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Editorial

By Prof. Dimosthenis Sarigiannis, MEASEP President

The 19th International MESAEP Symposium on Environmental Pollution and its Impact on Life in the Mediterranean Region has experienced a considerable growth in the number of papers presented at the Symposium. This time the Symposium was held at the National Research Council (CNR) headquarters in Rome from October 4 to October 6, 2017.

It built upon the series that began in Athens in 1981 and followed by others eighteen biannual Symposia organized in various countries of the Mediterranean Region to provide a forum for scientists, engineers and decision and policy makers to meet and discuss the latest developments in the research field related to control and preserve natural resources, protect the environment and human health and combat pollution and climate change. An important benefit of these conferences has been to encourage interactional collaboration between researchers in order to advance the frontiers of these fields.

The overall aim of the MESAEP Symposia are:

- to bring together its members and other interested persons from all scientific disciplines, of politics and economics to examine the current problems of environmental protection in the Mediterranean region. They investigate solutions to these problems on regional, national and international basis. For this purpose MESAEP makes critical appraisals of the problems concerning the protection of man, animals and plants in the Mediterranean region from harmful effects of chemicals and physical agents, both natural and manmade.

- to give suggestions and recommendations concerning environmental quality and safety so as to enable the regulatory bodies of the various Mediterranean Countries to make proper decisions regarding the evaluation of safety of chemicals and physical agents.

- to provide a forum for interested individuals from the field of the environmental sciences carrying out research related to chemical contamination and the other sources of pollution in the Mediterranean environment, and also those in economics and politics.

For this purpose, the association considers all the problems concerning the protection of life in the region from harmful effects of chemical and physical agents, both natural and man-made. Regulatory bodies in the Mediterranean regions are supported and advised by MESAEP to make proper decisions for improvements in environmental quality and safety.

Each MESAEP symposium brings together around 300 scientists from Mediterranean countries representing different organizations involved in the different facets of “Environmental Pollution and its Impact on Life in the Mediterranean Region”.

The focus of the 19th Symposium was on “Environmental and health inequity; science in the service of society”. This Special Issue presents a collection of the papers presented at the 19th MESAEP Symposium. The main themes covered in this book include:

- Climate change mitigation and pollution abatement
- Ecotoxicity and biodiversity
- Energy, environment and sustainability
- Environmental and health inequities
- Environmental economics, policy and education
- Environmental health and well being
- Indoor and outdoor air pollution
- Natural and man-made environmental disasters
- New and emerging technologies
- Sustainable natural resource and waste management
- Water and soil pollution and control
The conclusions of the overview of the 19th Symposium sessions was that the state of the environment in the Mediterranean region is under pressure. Positive steps have been taken in terms of addressing the most important issues linked to clean water scarcity, climate change and air and soil pollution. However, current policies and technical and non-technical measures fail to capture and appropriately reduce the totality of exposures affecting human life quality. Thus, additional work and resources are needed in the area of human exposome, i.e. the totality of exposures over one’s lifetime, linking organically diet, environmental conditions, and consumer good consumption, especially when considering the projected effects of climate change in the region. Clearly, socio-economic and institutional aspects play an important role in integrated environmental management for improved public health and well-being.

On that note, and in addition to the regular scientific sessions, a round table and panel discussion on migration and the consequent pressure on environmental and health inequity was organized, outlining many of the salient socio-economic, climatic, natural resource and environmental hygiene aspects of the migratory fluxes across the Mediterranean. Symposium participants and migration experts from Greece and Italy discussed the needs for improved welcome structures in the EU Member States and highlighted the enhanced pressure on the health care and environmental management systems linked to these migratory fluxes. It was made clear at the ensuing discussion that societal and equity aspects of environmental pollution have to be integrated into modern day environmental and health policies, especially in view of properly managing the effects of rapid societal change across the countries of the region.

The Symposium was organized in collaboration with the Institute of Advanced Study in Pavia, Italy; Aristotle University of Thessaloniki, Greece; Politecnico di Torino, Italy; Akdeniz University and Technical University of Istanbul, Turkey; Helmholtz Zentrum München, Germany; Public Health England United Kingdom; Istituto Superiore di Sanità, Italy; Consiglio Nazionale delle Ricerche, Italy; Università di Roma la Sapienza, Italy and the ICARUS H2020 Project consortium.

I would like to take this opportunity to thank the Conference Organising Committee, the International Scientific and Advisory Committee and the Editorial Panel for their invaluable advice. The smooth implementation of the paper review process was only possible because of the timely responses from a large number of external reviewers.

Most of all, I would like to express my sincere thanks to all the researchers who have contributed to the success of this conference and the scientific work of whom made this special issue feasible. Many thanks are due also to the all the members of the Executive Committee of MESEAP for their outstanding work and close collaboration during the preparation of this volume.
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SESSION I
ENVIRONMENTAL AND HEALTH INEQUITIES
GIS BASED INVENTORY AND DOCUMENTATION OF MONUMENTAL TREES IN BLACK SEA REGION OF TURKEY

Dursun Zafer Seker1,*, Nuket Sivri2, Mehmet Demir2, Abdulkadir Baytimur1, Enes Gunduz1, M Faruk Eroglu1

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ABSTRACT

Main objective of this study is documentation of the monumental trees has been a part of human life for a long time for many different aspects such as contributing to ongoing nature conservation in Black Sea Region of Turkey. Additionally, it is aimed to contribute creating awareness for the protection of monumental trees and provide a guide line for future studies related to GIS based documentation of the monumental trees. All types of monumental trees have different features and they are basically classified into four main groups in terms of their historical, mystic, folkloric and dimensionally characteristics. In this study, initially a GIS data base was created using in-situ collected data related to monumental trees such as the crown diameters of trees, diameter of body, heights and estimated ages of 334 monumental trees layed in the study region. Among these monumental trees, Platanus orientalis is recorded as the most common genera with the amount of 157. Basics statistical evaluations and analysis according to their attributes were also realized and visualized. Spatial distribution and geostatistical analysis were carried out using GIS database which can be considered as an important tool in the inventory and documentation process of the monumental trees.

KEYWORDS: Monumental trees, Platanus orientalis, Documentation, GIS, Black Sea Region.

INTRODUCTION

The huge and old monumental trees have attracted the attention of societies throughout the history of mankind. Moral and cultural values, Folkloric aspects, Mystical aspects, Historical aspects, Mythological aspects and Contribution to the culture and art are the most important contribution of these trees to social and economic life of them [1-2]. Contribution to the environment and scientific researches should also be considered. Trees have specific values, in relation to their aesthetic, cultural, historical, scientific, architectural, landscape and irrespective of the species [3-4]. Older trees are relatively rare and are therefore very valuable for the urban environment. Evaluation criteria should be set up before the study of the monumental trees. The most important criteria are the iconic character, the memorial status and/or the cultural historical value. Monumental trees have much larger size than the common size of their species in terms of age, diameter and height. They definitely have a special place in the history and culture [5-6]. They are naturally old enough to provide communication between past to present and also present to future. Currently, many of the monumental trees have been discovered and conserved in all around the world. While some of the previously recorded monumental trees are destroyed; some new ones have also been discovered. Thus, documentation of these trees is becoming extremely important [7-8].

Trees, which are the main source of ecosystem, have a great contribution to improve quality of life for many communities. Due to monumental trees are the main part of the cultural life, they should be documented [9]. A series of new policies are required to prevent the loss of monumental trees in forests worldwide. Most of time monumental trees are the part of disappearing cultural landscapes. Thus, to preserve these kind of landscapes, where there is still a high density of monumental trees new policies and regulations should be applied by the local or central governments and priorities should be define for them in order to conserve their unique biodiversity [10].

In Turkey, the studies related to monumental tree inventory has been started in 1999 by the Ministry of Forestry but up to date a complete study for whole Turkey has not been realized. Monumental trees, according to Article 6 of the Law No. 2863 on the Preservation of Cultural and Natural Assets are defined as “… tree and tree communities that featured indicative; immovable natural assets are examples”. According to the 2nd paragraph of Article 11 of the Regulation on the Procedures and Principles Regarding the Detection, Registration and Approval of Protected Areas, monumental trees are
FIGURE 1
The study area

Monumental trees are important for sustaining various communities regarding their structural and functional characteristics. Most of the time, disappearance of these trees because of any reason, may cause the loss of organisms and disappearance of rare and endangered species. Even though the listing of monumental trees in Turkey is done for a long time, there is not reliable database which cover all related information for whole monumental trees of Turkey [3, 11].

Monumental trees perform very important ecological role. All existing monumental trees need to be properly documented and protected. Due to the replacement of these trees is very difficult when they are lost, implementation of a functional management in countrywide is urgent to prevent the decline of monumental tree population [12].

This is an educational study based on a graduate project carried out Geomatics Engineering Department of ITU and Environmental Engineering Department of Istanbul University-Cerrahpasa [13], Turkey aiming documentation of monumental trees located in the Black Sea Region of Turkey for updating and disseminating the information related these cultural and natural assets by means of a geographical information system (GIS). This preliminary study is going to be a pioneer for further inventory studies carried out in the other regions of Turkey. This list is included complete records of 334 monumental trees. The most abundant species were Platanus orientalus, Pinus nigra, Pistacia terebinthus, Tilia tomentosa and Magnolia grandiflora. Location, estimated age, height, diameter of crown and diameter of body were measured for each monumental tree.

MATERIALS AND METHODS

Data. In the study, Black Sea Region of Turkey which covers 18 provinces has been selected as study area. This region is the greenest region among the seven geographical region of Turkey. The study area is presented in Figure 1. In this figure recorded monumental trees is also represented with different tones of green color.

Number of monumental trees is approximately ten thousand across Turkey although forested areas cover 27.6% of the country. Black Sea Region is the region the most extensive forests of Turkey, but the number of monumental trees is relatively limited. In the study, 334 separate monumental trees were documented by means of in-situ measurements. Genera, age, height, diameter of crown and diameter of body were measured and recorded. Size measurement of monumental trees were realized with Blume-Leiss size meter, peak diameter measurement were found that divided into two to these measurements were summed to carry out the peak diameter measurement from four direction. The body diameters were determined the average that measured from two directions with the aid of a caliper. Since the use of incremental bruising would damage trees of this age, the age determination was estimated by taking advantage of the information gathered from the people living in the area, taking into consideration the age determinations of some trees [13]. Registered monumental trees is only addressed but registered communities trees have not been examined on this article. Monumental trees are generally affected more than the other types of trees as they exist as single trees rather than appearing in clusters.

Methodology. Coordinates of the monumental trees were taken from the reports of the General Directorate for Protection of Natural Assets, "Determining the Current Situations of the Trees in Monumental Trees and Registered Tree Communities". Additionally, geographic coordinates of these trees were observed and this information is stored in
GIS geodatabase to be used further analysis. Geodatabase is a collection of geographic datasets of various types held in common file system folder. From a user perspective, the file geodatabase is essentially a database structure but contains geospatial information as well as rows and columns; besides, it is one of the fundamental elements of software. Google Earth view has been used as a base map in order to overlay monumental trees on it.

Reference ellipsoid WGS84 has been chosen as a datum for the study. After that, using geographic coordinate of all trees were added on base map. Data that contains coordinate of the monumental trees was prepared as an Excel file, each data was added separately with selecting X and Y values from the list. Same file also cover data about monumental trees such as province, district, street, Turkish and English genera, age (years), height (m), peak diameter (m) and body diameter (cm). After adding all points this layer exported and saved as a shapefile. Obtained shapefile was opened in with Google Earth to observe points and checking if there were any errors in their locations.

Due to unmeasured elevation values of the monumental trees, this data was extracted from SRTM (Shuttle Radar Topography Mission) data.

RESULTS

Distribution of monumental trees is given in Figure 2. Among these cities while Tokat Province has 47 monumental trees inside the administrative boundary, there is no recorded monumental tree in the Bayburt Province. Average monumental tree distribution of these provinces of the Black sea Region of Turkey is calculated as 35 trees for each province.

It shows that Platanus orientalis is the most common type of monumental tree in Turkey with number of 157. Other dominant species which are widely found in the study area are; Pinus nigra, Pistachia terebinthus, Tilia tomentosa and Magnolia gransiflora.

117 of monumental trees are classified as other species which cover Camellia japonica, Carpinus betilus, Fagus orientalis, Fraxinus excelcior, Castanea sativa, Taxus baccata etc. Genera distribution of the monumental trees is displayed in Figure 3. Age distribution of the monumental trees are presented in Figure 4. The oldest tree is around 1640 years old while the youngest one is around 100 years old.

Ground elevation of monumental trees were not measured during the data collection step. To find the elevations of these trees SRTM DEM data was used and elevation of each tree was extracted from this data. When the obtained results were evaluated it was clearly seen that more than %50 of them are under the 450 m elevation. The mean elevation value of all monumental trees is 431 meters. Highest elevation point of a monumental tree is 1741 meters while the lowest elevation point is almost at sea level. Height of the trees are presented in Figure 5. As clearly indicated in this figure, height distribution of monumental trees are normally distributed [13]. Province based species distribution were prepared and obtained results was presented in Figure 6.
Although inventory and documentation of monumental trees in Turkey, have been considered in several studies, there is no more study using GIS for documentation and inventory of them. Monumental trees in Akcakoca District located in Black Sea Region of Turkey were determined and evaluated within the framework of ecotourism [14]. In [3], a new inventory technique for monumental trees documentation was proposed. In [15], the authors discussed the GIS usage for inventory of the monumental trees in the Bogazici University Kandilli campus.

CONCLUSIONS

The number of specialists required for the determination of monumental trees is in short supply. Therefore, the determination and registration procedures can’t progress fast enough. TS 13137 standard does not include some of the local trees in the region. Therefore, the standard which includes some of the local trees in the region needs to be updated. For example, the Buxus sempervirens in the Eastern Black Sea Region, Tilia argentea, Morus nigra, Aesculus hippocastanum are not exist in the TS 13137 standard.

In order to preserve the richness and diversity of the cultural landscapes, new policies and regulations should be the priority issue of the central government of Turkey. Categorizing the monumental trees located in varied regions of Turkey has a critical role in their documentation. This effort will contribute to the protection of monumental trees.

Not only monumental trees but also other types of trees in need of protection are a complementary part of green nature. Damage caused by human beings is the main factor affecting their lives negatively. Also, treasure hunters may demolish the monumental trees since it is considered that precious treasures are buried in their bodies or in their surroundings.

The natural genera of monumental trees in the Black sea Region of Turkey were represented and visualized in the study. This study is considered as a pioneer study in this field in Turkey and it might be used a guideline for the future works. It is proposed that a national survey of monumental trees should be realized and necessary policies and necessary instruments should be urgently defined to protect these trees. Documentation process should regularly continue with the help of technological tools such as GIS.
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EXAMINATION OF THE GREEN SPACES BASED ON SPATIAL SUFFICIENCY AND ACCESSIBILITY THROUGH GIS

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ABSTRACT

Ecologically and socio-economically beneficial to cities, and covering a large fragment of land use pattern in developed countries, the green areas are under risk of zoning for building due to rapid and unplanned urbanization, policies aiming at rent and non-applicable zoning ordinances. Sufficiency of active green areas is validated with the standards of 10 m² minimum green area per person in the Spatial Plans Regulation. While analyzing the green areas for recreational needs in the city, in addition to the spatial extent, some other criteria as the population served, location, walking distance, walking time, variety, functionality and aesthetics should also be taken into the account. Thus demands for improving the life quality in any terms in cities can be met and citizens are satisfied by a systematical planning of the green areas in accordance with these criteria. In this study, existing active green spaces in Avcilar district, which is located at western part of Istanbul, were evaluated in terms of their spatial extent, area per capita and accessibility regarding their service domains. The relationship between population density, active green areas and their service domains were examined using spatial analyses methods provided by the use of geographic information technologies. The results of the study outlined that the active green area per capita in Avcilar is 1.8 m², significantly lower value than the accepted standards. Additionally, spatial extent of the active green areas is insufficient and their locations are messy with limited functionalities. The results clearly introduced that a comprehensive planning of green areas is urgently required in Avcilar for improving the prosperity of the local population.

KEYWORDS:
Urban planning, green areas, spatial sufficiency, accessibility, GIS.

INTRODUCTION

The two basic elements of the cities are the constructions and the gaps between them. The relationships of these elements are formed as structured-unstructured or empty-filled by considering the parameters such as depth, width and height of the constructions [1]. Open space is any open piece of land that is unbuilt (has no buildings or other built structures) and is accessible to the public [2-3]. Open space can include; green spaces, schoolyards, playgrounds, public plazas and etc. Green spaces are formed by the land that is partly or completely covered with grass, trees, shrubs, or other vegetation. These spaces provide recreational areas for residents and help to improve the visual and environmental quality of neighborhoods. As one of the most important elements of urban texture, open-green spaces are social interaction points where people with different socioeconomic characteristics [4]. So that, more green space exposure supports the formation of a stronger community development [5]. When the urban settlement plans are examined, open-green areas located in the city can sometimes form spontaneously and unplanned as distributed green areas or within certain plans as green belts [6]. In any existence open-green spaces structure the city with its green texture, topography, morphology, and climate based on the urban political decisions and development strategies [5].

Green spaces have various functionalities contributing to improve the quality of the city life by changing air quality, promoting physical activities and social contacts, reducing stress, mitigating noise and regulating heat and humidity [7-9]. Along with all the outdoor areas participating in the physical structure of the city, green areas serve as buffer between different land use areas; distinguish them in the most positive way. As each building occupies air in the city based on its volume, a balanced and planned green space distribution can regulate the number and density of buildings. Additionally, green spaces play a significant role in city life with its benefits on public health [9]. James et al. provided pathways for explaining relation between functions of the green...
was set as 10 m² per person. Additionally, in the pace of the renewal, the minimum area standard for green area per person was considered as 7 m². With the renewed planning purposes [12], the contributions of the GIS technology facilitating the decision-making processes by the efficient use of spatial analysis and modelling methodologies for urban and regional planning purposes [12]. The contributions of the GIS to urban and regional planning have been confirmed by many research studies; i.e. for the determination of the sensitive areas [13], examination of the highly urbanized cities in terms of urbanization, disaster management and etc. [14-16].

This study aims to draw attention to the necessity of planning systematic green spaces for the local governments preparing the development plans that shape the cities, so that high quality and healthy cities can be formed. In this context, the spatial sufficiency and accessibility of the active green spaces in Avcılar District, Istanbul were evaluated using GIS technology. The following section of the paper includes the general overview of the methodology together with the definition of the study area and the data used. The results of the study were presented in the third part of the paper and it is concluded in the final part with comments and recommendations.

### MATERIALS AND METHODS

Avcılar district which is located by the Küçükçekmece Lake and Marmara Sea at south western part of Istanbul was selected as the study area as presented in Figure 1. Total area of Avcılar is approximately 4,202 hectares and its population is 430,770 based on the 2016 dated census statistics provided by Turkish Statistical Institute. The district is surrounded by Küçükçekmece District at the east, Beylikdüzü and Esenyurt at the west, and Başakşehir districts at the north. Avcılar included 10 neighborhoods as Üniversite, Ambarlı, Cihangir, Denizköşkler, Firuzköy, Yeşilkent, Gümüşşapalı, Merkez, Mustafa Kemal Paşa and Tahtakale as presented in the Figure 1. A variety of functional areas as archeological sites, industrial and commercial areas, natural sites, universities and filling facilities are included in the district as well as settlement areas.

In order to make an assessment of the efficiency and the accessibility of the open-green spaces in the district, geometric data in vector and raster format and tabular data were used as the input of the performed GIS analyses. Vector data of the study included locations of the parks, road centrelines, building stock database and administrative boundaries. Except for the locations of the parks which was provided by the Avcılar Municipality, all vector data were provided by Istanbul Metropolitan Municipalite.

### TABLE 1 Minimum areal standards by countries [7]

<table>
<thead>
<tr>
<th>Function</th>
<th>USA</th>
<th>Amsterdam</th>
<th>Stockholm</th>
<th>Rome</th>
<th>Warsaw</th>
<th>UK</th>
<th>France</th>
<th>Turkey**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Children’s play ground</td>
<td>*</td>
<td></td>
<td>56</td>
<td>3.2</td>
<td>-</td>
<td>*</td>
<td>3.5</td>
<td>1.5</td>
</tr>
<tr>
<td>District/Neighborhood park</td>
<td>3.9</td>
<td>-</td>
<td>-</td>
<td>5.5</td>
<td>15</td>
<td>20</td>
<td>4.2</td>
<td>2</td>
</tr>
<tr>
<td>City/Town garden</td>
<td>13.2</td>
<td>9</td>
<td>23.8</td>
<td>11.6</td>
<td>5.3</td>
<td>40</td>
<td>10</td>
<td>3.5</td>
</tr>
<tr>
<td>Green zone near the city</td>
<td>60</td>
<td>30</td>
<td>48.1</td>
<td>18</td>
<td>17.5</td>
<td>8</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Playground</td>
<td>*</td>
<td>6.5</td>
<td>10</td>
<td>7.5</td>
<td>7.5</td>
<td>10</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>Total</td>
<td>77.84</td>
<td>45.5</td>
<td>87.5</td>
<td>48.8</td>
<td>45.3</td>
<td>78</td>
<td>35.7</td>
<td>10</td>
</tr>
</tbody>
</table>

* Included in to park areas  
**Values based on regulation dated 1985 and modified and published in the Official Gazette
ity for the use of the study. Metropolitan municipality also provided 2015 dated satellite imagery of the study area as raster format to be used for producing the polygons of the green spaces based on their locations by digitization. The attribute data used in the study included census data for the year 2016, names and the addresses of the parks in the study area. These data provided by Turkish Statistical Institute and Avci lar Municipality respectively.

The main methodology of the study encompasses two basic steps. The first step is the data preprocessing and enrichment. As presented in Figure 2, the data obtained from the different data sources in different formats were organized in order to be integrated in to GIS implementation established within the study. In this step, road network was produced using road centerlines, green spaces polygons were obtained by digitizing the satellite imagery, building geometries were corrected as closed polygons for obtaining their areas accurately during performed GIS analysis. Additionally, population and density information were assigned to each building. All these pre-processing works and the second step of the study were succeeded in GIS environment using ArcGIS 10.X software released by ESRI. The second step of the methodology is presented in Figure 3. This step basically implemented by the efficient use of spatial analyses tools of GIS. For this purpose, overlay, clip and network analyses were implemented in practice. As the main output of the step, green spaces per capita were determined as m² using overlay analysis of vector data of green spaces produced in the first step of the study with neighborhood polygons obtained by integrating census data. Additionally, in order to perform network analysis, a network topology was built using road geometries. Produced road network data were used to identify the service domains of green spaces by determining areas with 500 m accessibility to parks and green areas through network analysis. The maximum walking distance for the accessibility of the services set in the “Spatial Planning Regulation” were used as threshold value in service domain determination.

![FIGURE 1](image)

**FIGURE 1**
Study area

![FIGURE 2](image)

**FIGURE 2**
Workflow of the first methodology step

As the final step of the methodology, total population and the buildings served by each green space were determined by clipping service domains and building polygons through GIS. Interpretation of the analyses results were performed in order to make decisions on feasibility and accessibility of the active green spaces in Avcılar District in Istanbul.

**RESULTS**

The examination of the existing green spaces in Avcılar District resulted with 65 active green spaces ranging from 126 m² to 311,072 m² in size. The highest amount of these green spaces (30 of them 46%) vary in between 1,000 m² and 4,000 m² in size. This amount is followed by 14 (22%), 13 (20%), 5 (8%) and 3 (5%) and related areal ranges are below 1,000 m², 4,000 m² – 12,000 m², 12,000 m² – 80,000 m² and larger than 80,000 m² respectively. Figure 4 presents the spatial distribution of the active green spaces in the study area.

The evaluation of the functional characteristics of the active green spaces resulted that almost all of the green spaces in the district is children’s playground and include sports equipment. Children’s play areas are mostly suitable for children older than 7 years old. Therefore, green spaces for the use of children under the age of 7 is not sufficient in the district. There are 17 basketball, 10 football, 2 volleyball fields and 6 tennis courts actively in use in the study area.
According to the results obtained by the general evaluation of the district the following results are obtained: In Avcılar District, active green areas (771,792 m²) constitute 5.8% of the residential area (13,199,773 m²). The amount of active green area per capita in the study area was calculated as 1.8 m² by dividing the total amount of green space calculated for the district by the total population. Resulted value of green area per capita is considerably lower than the standard of 10 m²/person in the “Regulation on Spatial Plans”. Based on this result, the study area requires to be provided 3,535 808 m² of green space in order to provide 10 m²/person standard. In the year of 2000, total population of the district was 236,885 people, the active green areas in the district were 351,140 m², and the amount of active green area per capita was 1.5 m² [7]. When the obtained values are compared, it is introduced that the size of the active green area increased from 351,140 m² to 771,892 m² with 20% increase in active green space per capita while the population growth in the study area is 82% for the same period.

In addition to district base evaluation, neighborhood evaluation of the active green spaces were also performed within the study. According to these results: Denizköy is the neighborhood with the highest amount of active green space per capita (7.2 m²/person). The amount of active green space per capita in Ambarlı (3.6 m²/person) and Gümüşpala Quarter (3.3 m²/person) is more than other neighborhoods. The reason of the high ratio in Denizköy and Ambarlı Quarters based on “Coastal Law” which defines first 50 meters of the coastal area and the shoreline as a green area. The amount of green space per capita in Firuzköy and Tahtakale Quarters is 1.1 m² per capita, well below the standard. Although there is a regular and planned construction at the Ispartakule region of Tahtakale Quarter, the amount of active green space per capita is calculated low due to the fact that the green areas in the housing estate are not included in to account during calculation process since they are not public green spaces. In Cihangir (0.2 m²/person), Üniversite (0.4 m²/person), Merkez (0.4 m²/person), Mustafakemalpaşa (0.1 m²/person) and Yeşilkent (0.7 m²/person), the amount of active green area per capita is less than 1 m². The main reason of these low amounts of active green space per capita in Cihangir and Yeşilkent quarters is the high population density of these neighborhoods. The reason for the low amount of active green space per capita in the Üniversite (426 person/ha), Merkez (450 person/ha) and Mustafakemalpaşa (546 person/ha) is the fact that there is a dense
and high density building texture in these neighborhoods and the population density is high. Although the density is very high in Gümüşpala Quarter (502 person/ha), the existence of Paşaşı and İğdelik Parks with large areas in this neighborhood increases active green area per capita.

The neighborhood based comparison of the active green spaces per capita and population density by neighborhood presented in the Figure 5.

In the Figure 5 the inner circle symbols with lighter color indicate the amount of the green space per capita in the study area and the outer circle with darker color represent the green space standard in Turkey as 10 m²/person.

Examination of the service domains of the green spaces resulted that, 16,406 (68.5%) of total residential buildings (23,945) located in the Avciğer District are within the 500-meter service area of active green areas and the number of buildings without service is 7,539 (31.5%). Based on this result, it is concluded that 336,488 (78.2%) people living in the Avciğer District can receive services from active green areas while 94,282 people (21.8%) do not receive services comfortably. The map depicted in Figure 6 presented results of accessibility analysis.

CONCLUSION

When active green spaces (park, children’s garden, playground, recreation area) in Avciğer District are examined, it is concluded that the amount of active green area per capita is 1.8 m². The green spaces in Avciğer District are scattered and in small pieces and do not show integrity. Policies promoting unearned income in construction works always damage the zoning activities in cities. Green spaces are mostly affected by these policies and they are mostly occupied for other purposes. One of the main reasons of the insufficient amount of green spaces in Avciğer is that the areas assigned as green spaces in zoning plan are mostly occupied by increasing population for housing. These occupied areas were then included into zoning plans with the new releases of “zoning laws” in different periods. Recovery of the green spaces in the zoning plan is one of the main solution to existing situation in Merkez, Cihangir, Yeşilkent, Tahtakale, University and Mustafakemalpaşa quarters. Recovery can be provided by expropriation of the occupied green areas in the zoning plan. Additionally such policies should be abandoned in order to provide sustainable green spaces in cities.

In order to provide a planned conversion in the study area, graduation of green spaces should be provided to form a green space system that is increasingly complex in size and function from the green areas at the housing level, which is the smallest unit,
and green bands that link those systems to each other and to the coastal areas. Based on the results of the study the diversity of the children's playgrounds were not provided in the study area. Therefore, in addition to the improvements on the quantity of the play areas for children, quality of the existing ones should also be increased to meet the needs of children indifferent age groups and increase their creativity. In primary school domains, sports and play grounds should be planned attached with the primary school. Similar facilities should be maintained for older children together with the secondary schools and high schools.

Finally, when green areas are planned, random site selection decisions should not be made; property status, service domain, minimum size, security, design elements, socio-cultural texture, etc. criteria must be taken into consideration for providing an efficient green space plan.

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PROSPECTS OF USING GARLIC EXTRACTS FOR PEST CONTROL IN SUSTAINABLE AGRICULTURE

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ABSTRACT

In accordance with the Directive 2009/128/EC, the spreading of biological methods based on the sustainable use of pesticides is one of the main objective aimed at limiting the risks caused by the use of pesticides on environment and health. Plant extracts offer significant advantages in terms of sustainable agriculture and represent a feasible alternative against infestant weeds and pests for disease control of crops. Garlic (Allium sativum L.) is known for its stimulating properties on plant growth and also protects plants due to its bactericidal and fungicidal activity.

In this study, the antioxidant properties of aqueous extracts of garlic were evaluated by DPPH method, for the ability to provide stress resistance in plants. Moreover, the bio-stimulant and repellent effect of 1% (w/v) aqueous extract was evaluated on plants of zucchini (Cucurbita pepo L.) in an open field test, under the spontaneous attack of parasites and pathogens. The vegetative conditions of plants were assessed by measuring the chlorophyll content in vivo using the fluorimeter SPAD 5200. To evaluate the antioxidant properties of fruits, generally stimulated by abiotic environmental stress, we determined the antioxidant activity on zucchini harvested, using the same DPPH method.

The results showed a higher fruit yield in treated plants due to higher vegetative vigour, higher chlorophyll content in their leaves and better flower induction compared to control plants. The zucchini plants seemed to have taken advantage from the repellent effect against insect vectors and the preventive effect of garlic extract used. Moreover we found that zucchini fruits had lower antioxidant activity in treated plants than in control plants, due to their better physiologic conditions.

The introduction of plant extracts to replace conventional chemicals, could provide significant benefits on the environment and human health.

KEYWORDS:
Allium sativum, zucchini crop, protection, antioxidant activity.

INTRODUCTION

Plant extracts seem to be particularly effective in the control of pests and diseases of agricultural plants, while not showing any toxic effect [1, 2]. These extracts are a combination of compounds, and display a higher activity compared to the single active substance, which lead to a more effective response. This phenomenon called synergism, has been recently observed for the constituents of essential oils [3, 4] which proved to give better and longer lasting results when used as mixtures compared to the additive effect of the individual components [5].

Garlic is known for its stimulating properties on plant growth and also protects plants due to its bactericidal and fungicidal activity (depending on Allicin and Alliin), as confirmed by several scientific studies [6, 7, 8]. Garlic promotes their self-defense against attacks by fungi and bacteria [9] [10]. Aqueous and hydroalcoholic garlic extracts have been shown to be effective in agriculture.

Moreover, garlic extract has good antioxidant properties [11, 12, 13]. Antioxidant activity is important against stress in the plants, showing a positive correlation between increased antioxidative components and different stress tolerance [14]. Plant extracts used as biostimulators benefit plant productivity by interacting with plant-signaling cascades thereby reducing negative plant reactions to stress [15, 16].
Except for legumes, garlic can be sprayed directly on the leaves. It is used in organic farming as a preventive substance, due to its repellent action against pest arthropods (mites, aphids, moths, termites, beetles, red spider mites, mosquito larvae, etc.) and snails. Garlic is not active against useful arthropod (bees, bumblebees, ladybugs, spiders, etc.). In order to protect plants against some species of nematodes, garlic is added to the soil directly.

In this work, the antioxidant properties of garlic aqueous extracts were evaluated as concerns their ability to provide stress resistance in plants. The bio-stimulant and repellent effects of a garlic aqueous extract were both evaluated on zucchini (Cucurbita pepo L.) crop and the antioxidant properties of fruits were also determined.

### MATERIALS AND METHODS

**Preparation of garlic aqueous extracts.** Extracts were prepared using dried garlic powder (Allium sativum L.) at two concentrations 1% and 2% (w/v), namely 1g 100mL⁻¹ and 2g 100mL⁻¹ respectively, using water at room temperature or at 40°C. Each mixture was allowed to stand for 2h to allow a complete extraction process. The extracts were filtered with filter paper and then centrifuged at 3500 rpm for 10 min.

**Measurement of antioxidant activity.** The antioxidant activity of garlic aqueous extracts was evaluated by DPPH (1,1-diphenyl-2-picryl-hydrazyl radical) method [17] [18]. DPPH is a purple dark-colored crystalline powder containing stable free-radical molecules. It changes its colour into yellow following reduction by an antioxidant. Free radical scavenging activity of plant extracts has been extensively evaluated by DPPH method.

1 ml of a 0.15 mM DPPH methanolic solution was mixed with increasing doses of extract (ranging from 100 to 500 μL), and adding methanol to the final volume of 1.5 mL. The mixtures were shaken vigorously and left standing at room temperature for 30 min in the dark, and then the absorbance was measured at 517 nm, using methanol as blank. Spectrophotometric measurements were performed by UV-VIS double-beam spectrophotometer (Uvikon XL Secomam S.a.s. ®, Alés Cedex, France); analyses were performed in triplicate.

The antioxidant activity was expressed as a percentage of inhibition of DPPH radical calculated according to the following equation:

\[
\% \text{ antioxidant activity} = \frac{(A_0 - A_S)}{A_0} \times 100
\]

where \(A_0\) is the absorbance of the control (containing all reagents except the extract), and \(A_S\) is the absorbance of the tested sample.

**Field experiment.** The effects of garlic aqueous extract at 1% (w/v) concentration were evaluated on plants of zucchini (Cucurbita pepo L.) in an open field experiment, under the spontaneous attack of parasites and pathogens.

The solution used for the field application was prepared by adding the powder of dried garlic (Allium sativum L.) to distilled water to make the final concentration of 10 g L⁻¹ and left standing for 48 hours. After filtration with paper filter, the aqueous extract can be used immediately or stored for 6-7 days at +4 °C.

Zucchini plants (Cucurbita pepo L.) var. Augusto (Romanesco type) were planted in open field in April 2014 and cultivated under integrated farming system, divided into 3 plots of 4 plants (two treated with plant extracts and two untreated as controls) with three replicates in a random design.

At the beginning of the test, the chemical characteristics of the soil were analyzed according to the official methods of soil chemical analysis [19]. The results showed that the soil had a clay-loamy texture, with sub alkaline pH (7.6), and a high cation exchange capacity (31.41 meq 100 g⁻¹).

At the transplant, a single local fertilization was carried out, by distributing 30 g of bi-ammonium phosphate (DAP 21-54) per plant. The plots were treated weekly with the aqueous extract of garlic at 1%, for an overall period of two months. The plants of each plot were also inspected daily to check for outbreaks of fungal infection or for disease caused by the attack of insects. The fruits were collected during the months of June and July (12 harvests), weighed and measured (length and diameter).

The vegetative conditions of each plant were assessed by measuring the chlorophyll content in vivo, using the fluorimeter SPAD 5200 (Konica Minolta ® Business Solution Italia S.p.a., Milan, Italy); for the calibration in the laboratory, the spectrophotometric measurement of chlorophyll content was performed as described: 0.5 g of fresh leaves were homogenized in an aqueous solution of 80% acetone. The extract was analyzed in the spectrophotometer UV-VIS Uvikon XL (Secomam S.a.s. ®, Alés Cedex, France), against a blank consisting of 80% acetone, at wavelengths of 660.0 nm and 642.5 nm (Fig. 1).

The value of total chlorophyll, expressed in mg L⁻¹ was given by the formula:

\[
\text{Total chlorophyll} = 7.12 A(660.0) + 16.8 A(642.5)
\]

where \(A(660.0)\) and \(A(642.5)\) are, respectively, the absorbance values at 660.0 nm and 642.5 nm.

To evaluate whether garlic extract treatments have led to variations in the antioxidant properties of fruits, we determined the antioxidant activity on zucchini harvested, using the same DPPH method described above with the following revisions. Six fruits were collected in the last harvest.

Each sample was prepared weighing 3 g of fresh fruit (including its pulp and peel) and adding 30 mL ethanol 80% to have a final rate 1:10 w/v. The mixture was homogenized, filtered with filter paper,
TABLE 1
Production of zucchini squash, number of fruits and fruit weight (mean data per plant).

<table>
<thead>
<tr>
<th>Treated plants</th>
<th>Untreated plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (g)</td>
<td>3891.3*</td>
</tr>
<tr>
<td>Number of fruits</td>
<td>17.5</td>
</tr>
<tr>
<td>Fruit weight (g)</td>
<td>222.4</td>
</tr>
</tbody>
</table>

* Significance (p<0.05) to the test t for paired samples

TABLE 2
Lowest air temperature values recorded during the month of June (°C).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>17</td>
<td>17</td>
<td>18</td>
<td>20</td>
<td>19</td>
<td>14</td>
<td>14</td>
<td>15</td>
<td>15</td>
<td>19</td>
<td>20</td>
</tr>
</tbody>
</table>

TABLE 3
Chlorophyll content in SPAD units, average number of leaves and fecund flowers.

<table>
<thead>
<tr>
<th>Treated plants</th>
<th>Untreated plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPAD units</td>
<td>39.2*</td>
</tr>
<tr>
<td>Number of leaves</td>
<td>22.3</td>
</tr>
<tr>
<td>Number of fecund flowers</td>
<td>35.3*</td>
</tr>
</tbody>
</table>

* Significance (p<0.05) to the test t for paired samples

centrifuged at 3500 rpm for 10 min thus obtaining the supernatant that was used for the analyses. Increasing volumes of supernatant extract (ranging from 100 to 500 μL) were mixed with 1 ml of 0.15 mM DPPH methanolic solution, and adding methanol to obtain a final volume of 1.5 mL to give concentrations ranging from 6.67 to 33.33 mg f.w. ml⁻¹. Spectrophotometric measurements and expression of the results have already been described above.

Statistical analysis. Since two plants, on the half plot, were treated with garlic extract and the other two plants were not, an experimental spatial dependence as results of the closeness of plants has been introduced in the design. The plots were repeated for three times at different points of the area of the field test. The differences observed as regards data between treated and not treated plants were tested statistically using the t-test for paired samples, as a result of the spatial dependence between the treatments.

RESULTS

Extracts Antioxidant activity. The antioxidant activity of garlic extracts shows a similar trend by increasing the dose of extract in all the examined extracts, while the garlic extracts at 2% (w/v) concentration displayed higher antioxidant activity showing a dose-related increase of activity with increasing extract concentration (Fig. 2).

We chose to use the cold 1% extract in the field trial, because it has the highest antioxidant activity (higher than 60%) and it is cheaper as it allows to use only half the amount of dried garlic with respect to the 2% concentration. The use of moderately heated water (around 40 °C) did not affect the antioxidant activity of the extracts that maintain a similar behaviour in both cold and heated solutions (Fig. 2).

Field production. The results showed a higher fruit yield, with higher diameter and lengths in treated plants (data not shown) compared to control plants. However, the difference in the average production per plant was statistically significant (Tab. 1). Examining the data collected for the single harvests, as highlighted in four of these, the t-test showed statistically significant differences in treated plants compared to not treated ones (Fig. 3).

In one harvest, namely the number 7 (June, 24) the zucchini production was much lower than the others for both treatments, due to a strong reduction of the minimum air temperature in the days prior to the harvest (Tab. 2). Moreover, the plants of zucchini treated with garlic extract had higher vegetative vigour, higher chlorophyll content in their leaves and better flower induction (Tab. 3).

Biostimulators often increase chlorophyll content, which is crucial for proper course of photosynthesis. This effect was observed in cowpea seeds after pre-soaking in carrot extract [20] and in rocket (Eruca sativa) treated with Moringa oleifera extract [21].

Other authors found that algae filtrates from Ascophyllum nodosum stimulated growth and nutrition of the treated plants and laminarin extracted from Laminaria digitata induced natural defense reactions [22]. The studies on their mode of action showed that these products acted as phytoactivators. First, the filtrates stimulated the nitrate reductase and root phosphatases involved in both N and P nutrition. Such stimulation resulted in better plant growth and increased chlorophyll content.

Fruits from treated plants had lower antioxidant levels compared to the control plants (Fig. 4). This
may suggest that the best conditions of treated plants have led to less accumulation of antioxidant substances in fruits, generally induced under stress.

DISCUSSION

The high antioxidant activity of garlic has been reported in several studies [11, 12, 13] and depends on the combination of a number of components. The DPPH radical scavenging method could be a good way for comparing the antioxidant properties of different garlic extracts. Although the DPPH reaction has low specificity for the detection of specific antioxidant components, it allows to measure the overall antioxidant capacity in a sample.

The antioxidant activity of polyphenolic components in plants is well documented. A recent study showed the correlation of the antioxidant properties with the presence of phenolic compounds in Allium sativum L. [13].

The application of garlic extract to zucchini crop resulted in a biostimulant effect on plant growth and better yield and quality of zucchini. The biostimulant effect on zucchini plants may depend on its protective effect against the oxidative stress.

Many natural extracts displayed biostimulant properties due to their various components, thus improving and stimulating plant life processes through mechanisms that are different from those of fertilizers or phytohormones. The different activated mechanisms depend on the wide range of molecules contained in the solution [16].

Moreover, zucchini fruits are vegetables with high nutritional value and many of their useful properties are attributed to the antioxidant activity of the components they contain. Many reports indicate that oxidative stress may cause excessive formation of ROS (Reactive Oxygen Species) under unfavourable environmental conditions. The abiotic stress may activate the production of antioxidant molecules like ascorbic acid, phenolic compounds and carotenoids, that are involved in the plant defence response [23]. In fact, we found that zucchini fruits had lower antioxidant activity in treated plants than in control plants, due to their better physiologic conditions. The antioxidant activity of plants is therefore stimulated by the abiotic environmental stress.

The zucchini plants seemed to have taken advantage from the repellent effect against insect vectors and/or the preventive effect of garlic extract used. The effects of the garlic aqueous extract are due to the synergistic action of the mixture of its chemical components, and are superior to those given by pure allicin.

![FIGURE 1](image1.jpg)
Calibration SPAD units towards real chlorophyll content (mg L⁻¹) with eight leaf samples.

![FIGURE 2](image2.jpg)
Antioxidant activity of garlic extracts at the concentrations of 1% and 2% w/v obtained by cold or heating. Values are expressed as mean ± SD (n = 3).
The gradual replacement of conventional chemicals with organic products such as plant extracts, experimentally tested and produced on a large scale with less expensive processes will provide significant benefits in terms of natural resources, environment and human health, and will also lead to the opening of new and attractive markets [2]. To achieve this, it will be necessary to improve the control of quality of the products, and to implement appropriate strategies for process standardization.

A number of green agricultural chemicals (fertilizers, herbicides and fungicides) were launched on the market in many Countries including Turkey, Germany and Bulgaria. But it is in the Mediterranean Countries, that are particularly rich in endemic plants and biodiversity, these pesticides are expected to have the greatest impact on a system of integrated agricultural management, due to their safety for humans, non-target organisms and the environment.

CONCLUSION

An interesting aspect was the absence of insect pests attacks on the plants, such as fungal and bacterial diseases, despite the high rainfall and the high moisture content of the air in the period in which the test was held. Garlic extracts used in this study seemed to have beneficial effects on growth of plant and fruits, along with their repellent and/or preventive effect against insect vectors.

The gradual replacement of conventional chemicals with organic products such as plant extracts will bring significant benefits with regard to natural resources, environment and human health. In the Mediterranean Countries, that are particularly rich in endemic plants and biodiversity, these pesticides can have their greatest impact on a system of integrated agricultural management.

REFERENCES


ASSESSMENT OF THE RELATIONSHIP BETWEEN LAND USE/COVER CHANGES AND LAND SURFACE TEMPERATURES: A CASE STUDY OF THERMAL REMOTE SENSING

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Istanbul Technical University (ITU), Faculty of Civil Engineering, Department of Geomatics Engineering, Turkey

ABSTRACT

Rapid and uncontrolled urbanization is one of the most important land cover change phenomenon, which has important environmental impacts on ecosystem and climate. Due to the urbanization, green areas and natural permeable surfaces transform into non-permeable impervious surfaces, yielding an increase in urban land surface temperatures (LST). This causes an environmental phenomenon called urban heat islands (UHI), where urban temperatures are higher than the surrounding rural areas. Satellite remote sensing technology is an effective tool to monitor and quantify the effects of urbanization process with synoptic viewing capability and high temporal resolution. This study focuses on determining the land surface temperature and land use/land cover (LULC) changes in Istanbul for the last three decades and identifying the relation between these parameters using multi-temporal optical and thermal remote sensing data. The study is conducted using Landsat 5 TM and Landsat 8 OLI/TIR images, which were acquired on June 1984 and June 2017 respectively. In order to assess the land cover change between 1984 and 2017, a vegetation impervious surface-soil (V-I-S) model was applied to the fraction images obtained from linear spectral unmixing process. End-member spectra used in linear spectral unmixing were extracted from ASTER spectral library and resampled to band passes of Landsat 5 TM and Landsat 8 OLI data. In addition to V-I-S model outputs, normalized difference vegetation index (NDVI) and normalized difference built-up index (NDBI) images were produced. A maximum-likelihood classification was also performed to multi-spectral bands in order to derive the LULC maps. Water bodies were extracted from imagery using automated water extraction index (AWEI). Thermal infrared bands of Landsat 5 TM and Landsat 8 are used for the derivation of land surface temperatures. The results of the study indicates that, the amount of impervious surfaces substantially increased along with land surface temperatures over three decades.

KEYWORDS:
Spectral Unmixing, Thermal Remote Sensing, Land Use/Cover

INTRODUCTION

According to the World Urbanization Report published in 2014 by the United Nations, 54% of the world’s population live in urban areas and it is predicted that this ratio will grow rapidly in developing countries and will reach to 60% in 2050 [1]. In parallel to the rapid increase in the world population, the impacts of human on nature is also increasing. New agricultural areas have opened and residential areas expanded in order to meet the needs of the increasing population that results with forest destruction. Many studies have shown that, in addition to natural processes, anthropogenic land cover changes also have a significant impact on the climate. One of the main anthropogenic land cover change is the urbanization, which influences biodiversity, ecological system and climate in regional scale, therefore dramatically affecting human health and quality of life [2]. As urban areas expand, permeable and moisture-holding lands transform into impervious surfaces such as concrete and asphalt. Changes in the land use/land cover (LULC) have direct impact on thermal characteristics. At this point, remote sensing technology provides great opportunity to analyze the urban thermal environment with its synoptic vision capability. Many studies have been conducted on the impacts of land cover change to urban thermal condition using remote sensing [3-7].

Istanbul is one of the biggest metropolitans around the world. According to Turkish Statistical Institute (TUİK) census database, while the population of the city in 1980 was around 4.7 millions, it reached to 14.8 millions in 2016 and expected to reach 21 million by 2050 [8]. Over three decades, the large-scale growth in population of the city lead to a dramatic increase in urbanization [9, 10]. Natural landscapes transformed into residential areas with impervious surfaces causes increase in land surface temperatures, which is one of the main components
of urban heat islands [11]. Depending on the location, the rate of land use/land cover change varies for different districts in Istanbul.

In this study, the land cover change and its impacts on Istanbul’s thermal condition was investigated using optical and thermal satellite images for 33 years period.

STUDY AREA

The study area was selected as Istanbul, which is located in Marmara region of Turkey (Figure 1). The city lies on two continents as Europe and Asia divided by Bosphorus, an important 29.9 km long waterway for trading and international affairs connecting Black Sea to Marmara Sea. Istanbul covers 0.7% of Turkey with an area of 5,343 km² [12, 13].

General characteristics of Mediterranean climate is dominant in southern parts of Istanbul, where the intense urbanization occurs. The northern side of the city is mostly covered with forests and the climate is affected by Black Sea and northerly colder air masses of maritime [14].

FIGURE 1
The Study Area

METHODS AND RESULTS

Image Preprocessing. The Landsat C1 Higher-Level surface reflectance data is delivered as 16-bit signed integer. In order to convert these values into actual reflectance values, all pixels of the data were multiplied with a scale factor of 0.0001 as described in LEDAPS and LaSRC product guides [15, 16]. Following the scale conversion, waterbodies in the study area were masked using Automated Water Extraction Index (AWEI) [17].

Emissivity and Land Surface Temperature Maps. Land surface temperature (LST), often defined as skin temperature, is the estimation of kinetic temperature of earth’s surface using thermal infrared radiation. Although, LST is defined as skin temperature, it is far from being a two-dimensional surface [18]. In medium-resolution remote sensing images such as Landsat, pixels are composed of different types of surface components.

For thermal infrared remote sensing, derivation of LST is based on Planck’s radiation function, which is related with radiation emitted by black body at temperature T, where the emissivity is equal to 1 [19]. To retrieve land surface temperature from thermal imagery, an emissivity correction must be performed to atmospherically corrected TIR bands. For Landsat TM sensors, an NDVI_{THM} (NDVI Thresholds) method is proposed to obtain land surface emissivity maps [20]. The NDVI_{THM} is based on thresholding the NDVI values according to three intervals that are defined for soil, vegetation and mixed pixels. Pixels with NDVI values smaller than 0.2 are considered as soil and the mean emissivity spectra for soil is assigned to corresponding pixel. Pixels with NDVI values greater than 0.5 are considered as full vegetation cover and related mean emissivity spectra is assigned to corresponding pixels. Pixels with NDVI values between 0.2 and 0.5 are considered to be a mixed pixel composed of vegetation and soil.

The emissivity estimation were performed by linear spectral mixture analysis (LSMA) based spectral unmixing and by use of mean emissivity of end-members. A constrained linear spectral unmixing model was applied in order to estimate the fractions of each pixel according to given end-members. The end-members extracted from ASTER spectral library and convolved to Landsat 5 TM and Landsat 8 OLI band-passes using following equation [21]:

$$L_b = \frac{\int_{\lambda_1}^{\lambda_2} L_S(\lambda) f(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} f(\lambda) d\lambda}$$  \hspace{1cm} (1)

where, \(L_S(\lambda)\) denotes the reflectance of spectra in wavelength (\(\lambda\)), \(f(\lambda)\) denotes the relative spectral response of the sensor on wavelength (\(\lambda\)), \(\lambda_1\) and \(\lambda_2\) denotes the upper and lower wavelength boundaries of given band b and \(L_b\) denotes the band equivalent reflectance value of the spectra in band b.

Extracted spectra were classified into classes as vegetation, impervious and soil. For impervious surface structures, man-made material spectra from John Hopkins library were used. Man-made material spectra are classified as concretes, road asphalt - tar and roofing materials, while vegetation cover is classified as conifer, deciduous and grass.

After derivation of band-equivalent values of end-members, mean emissivity values for man-made materials, soil and vegetation were calculated. For impervious surfaces, mean emissivity value of 0.92 ± 0.03 and for vegetation, mean emissivity value of 0.98 ± 0.01 were used [22]. For soil spectra, an emissivity value of 0.973 ± 0.004 was used [20]. A constrained LSMA was applied to C1 Higher Level atmospherically corrected Landsat visible and infrared bands by using end-members given in Table 1. After the derivation of resultant fraction map for each end-
member, emissivity maps were obtained by using following equation;

\[ \varepsilon_p = \sum_{i=1}^{N} f_i \varepsilon_i \]  

(2)

where, \( \varepsilon_p \) is the emissivity value of pixel \( p \). \( f_i \) is the fraction value of end-member \( i \), and \( \varepsilon_i \) is the known emissivity value of end-member \( i \). \( N \) is the number of end-members.

### TABLE 1

<table>
<thead>
<tr>
<th>Band Center Wavelength (micrometers)</th>
<th>Vegetation</th>
<th>Impervious</th>
<th>Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.479</td>
<td>0.0533</td>
<td>0.1634</td>
<td>0.0708</td>
</tr>
<tr>
<td>0.561</td>
<td>0.0913</td>
<td>0.1841</td>
<td>0.1290</td>
</tr>
<tr>
<td>0.661</td>
<td>0.0514</td>
<td>0.1944</td>
<td>0.1936</td>
</tr>
<tr>
<td>0.835</td>
<td>0.5087</td>
<td>0.2027</td>
<td>0.2730</td>
</tr>
<tr>
<td>1.650</td>
<td>0.2819</td>
<td>0.2743</td>
<td>0.4363</td>
</tr>
<tr>
<td>2.208</td>
<td>0.1361</td>
<td>0.2663</td>
<td>0.4064</td>
</tr>
</tbody>
</table>

In order to obtain the land surface temperatures, thermal infrared bands of Landsat 5 TM (band 6) and Landsat 8 (band 10) were atmospherically corrected as initial step.

For Landsat 5 TM imagery acquired in 1984, a mono-window LST retrieval algorithm was applied on band 6 to obtain the LST values [16]. The algorithm is formulated as follows;

\[ T_2 = \frac{a_6(1-C_6-D_6) + (b_6(1-C_6-D_6) + C_6 + D_6)T_6 - D_6T_6)}{C_6} \]

(3)

where, \( a_6 \) and \( b_6 \) are the model constants (-67.355351 and 0.458606), \( \varepsilon_6 \) is the emissivity value of pixel in band 6 of Landsat TM, \( \tau_6 \) is atmospheric transmittance on band 6 of Landsat TM, \( T_2 \) is top-of-atmosphere (TOA) brightness temperature on band 6 of Landsat TM, \( T_a \) is the mean atmospheric temperature in study area and \( T_3 \) is the land surface temperature of Landsat band 6 pixel.

Atmospheric transmittance \( (\tau_6) \) derived from water vapor content as described in [23]. Water vapor and \( T_a \) was calculated using in-situ radiosonde measurements obtained from local meteorological station. For Landsat image acquired in 2017, a radiative transfer equation based methodology was performed to obtain LST values. A web-based atmospheric correction parameter calculator provided in URL-1 was used to derive atmospheric transmittance, upwelling and downwelling radiances. This atmospheric parameter calculator tool uses National Centres for Environmental Prediction (NCEP) profiles and MODTRAN radiative transfer code and performs simulations with given sensor information, data acquisition date and surface conditions [24]. Results of web based atmospheric correction parameter calculator for the study area is given Table 2.

### TABLE 2

<table>
<thead>
<tr>
<th>Acq. Year and WRS Row/Path</th>
<th>( \tau ) (transmittance)</th>
<th>Upwelling Radiance (W/m²²st r²μm)</th>
<th>Downwelling Radiance (W/m²²st r²μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2017-180/31</td>
<td>0.67</td>
<td>2.67</td>
<td>4.21</td>
</tr>
<tr>
<td>2017-180/32</td>
<td>0.74</td>
<td>2.12</td>
<td>3.44</td>
</tr>
</tbody>
</table>

Following the derivation of transmittance, upwelling and downwelling radiances, radiative transfer equation was applied to obtain atmospherically corrected surface radiance map for the Landsat thermal band acquired in 2017 [25]. After obtaining atmospherically corrected radiance image in thermal band, an inverse Planck’s function was applied to derive LST images. The Inverse Planck function is given as;

\[ T = \frac{K_2}{ln \left( \frac{K_1}{\tau_{atmcor}} + 1 \right)} \]

(4)

where, \( K_2 \) and \( K_1 \) are thermal constants specific to thermal sensors and \( L_{atmcor} \) is atmospherically corrected radiance values in thermal band. Resulting LST maps are shown in Figure 2.

![FIGURE 2 LST maps of Istanbul.](image)

**Land Use/Cover Maps.** Land cover is defined as natural and anthropogenic features that exists on earth’s surface like forests, water bodies, urban areas, grasslands and etc. Land cover changes, espe-
cially caused by human activities, are important factors that play significant role on local and global environmental characteristics [26].

In this study, maximum-likelihood supervised classification algorithm was performed to obtain land cover maps [27]. Three information classes were chosen for the study area with respect to CORINE land cover classification system which are; Forests and Vegetation, Soils (Semi-natural areas referring to open space bare-soils, grass-lands beaches, and sparsely vegetated areas) and Impervious Surfaces (Urban areas) [28]. For each class, a minimum of 30 training samples, each containing at least 50 pixels were selected. The land cover maps produced by supervised classification for 1987 and 2017 are shown in Figure 3.

![Image](image_url)

**FIGURE 3**

Land cover maps of Istanbul.

**TABLE 3**

Total area and area percentage of each land cover class from 1984 to 2017.

<table>
<thead>
<tr>
<th>Land Cover Classes</th>
<th>1984</th>
<th>2017</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>km²</td>
<td>%</td>
</tr>
<tr>
<td>Forest &amp; Veg.</td>
<td>2561.0</td>
<td>48.4</td>
</tr>
<tr>
<td>Impervious</td>
<td>246.3</td>
<td>4.6</td>
</tr>
<tr>
<td>Soil</td>
<td>2489.5</td>
<td>47</td>
</tr>
</tbody>
</table>

In order to investigate urban expansion in district level using LSMA fraction images, the administrative boundaries vector file for 38 districts of Istanbul was used. Mean values of fractions (vegetation, impervious and soil) in each district were calculated for 1984 and 2017, using zonal analysis function of ArcGIS software. Results of zonal analysis indicates that, during 33 years period, a 50 percent of increase in impervious surface fractions occurred in 4 district of Istanbul that are Atasehir, Bagcilar, Basaksehir and Esenyurt. Some of these districts like Atasehir, Basaksehir and Esenyurt are known as new urbanization areas of Istanbul with highest population increase rate.

The V-I-S model was also utilized for these 4 districts using the components of LSMA results to determine the direction of impervious surface change at end-member level. As seen in Figure 4, from 1984 to 2017, the ratio of fractions converge on upper left side of the ternary diagram. This states that, the ratio of impervious fractions increases as the vegetation cover decrease in these districts.

![Image](image_url)

**FIGURE 4**

VIS Model of 4 districts, (1) Atasehir, (2) Bagcilar (3) Basaksehir, (4) Esenyurt

The results of LST maps show that, mean LST values of Istanbul ranges from 297 °K to 306 °K and 307°K to 323°K respectively in 1984 and 2017. The temperature changes especially in 16 districts vary from 16°K to 20°K. These districts are mainly
known as new residential areas that have a rapid urbanization and population growth rates.

**Correlation Analysis of LST with NDVI and NDBI.** In addition to land cover classification and LSMA analysis, NDVI and NDBI algorithms were utilized on the images to evaluate the relationship between impervious surface - vegetation cover distribution and land surface temperatures [29]. For this purpose, correlation and regression analysis between the LST and NDVI - NDBI were performed taking the 1984 dataset as reference. The relationship between LST, NDVI and NDBI images were determined by use of randomly distributed 300 points. The scatter plots of NDVI vs LST, NDBI vs LST and the linear regression models are given in Figure 5. As seen in figure, fitted linear regression models satisfy correlation between NDVI and LST ($r^2 = 0.732$) and correlation between NDBI and LST ($r^2 = 0.7528$). From these results, it can be asserted that, land surface temperatures tend to negatively correlate with NDVI, while positively correlate with NDBI values.

![Figure 5](image)

**FIGURE 5**
Relationship between normalized indices and mean LST for 1984 (a) NDVI vs LST, (b) NDBI vs LST

**CONCLUSION**

In this study, multispectral and TIR bands of Landsat 5 TM and Landsat 8 OLI satellite images were used to derive the land cover maps, LSMA fraction maps, NDVI, NDBI maps and LST maps to analyze the urban land cover changes and their impacts to land surface temperatures in Istanbul between 1984 and 2017.

The results indicates that, in parallel to rapid population and economic growth in Turkey, urbanization in Istanbul metropolitan increased dramatically with an annual rate of 4.59% during 33 years of period. The increase in urban areas in 33 years covers 16% of the total study area. This urbanization resulted with a significant decrease in surrounding semi-natural areas and forest areas especially in the northern parts of the city, which will most probably lead environmental problems in the near future. The V-I-S model derived from LSMA also shows that, the increase in impervious areas match up with the results of land cover maps. The zonal analysis of LST maps along with LSMA fractions in district level reveals that the highest mean LST differences ranging from 16°K to 20°K occurs in districts which are also known as new residential areas, where the impervious fractions increase more than 50 percent. These results reveals that, mean LST values increase with the expansion of urban areas. Additionally, the negative correlation between NDVI and LST, and positive correlation between NDBI and LST indicates that the vegetation cover causes decrease in land surface temperatures.

With its spatial and temporal resolution features and continuous data availability, remote sensing technology provided a great opportunity in exploration of urban process and monitoring the impacts on environment. In this study, the determination of land cover changes in Istanbul metropolitan area and its influences on urban land surface temperatures could be investigated using multi-temporal satellite remote sensing data. The results of this study will provide a baseline for further urbanization investigations about Istanbul.

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ABSTRACT
This study aimed at introducing the efficiency of the health services in Turkey by providing province-based analysis using Geographic Information System (GIS) technology. In this context, quantitative data, derived from official health reports published by Turkish Ministry of Health, for the years 2001, 2007 and 2015, were evaluated. Stated data included indicators of the delivery of health services as number of hospitals (private and state hospitals) and their bed capacity, number of the employee in charge (specialist and practicing physicians and allied health personnel). Additionally, infant and child mortality data was considered as criteria for evaluating the efficiency of the health services by province. Thematic maps presenting spatial distribution and density of the provided services were produced through GIS and these maps were interpreted in order to evaluate the efficiency of health services. This study resulted that, as expected, the health services are in better conditions at the central and western regions of Turkey with respect to eastern regions. Compatibly, infant mortality rate was also increased in the eastern regions during the study period. Province based results of the study may be considered as an input for further studies to be applied in order to improve the quality and quantity of the health services in Turkey for providing health services to all citizens on an equal basis.

KEYWORDS: Health services, GIS, quantitative analysis, open source.

INTRODUCTION
Health services, which encompass and reflect the economic conditions and socio-cultural characteristics of a country and its society, include all services dealing with the diagnosis and treatment of disease, or the promotion, maintenance and restoration of health. The World Health Organization (WHO) defines the primary health care services as personal and non-personal health services built on adequate methods and technology in a practical, scientifically sound, and socially appropriate manner universally presented to families and individuals within the community. Service provision refers to the way inputs such as supply, employee in charge, equipment and drugs are combined to allow the delivery of health interventions [1]. Improving access, coverage and quality of services depend on these key resources being available. With the adoption of the Law No. 224 on the Socialization of Health Services in 1961, providing a prosperous health system targeted in Turkey [2]. However, it is clear that, this target could not be accomplished in an inclusive manner at every part of the country, because of the disparity in social and economic conditions. Therefore, qualitative and quantitative analysis of the provided health services should be performed for minimizing the potential inequalities on receiving these services in public.

Organization and the management of the health services in countries are examined within the context of the medical geography, which uses concepts and methodologies from the geography discipline to investigate health-related topics, as well as the monitoring and the surveillance of the diseases [3-4]. Medical geography is the branch of human geography dealing with the geographic aspects of health and healthcare by executing studies on geographical distribution and causes of diseases linked with natural environment-human interactions, the percentage of population under risk, and the healthcare services available in these geographies as a whole [5]. As the whole context has direct relation with the geographic locations of the health related phenomenon, the widespread use of Geographic Information Systems (GIS) technology in public health studies have been adding value to existing epidemiological researches [5-7]. GIS capabilities on analyzing spatial data and presenting information derived from the stated data as thematic maps and other works of arts promoted and increased the popularity of the technology in time [8-10].

This study basically aims to evaluate the efficiency of the health services in Turkey by providing province-based analysis using GIS technology. For this purpose, GIS based examination of the indicators on the delivery of the health services performed. For this purpose, the basic methodology was explained in the following section together with the used data and then the results of the study were explained based on the thematic maps produced by the use of GIS. Further discussions were also included in order to evaluate the provided services by considering the existing socio-economic conditions at different parts of Turkey.
MATERIALS AND METHODS

Turkey included 81 provinces located in seven geographical regions. The study covered the whole country in order to make a general, province based, evaluation of the health services. In this context, spatial and tabular (semantic) data were used as indicated in the methodology flowchart presented in Figure 1.

Geometric data used in the study included vector geometries of provinces and the other reference data as polygons representing waterbodies and neighboring countries. The quantitative health data by province for the years 2001, 2007 and 2015 was used together with the census data of selected years. The health data compiled from official health reports published by Turkish Ministry of Health and included indicators of the delivery of health services as:

- number of hospitals by type (private and state hospitals),
- bed capacity of hospitals,
- number of employee in charge (specialist and practicing physicians and allied health personnel).

The number of the infant deaths by gender and child deaths classified in three age groups (0-4, 5-9, 10-14) were also considered as another indicator for evaluating the efficiency of the health services in Turkey.

Figure 1 presented the methodology of the study in three main steps: Data collection, data analysis and interpretation of the results. In the first step of the methodology, the acquired geometric and tabular data integrated in to a GIS database for the use of GIS analyses to be applied. In order to perform substantive evaluations based on the input data, rates of changes in selected health indicators was determined as percentage values for the study periods 2001-2007 and 2007-2015.

For this purpose the following equation was used in order to determine province based increase rates in the number of hospitals and employee in charge.

$$\frac{x_{t2} - x_{t1}}{x_{t1}} \times 100$$ (1)

where $x_{t2}$ and $x_{t1}$ represent the assigned values of the examined indicator at the end and beginning of the analysis period respectively.

Additionally, mortality rates of the infants and the children were calculated per 10000 capita. In the second step of the methodology, thematic maps providing quantitative information of the health services were produced using data analysis and visualization tools of GIS. In the final step, stated maps used after a detailed examination for the interpretation of the changes observed during the study period in health services.

RESULTS AND DISCUSSION

Changes in the quantity and the quality of the public health services were evaluated in this study by analyzing spatial distribution and the temporal changes of selected health indicators. Province based analysis applied for each indicator resulted with thematic maps.

Interpretation of the data and thematic maps presenting temporal and spatial variations in the number of hospitals by province outlined that the average numbers of hospitals per province were 15, 16 and 19 in 2001, 2007 and 2015 respectively. The map in Figure 2 presented total increase rates in the number of hospitals from 2001 to 2015 and changes by period as bar chart. Based on the map, although the average number of the hospitals increased in most of the provinces during the study periods, significant decrements in the numbers of hospitals were observed in some provinces as Nevşehir, Kırşehir, Edirne, Kırklareli, Rize, Kastamonu, Karabük and etc. In this context, the most significant decrease observed in Nevşehir. Based on the annual reports officially published, in 14 years’ time 4 of 10 hospitals were closed in the city. On the other hand, Yalova had the highest increase rate with 500% increment because although there was only 1 state hospital in 2001, private hospitals established in the city and the total number of the hospitals reached at 6 during the study period. Additionally, the second highest increase rate for the same period was 300% observed in Iğdır. When the results were evaluated by geographic region; beside the increments in the numbers of hospitals throughout the country, total numbers of the hospitals were still below the country average in most parts of Western Black Sea, Eastern Anatolia and Southeastern Anatolia regions.

The other indicator considered for evaluating the efficiency of the hospitals was the bed capacity of hospitals. In the study, the number of beds per
10,000 population was examined and according to results, Iğdır, Ağrı, Muş, Şanlıurfa, Mardin, Şırnak, Hakkari had the lowest values for 15 years compared to the other provinces. The increase rate in the number of the beds in hospitals was compatible to the rate of the number of the hospitals as expected. Significant decrement observed in Artvin and Kastamonu as the number of the hospitals decreased drastically during the period.

Sufficient number of physicians ensures fast, efficient and comfortable delivery of health services [11]. Therefore, the number of the physicians (specialist and general practitioner) and the number of people per physician were the other indicators examined for the efficiency assessment of the health services within the study. Figure 3 and Figure 4 presented the maps produced for the years 2001 and 2015 respectively. The study outlined that total number of physicians increased by about 60%. However, the number of the physicians were not sufficient in the provinces with lesser population especially in the year of 2001. As presented in the Figure 3, total population per physician was significantly higher in Eastern parts of Turkey than the Central and Western regions. When maps presented in Figure 3 and Figure 4 compared, it is introduced that health services improved in terms of the number of physicians during the study period and in 2015 most of the provinces were in better conditions with respect to the conditions in 2001. In addition to number of physicians, the number of health personnel, nurses and midwives were examined as health officers in the study because the health service is a teamwork and the qualification and the skills of the team members are very important for providing efficient service to public [12]. Figure 5 presented the increase rate of the health officers by province during the study period. As presented in the figure, total number of health officers increased with higher rates in South-eastern regions in Turkey. Istanbul had the similar increase with the highest value within western provinces.
As the final indicator, data on infant and children mortality were examined, because these parameters have been acknowledged as the crucial indicators that reflect the quality of the health care delivery system and progress of the country in terms of health services [13-14]. Examination of the infant mortality data resulted that the mortality rates in big cities as İzmir, Eskişehir, Adana, Gaziantep and Ankara were high in 2001. Although the rates reduced in most provinces by the year 2007, they significantly increased in especially southeastern part of Turkey.

Figure 6 presented the map showing the increase of the infant mortality during the study period in Turkey. As indicated in the map, while no increase in infant mortality observed in Bolu, Zonguldak, Karabük, Gümüşhane, Erzincan and Iğdır, Muş and Şırnak were the provinces with highest increases in infant mortality. Although a significant decrease in infant mortality was observed in İzmir, a slight increase was seen in other provinces located in Aegean Region at the Western part of Turkey. Other provinces with significant decrement in infant mortality were Edirne, Eskişehir, Ankara, Kırıkkale, Kastamonu, Samsun, Malatya, Tunceli and Adana. As stated by Kormaz et al., the infant mortality in Turkey is basically originated by neonatal mortality, which is mainly caused by prematurity and its complications. In order to achieve a further decline in the infant mortality rate, preterm births should be decreased or prevented in the future [15]. Similar results were also observed for the children mortality as a result of the study as presented in Figure 7. In general, although the number of children deaths has declined during the first study period (2001-2007), it has risen in the second study period from 2007 to 2015. The increases were significantly higher in Regions of Southeast Anatolia and Eastern Anatolia than the other regions. As stated in references, inadequate vaccination, diarrhea, measles [16].
inadequate antibiotic use, malnutrition and, most importantly, lack of education are among the causes of child mortality [17-18]. Therefore the provincial health directorates should plan and perform studies for raising awareness of the society especially in provinces where children and infant deaths are high.

CONCLUSION

In this study, quantitative evaluations of the health services were performed and substantial results were presented. The study introduced that most of the health services in Turkey provided by public hospitals. Although there is a significant improvement in providing services and qualified personnel, the study presented the unsatisfactory results in overall. In particularly, the increase in infant and children mortality in some regions of the country is a significant problem that should be addressed as a priority. This result shows that in addition to improving general practices, the quality and quantity of health services delivered during prenatal and postnatal periods should be increased, especially in the provinces with increasing infant and children mortality rates. Measures should be taken in these provinces by observing the growing conditions of the provinces with decrement in children and infant mortality.

As a conclusion of the study, although a significant improve on the quantity of the health services were observed in Turkey during the study period from 2001 to 2015, significant inequities in providing health services were also seen within the geographic regions. In order to overcome these inequities, the quality and quantity of the health services
should be improved in Eastern and Southeastern regions of Turkey. In addition to improving the quality and the quality of the health services, people living in these regions should also be supported by intensive education programs in order to decrease the infant and children mortality. However, because of the limited data availability, this study considered a limited part of the indicators to be analyzed in the assessment of the quality and quantity of the health services. Therefore, additional parameters should be taken into account to make a more detailed and precise evaluation of the health services in Turkey.

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GEOGRAPHIC DISTRIBUTION AND EXPANSION OF HEPATITIS A AND A DYSENTERY CASES IN BLACK SEA CATCHMENT REGION IN TURKEY

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ABSTRACT

This paper focused on the investigation and mapping of water-related communicable diseases in the Black Sea Catchment area in Turkey by using Geographical Information System (GIS) technology. The official health statistics on Hepatitis-A and Amebic Dysentery from 2000 to 2009 were investigated and evaluated considering the incidence rates. Epidemic, hyper-endemic and endemic thresholds were set regarding the general trends of the incidence rates for both diseases. Time series maps were created to introduce the variation of the incidence rates using GIS. Results interpreting the thematic maps were confirmed with the Mann Whitney U Test statistical analysis and the Spearman correlation analysis. A significant and slight descending trend for Hepatitis A and A Dysentery was detected in the observation period. 16 provinces were assigned as high or low risk-areas regarding the epidemic potential. The downward trend observed could be explained as a result of the wide spread application of best water treatment technologies within the acquisition period for European Union.

KEYWORDS:
Spatial epidemiology, GIS, A Dysentery, Hepatitis A, health statistics, geographic distribution

INTRODUCTION

Epidemiology is the “scientific study of the distribution and determinants of disease frequency”, having three interconnected dimensions: Frequency, distribution, determinants [1, 2].

Frequency of a disease determined on the basis of incidence rate is an important parameter for monitoring the illness and determining the threshold values of endemic or epidemic characteristics. The threshold values are usually considered as the numbers of cases in a certain period beyond a predetermined value [3]. The attainment of a threshold should be recognized as a signal of an outbreak and should activate specific measures in epidemiology. The thresholds are generally set with case-specific provisions mostly depending on the local epidemiology and immunization programs.

The simplest method to determine the threshold values among several methods [4] relies on the visual inspection of the historical data [5].

Different studies on epidemiological investigation have been conducted to provide an integrated approach for disease control and surveillance at local, regional and national levels using GIS technology [6-10]. Alkoy et al. benefited from the capabilities of the GIS technology to determine the epidemiological aspects of air pollution [11]. The spatio-temporal patterns of dengue infection and chikungunya fever appeared in Taiwan were analyzed using GIS [12]. Similarly, spatial patterns of the Hepatitis A cases in Children in Turkey were also examined using geostatistical tools of GIS [13]. Ballas et al. performed health inequity analysis and spatial microsimulation by the use of GIS [14], whereas Alkoy et al. integrated GIS technology with quality assurance sampling methodology for monitoring vaccination coverage in Istanbul [15]. Oakes et al. proposed the use of administrative health care system records for community based population research [16]. All these studies confirmed the convenience of the GIS application in epidemiology.

The objective of this study is to explore the epidemic process of Amebic (A) Dysentery (Amebiasis) and Hepatitis A by analyzing the geographic distribution and expansion in Black Sea Catchment, Turkey in the period of 2000-2009. GIS was used as the technology to outline the spatial distribution and expansion of these waterborne communicable diseases. Health statistics were applied to confirm the GIS results for the use of decision makers and to create the required capacity to take measures on environmental, social and economic issues at stake [17, 18].

DATA AND METHODOLOGY

The study focused on the Black Sea Catchment (BSC) region in Turkey. The BSC catchment area...
covered 41 (Afyon, Aksaray, Amasya, Ankara, Ardahan, Artvin, Bartın, Bayburt, Bilecik, Bolu, Bursa, Çankırı, Corum, Duzce, Erzincan, Erzurum, Eskişehir, Giresun, Gumushane, İstanbul, Karabük, Kastamonu, Kayseri, Kirikkale, Kırklareli, Kırşehir, Konya, Kütahya, Kocaeli, Nevşehir, Ordu, Rize, Sakarya, Samsun, Sinop, Sivas, Tokat, Trabzon, Usak, Yozgat, and Zonguldak) among 81 provinces in accordance with the ENVIROGRIDS Project. An overview of the whole BSC territory including the study area is presented in Fig. 1.

**FIGURE 1**
Study Area in the Black Sea Catchment

The geographic distribution and the expansion of selected waterborne diseases were analyzed using relevant semantic and geometric data to introduce spatial characteristics of the diseases. The contextual data covered both health and census data of the provinces. The Turkish Ministry of Health officially provided the health data, for a period of 115 months starting from January 2000 to July 2009. The data on case numbers and deaths of the diseases were monthly gathered by the local health authorities and stored in the public health surveillance system. Census data were also obtained from the Turkish Statistical Institute (TSI) for the years 2000 and 2007–2010 to make an accurate interpretation.

Geometric data used for mapping were the vector data covering the administrative boundaries of 81 provinces in Turkey. The interconnection with the reference information in thematic maps was provided by using the vector data of neighboring countries and significant natural lakes in Turkey. The Universal Transversal Mercator (UTM) coordinate system defined for the zone 37 was applied and the World Geodetic System 1984 (WGS84) was selected as geographic reference.

The methodology applied in this study was illustrated in Fig. 2. As seen from the flowchart, raw data including the health and the census data were firstly used for determining the annual incidence rates of the Hepatitis A and A Dysentery cases. Annual incidence rates were then visualized as line graphs for studying the temporal trends of the diseases for a period of 10 years. Visual analysis was performed as a beneficiary tool to set the thresholds as endemic, hyper endemic or epidemic regarding the annual occurrences of the diseases. The thresholds were determined to identify the risk levels with high or low occurrence ranks in the provinces. A GIS database supported by SQL Server 2008 was established for storing, organizing and analyzing the data. GIS application was implemented using ArcGIS 10.x software for mapping and identification of the sensitive provinces based on time series maps. Health statistic procedures were also applied to confirm the results obtained by GIS technology.

Annual incidence rates of Hepatitis A and A Dysentery cases were calculated in each province. The incidence rates defining the number of new cases for a given time period [2] were calculated per 100,000 people for each province using Eq. (1):

$$ \text{Incidence rate} = \frac{\text{total number of cases}}{\text{total population at risk}} \times 100000 \quad (1) $$

The census data based on total population (2000, 2007–2010) provided by TSI were used for the estimation of the population for the years of 2000–2007 using the geometrical increase method as presented in Eq. 2:

$$ N_t = N_0 \times (1 + p)^t \quad (2) $$

where $N_t$ is the population at time $t$, $N_0$ is the initial population, $p$ is the growth rate, and $t$ is the time period.
Where;
N_t: population at the end of the study period,
N_0: population at the beginning of the study period,
P: yearly growth rate of the population [%],
t: number of years of the study period.

Threshold values were set following the temporal trends of the diseases in each province, as stated by WHO [3]. In this context, the reports on annual incidence rates were reviewed from previous years (115 months, or approximately a 10-year period) to determine the threshold values. The stable incidence rate was considered as the threshold between endemic and hyper-endemic levels. The incidence rate rarely exceeded was assumed as the threshold between hyper-endemic and epidemic levels. The endemic level was stated as the level of the lowest risk of disease occurrence, while hyper-endemic and epidemic levels were fixed as the highest risks of disease occurrence.

GIS technology was used for the production of the temporal distribution maps for selected illnesses. Vector data imported into a GIS environment were linked with the tabular data including annual incidences of diseases. Classification tools were exercised to classify and geographically visualize the data depending on the determined thresholds. Each class was visualized by using the value of the graduated color, representing the endemic, hyper-endemic, and epidemic levels. Consequently, time series maps were created for determining the timely changes in incidence rates.

The analysis of the incidence rates was conducted by applying Kolmogorov Smirnov Test on the epidemiological data. This test showed that the data was not in compliance with normal distribution. The study was continued with Mann Whitney U Test and Spearman correlation method to provide statistical justification of the incidences assigned as high risk and low risk of disease occurrence [19]. Spearman Correlation Analysis was also applied to three different data sets covering the study area (41 provinces), provinces out of the study area (40 provinces) and the entire country (81 provinces) to provide an extensive evaluation of the correlation between incidence rates and time [20-22].

RESULTS AND DISCUSSION

The incidence rates of the diseases were assessed by considering their temporal trends. The evaluation indicated that in 21 provinces the incidence rates of A Dysentery were fluctuating between 0-20 per hundred thousand people. In the rest, a much higher tendency in a wider range (0-120 per hundred thousand people) was noticed exceeding 20 at least once.

A similar temporal trend was also detected for Hepatitis A. The incidence rate, 10 per hundred thousand, was endemic for both diseases during the study period. This tendency has been used to score the common thresholds for both diseases as: <10 for endemic, 10 to 20 for hyper-endemic and > 20 for epidemic occurrence levels.

A detailed investigation on particular provinces yielded that Istanbul and Bayburt reflected endemic characteristics, whereas Kastamonu and Kutahya exposed higher incidence rates as illustrated in Fig. 3. The incidence rates at epidemic levels demonstrated a strong decreasing tendency until 2003, but an increasing trend after 2003 in Kastamonu and Kutahya. The increase continued approximately until 2007 in both provinces, but dropped immediately after 2007 in Kutahya and a year after in Kastamonu. The lower incidence rates were observed in 2009 for both provinces.

FIGURE 3
Annual incidences of A Dysentery in İstanbul, Bayburt, Kastamonu, and Kutahya
Time series maps indicating yearly geographic distribution of Hepatitis A and A Dysentery were designed as choropleth maps. These maps presented the incidence rates of the diseases in three main classes based on determined threshold values. The maps for Hepatitis A presented in Fig. 4 illustrated a downward tendency in incidence rates, although the number of epidemic provinces significantly increased in 2005 and 2007. A Dysentery revealed a different tendency; having a significant decrease in the number of epidemic provinces after 2007, the lowest numbers of epidemic provinces also drawn the attention for the years of 2002 and 2003.

Provinces with stable trends of being hyper-endemic and epidemic were considered at the high-risk level, whereas being endemic was identified as low-risk. The evaluation of the results yielded Kastamonu, Nevşehir, Kutahya, Ordu, Bayburt, Ardahan, Rize, and Kırklareli as high risk-provinces, on the contrary Istanbul, Bilecik, Kayseri, Giresun, Tokat, Afyon, Eskisehir, and Artvin as low risk-provinces.

**FIGURE 4**
Temporal and spatial changes in incidence rates of Hepatitis A in Turkey, 2000–2009
Statistical evaluation based on Mann Whitney U Test ($U = 0.000, p < 0.001$) indicated a significant difference in incidence rates between high and low risk levels for Hepatitis A. The mean rank of the incidence rates for high-risk provinces was calculated as 226.50, a value lower than the one obtained for low-risk provinces (Table 1). The significant difference between the mean rank values confirmed the preciseness of the risk levels classification.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Mean Rank</th>
<th>U</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Risk</td>
<td>226.50</td>
<td>0.000</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Low Risk</td>
<td>631.50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The same statistical analysis considering A Dysentery ($U = 0.000, p < 0.001$) revealed a significant difference in incidence rates between high and low risk level provinces. As given in Table 2, mean rank of the incidence rates was calculated as 649.00 for high-risk provinces, a much higher value than the calculated mean rank for low-risk provinces. This significant difference between the mean ranks again confirmed the assignment accuracy of risk levels.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Mean Rank</th>
<th>U</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Risk</td>
<td>649.00</td>
<td>0.000</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Low Risk</td>
<td>244.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Spearman Correlation Analysis applied for the assessment of temporal changes in incidence rates presented a significant inverse correlation between time and incidence rates for three different data set as outlined in Table 3.

<table>
<thead>
<tr>
<th>Coverage</th>
<th>rs</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entire country</td>
<td>-0.215</td>
<td>0.01</td>
</tr>
<tr>
<td>Provinces located out of the study area</td>
<td>-0.118</td>
<td>0.05</td>
</tr>
<tr>
<td>Provinces located in the study area</td>
<td>-0.434</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The results focusing on the provinces in the study area ended up with a weak correlation (rs) reflecting even weaker correlation for the entire country and outside the study area components. Consequently, the weak correlation indicated that the incidence rates of Hepatitis A had a descending trend from 2000 to 2009. This was also confirmed by the examination of the thematic maps presented in Fig. 4. The results of the Spearman Correlation Analysis of A Dysentery similarly outlined a weak correlation between time and incidence rates for the entire country and provinces out of the study area, on the contrary no significant inverse correlation was observed between time and incidence rates for provinces located in the study area.

## CONCLUSIONS

The scientific evidence summarized in the above sections clearly reveals that the geographic distribution and expansion of Amobic (A) Dysentery and Hepatitis A indicated a number of sensitive provinces with high and low risk of epidemics between 2000 and 2009 in Black Sea Catchment region of Turkey. A significant and downward trend in the incidence of the Hepatitis A and A Dysentery were resolved using health statistics and GIS studies. This downward trend in occurrence of waterborne diseases could be explained by the wide spread application of best water treatment technologies within the acquisition period for European Union.

This study confirms that GIS technology provides an efficient tool for end users at any level and decision makers by visualizing the results more understandable in thematic maps, although statistical results are considered more useful and understandable by the end users at expert level. Time series maps clearly represent the timely fluctuation of the diseases and increase users’ spatial cognition.

This study should be considered as one of the significant researches covering a large area among the existing studies particularly on the epidemiology of Hepatitis A in Turkey at local levels. The results could be improved by integrating accurate data for water quality and quantity with the expectation of having all the data publicly available. The data will greatly contribute to create the potential relationship between epidemic diseases and water quality and quantity.

## ACKNOWLEDGEMENTS

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MAPPING HAZELNUT TREES FROM HIGH RESOLUTION DIGITAL ORTHOPHOTO MAPS: A QUANTITATIVE COMPARISON OF AN OBJECT AND A PIXEL BASED APPROACHES

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ABSTRACT

This study investigates the suitability of object- and pixel-based approaches for extraction of hazelnut trees from high resolution digital orthophoto maps. For object-based approach, simple linear iterative clustering (SLIC) method was employed to segment image pixels into homogeneous regions. Features spanning spectral, spatial and textural domains were extracted from each segment then classification was performed by employing support vector machine (SVM) classifier. For pixel-based approach, the spectral reflectance information from all four bands were used as features and applied maximum likelihood (ML) classifier for classification of each pixel into hazelnut and other tree species classes. An area-based approach was used to evaluate the performance of the proposed method. The experiments showed that overall classification accuracy for object-based method was superior to the pixel-based method. Using object-based approach the overall accuracy obtained was 86% while pixel-based approach scored 76%.

KEYWORDS:
Tree species classification, simple linear iterative clustering, support vector machine, maximum likelihood

INTRODUCTION

Photogrammetric methods offer powerful tools, which can be exploited for mapping vegetation information over large geographic areas. The obtained information, such as tree species distribution, can play a vital role for applications related to forestry and agriculture. High resolution images containing such information content can be obtained with varying spectral, spatial, and temporal information using various sensors, including space borne, airborne, and drone-based [1]. Due to diversity of data sources, a method developed for one type of data may not produce optimal results for others. Therefore, it remains challenging to obtain best results on such diverse datasets. However, consistent efforts are being made, especially in last few decades, to develop new techniques that could benefit from data with higher spatial and temporal resolutions.

The recent advancements in the imaging technology has made it possible to examine tree species distribution over large geographic areas in fine details [2]. To exploit such detailed information, pixel-based methods rely on individual pixel values regardless of its neighborhood. A number of studies have investigated such methods for classification of remote sensing data [3 - 4]. For instance, [5] used a pixel-based approach and compared the performance of three non-parametric classifiers — SVM, artificial neural network (ANN), and random forest (RF), for tree species extraction and land cover/use classification from high resolution digital orthophoto maps. Similarly, a pixel-based method is integrated with SVM and ML classifiers for land cover classification in [6]. In [7] authors proposed to combine a pixel-based method with a probabilistic SVM for classification of hyperspectral images. Furthermore, by incorporating features spanning both spectral and textural domains they improved classification accuracy. Similarly, [8] employed RF classifier for delineation of ten tree species from Worldview-2 data using both object- and pixel-based approaches.

Although, each pixel provides vital information, however, grouping spectrally similar pixels in the vicinity may provide more semantics for real word object representation. In addition, inter-class spectral variations and intra-class spectral similarity pose more challenges for pixel-based approaches.

To cope with such situations, there has been more focus on geographic object-based image analysis (GOBIA), which has now become a new paradigm for remote sensing data analysis [9]. It not only reduces the semantic gaps of pixel-based approaches by incorporating the spatial relationship among pixels but also offers a natural representation of real world objects in images. This representation allows to extract more complex features which cannot be captured using individual pixels, such as structural, geometrical, and shape information [10]. These convenient features make object-based approaches first choice for image analysis for remote sensing data.
and often produce good classification results as compared to traditional approaches (pixel-based) [8]. For instance, [11] employed an object-based image analysis technique with RF classifier for classification of four tree species obtained from unmanned aerial vehicle (UAV) from Ontario, Canada. Similarly, [12] applied an object-based method for classification of land cover classes and species types for data obtained from three different multispectral cameras mounted on a UAV.

Machine learning approaches have been widely used for classification of remote sensing data due to their diversity and robustness. Most widely used classifiers include SVM [7], ANN [13], RF [14]. In this study, SVM has been used for classification as it is robust and has proved to show good performance even in presence of low training samples[15].

To the best of our knowledge, no method has been evaluated to date for extraction of hazelnut tree species from high-resolution digital orthophoto maps. Therefore, the focus of this study is to investigate the suitability of object- and pixel-based approaches for hazelnut tree species extraction with minimal human interventions from high resolution imagery data. The objectives of this study are multifold: 1) investigate applicability of pixel-based approach using ML, 2) examine efficiency of object-based approach with SVM classifier, 3) study effect of feature selection on classification accuracy for both approach and 4) perform comparative analysis of both methods using an area–based evaluation approach.

MATERIALS

The study area is situated in the central district of Giresun province located in the Northeastern part of Turkey which is known for high quality hazelnut production. Apart from vegetation, impervious surfaces and bare land could also be seen in the captured images. Figure 1 shows map of Giresun province and Turkey.

The data set used in this study consisted of ten high-resolution digital orthophoto maps, which were acquired using Ultracam-X digital camera mounted on an airplane on 06-04-2013. Since the overall atmospheric and weather conditions were similar throughout the capturing time, the images characterize similar spectral reflectance for objects of interest. The end and side laps were set to 70 % and 30 % respectively. The raw images were processed by EMI Group Inc. and delivered the final product as digital orthophoto maps along with their ground truth data for further analysis. Photogrammetric evaluated results have been converted into binary image to be used as a reference data. Figure 2 a) shows a whole sample image while b) shows its reference image for hazelnut trees in white while background in black color.

![Map of Giresun Province and Turkey](image)

**FIGURE 1**

Map of Giresun Province and Turkey

![A whole sample image Reference image](image)

**FIGURE 2**

a) A whole sample image b) Reference image

METHODOLOGY

The input images were first preprocessed to reduce noise before proceeding to other steps. The source of noise in images can be attributed to various factors affecting the capturing process such as sensor errors, illumination differences, camera angels etc. Therefore, it is convenient to reduce the effect of noise before proceeding to other steps. To achieve this objective, each band of the multispectral image was convolved with a Gaussian low pass filter of size 5x5. The net effect of the filter was so that it reduced undesirable elements such as salt and pepper noise from local neighbourhood.

The preprocessing step was then followed by features extraction step for pixel-based method. However, for object-based approach, images were segmented into homogeneous regions first and then features were derived from each segment. The segmentation procedure is described in following section.

**Simple Linear Iterative Clustering:** Image segmentation is fundamental task in object-based image analysis. Although, there is no general rule of
thumb for selection of a segmentation algorithm, however, an algorithm with good accuracy is highly desirable. For current study, SLIC algorithm was selected since it is efficient and easy to implement with low computational overhead [16]. In addition, fine-tuning SLIC is relatively simple, as it requires tuning of only one parameter, i.e. the number of superpixels (N). SLIC is based on localized k-means algorithm that first divides the whole image into N-segments and then apply k-means algorithm on each segment separately to form superpixels. Optionally, it also merges smaller segments in the close neighbourhood whose size are less than a predefined threshold value. A detailed description about the mathematical background of superpixels can be found in [16].

To select an optimal value for N, experiments were repeated several times until satisfactory results were obtained. A smaller value of N resulted in segments with larger size, which were more prone to errors especially towards the object boundaries. Therefore, relatively a larger value of N was selected which produced higher number of superpixels but they were highly homogeneous. An optional merging step was also included to merge objects based on spectral consistency and geometrical constraints. Two neighboring objects O_i and O_j were merged when the absolute difference between their mean values was less than a predefined threshold value T:

\[ O_i = \begin{cases} 
1 & \mid \mu_{oi} - \mu_{o\bar{j}} \mid \geq T \\
0 & \text{else} 
\end{cases} \]

Where \( \mu_{oi} \) and \( \mu_{o\bar{j}} \) represent mean values of object \( i \) and \( j \) respectively. The value of T was empirically calculated by visually analyzing the segmentation results. Figure 3 a) shows a portion of a sample image obtained by setting \( N=10,000 \) while b) shows results for \( N=100,000 \). It is obvious that a smaller value of N produced superpixels with relatively larger size. In some cases, it resulted in over segmentation and encapsulated even some parts of both vegetation and non-vegetation areas into one object. This issue was resolved by selecting a larger value of N. As shown in b), the size of resulting superpixels is relatively small yet they represent pure objects with some exceptions. The idea is to produce objects with sheer homogeneity.

**Feature extraction:** The purpose of feature extraction is to transforms the input data into such a representation (feature space) that machine learning algorithms can be applied on them. These features should be informative and non-redundant for obtaining good classification results [17]. The most widely used are spatial, spectral and textural features for remote sensing data classification. Many pattern recognition applications reported higher classification accuracies for these set of features (e.g. [7], [18]). Therefore, this study also adopted these features for hazelnut tree species extraction.

To encode spectral and spatial information, mean and standard deviation were calculated. These features were directly derived from gray values in each band of orthophoto images. However, texture features were derived using grayscale co-occurrence matrix (GLCM). Entropy, homogeneity, contrast, and angular second moment were selected as texture features as they have widely been used in the literature. GLCM can be constructed for a two dimensional data, therefore, for each segment an image was constructed by cropping the multispectral image using it bounding box. The resulting rectangular object image had some extra pixels as objects were not perfect rectangles. These pixels were considered background and their values were set to zero. It was observed that the additional background pixels had little effect on the quality of features extracted, since the ratio of background to foreground pixels within object image was very small as compared to object size. For pixel-based approach, however, the texture features were extracted by scanning the image with a small window of size 11 x 11.

![FIGURE 3](image)

**FIGURE 3**

SLIC results for different number of superpixels (N) a) N=10k b) N=100k

**Spectral Separability Analysis:** Generally, apart from other factors, the accuracy of any classifier depends on quality of features used for classification. Hence, features with great discrimination power are highly desirable. It is beneficial to evaluate the separability between features to assess if they provide valuable information that can be used to distinguish between classes of interest. Therefore, an investigation of discrimination power of features is imperative to achieve good classification accuracy. The objective is to remove non-informative or redundant features from the feature set [19].

In this study, forward sequential search was applied on features and Jeffries-Matusita (JM) statistical distance, which is related to the Chernoff upper bound in the Bayesian error [20], was employed as separability criteria to decide if features are highly informative or not. JM provides the average distance between two density functions, which can be expressed according to Bhattacharyya (B_{ij}) as:

\[ JM_{ij} = \sqrt{2(1 - \exp[-B_{ij}])} \]
The $B_{ij}$ of feature vector $x$ given distributions of two classes $\omega_i$ and $\omega_j$ can be calculated as:

$$B_{ij} = -\ln \left\{ \int \frac{p(x/\omega_i)p(x/\omega_j)}{p(x)} dx \right\}$$

where $p(x/\omega_i)$ and $p(x/\omega_j)$ are conditional probability density functions for the classes $\omega_i$ and $\omega_j$, respectively for the feature vector $x$. [21].

JM returns a value in the range [0-2]. The values closer to 2 indicate high separability while values close to 0 indicate a very low spectral separability among classes [22]. For current study, the features that produced relatively higher JM distance were selected for classification.

**FIGURE 4**
Statistics measured for training samples of both hazelnut and other trees in all four bands
(a) Mean reflectance (b) Standard deviation

Further statistical measures based on mean reflectance and standard deviation were calculated to visualize the spectral differences between hazelnut and other tree species (Figure 4). It is observed that the spectral reflectance encode vital information in each band of multispectral images which can be used to discriminate tree species.

**Classification:** In this study, two supervised classifiers were used for comparative analysis: SVM for object-based method and ML classifier for pixel-based approach. SVM classifier is a robust classifier and has proven its ability to deal with large amount of data efficiently even in presence of smaller training samples [5]. During training phase, the SVM classifier constructs a hyperplane to distinguish between classes and the margin of separation is maximized by selecting an optimal number of support vectors. It is primarily designed to deal with linearly separable data; however, it can also be used to classify non-linearly separable data. In such case, the data is first transformed into a higher dimensional feature space by applying a kernel function (e.g. polynomial, radial basis function), where the data is expected to be linearly separable. SVM can then find an optimal hyperplane to distinguish among classes.

For this study, the most widely used radial basis function (RBF) kernel was used with SVM classifier. The SVM Cost (C) and kernel parameter (gamma) were obtained by applying a grid search method. For experiments, libsvm [23] with its MATLAB interface was utilized. Further details about SVM can be found in [24].

For classification at pixel-level, ML classifier was selected as it has widely been used for tree species extraction from remote sensing data (e.g. [25], [26]). ML classifies a pixel into the corresponding class based on its maximum likelihood, which is defined by its posterior probability. It assumes that the data has a normal distribution and computes mean vector and covariance matrix for each class during training. It then computes the statistical probability of the pixel and assigns to the class with highest likelihood. The ML classifier was implemented in MATLAB platform. The obtained features (described in previous section) were prepared such that they can be used by classifier for classification. Given k-dimensional features with N labels, the training dataset was created by pairing each feature vector with corresponding label $(x_i, y_i)$, where $x \in \mathbb{R}^N$ and $y \in \{-1, +1\}$. In this study, other tree species were labelled as -1 while hazelnut trees were labeled as +1. The objective of classification method is to assign one of the labels defined in $Y$ to the test data.

A post-processing step was applied on the final classification map for both methods to omit the uneven patches and to improve the detection rate. Normalized difference vegetation index (NDVI) and normalized difference water index (NDWI) were applied to remove the non-vegetation and water bodies respectively. In addition, geometrical constraints were applied to remove isolated small regions and morphological opening operator was applied to fill small gaps within possible tree regions.

**RESULTS**

Experiments were performed on a dataset consisting of ten high resolution digital orthophoto maps. First, the data was prepared for training the
classifiers that was obtained from five randomly selected orthophoto maps. The objective was to utilize fewer number of images to obtained training samples and test on whole dataset. In addition, a fraction (~3% - 5%) of data was selected as training data for both object- and pixel-based methods. This simulates a real-world scenario where the availability of training data could be limited. For object-based method, total 525,868 superpixels were generated using SLIC for whole dataset out of which 4.3% (22,571) superpixels were selected as training samples. These training samples comprised of 60% (13,696) hazelnut while 40% (9,055) other tree species. Similarly, for pixel-based approach, 19,753,171 pixels were selected as training samples out of total 658,439,040 pixels, 59% (11,654,371) sample pixels representing hazelnut while 41% (8,098,800) pixels representing other tree species. The proposed method was evaluated using precision (P), recall (R), F-measure (FM), overall accuracy (OA) and Kappa coefficient (KC).

Table 1 summarizes the classification accuracy obtained for object- and pixel-based method. For the object-based method, the overall accuracy was 86%. The calculated Kappa coefficient was 0.75. The obtained precision, recall and f-measure were 84.46%, 82.97%, and 83.62% respectively. Similarly, for pixel-based approach, the overall accuracy was 75.63% and Kappa coefficient was 0.62. While, precision remained 73.13%, recall was 79.10% and f-measure was calculated as 75.49%. Obviously, the object-based method produced more conclusive results as compare to the pixel-based approach.

The thematic maps generated for hazelnut tree species were compared with the reference data using an area-based evaluation approach. Since, the reference data was available for hazelnut trees only, therefore, proposed method also produced binary maps for evaluation. Comparisons were made individually for each predicted map and its respective ground truth data. The process was repeated on whole dataset and the overall accuracy for both methods was obtained by averaging the accuracies for all maps.

Errors in the overall accuracy were mostly caused in areas where it was difficult to distinguish between spectral reflectance of hazelnut and other types of trees. The pixel-based method reported more errors compared to the objet-based method. This is reflected in the overall accuracy as object-based approach produced higher overall accuracy (85.99%) which is about 8%-10% higher than the pixel-based approach (75.63%). Figure 5 shows the final results obtained using both methods for a sample image, a) is a whole sample image, (b) shows reference image, (c) shows classification output obtained for object-based approach and (d) shows the results obtained for pixel-based approach.

### TABLE 1

<table>
<thead>
<tr>
<th>Method</th>
<th>Precision</th>
<th>Recall</th>
<th>FM</th>
<th>OA</th>
<th>KC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Object-based</td>
<td>84.46</td>
<td>82.97</td>
<td>83.6</td>
<td>85.99</td>
<td>75.6</td>
</tr>
<tr>
<td>Pixel-based</td>
<td>73.13</td>
<td>79.10</td>
<td>75.4</td>
<td>75.63</td>
<td>62.3</td>
</tr>
</tbody>
</table>

* OA: Overall Accuracy, KC: Kapa Coefficient, FM: F-Measure

### CONCLUSIONS

The main objective of this study was to find the suitability of pixel- and object-based approaches for delineation of hazelnut trees from high-resolution digital orthophoto maps obtained from Ultracam-X camera. To discriminate between hazelnut and other trees, features from texture, spectral and spatial domains were extracted. A feature selection method based on spectral analysis using JM distance measure was applied to obtain features with high discrimination power. For object-based approach, SLIC was employed for segmentation and SVM was used for classification while ML classifier was applied for pixel-based approach. Object-based method produced higher overall accuracy (86%) than pixel-based method (76%). It can be deduced from the obtained results that object-based approach and SVM combination is the most reliable method for mapping hazelnut tree species. Miss-classifications can be attributed to spectral similarity between two classes of interest. Overall, satisfactory results were obtained using object-based method and SVM. In future, we plan to consider convolutional neural network for automatic feature extraction and then classification can be performed using machine-learning classifiers to overcome the problem of manual feature selection approach.

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SESSION II
SUSTAINABLE NATURAL RESOURCE AND WASTE MANAGEMENT
THE EFFECTS OF SOME ORGANIC COMPOUNDS ON THE CATALYTIC PROPERTIES OF MnO₂ AND Mn²⁺ OXIDATION IN DRINKING WATER

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ABSTRACT

Oxidation of the manganese by atmospheric oxygen is a widely used method for drinking waters. The purpose of this study was to determine the effects of some organic substances (glutamic acid, vanillin and citric acid) on converting/stabilizing Mn²⁺ to and Mn⁴⁺.

This study has been carried out in two stages. All experiments were carried out in a condition of alkalinity; 1.2x10⁻² eq/L, pH=9.5, T=25°C, pO₂=0.21 atm, [Mn²⁺]=3 mg/L. In the first stage, catalytic effect of Mn⁴⁺ has been experimentally investigated when it’s increased up to about 400 mg/L, keeping Mn²⁺ constant at 3 mg/L with pH=9.5. In the second stage it has been studied how oxidation of Mn²⁺ and the catalytic effect of MnO₂ are affected by some organic matters. The effect of MnO₂ on Mn²⁺ oxidation in media containing organic substances (glutamic acid, vanillin and citric acid), was simulated and investigated experimentally.

In media without organic acids, MnO₂ increases the oxidation rate of Mn²⁺. When glutamic acid is added, the catalytic effect of MnO₂ clearly decreases and almost vanishes. This is considered to be a result of glutamic acid-forming complexes with MnO₂. In contrast, it is seen that vanillin does not affect the catalytic effect of MnO₂ and the oxidation rate of Mn²⁺. Citric acid slightly increases the catalytic effect of MnO₂.

KEYWORDS:
Manganese, organic compounds, catalytic effect, drinking water.

INTRODUCTION

Manganese (Mn) is one of the common constituents of surface water and underground waters. Manganese in many natural aquatic systems can exist in dissolved, colloidal and suspended forms, e.g. Mn³⁺, Mn⁴⁺ [1, 2]. In public supplies, Mn precipitates cause some difficulties and undesirable effects such as staining of clothes, increased turbidity, metallic taste, odor, colored stains on plumping fixtures [3,4]. Iron and manganese cause aesthetic problems even at low concentrations (0.05 and 0.02 respectively) [5, 6]. Furthermore, in recent years it has been determined that manganese causes neurotoxic effects [7, 8]. Manganese, even at low concentrations (0.25 mg/L), has been associated with defects in children [9]. High concentrations of manganese is often associated with organic matter of natural origin in many aquatic systems. Various oxidants are used in the oxidation of iron and manganese, such as oxygen, chlorine, ozone, or potassium permanganate. The precipitates is also removed in the sedimentation basin and sand filters [10]. One of the most widely used processes for the removal of manganese from drinking waters are oxidation of the manganese by atmospheric oxygen to the manganese(IV) [11, 12, 13]. The removal of Mn is efficiently catalyzed by, Mn(IV) dioxides in drinking water treatment [14, 15, 16].

The oxidation of manganese is affected by several factors such as Mn²⁺ and oxygen concentration, pH, temperature [17,18], organic matter [19,20] and other ions [21]. The transport and circumstances of MnO₂ colloids are affected by the surface reactions (i.e. adsorption/desorption and redox) in aquatic environments. Furthermore, surface reactivity of MnO₂, (e.g., adsorption, oxidation, and catalysis) colloids is noticeably changed by aggregation of MnO₂ colloids that come to be once they formed under certain circumstances [22, 23, 24].

The main purpose of this study is to investigate the catalytic effect of MnO₂ on oxidation of Mn²⁺, in addition, to see the effect of MnO₂ on Mn⁴⁺ oxidation in media containing organic substances experimentally.

MATERIALS AND METHODS

The oxidation of Mn²⁺ was investigated in 1 L volume batch reactors under same conditions as described before. The experimental set up is illustrated in Fig. 1. Chilern Hotplane model HS-31 magnetic stirrer was used to intensely mix the reaction vessel. NaHCO₃ was inserted into the distilled water in order to produce a solution with an alkalinity of 1.2x10⁻² eq/L. Air was given into the reactor using bubble diffusers. HACH HQ40d type of pH meter is used to measure the pH of the solution with
sensitivity of ± 0.01 pH unit. The dissolved oxygen level was monitored by a WTW oxygen meter. Immerging the reaction vessel into the water bath is done to maintain constant temperature.

**FIGURE 1**
Experimental set up

Mn²⁺ stock solution was prepared by dissolving MnSO₄·H₂O in 1 L demineralised water. During the experiment process sampling is done at planned times as measured from the start of the process were directly filtered and acidified following filtration with 1 mL of (1+4) H₂SO₄ (25% H₂SO₄ + 75% demineralized water). 0.22 μm membrane filter is used for filtration in a procedure which is described in Standard Methods (3010A) for the determination of Mn²⁺ [25]. Residual Mn²⁺ values were determined in samples. The detection limit for the AAS manganese measurement was 0.01 mg/L as Mn²⁺/L.

In this study, Mn²⁺ concentration was kept constant as 3 mg/L and the concentrations of glutamic acid were chosen as it can be seen from Table 1.

<table>
<thead>
<tr>
<th>Concentration of organic compounds and MnO₂</th>
<th>Glutamic</th>
<th>Citric acid</th>
<th>Vanillin</th>
<th>MnO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>200</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>400</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

The Catalytic Effect of MnO₂ on Mn²⁺ Oxidation. The results of experiments with initial Mn²⁺ concentration of 3 mg/L and with varying MnO₂ concentrations are given in Fig. 2. The catalytic rate constant k_cat was determined from the slope of the lines in Fig. 2 and shown in Fig. 3. MnO₂ affects the oxidation rate of Mn²⁺ without the presence of organic substances. The increase in the concentration of MnO₂ up to 400 mg/L caused the oxidation rate rise significantly. Before the addition of MnO₂ to the medium, the reaction completion time was 78 minutes and the k value was 0.0215 min⁻¹. When MnO₂ was 400 mg/L, the catalytic rate constant (k_cat) was 0.0503 min⁻¹ and the completion time of the reaction was 60 minutes, which is the highest value obtained. The oxidation rate reaches to maximum at MnO₂ concentration of 400 mg/L. Thus, the reaction time is reduced with increasing initial MnO₂ concentrations.

**FIGURE 2**
The effect of MnO₂ on Mn²⁺ oxidation

The Effect of Glutamic Acid-MnO₂ on Mn²⁺ Oxidation. It is known that manganese normally present in natural water together with organic substances. In this part of the study, the effects of oxidation on the different glutamic acid concentrations (0-10 mg/L) were investigated by applying the same conditions. Fig. 4 shows the Mn²⁺ concentration over time with presence of various glutamic acid concentration values between 0 and 10 mg/L. Mn²⁺ and time
values were plotted on linear and arithmetic scales; respectively. The addition of glutamic acid, however, with increasing glutamic acid concentrations, slowed down the oxidation rate.

![FIGURE 4]

The effect of glutamic acid on Mn$^{2+}$ oxidation

In other part of this study, a concentration of 5 mg/L glutamic acid, at which average rate of oxidation was selected. In the experiments with glutamic acid, MnO$_2$ concentration was varied from 0 to 400 mg/L by keeping Mn$^{2+}$ concentration constant at 3 mg/L. As it can be seen from Fig. 5, the rate of oxidation increased with increasing MnO$_2$ concentration. Where the accelerating effect of MnO$_2$ on oxidation is seen to be greater than the slowing effect of glutamic acid.

![FIGURE 5]

The effect of MnO$_2$ on Mn$^{2+}$ oxidation

The Effect of Citric Acid-MnO$_2$ on Mn$^{2+}$ Oxidation. In this part of the study, the effects of oxidation on the different citric acid concentrations (0-10 mg/L) were investigated by applying the same conditions. The results are shown in Fig. 6. With the addition of citric acid, with increasing citric acid concentrations accelerated the oxidation rate. After these experiments, study was carried out by changing the concentration of MnO$_2$ varying between 0 and 400 mg/L in the presence of 5 mg/L of citric acid. As it can be seen from Fig. 7, from which it appears that the accelerating effect of MnO$_2$ is greater than citric acid. The rate of oxidation increased with increasing MnO$_2$ concentration. It appears that the catalytic effect of MnO$_2$ combined with the effect of citric acid accelerator slightly reduced the reaction time.

![FIGURE 6]

The effect of citric acid on Mn$^{2+}$ oxidation

![FIGURE 7]

The effect of MnO$_2$ on Mn$^{2+}$ oxidation

The Effect of Vanillin-MnO$_2$ on Mn$^{2+}$ Oxidation. At this stage of the study, the effects of oxidation on the different vanillin concentrations (0-10 mg/L) were investigated by keeping the same conditions. In Fig. 8 the experimental results obtained for vanillin as organic substance are presented. It is clearly seen that addition of vanillin does not affect the oxidation rate Mn$^{2+}$. Following these experiments vanillin 5 mg/L was selected and oxidation experiments were carried out with MnO$_2$ at concentrations between 0-400 mg/L. As shown in Fig. 9, it appears that vanillin does not affect the accelerator effect of MnO$_2$. 

![FIGURE 8]

The effect of vanillin on Mn$^{2+}$ oxidation
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EYEWEAR WASTE MANAGEMENT: ISSUES AND TRENDS

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ABSTRACT

The most widespread disability in the world is impaired vision. Individuals in order to correct or to improve their vision problems they wear eyeglasses or contact lenses. Additionally, eyeglasses with colored or tinted lenses can protect the eyes from damaging or discomforting the eyes. During the 20th century eyewear (eyeglasses and sunglasses) from a practical necessity turned to a fashion accessory in their own right. Consequently, eyewear became a vehicle for design, individual expression, and enhancement of personal appearance. In eyewear market it is estimated that nearly three billion units are purchased every year. Eyewear are small and light items and it is difficult to imagine that their production and their waste generation may have a significant negative impact on the environment. This study demonstrates the findings of a research relative to eyewear waste management amongst the residents of the city of Thessaloniki (Greece). In this study 265 persons took part and they were: a) students from Alexander Technological Educational Institute of Thessaloniki (Greece), b) individuals (residents of Thessaloniki) and c) optical shops. The results from this study support that people need to have more and accurate information about eyewear waste management.

KEYWORDS:
Eyeglasses waste management, environment, eyewear recycling, and environmental sustainable development.

INTRODUCTION

Impaired vision is actually the most widespread disability in the world. Individuals in order to correct or to improve many types of vision problems they wear eyeglasses or contact lenses. By the 1950s, eyeglasses became a popular fashion accessory in Europe and United States. Nowadays, eyeglasses are an accessory not only for vision improving, but also a personality display. Optometrists recommend updating of eyeglasses every one to three years as needed. Despite the popularity of contact lenses and the advent of laser surgery to correct vision problems, many people find eyeglasses necessary or desirable for their personal needs. Improved technology in the manufacture of plastic lenses and frames and in the comfort of fitted frames made eyewear more enjoyable to wear. The fashion industry also actively supports eyewear frames as an added avenue for expressive designs and a popular method of stating personal style. It is obvious that energy requirements for their manufacturing and way of their discard has a negative impact to the environment. Usually, the discarded eyewear are sent to a landfill for a very long wait. Nowadays, in order to overcome this environmental problem new type of eyewear appeared in the market. This new type of eyewear has less negative impact on the environment during the manufacturing process and once the owner has finished with them. In this new type of eyewear the frames are made of:

a) composites of plastics and bio-based materials that maintain the properties of plastic frames (light, flexible, etc.) and
b) incorporation of natural materials that reduce the carbon footprint.

However, when it comes to eyewear a number of questions arise:

a) is there enough demand to support sustainable frames? and
b) are there enough stylish sustainable frames to support the demand for face jewellery?

This study presents the results and analysis on the determinants of eyewear waste handling behavior among residents of Thessaloniki (Greece) and involves qualitative research and quantitative research with face-to-face interviews. The clearest messages from this study was the need of more and accurate information relative to eyewear waste management.

MATERIALS AND METHODS

Background. According to Vision Council of America over 4 billion in the world wear eyeglasses [1]. The correction of people’s vision contributes to the advancement of their socioeconomic development. Children with vision problems are in major disadvantage in school because 80% of all of their learning in school occurs through vision [2]. Adults with vision problems if they fix their vision problem then they are able to support productivity increments because they remain in the workforce for a longer
period. In a study conducted in USA it is pointed out that taking in account the same average wage of people with normal vision then reduced labor force participation by people with visual impairment and blindness it can be annually measured at productivity terms as a lost of billions of dollars [3]. Accordingly, the provision of eyewear to children has a positive educational impact and the provision of eyewear to adults becomes an economic investment. It is obvious that eyeglasses are an object that presents a solution to vision correction.

Eyewear need to be updated nearly every one to three years [4] and the reasons are:

- Eyewear don’t give the clarity of vision that they used to,
- Lenses are scratched and distorted,
- Frames are outdated,
- Old glasses are uncomfortable,
- Excess glare makes vision difficult during day or night.

Eyewear is small and light items and it is difficult to imagine that they are having a significant negative impact on the environment. A typical pair of eyewear is fashioned from plastic (both the frames and the lenses). Plastic is versatile, lightweight, flexible, moisture resistant, strong, and relatively inexpensive. Plastic is durable and degrade very slowly and are waste with staying power. Eyewear becomes part of litter from careless disposal and eyewear decomposition rates in landfills can be extremely long. Consumers should be persuaded or required to divert these for recycling or other environmentally acceptable procedures.

Recycling of eyewear is desirable because this avoids eyewear accumulation in landfills. It is evident that the success of eyewear recycling is limited and it needs successful collection strategies. Consequently, the energy requirements by eyewear manufactures and the great number of discarded eyewear in landfills forced the industry to start to introduce a life cycle perspective. During the last decade, the manufacturers of eyewear, forced to choose more environmental friendly materials, so, they started to use for eyewear frames composites of plastics, bio-based materials, natural materials and recycled materials [5].

A consideration must be made for the end-of-life for individuals’ eyewear. This generates the need to start to re-use them when it is possible and to dispose them more wisely. Donation of eyewear is one solution as it prevents excess manufacturing and excess waste. This action contributes to the environment because old eyewear can be reused.

In Greece eyewear recycle is not fully utilized and there is not any study relative to eyewear waste number and eyewear waste management.

The only organization that recycles eyewear in Greece is the Greek sector of Lions Clubs International. Worldwide the Lions Clubs International collects eyewear since 1930. They collect new and gently used eyewear in special collection bins or boxes at a variety of locations including libraries, doctors’ offices, schools, sidewalks, banks and retail stores. The collected eyewear is then shipped to the nearest Lions Eyewear Recycling Centre, where volunteers sort them, clean them and determine their prescription strength. After carefully packaging the refurbished spectacles, they store them until the collected ones can be distributed to developing nations [6].

The overall objective of this study was to gather baseline information of the eyewear waste management in the area of Thessaloniki (Greece). In Thessaloniki during the last ten years the number of collected eyewear by Lions Clubs is about a thousand per year. In the year 2012 a large optical company donated one hundred sixty thousands pair of eyewear. During 2016 Thessaloniki’s Lions Clubs created a communication and development campaign aiming to increase the number of collected eyewear per year in order to:

- a) give them to people that they need them and
- b) reduce eyewear wastes.

In this study 265 Thessaloniki’s residents took part and studied their behavioral eyewear waste management.

Research Methodology. The whole research took place in Alexander Technological Educational Institute of Thessaloniki (ATEI-Th) and involved both quantitative and qualitative research. The participants divided in three groups:

- ATE-Th Students =120,
- Individuals (citizens of Thessaloniki) =125 ,
- Optical Shops =20.

ATEI-Th students’ age range was 18 to 25; individual’s age was over 25 and shops participants age was over 25 too.

The quantitative research used face-to-face interviews for setting baseline attitudes and behavior [7]. The overall objective of the study was to evaluate their eyewear waste management and it was based on:

- Awareness and understanding of eyeglasses waste management/treatment issues.
- Beliefs, attitudes and behaviors towards eyeglasses waste management/treatment issues.
- Type of service provision that they require.
- The main influencing factors.
- Actual behavior and responsibility of individuals based on eyewear disposal and recycling.

The objective of the qualitative research was based on exploring in depth and on interpreting the attitudes of the participants through the translation of their attitudes to behavior change concerning
eyewear waste handling. Additionally, questions relative to “what brings change; and what are the barriers that individuals see in the application of this activity” included.

As in Greece the only organization that recycles eyeglasses are the Lions Clubs so it was included participants’ reaction on Lions Clubs campaign’s Greek logo “The old glasses give the new life” which is a free translation of the Lions Clubs logo “Recycle for Sight”.

There were five areas of questions that have been addressed to participants. The question areas were: interpretation, perception, information, service and actions.

Area 1: Interpretation (present actions)
- What do you do for eyewear waste management?
- Why you do eyeglass/ sunglass waste management?
- Why you don’t do eyewear waste management?
- Do you know about the steps of eyewear waste management?

Area 2: Perception (attitude and behavior)
- What is your opinion about eyewear waste management?
- What is your opinion for people that are doing eyewear waste management?
- What influenced you to start eyewear waste management?

Area 3: Information (knowledge of eyeglasses and sunglasses waste management)
- From where did you get the information about eyewear waste management?
- Who gave you the information about eye wear waste management?
- What is your opinion about the received information?

Area 4: Service (provision means of service)
- Who provides the service of eyewear waste management?
- What is your opinion about the service of eyewear waste management?
- What can be done in order to increase your behavior on eyewear waste management?

Area 5: Action (decision to stop or to continue this process)
- What will stop you from eyewear waste management?
- What improvements eyewear waste management requires?
- What you will do to persuade other people to do eyewear waste management?

The participants did not represent the views of the population of Thessaloniki area as a whole. This study was tried to explore the opinions, practice and attitudes of Thessaloniki’s citizens on eyewear waste management.

For each group the time spent on the process was half an hour. Three meetings took place for each group and the discussion was based on the five categories of the above questions. In this process notes kept for analysis.

The participants in this study were 265 (Figure 1) and there were slightly more female participants than male. All the participants declared their general recycling behavior and also their eyewear recycling behavior. The group selection was based on the inclusion of a very cross-section of gender and age (Figure 2).

**FIGURE 1**
Groups of Participants (N= 265)

The age range of the participants (Figure 2):
(1) 18-28 (139; 52%)
(2) 28-38 (33; 12%)
(3) 38-48 (48; 18%)
(4) 48-58 (37; 14%)
(5) >58 (8; 3%)

**FIGURE 2**
The age of participants.

The participants were divided in two main categories: general recyclers (159; 60%) and non-recyclers (106; 40%). The recyclers were divided in two categories non eyewear recyclers (136; 86%) (Figure 3) and eyewear recyclers (23; 14%) (Figure 4).

For each group there were introductions and discussions about the five key areas of questions and these there were recorded and transcribed for analysis.
results and discussion

The main message that needs to be communicated is based on “what are the benefits of eyewear recycling”. Only 9% of all participants are involved in eyewear recycling. Other findings from the results that have to be mentioned and need a further study is about the 40% of the participants that do not recycle at all. From the non-recyclers (106; 40%) participants mentioned that there is a lack of understanding of what can or cannot be recycled (64; 60%), the type of recycling services that local authorities of Thessaloniki are provided (70; 66%) and finally what happens to the materials once have been collected (80; 75%). It is obvious that information about where the recycled items-materials are going after their collection has to be spread out to Thessaloniki’s citizens. This means that citizens need to understand that:

- their individual action is making a difference,
- the recycle myth “that recycling all ends up in landfill anyway” do not exist,
- they have to try to be green consumers in favour of recycled products.

The participants that do not recycle eyewear are not aware of any campaigns regarding this activity.

Finally, the majority of the participants did not show that recycling is not important for them and they pointed out that there is a need for campaigns or initiatives in the local area relative to eyewear recycling process (240; 91%). Their recycle behaviour is based on their inadequate information that they have on the recycle process and especially on eyewear recycle task.

The results show that there is a lack of awareness about eyewear recycling and not a lack of concern about environment. The significant of eyewear recycling is not the most pressing issue rather it is salience.

An important motivator, agreed by all the participants was eyewear recycling being or becoming a common behaviour. The non recycler eyewear students commented that it had to become a social norm or habit to take off, although they did not propose an approach that can be achieved. The non eyewear recyclers from the citizens saw it as a hassle for them and not a habit and some of the shops felt that by eyewear recycling they were leading the ways towards creating these good habits.

Most of the non eyewear recyclers felt that at the moment recycling was not an important enough issue for them.

In all groups the non eyewear recyclers and especially the students wanted to have more information about this process. They wanted to know what happens to the recycled eyewear. Most of the students mentioned that they did not know anything about Lions Clubs campaigns relative to eyewear
recycle activity. The students supported that there is a need for communication from the local media and with respect of general resources, television (72%), Social Media (64%), Radio (55%), National and Local Papers (49%), Websites (47%) and None of these (8%).

The younger ones (students) preferred Social Media (80%) and Websites (70%) and the other (individuals and shops) preferred television (65%) and National and Local Papers (55%). The plurality of the participants pointed out that eyewear recycling need information provision. In order to avoid the failure of this process the creation of awareness has to be with the provision of the required facilities. Furthermore, the provision of infrastructure including convenience there were the major determinants. The message that the non eyewear-recycle participants declared is:

- make the service right and convenient
- advertise the places where the eyewear recycle boxes are.

It is obvious that Lions Clubs have to present good eyewear recycle facilities and services in order to achieve a dramatic impact of Thessaloniki’s area residents’ eyewear recycle behaviour. Also, there were comments from the participants that eyewear recycle campaign should not be only under Lions Clubs responsibility but it has to be a shared responsibility of Municipality of Thessaloniki and the of Chamber of Commerce too.

All participants supported that eyewear recycling requires hard hitting messages as a more effective approach than personalised messages and engage directly with communities. All groups agreed that in all levels of Education there must be at least one eyewear recycle box in these establishments and especially educating children was an important element in encouraging eyewear recycling.

CONCLUSION

Examining the results from the three groups of participants and quantitative research converge that there is a need of more information. All of them agreed that “awareness” is the key for getting people to recycle eyewear. The participants in drivers and motivations approach agreed that the provision of information, the creation of awareness and the presence of good eyewear recycling facilities and services have a dramatic impact of participants’ eyewear recycling behaviour. Lions Clubs have to do a more dynamic campaign and also they have to integrate their efforts with the Municipality of Thessaloniki and the Chamber of Commerce.

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ABSTRACT

Biosolid application to pastures is generally considered the best option of management for their organic amendments and plant nutrients. Particularly pastures converted into poor quality pastureland, as a result of early and over grazing, can be regained their productive capacity by biosolid application. The aim of the study was to obtain the bacterial inactivation after biosolid application to pastures during winter conditions. Four levels of biosolids were topically applied at rates of 25, 50, 100 and 200 t ha⁻¹; one treatment was not amended that represented the control. The experimental design was a randomized block with three replications in the same plots during six months. Thermotolerant coliforms, *Escherichia coli* (*E. coli*), Enterococci and *Salmonella* ssp. were studied as the indicator microorganisms. Obtained results suggest that biosolid could be a safe and inexpensive substitute to inorganic fertilizer for poor quality pastures and standard application of biosolid on pastures is apparently at low risk.

KEYWORDS:

INTRODUCTION

Biosolid is the by-products of wastewater treatment plants and their production, worldwide, has steadily increased over the past years which disposed as waste in many countries. However, recycling of the biosolid as a product is necessary in terms of sustainability [1-3]. The general trend in recent years is utilization of biosolids in pasture as plant nutrients and organic matter, a shortest way to back to the naturel cycle that is the most environment friendly and more acceptable route [4-7]. Because biosolid contain considerable amounts of nutrients, especially nitrogen, phosphorus, sulphur, calcium and micronutrients, and are inexpensive when compared with commercial fertilizers [8]. Especially the use of adequate doses of biosolid could enhance the productivity of pasture and promote biodiversity [9]. In this way, production and continuity will occur in the pasture, high yield provided pasture can ensure significant improvement in cost in the livestock sector [10, 11]. Additionally, it will reduce the demand of available commercial fertilizers and fertilization programs that will provide saving. Thus an ecologi-cal management plan development economically sustainable and improved methods of solid waste will helpful to resolve serious problem of municipalities.

Nutrients present in biosolids can therefore make a substantial contribution to the nutrient demand in pastures. However, due to higher concentrations of heavy metals and indicator microorganisms which represented potential presence of pathogens, the use of biosolids to pastures became a big concern [11, 12]. Pertaining to successive application of biosolid result in heavy metals reaching environmentally toxic levels. This caused governing authorities to set limits to how much biosolid can be applied to agronomic lands. Thence sustainable biosolid management on pastures is based upon controlling and influencing the quantity, quality and characteristics of this material. Even when the biosolid is within the regulatory limits for heavy metals, the high number of pathogenic microorganisms can cause possible risk to the environment and endanger human health. Biosolid harbours a large variety of pathogens able to cause or spread a high number of transmissible diseases to both humans and animals [12]. Therefore pathogen elimination is substantial in order to diminish the potential risks during and after biosolid application.

Pathogen inactivation in biosolid is a time and energy consuming process that requires a practical, cost efficient method [13]. The inactivation mechanisms of pathogenic microorganisms are well defined according to time and temperature. Especially fecal microorganism inactivation via solarization has been studied at various experimental conditions in literature [14-18]. Exposure temperatures, in particular above the thermophilic range, are identified as the principal factor influencing pathogen inactivation in biosolid. It is generally accepted that increasing biosolid temperature has a direct impact on
m微生物 decay. Simply solarization appears to be an effective method to inactive biosolid indicator microorganisms during the hot summer periods. However inactivation of fecal microorganisms in biosolids in cold conditions after pasture application is an untouched study. Thus the main objectives of the study were to determine the inactivation rate of selected fecal microorganisms after biosolid application to pastures in cold weather conditions and to assess the environmental and health impacts of recycling biosolid through the land application. Data from this study will also improve our understanding of the effects of long-term application of biosolids as a fertilizer on soil biochemical and biological processes and the sustainability of soil fertility of pastures.

**MATERIALS AND METHODS**

**Experimental site and biosolid application.** The study was conducted on a pasture located in Akova (Sakarya-Turkey). The soil was classified as alkaline soil and the soil has silty texture with a composition of 24.3% sand, 51.8% silt and 23.9% clay. The biosolid used in the experiments was obtained from Sakarya Municipal Wastewater Treatment Plant. The current treatment facility in this plant is capable of treating a flow of 90,000 m³ day⁻¹ in an extended aerobic activated sludge process. After the thickening process, biosolid is dewatered using a belt filter to produce the end product which has 20% dry weight (DW) and stored at open-air for stabilization until the next disposition. Dewatered and stabilized biosolid cake was used in the experiment.

The experiment was conducted in randomized block design (RBD), having four different application rates of biosolid which were the equivalents to 25 t ha⁻¹, 50 t ha⁻¹, 100 t ha⁻¹ and 200 t ha⁻¹. One treatment was not amended that represented the control. Three replicates were performed for each treatment. The biosolid was hand applied in December to the soil surface. The changes in fecal microorganism’s populations were monitored for six month between December 2017 and May 2017. Soil samples were collected monthly after the biosolid application. In each plot, five samples from the 0–20 cm soil layer were collected at random design and pooled to form a composite sample. The experiment was carried out in the climatic conditions of Sakarya with a mean annual temperature of 14.5°C. During the six month of experiment period including December and May, mean temperatures were obtained such as 8.1°C and 17.4°C, respectively. Mean temperature of the six month test period is 10°C.

**Soil and biosolid analysis.** Oven dried (70°C), ground and sieved with 2 mm mesh size biosolid and soil samples were used in the analysis. pH was measured with a pH-meter at the 1:5 (w/v) ratio of soil water suspension [19]. The electrical conductivity (EC) was measured with an EC electrode at the 1:5 (w/v) soil water suspensions [19]. Organic matter (OM) and organic carbon (%) were measured according to Walkley and Black method [20]. Total N was determined by the Kjeldahl method [19]. Phosphorus was measured spectrophotometrically according to Bingham method [21] and potassium was obtained at ICP-OES (Spectro Arcos, Kleve- Germany) by employing ammonium acetate method [20]. Cation exchange capacity was obtained according to BaCl₂ extraction method [22]. Dried soil/biosolid samples (250 mg) were digested in a Microwave Digestion System (Sorisingle-Bg Italy) using 6 ml of HNO₃ (65 %), 1 ml of H₂O₂ (30 %) acid mixture and then total heavy metal contents and micro nutrients were determined with an ICP- OES (Spectro Arcos, Kleve- Germany) [19].

The determined chemical and physicochemical properties of the soil were a texture saturation of 78%, pH of 8.4, EC of 475 µS cm⁻¹, OM content of 2.41%, total N content of 0.174%, P content of 17.11 ppm, K content of 532 ppm, and CaCO₃ content of 11.5%. The elemental composition of the soil was found to be 3.7 mg kg⁻¹ Cu, 1.17 mg kg⁻¹ Zn, 4771 mg kg⁻¹ Ca, 652 mg kg⁻¹ Mg, 6.1 mg kg⁻¹ Fe, and 2.01 mg kg⁻¹ Mn.

The obtained physicochemical properties of the biosolid were a pH of 7.1, EC of 1978 µS cm⁻¹, OM content of 55%, Kjeldahl N content of 3.34%, P content of 3.06%, K content of 0.99%, CEC of 7.09 cmol (+) kg⁻¹, organic carbon content of 33.11%, and a C/N ratio of 8.09. The heavy metal content of biosolid was found to be 21 mg kg⁻¹ Cu, 1574 mg kg⁻¹ Zn, 251 mg kg⁻¹ Cr, 84 mg kg⁻¹ Ni, 39 mg kg⁻¹ Pb, and 3.8 mg kg⁻¹ Cd.

**Microbiological analysis.** Microbiological analysis were performed using chromogenic ready-made media. The reason for choosing this method is more sufficient to work and count for high volume samples and faster than classical procedures. In this method, the microorganism after adequate dilutions is placed on a selective medium according to the type of microorganism. After incubation for 24 hours at 35 °C and 41 °C, counts were made through the squares on the substrate and the amount of thermotolerant coliforms, *E. coli* and Enterococci were determined as CFU/1 gr (dry matter) [23-25]. Simple dry culture medium was used that qualitatively identified *Salmonella ssp.* based on its specific character, such as its biochemical reactivity and mobility [26].

**Statistical analysis.** Inactivation rates of each microorganisms throughout the experiments were calculated using the ratio of log N/N₀, where N₀ is the concentration at time 0 and N is the concentration at time t. The GlnaFiT inactivation model fitting tool was used to determine the types of microbial inactivation models which fitting best with obtained data.
Thermotolerant coliform number was significantly reduced in the experiments. The average numbers of thermotolerant coliforms were $40 \times 10^2$ CFU/1gr DM in 25 gr biosolid application rate, $45 \times 10^2$ CFU/1gr DM in 50 gr application rate, $90 \times 10^2$ CFU/1gr DM in 100 gr application rate and $150 \times 10^2$ CFU/1gr DM at the beginning of the process were decreased considerably to $2 \times 10^2$ CFU/1gr DM within the period (Fig. 1). Depending on this, approximately 98-100% inactivation efficiencies were obtained for thermotolerant coliforms. The decimal decay rate ($T_{90}$) measured from the regression analysis were 126d and 121d for thermotolerant coliforms, respectively at 25 and 50 gr biosolid application rates (Table 1). The effective boundary for inactivation rate and $T_{90}$ value was obtained at 25 and 50 gr application rates for thermotolerant coliforms that increased biosolid amounts extended the shoulder point of the inactivation curve (Fig. 1).

The most suitable model has been the log-linear regression plus shoulder model for each fecal micro-organism. The error squared averages (RMSE) were used to determine the most appropriate inactivation curves. The inactivation rate $k_{max}$ and $T_{90}$ values (time to inactivate 90% of the population) were calculated using the best fitting model in GItaFiT.

### RESULTS AND DISCUSSION

Obtained results showed that agronomic characteristics of biosolid like pH, EC, CEC and organic matter contents were found in acceptable range and good for subsequent plant growth. Additional fertility distinctiveness, such as NPK level, organic carbon and C/N ratio were also fairly reliable. The heavy metal content of biosolid was also obtained much lower than the limits recommended by the Turkish Soil Pollution and Control Regulations for agricultural usage (2001) either with the EU (2005) or by the USEPA (2002). Thus, biosolid can be contem-plateable as a perfect amendment for agricultural usage.

Inactivation of thermotolerant coliform, *E. coli* and Enterococci in the biosolid at different sludge application rates were presented in Fig. 1., Fig. 2. and Fig. 3., respectively. Estimated maximum inactivation rate ($k_{max}$/day), decimal decay rate ($T_{90}$ day) and root mean squared error RMSE of regression lines for indicator microorganisms were represented in Table 1. Application of biosolid to pasture for six months was highly effective to reducing the population densities of thermotolerant coliforms, *E. coli* and Enterococci species. The survival rate over the treatment period was obtained in the sequence of *E. coli* < thermotolerant coliforms < Enterococci. Thus, the reduction in bacterial strains was achieved at different times throughout the experiment. Microorganism’s densities obtained in biosolid were $25 \times 10^5$ CFU/1gr DM thermotolerant coliform, $15 \times 10^5$ CFU/1gr DM *E. coli* and $7 \times 10^5$ CFU/1gr DM Enterococci. And populations determined in pasture soil were $10 \times 10^2$ CFU/1gr DM thermotolerant coliform, $4 \times 10^2$ CFU/1gr DM *E. coli* and $1 \times 10^2$ CFU/1gr DM Enterococci. *Salmonella ssp.* was not detected initially in soil nor biosolid.

### TABLE 1

<table>
<thead>
<tr>
<th>Treat.</th>
<th>$T_{90}$</th>
<th>RMSE</th>
<th>$k_{max}$</th>
<th>$T_{90}$</th>
<th>RMSE</th>
<th>$k_{max}$</th>
<th>$T_{90}$</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>0.02c</td>
<td>178a</td>
<td>0.14</td>
<td>0.08c</td>
<td>116a</td>
<td>0.53</td>
<td>0.03c</td>
<td>70c</td>
</tr>
<tr>
<td>S25</td>
<td>0.16b</td>
<td>126b</td>
<td>0.68</td>
<td>0.44b</td>
<td>46b</td>
<td>4.22</td>
<td>0.16b</td>
<td>83c</td>
</tr>
<tr>
<td>S50</td>
<td>0.17b</td>
<td>121b</td>
<td>0.52</td>
<td>0.66ab</td>
<td>43b</td>
<td>1.93</td>
<td>0.23a</td>
<td>100b</td>
</tr>
<tr>
<td>S100</td>
<td>0.17b</td>
<td>70c</td>
<td>0.84</td>
<td>0.85a</td>
<td>41b</td>
<td>4.14</td>
<td>0.27a</td>
<td>106b</td>
</tr>
<tr>
<td>S200</td>
<td>0.32a</td>
<td>52c</td>
<td>2.09</td>
<td>1.10a</td>
<td>41b</td>
<td>4.14</td>
<td>0.27a</td>
<td>112a</td>
</tr>
</tbody>
</table>

(S0: control; S25: 25 t ha$^{-1}$; S50: 50 t ha$^{-1}$; S100: 100 t ha$^{-1}$; S200: 200 t ha$^{-1}$)

Values followed by different letters are significantly different for $p<0.05$
FIGURE 2
Inactivation of E. coli

The inactivation of E. coli population showed similar reduction effectiveness to the thermotolerant coliforms at both biosolid treatments. Initially obtained mean numbers of E. coli populations were 17x10^2 CFU/1gr DM in 25 gr rate, 30x10^2 CFU/1gr DM in 50 gr rate, 35x10^2 CFU/1gr DM in 100 gr rate and 47x10^2 CFU/1gr DM in 200 gr rate were decreased to 3x10^2 CFU/1gr DM within the experimental period (Fig. 2). Inactivation efficiencies were estimated 96-100% for E. coli. While in E. coli inactivation curves, more apparent shoulders were obtained at 25, 100 and 200 gr application rates, this is not obvious in 50 gr application rate (Fig. 2). The decimal decay rate (T90) measured from the regression analysis was ranged from 41-46d for E. coli (Table 1).

The viable cell counts of Enterococci was ranged for 100x10^2 CFU/1gr DM in 25 gr application rate, 120x10^2 CFU/1gr DM in 50 gr application rate, 150x10^2 CFU/1gr DM in 100 gr application rate and 200x10^2 CFU/1gr DM in 200 gr application rate at beginning of the experiment where decreased to 2x10^2 CFU/1gr DM within the experimental period (Fig. 3). Inactivation efficiencies were estimated 99-100% for Enterococci. Although a small increase in whole microorganism populations were determined during the first month of the experiments, this increase was obtained more specific in Enterococci and further destructions were minimal. Comparing the inactivation curves, T90 values, RMSE values and inactivation rates, kmax, Enterococci were obtained more resistant to outdoor conditions (Fig. 3) (Table 1). In contrast, E. coli declined rapidly, with lower T90 values, but the residual population numbers was obtained similar to the residual numbers of thermotolerant coliforms (Table 1). Similar results were obtained by Ozdemir et al. in 2013 [13] and Watcharasarukarn et al. in 2009 [28]. And were continuing to decrease to concentrations below the detection limits.

Previous studies have also reported the sigmoidal inactivation curve of Enterococci [29], in contrast shoulder curve obtained in this study which attributed to the resistance of this microorganism to adverse soil microbial variety rather than temperature. Especially despite the significant reductions in counts, thermotolerant coliforms and Enterococci populations were not reduced to undetectable levels via solarization, probably due to the adaptive nature conditions of pasture soil, where temperature increases were slower. Because introduced pathogen inactivation in soil is affected not only by temperature increase, but also by many soil environmental factors capable of suppressing pathogenic microorganisms or of pathogen destruction. Biosolid pathogen reduction in soil without solarization has been reported by several researchers, but it requires several months to reduce the microbes to undetectable levels [30].

CONCLUSION

Obtained results suggest that bacterial populations of fecal origin were increased immediately after the biosolid application but progressively decreased as time went by, reaching values similar to the controls within six month period and to meet the regulations for Class A Biosolids for agricultural reuse. However, this low decrease in the number of Enterococci is attributed to the continuation of the presence of the fraction showing adaptation to the soil environment. When long time applications and mineralization process were considered, biosolid doses of 25-50 ton ha^-1 year^-1 can be said to provide more beneficial results than the synthetic fertilization's highest dose which is suggested for pastures.

The significant reduction of selected indicator microorganisms was attributed to not only by temperature increase but also by many soil environmental factors capable of suppressing pathogenic microorganisms or of pathogen destruction such as pH and microbial activity. Supporting this hypothesis, Al-Kayssi [31] reported that increasing the CO2 level in soil enhanced the pathogen destruction. In addition,
acidification of soil and root zone via secretion of organic acids from rhizosphere, is an important parameter in pathogen destruction. As a result biosolid could be a safe and inexpensive substitute to inorganic fertilizer for poor quality pastures and standard application of biosolid on pastures is apparently at low risk.

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SECOND HOME OWNERS PERCEPTIONS TOWARDS ENVIRONMENTAL EFFECTS

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ABSTRACT

The aim of the study is to identify second home owner’s perceptions towards environmental effects. Also it’s aimed to reveal their perception about sustainable environment to understand better whether their perception about environmental effects is satisfactory or not. In this study, a qualitative method was applied on the sample group consisted of second home owners in the village of Eriklı, Keşan in Bay of Saros. The problems were identified after investigating related studies on environmental effects in the literature and gathering opinions of researchers who conducted studies on perceptions towards environmental effects and then a semi-structured interview questionnaire was formed. The data was examined using qualitative descriptive analysis and meta-analysis. As a result, it has been found that second home owners perceive environmental effects negatively and they are not aware of their negative effects on the sustainable environment while they are realizing what the sustainable environment means.

KEYWORDS:
Second Home Owner, Second Home, Environmental Effect, Sustainable Environment,

INTRODUCTION

The increase in leisure time affects people's lifestyle and housing preferences around the world [1]. People want to go to rural areas to escape from the stress, noise and crowd, especially from big cities, but not everyone is totally away from the cities due to job opportunities. Nevertheless, renewing at certain periods of the year, at least in order to rest, they prefer to own second home. This leads to the emergence of second home vacation. It is expressed by many researchers that it is difficult to measure the share of environmental impacts caused by second home vacation. However, the construction of second homes leads to consumption growth related to the use of transportation, increase of land and infrastructure usage and consumption of non-renewable natural resources. The rapid increase in the number of second homes, which people are forced to escape from the intense pressure of cities and live in natural environments, is a distinct paradox. Second home owners are able to recreate the pressure and stressful environments they are trying to escape. For this reason, to reduce the environmental impact of second home tourism and to ensure a sustainable environment, it is important to understand the environmental effects within the perception of second home owners.

This study aims to investigate the perception of second home owners towards environmental effects in Eriklı. Also it’s aimed to reveal their perception about sustainable environment to understand better whether their perception about environmental effects is satisfactory or not. It is important to verify that second home owners understand the meaning of sustainable environment satisfactory, so that they can explain the environmental effects of second home. Despite being an independent academic study, the results of this research can be used as a theoretical resource by policy and planning experts to develop a consistent framework for monitoring second home development and its environmental impacts. In addition, this research, built on the experience and theoretical approach in the western countries, can enrich the results of previous studies and contribute to knowledge and accumulation on both Turkey and international second home tourism.

In the study, the literature on the perception of environmental effects of second home tourism has been reviewed in order to establish the theoretical framework of the study. This literature review covers, examples of previous studies on second home tourism, sustainable environment and perceptions towards environmental effects. After the literature review, results based on qualitative research using interview technique is presented. In the study, 13 second home owners in Eriklı were interviewed to see how they perceive environmental effects and sustainable tourism. A thematic analysis was conducted on the answers given to the open-ended questions by the participants.
THEORETICAL FRAMEWORK

The concept of second home is a key issue discussed in many previous researches. Second homes are named as holiday houses, secondary home, villas and so on [2-4]. In this study "second home" term was used. It is difficult to define the second home concept. Considering the current literature, researchers working on this issue [3,5-6] seem to be challenged. It is difficult to identify second home because many factors are influential even in defining the house and the definitions comprise different limitations. Despite the fact that the definition of second home is a very difficult subject, some issues have been agreed upon. Second homes are defined as residences owned by people or rented for a long time, as residences that are used elsewhere and are used less frequently than areas where the permanent residence is located [7-11].

Second home tourism affects environment, landscapes and nature in various forms. Some environmental variables include population, marine pollution, parks, cultural and architectural wealth, landscape, waste, coastal roads, motorized mobility between home and second home, energy consumption, erosion of natural areas, loss of biodiversity, consumption of non-renewable natural resources, reduction of fish species, seawater pollution caused by motorboats problems caused by overcrowding (n. cars) traffic congestion, tourist population consumes a certain amount of resources (fresh water, energy, etc.) and noise [12-13]. Since second homes are often located along the coast, second homes and users contribute to threatening these natural habitats [14]. Despite some benefits for local communities, second homes are causing unsustainable environment by buildings that is used a few days in a year by occupying large areas. Therefore, sustainable environment is important for both second home owners and local people.

The concept of sustainability is based on the principle of economic development to protect environmental resources and values and to transfer them to future generations. On the other hand, sustainable environment, means ensuring the continuity of natural resources. The level of resources used is the incidence at which these resources renew themselves; the proportion of released pollutants must not exceed the rate at which natural resources are able to process these pollutants. Bio-diversity; human health; air, water and soil quality; protection of animal and plant life is also included in environmental sustainability [15]. Nature has the ability to renew itself, but this is limited. For this reason, it is very important to ensure the continuity of life, to hand down a healthy environment where natural resources have not been destroyed for future generations, to learn how to live in harmony with the natural environment and to prevent the deterioration of existing ecological balances [16].

Environmental perception refers to the subjective ways in which individuals or groups perceive and evaluate their environments [17]. Individual perceptions are more broadly associated with collective cultural beliefs, values, and aesthetic judgments about natural environments [18]. The closest synonyms to the term of perception used in this study are "opinion", "thought" and "understanding".

LITERATURE

There are a number of studies examining the perceptions of second home owner’s environmental effects of second homes. Kaltenborn et al. [19] measured the environmental attitudes of second home owners and concluded that second home owners did not perceive second homes as the reason of environmental impact. However, they found that they were somewhat worried about the environmental changes caused by the expansion in second homes areas. In their research of Halseth and Schwamborn [20], most of the respondents (77%) stated that second home life styles are not environmentally problematic. Only four of the participants think there are adverse environmental impacts. Almost two-thirds say "no" when they realize that there is no environmental problem in the second home area. Although Halseth and Schwamborn [20] found that many second home owners’ lifestyles do not cause too much environmental impact, they are inadequate in the elimination of solid and domestic wastes and often use motor vehicles in the lake or in the forest, at least an hour between the primary and second home and damage to the environment [20]. Pitkänen et al. [21], stated that the second home owners are aware that the protection of natural resources is important for future generations and even some local protection measures. Nevertheless, it has been determined that the conservation concept of second home owner’s may be significantly different from the scientific conception of nature conservation. Long and Hoogendoorn [22] have examined the perceptions of second home owners in South Africa on the impacts of lifestyle of second home owners on a lake. It is considered that second homes have a general influence on the environment through housing construction, transportation between permanent and second home, water and electricity use and solid waste. However, the majority of second home owners are unaware of their own environmental influences and they think that they do not have any influence on the environment or that others are responsible for the environmental effects. Long and Hoogendoorn [22] concluded that second home owners affected environmental deterioration but did not know that they had the potential to reduce this environmental effect.

As the previous studies mentioned above, general inconvenience and negative effects in the nature are usually overlooked in the second home owner’s
environmental perceptions. Moreover, the previous literature suggests that environmental perceptions about individual behavior and second-home tourism are often contradictory. While second home owners are sensitive to the environment, they do not reflect that on their lifestyle preferences and daily activities. Instead, second home owners think that, industry, agriculture or other people are causing environmental problems or rural environmental change [21-22].

MATERIALS AND METHODS

Study Area. The geographical focus of this research is on Eriklı village. Eriklı is a settlement on the coast of Saros Gulf, one of the exceptional gulfs with self-clearing features, is located in Edirne province of Turkey, close to Istanbul, which is Turkey's most populous city, still has unspoiled natural resources, as there are no enough accommodation facilities, the majority of the accommodation takes place in second homes. There are many second homes in this area. It is usually preferred by local tourists. It's very crowded in the summer months. It is a developing area. For these reasons Eriklı was chosen as a study area.

Eriklı is a village founded in 1893. There are 65 local household in Eriklı and the local population is 362. It was pasteur area and field before it was allowed to construction in 1960. Afterwards, due to its proximity to the settlements, it became a small resort in time, then the village was later converted into a town [23]. While the number of secondary houses in Eriklı was approximately 4270 in 2005 [24], this number grew rapidly in recent years and reached nearly 7,000 by 2018. Despite the fact that only local people live in Eriklı during the winter times, this number reaches nearly 80,000 in the summer [23].

Saros Gulf is located in the Aegean Sea, north of the Gallipoli Peninsula. The Gulf is in the shape of a "U" and extends into the Thrace peninsula along the northwest direction. The gulf is connected by a width of approximately 36 km to the North Aegean Sea. Its length is approximately 61km and narrows inward. There are no waste discharges from industrial plants in Saros Gulf. However, there are no infrastructure facilities in the area except the Eriklı and Yayla on the coastal area where the second homes are located. The distances of the coastal shrines of the village settlements in the region vary between 3-7 km. It is observed that the number of people living in the region during the summer season is increasing due to the fact that the second homes on the coast are generally used in summer. Eriklı, the most popular summer coastal settlement in the Saros Gulf, is under the pressure of second home owners and has some problems such as unplanned settlement, density of housing and inadequate local government services.

Research Methodology. This study aims to investigate the perception of second home owners towards environmental effects. Also it’s aimed to reveal their perception about sustainable environment to understand better their perception about environmental effects. Although there have been many comprehensive research on tourism impacts, most of these studies have adopted a quantitative approach and have used survey-based methods to examine the connection between various variables. Such an approach is appropriate for achieving high level generalizability, but qualitative methods are the most appropriate method of providing rich data and information to investigative research on a smaller sample [25]. Because of the limited capacity of the quantitative methods to present satisfactory views on the perception of second home owners about the environmental effects of second homes, this study was conducted by qualitative data collection. Qualitative interviews are seen as a convenient method because it is the open way of allowing people to talk about themselves and their own experiences. The research took place in Eriklı between April and September 2017. Structured interview data collection method was used in the research. The interviews were terminated when the data from the interviews began to repeat. From different parts of Eriklı, 7 males and 6 females (n = 13) second home owners were interviewed. As the second home owners in Eriklı are mostly composed of middle-aged people, the people to be interviewed were selected randomly from middle-aged living in different parts of Eriklı. Each interview took a relatively long time to establish a reliable relationship with interviewees. Although there was a certain format for the interview, the interview was conducted with maximum flexibility according to subject and the characteristics of the interviewee. The aim was to encourage interviewees to talk and to provide enough time and freedom to express their ideas, thoughts and feelings. Flexibility is an important factor when the interviewees' have different levels of education and knowledge or awareness of the research are taken into consideration. In the interview process, participants were pre-agreed and volunteered to participate. The interviews took between 35 and 120 minutes, all the interviews were recorded digitally, then the data file was created by transferring them to the word file. The evaluation of the collected data was made by qualitative descriptive analysis and content analysis were discussed and suggestions were presented in conclusion.

Research Questions. The survey questions were adapted from the studies of Radulescu [26] and Hiltunen et al. [12]. The semi-structured questionnaire was designed based on the initial research objectives and on the thematic issues identified during the literature review. The questions consist of four parts.
Section 1 Questions about the demographic characteristics of second home owners

Section 2 Questions about the motivation of second home owners to purchase a second home

Section 3 Questions about second home owners perception about environmental protection and sustainable environment.

Section 4 Questions about the perception of environmental effects of second homes and about change in Erikli and opinions about more second home construction in Erikli.

With these questions above, it is aimed to get information from the second home owners to understand their demographic characteristics, the motivation to purchase a second home, the perceptions of second home owners about environmental protection and sustainable environment and the perception about environmental effects of second homes, perception about change in Erikli and their willingness for more second home construction in Erikli. Such information may contribute to a better understanding of whole perception about the environmental effects of second home owners.

RESULTS AND DISCUSSION

According to demographic characteristics of participants, the education level of second home owners is high, the average age is 57. mostly they are retired, and the others are civil servant, teacher, academician, and housewife. The distance between the primary residence and second home varies between 90 km and 900 km. The majority of second home owners in Erikli are from Istanbul and Edirne. Some second home owner visit their permanent residences at least once a week and return back. These visits are one of the indirect negative effects of second homes in terms of carbon emissions. In addition, the participants stated that they used their second homes for an average of 3 months and the second homes are empty during winter. This leads to the idle use of the areas where second homes are located.

The Motivations of Second Home Owners to Purchase a Second Home. Participants have three reasons for choosing Erikli. These are; "Beauty of the sea" (P1, P2, P3, P4, P5, P6, P8, P9, P10, P11, P12, P13) "the existence of relatives and friends" (P3, P4, P5, P10, P12, P13) and "closeness to permanent residence" (P2, P6, P8, P9, P11, P12, P13). 3 themes have emerged. Examples of preference reasons are given below;

"The only reason is the beauty of the sea, besides, my nephew here, my brother here, my friends here" (P4).

"Other places may be preferred as it is close to the region we live in and the sand and the sea are beautiful and the season is short, but it is our preference for us to be close to where we live and work" (P6).

"It is because of Saros Bay which is one of the 3 seas which cleans itself in the world and the most beautiful sea in the Marmara region" (P7).

"First of all, the sea is very clean and close to Istanbul. Plus, I like fishing, I like cooking fish and eating fish. You can not go to Bodrum in 3 hours from Istanbul but you can come here" (P11).

"Close to Istanbul, beautiful sea, fish and relatives of my wife live here” (P12).

Second home owners often buy second homes in Erikli for such factors as natural beauties, the presence of friends and relatives, and the proximity to where they live. This means that natural beauty, relatives and friends and proximity are the important factors for second home owners to purchase a second home in Erikli.

Second Home Owners Perception About Environmental Protection and Environmental Sustainability. Participants were asked about what "environmental problem" mean. According to the answers given, "pollution of air, water and soil" (P4, P6, P12, P13), "garbage that people throw to their environment" (P3, P5, P7, P8, P9, P10, P11) and "Noise" (P1, P2, P4). 3 themes have emerged. Examples for environmental problem perception are given below;

"Tap water pollution, sewage in the infrastructure sometimes smells at nights and noise” (P4).

"As for the environmental problem, pollution such as visual pollution, chemical pollution, sea, soil, air pollution, noise pollution are obvious” (P6).

"The environmental problem is that people pollute the environment and destroy the nature. People are destroying nature entirely. All agriculture fields are transformed into buildings, green areas are damaged and become a stone pile” (P7).

"Non-collected garbage, polluting the sea, garbage that people throw to their environment” (P3, P5, P10).

"Air, water and soil pollution. When the water is bad, the material in the ground is deteriorated and the chemicals used in the soil spoil water. For example, here is something that has changed this year. Every year it is getting worse, but this year I think something infecting the soil with a chemical, so all the plants dried up. When we came here in the spring, all the plants were green. There was no problem. But then the plants dried up as I used water. The lake in which the water is provided may also be chemically disinfected to protect the micropotent, and the pesticide may be contaminated with water. This leads to environmental problems” (P12).

Participants define sustainable environment as the habitable world for future generations and the unspoiled use of nature. This indicates that participants
are aware of the meaning of sustainable environment.

Perception of meaning of Environmental Sustainability. Participants were asked about what “sustainable environment” mean. According to the answers given; “habitable world for future generations” (P1, P6, P7, P9, P10, P12, P13) and “intact use of nature” (P2, P3, P4, P5, P8, P11). 2 themes have emerged. Examples of perceptions of environmental sustainability are given below.

“There are many things that can be done without spoiling the nature. For example, in Eriklı there is a lake at the back, it can be cleaned, flamingos go there, you can not see flamingo everywhere. It may be arranged and presented to the public use. no need to cut trees and construct buildings” (P2).

“There is a saying, the environment is not ours but our grandchildren entrusted to us. Soil, water, air, and green areas must remain for future generations” (P6).

“First of all we need to protect the environment very well as human beings. We have not been able to provide that world for our young people, our ancestors left us a very beautiful World, but we could not protect it. I hope the next generation can protect and watch, they can create a habitable world. But if it goes this way, unfortunately there will be no world to live” (P7).

“What we have taken, what we can give the children. It was very different 20 years ago, even before the last 5 years. We must hand down a habitable environment for our children” (P12).

“Protecting the nature, taking advantage of the natural environment without deteriorating the ecological balance, handing down a beautiful world for future generations” (P13).

Participants define sustainable environment as the habitable world for future generations and the unspoiled use of nature. This indicates that participants are aware of the meaning of sustainable environment.

The Environmental Effects of Second Homes, Perception About Change in Eriklı and More Second Home Construction in Eriklı. According to the answers of the question “what is the environmental problems in Eriklı”; participants state that; “unplanned construction of superstructure” (P1, P3,P6, P13), “lack of clean and healthy city water” (P1,P2 P3, P7,P10, P13), “noise” (P1,P3,P5) “inadequate of sewage treatment” (P1, P2, P3, P6, P10, P11), “The pollution of the environment by day-to-day vacationers” (P1, P3, P4, P11). Interestingly, air pollution and transportation are not seen as environmental problems in Eriklı. 5 themes have emerged. Examples of environmental problems in Eriklı are given below.

“Due to the disputes from the bureaucracy, unregistered houses, there is a water problem, the water is salty and dirty, the environment is neglected, people pollute the environment very much, for example, there are people who change diapers and throw it to sandy beaches. There is noise in the morning you can wake up with screams. Vehicle noises, Insufficient purification” (P1).

“The beach needs to be cleaned more, lack of visual beauty that the sea deserve, only a little more service quality needs to be increased, infrastructure problem is serious, water is not drinkable even one can not take a shower” (P2).

“The water is dirty, besides that the sewage smell is also terrible. There was no smell before. They discharge the wastewater into the lake, and they release it to the lake without purification. What causes yellow water? A water smelling like a dirty toilet flows through the tap water. I think it was given without complete purification. There is a lot of noise. Music is playing loudly up to 3 in the morning. People coming from outside pollute the environment they throw plastic bottles and bags, also irregular urbanization” (P3).

“People spread out on the beach for a picnic, they drink, but where are they throwing the garbage, the sea is getting polluted. Indeed, at the sea there are human scum, which is why we hate it, so now we are looking for other places to move” (P4).

“Noisy, I even went to Istanbul to sleep at 3 o’clock in the morning” (P5).

“Unplanned construction, as it is not planned at the beginning, trying to get into a plan later is insufficient, it does not mean much because the unplanned construction is wrong. There is a lack of infrastructure There was sewage problem for many years, there was no sewage, tried to solve this problem with cesspit. Later, in the recent past, sewage was built several years ago. But where did the waste of these sewers go, a biological treatment was done for it, but this is not enough for the number of residential settlements and it really smells bad” (P6).

“There is no drinkable city water in Eriklı. Here the water is supplied from the wells of Korakolu village about 7 km away. It is brought here but it is arguable how sanitary the wells water is. Because it passes through arable land, every kind of pesticide is thrown in those fields finally goes to those wells, and people use that water. Here, we use the water only for the purpose of washing laundry and dishes. The water is not drinkable” (P7).

“The water problem, the bad smell, the purification is not enough. Everything will be nice if water is provided to Eriklı. Even our flowers were dry” (P10)

According to participant’s perception about environmental effects of second homes are; the unplanned development of the superstructure, the lack
of clean and healthy city water, the inadequate sewerage system and the pollution caused by day to day visitors.

The Perceived Change in Eriklı Participants have been living in Eriklı for 21 years in summer season. Participants were asked how they perceive the change in Eriklı; “increase in population” (P1, P2, P3, P6, P10, P12), “increase in concrete structures” (P4, P6, P8, P10), “increase of environmental pollution” (P6, P7, P11, P13) “change in tourist profile” (P6, P7, P9, P10) and "more noise" (P1, P7, P11). 4 themes have emerged. Examples of perceived change in Eriklı are given below:

“IT became very crowded, an irregular image increased, pollution increased, tourist profile changed, tourist profile slightly get worse. Sustainable tourism, unfortunately, became an unconscious mass that would make it unsustainable. So Eriklı did not develop positively We work weekdays so we can go to the sea on weekends. But the weekends are so crowded and so polluted that we do not want to come to Eriklı” (P6).

“There is a huge difference. Especially in the last five years the quality of the human being has dropped here. People who do not have second home cultures have come with cars and minibuses, sleeping in minibuses without accommodation, or even sleeping on people’s balconies when people are sleeping in a certain hour at night. they undressing in front of the people’s house, even they open music loudly in front of people when second home residents are sitting on the balcony, and having their breakfast, they are undressing and dressing everywhere. the sea is filthy. Such a group started to visit” (P7).

“There is a difference, of course, it was more peaceful, the number of buildings has increased, infrastructural problems have increased. The quality of the people has dropped. There is no green space anymore and, everywhere is building” (P10).

“There is a lot of difference in Eriklı between 1994 and now. There is a lot of difference with Eriklı even 2 years ago. Two years ago, it was cleaner and cleaner. For example my brothers have second homes and both of them will sell their homes. They say they will not come to Eriklı anymore” (P13).

Participants think that during the last 20 years, pollution caused by concrete construction, environmental pollution and noise have increased and that the tourist profile has changed. This shows that because of construction of new second homes the environment have been polluted. Te construction of new second homes also caused noise and change of tourist profile.

Participants were asked, “How Eriklı will be effected if more second home built in Eriklı in the future?” “It will definitely be a negative environmental impact” (P1, P3, P4, P7, P10), “there will be no negative environmental impact if it is planned well”(P2, P5, P6) and " Day to day visitors will protect the environment much better if they have their own home” (P8, P9, P11). 3 themes have emerged. Examples for the perception of more second home construction in Eriklı are given below.

“I think it will be negative, the increase in second home will increase the already inadequate infrastructure problem” (P1)

“I do not think it will be a negative effect as long as it is done in a planned way.” (P2)

“It gets worse. It gets so bad, Eriklı disappears. The environment gets dirty” (P3).

“It can be done, but the infrastructure has to be fixed first, at some point it should not be allowed anymore” (P6).

“We barely breathe, no greenery: It will have environmental effects. Second home owners are renting their houses; foreign people are coming. For example, even though there is a balcony at the rear; they hang the front of my house on the trees they have pulled out of the laundry machine. Even though they have a garbage can they throw their garbage in front of the door when they leave” (P10).

“People better protect their environment when they own their own home” (P11).

Participants think that new second homes will adversely affect the environment but according to them if it is planned well, the environment will not be negatively affected and that the environment will be better preserved if day to day visitors own their own second homes. This indicates that the second home owners think the environment is effected negatively but they feel that they are not responsible for that negative environmental effects.

CONCLUSION

The environmental effects resulted from second homes are considered difficult to measure by a lot of researchers. On the other hand, building second homes causes to increase usage of land and infrastructure and die out non-renewable natural resources. For this reason, it is important to discuss the environmental effects of second home tourism and investigate the perceptions and opinions of second home owners so as to understand what to do for the negative effects on the environment.

This study aims to investigate environmental effects of second homes and it focuses on measuring perceptions of second home owners regarding the environment. In spite of being an independent research, the results of the study can be used as a theory based resource by the politics and planning experts to create a consistent frame in the process of observing evolution of second homes, their environmental effects and social attitudes towards them. In addition, this study which was based on the experience and theoretical approaches in western countries can enrich the results of existing studies and it can contribute to both national and international literature of second home tourism.
In previous studies, Kaltenborn et al. [19], Hals- seth and Schwamborn [20], Long and Hoogendoorn [22], it has been observed that second homes are not perceived as causing environmental effects. In this study as well, second homes are not perceived as causing environmental impact. Similar results of the study of Halseth and Schwamborn [20], many second home owners are aware of their inadequacy in the destruction of solid and domestic wastes, although they do not think that their hostile lifestyle is causing too much environmental impact. Pitkanen et al. [21] revealed similar results with the results of our study; that the second home owners expressed their awareness of the importance of conserving natural resources for future generations. In our research, the participants expressed environmental sustainability as unspoiled natural resources for future generations. In addition, the participants said that although they have not protected, the natural environment is in their responsibility for future generations. Even if the second home owners are sensitive to the nature, this sensitivity is not reflected on their behavior. For example, it is seen that in Erikkå, solar energy in terms of sustainable energy and renewable energy are not in use in second homes.

Second home owners think that they are not responsible for the negative environment affect. They think that the day-to-day tourists are responsible for the negative environmental problems. As long as it is planned, second homes will not cause environmental degradation. Nonetheless, population increase, inadequate infrastructure, sewage smell, dirty and unhealthy water are the changes that took place in Erikkå over the years.

It is determined that second home owners are not aware of their environmental effects. In terms of environmental sustainability, it is necessary to get rid of the idea that the second home owners have no influence on the environment. For this reason, it is proposed to provide training by specialists in order to alleviate some of the environmental effects, and to develop projects in which relevant stakeholders can work together. Environmental sustainability should be adopted as the most important principle in the planning of municipal services and settlement.

As a result, it is an indisputable fact that the settlements in which the second houses are located lead to many problems mentioned in this study. What is important is that to be aware of the environmental effects of these settlements and that future initiatives will not create new problems but will overcome them. What is important is that to be aware of the environmental effects of these settlements and that future initiatives have a character that will not create new problems but will overcome them. It seems that Erikkå have many environmental problems such as soil, water pollution, sewerage, superstructure. In order to create a sustainable environment in Erikkå, sustainable planning studies should be done by the participation of all stakeholders. Even if they are not accepted as local people it would be beneficial for second home owners to be recognized as one of the stakeholders of the region and participate as a stakeholder in sustainable tourism planning since they own property in that region and live there in summer time much more longer than a regular tourist. At the same time, the fact that second homes are spread all over the country and that their purpose of use varies according to the qualifications of the regions, many studies need to be conclude with different samples. Also in the future studies, the different dimensions of issues such as socio-cultural effects of second home tourism, managerial problems and control barriers in the second home areas can be investigated.

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ENVIRONMENT AND HUMAN FRIENDLY ENERGY SYSTEM IN TURKEY: BIOGAS

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ABSTRACT

Energy is an important necessity for the continuity of human life. While energy contributes to human life, it can also harm the environment and human health. The method of obtaining energy, inputs and outputs in production are the most important elements. As an environment and human friendly alternative energy, biogas is the product of the digestion of organic materials under anaerobic conditions. On the whole, electricity produced from biogas generates much less carbon dioxide than conventional energy. Shortly, Biogas is a carbon neutral way of energy supply. Turkey’s energy demand has increased over the years and Turkey’s importance in world energy market has been growing both as a regional energy transit hub and as a consumer. The increasing energy consumption of Turkey makes it dependent on foreign sources year after year. Renewable energy projects have been attractive for a few years as Turkey aims to reduce its dependence on external sources. Today, Turkey has high biogas potential and infrastructure that will provide enough input for biogas production and energy generation. Raw materials are mainly procured from animal livestock (e.g. manure from cattle or manure from poultry) agricultural areas (e.g. straw of cereals, sugar beet leaf or tomato waste) and residues from food, fruits and vegetables (e.g. press cake of sugar beet, olive press cake). Because it is a very useful and economic energy in terms of the use of organic wastes Biogas is preferred in terms of clean energy alternatives. Turkey is one of the livestock and agricultural zone in the world therefore has a large biogas potential more than European Countries. Today, Turkey has the potential of 2000 biogas plants which will operate in animal waste. According to official information biogas in Turkey, convertible biomass weight is 117 million tons/year. This study describes the situation and the importance of energy production via biogas in Turkey, an agricultural country. The current status of bio-energy and requirements in biogas production which plays important and vital role for human life and the environment, has been examined.

KEYWORDS:
Environmental health, clear energy, natural source.

MATERIALS AND METHODS

Biogas is a mixture of colorless and odorless gases. It can be produced through fermentation from any degradable material (substrate) with the help of different types of tiny microbes/bacteria. It can be produced in a concealed chamber/digester in the absence of atmospheric oxygen. Biogas is a mixture of different gases, major portion in biogas being methane (CH4) and carbon dioxide (CO2). It also contains traces of other gases like hydrogen (H2), moisture (H2O), hydrogen sulphide (H2S) etc. Improved digesters used for anaerobic digestion can produce biogas with 65% - 75% methane content. The use of methane gas plants as a source of fuel and fertilizer is a practice only recently introduced in this century [1].

FIGURE 1
Biogas Production Cycle [2]

Biogas is a carbon neutral way of energy supply. The production of biogas is sustainable, renewable, carbon neutral and reduces the dependency from imported fossil fuels. The substrates from plants and animals only emit the carbon dioxide they have accumulated during their life cycle and which they would have emitted also without the energetic
utilization. On the whole, electricity produced from biogas generates much less carbon dioxide than conventional energy. 1 kW of electricity produced by biogas prevents 7000 kg CO2 per year. It can be said that this is environment and human friendly energy system. The use of biogas supports the objectives of the European Union of 20 % of renewable energy by 2020.

FIGURE 3
Thermochemical processes to convert biomass into energy

ENERGY SOURCES IN TURKEY

Energy is an essential factor to achieve sustainable development. So, countries striving to this end are seeking to reassess their energy systems with a view towards planning energy programs and strategies in line with sustainable development goals and objectives [4].

Turkey is an energy importing country, with more than half of the energy requirement supplied by imports. Oil accounts for the biggest share of the total primary energy consumption. Due to the recent diversification efforts in the energy portfolio, the use of natural gas, introduced into the Turkish economy, has been growing rapidly. Turkey has large reserves of coal, particularly of lignite. The proven lignite reserves are 8.0 billion tons, with estimated total possible reserves of some 30 billion tons. Biogas from biomass appears to have potential as an alternative energy in Turkey, which is potentially rich in biomass resources.

The energy demand of Turkey doubled between 2000 and 2010, and increase fivefold by 2025. This rapid increase in demand is due to the high economic development rate of Turkey [5].

Primary energy production and consumption rates of Turkey are given below:

FIGURE 4
Energy Consumption in Turkey

FIGURE 5
Energy Production in Turkey [6]
In addition to the commonly used energy sources, it is clear that Turkey needs renewable and sustainable clean energy sources. Among the renewable energy sources, biomass is important because its share of total energy consumption is high. And Turkey has more than enough resources for producing this type of clean energy.

FIGURE 6
Distribution of Turkish soils

**RAW MATERIALS FOR BIOGAS PRODUCTION**

Biomass resources include plant and animal material such as wood from forests, material left over from agricultural and forestry processes, and organic industrial, human and animal wastes. Biomass comes from a variety of sources which include:

- Wood from natural forests and woodlands
- Forestry plantations
- Forestry residues
- Agricultural residues such as straw, stover, cane trash and green agricultural wastes
- Agro-industrial wastes, such as sugarcane bagasse and rice husk
- Animal wastes
- Industrial wastes, such as black liquor from paper manufacturing
- Sewage
- Municipal solid wastes (MSW)
- Food processing wastes

Biomass energy projects provide major business opportunities, environmental benefits, and rural development. Feedstocks can be obtained from a wide array of sources without jeopardizing the food and feed supply, forests, and biodiversity in the world [7].

**Agricultural Residues**. Crop residues encompasses all agricultural wastes such as bagasse, straw, stem, stalk, leaves, husk, shell, peel, pulp, stubble, etc. Large quantities of crop residues are produced annually worldwide, and are vastly underutilized. Agricultural residues are characterized by seasonal availability and have characteristics that differ from other solid fuels such as wood, charcoal, char briquette. The main differences are the high content of volatile matter and lower density and burning time [7].

**Animal Waste**. There are a wide range of animal wastes that can be used as sources of biomass energy. The most common sources are animal and poultry manure. In the past this waste was recovered and sold as a fertilizer or simply spread onto agricultural land, but the introduction of tighter environmental controls on odor and water pollution means that some form of waste management is now required, which provides further incentives for waste-to-energy conversion. The most attractive method of converting these waste materials to useful form is anaerobic digestion which gives biogas that can be used as a fuel for internal combustion engines, to generate electricity from small gas turbines, burnt directly for cooking, or for space and water heating [7].

**Forestry Residues**. Forestry residues are generated by operations such as thinning of plantations, clearing for logging roads, extracting stem-wood for pulp and timber, and natural attrition. Harvesting may occur as thinning in young stands, or cutting in older stands for timber or pulp that also yields tops and branches usable for biomass energy. Harvesting operations usually remove only 25 to 50 percent of the volume, leaving the residues available as biomass for energy. Stands damaged by insects, disease or fire are additional sources of biomass. Forest residues normally have low density and fuel values that keep transport costs high, and so it is economical to reduce the biomass density in the forest itself [7].

**Wood Wastes**. Wood processing industries primarily include sawmilling, plywood, wood panel, furniture, building component, flooring, particle board, moulding, jointing and craft industries. Wood wastes generally are concentrated at the processing factories, e.g. plywood mills and sawmills. The amount of waste generated from wood processing industries varies from one type industry to another depending on the form of raw material and finished product [7].

**Industrial Wastes**. The food industry produces a large number of residues and by-products that can be used as biomass energy sources. These waste materials are generated from all sectors of the food industry with everything from meat production to confectionery producing waste that can be utilized as an energy source [7].

**Municipal Solid Wastes and Sewage**. Millions of tons of household waste are collected each year with the vast majority disposed of in open fields. The biomass resource in MSW comprises are the putrescible papers and plastics, and averages 80% of the total MSW collected [7].
ANIMAL WASTES CAPACITY FOR BIOGAS PRODUCTION IN TURKEY

Wet waste per day according to the number of animals and animals in designated provinces in Turkey in 2009 with a map showing the values of the total waste is given in Fig. 7. When the map is examined, the regions with high potential for waste are concentrated in Eastern Anatolia Region for cattle farming, Aegean and Central Anatolian Regions for poultry. The amount of animal waste collected for Biogas facilities varies from region to region.

There are three provinces that have the potential of 4 million t year⁻¹ waste when the total amount of wet waste of provinces is examined. These are: Balikesir, Erzurum and Konya. The provinces that have the potential of 3–4 million t year⁻¹ waste are Izmir, Van and Kars. Afyon, Sanliurfa, Agri, Bolu, Manisa, Ankara, Aydin, Samsun, Sivas, Diyarbakir and Mus are the provinces that have the potential of 2–3 million t year⁻¹ waste. Turkey’s total number of agricultural holdings and characteristics are given in Table 1 [8].

According to agricultural census done in 2001, Turkey has a total of 3076650 agricultural holdings. While 67.43% of these enterprises make animal and vegetable production, 1.77% of them only makes animal production. Approximately 70% of agricultural livestock enterprises are operating in Turkey. According to the Turkish Statistical Institute (TUIK) in Turkey, raising the number of animals is given in Table 2 for 2016. Approximate animal waste capacity is also given on the same table [9].

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>The number of agricultural holdings of Turkey [8]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristics of Agricultural Holdings</td>
<td>Number</td>
</tr>
<tr>
<td>Animal production</td>
<td>54,523</td>
</tr>
<tr>
<td>Animal + crop production</td>
<td>2,074,439</td>
</tr>
<tr>
<td>Crop production</td>
<td>929,582</td>
</tr>
<tr>
<td>Fisheries and hunting holdings</td>
<td>18,106</td>
</tr>
<tr>
<td>Total</td>
<td>3,076,650</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE 2</th>
<th>The number of animals and waste capacity in Turkey (2016) [9]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Animal Type</td>
<td>Number of Animals</td>
</tr>
<tr>
<td>Cattle</td>
<td>14,222,000</td>
</tr>
<tr>
<td>Small ruminants</td>
<td>41,329,000</td>
</tr>
<tr>
<td>Poultry</td>
<td>323,000,000</td>
</tr>
</tbody>
</table>
TABLE 3

Turkey’s annual main agricultural biomass production [10]

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Annual Production (million tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat straw</td>
<td>26</td>
</tr>
<tr>
<td>Wood/woody materials</td>
<td>12</td>
</tr>
<tr>
<td>Cocoon shell</td>
<td>1</td>
</tr>
<tr>
<td>Hazelnut shell</td>
<td>0.35</td>
</tr>
<tr>
<td>Total</td>
<td>39.35</td>
</tr>
</tbody>
</table>

AGRICULTURAL WASTES CAPACITY FOR BIOGAS PRODUCTION IN TURKEY

Agriculture is the backbone of economic and social development in Turkey. As a source of biomass energy production, several agricultural wastes are accessible in Turkey. As seen in Table 3, Turkey has an important potential of wheat straw which is almost 66.07% of total bioenergy sources [10].

These agricultural wastes can also be transformed to ethanol, biodiesel, hydrogen-and-methane-rich gaseous products by the hydrolysis methods and these products are considered to be the best fuel for electricity production. Furthermore, biogas systems are considered to be strong alternatives to the traditional space heating systems in rural Turkey [4].

Bioethanol can be produced from sugar beets and residues, potato, molasses, wheat straw, corn and cornceobs. More recently, lignocellulosic biomaterials are used through hydrolysis of cellulose into simple sugars and subsequent bioconversion to ethanol.

Biodiesel is another bioenergy product gained from oleaginous seeds such as canola, safflower, sunflower and microalgae. Being environmentally friendly, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content and higher biodegradability constitute the biggest advantage of using biodiesel. However, the number of biodiesel refinery plant was decreased in the last decade in Turkey. By 2006, amount of biodiesel planting was 54000 decare in 6.6 million decare oily seed planting and 12600 tones (0.45%) in 2.8 million tones oily seed production in the country. In 2011, approximately 12 thousand tons of biodiesel was produced by a biodiesel license holder and 10 thousand tons were sold to distributor license holders. Besides, providing via import established 40% of the total of the distributor license holders. It is believed that the amount in the fuel distribution market has a trend to decrease. The total market share of the companies was 80% in 2009, 76.8% in 2010 and 74.5% in 2011.

Biogas, produced from organic substrates after anaerobic fermentation and accounts for mostly methane and carbon dioxide and lower amounts of hydrogen sulfide, hydrogen, nitrogen, carbon monoxide mixtures and this gas mixture can be used directly in gas turbines and fuel cells to produce electricity with less environmental pollution than fossil fuel. As a result of its advantages, biogas production studies are highly increased in Turkey. Biogas manufacturing only from animal residues is calculated to be 2.2-3.9 billion m³ in the country [10].

ADVANTAGES OF BIOGAS PLANTS AND BIOGAS AS FUEL

Benefits of biogas plants are explained as below;
- Reduces burden on forests and fossil fuels,
- Clean fuel reduces air pollution,
- Provides nutrient rich manure for plants,
- No residue produced
- No smoke produced
- Less greenhouse gas emission
- Reduced nuisance from odors and flies
- Controls water pollution by decomposing sewage, animal dung and human excreta

And advantages of biogas as fuel are also given as below;
- High caloric value
- Provide benefits for farmers
- Increases productivity in agriculture
- Improved fertilization efficiency
- Cheap and environmentally sound waste-recycling
- Positively affects environmental health in rural areas
- Economical
- Can be supplied through pipe lines
- Burns readily has a convenient ignition temperature [11].

Due to these advantages, biomass has been considered as the best source for renewable energy in worldwide for the last 20 years.

In Turkey, new strategies are being planned along with the reported studies since 1990s, parallel to approaches worldwide and biomass energy production also enhanced in the last decade in the country. Only 41.26% of total biomass potential which is 16920 ktoe (Table 4) was used for bio-energy production in 1998 and it was increased by 6.19% in 2010. Moreover the projected biomass potential is predicted to be 8205 ktoe (Table 5) and biomass energy production will be increased by 10.67 % by the end of 2030 in Turkey.
The annual biomass energy potential of Turkey has been estimated to be 32 Mtoe and the total biomass consumption in Turkey was 4.8 Mtoe/year. But the largest portion of this product is used in rural areas for heating and cooking in a primitive way. Turkey has a great potential, but energy crops sometimes is required to minimize biomass collection and supply chain risks to bio based industries [13].

**Effective heat of 1 m³ Biogas**

- 3.47 kg Wood heat
- 0.62 lt Kerosene heat
- 4.7 Kwh Electricity heat
- 1.46 kg Wood Coal heat
- 0.43 kg Butane Gas heat

**In Turkey, by the end of 2015:**

- Electricity consumption = 263.8 billion kWh
- Installed power = 73.147 MW
- Renewable energy = 52 billion kWh (%19.8)
- Biogas Energy = 1.5 billion kWh (%0.57)
- Total biogas plants power = 203 MW
- Number of Biogas Plants = 43

<table>
<thead>
<tr>
<th>Million tons of oil equivalent (Mtoe)</th>
</tr>
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<tbody>
<tr>
<td>1 Mtoe = 11630000000 kWh</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thousand tons of oil equivalent (ktoe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ktoe = 11630 MWh</td>
</tr>
</tbody>
</table>

**CONCLUSION**

Turkey, with its young population and growing energy demand per person, its fast growing urbanization, and its economic development has been one of the fast growing power markets of the world for the last two decades. Turkey is heavily dependent on expensive imported energy resources that place a big burden on the economy and air pollution is becoming a great environmental concern in the country [12].

Energy crops might offer significant advantages along the supply chain of any project of biogas, biofuels or bio power in Turkey. As residues are highly available in some regions, dedicated plantations may add more biomass and allow projects to add values like this:

- Higher biodiversity
- Reforestation programs
- More options reducing supply risks
- Integration with forest and agri-industries and providing rural income and local solutions
- Annual and perennial herbaceous crops integrated with existing farming activities (residues, crops, food and synergies between them)
- A multi-feedstock approach reducing uncertainties for bio-based industries
- Woody crops and short rotation coppice alternatives.

Biogas is a clean source energy. Biogas plants have been in operation for a long period of time, especially in rural areas around the globe. The research organizations should focus on newer efficient low cost designs. Turkey have to obtain and use its own human-friendly energy for a clean environment. It has enough raw material for it. Turkish government can play an important role by introducing different legal frameworks, education schemes and the availability of technology and simultaneously creating more awareness and providing more subsidies for Turkey and the world.
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tials_of.42.0.html?&L=0

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CARBON FOOTPRINT IN DATA CENTER: A CASE STUDY

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ABSTRACT

In today's world, which is becoming more digital everyday, it is crucial to address the sustainable environmental awareness during the increasing production, consumption and disposal of IT technologies. These technologies, which consist of software and hardware components, are known to have created a carbon footprint in their lifecycle due to their energy use. New generation technologies such as computer-server virtualization technology and cloud technology are being developed in order to minimize this trail in data centers. In recent years, in order to reduce the carbon footprint, the Hitit University data center has aimed to reduce the carbon footprint by adopting environmentally sensitive technologies. In this study, electrical energy usage data of servers and storage systems were collected from data center of Hitit University. From these data, a comparative carbon footprint has tried to be calculated using a value of 0.443 kg, which is the carbon emission value per kWh of the European Union energy mix. As a result, it is determined that the carbon footprint value is 4.82 kg of the information systems created in traditional architecture until 2012, while the carbon footprint value of the information systems transformed with new generation environmental technologies after 2012 is reduced to 2.20 kg.

KEYWORDS:
Information technologies, Computer hardware, Sustainability, Server virtualization, Carbon footprint.

INTRODUCTION

Although technological developments aimed at increasing the quality of life provide innumerable advantages, many environmental problems such as, increased energy demand, environmental pollution, wasting natural resources and increased greenhouse gas emissions are also accompanied. As a result of which the ecological balance is deteriorating. Diversification and efficient use of energy resources to maintain this balance has brought about the concept of sustainability.

The concept of Ecological Footprint, which enables to make environmental sustainability measurable, deals with a new perspective on the relationship between nature and human beings. It is foreseen that in the future Turkey will live economic difficulties due to biological capacity. The information gained through Ecological Footprint resource accounting to prevent these troubles is a guide for making strategic decisions about resource management. CO2, one of the most important greenhouse gases that accumulate in the atmosphere, also causes other ecological problems such as acidification of the oceans as well as climate change that is one of the biggest environmental problems in history [1].

The reduction of Ecological Footprint is not enough to reduce the ecological deficit, the biological capacity should be invested at the same time to end the limit, the productivity of the productive areas should be increased. Public agencies, the private sector, non-governmental organizations, universities and other relevant groups should act jointly to address environmental issues. 46-49% of total Ecological Footprint resulting from consumption in Turkey constitutes (1.24-1.36 kha per person) carbon footprint. Approximately 21% of the country's CO2 emissions are attributed to products, 19% to personal transportation and 17% to food consumption. In addition, apart from personal carbon footprint, capital accumulation also has a significant share and constitutes 20% of total carbon footprint [1].

In recent years, the idea of being sensitive to the environment, in addition to its cost and technical characteristics, has become important during the selection, design and use of information systems. The installation and living costs of information systems are quite high [2]. It is also known that these systems created a carbon footprint during their life cycle [3]. In order to lower this carbon footprint to lower levels, everyone is tasked in both individual and institutional sense.

According to Yilmaz (2014), there is a relationship between energy demand and emission output in the four major phases of a product life cycle. These four stages are as follows; The raw material production from raw material is the first stage, the product development process from the material is the second stage, the third stage which is the product usage period and finally the product life cycle is completed and the product is recycled. In addition, the building
is referred to as heating and cooling system, electrical household appliances and vehicles are active products, and these products consume more energy than the other phases in the third phase of use [4].

The main pillars of the concept of green ergonomics are the construction and architectural qualities of the working environment, the recycling of office equipment to be appropriate and environmentally friendly, and the selection of computers and other equipment not to threaten the environment and human health [5].

Institutional data centers where information technologies (IT) take place at different scales need to be created within the concept of green ergonomics and sustainable environmental awareness. Data center electricity consumption was first studied by Koomey and it has been mentioned that data centers used 1.5% of global electricity in 2010 [6]. Advances in information and communication technologies (ICT) are also changing the preferences of users. As shown in Figure 1, over a period of 5 years, these preferences are an increase in the use of networks and the expansion of data centers where these networks are located. Therefore, it increases the energy consumption of data centers. In the above Figure 1, the demand for electrical energy for data centers with server-based information systems has increased from 15% to 21% over a period of 5 years. It is believed that the reason for this increase is due to the management of systems centrally via servers and increasingly digital lifestyle.

The data shown in Figure 1 were tried to be summarized in Graph. 1, taking into account the variation of four different factors with respect to two different levels. Accordingly, the biggest change is the increase in amount of network and data centers.

The data centers operate 24/7 and requires a large amount of energy. In 2006, data centers in the United States reached 61.4 billion kWh of energy consumption, which is equal to the manufacturing sector and transportation sector (automobile, airplane, ship and road) [8]. Data centers in Western Europe consumed a weighty 56 TeraWh of power per year in 2007 [3].

As shown in Figure 2, looking at the worldwide, in 2016, energy consumption of data centers was 401.7 billion kWh. If consumption continues this way, it is estimated that will be 507.9 billion kWh in 2020. It shows that as the electricity consumption increases, the carbon footprint will increase.

Universities are one of the centers where information systems are heavily used. In today’s world, where all stages of campus life are digitized, energy is needed to run computers, servers, network devices, mobile terminals and many more. Although some international organizations specify the standards for the energy use of computer equipment, it is considered that these standards can’t be fully met in different environment conditions and load values of the devices. For this reason, it is important for corporate managers and IT staff to make decisions by considering the energy consumption data of the devices for a sustainable environmental policy.
Hitit University has decided to invest in IT, which it has done in recent years, within the scope of sustainable environmental awareness. With this awareness, we take into account the values that international standards have been set for the selection and use of servers, computers and network devices and incorporate them into the life cycle. In this context, important steps are being taken such as determining the systems that are suitable for the energy and signal values of the wireless network devices due to the server virtualization system, cloud architecture and increasing mobile usage needs in campus life. In addition, with some interdisciplinary studies [10] has determined the geographical features of the settlement area. Then wireless network devices have been located in area by signal visibility analysis. It is known that electricity produced and consumed in daily life causes a carbon emission. The European Union specifies that the CO₂ emissions per kWh of the electrical energy mix (such as coal, natural gas, hydroelectricity and nuclear) is 0.443 kg. [4]. Energy related carbon dioxide emissions account for 60% of global carbon dioxide emissions [3].

In this study, electrical energy usage data of servers and storage systems were collected from data center of Hitit University. First, the energy consumption and carbon emission of servers and storage units of the data center established in 2007 by traditional methods was calculated. Next, these values of the system established in 2012 by server virtualization method, which is a new generation method, was calculated. By comparing these two values, we have tried to interpret the change in energy consumption and carbon footprint.

**LITERATURE REVIEW**

The carbon footprint concept, which has been on the agenda for many years and has gained more importance in recent years, is quite a new research in IT. In particular, the increasing use of internet services has increased the energy demands and the environmental impacts [7].

The carbon emissions from energy consumption in data centers are shown in Fig. 3. According to this figure, the total carbon emissions of data centers, computers and network devices as a result of the energy consumption seems to be approximately equal to the total emission of Nigeria, Iran and Poland. Data centers alone consume almost 0.5 percent of the world's energy, and this figure is expected to increase fourfold by 2020 [11].

Kiruthiga and Vinoth (2014) emphasize the need to shift to green computing technology, a nature-friendly approach to energy efficiency and electronic waste reduction. Besides, it is emphasized that CPU used in computer, servers in data center and peripherals connected to them should be converted into low energy consumption devices [12].

In a study by Williams and Tang in 2011 on the environmental impact of the Microsoft Windows operating system, a model has been developed that re-
duces the power consumption of the drives. Implementation of this model provided over 22,000 tons of CO$_2$ reduction per year from 50,000 desktop computers [13]. In the study of Sheikh and Lanjewar (2010), it is stated that data centers produce 150 metric tons of CO$_2$ per year [14].

Vashishtha, et al. (2014) talked about the importance of green computing and virtualization in their work. In the study, it is stated that with virtualization, energy efficiency per user is reduced by 90% and hidden environmental cost e-waste by 98% [15]. In the article of Malviya and Singh (2013), one of the most important solutions for power reduction and ecological problems in ITC is the green information technology [16]. Flynn and Hoover (2010) report that with desktop virtualization, energy efficiency can be achieved in schools and universities, reductions in the amount and cost of energy consumption can be achieved, and computers can be managed more easily [17].

In the study of Çetin and Akgün (2015), the energy consumption of all the systems in first laboratory that are running separately (safe, monitor and running software) was measured. In the second laboratory where virtualization is performed, was measured, as a result, they emphasize that 81% energy saving is achieved alone [17].

In a survey of 360 participants, 63.9% of the respondents answered that they fully agree with the statement "I am going to prefer a less harmful product for the environment". When a statistical evaluation is made, it can be said that when the expressions with the highest percentage in terms of frequency distribution are examined, the participants are trying to turn their sensitivity towards the environment into behavior. Besides, it is also emphasized that this ratio should be increased further [18].

**CONCEPTUAL FRAMEWORK**

**Sustainable Environmental Awareness.** The concept of sustainability, which has recently increased in importance every day [19]; is defined as the continuation of the human being and the environment in which he lives, without being interrupted, without weakened and without causing any loss of quality. By this way, a minimum sustainability criterion is obtained by comparing ecological footprint and biological capacity values [1]. 3R (Reducing, Reusing and Recycling) approach seems to be important in providing a sustainable environmental consciousness [20]. With this approach, resources' are considered to be a life cycle [21].

**Carbon Footprint.** Due to the use of fossil fuels during energy production and consumption, into the atmosphere release of Carbon Dioxide-CO$_2$, Methane-CH$_4$, Nitrous Oxide-N$_2$O, HydroFluoro Carbons-HFCs and Sulfur HexaFluoride-SF$_6$ greenhouse gases occurs. The carbon footprint is called the amount of the effect of the release of CO$_2$ gas, which occurs during the human activity and a product’ life cycle, on the environmental effect of the carbon dioxide.

Turkey's greenhouse gas emissions for 2011 are estimated to be 422.4 million tons (Mt) based on carbon dioxide equivalent, which is quite high. In the same year, World Bank data showed that Germany’s emissions were 810 Mt, 470 Mt UK and 420 Mt Italy. According to TUIK (Turkish Statistical Institute), Turkey’s per person greenhouse gas emissions rose from 3.42 tons in 1990 to 7.2 tons in 2011, an increase of 124 percent. Greenhouse gas emissions are rising in developing countries like Turkey, but decline in developed countries. For example, in India in 2011, it reached 1.6 ton / person, 6.7 ton / person in Italy, 9.9 ton / person in Germany and 7.5 ton / person in the UK. The United States is the country with the worst score both in countries and per capita emission. The share of global pollution in this country, where 5% of the world's population lives, is close to 25%. In the US, greenhouse gas emissions are now at 17 tons per person, 15 years ago was at 20 tons per person [4].

**Information Systems and Data Center.** Information systems are generally known as computers, but they consist of computers, servers, storage devices, network devices, other devices and software. It is possible to encounter most of these equipment in houses. Institutions create data centers where more extensive processes are carried out and many computer equipment are involved.
TABLE 1
Servers in data center of Hitit University

<table>
<thead>
<tr>
<th>Server</th>
<th>Num.</th>
<th>Energy Consumption (~Wh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sun Fire x2100</td>
<td>2</td>
<td>844</td>
</tr>
<tr>
<td>Sun Fire x2200</td>
<td>3</td>
<td>1266</td>
</tr>
<tr>
<td>Sun Fire x2250</td>
<td>2</td>
<td>844</td>
</tr>
<tr>
<td>Dell PowerEdge R720</td>
<td>1</td>
<td>422</td>
</tr>
<tr>
<td>HP DL160 Gen9</td>
<td>1</td>
<td>422</td>
</tr>
<tr>
<td>HP DL380 Gen8</td>
<td>2</td>
<td>1266</td>
</tr>
<tr>
<td>FUJITSU RX224OM2</td>
<td>3</td>
<td>844</td>
</tr>
<tr>
<td>IBM X365 M3</td>
<td>5</td>
<td>2110</td>
</tr>
<tr>
<td>OEM</td>
<td>2</td>
<td>844</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>21</strong></td>
<td><strong>8,862.0</strong></td>
</tr>
</tbody>
</table>

(1) The energy consumed by a server in average load and configuration

TABLE 2
Storages in data center of Hitit University

<table>
<thead>
<tr>
<th>Storage</th>
<th>Num.</th>
<th>Energy Consumption (~Wh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sun StorEdge 3500</td>
<td>1</td>
<td>422</td>
</tr>
<tr>
<td>HP 3Par 7200</td>
<td>1</td>
<td>482**</td>
</tr>
<tr>
<td>FUJITSU Eternus DX60</td>
<td>1</td>
<td>530***</td>
</tr>
<tr>
<td>EMC vxv5300</td>
<td>1</td>
<td>574****</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>4</strong></td>
<td><strong>2,008.0</strong></td>
</tr>
</tbody>
</table>

(1) The energy consumed by a storage in average load and configuration
(2) EMC VNX 5000 Series Storage Device Product Catalog [23]
(3) HP 7000 Series Storage Device Product Catalog [24]
(4) Fujitsu Eternus DX60 Series Storage Device Product Catalog [25]

The construction and operation of a green data center includes advanced technologies and strategies. These technologies are shown in the Figure 4.

MATERIALS AND METHODS

The amounts of energy consumed by the information systems in the data center of Hitit University were prepared according to their energy consumed values suggested by their producers and the following Table 1 and Table 2 were prepared. The reference server model is Dell PowerEdge R720.

In these tables, the energy consumption quantities of servers and storages have been calculated assuming that they all have the same value, taking into account average load and average disk capacity. Even if different brand and model servers have different energy consumption.

It is stated that the average power consumption of referenced server in the product catalog is between 2536 kW and 4852 kW per year [22]. The average Server / Storage Energy Consumption for year (SECy) of these values according to catalog values;

\[
SEC_y (Average) = \frac{(2536 \text{ kWyear} + 4852 \text{ kWyear})}{2} = 3694 \text{ kWy}
\]

As shown in Table 1, the names and models of the servers in the data center are given together. In the following formula (1), one hour of energy consumption is calculated from the values given in the catalog of the referenced server. Server/Storage Energy Consumption for hour (SECh);

\[
SEC_h = \frac{SEC_y}{(365 \times 24)} \quad (1)
\]

\[
SEC_h = \frac{3694 \text{ kWy}}{(365 \times 24)} = 0.42168 \text{ kWh} = 422 \text{ Wh}
\]

In Table 2, the brands and models of storage in the data center are given. The energy usage values of the storage devices in this table vary depending on the disk type (SCSI, IDE, SAS and SSD) and capacity, controller model, processor model, other additional hardware and process load. For this reason, the catalog data of the devices are used as standard Carbon emission values from energy consumption of the devices in Table 1 and Table 2 were taken as 0.443 kg per kWh [4]. This value was used when the carbon footprint was calculated and findings were obtained.

FINDINGS AND RESULTS

In this section, total carbon emission value has calculated based on the electricity consumption values of the servers and storages used in the data.
center. Firstly, in Table 3, the data center emissions between the years 2007-2012, established with the traditional server architecture, are calculated.

In traditional architecture, there is a server setup for at least one task. For this reason, 21 servers and 4 storages were used in the data center created with the previous architecture. The total energy consumption of these devices, as shown in Table 3, is 10.87 kWh and the carbon footprint resulting from carbon emissions is 4.82 kg.

In Table 4, server virtualization technology has been implemented with the help of new generation server architectures. With this change, from 21 servers and 4 storage are reduced to 8 servers and 3 storage. In this case, the consumption of electric energy was reduced to 4.96 kWh, while the carbon footprint was reduced to 2.20 kg.

In 2007, while 21 servers and 4 storages devices were consuming 10.87 kWh energy, this ratio was reduced to 4.96 kWh with the new system established in 2012. So the carbon footprint was reduced from 4.82 kg to 2.2 kg. This result is very important for us. Because we have seen what we did was right.

Amounts of change in energy consumption and carbon footprint have been tried to be summarized in Graph 2.

**TABLE 3**

<table>
<thead>
<tr>
<th>Hardware</th>
<th>Energy Consumption (kWh)</th>
<th>Carbon Footprint (CO₂)(Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Server</td>
<td>8.862</td>
<td>3.926</td>
</tr>
<tr>
<td>2 Storage</td>
<td>2.008</td>
<td>.890</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>10.870</strong></td>
<td><strong>4.816</strong></td>
</tr>
</tbody>
</table>

**TABLE 4**

<table>
<thead>
<tr>
<th>Hardware</th>
<th>Energy Consumption (kWh)</th>
<th>Carbon Footprint (CO₂)(Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Server</td>
<td>3.376</td>
<td>1.496</td>
</tr>
<tr>
<td>2 Storage</td>
<td>1.586</td>
<td>.703</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>4.962</strong></td>
<td><strong>2.199</strong></td>
</tr>
</tbody>
</table>

**CONCLUSION**

In 2012, sustainable environmental awareness began to emerge with the help of decisions made by the university administration about the adoption and use of environmentally-sensitive technologies. Thanks to this awareness, this change has become more evident in the area of information technology. While the hourly 10.87 kW energy consumption was made at the university data center established in 2007, this value was decreased to 4.96 kWh in 2012. As a result, there was a decrease in the carbon footprint of more than half. This sustainability of our university have emerged to address global warming and reduce emissions through product uses and process improvements.

As a Hitit University, decisions have been made in the framework of these expressions, which are also included in the literature in the establishment of information systems in data center. Data center of Hitit University in which;

- Reductions in energy use of 40% to 50% with next generation Information technologies
- All purchased IT products are within international standards (EnergyStar, MercuryFree, RoHS…).
- The mechanical, lighting, electrical and computer systems are designed of maximum energy efficiency and minimum environmental impact.

According to the ecological footprint calculations made by the Global Footprint Network, we will need a world equivalent to three worlds by 2050, as long as we continue our non-sustainable production and consumption patterns today [26].

According to Gartner, the IT industry produces 2% of global CO₂ emissions parallel to the aviation industry. For this reason, reducing even a small portion of the energy consumption in IT leads to significant savings in eco-system financial and carbon emissions [27].
The use of information technology in other sectors also plays an important role in reducing emissions. According to the forecasts, active use of information technologies in greenhouse gas reduction will result in a reduction of 2.03 Gt CO₂ on a global scale [17]. GeSI Smarter 2020 report stated that greenhouse gas emissions could be reduced by 16.5% (9.1 Gt CO₂) with effective use of IT. It is also pointed out that with this decline, 29.5 million jobs and savings of $1.9 million can be achieved worldwide [28].

**SUGGESTIONS**

People who have a big share of the consumption of environmental resources need to be conscious about reducing the consumption and turning to different sources. It is important to have a positive approach to green environment in the process from energy use to waste management, and to acquire individuals with a sustainable environmental awareness starting from the first stages of education.

The wastes that are caused by individual consumption today pollute the environment. Given the obligation to consume every individual and community in society, the role of the decision and conduct of procurement, use and disposal in the preservation and pollution of the environment is indisputable. When environmental education is thought to have begun at the family, new gains can be gained in the school and the surrounding environment. Particularly in the 11-19 age range, family members who are easier to adopt new ideas should be given "ecological responsibility". The acquisition of this responsibility must be one of the aims of consumer education [20].

With this approach, it is necessary to carefully follow the steps from the acquisition of information technologies until they are disposal and to be more sensitive. In this process, brands that manufacture in international standards should be purchased, energy load balancing systems supported by information technologies in energy consumption should be followed, new generation technologies should be followed, and efficient usage architectures should be adopted instead of numerical increase in number of devices. Server virtualization and cloud architectures that have developed in recent years should be supported in this area and contributed to its development.

According to some research results, it is stated that data centers can reduce the energy use demand by 38% in 2020 thanks to the spread of cloud computing [29]. Moreover, when the energy needs of the data centers are supported by renewable energy sources, it is considered that the energy consumption and the emission ratio will be lowered further. In addition, the use of processors, RAMs and HDDs that require faster and less energy can further reduce these carbon emission values. Greener systems should be adopted by investigating the climate, fire extinguishing and other components used in data centers.

In addition to this work, a more comprehensive carbon footprint calculation can be made by determining the carbon emissions from the emission of the heat energy generated by these equipment and the carbon emissions generated by the air conditioning systems used to balance this heat.

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IMPACTS OF PUBLIC PARTICIPATION ON THE ENVIRONMENTAL IMPACTS OF LANDFILLS

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ABSTRACT

As a result of human activities, massive amount of municipal wastes is produced daily. There are several management options for these wastes. According to the general accepted hierarchy, landfills has the lowest priority as the environmental impacts are significant. On the other hand, landfills and wild dumping play a very important role in municipal solid waste management in developing countries and, especially wild dumping is the major disposal art for municipal solid wastes. In these countries the rate of source separation is generally very low and the major disposal method of the commingled collected wastes is the uncontrolled landfilling. The major environmental impacts of landfills are leachate and landfill gas production. The main idea of this study is to minimize the environmental impacts of these sites. Environmental performances of the alternatives are compared by using SimaPro 7.1 LCA software. The results indicate that source separation with high public participation together with biodegradable waste management are the major issues which will enhance the efficiency of waste management and lead to minimize the environmental impacts.

KEYWORDS:
Environmental impacts, Landfilling, Life cycle assessment, Municipal solid waste; Sustainable waste management

INTRODUCTION

Throughout the history, the most commonly used method for waste disposal in the world by far is landfilling. According to the Environmental Protection Agency in the U.S. there were 7,683 dumps in 1986 which is reduced to 1,908 by 2009. EPA estimates the total amount of MSW generated in the United States in 2010 as 250 million tons whereas 135.5 million tons of MSW were deposited in landfills [1]

The rate of municipal waste landfilling for the 32 EEA member countries was 34 % in 2014. The performance of individual countries varied. In Austria, Belgium, Denmark, Germany, the Netherlands, Norway, Sweden and Switzerland, virtually no municipal waste is sent to landfill. On the other hand Cyprus, Croatia, Greece, Latvia, Malta and Turkey still landfill more than three quarters of their municipal waste. Overall, the rates of landfilling decreased in 27 out of 32 countries between 2004 and 2014 [2]. In contrary to the decreasing demand on landfilling in the EEA countries, in most of the developing countries uncontrolled dumping is the common rule of disposal. Besides the huge amount of land, which is occupied by dumping of the wastes, landfill gas (LFG) produced by landfilling of waste (controlled or wild dumping) is the major environmental hazard that the managers have to deal with.

Worldwide methane (CH₄) produced from the landfilling of municipal solid waste (MSW) represented over 12 percent of total global CH₄ emissions. Global CH₄ emissions from landfills are expected to grow by 9 percent between 2005 and 2020 to 817 MtCO₂eq. Most industrialized countries have regulations that will constrain and potentially reduce future growth in CH₄ emissions from landfills. However, it can be expected that especially in developing countries steady growth in landfill CH₄ emissions will take place in the future [3].

The economic welfare of a country is a key influencing factor of the art of disposal: Industrialized countries traditionally have the highest per capita waste generation rates and have accounted for the dominant share of global MSW production each year. On the other hand these countries have adopted sanitary landfills, employing waste compaction, daily cover and final caps as well as leachate and LFG management. Developing countries historically have high population growth rates but use open dumps for waste disposal because of decentralized waste management programs and cost factors [3]. The tendency in the countries with emerging economies is constructing sanitary landfills and rehabilitating the existing uncontrolled dumping places. However sanitary landfilling enables more waste to be decayed in an anaerobic environment, which ultimately leads to an increase in CH₄ production. Additionally, economic growth in developing countries may result in increased migration from rural communities to larger urban settings. Larger amounts of...
waste landfilled in the sanitary and managed dumps in these larger urban cities may potentially increase the amount of \( \text{CH}_4 \) generated.

In industrialized countries’ emissions factors for landfills are projected to decrease. As these countries continue improving their waste management practices, most of the organic waste will be taken out of the MSW disposed of at landfills, thereby lowering the landfill’s \( \text{CH}_4 \) generation potential. One example is the EU Landfill Directive, which has limited the amount of organic matter that can enter MSW facilities. Additionally, steady economic growth and small or negative population growth may again lower emissions factors for landfills in industrialized countries [3]. On the contrary emissions factors for developing countries’ landfills will increase as these countries move away from open dumps toward sanitary landfills. Sanitary landfills typically do not allow for scavengers to reduce the organic composition of the MSW. This possibility, in combination with the lack of established recycling programs (formal recycling programs typically follow the adoption of sanitary landfills), could lead to a dramatic increase in the emissions factors for these landfills.

\( \text{CH}_4 \) emissions, as well as the overall environmental impacts from landfills can be reduced by using two approaches: i) Changing waste management practices to reduce waste disposal at landfills by comprehensive recycling-and-reuse programs plus composting, ii) Capturing the \( \text{CH}_4 \) and flaring it or use it for energy [3].

The main goal of this study is to evaluate the possibilities, which will help to minimize the environmental impacts of landfills using Life Cycle Assessment (LCA) methodology. LCA is a powerful tool and assists the decision makers to evaluate the different management systems according to their environmental performance. It is intensively used as decision support tool in comparison of municipal solid waste treatment technologies [4], comparison of the LCA models developed for solid waste management systems [5], evaluation of solid waste management strategies and options [6, 7, 8, 9] and in evaluating waste-to-energy systems [10].

In this study the waste management system of Antalya City with 1.2 million inhabitants, located at the Mediterranean Coastal Zone of Turkey is evaluated. In order to improve the existing situation, several waste management scenarios which includes the effects of different source separation/public participation options are developed and evaluated by using Life Cycle Assessment (LCA) approach.

**MATERIALS AND METHODS**

**Antalya City.** In recent years based on the population increase rate, the City of Antalya is the second highest after Istanbul in Turkey. Currently approximately 1.2 million people are living within the boundaries of the Metropolitan Municipality, which consists of five district municipalities. In addition, the region receives more than 10 million foreign tourists each year.

**Solid waste management in Antalya City.** Within the borders of the Metropolitan Municipality of Antalya, 1650 tons and 1175 tons of municipal solid wastes are produced during summer and winter period respectively. The majority of these wastes are collected commingled at homes and deposited in the street containers without any separation. The containers are emptied by the district municipalities into pressurized collecting trucks and transported to the sanitary landfill of the city and buried. This 67-hectare site is located about 30 km from the city center. The leachate is collected and treated biologically in the treatment plant located within the landfill site and transported by a pipeline system to the nearest wastewater treatment plant of the city and finally discharged to the sea environment together with the treated waste water of the city. The effluent complies with the relevant discharge criteria. The landfill gas is collected in passive system by vertical vents and discharged to the atmosphere.

Besides this commingled collection system of the wastes conducted by the district municipalities, there are two other actors, who also play important roles in the management system. The first one is the licensed collection companies that are entitled to collect the home separated packaging wastes in each district. The second actor is the irregular street collectors, who collect the majority of the packaging wastes.

In the framework of this study, the composition of the municipal wastes is determined by a field study lasted one year. For this purpose, selected waste containers are collected early in the morning before the street collectors were active, transported to the landfill site and composition is determined according to the prescribed method of the Ministry of Environment and Forestry of Turkey [11].

**Waste management scenarios.** In framework of this study, three waste management scenarios based on the ratio of the public participation, are developed:

**Source separation.** Source separation is the most essential element of a successful waste management plan. Normally the public participation to source separation projects is significantly low (to a greater extent neglected) in developing countries. In Antalya several projects have been implemented for motivating the residents to collect their wastes separately, which should be collected by the licensed companies also separately and after processing in a recovery plant the recyclable materials are send to
the industry as raw material, during the last five years unfortunately with limited success. Three scenarios are developed for evaluating the effects of public participation on overall environmental impacts of a waste management scheme in Antalya.

For the LCA procedure the unit waste production is assumed to be 1.0 kg/cap, day for all scenarios. The economic life of the plant is assumed to be 25 years. The flowchart of these three scenarios is illustrated in Figure 1. Valid for all three scenarios: Leachate produced during the landfilling process is collected and treated in the treatment plant located in the site. Landfill gas is collected by passive wells and discharged to the atmosphere.

**Scenario 1.** The municipal wastes are collected commingled, transported in pressurized trucks to the 30 km away from the city center located landfill site and buried without any recovery. The landfill gases are released to the atmosphere without any treatment.

**Scenario 2.** The municipal wastes are separated at source. The public participation rate is assumed to be 30% that can be easily reached in Turkey with public awareness campaigns. During this separation process, the produced wastes at home, will be collected in two “wet” and “dry” bins. The wastes in the wet bins will be discharged into the containers on the streets, collected by the municipality and transported to the landfill site to be buried. The landfill gases are released to the atmosphere without any treatment. The “dry” fraction will be collected by the licensed company and processed further in a material recovery facility (MRF). The recoverable materials will be sent to the industry whereas the unrecoverable materials will be transferred to the landfill and buried.

**Scenario 3.** The public participation ratio is increased to 70%. This goal can be reached by means of a long term intensified public awareness campaign. The “dry” and “wet” fractions collected separately by the municipality will be delivered to the Mechanical-Biological Treatment (MBT) facility. Dry and wet fractions the waste will be processed separately and the recoverable materials will be transferred to the industry, whereas the biodegradable fraction will be processed in the composting unit of the plant. Produced compost will be used in the agriculture. The unrecoverable materials remaining from the dry and wet fractions will be transferred to the landfill and deposited there.

**Life Cycle Assessment Approach.** LCA is a methodology that corresponds to the demands for selecting the best environmental friendly solution [12]. A LCA study includes four phases: goal and scope definition, inventory analysis, impact assessment, and interpretation. In the goal and scope definition phase, the purpose of the study, the functional unit to which all data/calculations is referred, and system boundaries are defined. The inventory analysis includes data collection and calculation procedures to quantify relevant inputs and outputs of a product system. These inputs and outputs may consist of resource consumption and releases to air, water, and soil related to the system. In the impact assessment phase, the collected and processed data in the inventory analysis are evaluated by a systematic procedure and checking is realized to be ascertain whether all requirements described in the goal and scope phase could be met or not.

The environmental impact assessment comprises of three phases: Classification, characterization, and normalization. In the classification step, all released emissions are distributed into impact categories according to their environmental effects. Subsequently, emissions within each impact category are aggregated by using characterization factors that compared to the effect of a specific emission with a reference [13].

Selected impact categories in evaluation of the scenarios are:
- **abiotic depletion**
- **acidification**
- **global warming**
- **ozone layer depletion**
- **human toxicity**
- **terrestrial ecotoxicity**
- **photochemical oxidation**

The normalization step provides easier comparison of the impact categories by dividing the results into a selected reference value. In the interpretation phase, the results of the inventory analysis are evaluated and the impact assessment for the selection of the preferred product, process, or service is generated.

In this study, the environmental performances of waste management based on public participation ratios are compared by using SimaPro 7.1 LCA software. The inventory data for alternatives evaluated in this study are obtained from the EcoInvent V.2 database, which provides data from various treatment systems. For the impact assessment phase CML baseline 2000 developed by Centre of Environmental Science of Leiden University is used. The data derived from the EcoInvent V.2 database are processed with CML baseline 2000 method implied by SimaPro 7.1 software.

**RESULTS AND DISCUSSION**

**Waste Management.** According to the composition determination works of the municipal wastes in Antalya it is determined that the organic fraction (food and garden wastes) contribute to 55% of the total and the recoverable portion of the wastes is determined as 37.9%. This high value indicates that in
case of good management practices and applying the principles of sustainable waste management, it will be possible to recycle significant amount of recoverable wastes, to decrease the landfill space required and minimize the emissions produced in the landfills.

The impacts of the waste management scenarios on the material flow are summarized in Figure 2. As seen in Scenario 3 which is the most appropriate management scenario for Turkish conditions, only 12% of the wastes have to be landfilled whereas the rate of recoverable/recyclable packaging materials will amount to 41% and remaining organic materials (47%) will be processed in the composting unit. As these organic wastes already separated at source, it is to expect that the produced compost will be of high quality.

The results of the LCA studies are shown in Figures 3 and 4. As seen from the characterization phase, the Scenario 1, in which the wastes are collected without any separation and landfilled, represents the worst case regarding the environmental impacts. It is possible to increase the source separation rate to 30% by conducting minor public awareness raising campaigns (Scenario 2). In this case, as expected, the environmental impacts decrease but it will not be enough to comply with the discharge standards of the emissions. In Scenario 3, it is foreseen that the public participation and the source separation rate will increase to 70% by conducting more intensified public awareness campaigns at larger scale supported by necessary legislative changes. In this case the produced emissions are significantly low. 41% of the recoverable/recyclable materials will be sent to the industry as raw material. In addition, 47% of the produced wastes will be processed in the mechanical-biological treatment plant and relatively good quality compost will be produced.

![FIGURE 1](image1.png)

**FIGURE 1**
Flowcharts of the scenarios

![FIGURE 2](image2.png)

**FIGURE 2**
Impact of waste management scenarios on the material flow

The results of the scenarios regarding the impact categories are summarized below:

**Abiotic depletion.** The least depleting alternative of the abiotic resources is the 3rd scenario as the demand of raw materials in construction and operation phases are low. Landfill area requirements are quite lower than other scenarios due to sending of unrecoverable materials to the landfill only. In addition, through material recovering abiotic resources can be saved in the long-term.

**Acidification.** SO₂, NOₓ, NH₃ and SOₓ emissions produced in the landfill cause acidification. Acidification impact category is least affected in the 3rd scenario, as NH₃ is fixed during composting.

**Global warming.** As a part of CH₄ is oxidized in composting unit and fossil fuel consumption is less in the construction phase due to decreased landfill area requirements, 3rd scenario is the least affecting alternative to global warming.
Ozone layer depletion. Since material recovery can decrease direct emissions (such as released emission in landfill construction and operation) and indirect emissions (releases during recoverable material production in industry) source separation improves the environmental effects on this category.

Toxicity. Toxic emissions are mainly released during construction phase. Also, these emissions can be released via LGF and leachate water during operation phase. Landfill sites of the 2nd and 3rd scenarios will occupy less area as less waste will be delivered. Additionally, some toxic compounds can be recovered; therefore, in the 2nd and 3rd scenarios, toxic releases are reduced as a result of increasing public participation to source separation.

Photochemical oxidation. The products of photochemical oxidation can be converted into refractory and toxic compounds with UV effect. These compounds are mainly released in landfill construction phase due to fossil fuel consumption and influence quantity of this category depends on landfill area requirement.

From the findings mentioned above it can be concluded that low level of public participation to source separation does not lead to significant improvement regarding environmental impacts (Figure 3 and 4). Higher levels of public participation (i.e. 70%) will significantly lead to minimization of acidification, global warming, and human health and toxicity categories.

CONCLUSION

LCA is a powerful tool and assists the decision makers to evaluate the different management systems according to their environmental performance. It is outlined that in case landfilling is applied as the only and final disposal art of commingled collected
municipal wastes, it will result with the highest environmental impacts. Thus, landfilling alone is considered as the worst case scenario.

LCA approach demonstrated that source separation, recycling and diverting organics from the landfills (composting) are the most preferable alternatives. The findings in this study indicated that the key element of reducing the environmental impacts in a sustainable way is the level of public participation (PP). Low levels of PP do not lead to desired decrease in environmental impacts. Though not included in this study, it can be expected that low levels of PP also is not appropriate from economic point of view. Relatively high PP will lead to decrease the environmental impacts in a sustainable way. High amounts of good quality recyclables and compost will be the major “by products” which will contribute to the economic sustainability.

The major negative impact of landfilling is the production and uncontrolled release of CH₄ to the atmosphere. As mentioned above change of waste management practices to reduce waste disposal at landfills by adding recycling-and-reuse programs and composting has priority in reducing CH₄ emissions from landfills.

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INVESTIGATION ON USABILITY OF BIOMASS ENERGY POWER PLANT ASHES FOR PATHOGEN REMOVAL FROM POULTRY MANURE

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ABSTRACT

In this study poultry manure and biomass ash at various ratio and temperatures were mixed and effects of hot biomass ash on removal of pathogens from poultry manure were investigated. Microbiological analysis carried out within the context of the study for pathogen examination (Termotolerant Coliform, Salmonella, E.coli Enterokok) in samples were performed by using ready media. According to the results obtained in the study, Salmonella and E. coli were not found in pure poultry manure and all other mixtures. However, 25x10^3 cfu/g Thermotolerant Coliform and 7.2x10^3 cfu/g Enterococcus were detected in pure poultry manure. The Thermotolerant Coliform and Enterococcus contents, initially detected on raw poultry manure were completely removed in applications using 50% biomass ash at all the temperatures. However, in applications of 200 °C and 250 °C, it was sufficient to use 40% of the biomass ash to completely remove both the Thermotolerant Coliform and Enterococcus contents. The results show that the hot biomass ash can be used to eliminate the pathogen microorganism content of poultry manure.

KEYWORDS:
Poultry manure, biomass ash, pathogen microorganisms, pathogen removal

INTRODUCTION

Groundwater and surface water resources are polluted by the absence of uncontrolled and fugitive poultry manure left in the natural environment, and this poses a significant risk to human health [1,2]. However, poultry manures have an important potential to meet the need for fertilizer, one of the most important inputs for agricultural production, thanks to the macro and micro plant nutrients in high ratio [3]. Today, however, the use of poultry manure for this purpose is very limited. The main reason for this is that the high level of ammonia contained in raw chicken manure is detrimental to plants in direct use, leading to problems such as the presence of pathogenic microorganisms, odor and vector attractiveness. In addition, these problems make it difficult to store and to reach the consumer by being packed like alternative fertilizer varieties. On the other hand, methods applied to alleviate the aforementioned problems, such as open-air drying and composting, reduce the nutrient content and organic matter of poultry manure, mainly nitrogen [5].

These practices cause removal of ammonium (NH₄-N), which constitutes one third of the nitrogen content, by converting ammonia (NH₃), and a reduction in the proportion of nitrogen in poultry manure [6,7]. In studies conducted on this subject, it is stated that the most effective method to reduce the pathogenic microorganism and odor problem, while the nitrogen content of poultry manure is protected as much as possible, is to dry raw poultry manure at appropriate temperature as soon as it is out of the coop [8].

In addition, power plants that use biomass resources such as agriculture-based organic wastes and forestry industrial wastes as fuel are rapidly becoming widespread due to ease of establishment and operation and fewer emissions compared to power plants operating with fuels such as coal and petrol [9]. The rapid increase of these plants causes a lot of biomass ash. According to process, ashes formed at high temperatures, needs to be cooled down and disposed properly [10].

In this study, we investigated the pathogen removal efficiency of hot biomass power plant ash during mixing with poultry manure at various wasted ash temperature from 100 to 250 °C.

MATERIALS AND METHODS

The broiler poultry manure samples used in this study, were supplied from a poultry farm located in Sakarya / Turkey. This breeding farm raises the fattening hen by the method called broiler and it has a capacity of 25 thousand hens for a breeding period. In broiler breeding, the so-called floor substrate is laid to create a suitable environment for hens. In the farm where the samples are taken from rice husk that
is used as bedding material. The farm is equipped with climatization, feeding and watering automation systems. Poultry manure samples (10 kg) were obtained from poultry farm just after the broiler production cycle. The collected samples were homogeneously mixed and then stored in the laboratory at 4°C until analysis time.

Biomass ash samples were obtained from a power plant that uses organic wastes of agricultural origin as fuel. These central biofuels burn down in the fluidized bed combustion unit at 800 °C and produce energy. The ash samples were sieved and heated in the ash oven with the aim to reach the desired temperature (100, 150, 200, 250 °C) for the experiments. When mixed with ash and manure at different ratios, 74.77% of the dry matter content of poultry manure was taken into consideration and the mixing ratios varying by weight (10, 20, 30, 40, 50) were applied.

The moisture content of the samples was determined by the change in the sonar weights from the dried to the constant weighing at 105 °C [11]. The pH values were measured using a pH-meter in a 1:5 sample and pure water mixture as described in European Union standard methods [12]. Similarly, 1:5 ratio of pure water sample mixtures was shaken and then filtered through the vacuum pump and electrical conductivity measurements were performed taking into account the temperature in the resulting filtrate [12]. The total organic matter was calculated according to principle of burning oven dry (105 ºC) samples at 550 °C for 4 hours [13].

Microbiological analysis of the samples, to determine the effects of the hot biomass ash used in the study on the removal of pathogenic microorganisms in the poultry manure, were carried out with pathogen examination in the samples (Termotolerant Coliform, Salmonella, E. coli Enterococcus). Microbiological assays were performed using ready-to-use media. After the intake samples were diluted, the specimens were inoculated to the specially prepared media and the media incubated for 24 hours. Microorganism count was then determined as cfu / 1 g (dry substance) [1, 2]. Bacterial numbers were converted to logarithmic tab to ensure homogeneity.

All analysis in the study were conducted with three replications and the results were provided as the average of three replications in ± SD. The dependent pathogen removal variables were fit to a best reduced model using a backward stepwise regression model, which contained all 6 possible independent variables. The independent variables consisted of temperature, ash ratio, moisture content, pH, electrical conductivity and total organic matter. The resulting best reduced models included only the statistically significant terms at p<0.001.

### RESULTS AND DISCUSSION

The broiler poultry manure is a mixture of chicken droppings and bedding materials. The use of various organic materials as a substrate in broiler poultry breeding can cause the characteristics of poultry manure to differ [4]. Similarly, differences in biofuel species used in biomass power plants can affect the properties of biomass ash. Some characteristics of poultry manure used in the study and biomass ash are shown in Table 1. The moisture content of raw poultry manure was found to be 25.23% and organic matter was 76.92% DM. The pH and electrical conductivity (EC) values of poultry manure and biomass ash are quite high. The pH and EC were 8.1 and 6.76 dS/m, and 12.4 and 14.28 dS/m, in poultry manure and biomass ash, respectively. When these values are compared with the results in studies using broiler poultry manure and biomass ash in the literature, it can be said that the results are similar [14-16].

### TABLE 1

<table>
<thead>
<tr>
<th>Properties</th>
<th>Poultry Manure</th>
<th>Biomass Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Matter (%)</td>
<td>74.77</td>
<td>100</td>
</tr>
<tr>
<td>Moisture Content (%)</td>
<td>25.23</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>8.1</td>
<td>12.4</td>
</tr>
<tr>
<td>EC (dS/m)</td>
<td>6.76</td>
<td>14.28</td>
</tr>
<tr>
<td>Organic Matter (%) DM</td>
<td>76.92</td>
<td>-</td>
</tr>
</tbody>
</table>

Besides, the content of pathogenic microorganism of raw poultry manure was examined and the results are presented in Table 2. *Salmonella* and *E. coli* were not found in the poultry manure, the number of *Enterococcus* was 72x10² and the most detected microorganism strain was *Termotolerant Coliform* with 245x10².

### TABLE 2

<table>
<thead>
<tr>
<th>Microorganisms</th>
<th>Poultry Manure (cfu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Termotolerant Coliform</em></td>
<td>25x10⁰</td>
</tr>
<tr>
<td><em>Salmonella</em></td>
<td>0</td>
</tr>
<tr>
<td><em>E. coli</em></td>
<td>0</td>
</tr>
<tr>
<td><em>Enterococcus</em></td>
<td>7.2x10³</td>
</tr>
</tbody>
</table>

As the ash content and the temperature used in the mixtures increased, a significant decrease in the humidity ratio of the poultry manure was observed. In the application where the highest rate and temperature (50% biomass ash at 250 °C) biomass ash was used, the humidity of the poultry manure was reduced to 9.82% (Figure 1). It is clear that this reduction in moisture content will make a significant contribution to the elimination of the negative properties.
of poultry manure when considering the fact that humidity in poultry manure is the root of pathogen microorganism growth, odor and rapid differentiation. In addition, it is desirable that ideal humidity is 10-15% in terms of ease of application for use of the poultry manure in agriculture [17].

The changes in the pH and electrical conductivity values of the poultry manure and biomass ash mixtures at different temperatures and ratios are given in Figure 2 and Figure 3.

The pH and electrical conductivity (EC) values of the biomass ash are higher than those of the poultry. This caused increase in pH and EC values of mixtures with the increase in biomass ash used in mixtures. The highest pH value was 9.3 determined in the application used 50% biomass at 100 °C while the highest EC value was determined as 10.92 dS/cm in application in which 50% biomass ash was used at 250 °C. In the literature studies, the pH value of raw poultry manure is given in a wide range between 7.8-9.65 [18,19]. Taking this into account, the pH results obtained in all applications, including the application in which the highest pH value is observed, are found in the range of values given in the literature. Additionally, in some studies it is reported that drying process affects pH of poultry manure [20].

Biomass ash reduced amount of organic substances of poultry manure up to 33.68%. During applications the lowest organic substances value was found in the experiment with the highest temperature (250 °C) and the highest mixture ratio (50% biomass ash). On the other hand, decrease ratio of organic substances increased with the temperature. This shows that organic substance is not only affected by mixture ratio but also by the temperature of ash (Figure 4).

Broiler poultry are known to use antibiotics at high rates to prevent poultry diseases. The use of this antibiotic also affects the number and types of microorganisms in chicken droppings. Nonetheless, the studies carried out indicate the presence of an important microorganism in poultry manure, including pathogenic microorganisms [19,21].

The results of the effects of the hot biomass ash on the removal of pathogenic microorganisms in chicken poultry are presented in Figure 5 and Figure 6. In mixtures of poultry manure and biomass ash prepared within the context of this investigation, pathogen microorganisms found most commonly in broiler chicken droppings, which are *Termotolerant Coliform*, *Salmonella*, *E.coli* and *Enterococcus* were investigated [22]. Although there was no possibility of microorganism content in the biomass ash burned at high temperatures, the ash samples were
microbiologically examined for the possibility of contamination and pathogenic microorganisms were not found. *Salmonella* and *E. coli* were not found in raw chicken manure and in the other applications. Although previous studies on the subject have indicated that *Salmonella* and *E. coli* are typical pathogenic microorganisms found in broiler poultry manure, the numbers of these microorganisms have been reported to vary depending on the age of the poultry and the production conditions [22]. As in this study, there are studies in which *Salmonella* and *E. coli* were not present in the broiler poultry manure. However, 25x10^3 cfu/g Thermotolerant *Coliform* and 7.2x10^3 cfu/g *Enterococcus* were detected in pure chicken manure.

**FIGURE 5**
The effect of biomass ash at different ratios and temperatures on the removal of Thermotolerant *Coliform* in chicken manure

**FIGURE 6**
The effect of biomass ash at different ratios and temperatures on the removal of *Enterococcus* in chicken manure

The Thermotolerant *Coliform* and *Enterococcus* content, initially detected on raw chicken manure, was reduced to half in applications using 20% biomass at all temperatures and it was removed in completely applications using 50% biomass ashes. On the other hand, in applications of 200 °C and 250 °C, it was sufficient to use 40% of the biomass ashes to completely remove both the Thermotolerant *Coliform* and *Enterococcus* content. This suggests that as both the temperature and the biomass ash ratio in the mixtures increase, the amount of Thermotolerant *Coliform* and *Enterococcus* content in chicken manure is reduced. Additionally, stepwise regression analysis was performed with the aim of determining the most effective parameters for pathogenic microorganism removal, temperature, ash ratio and pH were found to be the most effective parameters for Thermotolerant *Coliform* and *Enterococcus* removal.

Thermotolerant *Coliform* = -132.66 – 0.01557*T + 19.7042*pH – 0.953366*AR (R^2=0.94; p<0.001)  
*Enterococcus* = -19.623 – 0.220318*AR + 3.43775*pH – 0.00701647*T (R^2=0.956; p<0.001)

Besides, when the results obtained are examined according to European standards of organic fertilizers and soil improvers, it appears that all microorganism species are below the limit values of chicken manure and hot biomass ash applications [23].

**CONCLUSION**

The application of hot biomass ash had significantly considerable benefit in removing pathogenic microorganisms from poultry manure. For all temperature values, it was found that in applications in which the biomass ash was used at the highest level none of investigated pathogenic microorganisms were detected in the mixtures.

When all the results obtained are examined according to the objectives to be achieved in the study, an alternative assessment method for the ashes of power plants using biomass fuel is proposed and have contributed to the broiler poultry fertilizers for the use of agricultural production without adversely affecting the natural environment and human health in terms of the presence of pathogenic microorganisms.

Additionally, it is believed that the macro and micro elements in the biomass ash will enrich the content of the plant nutrient elements of the poultry manure.

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FINDING THE BEST LOCATIONS FOR PHOTOVOLTAIC PANEL INSTALLATION IN URBANIZED AREAS

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ABSTRACT

Social and economic development has proceeded in parallel with energy production and this progress is influenced by the types of used energy sources. Increasing environmental problems originated by the widespread use of fossil fuels, have promoted the use of clean and renewable energy sources as solar energy and related technologies as photovoltaic panels and the photovoltaic applications. However, the use of these technologies is not that much common in urban areas with limited spaces for solar panel installation. In this context, building rooftops and facades are considered a potential installation spaces but the best locations for panel installation should be determined to understand the feasibility of the potential system installations in practice. This study basically aims to present a Geographic Information System based methodology for making a decision of photovoltaic installations on building rooftops in urban areas. For this purpose, a model was provided for determining the spaces available for photovoltaic panel installations on building rooftops and for performing feasibility analyses. The model used three dimensional point cloud data of the study area as input and produced building rooftops classified based on their availability for photovoltaic panel installation as a result of a Multi-Criteria Decision Making process.

The proposed model implemented in the study area including 7 units pitched roofs. As a result total available space, at high suitability rank, was determined as 653.25m², making up 24% of all eligible areas. The number of panels to be used was calculated as 335 pieces. Efficiency analysis applied for a single rooftop confirmed that 70% of the energy consumed in July could be covered by solar energy systems.

KEYWORDS:
Solar energy, photovoltaic, geographic information system, site selection, MCDM.

INTRODUCTION

Energy is an indispensable necessity in today's conditions for especially growing populations of the civilized cities to maintain the quality of the living standards. The increasing energy demand has mostly been supplied by finite energy sources such as fossil fuels as coal, oil or natural gas reserves. However, the use of fossil fuels has significant environmental impacts as accelerating the global warming and air pollution due to increasing greenhouse gas emissions. According to International Energy Agency (IEA), World Energy Outlook Special Report (2015) [1] “Greenhouse gas emissions from the energy sector represent roughly two-thirds of all anthropogenic greenhouse-gas emissions and carbon dioxide emissions from the sector have risen over the past century to ever higher levels.” Another important point mentioned in the IEA report is “to preserve a 50% chance of limiting global warming to 2°C, the world can support maximum CO₂ emissions “budget” of 3000 gigatonnes (Gt), of which an estimated 1970 Gt had already been emitted before 2014” [1]. Potential solutions to current environmental problems have identified along with Renewable Energy Sources (RES) and related technologies since they can provide a reliable and sustainable energy supply almost indefinitely. Improvements of the solar photovoltaic (PV) system, the direct conversion of sunlight into electric power by a solid-state device, have progressed rapidly since the launch of the first satellite in 1950s. Developments in PV technology paved the way for usage of solar energy [2]. As a result, several types of energy generation systems have been implemented for solar energy supply on building rooftops and facades or at installed solar farms. One of the most crucial concerns of RES management is selecting the sites available for an efficient energy supply. The locations with the highest solar energy potential are not always feasible sites for installing energy plants. The efficiency of the installed plant is not only related to energy potential but also has a strong relationship with the requirements of meteorology, economics, environment, and society [3].

Geographic Information System (GIS) integrates current data acquisition, storage, analysis,
and management tools in applications that solve problems related to geospatial information [4]. GIS allows working with multiple spatially referenced variables and enables the use of Multi-Criteria Decision-Making methods (MCDM). The purpose of these methods is to analyze a number of alternatives based on determined criteria and conflicting objectives [5]. This study focused on proposing a GIS-based model applying MCDM in order to obtain the spaces on the building rooftops available for photovoltaic systems’ installation.

Power plants are often installed away from settlements, depending on the size of the plant, human health, and source of energy. The in situ energy production is benign for the transmission expenditure. When the Sun is preferred as an energy source, the idle areas within the urban could be included in energy production. Solar PV panels and selecting suitable areas are the critical parameters in solar energy production. For this selection, one of the significant GIS-based solar energy applications is SUN-AREA research project implemented in Osnabrück, Germany [6]. The method is based on the ArcGIS ModelBuilder from ESRI which gives the user an interface to implement necessary data and tools to model solar power. Other important sources related to the subject is studied by Bayrakci Boz et al. [7] as an automated model for rooftop PV systems assessment in 2015.

This study basically aims to present a Geographic Information System based methodology for making a decision of photovoltaic installations on building rooftops in urban areas.

This study proposed a GIS-based model for the determination of the rooftop spaces available for photovoltaic panel installations. Proposed model is also capable of performing feasibility analyses of potential PV system installations in order to support decision making processes. Total area of the rooftop space available for PV installation, number of PV panels to be installed on that spaces, average electricity consumption of the building were basically used within the context of feasibility analyses.

**METHODOLOGY**

The Ayazaga Campus of Istanbul Technical University located in Maslak, was determined as the study area and the implementation was realized at a specific part of the campus area including university residences with different variety of roof structures for running the proposed model (Figure 1).

The main input data of this study were vector polygons representing the building rooftops and 3D point cloud data which was used to produce digital surface model (DSM) of the roof geometries. The stated data sources were referenced in Transverse Mercator grid zone with central meridian 30 based on the International Terrestrial Frame 1996 datum. The proposed methodology estimated the suitability of the rooftop areas for PV installation and it also aimed to introduce the feasibility of this installation. The suitability and feasibility analyses workflow of the study was presented in Figure 2. As presented in the figure the outputs of the suitability analyses were considered as the input of the feasibility analyses together with the general energy consumption information of the building and the cost of the installation and maintenance of the PV system.

The proposed methodology was implemented using ArcGIS 10.X software, the ModelBuilder extension which is a visual programming language allows creating individual tools [8]. The main parameters used to determine the suitability of the roofs for PV panel installation were rooftop size, shape, slope, aspect, and received solar radiation. Performed analysis was based on DSM produced using 3D point cloud data which was obtained by the use of Unmanned Aerial Vehicle. Since the study area contained two types of roof tops, they were...
FIGURE 2

The suitability and feasibility analysis workflow of the study.

classified based on the average slope they had. Based on the criterion, roofs with an average slope greater than 25° were assigned as pitched roofs while the roofs with an average slope less than 25° were assigned as flat roofs [9]. Based on the proposed methodology such a classification of rooftops was required because of the differences in the spatial analyses applied for different types of rooftops. In this context, while aspect, slope and solar radiation analyses were required for the pitched roofs, only slope analysis was performed for the flat roofs.

The power contained in the sunlight and the angle between the module and the sun were important for the energy collection of solar PV panels hence, the optimum tilt angle played an important role for energy production. Result of the studies completed by Gunerman and Hepbasli in 2007 were used for tilt angle determination in this study [10]. In the fixed-tilled systems, to utilize solar energy throughout the year, the optimum tilt angle were taken to be equal to the latitude of the location. The south-facing slopes received the best sun expose [3], so in the northern hemisphere, the optimum orientation were considered as south facing in the study. The solar radiation intensity falling on a surface was called irradiance or insolation, and it was measured in W/m² or kW/m². Irradiance is the amount of solar energy incident per unit area per unit time and the most suitable criteria in the assessment of the solar resource at a geographical location [11].

GIS is a tool to solve the complicated decision-making problems with MCDM methods which provides a systematic tool for decision-makers in selecting the best alternatives between different options [12]. The implementation of the MCDM methodology through GIS makes it a significant tool as the Decision-Support System (DSS) for the use of spatial decision-making processes such as site selection, resource management and etc. [13]. The weighted overlay analysis is one of the MCDM purposes. In the analysis, the input layer with different scores according to their influence is combined with a percentage weight in a single layer. The sum of the total percentage of influencing weight values of all the layers in the weighted overlay analysis must be equal to 100 % [14].

The slope is the inclination of the surface and it was calculated with clipped DSM due to the rooftop outline. The range containing the latitude value is considered to have the highest suitability, and the classification is made. For the pitched roofs, 30-45 degree was accepted as most suitable range. For the use of flat roofs, slope analysis was performed to find the precise available area on the roof due to eliminate the structural components. Between 0-15 degree was accepted suitable. Since 60 degrees and above are very steep angle values in terms of installation and production, this value and the above were classified as not suitable [9]. The new values were assigned from high suitability to low suitability and presented in Table 1.

<table>
<thead>
<tr>
<th>Slope Degree</th>
<th>New Values</th>
<th>Slope Degree</th>
<th>Assigned Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pitched Roof</td>
<td>Flat Roof</td>
<td>0-15</td>
<td>4</td>
</tr>
<tr>
<td>15-30</td>
<td>3</td>
<td>15-60</td>
<td>2</td>
</tr>
<tr>
<td>30-45</td>
<td>4</td>
<td>60-90</td>
<td>1</td>
</tr>
<tr>
<td>45-60</td>
<td>1</td>
<td>55-70</td>
<td>1</td>
</tr>
</tbody>
</table>

Slope directions calculated according to aspect analysis results and the reclassification was
implemented. N, NE, NW is less suitable directions, E and W directions are medium and S, SE, SW is the most suitable directions (Table 2) [7].

### TABLE 2
The assigned values of aspect

<table>
<thead>
<tr>
<th>Slope Direction</th>
<th>Assigned Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pitched Roof</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>2</td>
</tr>
<tr>
<td>NE</td>
<td>2</td>
</tr>
<tr>
<td>E</td>
<td>3</td>
</tr>
<tr>
<td>SE</td>
<td>4</td>
</tr>
<tr>
<td>S</td>
<td>4</td>
</tr>
<tr>
<td>SW</td>
<td>4</td>
</tr>
<tr>
<td>W</td>
<td>3</td>
</tr>
<tr>
<td>NW</td>
<td>2</td>
</tr>
<tr>
<td>N</td>
<td>2</td>
</tr>
</tbody>
</table>

Area solar radiation tool of ArcGIS software was used to calculate the Global Radiation. The solar radiation analysis tools are defined as a methodology based on the hemispherical view shed algorithm developed by [15, 16]. Solar radiation analysis tool can calculate a particular location or selected area. The calculation of direct, diffuse, and global insolation is for each feature location or every location on the surface, producing insolation maps for an entire geographic area [17]. Solar radiation data was used to classify regions where the radiation is high (Table 3). It was not taken into account in the electricity generation.

### TABLE 3
The assigned values of solar radiation

<table>
<thead>
<tr>
<th>Solar Radiation (MWh/m²)</th>
<th>Assigned Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-250</td>
<td>2</td>
</tr>
<tr>
<td>250-500</td>
<td>2</td>
</tr>
<tr>
<td>500-800</td>
<td>3</td>
</tr>
<tr>
<td>800-1100</td>
<td>3</td>
</tr>
<tr>
<td>1100-9999</td>
<td>4</td>
</tr>
</tbody>
</table>

Feasibility analyses include the initial cost, potential savings, annual income and expenses, depreciation [18]. The suitable area calculations and classifications, which are required for feasibility analysis, were made with GIS analyses. Those analyses include slope, aspect, weighted overlay and area calculations.

The installation and maintenance costs of the CWT270-60P 270W panel were considered as the input of the feasibility analyses within the study. The peak power of the panel was taken consideration, so the high-value regions of the roofs were put in practice. The area covered by a single PV module covers 2m² area on average. The number of panels to be installed was decided only for pitched roofs. The analyses were carried out considering the architectural structure of the roof for PV installation without adding any additional constructional elements. The cost of the panel was required from the production company. The average price of a single module was given 143.15. The average sunshine duration of Sanyer is 6.50 h and was taken from the Solar Energy Potential Atlas (GEPA) [19]. The average sunshine duration was used to calculate daily electricity production. In this study, the production of the electricity is dependent on the total number of panel module used. The other components of PV system, inverters, support equipment, cables were not taken into account for the feasibility analysis in this study. So the determined cost can be considered as the minimum installation cost in practice. The stated cost of the panel varies based on the purchase amount of panels, production supply, and shipping type.

In the study area, 11 buildings were analyzed, and 7 of them have pitched roof while 4 of them have flat roof. In the panel installation, it was accepted that the installation process would be done with the current roof orientation. Feasibility studies were made on pitched roofs, considering the extra cost of providing flat roofs to suitable orientation. Results of analysis as slope, aspect and solar radiation were reclassified and one of the MCDM, the weighted overlay analysis was implemented. The reclassification values assigned relative importance of each factor. The classification range is between 1 and 4. The highest weight value was assigned as 4 with maximum potential magnitude. 1 value was assigned as inapplicable area, and it was not considered in weighted overlay process. Then, the weighted overlay process was performed by accepting the resultant effects at different percent. The reclassification outputs of slope, aspect and solar radiation were used as inputs of weighted overlay process. The influence percent was selected 20%, 60% and 20%, respectively. The overlay analysis result was converted from raster to feature, and spatial join process was done to attend the building ID. Building ID is necessary to combine the segments which are the same roof and the same suitability value.

Based on Ludwig et al., [6], the roof size should be at least 15m² to be suitable due to economic reasons and according to Bayrakci Boz et al., [7] the minimum area of rooftop depends on the total roof area commonly acceptable area is 10 m². However, when the panel dimensions are examined, it has seen that the single bridging module covers approximately 2 m² area. Therefore in this study, unlike the studies mentioned above, areas larger than 2 m² were included in the calculation. Depend on the average area covered by a panel, the area of rooftops is less than 2 m² was eliminated because of the panel area. After the elimination process, the suitability map was generated (Figure 3).
RESULTS

As a result of the applied methodology, the classification according to the suitability of each of the 11 rooftops is shown in the map in Figure 3.

For the buildings considered in the study area, the total available area and the total panel module count were determined as is 678 m² and 335 respectively. If the daily sunshine duration was accepted the average of the year, 6.5 h [19], the total energy production was calculated 653.25 kW/day. The electricity consumption of building 5 was used in the detailed feasibility calculations. The electricity consumption in July 2016 was 3208 kWh (Table 3). The sunshine duration in July is 10.72 h [19]. If the calculation was made according to the sunshine of July, the monthly electricity generation related to the installed capacity would be 4515 kWh.

However, it should not be forgotten that the panels cannot work with 100% efficiency, that the production changes according to the incoming solar radiation and those energy losses due to the transmission are experienced. Even if it is thought that the production of these losses is around the 50%, it is possible to cover the 70% of the electricity consumption of the building 5 from the roof PV panel systems.

When the calculations of buildings according to the yearly average electricity consumption of the building number 5 are made, the annual electricity consumption is 46 116 kWh and the invoice amount paid is 12 420 TL approximately 3 253 dollars. It is estimated that the annual electricity generation of the installation at most suitable locations, which is supposed to be built at building number 5, is 32 853 kWh/h. When averages are taken on a monthly basis, the electricity consumption is 3843 kWh, the paid amount is 1035 TL, about 271 $. It is seen that the production produces more than the annual value, and if it is considered that the system sells electricity depending on the network, on-grid PV system, electricity sales of 13 260 kWh per year can procurable. The distinction between consumption and production is equivalent to about 4 months of electricity consumption, it can be considered that 4 bills and the income per year earned will be 4 140 TL, about $ 1 084. Only the cost of purchasing the panel is $ 7 441, and the period of depreciation time can be calculated as 28 months. Calculations were performed as profit on invoice and costs might be changed depending on the on-grid or off-grid installations. It should be considered that costs that will arise outside of the panel cost as, inventor, installation, transportation, official permission,
maintenance, and in the necessary cases the storage costs were not into taken consideration.

CONCLUSION

This study proposed a methodology for determining the installments of the solar energy production systems in urban areas. The method determined the suitable rooftops based on slope and aspect analyses. The efficiency of the potential installations were also estimated by the proposed methodology in order to contribute decision making mechanisms for motivating the investments for the use of solar energy sources in the cities.

There are a number of deficiencies in the development of the model at the next stage of this study. One of the fundamental deficiencies of the model, which cannot be realized in this study, is shadow analysis. The environmental impact of the shadow should be considered as a weighted overlay factor. The other rooftop components as chimney can be extracted before the spatial analysis.

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ASSESSMENT OF POLLUTION PROFILE AND WASTEWATER CONTROL ALTERNATIVES OF A PHARMACEUTICAL INDUSTRY

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Environmental Engineering Department, Civil Engineering Faculty, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

ABSTRACT

In this study, characterization and biological treatability of tablet production wastewaters of a pharmaceutical industry were assessed. Source-based wastewater characterization of tablet, pastille, effervescent tablets, and chewing tablet productions indicated variable strength of wastewaters with COD values between 1030 and 6700 mg/L. Biological treatability studies conducted on these wastewaters showed that the wastewater having BOD/COD ratios above 0.4 could be effectively treated using activated sludge process at 0.21-0.25 g COD/(g VSS d) organic loading. One of the tablet production wastewaters was found to be practically non-biodegradable. Ozonation of this wastewater yielded a limited increase in biodegradability. 60% COD removal could be obtained by biological treatability experiments at organic loadings of 0.06 to 0.1 g COD/(g VSS d) using composite samples prepared as a mixture of ozonized and non-ozonized tablet wastewaters.

KEYWORDS:
Biological treatment, Ozonation, Pharmaceutical industry, Source-based characterization, Tablet production wastewater

INTRODUCTION

Pharmaceutical industry wastewaters pose several problems in terms of handling and treatment [1-3]. These problems mainly originate from the diversity of sources, wastewater strength and more importantly from limited biological treatability. While pharmaceutical industry subcategories such as chemical synthesis, fermentation have been studied relatively more extensively due to high strength of their wastewaters, less attention has been paid to formulation plants. Formulation plants generate wastewaters to deal with more easily. However, the formulation plants actually are of a more complex nature. This is mostly due to a very broad range of product spectrum and change of production profiles with seasons. On the other hand, strength of wastewater may be unexpectedly high reaching several thousand mg/L of COD and biological treatability varies in a great range. The most common application for the treatment of formulation plant wastewater is to employ a central activated sludge system with low organic loading. Generally, no wastewater segregation or pretreatment has been practiced [4]. However, this approach seems to be no longer adequate in complying with the new regulations and effluent discharge standards that have become more stringent. Control of pollution by modifying the production processes has reached a wide application and is one of the most effective means against pollution of the aqueous environment. Within this context there have been attempts to search for new and effective means of treatment for pharmaceutical wastewaters and other industrial wastewaters containing recalcitrant compounds. Zwiener and Frimmel [5] studied oxidative treatment of pharmaceuticals in water using clofibric acid, ibuprofen and diclofenac as model compounds. Direct ozonation was found unsuccessful for diclofenac with almost complete reduction while other compounds were treated by the combined ozone and hydrogen peroxide to obtain satisfactory degradation efficiencies. Ozonation as a pretreatment was also used for several other difficult wastewaters for partial treatment and to increase the biodegradability. Alvares et al. [6] reviewed studies on ozonation for removal of recalcitrant compounds from wastewaters. Preozonation to enhance the biodegradability was evaluated from the data for organic compounds such as halogenated heterocyclic or nitrogenous aromatics, and a variety of wastewaters. Stockinger et al. [7] studied the ozonation of chloro and nitro aromatic wastewater compounds in synthetic wastewater and determined optimum operating conditions. Tosik and Wiktorowsky [8] applied ozonation to dyeing wastewaters to increase the biodegradability. Information about biological treatability of pharmaceutical wastewater is still limited. El Gohary et al. [9] experimentally studied the treatability of pharmaceutical and chemical factory wastewater for its final disposal to surface water or for reuse in irrigation. Raj and Anjaneyulu [10] evaluated the biological treatability of pharmaceutical wastewaters employing coagulation as a pretreatment. Tunay and Ovez [1] studied biological treatability of a variety of pharmaceutical wastewaters and emphasized the different characters of wastewaters from different sources. Kabdasli et al. [2] developed a source-based approach aiming at the definition of biodegradability for the sources by which a general scheme of treatment system could be obtainable.
In this paper results of characterization and treatability studies conducted on tablet formulation wastewaters of a pharmaceutical industry were presented. The study was carried out on the wastewaters supplied from a pharmaceutical company located in Istanbul. The scope of the study included characterization of different sorts of tablets and assessment of their biological treatability. For one wastewater source modification of biological treatability was carried out using ozonation.

**MATERIALS AND METHODS**

**Description of the plant and wastewater generation.** All products generating the wastewaters investigated in this study follow the same production steps of: weighing, granulation, drying, mixing, tablet pressing, tablet coating and packing. Only for chewing tablets the granulation step was not involved.

Four types of products from the tablet group were selected for the experimental study. First type was tablet. In this type, three products were represented. Product IA was a paracetamol based analgesic. Product IB exhibited the same composition as Product IA except for an additional auxiliary chemical. Product IC was a sulfonamide based antibacterial. Product II was an o-phantenol based pastille. Product III was an effervescent tablet containing ascorbic and citric acid as active materials. Product IV was an alkali based antacid.

All processing steps except coating contribute to wastewater generation which is totally caused by equipment washing. Carts are used to transfer the material between the equipments. Cart washings are also wastewater sources. Only a detergent is used in the washing, final rinse is always with deionized water. Unit amount of wastewater, on the basis of operation or per batch is given in Table 1 for all productions.

**Sampling and wastewater characterization.** Composite samples representing each production process were prepared for wastewater characterization and treatability experiments. For each composite the wastewater samples taken from all process steps were combined in a flow-weighted manner. Since the wastewaters originated from washing and rinsing, the samples collected in each process step were prepared from a group of individual samples taken through the washing period.

All analyses were made in accordance with Standard Methods [11] except COD analyses. COD measurements were performed as defined in ISO 6060 [12].

**Biodegradation experiments.** Product II and product III wastewaters were, although strong, highly biodegradable as their BOD<sub>5</sub>/COD ratio indicated. These wastewaters were directly fed into activated sludge system after pH adjustment and nutrient additions. Product IV also exhibited biodegradable character, but it contained a high concentration of suspended matter of settleable character. Therefore, this wastewater was fed into biological treatment after gravity settling. A wide range of organic loading was applied for Product II, Product III and Product IV samples in order to evaluate biological treatability. Product IA wastewater showed degradable character. For wastewater originating from Product IC no biodegradability was indicated. However, biodegradability of organics contained in this wastewater was determined in the activated sludge system. An activated sludge system acclimated to Product IA wastewater was fed with a mixture of Product IA and raw Product IC wastewater. Content of Product IC in the feed varied between 10 and 25% on a COD basis. Each trial with this wastewater lasted for 1-2 weeks but no COD removal was observed. This indicated that raw Product IC wastewater was not biodegraded while totally blocking the metabolic activity to remove otherwise biodegradable COD of Product IA. Upon the results Product IC wastewater was ozonated to improve its biodegradability. Ozonated Product IC sample was not directly fed into activated sludge considering its still low BOD/COD ratio, instead it was mixed with Product IA or Product IB wastewater in proportion with their flows as shown in Table 1. Biological treatability experiments were conducted on these mixtures (Composite I and Composite II).

<table>
<thead>
<tr>
<th>Wastewater Generation for All Productions (m³ per Operation)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tablet</strong></td>
</tr>
<tr>
<td>Product IA-IB</td>
</tr>
<tr>
<td>2.345</td>
</tr>
</tbody>
</table>
Biological treatability studies were run in 5 liter fill and draw reactors equipped with porous stone diffusers at the bottom to supply air and to provide completely mixed conditions. Activated sludge seed was provided from wastewater treatment plant of the pharmaceutical industry. The seed was further acclimated to all process samples separately. Acclimation was conducted at 0.3 g COD/(g VSS d) F/M for all wastewaters except Product IC wastewater. Initial concentrations of both Composite I and II were diluted about 15-20% due to microorganism addition. Acclimation period was 4-6 weeks for all samples. After acclimated period, the sludge was used for biological treatability experiments. The systems were operated for the determined organic loading for a period to obtain steady operation and consistent effluent quality. VSS concentrations and aeration periods employed for Product II, Product III, Product IV and Tablets were: 3600-6000 mg/L and 1.5 days, 3000-5000 mg/L and 2-4 days, 2000-4000 mg/L and 1-3 days, 1000-2000 mg/L and 2-3 days respectively. VSS concentrations were kept at given ranges by withdrawing sludge. A mixture of $K_2HPO_4$, $KH_2PO_4$ and $NH_4Cl$ was added to wastewater to provide phosphate and ammonia and to buffer the pH between 6.9-7.2. Although, the systems were buffered, pH decreases were observed for Product II and Product III wastewaters during the course of aeration. To overcome this difficulty pH changes were monitored and corrected by addition of NaOH solutions. Foaming observed during the operation of activated sludge systems was suppressed using silicon type defoaming agent. System performance was evaluated on the basis of soluble COD which was determined by filtration using Millipore AP40 glass fiber filters.

### Sedimentation experiments

Sedimentation experiments were conducted in Imhoff cones for one-hour duration. Two samples of Product IV wastewater were subjected to the sedimentation.

### Ozonation

Product IC wastewater was ozonized at the original pH to increase its biodegradability. Foaming was abated by adding silicone type defoaming agent in small increments. Ozone was provided using GL-1 brand PCI Model ozone generator that was fed with air at the capacity of 0.57 m$^3$/h. All connections in the ozonation set up were made using Teflon fittings. The ozonation reactor was made of Pyrex glass with 4.5 cm internal diameter and 120 cm height. The ozone-air mixture was fed through the sintered glass diffusers placed at the bottom of the reactor. Off-gas ozone was trapped using two serially connected gas-washing bottles containing 2% KI solution. The sample volume was taken as one liter in all experiments. Ozonized Product IC was aerated to remove ozone and mixed with Product IA wastewaters on a flow weighted basis (i.e. in proportion with the flows indicated in Table 1), and prepared for activated sludge feeding.

### RESULTS AND DISCUSSION

A source-based wastewater characterization was carried out using the parameters selected considering the structure of raw materials of production. Analysis results are given in Table 2. Product IA and Product IB production is identical except for the addition of small amount of an auxiliary material to Product IB. Therefore, their wastewater characteristics were expected to be similar. However, Product IB wastewater was stronger than Product IA wastewater. BOD/COD ratio was in the same order of magnitude, although Product IA exhibited a slightly higher ratio of 0.273 vs. 0.138. A relatively high ratio of BOD/COD indicated biodegradability of paracetamole as pointed out in the literature [2]. Suspended solids (TSS) were totally of organic origin. Nitrogen requires addition of nitrification-denitrification in biological treatment. Product IC was also associated with a strong wastewater exhibiting high concentration of suspended solids which was also organic in nature. Nitrogen was, in a similar manner to Product IA, high. No BODs value could be detected indicating its resistance to biological degradation. This non-biodegradable character was also checked before biological treatability experiments had been started for Product IC.

Product II wastewater was also strong with high biodegradability as indicated by the high BOD/COD ratio of 0.5. Suspended solids although high were in colloidal form and did not show the tendency of separating by gravity. Product III wastewater had characteristics very similar to Product II wastewater in terms of all parameters except nitrogen. Biodegradability characteristics of the two samples were in the same range. Two wastewater samples from Product IV production had similar characteristics. They were strong in terms of organic matter and highly biodegradable. Product IV wastewater contained very high suspended solids that was observed to settle readily under quiescent conditions. In general, strength of wastewaters was in the order of a couple of thousands of mg/L COD being comparable to the literature data [4].

Results of sedimentation experiments are given in Table 3. In both samples very high suspended solids removal was obtained. Product IV wastewater, although representing only 7.5% of the total tablet wastewater, has a very high suspended solids content. Therefore, its suspended solids concentration needs to be reduced before the biological treatment. Sedimentation proved to be a proper application as a pretreatment for this waste stream providing very high suspended solids removal accompanied by a COD removal of 450-700 mg/L.
TABLE 2
Wastewater characteristics of the selected products of tablet production

<table>
<thead>
<tr>
<th>Product Name</th>
<th>pH</th>
<th>COD (mg/L)</th>
<th>S.COD* (mg/L)</th>
<th>BOD₅ (mg/L)</th>
<th>TSS (mg/L)</th>
<th>VSS (mg/L)</th>
<th>TKN (mgN/L)</th>
<th>TP (mgP/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tablet Product IA</td>
<td>6.7</td>
<td>1030</td>
<td>770</td>
<td>210</td>
<td>200</td>
<td>200</td>
<td>55</td>
<td>1.0</td>
</tr>
<tr>
<td>Tablet Product IB</td>
<td>3.7</td>
<td>4070</td>
<td>3980</td>
<td>550</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>170</td>
<td>0.9</td>
</tr>
<tr>
<td>Tablet Product IC</td>
<td>6.0</td>
<td>2250</td>
<td>1050</td>
<td>-</td>
<td>900</td>
<td>900</td>
<td>216</td>
<td>0.7</td>
</tr>
<tr>
<td>Pastille Product II</td>
<td>4.9</td>
<td>6700</td>
<td>5950</td>
<td>3000</td>
<td>800</td>
<td>420</td>
<td>&lt;5</td>
<td>0.9</td>
</tr>
<tr>
<td>Effervescent Tablet Product III</td>
<td>3.5</td>
<td>5900</td>
<td>4700</td>
<td>3300</td>
<td>420</td>
<td>420</td>
<td>&lt;5</td>
<td>2.5</td>
</tr>
<tr>
<td>Chewing Tab- le Product IV Sample I</td>
<td>9.8</td>
<td>2500</td>
<td>2000</td>
<td>1200</td>
<td>4150</td>
<td>1100</td>
<td>&lt;5</td>
<td>0.3</td>
</tr>
<tr>
<td>Chewing Tab- le Product IV Sample II</td>
<td>9.7</td>
<td>4300</td>
<td>3500</td>
<td>2000</td>
<td>6500</td>
<td>1700</td>
<td>&lt;5</td>
<td>0.6</td>
</tr>
</tbody>
</table>

* S.COD : Soluble COD

TABLE 3
Results of gravity settling experiments of Product IV wastewater

<table>
<thead>
<tr>
<th>COD (mg/L)</th>
<th>TSS (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent</td>
<td>Effluent</td>
</tr>
<tr>
<td>Sample I</td>
<td>2500</td>
</tr>
<tr>
<td>Sample II</td>
<td>4300</td>
</tr>
</tbody>
</table>

Results of the ozonation of Product IC wastewater sample are outlined in Table 4. Ozonation was applied for 1 and 3 hours. This treatment reduced pH to almost 3.0. Ozonation was extended to 3 hours to determine whether COD removal efficiency had been changed, however no large additional decrease in COD was determined. The amounts of removed COD concentrations (620 and 670 mg/L, respectively) were in proportion to the amounts of utilized ozone, which were also quite similar both ozonation periods, however. While no BOD₅ was detectable in raw Product IC sample, a BOD₅ concentration of 200 mg/L was measured after 3 hours ozonation. This corresponded to a BOD₅/COD ratio of approximately 0.13 indicating that the sample had gained some degree of biodegradability. Composite I and II were prepared using ozonized Product IC and Product IA mixture and ozonized Product IC and Product IB mixture, on a flow weighted basis, respectively.

Results of biological treatability for Product II wastewaters are delineated in Table 5. The wastewater was rapidly and readily biodegraded providing over 95% COD removal even at a very high organic loading of 0.64 g COD/(g VSS d). Product II wastewater was similar in strength to Product III. A comparison of the results obtained with both wastewaters (Table 5) indicated that their biological treatability characteristics were also quite similar. 0.3 g COD/(g VSS d) organic loading also seems to be an optimal loading for Product II wastewater. It may be assumed that residual COD of around 200 mg/L is recalcitrant.

As seen from Table 5 Product III wastewater was strong, its COD was approaching to 6000 mg/L. It was highly and readily biodegradable as indicated by its relatively high BOD₅/COD ratio (Table 2). Rapidly biodegradable part of wastewater was almost completely removed at 0.3 g COD/(g VSS d) loading. Above this loading removal was decreased resulting in higher residual effluent COD values. For lower loading of 0.23 g COD/(g VSS d), however, the additional COD removal was limited. The differences between final COD values obtained for sludge loadings of 0.23 and 0.3 g COD/(g VSS d) values implied that, similar to Product II, an inert or slowly degradable part of COD was remaining at sludge loadings below 0.3 g COD/(g VSS d). For this wastewater a loading around 0.3 g COD/(g VSS d) could be assumed as an optimum value.

Both, Sample I and II of the Product IV wastewater exhibited the same high biodegradability characteristics (Table 5). High COD removals were also obtained with relatively high organic loadings of about 1.0 g COD/(g VSS d). An effluent COD around 80 mg/L which corresponded to 98% COD removal was reached with 0.7 g COD/(g VSS d) loading and this COD could not be reduced by lowering the organic loading to 0.1 g COD/(g VSS d).

TABLE 4
Results of the ozonation experiments of Product IC wastewater sample

<table>
<thead>
<tr>
<th>1 Hour Ozonation</th>
<th>3 Hour Ozonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>BOD₅ (mg/L)</td>
</tr>
<tr>
<td>1630</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 6 shows the biological treatability results of Tablet production wastewater composites prepared from ozonized Tablet IC wastewater and non-ozonized Product IA or Product IB wastewaters (Composite I and Composite II, respectively). Ozonation increased the biological treatability of Product IC to a limited extent, providing a BOD5/COD ratio of about 0.13 (calculated from data in Table 4) which is in the same order of magnitude as those established for treatment of Product IA and IB as can be calculated from Table 2. Treatability results of Composite I indicated that at the highest organic loading of 0.21 g COD/(g VSS d) the COD removal was far from being satisfactory. COD removal percentage gradually increased with reduced organic load and 65% COD removal was obtained at 0.06 g COD/(g VSS d). 65% COD removal may be deemed satisfactory and may justify the use of biological treatment of this mixture. Lower organic loadings were not tested due to turbid effluent of activated sludge at 0.06 g COD/(g VSS d) loading. Although treatability results of Composite II exhibited a similar picture, COD removals were higher than in Composite I at corresponding organic loadings. Although effluent COD of 780 mg/L at 0.11 g COD/(g VSS d) loading was high, a biological treatment in a similar manner to that of Composite I can still be an alternative maybe as an intermediate step. Lower organic loading than 0.11 g COD/(g VSS d) was not tried due to the deteriorating settling characteristics.

In another study, the treatability of high strength pharmaceutical wastewaters (with high contents of COD, chloride and phosphorus) in a Thermophilic Aerobic Membrane Reactor (TAMR) was investigated [14]. The experimental research was carried out using a pilot plant, in which different mixtures of liquid wastes were fed. The hydraulic residence time varied from 5 to 10 days and the organic loading rate varied between 1.5 and 5.5 kgCOD/(m³ d). The main results of the study were summarized as: a) extremely high COD removal rate (up to 98%); b) very low sludge production (~0.016 kgVSS produced/kgCOD removed); c) suitability as a pre-treatment to a conventional (e.g. activated sludge) biological treatment and d) high phosphorus removal (up to 99%).

In the study of Germirli Babuna et al. [15], the biodegradability of wastewaters originating from a paracetamol active ingredients production factory (COD=18380 mg/L; SCOD=18180 mg/L; TP=10.5 mg/L; TKN=886 mg/L; pH=4.2). Aerobic and anaerobic treatment alternatives were comparatively evaluated in terms of the lowest achievable COD levels after bio-treatment. Aerobic treatment yielded a residual COD of 355 mg/L. However, the wastewaters were observed to be highly inert under anaerobic conditions. Anaerobic treatment effluents yielded almost 16000 mg/L of COD.

As aforementioned, chemical and pharmaceutical industries are allocated to a large group of industries and various processes and a wide range of raw

---

**TABLE 5**

Biological treatability of Product II, III and IV wastewaters

<table>
<thead>
<tr>
<th></th>
<th>F/M (g COD/(g VSS d))</th>
<th>Effluent COD (mg/L)</th>
<th>COD Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product II</td>
<td>0.18</td>
<td>190</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>0.22</td>
<td>215</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>0.29</td>
<td>260</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>0.64</td>
<td>350</td>
<td>95</td>
</tr>
<tr>
<td>Product II</td>
<td>0.23</td>
<td>260</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>280</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>0.36</td>
<td>450</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>0.73</td>
<td>990</td>
<td>83</td>
</tr>
<tr>
<td>Product IV</td>
<td>0.1</td>
<td>90</td>
<td>96</td>
</tr>
<tr>
<td>Sample I</td>
<td>0.15</td>
<td>85</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>85</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>0.90</td>
<td>140</td>
<td>93</td>
</tr>
<tr>
<td>Product IV</td>
<td>0.56</td>
<td>80</td>
<td>96</td>
</tr>
<tr>
<td>Sample II</td>
<td>0.70</td>
<td>85</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>1.32</td>
<td>130</td>
<td>96</td>
</tr>
</tbody>
</table>

The O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process, the organic pollutants were effectively oxidized with 0.5 of H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> molar ratio and 15 min of reaction time. The results of the study indicated that the anaerobic/aerobic MBBRs combined with the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process were effective for wastewater process from the pharmaceutical industry and the treated water could be reused for cleaning machines (either after a single production or for a final cleaning).

In another study, the treatability of high strength pharmaceutical wastewaters (with high contents of COD, chloride and phosphorus) in a Thermophilic Aerobic Membrane Reactor (TAMR) was investigated [14]. The experimental research was carried out using a pilot plant, in which different mixtures of liquid wastes were fed. The hydraulic residence time varied from 5 to 10 days and the organic loading rate varied between 1.5 and 5.5 kgCOD/(m³ d). The main results of the study were summarized as: a) extremely high COD removal rate (up to 98%); b) very low sludge production (~0.016 kgVSS produced/kgCOD removed); c) suitability as a pre-treatment to a conventional (e.g. activated sludge) biological treatment and d) high phosphorus removal (up to 99%).

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As aforementioned, chemical and pharmaceutical industries are allocated to a large group of industries and various processes and a wide range of raw
TABLE 6
Biological treatability results of tablet wastewater subsequent to blending ozonized and non-ozonized streams

<table>
<thead>
<tr>
<th></th>
<th>Composite I</th>
<th></th>
<th>Composite II</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F/M</td>
<td>Influent COD</td>
<td>Effluent COD</td>
<td>COD Removal</td>
</tr>
<tr>
<td></td>
<td>(g COD/(g VSS d))</td>
<td>(mg/L)</td>
<td>(mg/L)</td>
<td>(%)</td>
</tr>
<tr>
<td>0.06</td>
<td>1200</td>
<td>420</td>
<td>65</td>
<td>0.11</td>
</tr>
<tr>
<td>0.07</td>
<td>1040</td>
<td>500</td>
<td>58</td>
<td>0.22</td>
</tr>
<tr>
<td>0.09</td>
<td>1195</td>
<td>610</td>
<td>49</td>
<td>0.56</td>
</tr>
<tr>
<td>0.21</td>
<td>1195</td>
<td>825</td>
<td>31</td>
<td></td>
</tr>
</tbody>
</table>

As a result, a large number of effluents with different characteristics and volumes are produced as also presented in this study. Biological and physical-chemical methods used for the treatment of pharmaceutical industry wastewaters are the main processes each with their own traits. It is neither feasible to employ a single biological or physical-chemical method to treat pharmaceutical industry wastewaters [13].

CONCLUSION

In this study, wastewaters originating from formulation of different tablets within a pharmaceutical company have been experimentally evaluated. Different kinds of tablet formulation and their wastewaters were the basis of the experimental work. Emphasis was placed to a source-based assessment in terms of wastewater characterization, treatability and pretreatment requirements. Product groups were taken as the first step of segregation of flows. Following conclusions can be drawn from the results of the study:

- Wastewaters originating from different tablet formulations had different organic content with varying biodegradation characteristics from highly and rapidly biodegradable to practically non-biodegradable.
- The wastewater streams having BOD/COD ratios above 0.4 could be treated by the activated sludge with COD removal efficiencies over 95% at sludge loading rates of 0.21-0.25 g COD/(g VSS d), while tablet formulation wastewaters with BOD/COD ratios of 0.1-0.2 exhibited COD removal efficiencies of only 30-40% at similar sludge loading. An organic loading around 0.3 g COD/(g VSS d) can be assumed to be an optimum for Product II and III wastewaters.
- Product IV wastewaters contained high concentrations of suspended solids which could be successfully removed by sedimentation. After sedimentation, the wastewaters were also found to be highly biodegradable and could be treated by the activated sludge process employing organic loadings in the range of 0.25-0.5 g COD/(g VSS d).
- Product IC wastewater was found to be practically non-biodegradable. Ozonation of these wastewaters provided a limited increase in biodegradability. Composite samples prepared by the mixtures of ozonated Product IC wastewaters and non-ozonated Product IA and IB wastewaters.

Products IA and IB. However 60-65% COD removal could be obtained at 0.06-0.1 g COD/(g VSS d) organic loadings with composite samples prepared by the mixtures of ozonated Product IC wastewaters and non-ozonated Product IA and IB wastewaters.

These findings indicate the need and importance of source-based wastewater characterization and assessment of pretreatment requirements for pharmaceuticals formulation industry wastewaters. Such an assessment will help defining the most effective yet feasible means and schemes for wastewater treatment, particularly the design of central biological wastewater treatment unit and the need of polishing treatment before the final discharge of the effluent.

REFERENCES


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SESSION III
INDOOR AND OUTDOOR AIR POLLUTION
URBAN AIR QUALITY AND POPULATION EXPOSURE IN EUROPE

Dimitrios Kotzias*

Former Senior Official of the European Commission’s Joint Research Centre Institute for Health and Consumer protection, Ispra, Italy

ABSTRACT

Assessing the state of air quality in urban and suburban areas over the last decades in Europe we can generally say that a clear improvement of many pollution indicators has been achieved. Nevertheless local and national authorities often record increased concentrations of ozone, suspended particles (PM 2.5, PM 10) and carcinogenic compounds, e.g. benzene and polycyclic aromatic hydrocarbons, in urban air. Efforts and progress made on indoor and outdoor air quality with the aim to reducing air pollution and exposure of humans to harmful pollutants in Europe will be briefly reviewed and discussed.

KEYWORDS:
Air quality, population exposure, European directives, WHO guidelines

INTRODUCTION

Air pollution has been considered for many decades one of the main environmental problems with political, economic and social impacts in Europe and other regions of the world. Air pollution is harmful to health and the environment. It is mainly caused by economic activities (industry, transport, energy and agriculture) as well as by household activities, e.g. heating. The air is cleaner today than it was for the last three decades. For example, sulfur dioxide emissions - the main cause of acid rain - have dropped significantly (> 80%). However, more action is needed to make further progress: suspended particles (PM 2.5, PM10) and tropospheric ozone continue to cause human health problems and adversely affect our natural environment. The most recent analysis (European Environmental Agency 2016 report) shows that about 520,000 premature deaths were attributable in 2013 to atmospheric pollution (from exposure to PM 2.5, NO2 and O3) in the European Union Member States. [1]

The European Union's strategy on air quality combined with relevant actions of the Member States aims to develop and implement appropriate measures against air pollution. Monitoring of emissions from mobile and stationary sources, improving fuel quality and promoting and integrating environmental protection requirements in the field of transport and energy are part of this strategy. [2]

At present, about 75% of Europe's population live in cities. For the coming decades this percentage is projected to increase further due to migratory waves from Near East and African countries. Urban population growth is linked to a steady increase in macro- and microeconomic activities in cities, including energy production and transport, construction, etc. Increases in emissions and the accumulation of large quantities of pollutants in the atmosphere of urban and suburban areas are expected. As a result, citizens in urban and suburban areas, mostly from big cities, often face serious problems from high concentrations of air pollutants.

The overall strategy for improving air quality was initially focused on the characterization and quantification of major air pollutants, e.g. ozone, NOx, SO2 as well as of particulate matter (PM 2.5, PM 10) and, finally, on the establishment of limit values for these pollutants in the atmosphere. In a second phase, the aim was to evaluate the effectiveness of strategies to improve air quality as well as to better understand the way ozone and other photochemical oxidants are formed/produced and to better apply photochemical models.

MATERIALS AND METHODS

The role of volatile organic compounds for the production of ozone and other photo-oxidants. It is known that volatile organic compounds (VOCs) e.g. alkanes, carbonyl compounds, aromatic hydrocarbons, play an important role for the formation of photochemical oxidants (e.g., ozone, peroxy-acetyl nitrate) in the atmosphere (Table 1).

However, the measurement of total non-methane hydrocarbons (TNMHC) hydrocarbons does not provide sufficient and accurate information about their photochemical activity. Due to the particular dynamic/capacity of (certain) volatile organic compounds to contribute to the formation of ozone and other photo-oxidants as well as due to their constantly changing presence/concentration in the atmosphere, it is necessary to identify and quan-
tify the individual hydrocarbons involved in photochemical processes.

### TABLE 1

**Reactions (selection) of atmospheric pollutants contributing to the formation of ozone and photochemical oxidants**

<table>
<thead>
<tr>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NO}_2 + hv \rightarrow \text{NO} + \text{O}^* )</td>
</tr>
<tr>
<td>( \text{O}^* + \text{O}_3 + \text{M} \rightarrow \text{O}_2 + \text{M} )</td>
</tr>
<tr>
<td>( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 )</td>
</tr>
<tr>
<td>( \text{Alkenes} + \text{O}_3 \rightarrow \text{RCHO} + \text{HCHO} + \text{HO}_2^* + \text{RO}_2^* + \text{HO}^* + \text{RO}^* )</td>
</tr>
<tr>
<td>( \text{Alkanes} + \text{HO}^* \rightarrow \text{R}^* + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>( \text{R}^* + \text{O}_3 \rightarrow \text{RO}_2^* )</td>
</tr>
<tr>
<td>( \text{RO}_2^* + \text{NO} \rightarrow \text{RO}^* + \text{NO}_2 )</td>
</tr>
<tr>
<td>( \text{RO}^* + \text{O}_3 \rightarrow \text{R}^<em>\text{CHO} + \text{HO}_2^</em> )</td>
</tr>
<tr>
<td>( \text{HO}_2^* + \text{NO} \rightarrow \text{HO}^* + \text{NO}_2 )</td>
</tr>
<tr>
<td>( \text{CH}_3\text{CHO} + \text{HO}^* + \text{O}_3 \rightarrow \text{CH}_2\text{C(O)OO}^* + \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>( \text{CH}_3\text{C(O)OO}^* + \text{NO}_2 \rightarrow \text{CH}_2\text{C(O)OO}_2\text{N} )</td>
</tr>
</tbody>
</table>

At the beginning of the 1990s, a list of those compounds, which largely govern the production of ozone and other photochemical oxidants in the atmosphere was drawn up in order to include them in European network measurement programs in addition to classical atmospheric pollutants mentioned above (NOx, SO2, PM) [2,3] (Table 2).

Although the scientific basis on the role of the aforementioned volatile organic compounds in the production of ozone and other photo-oxidants in the atmosphere was evident, it was initially not possible to include their control as a requirement in the Air Quality Directive because only a few Member States had the technical capabilities and well trained staff to comply with the implementation of the Directive.

Sampling and analysis of a wide range of VOCs are problematic because of the large differences in their physicochemical properties. Compounds of 1,2,3,4 carbon atoms per molecule are gases (e.g., ethane, propane, ethylene, propene, butane, formaldehyde), while aromatic compounds (e.g., benzene, toluene) are liquid. Besides, the concentration of volatile organic compounds in the atmosphere is usually low (ppb, ppt), which inevitably requires specialized methodologies and techniques for sampling (a large volume of air from 50 ml to some liters is required) and analysis (through gas and liquid chromatography, mass spectroscopy, etc.).

Directive 2008/50 / EC on ambient air quality and cleaner air for Europe basically includes monitoring of the compounds according to the list (Table 2) so that a more reliable information can be provided for the production of ozone and other photo-oxidants in the atmosphere.

**Achievements in the past and priorities for the future.** Over the last twenty-five/thirty years, many studies were conducted, limit values were established and guidelines have been put in place, which significantly contributed to improved air quality and quality of life, particularly for urban residents. In addition, the development of more accurate sampling and analytical methods (capillary gas chromatography, mass spectroscopy, specialized detector assemblies etc.) as well as the improvement of our knowledge about chemical, physical and toxicological properties of various pollutants substantially helped to understand relevant factors and causes of atmospheric pollution and its impact on health. At European level, however, there are differences between Member States in fighting air pollution, which are based primarily on economic considerations and on problems related to the strict application of technical specifications as they result from the formulation of Community directives.

In the latest European Air Quality Agency (EEA) report (2016) on air quality in Europe, the percentage of the EU-28 urban population exposed to atmospheric pollutant concentrations higher than certain EU and WHO (World Health Organization) reference concentrations is reported. EEA data show significant fluctuations in urban exposure rates to specific pollutants during a period of three years (2012-2014) (Table 3).

### TABLE 2

**Measurements of ozone precursors cover at least the oxides of nitrogen (NO and NO2) and the appropriate volatile organic compounds (VOCs), which are contributing to ozone and photo-oxidant formation. A list of VOCs recommended for measurement is given below.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Isoprene</th>
<th>Ethyl benzene</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butene</td>
<td>Ethane</td>
<td>n-Hexane</td>
<td>m,p-Xylene</td>
</tr>
<tr>
<td>Ethylene</td>
<td>cis-2-Butene</td>
<td>i-Hexane</td>
<td>o-Xylene</td>
</tr>
<tr>
<td>Acetylene</td>
<td>1,3-Butadiene</td>
<td>n-Heptane</td>
<td>1,2,4-Trimethyl benzene</td>
</tr>
<tr>
<td>Propane</td>
<td>n-Pentane</td>
<td>n-Octane</td>
<td>1,2,3-Trimethyl benzene</td>
</tr>
<tr>
<td>Propene</td>
<td>i-Pentane</td>
<td>i-Octane</td>
<td>1,3,5-Trimethyl benzene</td>
</tr>
<tr>
<td>n-Butane</td>
<td>1-Pentene</td>
<td>Benzene</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td>i-Butane</td>
<td>2-Pentene</td>
<td>Total non-methane hydrocarbons</td>
<td></td>
</tr>
</tbody>
</table>

* Each Member State shall ensure that at least one sampling point is installed and operated in its territory to provide data on concentrations of precursors of ozone. Each Member State shall determine the number and location of the stations to measure concentrations of ozone precursors. (Directive 2008/50 / EC) [2]
TABLE 3
Percentage of the EU-28 urban population exposed to concentrations of air pollutants above certain EU and WHO reference concentrations (2012-2014) [1].

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>EU reference value (a)</th>
<th>Exposure estimate (%)</th>
<th>WHO / AQG (a)</th>
<th>Exposure estimate (%)</th>
<th>Pollutant</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM 2.5</td>
<td>year (25)</td>
<td>8-12</td>
<td>year (10)</td>
<td>85-91</td>
<td>PM 2.5</td>
</tr>
<tr>
<td>PM10</td>
<td>day (50)</td>
<td>16-21</td>
<td>year (20)</td>
<td>50-63</td>
<td>PM10</td>
</tr>
<tr>
<td>O₃</td>
<td>8-hours (120)</td>
<td>8-17</td>
<td>8-hours (100)</td>
<td>96-98</td>
<td>O₃</td>
</tr>
<tr>
<td>NO₂</td>
<td>year (40)</td>
<td>7-9</td>
<td>year (40)</td>
<td>7-9</td>
<td>NO₂</td>
</tr>
<tr>
<td>BaP *</td>
<td>year (1)</td>
<td>20-24</td>
<td>year (0.12) (RL)</td>
<td>88-91</td>
<td>BaP *</td>
</tr>
<tr>
<td>SO₂</td>
<td>day (125)</td>
<td>&lt;1</td>
<td>day (20)</td>
<td>35-49</td>
<td>SO₂</td>
</tr>
</tbody>
</table>

(a) In μg / m³; * except BaP (benzo (a) pyrene), in ng / m³. WHO / AQG [WHO / Air Quality Guidelines], RL [reference level]; Source: EEA, 2016f [1]

The differences between EU and WHO in the population exposure rates for various pollutants are due to differences in the reference concentrations/limit values between EU and WHO. While e.g. for particulate matter PM 2.5, the limit value according to EU Directives is 25 μg / m³ on annual basis, for the same pollutant the WHO AQG is 10 μg / m³. This implies that, based on the WHO reference value a larger proportion of Europeans are exposed to PM 2.5. Similar differences in population exposure based on EU and WHO reference and guideline values are also found for other pollutants too.

Towards a future strategy for air quality assessment and management, particularly in urban areas, efforts at European level must be continuous. This will contribute to a better understanding and control of the key factors/elements that determine and affect air quality and have a direct impact on human health and ecosystems. In addition, the socio-economic impact due to the implementation of the measures and policies needs to be assessed. In this context, issues that need to be studied in the future for a comprehensive European policy on the problem of air pollution are identified in the following points:

- What are the main sources of pollutants in the different regions of Europe? What differences and similarities exist? What kind of source testing is suggested?
- What "tools" do we have to control pollution? What can they offer us? Are they used in all areas? If not why, what are the possible obstacles? How can control be linked to regulatory work to reduce exposure to pollutants?
- What modeling tools exist, how reliable are they and what needs still to be developed?

**Human exposure to gaseous pollutants.** One of the main objectives of the implementation of air quality directives is to reduce/eliminate human exposure to air pollutants. Human exposure to air pollutants has a direct impact on health, well-being and living in general. The focus of atmospheric pollution scientists and air quality managers has so far been mostly focused on the quality of outdoor air.

People spend, however, 85-90% of their time indoors in homes, schools, offices, etc. Thus, a large amount of air enters the human body while staying indoors. This led to the introduction of the concept of Total Human Exposure to air pollutants, which takes into account the individual's stay in various environmental compartments (indoor and outdoor). There are few studies at European level only, that can be considered as representative of the overall human exposure to air pollutants (EXPOLIS, MACBETH, German Envir. Survey, AIRMEX). [4,5,6,7]

TABLE 4
Table 4. Concentrations for several classes of compounds in different environments (μg /m³), CO (mg/m³)

<table>
<thead>
<tr>
<th>Class</th>
<th>In³</th>
<th>W¹</th>
<th>Out³</th>
<th>P³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>2-13</td>
<td>4-14</td>
<td>1-21</td>
<td>3-23</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1-90</td>
<td>2-8</td>
<td>1-4</td>
<td>2-46</td>
</tr>
<tr>
<td>Styrene</td>
<td>1-6</td>
<td>3-7</td>
<td>1-2</td>
<td>1-5</td>
</tr>
<tr>
<td>Toluene</td>
<td>15-74</td>
<td>25-69</td>
<td>3-43</td>
<td>25-130</td>
</tr>
<tr>
<td>m&amp;p-Xylenes</td>
<td>4-37</td>
<td>25-121</td>
<td>2-23</td>
<td>25-55</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>2-12</td>
<td>7-29</td>
<td>1-8</td>
<td>8-15</td>
</tr>
<tr>
<td>Aldehydes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>10-18</td>
<td>3</td>
<td>1-2</td>
<td>8</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>7-79</td>
<td>12</td>
<td>2-4</td>
<td>21-31</td>
</tr>
<tr>
<td>Terpenes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Pineene</td>
<td>11-23</td>
<td>1-17</td>
<td>1-7</td>
<td>7-18</td>
</tr>
<tr>
<td>Limonene</td>
<td>6-83</td>
<td>11-23</td>
<td>5-9</td>
<td>19-56</td>
</tr>
<tr>
<td>Classical pollutants</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.5-1</td>
<td>1</td>
<td>2</td>
<td>0.8-1.7</td>
</tr>
<tr>
<td>NO₂</td>
<td>13-62</td>
<td>27-36</td>
<td>24-61</td>
<td>25-43</td>
</tr>
</tbody>
</table>

¹ In, W, Out, P = Indoor, workplace, outdoor and personal exposure concentrations
In the context of the INDEX project population surveys and standard concentrations for several classes of compounds in various environments, as well as concentrations related to personal exposure to these compounds are included (Table 4). [7,8]

These data primarily cover organic compounds as well as classical pollutants, such as CO and NO2. Comparative analysis of concise results shows that indoor concentrations are often higher than outdoor concentrations, and personal exposure concentrations are some times higher than the previous two. The work environment is generally characterized by slightly higher levels of pollution than residential areas, probably due to the presence of strong sources of pollutants in the confined working places.

In 2010, WHO presented guidelines for the protection of public health from compounds found often in confined spaces (WHO Guidelines for indoor air quality: selected pollutants, 2010). [9]

The compounds included in the guidelines (benzene, carbon monoxide, formaldehyde, naphthalene, nitrous oxide, polycyclic aromatic hydrocarbons (mainly benzo-a-pyrene), radon, trichloroethylene and tetrachloroethylene) were selected:

- on the basis of sources for these substances indoors;
- due to the availability of toxicological and epidemiological data; and
- due to exposure levels (concentrations) that may cause problems for human health.

The guidelines are addressed to professionals involved in public health, as well as to experts and authorities involved in the design and use of buildings and the development of materials and products for indoor use. The guidelines have the character of recommendations. However, countries may wish to use the guidelines as a scientific basis for (legally) applicable standards. Evidence supporting the guidelines includes for each of the selected pollutants the assessment of indoor sources, local indoor concentrations and their relationship to the corresponding levels (concentrations) in the external environment, as well as a summary of data on metabolism, kinetics, and health. Based on the accumulated evidence, the experts made an assessment of health risks and agreed on the guidelines for each of the above mentioned pollutants.

CONCLUSION

Over the past twenty-five to thirty years, significant efforts were made to improve air quality, particularly in urban areas with relatively good results. This is due to a series of measures, such as the introduction of catalysts in cars, the application of best available technologies for industrial installations, the improvement of fuel quality and, finally, due to changes of the infrastructure in European cities. However, overrun values e.g. for ozone, micro-particles and some other pollutants are recorded in many urban and suburban areas in Europe and more often in southern Europe. The various directives and proposals of the European Commission towards a single strategy on air quality have substantially contributed to the development of the methods and tools for an effective assessment and management of air quality in Europe. Within this framework, the study of Total Human Exposure to air pollutants is a difficult and demanding task. But it can also be seen as a powerful criterion for assessing and managing urban air quality providing useful information by the application of anti-pollution measures and on the effects for human health directly or indirectly related to the presence of gaseous pollutants and particles.

REFERENCES

[6] German Environmental Survey (GerES): http://www.uba.de/GerESs


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PHYSICAL AND GEOCHEMICAL ASPECTS ON STRONTIUM TRANSPORT FOR SAFETY ASSESSMENT STUDIES

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ABSTRACT

In nuclear safety studies, the transport of radionuclides in environmental matrices (e.g. soil, groundwater, surface water, etc.) is one of the key issues to consider. Safety assessment aims to foresee and manage the environmental and radiological impact of possible radionuclide releases into the environment. In particular, the prediction of radionuclide dynamic due to its interaction with the subsoil and to the impact of meteorological conditions must be investigated. Several techniques can be used to perform these analysis, such as experimental data and/or simulation tools. In this work, the impact of different ground covers (e.g. grass, pasture, wheat) on the mobility of strontium in space and time was investigated focusing on its behaviour in the unsaturated zone. The results highlight the impact of different ground covers on the absorption of strontium by plant roots. They can be useful to evidence the factors affecting the transfer of radionuclides from environmental matrices to the food chain and to support Safety Assessment studies about nuclear plant activities during its life cycle.

KEYWORDS:
Strontium transport, Safety Assessment, Hydrus 1D

INTRODUCTION

Nuclear energy is an important power source worldwide, but the problem of safe disposal of radioactive waste is still a major environmental challenge. For what concern the low level radioactive waste containing short-lived radionuclides, near-surface repository is the solution currently employed to face the disposal, with particular attention to the safety issues related to realization, operation, and post-closure phases of the nuclear facility. During the lifetime of a near-surface repository, as during the life cycle of any nuclear plant, radionuclides that may be leached from waste or facility internal structures can pollute surface water, soil and groundwater, reach the biosphere and cause a radiological contamination to food chain and human beings.

Nowadays, the safety of a near-surface disposal and related activities is evaluated and demonstrated by means of a safety case and related safety assessment, among different projects and disposal options. Safety case is the collection of all the scientific, technical, administrative and managerial arguments and evidences justifying the safety of a nuclear facility or nuclear activity. Safety assessment, that is an integral part of the safety case, quantifies radiation dose to human beings and related radiation risks, for comparison with safety criteria [1]. Safety case and safety assessment, although they evolve with the development of the nuclear plant life cycle, constitute the basis to demonstrate its safety and are the fundamental parts of the licensing process, supporting the siting and the designing process. Safety assessment normally includes the modelling activity, to simulate the release of radionuclides from the multi-barrier system of the nuclear facility, the following migration in environment and the calculation of possible radiological dose to population.

A key process to consider in safety analyses for near-surface disposal concerns the definition of future possible scenarios and the probability that they will occur. Scenarios represent a set of assumed features, conditions, events/processes and their possible evolution, regarding the repository and surrounding environment, which may reasonably be expected to occur in normal conditions or disturbing events. To perform a correct definition of scenarios, it is fundamental to characterize the existing relations among facility, near-surface geosphere and biosphere. Scenarios normally represent a wide range of conditions and support the safety decisions in normal and accidental contexts, as in present and future conditions. In addition, they support the evaluation of the migration of any radionuclide outside the plant and the subsequent impact on environment and human beings.

Radionuclide migration through an environmental matrix is one of the aspects to consider in assessing the radiological impact of the repository activities. Food contaminated consumption is an important pathway for radiological contamination of
people, therefore radionuclides transfer from soil to crops and vegetal is one of the key issue to consider in assessment of nuclear safety. For this reason, one-step in safety assessment is the evaluation of radionuclide adsorption by plant roots, from quantitative and qualitative point of view, to calculate the possible radiological dose to population in normal and accidental situations. The adsorption of radionuclides by plants roots is strongly related to its concentration in soil solution. It depends on the distribution coefficient, and so to the presence of radionuclides in adsorbed state or in exchangeable state; but the uptake is also related to the plants physiological aspects, to its selectivity in ions uptake, to the presence of chemical competitive species in soil. Many other external processes influence relationships between plants and soil: climate and meteorological variations modify the transfer factors and the bioavailability of radionuclides. These processes cannot be simply discriminated.

Radioactive isotope of strontium and cesium are often modelled in soil and groundwater for nuclear safety analysis purpose. Their importance regards their medium half-life and particularly their radiological effects, due to their high biological interaction. Strontium dynamic in environment is relevant because it is one of the most hazardous fission products of nuclear reactor and because of its high mobility in soil, groundwater and in vegetal, permeating vegetal tissues [2]. Its safety importance is also referred to the long-term radiological health impact, due to its chemical similarity with calcium and magnesium [3-4].

The purpose of this study was to evaluate the strontium dynamic in the subsoil, within scenarios characterized by different ground covers. In the context of nuclear safety analysis, the results can be useful to evidence the importance of the factors affecting the transfer of radionuclides from environmental matrices to plants and the food chain. In addition, the investigation of prediction scenarios can support decisions of operators about nuclear plant activities during its life cycle and Safety Assessment studies.

**INVESTIGATED SITE**

The experimental area is located near the ENEA Saluggia Research Centre, Vercelli (Italy) where the EUREX nuclear fuel reprocessing plant is located, which is currently being decommissioned by Sogin S.p.a., the Italian Waste Management Organization. The site is not suitable and is not intended to host a near-surface repository for radioactive waste, but it has been chosen for this study due to available geological and hydrogeological data acquired in the past, during ENEA research activities. The site is located in the flood plain of the Dora Baltea River, where alluvial deposits overlap fluvioglacial deposits, to a depth of about 45 m. The hydrogeological system is featured by a shallow aquifer, with a mean thickness of 45 m, characterized by a free-water table, whose mean depth from the ground surface is about 3.5 m [5]. The investigated subsoil stratigraphy and the grain size distribution for each layer is reported in Table 1. The main geochemical properties, such as pH, Organic Carbon (OC) and Cation Exchange Capacity (CEC) were also determined by experimental analysis performed by ENEA, and they are reported in Table 2. The water infiltrating in unsaturated zone above the free-water table was sampled with lysimeters from 20 cm to 125 cm depth from the soil surface.

In-situ measurements, performed in late spring 2000, were carried out to collect the concentrations of different anions and cations (e.g. F-, Cl-, NO₂-, NO₃-, Br-, HPO₄²-, K+, Cs+, Mg²+, Ca²+, Sr²+, Ba²+). As example, the measured concentrations in [mg/l] of strontium and magnesium varying in depth and time are reported in Table 3 and Table 4.

### TABLE 1

<table>
<thead>
<tr>
<th>Layer</th>
<th>Soil type</th>
<th>Depth [cm]</th>
<th>Sand [%]</th>
<th>Silt [%]</th>
<th>Clay [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Loamy sand</td>
<td>0-25</td>
<td>77</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>Sandy loam</td>
<td>25-50</td>
<td>68</td>
<td>29</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>Sandy loam</td>
<td>50-75</td>
<td>67</td>
<td>31</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>Loamy sand</td>
<td>75-100</td>
<td>81</td>
<td>17</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>Sand</td>
<td>100-125</td>
<td>91</td>
<td>8</td>
<td>1</td>
</tr>
</tbody>
</table>

### TABLE 2

<table>
<thead>
<tr>
<th>Layer</th>
<th>pH [-]</th>
<th>OC [g/kg]</th>
<th>CEC [mEq/100g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.5</td>
<td>4.3</td>
<td>10.02</td>
</tr>
<tr>
<td>2</td>
<td>7.8</td>
<td>5.5</td>
<td>6.75</td>
</tr>
<tr>
<td>3</td>
<td>7.9</td>
<td>2.5</td>
<td>8.95</td>
</tr>
<tr>
<td>4</td>
<td>8.1</td>
<td>1.5</td>
<td>9.39</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>0.6</td>
<td>8.11</td>
</tr>
</tbody>
</table>
### METHOD AND MODEL

This study analyses scenarios characterized by different ground covers, to evaluate the strontium dynamic in the unsaturated zone, by means of simulations and geochemical data about solutions circulating in soil. The time of sampling is referred to late spring but it should be extended to comprehend more aspects of water dynamic in the topsoil. The chemical analysis was performed to determine the total content of most important anions and cations. Strontium was determined as total stable strontium in soil solution sampled in unsaturated zone. Previous studies have highlighted that the proportion between radioactive and stable strontium in plants (especially for what concern rice and wheat) has a quite constant value, that permits to use stable elements in assessment of soil-to-plant transfer [6-7].

The study was performed in two steps: calibration of the model and development of prediction scenarios. The modelling was carried out by means of HYDRUS-1D software [8]. First, a calibration model was developed imposing concentration and pressure head the 27th April 2000 as initial condition. The geological and geochemical data (Table 1, Table 2) were introduced, such as the interaction between soil and solutes, as distribution coefficient. In particular, for what concern the strontium behaviour in soil, the distribution coefficients for strontium for each investigated layer were estimated by means of relationship proposed in [9]. The estimated distribution coefficients of strontium for each layer are shown in Table 5.

After the calibration of the model, prediction scenarios were investigated. In particular, the impact of different ground covers (e.g. grass, wheat, maize, rice, etc.) on the adsorption of strontium by plants roots was assessed. These aspects have to be considered key issues in activities supporting the safety analysis of nuclear plants activities, with particular reference to near-surface radioactive waste repository.

Concerning the modelling of root uptake in HYDRUS 1D, Feddes model was implemented, considering the characterizing parameters of each different ground covers provided by HYDRUS 1D database [8]. The root growth model was also considered, identifying functions in time of the growth of crop height and root depth.

### RESULTS AND DISCUSSION

The mobility of strontium in space and time has been investigated focusing on its behaviour in soil. First, the model was calibrated both from the hydraulic and mass transport point of view. Then, impact of different ground cover has been assessed, in order to understand the possible transfer of strontium into the food chain and to evaluate different occurring scenarios.

**Calibration model.** The model was calibrated from an hydraulic point of view, starting from the data analysed in [10]. Instead, as far as the solute transport is concerned, the comparison between measured data and simulated data for strontium and magnesium are reported in Figure 1 and Figure 2. Concerning the strontium dynamic, its transport calibration shows a good agreement between measured and simulated concentrations up to 7th June. The 6th

---

**TABLE 3**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>-20</td>
<td>2.6</td>
<td>1.9</td>
<td>1.2</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>-40</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>-</td>
</tr>
<tr>
<td>-60</td>
<td>2.7</td>
<td>2.7</td>
<td>2.3</td>
<td>3.7</td>
<td>3.8</td>
</tr>
<tr>
<td>-80</td>
<td>3.3</td>
<td>3.3</td>
<td>2.4</td>
<td>2.2</td>
<td>3.4</td>
</tr>
<tr>
<td>-100</td>
<td>2.8</td>
<td>2.7</td>
<td>2.4</td>
<td>2.4</td>
<td>2.7</td>
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<tr>
<td>-120</td>
<td>1.9</td>
<td>2.6</td>
<td>2.6</td>
<td>2.3</td>
<td>2.6</td>
</tr>
</tbody>
</table>

**TABLE 4**

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**TABLE 5**

<table>
<thead>
<tr>
<th>CEC [mEq/100g]</th>
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July a discrepancy between measured and simulated data has been revealed in the first 60 cm; this is probably due to the high evaporation/transpiration from soil surface. The hydraulic consistency of results suggests that, for what concern the concentration, it was necessary an additional on-site measurement to confirm the strontium behaviour and the previous hypothesis. A more precise investigation of the interaction between strontium and soil could improve the modelling of its dynamic in soil itself. Instead, magnesium transport calibration shows a better agreement between measured and simulated concentration than strontium. This can be due to the more strong interaction between strontium and the soil than between magnesium and soil. On the 9th May, below 80 cm from the ground, magnesium transport shows a higher discrepancy between measured and simulated concentration; this is probably due to the response of the model at the beginning of the simulation.

**Prediction scenarios.** After the calibration of the model, different prediction scenarios were investigated considering various ground covers. This analysis represents a key point in activities supporting safety assessment of nuclear facilities. In particular, with reference to near-surface radioactive waste repositories, this investigation makes it possible to understand how to manage the nuclear site after its closure, to evaluate the risk of contamination of crops and thus the possible transfer of radionuclides into the food chain.

First, grass and pasture covers were introduced to investigate if these simple ground covers have an impact on the absorption of strontium. The performed simulations have underlined that almost no absorption by roots occurs in a similar scenario. The strontium eventually released into the environment remains in soil; in case of no-ageing effect, that strongly retain radionuclides in soil particles, it may be leached toward the free water table. Then, other crops were investigated, such as corn, small grain, wheat. These ground covers show an impact on the strontium absorption, in particular the wheat is the crop that has higher effect on strontium absorption. Several simulations were performed for each crops changing crop height, root depth, growth models, etc. Two different cases of wheat growth are described and reported in this paper, to highlight the major discrepancies between a ground without and with wheat cover. In Table 6 and Table 7, two different functions of wheat growth are reported. In these tables, the crop height and root depth varying in time...
are reported. For the case 1, the comparison between concentrations without and with wheat is shown in Figure 3. The slightly difference between the condition without crop and with wheat is evident. To quantify the impact of wheat cover, the percentage discrepancies between the condition without and with wheat for the two reported cases are shown in Table 8. Comparing the two cases, the second function of wheat growth has a higher impact on the absorption of strontium. Discrepancies between situation without and with wheat are more evident in the first two layers, because the higher root uptake occurs near the ground.

To summarize, different ground covers were considered: grass and pasture have shown the lowest absorption of strontium; wheat cover has an evident effect on strontium absorption by the roots and represents the worst scenario in the examined context for its possible transfer to food chain.

### CONCLUSION

Physical and geochemical aspects about strontium transport in soil and sorption in plant roots, for safety assessment studies in nuclear field, were investigated, near a decommissioning nuclear plant. The investigated area is not suitable and is not intended to host a near surface repository for radioactive waste disposal. In particular, the evaluation of radionuclide absorption by plants, from quantitative and qualitative point of view, to calculate the possible radiological impact to population in normal and accidental situations must be considered as a key point in future Safety Assessment studies. The effect of different ground coverings was assessed and it has shown an evident impact on the absorption of radionuclides by plant roots and then on future possible scenarios to consider. One of the main influencing crops on strontium absorption is wheat. Identifying the main affecting crops on radionuclide absorption in soil allows to perform more detailed future scenarios in the context of safety analysis, and to reduce radiological risk for population, since the absorbed radionuclides may enter into the food chain.

#### TABLE 6

<table>
<thead>
<tr>
<th>Case 1: function of wheat growth.</th>
<th>Crop height [cm]</th>
<th>Root depth [cm]</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
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</tr>
<tr>
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<td>5</td>
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<tr>
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<td>90</td>
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<td>50</td>
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</tbody>
</table>

#### TABLE 7

<table>
<thead>
<tr>
<th>Case 2: function of wheat growth.</th>
<th>Crop height [cm]</th>
<th>Root depth [cm]</th>
</tr>
</thead>
<tbody>
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<tr>
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<td>72</td>
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<td>50</td>
</tr>
<tr>
<td>90</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

#### FIGURE 3

Comparison between simulated concentrations without (dashed line) and with (straight line) (case 1) wheat.

#### TABLE 8

| Percentage discrepancy between the two conditions (without and with wheat). |
|------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| [ % ] | Case 1 | Case 2 | Case 1 | Case 2 | Case 1 | Case 2 | Case 1 | Case 2 |
| Layer | 9th May | 7th June | 6th July | 25th July | 9th May | 7th June | 6th July | 25th July |
| 1     | -2.6    | -0.9     | -10.5    | -11.5     | -2.6    | -5.1     | -24.2    | -20.9     |
| 2     | -0.7    | -1.7     | -4.8     | -16.9     | -0.7    | -1.1     | -23.7    | -44.4     |
| 3     | -0.4    | -1.4     | -2.0     | -5.9      | -0.4    | -1.1     | -5.0     | -32.8     |
| 4     | -0.3    | -1.3     | -1.5     | -6.1      | -0.2    | -1.0     | -4.0     | -25.6     |
| 5     | -0.1    | -1.2     | -1.3     | -6.1      | -0.1    | -1.0     | -3.5     | -22.4     |
The presented work is a preliminary study, that can be implemented in future, introducing the effect of other solutes on the strontium behavior. For example, the geochemical behaviour of strontium is very similar to the behaviour of calcium. The uptake of strontium in soil by plant roots strongly declines in presence of calcium, because absorption of strontium by vegetal is closely tied to the calcium concentration in topsoil. On the counterpart, an increase of calcium and magnesium in soil solution reduces the sorption of strontium in sediments and so augments its migration rate; there is a direct proportionality between the strontium migration rate and the calcium and magnesium concentration in soil solution [11]. These aspects can be key issues in safety considerations about a near-surface disposal for low level radioactive waste.

REFERENCES


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MICROBIOLOGICAL AIR SAMPLING OF OPERATING ROOMS IN A VETERINARY HOSPITAL

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ABSTRACT

There is a gap in the literature with regard to the numerical standards of indoor air quality of operating rooms in veterinary hospitals. As an effort to fill this gap, the aim of this study is to determine the quantity of Culturable Airborne Bacteria (CAB) from different operating rooms of an operation unit in a veterinary hospital and to assess variations in microbial counts at different times and locations within this operation unit. For this purpose, we have determined appropriate procedures that could be pursued in a veterinary hospital by evaluating different sampling techniques and culture methods. Using Microbial Air Monitoring Sampler™, indoor air samples were taken from the rooms of the operation unit twice a month in a period of four months. Colonies on Blood Agar or Plate Count Agar (PCA) plates were counted and CAB concentrations (cfu/m³) were calculated according to Feller Correction Table. By this pilot study, the sampling techniques and culture methods were evaluated and we had a chance to decide on the adequate procedure that could be applied in a veterinary hospital. As a result, in terms of bacterial load, we found that the bacterial load in the samples taken after the operation had higher values than the ones taken before the operation. The importance of the indoor air quality and of the establishment of permanent standards are becoming more apparent, when it is considered that different operations of different animal species can be performed in any veterinary clinic.

KEYWORDS:
Air sampling, Culturable Airborne Bacteria (CAB), Operating rooms, Veterinary hospital

INTRODUCTION

Complications arising in the surgical area after surgical interventions have an important place in veterinary medicine. Airborne microorganisms effective in the hospital environment may cause infections in susceptible individuals [1, 2, 3]. Surgical suctions tips used in veterinary surgeries can be contaminated by indoor airborne bacteria and this can create a favourable environment for the development of infections in the surgical intervention areas [4].

Previous researches show that the complications that arise after surgical interventions originate from the deficiencies and errors made in the asepsis and antisepsis protocols within pre-operation, operation and post-operation. The most common causes of wounds and complications in the surgical area are; (i) the scope of the surgical procedure, (ii) the presence or absence of foreign bodies in the area, (iii) the duration of the operation, (iv) the duration or adequacy of the antimicrobial therapy, (v) the immunity status of the patient, and (vi) the indoor air quality of operating rooms [3, 5, 6]. Lidwell et al. [7] examined the relationship between postoperative wounds and indoor air quality in 19 different hospitals and found a significant correlation between joint sepsis ratios and bacterial airborne contamination. Researchers indicated that most of the bacteria detected in the operation wounds after the prosthetic surgeries reached the surgical area through air. It is observed in developed countries that contamination during operations decreases to a minimum, parallel to the increase in the design quality of operating rooms [8]. Further, it is emphasized that decreases are observed in postoperative complications by the contribution of ultra clean air facilitators. It is also underlined that identifying the bacterial diversity and bacterial load in the regularly and heavily used operating rooms in further studies shall reduce the risk of this type of contamination.

In this study, indoor air samples were taken twice a month between August 2016 and November 2016 to determine the concentration of CAB of the operation unit in a research and application hospital within a veterinary faculty. Heavily used operating rooms were classified according to their location, the time spent in the operations of different animal groups, and the material/device used. Another purpose of the study was to determine the appropriate method of active air sampling for the selected rooms as different methods could be preferred for different environments to determine the concentration of indoor airborne bacteria. The last purpose of the study
was to identify the possible change of CAB concentration before and after the operation.

MATERIALS AND METHODS

Choice of Operating Rooms. Three operating rooms were selected in accordance with the systematic-purpose sampling method. There were both UV lamps and air conditioning units in all rooms, but they were placed differently in each one. A unit sketch is presented in Figure 1 to visualise the characteristics of the selected operating rooms clearly.

The main entrance of the operation unit opens to the same corridor as the section where the clinical examinations are performed. Only the Surgery Department staff and the selected students who assist an operation have access to the main entrance. As a general rule, 2-3 members of staff take part in each operation and a maximum of 2 students can assist. There is a common space or patient waiting area next to the entrance, where a member of staff is permanently on duty. Operating room 1 was regarded as the most distant room to the common space. Operating room 3 was preferred because of its location and for being a transit route between the common area and the operating room 4. Operating room 5 was chosen since it was directly connected to the common area and could be more easily affected by environmental factors. The common area was also included in the sampling in order to study the possible effects of this area on CAB concentrations. The others were non-operative rooms located in the unit, such as cleaning and storage rooms, and were not included in the sample, since they were analogous spaces.

Measurement Method. In indoor air quality studies, the ‘culture method’, which is based on counting the colonies that develop as a result of incubation of microorganisms in airborne samples in the medium at a certain temperature and in a certain amount of time, is one of the most preferred methods. However, the frequently preferred ‘Sedimentation Method’ was used for air sampling in the first place in the study, petri dishes were kept open on the table for 30 minutes in selected operating rooms (Open Petri Dish Method). First, “Impinger Sampling Method” was adopted after the second sampling, once it was decided that the sedimentation method was insufficient to determine the CAB concentration [9]. For this purpose, AES Sampl’air™ (Aes Laboratoire Sampl’air Lite-France) Air Sampler Device was used, which consisted of 258 holes with a diameter of 0.7 mm each and was adjusted to draw 50 L of air per minute. This air sampler was tested by the British Health Protection Agency and validated according to ISO 14698-1 [10, 11]. Prior to air sampling, the top cover of the device was disinfected with alcohol, which was repeated for each operating room to avoid the risk of contamination among the sampling units. Entries to and exits from the rooms during sampling were either completely stopped or minimized. For sampling, the position of the device was fixed at a minimum human breathing level of 1.5 meters and at a 45° angle to the centre of the indoor environment. Meanwhile, measures were taken not to have natural or device-based ventilation in the indoor environment. From the moment they were taken, the samples were carried in cold chain until delivered to the lab [10, 11].
Evaluation. After confirming the Impinger Sampling Method as the method of the study; the number of samples was updated with two separate samples taken on the same day for both pre-operation and post-operation periods from each operating room.

Nutrient agar (HiMedia M 001) supplemented with 5% sheep blood was used in the first samples and Plate Count Agar (PCA, Merck 1.05463) was used in the third samples in order to determine the CAB values. The sampled media was left to incubate at 37°C ± 0.5 for 48 hours.

The colonies were counted after 48 hours. Counts of all incubation results were recorded by taking an average. In all samples, except the ones taken in the first sampling in which sedimentation was used, the CAB values were given as ‘CAB concentration cfu/m³’ (Colony Forming Units per cubic meter of air) using the Feller Correction Table [10].

RESULTS AND DISCUSSION

The highest CAB values were found in the first sample of the operating room 5 with 49x10³ (49540) cfu/m³ regardless of the environment difference. The lowest value was the result of the first sampling of the operating room 1 with 20 cfu/m³. Commonly, CAB concentrations in samples taken in the morning hours before operations were found to be higher than the ones taken after the operations. The results are shown in Table 1.

Reliability in Selecting the Method of Study.

Although there are standards issued by the European Union covering clean room classifications, there are no methods and standards for assessing the quality of microbial air both in human and animal hospitals. Similarly, there is no consensus on airborne microflora concentration that could increase the risk of infection [2, 5]. The number of colony forming units (cfu) is the most important parameter that can detect viable biogenic microorganisms [12]. Factors that may inhibit colony formation, such as the suitability of sampling device, should be considered. The device used in sampling may vary depending on several parameters, like microbial determination and the ones that impact determination activity. Parameters such as inlet efficiency and particle collection efficiency, collection line and drying amount, collection microorganisms crashing speed during sampling, and collection microorganisms’ surface density may shadow colony existence. In this study, sedimentation method was used in the first sample. However, we decided to change the air sampling method when the low values of the detected colony numbers raised questions over reflecting the actual values. The impinger method proposed by ISO standards was tried and then the study was continued with this method upon positive feedback. The difference between the sedimentation and impinger methods, and the significance of the effects of this difference on sampling is revealed in numerical values (Table 1). Based on the results of this study, the impinger method can be suggested as an effective method for future air quality studies.

Selectivity in the Choice of Operating Rooms. Research on the effects of airborne total aerobic bacteria concentration and environmental factors in indoor and outdoor milieus are limited in Turkey [13, 14, 15, 16]. The lack of data in studies conducted on veterinary clinics, animal hospitals, and other settings is clearly recognized in the literature. It is not possible to compare the studies in Turkey with standard values, since neither the national air quality standard of Turkey nor the indoor air quality values are determined. In this study, it was aimed to evaluate the results of air samples within the framework of the study and to present possible problems before and after operations along with their solutions. Total bacterial counts obtained during the research were observed to have higher values when compared to similar studies performed abroad [2, 8]. These differences may be related to different variables, such as sampling and bacteriological examination methods, disinfection and sterilization methods used in operating rooms, number of operations performed in rooms, operation types, and working personnel.

The selection of the research areas according to scientific sampling method was an important step that eliminated sampling bias, and hence, enhanced the validity of the research [16, 17]. The difference between the CAB values of selected stations found in this study allowed the identification of rooms where significant operations should be performed to eliminate infection risk. Operating rooms 1 and 4 showed similar characteristics during the sampling process and these two operating rooms have proved to be the cleanest areas according to the research findings. Likewise, operating rooms 2 and 3, which had similar characteristics, had a relatively dense bacterial concentration. The operating room 5 had the highest bacterial concentration according to the findings, which drew the most attention among other findings.

Selectivity in Sample Acquisition Time for Study. The bacterial load in the air in an operating room can vary from one day to another, or even at different times within the same day [2, 5]. The staff working in operating rooms had limited information on this issue, since there was no such research conducted in Turkey before as found by the literature review conducted for the study. At first, sampling was planned to be carried out once a day at a time interval close to the starting hours of the operations, therefore, the range of the CAB values could be determined. However, when the observed CAB values, as
TABLE 1
Culturable Airborne Bacteria Colony Counts (cfu/m³) According to Months

<table>
<thead>
<tr>
<th>Month</th>
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<th>No</th>
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<th>AO</th>
<th>BO</th>
<th>AO</th>
<th>BO</th>
<th>AO</th>
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<td>NM</td>
<td>NM</td>
<td>NM</td>
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<td>480</td>
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<td>5</td>
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<td>200</td>
<td>120</td>
<td>360</td>
<td>49540</td>
<td>300</td>
<td>20</td>
<td>280</td>
</tr>
</tbody>
</table>

Letters denote: NO: Sampling Time; NM: Not Measured, BO: Before Operation, AO: After Operation

the measure of bacterial load, showed high levels by ranging from 860 to 2080 cfu/m³, the number of samples was doubled by the approval of the staff in order to detect the differences in the bacterial load before and after operations. It was observed that the microbial load in the operating rooms varied during the day prior to and after operations vis-à-vis the sampling time.

The pre-operation CAB values of 500 cfu/m³ for room 1, 1260 cfu/m³ for room 3, and 8020 cfu/m³ for room 5 in the 5th sample were found to be 260 cfu/m³, 240 cfu/m³, and 300 cfu/m³ after operations in the same sample, respectively. These results were discussed with the department staff and they were requested not to enter the operation unit before the researchers and until sampling was completed. When the CAB values were obtained by the consideration of the hourly changes, it was observed that the values determined in the pre-operation samples were lower than the post-operation samples. On the 5th sampling day, relatively higher values might have been determined as a result of a large number of entries and exits prior to operations, or a possible disruption of disinfection and sterilization phases the day before. In addition, on the 8th sampling day in operating room 5, the CAB values prior to the operation reached the highest figures of the whole study. An emergency case was dealt on the day of sampling in this operating room and the operation was started at very early hours for that reason. Hence, the intensive activity before the sampling in room 5 might account for higher CAB values.

Sanitation Before and After Taking Samples for the Study. Harper et al. [2] collected air samples twice a day, in the morning and evening, and reviewed the number of total bacteria. There was no significant difference between the rooms regarding the samples, which were collected immediately after cleaning in the morning hours. However, regarding the subsequent afternoon samples, it was found that the total number of bacteria showed differences depending on human or animal activity in the rooms. In this study, the samples collected in the morning hours before operations were considered in the category of ‘after cleaning and sterilization samples’ and post-operative samples were deemed as ‘before cleaning and sterilization samples’. According to this classification, CAB values after sterilization were usually found at lower levels.

Harper et al. [2] also found in the same study that the CAB values in post-cleaning samples in two rooms were higher than the pre-cleaning values. They reported that one of the rooms, where this unexpected situation was experienced, had 3 walls, and its door was facing the corridor and the room might have been contaminated by the air flow coming from the corridor. Likewise, in our study, the design of the operating room 5 was directly connected to the common area, while the other rooms were more isolated, as can be seen from Figure 1 above. It can be argued that the numerical increase above expectations encountered in this room might have been caused by this feature of the room. When the results of the 5th sampling were evaluated, it was observed that the values of the samples before the operations were higher. Beginning from the 6th sampling, within the knowledge of the authorities, the samples were taken in the early hours before the staff arrived. This practice had revealed another problem. As the first person entering the operating rooms were shutting down the UV lamps, they noticed the misplacement of the UV lamp reflectors and they only continued taking samples once this mistake was corrected. After the 6th sampling, it was observed that there was a general decline in the CAB concentration values in pre-operation samples in all rooms. This experience re-emphasized the importance of proper sterilization.

In majority of cases of surgical intervention infections, when isolated bacteria are examined, it is
seen that these pathogens originate from the normal skin flora of patients or staff. Skin rashes and other dust particles come together in the air of the operating room and accumulate on the surfaces by turbulent air currents [5]. As the number of employees and the motions of these people increase, the skin rashes carrying bacteria also spread across the operating room [8]. Thomas et al. [8] found that the number of total bacteria obtained in air samples in empty operating rooms increased due to the increase in number and movement of personnel during operations. Eugster et al. [1], in their study on retrospective evaluation of postoperative complications, argued that the risk of complications with each additional person in the operating rooms increased 1.3 times. For this reason, it was emphasized that the number of personnel in the operating rooms should be limited only to the people required for that operation and the requirement of preventing unnecessary entries and exits during operations should be paid attention. It was observed in Thomas’ et al. [8] study that the CAB values were lower in morning hours and increased at the end of the day, depending on the increase of entries and exits, and the activity inside the room. Also, it was found that these pathogens also reduce the aforesaid risk of contamination. Determination of bacterial diversity and bacterial load in regularly and heavily used operating rooms will reduce the risk of this type of contamination and contribute to the control of postoperative problems.

In Turkey, it is necessary to support aero-microbiological research that aim monitoring indoor and outdoor airborne aerobic bacteria concentration and environmental factors, which are still in limited numbers. Along with the increase in such studies and by the improvement in indoor air quality, well-being and better living conditions will be provided also in veterinary medicine.

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REFERENCES


ASSESSMENT OF THERMAL COMFORT CONDITIONS AND ENERGY PERFORMANCE OF AN INDOOR ATHLETIC CENTER

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ABSTRACT

Sport centers present considerable amounts of energy consumption, related with the specific requirements of the thermal environment, as well as the significant loads imposed by the spectators. In the relevant literature, the issue of energy effective athletic centers has been studied. Even though these studies deal with energy issues, the analysis in most cases does not go into the quality of the thermal environment. In this work, the ventilation level and internal comfort conditions of an indoor athletic center is studied on an experimental basis. Measurements include temperature, humidity and CO2 in different positions of the conditioned and external space through operation and non-operation periods. On energy terms, the analysis evaluates the performance of the center according to an established simulation method. The elaboration of the thermal comfort and energy results, identified the corrective actions towards the upgrade of the thermal environment and energy performance; the proposed measures include energy saving and Renewable Energy Sources interventions.

KEYWORDS:
Thermal comfort, energy performance, athletic center, energy saving, Renewable Energy Sources

INTRODUCTION

Sport centers comprise spaces of special interest, regarding the type of activities taking place, the presence of people of different type of activities (e.g. athletes and spectators), the building geometries, noting that usually spaces of large volume are met, while critical is the thermal comfort level. The above factors are reflected onto the energy consumption, noting that considerable amounts are referred to in the relevant literature [1], while works aiming at the energy upgrade of sport centers [2], including the use of Renewable Energy Sources (RES) as well [3], [4] are also referred to.

The number of works investigating thermal comfort parameters in sports centers are quite limited; their number becomes negligible considering the combination of thermal comfort analysis results with the proposal of interventions for improvement. This is the case of the work of Bernando et al. [5], assessing indoor climate in order to identify potential corrective measures to problems related to indoor air quality and thermal comfort; it should be noted though that their method is implemented on a school building. Rajagopalan and Luther [6], analyze and assess the thermal environment parameters on a sports hall, on experimental and numerical basis, while proposing natural as well as forced ventilation solutions. A study for the development of a comfort-based smart metering system for sport facilities that would allow the correlation of the energy consumption with the achieved thermal comfort, is presented by Revel and Arnesano [7]; an example applied to a swimming pool is shown. Investigation of the critical comfort parameters for the specific system is also referred to [8].

In this work, the ventilation level and internal comfort conditions of an indoor athletic center are studied on an experimental basis. The presented research is part of a greater investigation at the specific athletic center, including the presence of substances responsible for internal pollution [9].

On energy terms, the analysis evaluates the performance of the center according to the monthly method provided by EN13790 [10]. The elaboration of the thermal comfort and energy results, contributed to the formulation of the action plan towards the upgrade of the thermal environment and energy performance. The proposed measures mainly concentrate on energy saving ones, as well as to the increase of RES contribution.

The proposed approach uses easy to implement methodological tools, allowing the improvement of the thermal environment in a demanding application, as the one of an indoor athletic center.
MATERIALS AND METHODS

Location and description of athletic center. The athletic center (Picture 1) is located in the Lefkovrysi municipal district, 3 km away from the city of Kozani. Kozani lies upon the Western Macedonia region, characterized by the presence of major coal-fired (lignite) electrical power production units. Even though the sports center has been inaugurated by year 2009, until 2016 it had also been used for the hosting of two cultural events. Following that year, the center was set to operation; nevertheless regular operation has not yet been achieved. One of the major constraints regarding the regular use of the center is the energy cost.

The center has a capacity of 2,724 spectators. It constitutes of one (1) floor; the main sports hall presents area of 3,432.9 m² (Picture 2), while the auxiliary places lay on the surround, presenting an area of 3309.8 m². The total area is 5,141.7 m².

![Picture 1](general-view-of-the-sports-center-outdoor.jpg)

![Picture 2](general-view-of-the-sports-center-indoor.jpg)

The structure consists of reinforced concrete and brickwork, noting that the enclosed insulation is thermally adequate. Double glazing aluminum frames are used as openings.

Installed energy systems. Regarding energy systems, the center has a central air conditioning unit. The unit is responsible for the supply of fresh conditioned air to the main hall, through the air ducts. A cooling unit and a boiler enable the treatment of cooling and heating loads, as well as hot water load. The boiler consists of three branches; supplying hot water to the air conditioning unit (air-to-water heat exchanger), hot water to the heating units of the auxiliary places, as well as charging the boiler for hot water use. Renewable energy sources systems are not installed.

For the controlling of the operation of the energy systems, a Building Energy Management System (BEMS) is installed. Input parameters include the temperature and humidity measurements of the supply air and return air on the air-conditioning units, as well as the temperature and humidity of the main space. Safety operation and alarm points for the boiler and the chillers are also controlled through the BEMS.

The electrical loads refer to lighting demand, as well as to the consumption of electrical appliances. Fluorescence light bulbs and halogen headlamps are used, while the energy demand of the circulators/pumps on the boiler room and fans on the air-conditioning unit are significant.

It should be noted that energy consumption data are not available, due to the fact that the sports center is not operating on regular basis.

Experimental analysis of thermal comfort parameters. The estimation of thermal comfort parameters was based on a series of measurements. The measurements were performed throughout a period slightly greater than one month (17/9-21/10/2016), divided in two sub-periods surrounding the days that events took place; the event days are on 16/9, 17/9 and 18/9, as well as on 8/10 and 17/10. The measured quantities refer to temperature and humidity of indoor area, indoor CO₂ concentration (Picture 3), while a meteorological station (Picture 4) was installed on the surrounding area, for estimating the ambient air climatic parameters.

![Picture 3](temperature-humidity-and-co2-concentration-sensors-sensors-a-and-2.jpg)

![Picture 4](meteorological-station.jpg)

In Figure 1, one may see the positions of the sensors, while in Table 1 the respective quantities and the indication of sensors are presented. According to Figure 1, the sensors have been installed on the perimeter of zone 1 (sports hall). More specifically on the South side sensor A is installed, on the North side sensor B and on the West side sensor D, while the Hobo sensors 2, 3, 4 are installed on the portable seats on the East side.

Energy Analysis. The calculation of the energy demand and energy consumption requires the
respective efficiencies of the subsystems; these efficiencies refer to the generation of energy (e.g. boiler efficiency or COP), the heat losses as well as the efficiency of the terminal units [11].

The energy analysis is performed according to the monthly based model proposed by EN13790 [10]. The energy demand is calculated throughout the appropriate sum of energy gains (solar and internal) and energy losses (transport losses throughout the envelope and ventilation losses).

The model needs the input of specific parameters as:
- The number of athletes and spectators, being equal to 30 persons in total on an hourly basis.
- The number of athletes (for calculating the domestic hot water uses), being equal to 200 on a daily basis.
- The fresh air ventilation rate (set equal to 13,000 m³/h; according to air velocity measurements performed).

RESULTS AND DISCUSSION

Experimental analysis of thermal comfort parameters. Table 2 presents the mean, minimum and maximum values for the measured parameters of indoor and ambient conditions. In Figure 3, the temperature and relative humidity of indoor air for the complete measurement period is presented. In Figure 4, the indoor air CO₂ is presented, indicating the values for the complete measurement period; focus on a typical day is also performed.

TABLE 2
Daily meteorological and athletic center thermal comfort parameters during sampling period

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Indoor</th>
<th>Outdoor</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>Mean</td>
<td>Min</td>
<td>Max</td>
<td>Mean</td>
<td>Min</td>
</tr>
<tr>
<td>T-RH (%)</td>
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<td>CO₂ (ppm)</td>
<td>470.8</td>
<td>294.8</td>
<td>1260.7</td>
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<td>-</td>
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<tr>
<td>Speed (m/sec)</td>
<td>0.96</td>
<td>0.40</td>
<td>2.88</td>
<td></td>
<td></td>
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</tbody>
</table>

The legend of the Figures 3 and 4 denotes the side of installation of each instrument and is in agreement with the instrument indication provided in Table 1; it is noted that additional indication for instruments lying on the same side of the building has been anticipated.

The values both for temperature and relative humidity demonstrate achievement of thermal comfort conditions (noting that the center was on operation by days 1 (preparation works), 2-3-4, 10 and 19).

Regarding temperature and relative humidity, the potential differences on the values of the sensors can be merely attributed to their accuracy (being equal to 0.5K for the specific temperature sensors and 5% for the relative humidity ones, taking into account ageing effects, as well), rather than on non-homogeneous spatial distribution. The relatively high temperature values on the NW side can be at-
tributed to the fact that the specific sensor was positioned next to the respective window, thus its indications were affected by solar radiation.

![Graph](image1)

**FIGURE 3**
Air temperature and relative humidity in various positions of the athletic center throughout the measurement period

![Graph](image2)

**FIGURE 4**
CO₂ concentration in various positions of the athletic center throughout the measurement period and during a typical event day

Regarding CO₂ concentration (Figure 4), one may note that there are some differences in the indications of the sensors; these differences can be largely attributed to the indicated accuracy of the sensors, being equal to 50 ppm or 5% [12]. Focusing on an event day, the behavior of the curve is in relation with the presence of people in the center. More specifically, there is a gradual increase until the time the center closes; following that time, the CO₂ concentration starts to decrease. The observed values denote in general sufficiency of ventilation rate, according to the relevant Directive by the Greek Government [13]. The presence of values above 800 ppm are expected to be eliminated through the implementation of specific interventions, described in the following section.

**Energy analysis.** In Figure 5, the annual energy demand and consumption with regard to the different uses is presented; the respective fuel consumption data are 65831.1 l of oil and 216.4 MWh of electrical energy. The results demonstrate the satisfactory energy performance of the building; the weak point is the absence of renewable energy sources systems, in order to limit the oil and electrical consumption, which is 127.9 and 56.6 kWh/m² respectively.

The predicted values are in agreement with data provided by the relevant literature [14]. Of course, the absence of actual consumption data does not contribute towards a more detailed and eventually accurate investigation of the building energy behavior.

![Graph](image3)

**FIGURE 5**
Annual energy demand and consumption

**Proposed Interventions.** Even though a few kms away from the center a well developed district heating network operates, connection of the center is not expected to be established in the near future, thus limiting the potential energy saving solutions, e.g. combining district heating with solar energy [15]. Within this context, a large scale upgrade scenario has been formulated, including some corrective actions on the existing infrastructure, as well as an energy saving and RES penetration plan. More specifically, anticipated measures include:

- An increase on the air flow rate of the fresh air, in order to eliminate potential values of CO₂ concentration above 800 ppm. Investigation showed that intervention on the existing fan system would be required.
- The inspection on the BEMS, as well as the potential differences on the indoor air thermal comfort parameters, demonstrated the need to increase the number of sensors used as input by the BEMS. At this time three temperature sensors and one relative humidity sensor are used; given the presence of two main zones (sports hall, auxiliary places) the number of sensors can increase.
Moreover, caution should be taken in order to shift operation between cooling and heating modes automatically.

Regarding the integration of RES, the following interventions should be implemented:
- The exploitation of ground source geothermal energy (heat pump technology), in order to eliminate the use of oil for heating reasons, while decreasing the electrical consumption for cooling.
- The installation of a solar thermal system for covering the hot water needs.
- The installation of PV panels for covering part of the electrical consumption.
- The replacement of the existing lighting system with energy efficient ones.

The dimensioning of the RES systems has been based on simple methodological tools. More specifically, the ground source geothermal energy intervention has been dimensioned according to the methodology proposed by Kavanaugh and Rafferty [16]. The drill length depends on the thermal load, including the performance characteristics of the selected ground source heat pump, the ground and piping heat resistances, as well as the temperature of the involved flows on the ground heat exchanger. For the specific analysis, ground heat conductivity of 1.3 W/mK has been assumed [17], while ground temperature data by [18] have been used. The results demonstrate 130 drills of 103 m each (total piping length of 80,182 m, on a total surface of 0.8 acres).

The thermal energy analysis regarding the hot water needs and their covering by a solar thermal system, has been based on the f-chart method [19]. Depending on the fraction of the total heating load that will be supplied by solar energy, the calculations demonstrated different values for the total collector surface. In particular, the calculations were accomplished taking into consideration the assumption that the solar thermal collectors would cover the total thermal energy needs for hot water during summer; this would allow, in principle, the elimination of oil consumption for hot water needs, as the hot water thermal load that cannot be covered by solar energy (by winter time) could be covered by the ground source heat pump. The above scenario led to the requirement of 20 m² of selective flat plate collectors (F_t (tu) = 0.75 and F_t UL = 4 W/m²K). The collectors would be installed on the inclined roof (inclination of 20°) of the sport center, at the South-East orientation.

The results indicate that for more than 6 months, the fraction of the covered thermal energy load exceeded 70%, while fraction of 59% on annual basis has been calculated. In Figure 6, the variation of the monthly thermal energy fraction by solar energy is presented.

For covering the electrical needs of the center, after the interventions, the installation of PV panels has been considered. More specifically, the energy saved through the replacement of the existing lighting system, the additional contribution of the geothermal heat pump system to the electrical consumption and the necessary electrical energy needs for the coverage of the rest of the thermal load of solar water heating by the geothermal heat pump, have been taken into account. As a result, the total electrical consumption was calculated equal to 186,562 kWh versus 216,407 kWh before interventions. The PV panels were assumed to be installed on the two inclined roofs (inclination of 20° each) of the building (at South – East and North – West orientation), while energy analysis has been based on the PV-f chart method [20].

The results show that the total surface area of the required PV panels is 240 m², installed at the South – East (100 m²) and North – West (140 m²) orientation, as well. The annual amount of the produced electrical energy was calculated equal to 48,094 kWh (22,334 kWh for the South – East and 25,760 kWh for the North – West oriented panels). The fraction of the electrical energy load, covered by the PV panels, varies according to the Figure 7. More specifically, in May, presenting minimum load requirements, the coverage is 100 %, while for four months the corresponding coverages exceed 50 %. The annual fraction of the electrical load, covered by the PV panels was estimated to be almost 27 %.

An economic analysis of the pay-back period, based upon the integration of the above technologies, led to a value of 12 years; the main intervention burdening the economical profitability is that of the ground source heat pump, as substantial effort on drilling and installation of the ground heat exchangers should be provided. Alternative scenarios may
consider limitation of the ground source heat pump load (and size) through the installation of solar thermal collectors. In any case, the proposed interventions could only be evaluated given the presence of specific data for the operation of the center. Within this context, priorities could be highlighted, making the discussion for the energy upgrade of the center more realistic.

CONCLUSION

The elaboration of experimental and simulation analysis contributed to the evaluation of thermal comfort and energy performance of the studied sports center, as well as to the proposal of specific interventions for improvement; the adopted approach uses easy to implement methodological tools.

Interventions, largely concentrating on RES integration, would contribute to the substantial decrease of conventional fuels consumption; oil consumption is expected to be eliminated, while electrical consumption would be decreased by 36%.

Economic analysis predicted a pay-back period of 12 years. One should note, however, the limitations related to the absence of actual consumption data, due to the non-regular operation of the sports center. Given the availability of reliable operation data, the simulation can be more detailed and the effectiveness of the proposed measures can be evaluated on a more realistic basis. Within this context, the information provided by Life Cycle Assessment (LCA) of the anticipated RES systems can be valuable.

ACKNOWLEDGEMENTS

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AIR QUALITY MEASUREMENTS IN A MEDIUM SCALE ATHLETIC HALL: DIURNAL AND I/O RATIO ANALYSIS

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ABSTRACT

Air quality of outdoor and indoor places is a continuing issue of major concern to scientists, local authorities and general population. Most of studies related to indoor air involve homes and workplace/school environments, but little attention is given to other places that people spend their time, like sport halls and aquatic centers, where many people are doing sports or watch athletic events. Within this context, in this study a mechanical ventilated medium scale indoor athletic centre (total capacity of 3,000 seats) of the city of Kozani, Greece, was chosen for investigating the air quality. For this reason, an extensive monitoring campaign took place during autumn period, including measurements of PM2.5, VOC, NO2, O3 for the indoor and outdoor area. The measurements for PM2.5 and VOC were performed simultaneously indoors and outdoors, in order to find potential, common or not, indoor sources of these two pollutants. In addition, chemical analysis was performed for the collected PM2.5 concerning ionic species and 17 metals (Be, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sb, Ba, Th, Pb, U and Fe). Results show that the PM2.5 concentration is slightly higher outdoors than indoors with values of 13.98 and 11.96 μg/m³ respectively. The I/O ratio was always under 1, indicating that the outdoor concentrations influence the indoor ones. On the other hand, the diurnal variation of VOCs concentration reveals increased levels during “event” hours, in comparison to “non-event” hours, for the indoor and outdoor area as well.

KEYWORDS:
VOCs, PM2.5, indoor air quality, athletic hall, ionic species

INTRODUCTION

Air pollution is still a vital environmental issue, which concerns the international scientific community and also the public authorities and the general population. This is strongly supported by the fact that recently the EEA (Air quality in Europe report 2017) estimates that for example, at the year 2014, the long term human exposure to PM2.5 concentration was responsible for about 428,000 premature deaths across Europe (over 41 countries) [1]. Taking into consideration that people spend more than 80% of their time indoors [2], the indoor air quality (IAQ) is a special issue and gains a lot of attention during the last decades. The IAQ mainly is affected by indoor sources like smoking, cooking, building and consumer products emissions, etc. as well as by the infiltration of outdoor air pollutants [3]. The most studied chemical categories that occur in the indoor air are volatile organic compounds (VOCs) and carbonyl compounds. Other important indoor pollutants are particulate matter (especially PM2.5), ozone (O3) and NO2 which are regulated by international organizations (EU, WHO); these are well studied and also related to health effects [4].

Most of studies related to indoor air involve homes and workplace/school environments [5-7] but little attention is given to other places that people spend their time like sport halls and aquatic centres, where many people do sports or attend athletic events [8]. According to Andrade et al. [9] in the period of 2000-2015, 23 studies were published, corresponding to 67.6% of the total published material relevant to indoor air quality of sport facilities and environments used for physical exercise. The level of the values of air quality parameters at places where people are doing sports can be very important due to the fact that: i) the inhalation rate increases while human exercises, so the amounts of pollutants inhaled increase proportionally [10], ii) the air flow velocity increases during exercise, so the pollutants are carried deeper into the respiratory system [11], iii) most of the inhalation is performed through mouth, so the normal nasal filtration is bypassing, thus, large particles and soluble vapours enter the respiratory tract, and iv) the pulmonary diffusion capacity has been shown to increase with exercise [12].

The importance of studying the air quality of indoor sport facilities is twofold: first, the number of people doing physical exercise is increasing, and consequently the total daily time spend inside such places is increasing, and second, the number of attendants of an athletic event is considerably large,
in the order of thousands. Most of the studies concerning the air quality of indoor facilities have been performed in school gymnasiums and deal with a limited number of pollutants [13, 14] or university sport facilities with more pollutants [10]. Moreover, studies performed by the time of an athletic event in large crowded athletic halls are very scarce [8].

The objective of this study was to conduct a comprehensive air quality investigation in a medium scale indoor hall and examine indoor/outdoor relation. Thus, in the present study a mechanical ventilated medium scale hall (total capacity of 3,000 seats) of the city of Kozani, Greece, was chosen to perform an extensive monitoring campaign during autumn period, including measurements of PM2.5, VOC, NO2, O3 for the indoor and outdoor area. During the campaign, a qualified round for the European Championship of Volleyball of 2016 was taken place for three days, presenting two games per day. The measurements for PM2.5 and VOC were performed simultaneously indoors and outdoors, in order to find potential, common or not, indoor sources of these two pollutants. Comparisons on event and non-event days/hours have also been made. In addition, chemical analysis was performed for the collected PM2.5 concerning ionic species and 17 metals (Be, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sb, Ba, Ti, Pb, Th, U and Fe).

MATERIALS AND METHODS

Location and description of the athletic hall. Kozani is the capital of the region of West Macedonia with about 48,000 inhabitants. The sampling site (40ο 27’ /21ο 78’) is located in Eordea basin, north-west of Greece, in which four large lignite-burning power plants operate with their coal mines. The location of the power plants is north to northeast (N,NE) of the sampling site and approximately 10.5 km away (figure 1). The athletic center is located in the Lefkovrysi municipal district, 3 km away from the city of Kozani. Even though the sports centre has been inaugurated by year 2009, until 2016 it had also been used for the hosting of two cultural events. Following that year, the center was set to operation; nevertheless regular operation has not yet been achieved. The center has a capacity of 2724 spectators. A thermal comfort and energy analysis performed by Panaras et al. [21] demonstrated the high thermal performance of the envelope and HVAC equipment.

Sampling and analysis. PM2.5 samples were collected simultaneously for the indoor and outdoor place of the athletic hall; measurements were performed from 16th to 22th of September 2016 (figure 1). Daily samples of suspended particulate matter were collected on 47 mm quartz fiber filters (Whatman), mounted in Low Volume Air Sampling System (Derenda LVS3.1/PMS3.1-15 and Teccora with a PM2.5 inlet) according to EN 12347 (CEN, 2014). Volatile Organic Compounds (VOCs) were collected for indoor and outdoor environment of the athletic hall, at the same time, during five days in September 2016 (16-20 September 2016). Air samples were taken every day at 09:00, 12:00, 18:00 and 21:30 using low volume personal pumps (SKC) and pre-conditioned glass tubes filled with Tenax TA (Chrompack) at flow rates of about 80 mL/min for 30 minutes.

FIGURE 1
Location of the Lefkovrişi athletic hall of Kozani (Google maps).
The grey areas are the lignite open mines. Also the locations of the five power plants are shown.

At the times of 18:00 and 21:30 an athletic event was taking place for the days of 16/9, 17/9 and 18/9. Samples were analyzed using a thermal desorption unit (Gerstel TDSA) coupled to a gas chromatograph (Agilent 6890N), equipped with a mass spectroscopy detector. NO2 and O3 were monitored on-line, on a daily basis, with a time interval of 30 minutes; measurements were performed with AEROQUAL (Series 500 IAQ) instrument using, NO2 and LOWO3 sensors respectively.

Extraction and analysis of ionic species. One half of the collected filter was ultrasonic treated with ultra-pure water. Details on the extraction procedure and analytical techniques are described in Tolis et al. [15].

Extraction and analysis of metals. The second half of the filter was heated at 70°C in a mixture of ultra pure HNO3 acid (6ml) and HCl acid (0.5ml) for 30 min. After the digestion, the mixture was filtered and the filtrate was diluted up to 25 ml with ultra-pure water (Millipore Direct Q, resistivity 18.2MΩ). The solutions obtained were injected to an ICP-MS (Agilent 7700x) instrument. Field and laboratory blank were routinely analyzed for metals and the results were subtracted from the sample values.
Weather conditions and meteorological data. The climate of Kozani area is continental Mediterranean, characterized by quite low temperatures during winter time (December to February) and high temperatures during summer time (June to August). The meteorological parameters were available during the campaign (16-9-2016 until 07-10-2016), from the University of Western Macedonia’s portable weather monitoring station which was located next to the athletic hall building. The average values for the two sampling periods concerning temperature, relative humidity, pressure and wind speed are presented in Table 1. Temperature values ranged between 7.3 °C and 26.2 °C, while relative humidity ranged between 33.3% and 100.0%. The prevailing wind directions during the sampling period were WSW and SW (21.6% and 15.9% of the observations respectively). The overall wind speed was at low levels during the whole sampling period, with an average value of 0.96 m/sec. Indoor comfort parameters (temperature and relative humidity) were continuously monitored with HOBO data loggers, which were also connected with Telair CO₂ sensors for the continuous monitoring and recording of the CO₂ concentration levels. The data loggers were programmed for a 5 min data logging interval (Table 1). CO₂ measurements were within acceptable limits for most of the time, noting the presence of relatively insufficient rate during the peak time of the events. The thermal comfort parameters analysis demonstrated acceptable values for temperature and relative humidity of indoor air, while ventilation has been proven to be sufficient for most of the time [21].

RESULTS AND DISCUSSION

PM concentration. The PM 2.5 concentration of indoor and outdoor environment of the athletic hall of Kozani, along with the Indoor/Outdoor ratio is listed in Table 2. The outdoor concentrations (mean value 14.13 µg/m³) were in general in low levels and almost two times lower (indicated value of 25.75 µg/m³ by Tolis et al. [15]) and more than three times lower (indicated value of 49 µg/m³ by Kallimeri et al. [7]) compared to previous studies which had taken place in Kozani during warm period but in different sampling sites. This can be mainly attributed to the location of the sampling point, as it was sited outside the city in an urban background place. The indoor PM 2.5 concentrations (mean value of 11.96 µg/m³) were lower than outdoor ones. As it is shown at Table 2, the I/O ratio for every sampling day was below 1.0, indicating that indoor sources are not present in the athletic hall. Concerning event and non-event days, it seems that there is a possible influence to the concentration of the PM2.5, as by the first three days there were two games per day, in contrast to the rest four days (Table 1). The above findings may be attributed to the sufficient air exchange rate achieved by the central HVAC system. The mean PM 2.5 concentration found indoor and outdoor did not exceed the EU established target value of 25 µg/m³, averaging one-year period (Directive 2008/50/EU), neither the recommended by WHO daily value of 25 µg/m³ [22].

Ionic composition of particulate matter. The average concentrations of water soluble ionic species, for the sampling period, concerning the indoor and outdoor area of the athletic hall of Lefkovrisi, are summarized in Table 3. The concentration of the measured ionic species, contributed for an average of 26.7% of the total mass for the

### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Indoor</th>
<th>Outdoor</th>
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</tr>
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<td>T (°C)</td>
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<td>RH (%)</td>
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<td>0.96</td>
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<tr>
<td>Rainfall (mm)a</td>
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<td>22.6</td>
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a. Accumulated precipitation

### Table 2

<table>
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<tr>
<td>22/9/2016</td>
<td>13.62</td>
<td>10.42</td>
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</table>
TABLE 3
Average value, standard deviation and range (in µg/m³) of ionic components of PM2.5 for indoor and outdoor air of the athletic hall.

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>Std</th>
<th>Range</th>
<th>Outdoor Avg</th>
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<td>Cl⁻</td>
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<td>0.03</td>
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<td>0.03</td>
<td>0.03</td>
<td>ND-0.09</td>
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<td>NO₃⁻</td>
<td>0.22</td>
<td>0.17</td>
<td>0.05-0.48</td>
<td>0.17</td>
<td>0.08</td>
<td>0.04-0.26</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>2.08</td>
<td>1.70</td>
<td>0.41-4.79</td>
<td>1.62</td>
<td>0.67</td>
<td>0.18-2.20</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.13</td>
<td>0.11</td>
<td>0.05-0.34</td>
<td>0.10</td>
<td>0.05</td>
<td>0.01-0.14</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.86</td>
<td>0.50</td>
<td>0.17-1.53</td>
<td>0.83</td>
<td>0.58</td>
<td>0.02-1.51</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.04</td>
<td>0.04</td>
<td>ND-0.10</td>
<td>0.05</td>
<td>0.04</td>
<td>ND-0.13</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.05</td>
<td>0.07</td>
<td>0.01-0.21</td>
<td>0.09</td>
<td>0.07</td>
<td>0.03-0.21</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.62</td>
<td>0.33</td>
<td>0.17-1.09</td>
<td>0.87</td>
<td>0.39</td>
<td>0.34-1.39</td>
</tr>
</tbody>
</table>

ND = Not Detected

TABLE 4
Average value, standard deviation, range (in µg/m³) and ratio of VOCs for indoor and outdoor air of athletic hall.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Indoor Avg</th>
<th>Std</th>
<th>Range</th>
<th>Outdoor Avg</th>
<th>Std</th>
<th>Range</th>
<th>I/O</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>1.00</td>
<td>3.17</td>
<td>0.07-14.41</td>
<td>0.31</td>
<td>0.28</td>
<td>0.03-1.18</td>
<td>3.24</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.94</td>
<td>1.97</td>
<td>0.11-9.16</td>
<td>0.60</td>
<td>0.51</td>
<td>0.16-2.26</td>
<td>1.57</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>0.02</td>
<td>0.05</td>
<td>ND-0.23</td>
<td>ND</td>
<td>-</td>
<td>-</td>
<td>&gt;&gt;1</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>0.03</td>
<td>0.04</td>
<td>ND-0.11</td>
<td>0.01</td>
<td>0.04</td>
<td>0.00-0.16</td>
<td>2.25</td>
</tr>
<tr>
<td>Octane</td>
<td>0.25</td>
<td>0.21</td>
<td>0.07-0.90</td>
<td>0.14</td>
<td>0.10</td>
<td>0.00-0.42</td>
<td>1.78</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.28</td>
<td>0.21</td>
<td>0.06-0.89</td>
<td>0.28</td>
<td>0.44</td>
<td>0.03-1.99</td>
<td>1.01</td>
</tr>
<tr>
<td>p,m-xylene</td>
<td>0.92</td>
<td>0.64</td>
<td>0.22-2.86</td>
<td>1.05</td>
<td>1.87</td>
<td>0.08-8.48</td>
<td>0.88</td>
</tr>
<tr>
<td>α-xylene</td>
<td>0.34</td>
<td>0.25</td>
<td>0.08-1.11</td>
<td>1.06</td>
<td>3.59</td>
<td>0.04-16.28</td>
<td>0.32</td>
</tr>
<tr>
<td>1,2,4-trimethylbenzene</td>
<td>0.30</td>
<td>0.24</td>
<td>0.04-1.02</td>
<td>0.40</td>
<td>0.69</td>
<td>0.03-3.11</td>
<td>0.77</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.43</td>
<td>4.84</td>
<td>0.19-22.27</td>
<td>1.31</td>
<td>2.08</td>
<td>0.02-9.02</td>
<td>1.86</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.21</td>
<td>0.41</td>
<td>ND-1.46</td>
<td>0.04</td>
<td>0.05</td>
<td>ND-0.18</td>
<td>4.71</td>
</tr>
<tr>
<td>a-pinene</td>
<td>0.27</td>
<td>0.33</td>
<td>ND-0.86</td>
<td>0.15</td>
<td>0.33</td>
<td>ND-1.27</td>
<td>1.71</td>
</tr>
<tr>
<td>b-pinene</td>
<td>ND</td>
<td>-</td>
<td>ND</td>
<td>ND</td>
<td>-</td>
<td>-</td>
<td>&gt;&gt;1</td>
</tr>
<tr>
<td>3-carene</td>
<td>0.43</td>
<td>1.56</td>
<td>ND-6.89</td>
<td>ND</td>
<td>-</td>
<td>-</td>
<td>&gt;&gt;1</td>
</tr>
<tr>
<td>d-limonene</td>
<td>0.13</td>
<td>0.21</td>
<td>ND-0.71</td>
<td>0.04</td>
<td>0.04</td>
<td>ND-0.13</td>
<td>3.67</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.04</td>
<td>0.03</td>
<td>0.01-0.13</td>
<td>0.04</td>
<td>0.06</td>
<td>ND-0.29</td>
<td>1.12</td>
</tr>
<tr>
<td>1,2,3-trimethylbenzene</td>
<td>0.09</td>
<td>0.07</td>
<td>0.02-0.28</td>
<td>0.10</td>
<td>0.15</td>
<td>ND-0.68</td>
<td>0.98</td>
</tr>
</tbody>
</table>

ND: Not detected

outdoor area, while for the indoor area this percentage was found to be 33.7%. Sulfate anion was the predominant ionic component for both indoor and outdoor sites, although the outdoor levels were laying lower than those of a study at an urban background area of Kozani [15].

Literature has connected sulfate anions with anthropogenic emissions (industrial units, central heating etc.) existing in the area [16]. In addition, previous studies demonstrate that the mass ratio of NO₃⁻/SO₄²⁻ is an indicator of the relative importance of stationary versus mobile sources for air pollution [17].

In this study, the mean mass ratio of NO₃⁻/SO₄²⁻ was 0.13±0.07 (range 0.05-0.23) indicating that stationary sources, such as industry emissions and especially coal combustion power plants that operate in the area (figure 1), may play an important role in atmospheric particle concentrations.

The indoor concentrations of the Cl⁻, NO₃⁻, SO₄²⁻, Na⁺ and NH₄⁺ ions were higher than the outdoor ones, in contrast to the K⁺, Mg²⁺ and Ca²⁺. The later could be attributed to the fact that the sampling point is an urban background site with croplands around, and the respective elements are part of the crustal earth composition.

FIGURE 2
(a) Average daily concentrations of trace elements in PM2.5 for indoor and outdoor air of the athletic hall. (b) Enrichment factors for elements in outdoor air of athletic hall.
PM2.5 associated trace elements concentration. The concentration of the associated PM2.5 trace elements is presented in figure 2. For all the measured trace elements, the outdoor concentrations are higher than indoor ones, indicating that for these species the outdoor concentrations influence the indoor area by penetration through ventilation process. A powerful tool to investigate the source and evaluate the contribution of anthropogenic and natural sources to the air pollution is the enrichment factor of trace elements (EF) [18]. EF is related with the element concentrations of the earth’s crust and is calculated by the following equation:

$$EF_x = \frac{C_x}{C_R_{aerosol}} / \frac{C_x}{C_R_{crust}}$$ (1)

Where \(C_x\) is the concentration of an element X and \(C_R\) is the concentration of a reference element measured at aerosol. The crust earth concentration for the elements was given by Wedepohl H. [19]. There is no widely accepted rule in the literature for the choice of the reference element; Si, Al and Fe are usually used [18]. In this study, Fe was used as a reference element. Results of the calculated EF(Fe), taking into account the average values of trace element measured at the outdoor area of the aquatic centre, is given in figure 2b. The EF values of Be, V, Mn, Co, Ba, Ti and Th were below 10, indicating that the presence of these elements can be mainly attributed to natural sources. The EF of Cr, As and U were between 10 and 100, revealing that both anthropogenic and crustal earth sources were important for these elements. Finally, the EF of Ni, Cu, Zn, Se, Sb and Pb were bigger than 100, indicating that they are mainly originated from anthropogenic processes such as vehicular emission and industrial emission. It is worth mentioned here that the highest EF was calculated for the day an athletic event took place, with the morning concentration being lower in the morning than during the evening and night. For the “non-event days” there is not such a diurnal variation, neither for the indoor or outdoor area as Figure 3 shows.

VOC concentrations. Table 4 illustrates the name and the mean value concentration of VOCs measured in this study, for indoor and outdoor places of the athletic hall of Lefkovrisi, Kozani; b-pinene was not detected, either at the indoor or the outdoor air of the athletic hall, while 3-carene and trichloroethylene were not detected at the outdoor air only. In general, the mean concentrations of VOCs were very low, especially for the outdoor values, except concerning the measurements by the days a sport event took place; by that time the values of VOCs increased. E.g. the sum of measured VOC for the 16th of September at 21:30 was 45.22 µg/m³, while for the rest two non-event days it was 1.00 and 0.7 µg/m³ respectively (figure 3). Toluene was the compound with the highest concentrations found indoors. Concerning outdoor concentrations, these were found in very low levels, indicating that toluene was the most significant outdoor pollutant, along with xylenes. To verify the possible indoor sources of the athletic hall area, the indoor-outdoor ratio (I/O) was calculated. Table 4 presents the numerical values of the I/O ratio for each monitored pollutant. Most of compounds gave a value of I/O ratio below 1, indicating that there are no possible indoor sources for these compounds, with the major source to be the outdoor concentration. In addition, styrene, d-limonene, with the maximum observed I/O ratio value of 4.71 and 3.67 respectively seems to have both indoor sources and an outdoor influence through the air exchange. Possible indoor sources are the cleaning process and the plastic substrate of the floor for the volley playing field. It is worth mentioned here that the compound with the maximum abundance identified by Mass Spectrometry was butyl glycol acetate, which is found at epoxy resins and in the manufacture of polyvinyl latex. This compound was not detected for the outdoor samples. The above findings can be supported by the Pearson coefficient correlation, which were found to be, for the compounds hexane, benzene, toluene, ethyl benzene, xylenes, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene and naphthalene, above 0.70.

Figure 3 illustrates the diurnal variation of the sum of measured VOC for indoor and outdoor concentration values. For indoor and outdoor concentration, it is clear that there is a diurnal variation for the days an athletic event took place, with the morning concentration being lower in the morning than during the evening and night. For the “non-event days” there is not such a diurnal variation, neither for the indoor or outdoor area as Figure 3 shows.

NO2 and O3 concentrations. Indoor and outdoor concentration of NO2 for the area of aquatic centre was measured for the period of 24 – 27 of September along with 7-10 of October 2016 and 27 September until 2 of October 2016 respectively. The average daily value of indoor concentration (8 days) was 72.61 (+5.46) µg/m³ while the outdoor concentration (6 days) was higher, reaching the value of 95.21 (+5.84) µg/m³. Although the measurements were not simultaneously done, it seems that the indoor concentration of NO2 was higher than outdoors. This is opposite to that observed in a similar investigation for the air quality inside large athletic halls [8]. Our observation can be attributed to the fact that the period of indoor measurements were performed when the athletic hall was closed, without any ventilation support, except for one day on October 8th when an athletic event took place. For this day, the diurnal variation of NO2 inside the hall, shown on figure 4, depicted a clear maxima started on noon and finished at afternoon hours.
while on the athletic event ours (20:00-23:00) the concentration seems to be abnormal. As it can be seen in figure 4, there is also a similar pattern, with a peak for the morning to afternoon hours, where the most anthropogenic activities performed. Regarding the indoor and outdoor concentration of O₃ for the area of the athletic hall, it was measured for the period of September 16th to 21st 2016 and October 02nd to 07th 2016, respectively. The average value of indoor concentration was 35.82 (±8.25) μg/m³ while the outdoor concentration was higher, reaching the value of 64.30 (±11.76) μg/m³. Although the measurements were not simultaneously done, it seems that the indoor concentration of O₃ was lower than outdoors, as Stathopoulou et al. [8] found in their investigation for a sport hall during event and non-event days. Figure 4 shows the diurnal variation for indoor and outdoor concentration of September 20th and October 6th respectively. The outdoor diurnal variation of O₃ reveals a clearly increasing trend, starting from 11:00, while starting to decrease by 19:00. The indoor diurnal variation seems to have a similar behavior (figure 4). On the other hand, it is known that ozone reacts with indoor surfaces and is easily removed if no other indoor sources are present [20]. This is also a possible explanation of the lower concentrations of O₃ indoors.

**CONCLUSION**

The air quality of the athletic hall of Lefkoviri si at Kozani municipality was investigated in this study, concerning common pollutants. Furthermore, the pollutants concentration of outdoor area was measured and the relationship between indoor and outdoor levels of air pollutants was considered. The particulate matter concentration of indoor environment was lower compared to outdoor, with both quantities being at low levels and under the daily limit value established be WHO. The indoor PM2.5 concentration seems to be influenced by the outdoor sources, even if a sport event takes place inside the hall. The same trend was also found for the trace elements composition of the PM species.
which support this finding. Concerning ionic species, the SO$_4^{2-}$ is the ion found in the highest levels for both the indoor and outdoor area. The VOCs were found at very low levels, both at indoor and outdoor air, with toluene to be the most abundant compound. An athletic event influences the VOCs concentration for the indoor and outdoor air, as derived from the diurnal variation. The O$_3$ concentration was higher at the outdoor environment than indoors, in agreement with the NO$_2$ concentration trend.

ACKNOWLEDGEMENTS

The proposed research was performed within the framework of the Research Program: “Energy upgrade and rational use of environmental resources in the athletic centers of the Municipality of Kozani, Western Macedonia” (duration: May 2016-January 2017), funded within the framework of the Specific Program for the Development of Western Macedonia Region and executed by the University of Western Macedonia, Mechanical Engineering Department, Environmental Technology Laboratory.

REFERENCES


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APPLICATION OF MCA FOR STUDYING AS THE LIFESTYLE AND THE AIR QUALITY CAN AFFECT FORMS OF SLEEP DISORDERED BREATHING

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2Institute of Methodologies for Environmental Research – CNR, 85050 Tito Scalo (PZ), Italy
3Engineering of the Environment, Land and Infrastructure Department, Polytechnic of Torino, 10129 Torino, Italy.
4Department of Molecular Medicine and Medical Biotechnology, University “Federico II”, Napoli, 80131, Italy

ABSTRACT

Despite an extensive research on the adverse effects of air pollution on human health, little was known about the mechanism by which air pollutants may affect sleep. Particularly for adults, it was proposed that particles influence sleep because they cause damages to the upper airways and because they have dangerous effects on the central nervous system. It was also suggested that environmental tobacco smoke exposure (active or passive) may be a cause of poor sleep and of sleep health disparities. In this study we present the application of the Multiple Correspondence Analysis (MCA) to analyze qualitative data regarding lifestyles of patients and the analysis of results obtained combining qualitative and quantitative data. In particular, Cluster Analysis (CA), and Principal Component Analysis (PCA) were used in order to investigate the potential relationships between PM10 concentrations and the occurrence of the Obstructive Sleep Apnoea Syndrome (OSAS), a particular respiratory disease consisting in a form of sleep disordered breathing. We used a database composed of polysomnography test performed on 295 patients living in Rome urban area, data about the lifestyles related to OSAS risk factors of the patients and PM10 daily concentrations measured by Air Quality Monitoring Network of Rome urban area in 11 sampling sites from 2008 to 2011.

KEYWORDS:
Air quality, Particulate concentrations, Respiratory disorders, Multivariate analysis

INTRODUCTION

Particulate matter (PM), a major component of air pollution, consists of a mixture of solid and liquid particles suspended in air [1]. PM remains one of the most harmful airborne pollutants of increased scientific and regulatory interest. Source complexity, transport phenomena and the atmospheric chemistry result in particulate matter of different size and chemical composition. Specific human activities result in significantly increased PM levels in the ambient and in indoor air [2].

Several studies have investigated the adverse health effects of air pollution by particulate matter [1, 3, 4, 5]. The ability of solid microparticles to penetrate deep into the human respiratory tract resulted in increased morbidity and mortality [6]. There was also evidence that car exhaust gases, an important source of PM, were directly involved in the pathogenesis of several health endpoints, including respiratory, cardiovascular, neurological, and allergic diseases, as well as asthma [7, 8, 9, 10].

Despite an extensive research on the adverse effects of air pollution on human health [11, 12, 13], little was known about the mechanism by which air pollutants may affect sleep. Some studies pointed out harmful effects of air pollution on the sleep in school-age children [14, 15, 16]. It was demonstrated that air pollution exposure had a negative impact on children’s sleep with a significant association between PM10 levels and sleep disturbance [17, 18]. For adults, it was proposed that particles influence sleep because they cause damages to the upper airways and because they have dangerous effects on the central nervous system [19]. It was also suggested that environmental tobacco smoke exposure (active or passive) may be a cause of poor sleep and of sleep health disparities [15, 19, 20].

In this study we present the application of a multivariate statistical procedure to investigate the relationships between levels of atmospheric particulate and Sleep Disordered Breathing (SDB). Particularly we studied the relationships between the Obstructive Sleep Apnoea Syndrome (OSAS), the risk factors associate to lifestyle of patients and levels of PM10 outdoor concentrations in the urban area of Rome (Italy). Our goal is to analyze the qualitative data throughout the Multiple Correspondence Analysis and to integrate the results obtained with this technique with results by application of PCA and Cluster Analysis to the quantitative descriptors.
MATERIALS AND METHODS

295 patients, living in Rome, were subjected to Polysomnography test (PSG) during the period 2010-2013 (data collected by the staff of Pulmonary Medicine Department, University Hospital A. Gemelli, Rome). Ten variables were taken into account (Table 1). PCA allowed identifying the correlation structure among the PSG variables. Three significant eigenvectors (Table 2) were identified, explaining 91% of data variance. It highlighted that snoring indices were weakly related with OSAS severity (measured by AHI).

On the base of residence zone in the last 10 years, each patient was assigned to one of the three zones in which was divided the urban area of Rome: Zone1-characterized by the lowest PM10 concentrations and the presence of green areas; Zone2-included urban and suburban areas with medium level of PM10 concentrations; Zone3-characterized by the highest level of PM10 (Table 3). This classification was obtained by Cluster Analysis of PM10 concentrations measured in 11 monitoring stations (MS) of Air Quality Monitoring Network of Rome urban area from 2008 to 2011 (data by ARPA Lazio agency).

Furthermore to each patient, a questionnaire on lifestyle was administered. It included nine descriptors with 22 modalities: six binary variables (gender G, exposure to second-hand smoke ExpSS, alcohol use AU, sedative consumption Se, rhinitis Rh and nasal septum deviation NSD) and three multi-modalities variables (age A with four modes: A-A patients less than 60 years old, A-B patients between the ages of 61 and 70, A-C patients between the ages of 71 and 80, A-D patients over 81 years; active smoke story ASS with three modes: ns-no smoking, low-patients who smoke less than 20 packs x year, high-patients who smoke more than 21 packs x year; Body Mass Index BMI with three modes: normal weight BMI<24.99 kg/m², overweight 25<BMI<29.99 kg/m², obese BMI>30 kg/m²).

The Multiple Correspondence Analysis was applied for analyzing the pattern of relationships among categorical dependent variables and consequently for highlighting risk factor profiles. In the first MCA run to questionnaire data, it was put in evidence that the first eigenvalue corresponds to the gender, explaining 12.1% of data variance or inertia. For better highlighting the role of the other variables in the patient profiles characterization, we excluded this variable and the patients were divided a priori in male (59%) and female (41%). The gender was the categorical variable that may be considered "binding" in the formation of the profiles. MCA was re-applied to male matrix MM = [174 male patients × p qualitative descriptors with q modes] and to female matrix MF = [121 female patients × p quantitative descriptors with q modes] (p is the number of qualitative variables, p = 8; q is the number of modes, q = 20). In order to individuate significant factors (patient profiles), we used a multiple criterion, combining \( \lambda \)-values and relative weight of each mode. In particular calling \( (q-p)/p \) the total inertia, we selected among the \((q-p)/p\) no trivial eigenvalues, the first ones in which at least two modes have relative weight higher than \( 1/p \).

**TABLE 1**

<table>
<thead>
<tr>
<th>m</th>
<th>OSAS variables by polysomnography test</th>
<th>u.m.</th>
<th>acronym</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Total Sleep Time</td>
<td>Min</td>
<td>TST</td>
<td>Measured</td>
</tr>
<tr>
<td>2</td>
<td>Total Snoring Time</td>
<td>Min</td>
<td>TSnT</td>
<td>Measured</td>
</tr>
<tr>
<td>3</td>
<td>Percentage of Snoring Time</td>
<td>%</td>
<td>PST</td>
<td>(TSnT/ TST)%</td>
</tr>
<tr>
<td>4</td>
<td>Apnoea Index</td>
<td>events/hour (ev/hr)</td>
<td>AI</td>
<td>Measured</td>
</tr>
<tr>
<td>5</td>
<td>Hypopnoea Index</td>
<td>events/hour (ev/hr)</td>
<td>HI</td>
<td>Measured</td>
</tr>
<tr>
<td>6</td>
<td>Apnoea Hypopnoea Index</td>
<td>events/hour (ev/hr)</td>
<td>AHI</td>
<td>AHI = AI + HI</td>
</tr>
<tr>
<td>7</td>
<td>Oxygen Desaturation Index</td>
<td>events/hour (ev/hr)</td>
<td>ODI</td>
<td>Measured</td>
</tr>
<tr>
<td>8</td>
<td>Snoring Index</td>
<td>events/hour (ev/hr)</td>
<td>SI</td>
<td>Measured</td>
</tr>
<tr>
<td>9</td>
<td>Snoring Index Obstructive</td>
<td>events/hour (ev/hr)</td>
<td>Slob</td>
<td>Measured</td>
</tr>
<tr>
<td>10</td>
<td>Percentage of sleep with haemoglobin saturation under 90%</td>
<td>%</td>
<td>T90</td>
<td>Measured</td>
</tr>
</tbody>
</table>

**TABLE 2**

<table>
<thead>
<tr>
<th>Descriptors</th>
<th>Explained variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor 1</td>
<td>PST, AHI, ODI</td>
</tr>
<tr>
<td>Factor 2</td>
<td>SI, Slob</td>
</tr>
<tr>
<td>Factor 3</td>
<td>T90</td>
</tr>
</tbody>
</table>
**TABLE 3**

Sub-groups of monitoring stations (MS) identified from Cluster Analysis; for each cluster the mean value of PM concentrations is shown

<table>
<thead>
<tr>
<th>Zone</th>
<th>Sub-groups of stations</th>
<th>PM level</th>
<th>Type area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone1</td>
<td>MS$^4$ - MS$^8$ - MS$^{11}$</td>
<td>Low PM$_{10}$; 26.7 μg/m$^3$</td>
<td>Green areas</td>
</tr>
<tr>
<td>Zone2</td>
<td>MS$^1$ - MS$^2$ - MS$^6$ - MS$^7$ - MS$^8$ - MS$^{10}$</td>
<td>Medium PM$_{10}$; 33.6 μg/m$^3$</td>
<td>Urban areas</td>
</tr>
<tr>
<td>Zone3</td>
<td>MS$^3$ - MS$^5$</td>
<td>High PM$_{10}$; 36.1 μg/m$^3$</td>
<td>Urban areas</td>
</tr>
</tbody>
</table>

**TABLE 4**

MCA results for the male sub-matrix.

<table>
<thead>
<tr>
<th>Characterizing descriptors</th>
<th>$\lambda_1$</th>
<th>$\lambda_2$</th>
<th>$\lambda_3$</th>
<th>$\lambda_4$</th>
<th>$\lambda_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P (\lambda_i)$</td>
<td>0.20</td>
<td>0.17</td>
<td>0.16</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>$P_{\text{cum}}$</td>
<td>13.4%</td>
<td>11.3%</td>
<td>10.4%</td>
<td>9.9%</td>
<td>9.1%</td>
</tr>
<tr>
<td>$P_{\text{cum}}$</td>
<td>24.7%</td>
<td>35.1%</td>
<td>45.0%</td>
<td>54.1%</td>
<td></td>
</tr>
<tr>
<td>$n_p$</td>
<td>14</td>
<td>8</td>
<td>1</td>
<td>31</td>
<td>1</td>
</tr>
</tbody>
</table>

Legend: $\lambda_i$ = i-th eigenvalue; $P(\lambda_i)$ = percentage of explained variance by i-th eigenvalue; $P_{\text{cum}}$ = cumulative percentage of explained variance; $F_{i\mu}$ = i-th factor, $n_p$ = number of patients. The acronyms of descriptors are listed in the abbreviations section.

**RESULTS AND DISCUSSION**

MCA results were summarized in Tables 4-5; for each factor, the characterizing descriptors were reported.

In the male-matrix (Table 4), MCA was able to identify three groups of patients ($F_{1\mu}$, $F_{2\mu}$, $F_{4\mu}$) and two isolated elements ($F_{3\mu}$, $F_{5\mu}$); the explained total inertia was 54.1%. $F_{1\mu}$ included heavy smokers (ASS high) aged less than 60 years ($A-A$). $F_{2\mu}$ included moderate smokers (ASS low) with nasal septum deviated (NS). In the factor $F_{3\mu}$ we found patients affected by rhinitis (Rh) and overweight or obese ($BMI \geq 25$). A patient from 61 to 70 years that make use of alcohol and sedatives and a patient with age over 80 years exposed to second hand smoke, were put in evidence as isolated elements.

For female-matrix (Table 5), we obtained five groups of patients ($F_1$, $F_2$, $F_3$, $F_5$, $F_6$) and three isolated elements ($F_4$, $F_7$); the explained total inertia was about 72%. $F_1$ includes patients with age under 60 years ($A-A$), exposed to second hand smoke (ExpSS); in $F_2$, we found non-smokers (ASS-no) women between the ages of 61 and 70 ($A-B$); $F_3$ comprised the group of woman under 60 years old ($A-A$), overweight or normal-weight ($BMI \leq 29.99$), affected by rhinitis (Rh) and that use sedatives (Se); $F_5$ included patients, with age over 70 years, that make use of alcohol; in the factor $F_6$, we found smokers (ASS low, ASS high). A patient with age over 80 years and nasal septum deviated and two women under 60 years old and with BMI $\geq 30$ were highlighted as isolated elements.

These results pointed out a marked gender difference in the risk factors for osas. For the men, the active smoke story, BMI and rhinitis play a discriminating role; on the contrary, for the women, age, exposition to second hand smoke and BMI are determining for characterizing the different profiles; use of alcohol and/or use of sedatives play a minor weight.

Furthermore for each subgroup selected by MCA, we allocated the patients in a cluster-zone on the base of their residence address. For all the cases, we calculated the mean values of OSAS parameters and we applied a small-sample pooled two-tailed t test to highlight the differences in which these mean values are significantly different by mean values calculated on the entire pool of patients. The results were summarized in Tables 6-7.

For male sub-matrix (Table 6), we noted that for the factor $F_{1\mu}$ (the heavy smokers), the sub-group of patients living in Zone2 (moderate pollution) presented high values of PST and SI and low values of AHI and ODI; on the contrary patients of the Zone3 (high pollution), showed all the values of the OSAS parameters higher than the mean values, particularly very high values of SI were observed. For the other factors, patients with nasal septum deviated or suffering rhinitis and obesity ($F_{2\mu}$ and $F_{4\mu}$ factors), showed very low values of OSAS parameters. These values increased in the patients living in Zone3 respect to the patients living in Zone2.
TABLE 5
MCA results for the female sub-matrix.

<table>
<thead>
<tr>
<th>( \lambda_i )</th>
<th>( \lambda_2 )</th>
<th>( \lambda_3 )</th>
<th>( \lambda_4 )</th>
<th>( \lambda_5 )</th>
<th>( \lambda_6 )</th>
<th>( \lambda_7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P(\lambda_i) )</td>
<td>0.19</td>
<td>0.18</td>
<td>0.17</td>
<td>0.16</td>
<td>0.14</td>
<td>0.13</td>
</tr>
<tr>
<td>( P_{cum} )</td>
<td>12.4%</td>
<td>11.9%</td>
<td>11.2%</td>
<td>10.4%</td>
<td>8.9%</td>
<td>8.8%</td>
</tr>
</tbody>
</table>

Characterizing descriptors

<table>
<thead>
<tr>
<th>np</th>
<th>F1f</th>
<th>F2f</th>
<th>F3f</th>
<th>F4f</th>
<th>F5f</th>
<th>F6f</th>
<th>F7f</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>12</td>
<td>3</td>
<td>3</td>
<td>49</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Legend: \( \lambda_i \) = \( i \)-th eigenvalue; \( P(\lambda_i) \) = percentage of explained variance by \( i \)-th eigenvalue; \( P_{cum} \) = cumulative percentage of explained variance; \( F_i = i \)-th factor, \( np = \) number of patients. The acronyms of descriptors are listed in abbreviations section.

TABLE 6
Mean values of OSAS quantitative descriptors calculated for different subgroups according MCA results and cluster analysis for the male sub-matrix.

<table>
<thead>
<tr>
<th>np</th>
<th>PST</th>
<th>SI</th>
<th>SIob</th>
<th>AHI</th>
<th>ODI</th>
<th>T90</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(%)</td>
<td>(ev/hr)</td>
<td>(ev/hr)</td>
<td>(ev/hr)</td>
<td>(ev/hr)</td>
<td>(%)</td>
</tr>
<tr>
<td>zone2</td>
<td>9</td>
<td>38</td>
<td>255</td>
<td>21</td>
<td>18</td>
<td>17</td>
</tr>
<tr>
<td>F1m</td>
<td></td>
<td>(0.03*)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zone3</td>
<td>5</td>
<td>32</td>
<td>127</td>
<td>42.5</td>
<td>37</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.17)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zone2</td>
<td>6</td>
<td>8</td>
<td>20</td>
<td>8</td>
<td>25</td>
<td>23</td>
</tr>
<tr>
<td>F2m</td>
<td></td>
<td>(0,20)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zone3</td>
<td>9</td>
<td>20</td>
<td>99</td>
<td>20</td>
<td>42</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0,20)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*significance level for small-sample pooled two-tailed t test

TABLE 7
Mean values of OSAS quantitative descriptors calculated for different subgroups according MCA results and cluster analysis for the female sub-matrix.

<table>
<thead>
<tr>
<th>np</th>
<th>PST</th>
<th>SI</th>
<th>SIob</th>
<th>AHI</th>
<th>ODI</th>
<th>T90</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(%)</td>
<td>(ev/hr)</td>
<td>(ev/hr)</td>
<td>(ev/hr)</td>
<td>(ev/hr)</td>
<td>(%)</td>
</tr>
<tr>
<td>F1f</td>
<td>zone2</td>
<td>6</td>
<td>25</td>
<td>45.5</td>
<td>13</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.20*)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zone1</td>
<td>4</td>
<td>6</td>
<td>19</td>
<td>1.5</td>
<td>18</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0,13)</td>
<td>(0,01)</td>
<td></td>
<td></td>
<td>(0,23)</td>
</tr>
<tr>
<td>zone2</td>
<td>7</td>
<td>26</td>
<td>118</td>
<td>13.5</td>
<td>26</td>
<td>25.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0,11)</td>
<td>(0,20)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zone1</td>
<td>10</td>
<td>29</td>
<td>147</td>
<td>20</td>
<td>37.5</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0,17)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zone2</td>
<td>27</td>
<td>15</td>
<td>77</td>
<td>14</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0,17)</td>
<td></td>
<td></td>
<td></td>
<td>(0,15)</td>
</tr>
<tr>
<td>zone3</td>
<td>12</td>
<td>11.5</td>
<td>45</td>
<td>16</td>
<td>26</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0,19)</td>
<td>(0,15)</td>
<td></td>
<td></td>
<td>(0,12)</td>
</tr>
</tbody>
</table>

*significance level for small-sample pooled two-tailed t test

CONCLUSIONS

In the present study we examined the relationships between Obstructive Sleep Apnoea Syndrome, a common form of apnoea, with the risk factors due to lifestyle of patients and outdoor PM10 concentrations. We applied a multivariate statistical procedure combining Multiple Correspondence Analyses with Cluster Analysis and Principal Component Analysis. MCA results have suggested dividing patients in male and female: the gender was the categorical variable that may be considered "binding" in the formation of the profiles. Both male and female patients showed severe OSAS symptoms if they lived in very polluted areas or if they lived in green areas, but there are differences between women and men. The first was that not smoker women show more evident OSAS symptom if they live in polluted areas. This behaviour was less clear for men because they were more sensitive to risk factors as smoke or obesity.
Another difference was that women living in polluted areas showed high \( T_{SO} \) values whereas for men this parameter was not conditioned by the pollution level of the area in which they live.

**ABBREVIATIONS**

MCA: Multiple Correspondence Analisys  
CA: Cluster Analysis  
PCA: Principal Components Analisys  
OSAS: Sleep Apnoea Syndrome  
PM: Particulate Matter  
SDB: Sleep Disordered Breathing  
PSG: Polysomnography test  
MS: Monitoring Stations  
MM: Male Matrix  
MF: Female Matrix  
TST: Total Sleep Time  
TsnT: Total Snoring Time  
PST: Percentage of Snoring Time  
Af: Apnoea Index  
Hi: Hypopnoea Index  
AhI: Apnoea Hypopnoea Index  
ODI: Oxygen Desaturation Index  
SI: Snoring Index events/hour  
SlOab: Snoring Index Obstructive

\( T_{SO} \): Sleep Time with haemoglobin saturation under 90%  
G: Gender  
AU: Alcohol Use  
Se: Sedative consumption  
Rh: Rhinitis  
NSD: Nasal Septum Deviation  
ExpSS: Exposure to Second-hand Smoke  
A: age  
A-A: patients less than 60 years old  
A-B: patients between the ages of 61 and 70  
A-C: patients between the ages of 71 and 80  
A-D: patients over 81 years  
ASS: Active Smoke Story  
ns-ASS: no smoker  
ASS-low: patients who smoke less than 20 packs x year  
ASS-high-patients who smoke more than 21 packs x year  
BMI: Body Mass Index  
Normal weight: \( BMI < 25 \) kg/m\(^2\)  
Overweight: \( 25 < BMI < 29.99 \) kg/m\(^2\)  
Obese: \( BMI > 30 \) kg/m\(^2\).

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**REFERENCES**


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DETECTION OF RADON EMISSIONS DURING 2016/2017 EARTHQUAKES IN ABRUZZO (ITALY)

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ABSTRACT

“Aracne” is an Italian monitoring network, part of the “Tellus” project, for the real-time detection of radon emissions from Earth’s subsoil. The Aracne network was launched in August 2015, with the first multi-parameter station in Pizzoli, in central Italy, followed in December 2016 by the one of Cagnano Amiterno and finally the station of Capitignano, which will be installed by early 2018. The stations provide data at 10-minute intervals, together with all meteorological values outside the station and at the exact measuring point, such as humidity and temperature measured at about 20 cm from the radonometer that is being used. The stations are identical both for instrumentation and for measuring place characteristics, designed in such a way to maintain constant temperature and humidity. This project makes the stations of the Aracne network unique in the world as far as detection methodology is concerned. The Pizzoli station provided very interesting data during the seismic crisis that hit central Italy on 24 August 2016, 30 October 2016 and 18 January 2017 with three earthquakes of Mw 6.0, Mw 6.5, Mw 5.5 respectively.

KEYWORDS:
Radon monitoring, Radon Emissions, Earthquake, Tellus Project, IARESP, ARACNE

INTRODUCTION

Radon is currently considered a very efficient marker of the dynamic phenomena that occur in the Earth’s crust [1-3]. However, radon emissions are influenced by many different meteorological factors, among which the most important are atmospheric pressure, temperature, humidity and wind speed [4-9]. A correct and accurate measurement of environmental factors is decisive for acquiring the capability of giving a real-time correlation, during the measurement of radon, with a possible earthquake future event. A thorough determination of radon emission rates from natural materials is necessary as well [10, 11]. In this regard, we have developed a software (AAD, Automatic Anomaly Detection) to automatically analyze the results and give a major contribution to speed-up the manual analysis of collected data [12].

For a more relevant and accurate data collection, the Tellus project involves the installation of 14 stations in a small area of about 625 Km² [12, 13]. Each station provides different data, depending on the geology of the subsoil and the presence in it of certain fluids that are relevant to determine the mobility of radon.

In this study we analyze the data of the Pizzoli station only. Those data have been continuously collected, starting from its activation date (August 2015) until today, with the exclusion of a few hours during the 6.0 Mw earthquake of 24 August 2016 at 01:36 UTC when, because of it, electricity was missing from the moment of the earthquake until the early hours of the afternoon.

MATERIALS AND METHODS

The Aracne-Tellus Network. The network was started in August 2015, and currently consists of two active stations and one has recently been completed [12]. Twenty-three areas have been identified in the Italian territory: one of them is in Sardinia, where the seismic activity is almost absent: this choice is justified by the need of having the possibility to measure a “background level” of the Radon emissions, i.e., those emissions that do not depend from seismic activity. The other 22 areas are sited in zones of high seismicity, throughout the Italian territory. Each of these zones, whose monitoring area is about 625 Km², will be equipped by a certain number of stations, namely between 9 and 14, according to the territorial specificities. The stations are equipped with a radon meter with a 1-liter ionizing chamber, a Davis-type weather station [14] with console - positioned next to the radon meter for the detection of temperature and humidity at the measuring point - a dehumidification system to keep temperature and humidity constant.

The cavity (where the radon meter is placed) can be considered almost hermetic, thanks to a special pressure lock. The radon meter and the weather station console are positioned at about 140
cm below ground level. Inside the cavity, there is also a high precision seismometer able to record seismic events even close to zero magnitude.

Outside the station, there is a central unit for detecting temperature, humidity, rain gauge, atmospheric pressure, wind speed and direction, in addition to the moon phases, powered by a small solar panel. These data are transmitted in Wi-Fi to the internal console every 10 minutes. Together with the data on the radon concentration, detected every 10 minutes too, they are transmitted to a dedicated server where the AAD software analyzes them and generates a complete graphic representation of all measured parameters. The analysed data and the plot are uploaded on a specific web page every 60 minutes. This frequent update permits an effective control of the parameters by the operators of the research group.

When the AAD system detects an abnormal pattern of the radon concentration curve, a special procedure starts. There is further processing and analysis of the environmental parameters, then a warning is sent to the control staff, by means of an email message that includes all the measured and processed data.

The aim of the Aracne network is to identify anomalies in radon emissions in order to associate them with the seismicity of the monitored territory, and to have a reliable tool to detect the preparation of large earthquakes, even in areas geologically close or bordering the seismogenic faults subject to monitoring.

Measurements and data evaluation. In August 2015, the multi-parameter station of Pizzoli (AQ) was installed and started up. The first days of November of the same year the tests were completed and the measurements were started [13]. Since then, they have been continuously collected, analysed and stored every 10 minutes until the present time. The amount of collected data is significant, and to date (December 2017) about 110,000 counts in total are stored and available.

This long period of observation has permitted to find evident correlations of the radon concentration with several environmental parameters. In particular, we have determined the correlation of radon concentration with atmospheric pressure, external humidity, external temperature and wind speed.

Thanks to the determination of these correlations, we have been able to discriminate among the anomalies measured by the station. The software is capable to predict – according to the measured values of the environmental parameters – an expected value of the radon concentration, which, as we stated before, can considerably vary depending on such parameters. Therefore, we can identify an “environmentally caused” radon anomaly. If a radon concentration significantly different from the predicted value is measured, the anomaly is classified among those worth of attention and further analyzed, since it could be of seismogenic nature. In fact, important anomalies have been recorded by our station on several occasions before some major earthquakes occurred during the seismic crisis that hit Central Italy from August 2016 to early 2017.

For a correct analysis of earthquakes, associated with radon anomalies, the Dobrovolsky formula [1, 15] can be used for a first assessment. The formula determines the radius in km of the zone within which precursor phenomena can occur.

\[
R = 10^{0.43M} \text{ Km} \quad (1)
\]

where \(M\) is the earthquake magnitude and \(R\) the radius in km. Applying the formula, we consider seismic events of all magnitudes if they are within a radius of 10 km from the station. For instance, instead, we can have precursor phenomena with earthquakes of \(M \geq 3.4\) up to 30 km, \(M \geq 4.1\) up to 60 km, \(M \geq 4.6\) up to 100 km, \(M \geq 5.4\) up to 200 km, \(M \geq 6.5\) up to 600 km from the station.

By combining the radon emission values with all the relevant environmental factors, it is therefore possible to have a first approach to the recognition of those anomalies that could be a seismic precursor. The anomalies can occur in different forms, such as increase or decrease of radon emissions.

During the 48 months of detection, we also noticed an interesting correlation between the large windy masses coming from the Northeast, which then invest the Apennine chain perpendicularly, with strong increases in radon emissions and strong earthquakes in 48/72 hours after the anomalous detection.

RESULTS AND DISCUSSION

In this section, we illustrate some of the main anomalies detected before, during and after the seismic crises that affected central Italy.

Two months before the earthquake of Amatrice, in a situation of seismogenic calm, a strong decrease in the emission of radon was detected. In the following 96 hours we recorded an earthquake of \(M \geq 2.8\) with epicenter in Barete (AQ) about 5 km North-West from the station of Pizzoli (AQ) with hypocentral depth of 14 Km (Figure 1).

In the 48 hours before the first major earthquake in Amatrice (RI) (Mw 6.0), two strong increases in radon emissions were recorded. The epicenter was identified between Accumoli and Amatrice, about 32 km north-west from Pizzoli station with a depth of 8 km.

Immediately after the strong earthquake, electric power net was lost and the station went off. After the re-ignition, which took place in the early
hours of the afternoon, the radon emissions were very high due, most probably, to the strong and continuous stresses due to the very high number of replicas of considerable magnitude (Figure 2).

In mid-October, the seismic sequence of Amatrice was greatly attenuated and the sequence of replicas was very low. The last major earthquake of Mw 4.0 dates back to 3 September. On 12 October 2016, we recorded a significant drop in radon levels and 40 hours later we recorded an earthquake of Mw 3.3 with an epicenter east of Amatrice about 21 km from Pizzoli station with a hypocentral depth of 11 km. Three days later, on the 15th of October, we recorded a new and more substantial decrease in radon levels and a new strong earthquake of Mw 4.0 less than 24 hours later from the anomaly. The earthquake had an epicenter to the north-west of Accumoli about 37 Km North-West from the Pizzoli station with a depth of 9 km (Figure 3).

On October 26, we recorded two earthquakes of 5.4 Mw and 5.9 Mw with epicenter in the northernmost area at a distance of about 57 km from Pizzoli. For these events, we did not find any
particular anomalies except for an average increase in the daily levels of radon. On 27 and 28 October we recorded two major anomalies, followed 48 hours later by the strongest earthquake of the Sequence (Mw 6.5) at a distance of about 46 Km from Pizzoli (Figure 4).

On 9 November 2016 an earthquake of Mw 3.1 was recorded, just 13 km from Pizzoli. About 48 hours earlier, we detected a strong decrease in radon concentration followed by a sharp increase.

On 12 and 13 November there were two earthquakes of Mw 4.1 at 32 Km from Pizzoli and Mw 3.3 at 16 Km from Pizzoli. Also on this occasion, we recorded a sharp decrease in the radon measurements, just a few hours before the events (Figure 5).
On January 18, 2017, the third sequence of the great seismic crisis of Central Italy began. Four earthquakes with a magnitude between Mw 5.0 and Mw 5.5, in a location north-west of the Pizzoli station are recorded at a distance between 5 and 10 km. About 48 hours before, the Pizzoli station recorded a very strong increase in radon (Figure 6).

On November 30, 2017 we found a new sharp decrease in radon levels followed by a new strong earthquake of 4.2 Mw within 72 hours after the anomaly, with an epicenter at about 20 km north of the Pizzoli station (Figure 7).
Starting from the early hours in the morning of December 13th, 2017, we noticed a strong decrease in radon emissions, which - in the following 72 hours – returned to average levels for the current period (Figure 8). This decrease has been successfully explained, and it is due to environmental factors. In particular, due to the hot winds coming from south, the outdoors temperature in those days exceeded the seasonal average, remaining constant for about 3 days without producing the usual day/night temperature variations.

In the following days, we have not detected earthquakes. This anomaly, for the reasons described above, cannot be considered a false positive: in fact, we identified its cause in the so-called «chimney effect» [16].

The chimney effect is due to the difference in temperature between inside and outside the building, depending on which a difference in pressure (ΔP) is formed. Because of this internal lower pressure, the cold air containing radon is absorbed from the ground, causing a decrease in the measured values of radon. The warmer the interior of the house and the colder the outside, the more intense the effect will be.

Often, this kind of anomaly of radon emissions occurs only concurrently with a phase of increasing temperature.

The ΔP can be calculated as follows:

\[ ΔP = α \left( \frac{1}{t_o + 273} - \frac{1}{t_i + 273} \right) \]  

where \( t_o \) and \( t_i \) are the outdoor and indoor temperatures, measured in °C, and \( α \) is a constant coefficient, equal to 3462 Pa. K.

The lower the outdoor temperature, instead, the greater the amount of radon detected.

In the specific case, shown in Figure 8, the increase in the outside temperature, constant over time, generated the opposite effect, with a decrease in the radon measurement, which has been successfully identified as an environmental anomaly.

At the end of our 2016/2017 data review, we would like to discuss the results and try to explain why we find, in some cases, sudden increase of the radon release just before an earthquake, while in other cases we have an increase or a decrease some days before or after the event.

The mechanism by which radon is released from rocks before an earthquake is – in theory – clear. Why, until now, no reliable method has been developed in order to actually predict earthquakes? This is due to an insufficient understanding of the other environmental causes (not dealing with earthquakes) that cause radon release. Some of these causes have a roughly daily cycle, while other ones depend on environmental factors that are not predictable with a daily periodicity. Therefore, anomalies do not always occur in the same direction, and it can happen that two environmental factors have effects that could partially erase each other.

For instance, on a daily basis, we find the maximum peak of radon early in the morning, when the temperature reaches the minimum and we have the maximum humidity. The minimum peak is detected in the afternoon hours, when the temperature reaches the maximum and humidity the minimum. However, if early in the morning we...
have a strong and sudden increase in atmospheric pressure, the effect should decrease the radon concentration which at the same time should remain high due to the low temperature and high humidity. In these cases it is more difficult to understand if a possible anomalous trend may depend on environmental factors or on seismogenic factors. In those rare occasions it is still necessary to wait about 3/4 days to detect possible seismic events. On the other hand, the "clean" anomalies, i.e., anomalous radon trends not depending on environmental phenomena, are immediately recognized by the software.

After a thorough analysis of the available data we can confirm that all the anomalies we did not explain in other ways have been always followed by an earthquake. On the occasion of the three most important earthquakes (Amatrice 6.0, Norcia 6.5, Capitignano 5.5) we found the three biggest anomalies in the records of the Pizzoli station.

On several occasions, instead, anomalies, even great ones, have been identified as caused by environmental factors and have not been followed by earthquakes. All the strong anomalies that have not been followed by an earthquake have a very clear meteorological explanation. However, on very few occasions, we have detected small anomalies, not explicable with meteorological factors, which have not been followed by an earthquake. However, since such anomalies should have been quite small, they are difficult to identify.

CONCLUSION

The multi-parameter station of Pizzoli, as it has been designed and built, has shown a perfect continuity and reliability in the detection task. The collected data turned out to be very useful for the purposes of our study. The expected behaviour of emissions has been determined throughout the period (over two years) identifying a daily harmonica that follows with extreme precision the daily trend of the external temperature/humidity. On several other occasions, not described in this work, the daily harmonic has allowed us to identify anomalous trends caused exclusively by environmental factors. In a few occasions, we could identify anomalous trends, in addition to those caused by environmental factors, with subsequent earthquakes of various relevance, located near the station itself.

Also the Cagnano Amiterno (AQ) station has shown complete reliability and on several occasions it has been possible to correlate the detected anomalies with those of the Pizzoli station: the two measurement complexes are at a distance of about 9 Km each other.

The Cagnano Amiterno station results have not been described in this work because the beginning of its activity dates to less than one year ago.

The Capitignano station too, which is planned to start operations in early 2018, will have the same instrumental characteristics of the previous two ones, and it will be located further north forming a perfect triangle with sides of about 9/11 Km.

The results we obtained demonstrate the great potential of this monitoring technique, if carried out in real time. In the future, it could provide a new interpretation key for the identification of anomalies of seismogenic nature, in order to anticipate an earthquake occurrence. In particular, the technique seems mature to determine if a sharp
anomaly in the radon emissions can be followed or not by an earthquake, roughly within the Dobrovolsky radius. The correlation between radon anomalies and earthquake energy has to be determined yet with an acceptable accuracy.

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ESTIMATION OF NO₂ CONCENTRATION VALUES IN A MONITORING SENSOR NETWORK USING A FUSION APPROACH

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³Department of Computer Science, ETS Computer Science, University of Málaga, Spain.

ABSTRACT

This study is focused on calculation of a reliable estimation of the hourly concentration value of NO₂ at a monitoring station based on a data fusion approach. Different feature selection procedures have been tested and their results were used as inputs to an artificial neural network (ANN) two-stage approach. The final aim is to develop a data fusion estimation tool in order to aid the decision-making in the monitoring process. ANN models were trained using backpropagation and early stopping in order to avoid overfitting. Furthermore, the study compares the different combinations of methods to estimate hourly NO₂ concentration values. The comparison was made using different performance indexes (R, d, MAE, MSE). The data from the Algeciras Bay was used as a case study. This approach may become a supporting tool for different purposes such as missing data imputation, automatic detection of decalibration or imprecise data in monitoring networks.

KEYWORDS:
Artificial neural networks, data fusion, atmospheric pollution.

INTRODUCTION

Air pollution has become an important environmental problem in metropolitan areas [1]. EU and many national environmental agencies define quality objectives for allowable levels of atmospheric pollutants [2]. An accurate air pollutants monitoring is required for air quality management to provide proper actions and control strategies [3]. The main urban-related pollutants are CO, NOₓ, hydrocarbons, and particles. Nitrogen dioxide (NO₂) is a very reactive toxic gas, which produces a strong odour, is highly corrosive and have great irritating power. NO₂ is the main responsible in the formation of the smog and acid rain in urban areas. In turn, it produces acute and chronic effects, particularly in sensitive people.

The control and reduction of the high levels of NO₂ are one of the main targets of governments.

Many atmospheric air quality reports have been regularly published in recent years. The meteorological conditions have a marked effect over the pollutants concentration as they diminish the ability of the atmosphere to disperse pollutants. The relationships between meteorological conditions and air pollutants may suggest estimating concentration values using a multivariate regression model. These relationships (pollution-weather) are very complex and may have nonlinear properties. Thus, better performance can be obtained using Artificial Neural Networks (ANNs) [4]. ANNs have become an alternative to traditional methods and they are an important tool to model air pollution with a wide range of pollutants at several time scales [5]. ANN approaches have been frequently used in atmospheric and air quality modelling studies [6]. Some studies have used ANNs to estimate air pollution peaks using meteorological variables [7].

Environmental monitoring is a very important task. An environmental monitoring network consists of a number of sensor nodes (few tens to thousands) working together to monitor a region to obtain data about the atmospheric pollution. Typically, network maintenance such as detecting failures is difficult and expensive since there are so many nodes. It is necessary to make these applications more reliable and robust in the real world. One interesting approach deals with the data fusion of the multiple sensors at the monitoring stations. Thus, sensor nodes can be able to self-organize and identify problems themselves. Data fusion has several advantages [8], mainly involving enhancements in data authenticity or availability. From network management and reliability perspectives, it is important that sensor nodes are capable of self-organizing themselves. Soft computing techniques have received an increasing interest in research on multi-sensor data fusion technology [9].

The main objective of the present work is to determine the concentration values of Nitrogen Dioxide (NO₂) at a certain monitoring station using a data
fusion approach of the meteorological variables, measured in other locations, and the concentration values measured in other monitoring stations located in the area of study. In this paper, authors have used different feature selection approaches in order to provide the best features as inputs to the following estimation stage. Different topologies of ANNs have been used in order to estimate the concentration values at a monitoring station as a function of the selected features. The different approaches have been compared using an experimental framework. Authors have also used a previously designed resampling procedure [10, 11] in order to statistically analyze and compare the results.

The rest of this paper is organized as follows: Section 2 describes the data and the region. Section 3 gives an overview of the feature selection methods. Section 4 gives a quick description of the artificial neural networks design. Section 5 presents the experimental framework. Section 6 discusses the results. Finally, Section 7 concludes the paper.

DATA AND AREA DESCRIPTION

This work is located in the Bay of Algeciras region, which is one of the most industrialized areas in Andalusia (South of Spain). Besides, Algeciras has the most important port of the Mediterranean Sea and a freeway (A-7), which links the entire region with almost 70,000 passenger cars and 4,000 heavy vehicles per day. It is a very populated region, with almost 300,000 people living in different towns, and many sources of particulate and gaseous air pollution are present. Despite that, there are only a few studies devoted to the study of air pollution in the region.

A monitoring network located in the area of study has supplied the database used in this work. This network is composed of fourteen monitoring stations. Additionally, five weather stations have supplied meteorological data. On the one hand, the monitoring stations have recorded an hourly database of NO\textsubscript{2} concentrations during a period of six years (2010-2015). These measures are controlled by the Environmental Agency of the Regional Andalusian Government (Spain). On the other hand, the meteorological information has been extracted from the weather stations located at three different sites, including a meteorological tower where the variables (wind speed and wind direction) have been measured at 60-meter height. No imputation methods have been used. Table 1 shows the stations that make up the monitoring network. Codes 1 to 14 indicate NO\textsubscript{2} monitoring stations, while codes W1 to W5 indicate weather stations. Figure 1 shows each station represented by its code. A description of each recorded variable can be found in Table 2.

<table>
<thead>
<tr>
<th>Code</th>
<th>Station name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EPSA Algeciras</td>
</tr>
<tr>
<td>2</td>
<td>Campamento</td>
</tr>
<tr>
<td>3</td>
<td>Los Cortijos</td>
</tr>
<tr>
<td>4</td>
<td>Esc. Hostelería</td>
</tr>
<tr>
<td>5</td>
<td>Col. Los Barrios</td>
</tr>
<tr>
<td>6</td>
<td>Col. Carteya</td>
</tr>
<tr>
<td>7</td>
<td>El Rinconcillo</td>
</tr>
<tr>
<td>8</td>
<td>Palmones</td>
</tr>
<tr>
<td>9</td>
<td>San Roque</td>
</tr>
<tr>
<td>10</td>
<td>El Zabal</td>
</tr>
<tr>
<td>11</td>
<td>Economato</td>
</tr>
<tr>
<td>12</td>
<td>Guadarranque</td>
</tr>
<tr>
<td>13</td>
<td>La Línea</td>
</tr>
<tr>
<td>14</td>
<td>Madrevieja</td>
</tr>
<tr>
<td>W1</td>
<td>La Línea weather station</td>
</tr>
<tr>
<td>W2</td>
<td>Los Barrios weather station</td>
</tr>
<tr>
<td>W3</td>
<td>CEPSA weather station (10 meters)</td>
</tr>
<tr>
<td>W4</td>
<td>CEPSA weather station (60 meters)</td>
</tr>
<tr>
<td>W5</td>
<td>CEPSA weather station (15 meters)</td>
</tr>
</tbody>
</table>

FIGURE 1
Location of the monitoring and weather stations.
Map data: Google, Data SIO, NOAA, U.S. Navy, NGA, GEBCO TerraMetrics.

FEATURE SELECTION METHODS

Two main approaches can be considered when the objective is to reduce data dimensionality: feature selection and feature transformation. On the one hand, feature selection has been widely studied in the last years in the literature [12]. Most researchers agree that there is not a best general method. Thus, a good method has to be found out in each particular problem. The performance of the feature selection methods relies on the performance of the learning method used afterwards and it can vary notably [13]. Therefore, the majority of the interesting comparative studies are focused on the problem to be solved [14]. Feature selection methods can be divided into three categories: filter, wrapper and embedded methods [15]. Among them, filter methods are based on the suppression of the least significant features.
On the other hand, feature transformation methods are based on the transformation of the existing features into a lower dimensional space.

In this work, two different approaches have been applied: feature selection using filter methods and feature transformation. Those approaches rely on the general characteristics of training data and carry out the dimensionality reduction process as a pre-processing step with independence of the learning algorithm. Specifically, the following methods have been used in this work:

1. Feature selection using filter methods:
   - Regression p-values: The p-value for each term in a regression analysis tests the null hypothesis that the coefficient is equal to zero (no effect). A low p-value (< 0.05) indicates that you can reject the null hypothesis. Conversely, a larger (insignificant) p-value suggests that changes in the predictor are not associated with changes in the response.
   - ReliefF [16]: It works by randomly sampling an instance from the data and then locating its nearest neighbour from the same and opposite class. The values of the attributes of the nearest neighbours are compared to the sampled instance and used to update relevance scores for each attribute.

2. Feature transformation methods:
   - Principal Component Analysis (PCA): A well-known orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components [17]. The first principal component has the largest variance. The new vectors are an uncorrelated orthogonal basis set.
   - Non-negative matrix factorization (NMF): It is a dimension-reduction technique [18] based on a low-rank approximation of the feature space.

Besides providing a reduction in the number of features, NMF finds nonnegative matrices W and H, respectively, that minimize the norm of the difference X – WH. W and H are thus approximate nonnegative factors of X, and the k columns of W represent transformations of the variables in X.

ARTIFICIAL NEURAL NETWORKS

Multi-Layer Perceptron (MLPs) are considered here since they have proven their efficiency to describe the nonlinear relationships between a set of input and output values. For these reasons, MLP is the most widely used neural network architecture for regression problems where all the neurons are organized in a layered feedforward topology. Feedforward ANNs using backpropagation [19] are proved to be universal approximators [20]. However, there is no a general way to determine the best ANN to solve a problem. The aim is to achieve the best generalization capability (for a test set of samples) avoiding overfitting. In order to do that, an early stopping has been used together with a resampling procedure using a cross-validation scheme [21].

EXPERIMENTAL DESIGN

The objective of this study is to develop a model to estimate the hourly concentration value of NO2 at the EPSA Algeciras monitoring station (see Table 1), according to the values of the rest of stations and the meteorological variables measured in the area of study. Thus, a database of 37 variables was used to obtain this estimation (see Table 2).

The use of soft computing techniques in engineering applications has increased over the last years [22]. In this context, the choice of the evaluation

<table>
<thead>
<tr>
<th>Variable number</th>
<th>Meaning</th>
<th>Variable number</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EPSA Algeciras - NO2 (mg/m³)</td>
<td>20</td>
<td>W2 - Wind direction (degrees)</td>
</tr>
<tr>
<td>2</td>
<td>Campamento - NO2 (mg/m³)</td>
<td>21</td>
<td>W2 - Relative humidity (%)</td>
</tr>
<tr>
<td>3</td>
<td>Los Cortijos - NO2 (mg/m³)</td>
<td>22</td>
<td>W2 - Rainfall (l/m²)</td>
</tr>
<tr>
<td>4</td>
<td>Esc. Hostelera - NO2 (mg/m³)</td>
<td>23</td>
<td>W2 - Atmospheric pressure (hPa)</td>
</tr>
<tr>
<td>5</td>
<td>Col. Los Barrios - NO2 (mg/m³)</td>
<td>24</td>
<td>W2 - Solar radiation (w/m²)</td>
</tr>
<tr>
<td>6</td>
<td>Col. Carteya - NO2 (mg/m³)</td>
<td>25</td>
<td>W3 - Relative humidity (%)</td>
</tr>
<tr>
<td>7</td>
<td>El Rinconcillo - NO2 (mg/m³)</td>
<td>26</td>
<td>W3 - Rainfall (l/m²)</td>
</tr>
<tr>
<td>8</td>
<td>Palomones - NO2 (mg/m³)</td>
<td>27</td>
<td>W3 - Atmospheric pressure (hPa)</td>
</tr>
<tr>
<td>9</td>
<td>San Roque - NO2 (mg/m³)</td>
<td>28</td>
<td>W3 - Solar radiation (w/m²)</td>
</tr>
<tr>
<td>10</td>
<td>El Zabal - NO2 (mg/m³)</td>
<td>29</td>
<td>W4 - Wind direction (degrees)</td>
</tr>
<tr>
<td>11</td>
<td>Economato - NO2 (mg/m³)</td>
<td>30</td>
<td>W4 - Temperature (C)</td>
</tr>
<tr>
<td>12</td>
<td>Guadarranque - NO2 (mg/m³)</td>
<td>31</td>
<td>W4 - Wind speed (km/h)</td>
</tr>
<tr>
<td>13</td>
<td>La Línea - NO2 (mg/m³)</td>
<td>32</td>
<td>W5 - Wind direction (degrees)</td>
</tr>
<tr>
<td>14</td>
<td>Madrevieja - NO2 (mg/m³)</td>
<td>33</td>
<td>W5 - Relative humidity (%)</td>
</tr>
<tr>
<td>15</td>
<td>W1 - Wind direction (degrees)</td>
<td>34</td>
<td>W5 - Rainfall (l/m²)</td>
</tr>
<tr>
<td>16</td>
<td>W1 - Relative humidity (%)</td>
<td>35</td>
<td>W5 - Atmospheric pressure (hPa)</td>
</tr>
<tr>
<td>17</td>
<td>W1 - Rainfall (l/m²)</td>
<td>36</td>
<td>W5 - Solar radiation (w/m²)</td>
</tr>
<tr>
<td>18</td>
<td>W1 - Temperature (C)</td>
<td>37</td>
<td>W5 - Temperature (C)</td>
</tr>
<tr>
<td>19</td>
<td>W1 - Wind speed (km/h)</td>
<td>38</td>
<td>W5 - Wind speed (km/h)</td>
</tr>
</tbody>
</table>
The technique is critical. In order to evaluate the performance of the model, cross-validation was used to determine when overfitting starts during supervised training of a neural network. This technique improves the performance and robustness for prediction applications as it has been proven empirically in a large number of works [23].

The values of the weights and bias were adjusted according to the Levenberg-Marquardt optimization algorithm. The original data set was preprocessed (only complete records have been used) and all the models were defined using a different number of hidden neurons (nhiddens) and trained using the 2-fold cross-validation (2-CV) as validation technique. This validation procedure was repeated 20 times, taking the average value of all of them, so that the randomness of the process was guaranteed. In order to select the optimal structure of the model, four statistical performance indexes have been measured: the standard correlation coefficient (R), the index of agreement (d) [24], the mean square error (MSE) and the mean absolute error (MAE). This resampling procedure has been applied in the proposed two-stage approach.

In the first stage, the different feature selection methods were tested using ANNs as an induction method, and the best models were selected. The four feature selection methods were applied to the original data set. In the case of regression p-values method, variables (see Table 2) were sorted according to their ascending p-values. For ReliefF Algorithm, variables were sorted according to their descending weights. In the case of PCA, a new space was obtained and the components were ordered by the proportion of variance explained. Finally, different approximations were obtained for NMF, which were ordered by their ranks. After that, the best possible model was obtained for every of the aforementioned selection methods using ANNs with a stepwise [23] inspired procedure. The approach was the same in the case of regression p-values, ReliefF and PCA, but had slight differences in the case of NMF:

- **Regression p-values, ReliefF and PCA**: Starting with a dataset composed only of the very best variable (or first component in the case of PCA), ANNs models were developed and their performance indicators were obtained. Additionally, a t-test was performed in order to determine if the data distributions of MSE and R were the same as the corresponding to the previous step. If the distributions were not the same and the statistical indicators were better, this second variable was kept. Otherwise, it was discarded. In further steps, new variables (or components) were added to the dataset and the process continued until all the variables (or components) were added to the dataset and tested.

- **NMF**: In this case, the difference relied on the fact that there was not an addition of new variables or components in each step. In contrast, the next rank approximation in ascending order was used.

In the second stage, the four best models (one from each feature selection method) were combined in a fuse ANN approach. In this approach, after finding the best model for each method in stage 1, each model was trained to get an estimation of the entire original dataset. Next, these four estimations were used as inputs of the second stage ANN model, and the best possible model was found. Finally, this model was trained and a final stage-2 estimation of EPSA Algeciras dataset was obtained.

**RESULTS AND DISCUSSION**

The results of the experimental procedure are presented in this section. In the first stage, ANNs based on backpropagation with early stopping have been used and here we compare their results with different feature selection procedures in order to determine the best model to estimate the hourly concentration values of NO\textsubscript{2} atmospheric pollutant at EPSA Algeciras monitoring station.

Table 3 shows the results obtained in the first stage. The four feature selection methods produce different results. Therefore, different ANN models can be selected in each case (using a different number of hidden units). Based on the values of the performance indexes, the good performance of ANNs models with early stopping is demonstrated. Table 4 shows the data set used in each best model of the first stage per selection method.

**TABLE 3**

<table>
<thead>
<tr>
<th>Method</th>
<th>nhiddens</th>
<th>R</th>
<th>MSE</th>
<th>RMSE</th>
<th>D</th>
<th>MAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCA</td>
<td>10</td>
<td>0.823</td>
<td>172.222</td>
<td>13.122</td>
<td>0.900</td>
<td>9.194</td>
</tr>
<tr>
<td>NMF</td>
<td>7</td>
<td>0.819</td>
<td>175.918</td>
<td>13.260</td>
<td>0.896</td>
<td>9.371</td>
</tr>
<tr>
<td>P-values</td>
<td>11</td>
<td>0.834</td>
<td>162.639</td>
<td>12.751</td>
<td>0.904</td>
<td>8.809</td>
</tr>
<tr>
<td>RELIEF</td>
<td>8</td>
<td>0.832</td>
<td>164.093</td>
<td>12.808</td>
<td>0.903</td>
<td>8.942</td>
</tr>
</tbody>
</table>
TABLE 4
Data set used in each ANN model of Table 3.

<table>
<thead>
<tr>
<th>Method</th>
<th>Variables numbers / Components / Rank approximation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCA</td>
<td>1, 2, 3, 4, 5, 6, 7, 8, 9, 12, 14, 15, 35, 37 (components)</td>
</tr>
<tr>
<td>NMF</td>
<td>32 (rank approximation)</td>
</tr>
<tr>
<td>P-values</td>
<td>4, 5, 7, 10, 12, 13, 15, 18, 20, 23, 28, 29, 30, 31, 32, 37, 38 (variable numbers)</td>
</tr>
<tr>
<td>RELIEFF</td>
<td>3, 5, 6, 7, 8, 10, 12, 15, 16, 18, 19, 20, 21, 23, 28, 29, 30, 31, 32, 33, 36, 37, 38 (variable numbers)</td>
</tr>
</tbody>
</table>

Table 5 shows the results obtained in the second stage. Stage-2 fuses the results obtained by the ANNs selected in Stage-1 using the best selected ANN models (in Table 2). As we can see, the ANN model of Stage-2 outperforms the models of Stage-1 in all the quality indexes measured. Considering the results, the introduction of the proposed two-stage approach achieved better prediction performance and were shown to be superior to the simple first stage models (composed by a feature selection method + ANN). The proposed procedure guarantees a better prediction performance of the concentration values at the Algeciras monitoring station.

TABLE 5
Results Stage-2. Fusion of the selected models of Stage-1. Best ANN model.

<table>
<thead>
<tr>
<th>nhiddens</th>
<th>R</th>
<th>MSE</th>
<th>RMSE</th>
<th>D</th>
<th>MAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.866</td>
<td>133.450</td>
<td>11.551</td>
<td>0.925</td>
<td>7.916</td>
</tr>
</tbody>
</table>

The results of the estimation of the two-stage approach for EPSA Algeciras monitoring station, using one month of the period as an example, are plotted in Figure 2. A good fit of this approach is shown with a closer adjustment to the observed values. The gaps in the figure indicate missing values.

FIGURE 2
Comparison of the observed and estimated values with the best model of the second stage.

CONCLUSIONS

A data fusion approach based on ANNs has been presented in this work in order to estimate the hourly concentration values of NO\textsubscript{2} at Algeciras (EPSA) monitoring station. A set of models with different inputs (coming from different feature selection methods) and configurations (number of hidden units) have been tested using a resampling procedure in two stages.

The results from the two-stage approach outperform those obtained by the single models. The results obtained demonstrated the utility of this data fusion approach. The application of this approach can become an efficient supporting tool to different purposes such as imputation of missing data, automatic detection of recalibration or calculation of concentration values in unseen or unregistered points where no monitoring station is located.

ACKNOWLEDGEMENTS

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SESSION IV
CLIMATE CHANGE MITIGATION
DYNAMIC MONITORING OF LAND COVER CHANGE: A RECENT STUDY FOR ISTANBUL METROPOLITAN AREA

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ABSTRACT

Climate change, rapid urbanization and industrialization have so far resulted in substantial loss of agricultural land, forestry and green areas that are environmentally of utmost importance. This is noted considerably in many coastal regions and highly populated cities such as metropolis Istanbul in Turkey. In that sense, there is an urgent need for evaluating the magnitude, pattern, and type of land cover/use (LCLU) changes for projecting future land development in the most sustainable manner in this highly crowded city. Remote sensing (RS), in conjunction with Geographic Information Systems (GIS), has been widely applied and recognized as powerful and effective tools of modern technology in detecting LCLU. Five satellite imageries acquired in 1975, 1987, 1997, 2007 and 2014 were classified and corresponding LCLU thematic maps were achieved. The change detection results revealed great loss in the green areas such as forests, and in turn, huge increase in urbanized and industrialized areas. Sharp increases were detected for land cover classes of urban fabric, industrial and commercial units, and for open spaces covered with slight or no vegetation, in ratios of 227%, 410% and 402%, respectively over time. Hence, such quantitative LCLU results of this strategically important region of the world are sufficiently robust to alert urban and regional planners to the urgent need of developing efficient management practices intended to prevent uncontrolled utilization and preservation of natural resources.

KEYWORDS:

INTRODUCTION

Rapid industrialization and urban growth directly cause significant decrease in agricultural lands, forest areas and green lands. Such loss has negative impacts on the well-being of the environment and the climate [1]. Lack of appropriate land cover/use (LCLU) planning and insufficient measures for sustainable development, diffuse urban growth, and massive disappearance of agricultural land, forests and green areas, introduce severe environmental consequences [2, 3]. Especially, metropolitan cities are highly exposed to LCLU changes [4]. Therefore, there is an urgent need for evaluating the magnitude, pattern and type of LCLU changes for projecting future land development [5].

Remote Sensing (RS) and Geographical Information Systems (GIS) have been widely used for monitoring the dynamic changes of the earth’s LCLU for decades [6, 7]. RS provides cost-effective, multi-spectral and multi-temporal data which can be converted into valuable information for understanding and monitoring land development patterns and processes, and for building LCLU information [8]. Additionally, GIS provides a flexible environment for storing, analyzing, and displaying spatial information necessary for change detection and database development. Moreover, stochastic modelling provides tools to predict the future changes and simulate their effects [9, 10].

Several algorithms have been developed to extract the thematic information from remotely sensed data. Classification is one of the basic and efficient techniques to produce LCLU information from satellite images. Classification algorithms mainly consist of mathematical models that evaluate the reflectance values of image pixels and assign them to possible LCLU classes [11, 12]. With the recent developments in satellite technology that introduced high-resolution images, former classification algorithms evolved to different ones, including object-based classification method [13]. However, when the long-term change analyses are of concern, there is always a need for mid/low spatial resolution archive imagery to derive LCLU information. Classification analysis of mid/low spatial resolution data mostly brings out some defects due to pixel heterogeneity and reflectance variations that result in misclassification of land objects or irregularities in object shape [14]. At this point, post classification analysis is generally used to increase the thematic and contextual accuracy of the classification results [15].
In this study, the main aims are 1) to determine the LCLU change in a selected part of Istanbul, which changed significantly in the previous years, and 2) to implement a reliable, robust GIS-RS framework to generate high accuracy thematic maps for each time frame. To fulfill these objectives, the LCLU changes at a pre-defined area of approximately 770 km$^2$ located at the European side of Istanbul Metropolis were determined using RS and GIS. The selected area has changed significantly over the past 40 years. Initially, five satellite image-ries acquired in 1975, 1987, 1997, 2007 and 2014 were rectified and classified to extract LCLU thematic maps. In order to cluster land cover classes, the international standard coordination of information on the Environment (CORINE) of year 2012 was utilized. It is a comprehensive quantitative LCLU data frame, providing consistent information on LCLU across Europe [23, 24, 25]. The 3rd level CORINE standards were implemented to acquire the relevant classes of the study area like urban fabric, industrial, commercial and transport units, dump sites and construction sites, forests, open spaces with slight or no vegetation cover, and marine environment [25]. Secondly, manual post classification enhancements were performed to improve the thematic accuracy of the class related polygons. Finally, areal statistics regarding each class were calculated for all the inspected dates in order to present the temporal changes regarding LCLU classes.

DATA AND METHODS

Study Area. Istanbul is one of the most crowded metropolitan cities of the world with approximately 15.03 million capita as of December 2017, according to the recent records of Turkish Statistical Institute (TUIK). The population was 14.38 million in 2014. The city’s importance lies in the fact that it bears significant economical, historical and socio-cultural aspects of the country. The city has been experiencing a tremendous migration in the past two decades due to developments in the industrial sector and to business opportunities. The city bridges the two continents, Europe and Asia; thus, commerce, labour and tourism oriented transportation rate is higher than any city in the country. While the northern part of the city is mostly covered with forests, southern part hosts new industrial and domestic residential areas especially established after the construction of the international highway that connects to Trans-European Motorway (TEM) network. This study basically focuses on the southern part of the European side of the city as illustrated in Figure 1.

Data Used and Pre-Processing. For this study, five multi-sensory satellite images belonging to 1975, 1987, 1997, 2007 and 2014 were used for determining the LCLU changes. Images from Landsat 2, Spot 1, Spot 2, Spot 4 and Spot 6 satellites respectively were geometrically corrected to ensure the location accuracy and reliable mosaicking of image set belonging to the same acquisition year. The geometric correction was performed with the use of ground control point (GCP) derived from historic ortho-photos and other vector databases according to 1st order polynomial model. The properties of the optical multispectral satellite images and their corresponding geometric correction information including the GCP number and root mean square error (RMSE) are provided in Table 1. The table mainly reveals acceptable RMSE values for all the satellite images, indicating that they are adequate and reliable to be further used in the next steps.

FIGURE 1
Geographical location of study area (Google Earth© 2017)
TABLE 1

<table>
<thead>
<tr>
<th>Satellite</th>
<th>Date</th>
<th>Spatial Resolution (m)</th>
<th>Ground Control Point (GCP)</th>
<th>RMSE (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Landsat 2</td>
<td>1975</td>
<td>60</td>
<td>12</td>
<td>8.0</td>
</tr>
<tr>
<td>Spot 1</td>
<td>1987</td>
<td>20</td>
<td>50</td>
<td>4.0</td>
</tr>
<tr>
<td>Spot 2</td>
<td>1997</td>
<td>20</td>
<td>55</td>
<td>4.0</td>
</tr>
<tr>
<td>Spot 4</td>
<td>2007</td>
<td>20</td>
<td>50</td>
<td>6.0</td>
</tr>
<tr>
<td>Spot 6</td>
<td>2014</td>
<td>1.5</td>
<td>50</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Following the geometric correction process, the image dataset for a specific year were mosaicked using weighted cutline and colour balancing on the overlap areas except for 1975-dated Landsat 2 image that covered the entire study area. In the last step of pre-processing, images were clipped according to the boundaries of the selected study area.

Classification and Post-Processing. Supervised classification is the method that can be applied when there is available ground truth information on the surface characteristics. Minimum distance, maximum likelihood, spectral angle mapper and support vector machine are among the popular algorithms that were used in the previous studies [16, 17, 24]. In this study, pixel based maximum likelihood algorithm, that is robust and already applied in several previous studies, was used. This preferred method assigns each pixel to a class that shows the maximum similarity according to probability calculation. Peer probability curve is defined for each class. The method evaluates the pixels not only according to their brightness value, but also to variance–covariance matrix value that shows their distribution in feature space. Previous studies reported that different algorithms provided similar accuracies for the classification of mid- or low spatial resolution (10m or lower) images [18, 19]. The spatial resolution of the satellite images used in this study failed in the mid/low range; thus, no experimental studies were performed to evaluate the efficiency of other algorithms.

The classification results presented that the method failed to create homogenous land cover patches in some regions especially when the majority of the area was covered by urban (impervious) surfaces. Manual polygon-based editing was applied to classification results to obtain homogenous land cover patches. CORINE methodology and criteria were taken into account in this process. While the original CORINE methodology is completely a manual process, the 2 step process (classification–manual editing) defined in this study could be accepted as a semi-automated systematic.

Accuracy Assessment. The accuracy of the classification process was evaluated using 200 stratified random points that were distributed according to class coverage and importance. Class labels of these points were compared by their ground truth values derived from closer dated ortho-photos and the original images to form the error matrix [20]. Moreover, producers and users accuracy and kappa statistics were calculated from the error matrix [21]. Table 2 presents the results of the accuracy assessment indicating that all images were classified with an acceptable accuracy of over 85%.

RESULTS AND DISCUSSION

When the classification results are examined, most of the CORINE LCLU classes available in the study area could be identified up to the 3rd level with 20m or higher resolution satellite images. Classes of “Forests” and “Open Spaces with Limited or No Vegetation” were determined at the 2nd level, as higher level sub-class identification requires multi-seasonal analysis within a single year. On the other hand, the spatial resolution of the Landsat 2 MSS satellite images was insufficient to determine the classes with small- sized objects such as roads, water courses, and mineral extraction sites. Resulting classified images are illustrated in Figure 2.

After performing the classification and the post-processing stages, results were evaluated in GIS environment to calculate the areal statistics. The resulting areal distribution of the LCLU classes is presented in Table 3. When the findings displayed in Figure 2 and Table 3 are examined, it can obviously be asserted that domestic and industrial urban lands increased over years dramatically and continuously. Rises occurred mostly on continuous urban fabric, and industrial and commercial units’ classes.

Effects of urbanization can be addressed with the major decrease of forests. Forest lands especially reduced by more than half between years 1975 and 1987. The land cover pattern showed a systematic conversion of destructed forest lands to non-irrigated arable lands between 1975-1987, and similar transformation of non-irrigated arable land to open spaces with limited or no vegetation was realized. An additional forest destruction occurred between 1987 and 1997.
FIGURE 2
Post-processed classification results of satellite images

<table>
<thead>
<tr>
<th>Year</th>
<th>Classification Accuracy (%)</th>
<th>Kappa Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1975</td>
<td>87.00</td>
<td>0.855</td>
</tr>
<tr>
<td>1987</td>
<td>95.91</td>
<td>0.951</td>
</tr>
<tr>
<td>1997</td>
<td>93.75</td>
<td>0.928</td>
</tr>
<tr>
<td>2007</td>
<td>94.00</td>
<td>0.931</td>
</tr>
<tr>
<td>2014</td>
<td>97.00</td>
<td>0.966</td>
</tr>
</tbody>
</table>

This fact holds true for the later years in which a continuous linear increment in the urban land was recognized. Moreover, industrial and commercial units increased enormously by a ratio of 410% between 1987 and 2014.

Within Table 3, the percent change of each class is expressed in comparison with the previous inspection period. Continuous and discontinuous urban fabric classes as well as the industrial and commercial units performed a significant increase within the observed period. The opposite trend was observed for the green areas as expected. This tendency was detected in several other studies that previously examined and focused on Istanbul Metropolitan area [22]. Green areas were transformed to non-irrigated arable lands, and in turn, barren lands were further converted to urban and industrial areas. However, this study revealed an exceptional trend; rise in ratios was realized after the transformation instead of gradual increase. This situation can be rationalized via the metrobus line that has been constructed and put into operation after year 2007.

CONCLUSIONS

This study demonstrated the dynamic monitoring of rapid urbanization and its effects on other land cover types in a selected region in Istanbul Metropolitan area. Results showed that areal metrics and transformation pattern of changes in the LCLU types could be determined effectively by use of satellite images over time. Supervised classification and manual post-processing of the images provided reliable results with accuracy over 85%. Istanbul has faced a high rate of urbanization through 1975 and 2014. This situation has negatively affected the forest lands that presented a dramatic decrease within the examined years. The temporal analysis provided an opportunity to discover the LCLU changes in a
TABLE 3
Statistics of CORINE LCLU derived by image classification

<table>
<thead>
<tr>
<th>Class*</th>
<th>Area (km²)</th>
<th>1975</th>
<th>1987</th>
<th>1997</th>
<th>2007</th>
<th>2014</th>
<th>% change</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1.1. Continuous Urban Fabric</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% change</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1.2. Discontinuous Urban Fabric</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>% change</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2.1. Industrial and Commercial Units</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% change</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2.2. Roads &amp; Railway Networks and Assoc. Areas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% change</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>1.2.4. Airports</td>
<td></td>
<td></td>
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<tr>
<td>% change</td>
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</tr>
<tr>
<td>1.3.1. Mineral Extraction Sites</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>% change</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.3.3. Construction Sites</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% change</td>
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<td></td>
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</tr>
<tr>
<td>2.1.1. Non-irrigated Arable Lands</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>% change</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1. Forests</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>% change</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3. Open Spaces with Slight or No Vegetation</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
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<tr>
<td>% change</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

stagedwise manner summarized as; initially the conversion occurred from forest to arable lands and open spaces, then from arable lands and open spaces to urban fabric and industrial/commercial units. Outputs derived from the study can be used as a reliable geospatial data for environmental researches and several management activities such as city planning or transportation network design.

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ANALYZING GRIDDING SYSTEMS FOR LAND COVER/LAND USE INFORMATION:
A STUDY CONDUCTED FOR GREEN AREAS

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ABSTRACT

Performing point-based land cover/use analysis traditionally compels converting thematic clusters into representative points located at their corresponding centroids. Yet, various spatial analyses require to grid thematic maps into smaller regular geometric grids such as square and triangle, where the attribute of the dominant land cover/use class is assigned as the grid value. Hence, the class is represented geometrically via the selected gridding system and the accuracy of the later intended spatial analysis is altered. Moreover, the grid size that provide acceptable errors within determined thresholds for each grid is also utmost importance, since it is necessary to represent the original land cover/use thematic, to reduce the complexity and computing time of the analysis. Both of these problems remained unsolved especially for the green classes such as vegetation, forest etc. This study proposes a methodology to identify the best suitable gridding system for green areas, where the relationship of scale for each gridding system is analyzed. The study grids a reference land cover/use map, where both square and triangle systems at 23 different scales are tested. The relative errors of each gridding system at each scale are found via comparing the areal results of each grid with the reference map. According to the achieved results, the triangle gridding system is identified as more accurate in providing areal representation. Furthermore, the developed model demonstrates the associated errors of each scale for both gridding systems. Thus, the developed model could be utilized to choose appropriate grid cell size according to the application.

KEYWORDS:
Land cover, land use, gridding, square, triangle

INTRODUCTION

Land cover/use information is vital, due to its interactions with climate, ecosystem processes, biodiversity, and even human activities, [1, 2, 3, 4]. Add to that, land cover/use change is a way to analyze future scenarios by modeling different future pathways [5]. Within cities, areas of the green areas, e.g. “arable lands”, “green urban areas” and “open space with little or no vegetation”, are dynamically changing requiring a continuous updated geo-database for modeling and analysis. Quantification of their exact change has always been a challenge, especially for scale dependent analysis [6, 7]. The problems with such applications emerge when big bulks of data are analyzed with various scales representing the land cover/use change. In order to increase computational performance and integrate spatial databases with various model resolutions such land cover/use classes are generalized. This approach results reduced resolution of the original thematic cluster areas. Hence, such procedure should be controlled and optimized to maintain the attributes of the original reference thematic map while guaranteeing minimum information lost.

In several GIS-based applications, the change in land use is analyzed and quantified via converting the raster land cover/use thematic maps to vector-based maps using different resolutions with different gridding systems such as square and triangle. The used resolution is usually determined by the aim and/or scale of the applied study [8, 9, 10, 11, 12, 13]. Each of these gridding systems has its own advantages when used to grid the reference land use thematic map. For instance, squares are advantageous due to their simplicity of definition, ease of resampling to different scales and providing easy relationship between cells. Moreover, it provides more contrasts between orthogonal and diagonal nearest neighbor interactions. Because of such reasons, square gridding systems are the most ubiquitous type of gridding systems in spatial analysis. However, inconsistencies of square grids are likely to undermine certain analysis that takes into account connectivity of edges. On the other hand, triangles have three edges and nine immediate neighbors. Mainly, they have advantages of; not having a uniform orientation, where some triangles could be pointed up while others could be pointed down. Moreover, the triangle grids can be very useful to follow orientations of non-uniform borders to maximize its efficiency [8, 13, 14, 15]. Due to such advantages in both gridding systems, the selection of best suitable gridding
system is a challenge. For that, the performance of each gridding system should be tested for the green areas classes of land cover/use and their relation to scale should be analyzed as well.

This research examines the square and triangle gridding systems for the green areas classes in the third level of CORINE standards, e.g. “arable lands”, “green urban” and “open space with little or no vegetation” classes, where the CORINE is the international standard for CoorDination of INformation on the Environment (CORINE) sites in Europe [16]. The expected best suitable gridding system is the one that provides minimum area errors via utilizing appropriate scale. The selected system should ensure minimum data complexity, storage and maximum analyze performance.

The methodology followed within this research is to extract a reference land cover/use map and to generate two gridding systems, namely square and triangle grids, using 23 various cell sizes. The resulted gridded maps are stored in a separate geodatabase for each scale. The relative areal differences in each scale are compared with the reference land cover/use map. Later, linear regression models representing the relation between area errors and scale for each grid are presented and discussed. The models are recommended to figure out the projected areal errors for each scale of the same green area class.

**METHODS**

Constructing an accurate model for area errors requires firstly extracting a highly accurate reference land cover/use thematic map. For that, a high-resolution Spot 6 satellite image with a spatial resolution of 1.5 meters is used. The image was acquired in 2014 and belongs to a part of Istanbul, Turkey as illustrated inside the red box in Figure (1).

![FIGURE 1](Image)

**FIGURE 1**
The selected study area, part of Istanbul- Turkey

The original land use thematic map is achieved using supervised classification of the satellite images of the study area. The resulting classified image is manually edited using corresponding orthophotos of the selected area to enhance its accuracy, resulting in an overall classification accuracy of 96%. The achieved accuracy is within the standards and high enough to be used as a reference map for the later comparison and analysis (Figure 2). The classification of satellite images has been carried out in accordance with the European Union established standard, CORINE. This standard land cover classification system has a hierarchical structure consisting of three levels under five main groups. These groups are artificial areas, agricultural areas, forests and natural areas, wetlands and water structures [16]. The group that needs to be classified in detail within the scope of the research are identified and used for later steps while the other classes are ignored.

Among the related classes, within the third level of the standards, “green urban areas”, “arable lands” and “open space with little or no vegetation” are selected. These classes are dispersed all around the study area as illustrated in Figure 2, where, the areal statistics of each class are represented in Table 1.

**TABLE 1**
Areal statistics of the relative classes of the reference thematic map.

<table>
<thead>
<tr>
<th>CORINE 3rd Level Class Type</th>
<th>Area (km²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green urban areas</td>
<td>1266.4</td>
</tr>
<tr>
<td>Arable lands</td>
<td>896.25</td>
</tr>
<tr>
<td>Open space with little or no vegetation</td>
<td>18027.42</td>
</tr>
</tbody>
</table>

![FIGURE 2](Image)

**FIGURE 2**
Extracted land use thematic map for the study area after the classification process

The raster land cover/use thematic map is converted into fishnets using the two different gridding systems (regular triangle and square) for 23 identified scales, each of which has a different cell size i.e. starting from a polygon resolution of 30*30 m², 40*40 m² till 250*250 m², resulting in a 46 different vector maps stored in different geo-databases. Such number of classes should be enough to help construct
a meaningful linear model of the results. The land use attribute for each cell is identified by the attribute of the dominant area in each cell. Each gridding system result some significant difference in assigning such attribute to its cells (Figure 3). As illustrated in the Figure 3, the same area is gridded using both systems. However, due to varying gridding systems, land cover/use classes have different areas and patterns. For example, at the lower right square of the original figure two areas of “green urban areas” and “open space with little or no vegetation” are shown. These two polygons were represented differently in both systems. The triangle system represented both of them with separated cells, while the square system kept only the cell of the green urban area. Similar results are achieved for all scales. Only one scale is illustrated in Figure 4, where the figure represents the resulted gridded maps at the scale of 100*100 m².

Later on, the results of the identified land cover/use classes from the previous step are compared for each gridding system at each scale and compared with the reference land use map as illustrated in Figure (2).
The achieved results are statically quantified by calculating the relative errors between each gridding system and the original information at each scale. According to the results, the relative errors of the triangle system are less in total and less in number in comparison to the square gridding system (Table 2). The relative errors for the triangle system are significantly less for the scales between 14 of 23 while the sum of relative errors for the triangle system is 0.228 in comparison to 0.331 of the square system (Table 2). After calculating the squared residuals in each scale, the same findings are also observed for the Root Mean Square Error (RMSE) for each system. The total RMSE for the triangle is found to be 271.44, while it is 387.32 for the square system. This also favors the triangle system compared to the square system. The errors for each system are modeled linearly as seen in the graph in Figure 5. The scales are illustrated in the x-axis and the relative area error in the y-axis.

DISCUSSIONS AND CONCLUSIONS

According to the Table 2, the triangle gridding system performed better compared to the square gridding system. The RMSE also boosted the relative errors in favoring the triangle system over the square system for gridding the green areas. The relative errors are projected in a linear relationship in Figure 5. The coefficient of determination ($R^2$) is a measure that its value shows the percentage of data linearly represented by the used model. The linear relationships show that value of the $R^2$ is higher for the square system than for triangle system, i.e. 0.627 and 0.430 respectively (Figure 5). Consequently, the square system provides more accurate mathematical data fitting model, where about 63% of the data is linearly presented via using the provided linear equation for square. However, the triangle grids provide less relative errors in applied scales, especially all of the scales after the 6th scale (Figure 5). The difference in their relative errors expands as scale gets smaller. Furthermore, the model points out that a relative error of 2% in the area is reached by the 15th scale (170*170 m) for the square grid system while the same error is reached by the 23rd scale (230*230 m) using the triangle grid system.

This results in reducing the number of points resulting from converting grids to points for the triangle grid while maintaining an area error of 2%.

The reason for that could be associated to the geometric properties of the modeled land cover/use classes and the ability of triangles with respect to capture the original shapes better. To illustrate this visually, the Figure (2) should be examined in detail. Most of the green area classes have irregular shapes that raise problems for the square grid having orthogonal boundaries. Actually, the square system is preferred for representing shapes of orthogonal similar

<table>
<thead>
<tr>
<th>Scale</th>
<th>Square Relative Error</th>
<th>Triangle Relative Error</th>
<th>(Square) – (Triangle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0020</td>
<td>0.0007</td>
<td>0.0013</td>
</tr>
<tr>
<td>2</td>
<td>0.0025</td>
<td>0.0002</td>
<td>0.0023</td>
</tr>
<tr>
<td>3</td>
<td>0.0047</td>
<td>0.0029</td>
<td>0.0018</td>
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<td>4</td>
<td>0.0047</td>
<td>0.0018</td>
<td>0.0030</td>
</tr>
<tr>
<td>5</td>
<td>0.0004</td>
<td>0.0017</td>
<td>-0.0013</td>
</tr>
<tr>
<td>6</td>
<td>0.0013</td>
<td>0.0096</td>
<td>-0.0082</td>
</tr>
<tr>
<td>7</td>
<td>0.0039</td>
<td>0.0015</td>
<td>0.0023</td>
</tr>
<tr>
<td>8</td>
<td>0.0019</td>
<td>0.0063</td>
<td>-0.0044</td>
</tr>
<tr>
<td>9</td>
<td>0.0134</td>
<td>0.0053</td>
<td>0.0081</td>
</tr>
<tr>
<td>10</td>
<td>0.0105</td>
<td>0.0044</td>
<td>0.0061</td>
</tr>
<tr>
<td>11</td>
<td>0.0001</td>
<td>0.0129</td>
<td>-0.0128</td>
</tr>
<tr>
<td>12</td>
<td>0.0260</td>
<td>0.0019</td>
<td>0.0241</td>
</tr>
<tr>
<td>13</td>
<td>0.0157</td>
<td>0.0053</td>
<td>0.0104</td>
</tr>
<tr>
<td>14</td>
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<td>0.0053</td>
<td>0.0104</td>
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<td>18</td>
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<td>0.0261</td>
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</tr>
<tr>
<td>19</td>
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<td>0.0253</td>
<td>-0.0020</td>
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<td>20</td>
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<td>0.0343</td>
</tr>
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<td>23</td>
<td>0.0478</td>
<td>0.0121</td>
<td>0.0357</td>
</tr>
</tbody>
</table>

**FIGURE 5**

A graph showing the area errors linear relationship for both grid
boundaries. Consequently, irregularity of shapes privileges the triangle grid, making its pointy edges more useful to capture original attributes of boundaries. By that, using triangle gridding for green areas results in minimizing data complexity, storage and area errors and increase the speed of related land cover/use analysis. The developed model is also useful to determine the relative area error at each scale. According to specific application, users could choose the appropriate scale according to allowed corresponding errors in their spatial analysis. Thus, this is very helpful to generalize a fixed error tolerance for all results in the spatial analyzes.

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SPATIO- TEMPORAL DETECTION OF ACCESSIBILITY CHANGE ON HEALTH CARE: A CASE STUDY FOR ISTANBUL

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ABSTRACT

Reaching health centers and hospitals in shorter traveling time is definitive for citizens. To assure that, cities heavily invest in enlargement and development of transportation infrastructure especially by constructing new links. The performance of such investments could be measured via spatial accessibility indices that quantifies the ease of reaching destinations. The most prominent accessibility indices are potential and daily accessibility that take into account development of urban networks and changes in land cover/use.

This paper proposes a method for evaluating the accessibility status of the existing hospitals of a selected study area in Istanbul using an integrated Geographical Information System (GIS) and remote sensing framework during the period of 2007-2014. Urban areas as origins and hospitals as destinations were spatially identified, projected on a map and later overlaid with the corresponding street network to perform an O-D matrix to calculate the accessibility indices. The results demonstrated changes in urban spatial distribution and urban road network for the selected area. The infrastructure investments have affected positively both accessibility indices with increase of 47.52% and 38.4% respectively. These changes also positively reflected on public services by decreasing the travel distance to the hospitals in the study area.

KEYWORDS:
Accessibility, Land cover/use, urban road network, index, potential accessibility, daily accessibility

INTRODUCTION

Cities are competing to establish hospitals and health care centers for citizens, primarily through implementing managed care financing, developing health care delivery strategies and increasing easy reachability for such services. In so doing, policymakers confront a central issue of how to ensure adequate access to hospitals/health care while controlling costs and equilibrium within districts. The major factors in controlling adequate access to such places are their locations in the city and the city’s road network, which assures easier reachability for citizens. Consequently, policymakers invest enormous resources in establishing accessible hospitals by developing their surrounding urban road network. To guarantee such investments are put in the right place, policymakers should evaluate their earlier decisions by quantitatively measuring the improvements on their set aims [1, 2]. Accessibility is a measure that combines both factors, locations of hospitals according to the urban road network and the road network itself, to analyze and quantify the progress in reachability of such origins-destinations analysis.

Relevant data and visualization aid policy makers and stakeholders to understand current travel demand, system performance and criticality. It also help city planners and engineers communicate with the related authorities in a clear yet substantive manner. However, all relevant data are useless if they are not crunched together to obtain easily understood measures which are used to evaluate current status of the relevant system. Accessibility is a clear understood measure to policymakers that helps them in understanding the interchange of land use, transportation mode and travel costs in urban areas. Accessibility, simply, refers to the possibilities of traveling to destination opportunities and the level of service associated with a wide range of travel options [3, 4]. Increasing travel options or improving their quality and performance spatially and/or temporally increase accessibility. Several potential uses for the accessibility measure can be obtained. First, it succinctly captures the quality of the existing state of the transportation system at many spatial levels. This allows for the identification of areas with relatively low accessibility which provides a basis for developing the transportation and land use proposals [5, 6]. Second, it delivers an estimation of the impacts due to proposed changes in the transportation system. Because of the multi-purpose character of this measure, it could assess changes to both road building and transit improvements. Third, it tracks and monitors changes in accessibility due to shifts in the distribution of land uses and can aid evaluation of the impact of alternative land use policies, such as the promotion of infill. Fourth, dimension-specific accessibility indices provide information for policy makers to
more effectively target investments for specific dimensions. Finally, it provides tools and important insights about the current levels of transportation performance and the impact of transportation improvements. This is useful especially in addressing issues poorly served by the domain of travel demand models, particularly with respect to use of non-motorized modes and public transportation [3, 4, 7, 8].

Istanbul is considered the biggest, most crowded city in Turkey. The urban fabric of the city changes continuously due to emerging of new industrial activities and the growth in population. Istanbul Metropolitan Municipality strive to keep up with such enormous increase in population by connecting all new urban settlements. The city also strives to provide its citizens with well-connected facilities such hospitals. However, a measure should respond to different changes occurring in the city to reflect the available quality of service. Because accessibility reveals the relationship between the transportation system and land use patterns, the index to measure accessibility should respond to changes in either, or both, of these elements. Accessibility indices exist in several categories each of which highlights different aspects of the network [3, 4, 7, 8, 9, 10, 11, 12]. Among these, relevant indices to this study, are the potential accessibility and daily accessibility indices. The potential accessibility index estimates the accessibility of opportunities in a zone to all other zones in which smaller and/or more distant opportunities provide diminishing influences. On the other hand, the daily accessibility is based on the notion of a fixed budget for travel in which a destination has to be reached to be of interest [12, 13, 14, 15]. Both of these indices are significant to illustrate the primary change of accessibility status due to network growth and land use change.

Hence the aim of the study is to quantitively calculate the change in accessibility of health centers due to urban transportation investments-mainly enlargement of the urban road network- using GIS environment. Within the context of this study, both indices, potential and daily accessibility, are used to estimate the accessibility change for hospitals and healthcare centers in a confined area in Istanbul within two different periods. The change of accessibility is obtained by comparing its status in both years 2007 and 2014. Origins are identified using GPS data while destinations are identified using classified multispectral imageries for the corresponding dates. Origins and destinations are converted to points representing their areas and overlaid with the street network to calculate the indices using an OD matrix. The paper explains the followed methodology in the next section in more details. The results of the calculated accessibility indices are provided in the third section. Finally, a discussion of the results and their effects on the hospitals are provided in the last section.

THE METHODOLOGY

Istanbul is considered to be the most economically important city in Turkey. Moreover, it is the most congested and crowded city in Turkey and probably within the region. The growth in population and economic activities led to big changes in the land cover/use of the city.[12, 16,17] To keep up with that, policymakers have been investing in urban infrastructure by building new hospitals and health centers and developing the city’s transportation system. Deciding the efficiency of these investments implies taking all these changes into account as a whole in one indicator/s e.g. potential and daily accessibility.

Accessibility to destinations as opposed to accessibility from origins is widely discussed as a measure of the transportation system from the perspective of users of that system [18]. The concept itself is variously explained depending on the aims and discipline of the implemented study [7]. Hence, the implemented indices, namely potential and daily accessibility, are introduced.

The value of potential accessibility indicator is calculated using two functions, the number and the cost of reaching destinations from origins and the attraction of destinations as shown in equation (1).

\[ A_p = \sum \frac{1}{c_{ij}} \]

where \( c_{ij} \) indicates travel time/cost between origin zone \( i \) and destination zone \( j \) in this study it is selected to be network distance solely. This measures the accessibility of a given volume of activity to a particular region and can be interpreted as the volume of activity to which a region has access, after the cost/time of covering the distance to that activity has been accounted for [19].

The daily accessibility indicator is similar to the potential accessibility indicator. Within this study, this measure is implemented to calculate accessibility of walkers to their destinations. According to Iacono [20], people are ready to walk to similar destinations up to a maximum distance of 3 km. The daily accessibility indicator is shown in equation (2).

\[ A_d = \sum \frac{\delta_{ij}}{(c_{ij})^\beta} \]

\( \beta \) is the distance decay parameter, while \( \delta_{ij} \) is a binary variable of daily accessibility, which equals 1 if \( c_{ij} \leq c_{max} \) and 0 if other. Finally, \( c_{max} \) is the daily accessibility threshold limiting the neighboring area. During the empirical measure of accessibility, critical parameters of the equations were determined using a heuristic approach and the distance decay parameter was set equal to 1, and the daily accessibility threshold was equal to 3 km as stated previously.
In order to test the indices, this study is implemented in a selected part of Istanbul, namely in the Büyükçekmece district. To extract the origin-destination matrix, land cover/use thematic maps for two dates are extracted. Two satellite images going back to 2007 and 2014 are acquired, rectified and classified up to the third level of CORINE standards, where it is an international standard for COoRdination of INformation on the Environment (CORINE) sites in Europe. The land cover/use classes of continuous and discontinuous urban fabric are gridded using a fishnet of 100*100 m² and converted to points in their centroids to be identified as the origins of the study in the accessibility calculations [13]. On the other hand, location data for hospitals and health care centers are acquired via GPS based measurements obtained from Here Maps® which are used to identify the destination points.

Urban road networks for both years are acquired as well, tested and modified, by checking the topological conditions. Well topologically checked street networks are significant to extract shortest path between origins and destinations later in the calculations. Origins, destinations and street networks are overlaid for corresponding years. Finally, origin-destination matrices for both dates are implemented and used to calculate potential accessibility and daily accessibility at each date as presented in Table (1).

### RESULTS AND DISCUSSION

The potential and daily accessibility results for both selected years are illustrated in Table (1), where the results are grouped to two sets being; using a distance constraint, which is set to be 3 kilometers, and without any distance constraint. In the study area, from 2007 to 2014, the number of origins increased for both conditions roughly 39.58% and 34.04% respectively. This is directly referenced to the land cover/use change within the study area, where land cover/use classes such as green areas and barren land were transformed to urban class. These are considered as new origins in year 2014. This transformation has positively influenced the accessibility results for the study area via increasing the number of citizens benefiting from neighboring hospitals.

Accordingly, the distances from origins to hospitals that contributed to the accessibility calculation increased as well, being 64.36% and 28.17% for both conditions respectively. The development and enlargement of the urban street network neighboring the hospitals have contributed to this result positively as well. However, the huge increase in the first condition is referenced to more alternatives during the walking mode.

The cumulative and interacting effect of both changes -land cover/use and urban road network- reveals the huge increase in their values, being 47.52% and 38.4% for daily and potential accessibility indices respectively. This huge growth was influenced by both factors, i.e. growth in origins and increased number of alternatives to reach hospitals. The walking mode benefited the most from the urban change within the area. This is referenced to construction of more short/local edges than collectors or arterials in the network. Policymakers were successful in constructing more routes and alternatives to walkers in order to reach hospitals more easily.

As the main result, traveling time and distances to reach hospitals reduced due to the emergence of new alternative roads/routes in the urban road network for the year 2014. A visual comparison between both urban networks of the same origin to reach both hospitals is illustrated in Figure (1), where the light-colored roads represent the newly emerged roads. Starting from the same origin, reaching the near two hospitals were illustrated in two different routes for both years. The traveling distance to reach hospital no.1 dropped from 2.69 to 2.47 km (9% decrease) and from 4.03 to 3.82 km (6% decrease) to reach the hospital numbered as 2 (Figure 1). The study calculated the travel time to reach hospitals assuming that the speed for all edges in the network is the same. Although, this assumption provides a preliminary indicator for the performance of the transportation investments within the study area, integrating average speeds on the network for day/night time could reveal more information on such policy decisions. Hence, the use of traffic speed information could enhance the achieved results. Furthermore, integrating other significant data in both indices helps in weighting destination based on their importance. Such step is recommended to follow in future works as well.

### TABLE 1

Results of number of origins, total destination between all origins and hospitals using all potential routes within constraints and accessibility indices

<table>
<thead>
<tr>
<th>Year</th>
<th>Using distance constraint (3 kilometers)</th>
<th>Without using any distance constraint</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of origins</td>
<td>1036</td>
<td>1446</td>
</tr>
<tr>
<td>Total distance (1000 km)</td>
<td>3488.85</td>
<td>5734.20</td>
</tr>
<tr>
<td>Index value</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daily accessibility</td>
<td>1.41</td>
<td>2.08</td>
</tr>
<tr>
<td>Potential accessibility</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CONCLUSION

Important accessibility factors such as land cover/use components and urban road network have changed significantly for Istanbul in the period of 2007-2014. The number of origins surrounding hospitals increased significantly, which illustrates the growth of urbanization and land cover/use change of the study area. Similarly, the development of urban road networks increased alternatives for urban road network users, thus increased the total distance covered from origins to the hospitals. However, short edges/local roads appeared more than collectors or arterials which benefited walkers more than other urban road network users. All these factors influenced the daily and potential accessibility indices, where a large increase in their values is observed. Consequently, the daily accessibility index increased more than the potential index due to more growth in both land cover/use and urban road network. Increasing the potential accessibility index in the study area compels developing more collectors and arterial roads. Generally, increasing the accessibility indices compels balanced growth in both factors of the surrounding destinations. The implemented policy in the study area helped in increasing relative public services surrounding hospitals and health centers, such as decreasing traveling time between hospitals and urban areas. The study calculated the travel time to reach hospitals assuming a constant speed for all edges in the network. In its next step, this research continues to collect real time average speeds of the network’s edges to determine more enhanced traveling time.

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INCREASING THE VISIBILITY OF TRAFFIC SIGNS IN FOGGY WEATHER

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ABSTRACT

Due to the growth in human population and number of vehicles, the traffic accidents on highways are drastically increased in both developed and developing countries, in recent years. In traffic accidents, the rate of accidents caused by bad weather has an important place. Among adverse weather conditions, driving under foggy conditions is one of the potentially dangerous activity. However, few studies have been reported the effect of foggy weathers in highway traffic accidents. In recent years, the driver support systems, in which several cameras and sensors are used to warn or help the drivers. In this study, it is suggested to use a real time defogging algorithm to preprocess the camera data before reflected to the driver support system screen. By this way, the traffic accidents occurred under foggy conditions is expected to be reduced.

KEYWORDS:
Traffic safety, traffic sign, image defogging, dehazing algorithm.

INTRODUCTION

Worldwide, 1.3 million people die and 50 million are injured each year due to traffic accidents. According to the World Health Organization (WHO) data collected from 178 countries, the traffic accidents are the most common cause of death among all age groups [1]. Traffic accidents are the first among causes of death according to the same report. For instance, the number of vehicles and traffic accidents have increased during the last decades in Turkey. It is very important to reduce the highway traffic accidents in developing countries, and therefore the traffic safety should be improved by the analysis of accident characteristics [2].

The causes of traffic accidents, human, road, vehicle and environment factors all over the world. Bad weather conditions play an important role among the environmental factors. The impact of bad weather conditions on road traffic safety is significant for transportation researches. Bad weather related crashes are occurred in the rain, sleet, snow, wet pavement, icy pavement and fog.

Driving in foggy weather affects drivers dangerously of all ability levels. Approximately 600 deaths and over 16000 injuries occur each year in fog related crashes as reported by The Federal Highway Administration (FHWA) [3]. It is reported that there is a 16% increase in personal injuries [4]. It is well known that fog reduces the contrast within the visual field which decreases the visibility. In addition, the low visibility caused by foggy weather can also reduce travel speeds and roadway capacity about 12% [5].

The literature review summarizes that the traffic fatality risk is much higher in accidents occurred in foggy weathers.

The study the relationship between air quality and fog incident in a nine year period was analysed for Istanbul-Yenibosna region [6].

The effect of experiences of drivers on speed allowance under foggy weathers are studied in [7]. It is reported that drivers with more experience drove faster in clear weathers, whereas, they reduce their speed in foggy weathers. Novice drivers, however have much longer responses to changes in weather conditions.

Ni et al. [8] investigated the effects of age in crash perception performance under foggy weathers. In this study, it is found that the older is the driver, the higher is the collision risk, due to the decreasing ability to react.

Ni et al. [9] under simulated foggy conditions, the car following performance of age differences have been studied. Since, the following distance is very important, especially in foggy weather, the results concluded that the older drivers drive at a dangerous following distance [9].

Abdel-Aty et al. [10] investigated the effects of visibility reduction on collisions, caused by smoke and fog. In this study, accident data of Florida (2003-2007) are used to determine the effects of smoke and fog by a multilevel order logistic model. This study concludes that the injuries are more severe, and more vehicles involve in the crash in foggy weathers,
when compared to the clear weather. The crashes are rarely occurred on high-speed roads with control, divided highways, roads with street lights. Brooks et al. under simulated fog, the speed choice and performance are studied. The drivers tend to drive at unsafe higher speeds, according to the results obtained from the simulator. Driving at unsafe speeds yields in lack of reacting [3].

Kang et al. [11] it is found that drivers tend to decrease the car following distance under foggy weathers.

Edwards studied the relationship between the weather conditions and severity of accidents [12]. It is concluded that the speed is the major factor in many crashes under foggy weathers.

Hao et al. [13] the effects of foggy weather on the severity of injuries is studied on data from FRA database. Based on a mixed logit modelling, this study detects the determinants of injury severity under foggy weather conditions compared to the clear weather conditions. It is reported in this study that the injuries are much more severe under foggy air conditions [13].

The early defogging algorithms are based on enhancement methods like histogram equalization. These methods cannot defog the images. Later, defogging methods using multiple images are proposed, in which the images of the same scene under different conditions are used [14-16]. It is concluded that the speed is the major factor in many crashes under foggy weathers.

Therefore, to defog the image before processing the visual information is very important. Moreover, in order to increase driving safety, driver support systems using various sensors and cameras are developed. The road can be reflected to a screen in front of the driver. Defogging before the image is transferred to the screen can help the driver to drive safely.

**MATERIALS AND METHODS**

The commonly used hazy image model is given below. [16-20]

\[
I_m = J_m t + A_m (1-t)
\]

Here \(I_m\) is equal to the \(m\) th band of the input hazy image, while \(J_m\) is the \(m\) th band of the fog free image, where \(A_m\) is the global air light value and \(t\) is the transmission which describes the unscattered data.

Therefore, the fog free image is recovered as

\[
J_m = \frac{I_m - A_m (1-t)}{t}
\]

In order to obtain the fog free image the transmission and airlight should be determined. The proposed defogging method consists of three steps. In the proposed method, first the proposed prior is calculated. Then, the airlight and transmission are estimated. By determining the two unknowns of (2), finally, the fog free image is recovered.

**The Multiscale Products Prior (MP).** First, the image is smoothed by a Gaussian filter [20]. The Gaussian mask used for this purpose can be given as [20]:

\[
G = \begin{bmatrix}
0.011 & 0.084 & 0.011 \\
0.085 & 0.619 & 0.085 \\
0.011 & 0.084 & 0.011
\end{bmatrix}
\] (3)

To obtain the first approximation subband, the input foggy image (I) is filtered by (3) as

\[
A_1 = I * F
\]

Here, \(A_1\) is the first approximation subband. In order to obtain the approximation subbands for further levels, the subband is filtered again as

\[
A_l = A_{l-1} * F
\]

Here \(A_{l-1}\) and \(A_l\) are the approximation subbands at level \(l-1\) and \(l\), respectively.

For L levels of decomposition, after obtaining the subbands, the multiscale products of these subbands are calculated as follows:

\[
MSP^n_A = A^n_1 A^n_2 \ldots A^n_l
\]

Finally the proposed prior is calculated by

\[
MP = \sqrt[1]{\sum_{m=R,G,B} MSP^n_A}
\]

Here, we take the Lth root of the MSPs to normalize the values.
**Air light and Transmission Estimation.** The air light is estimated with a similar manner described in [20, 21]. The air light estimation is equal to the mean of the brightest 0.1% pixels.

After air light estimation transmission should be estimated. The transmission is determined by the following steps:

- First, the input foggy image is normalized by the air light as:
  \[ I_n = \frac{I}{A} \]  
  \( (8) \)

- Then the MP of this normalized image is calculated by (7).

- The calculated MP is smoothed with the filter mask given in (1).

- Finally, the transmission is determined by the following equation.
  \[ t = 1 - A P \left( \frac{I}{A} \right) * F \]  
  \( (9) \)

In order to recover the fog free scene, equation given in (2) is used.

**RESULTS AND DISCUSSION**

The proposed method is applied to several images, along with Dark Channel Prior (DCP) method. Original fog free image is given in Fig.1.a, whereas the synthetic foggy image is given in Fig.1.b, and the defogging results obtained by the DCP and MP methods are given in Fig.1.c and Fig.1.d, respectively. It is obvious that the MP methods defog the image better than DCP method. The “BUS” sign in the closer region is more readable and the cars at the far region is more visible.

Moreover, to compare the methods quantitatively, Root Mean Square Error (RMSE) calculated between the defogging methods and original image is given in Table 1. According to table 1, the MP method is more close to the original image.

<table>
<thead>
<tr>
<th>Method</th>
<th>RMSE</th>
<th>Time(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCP</td>
<td>19.3615</td>
<td>23.070</td>
</tr>
<tr>
<td>MP</td>
<td>18.0994</td>
<td>1.318</td>
</tr>
</tbody>
</table>

**FIGURE 1**
(a) Original synthetic image (b) Synthetic foggy image, and Defogging results for (c) DCP method, and (d) MP method.

**TABLE 1**
The RMSE and time consumption for DCP and MP methods.
In addition, the time consumption of the methods are also included in Table 1. It can be seen that MP method is much faster than the DCP method. Therefore, the use of MP for driver support systems is more appropriate than DCP method.

For further defogging results, images taken outdoor are included. In Fig.2, a foggy weather with snow is demonstrated. The defogging result obtained by MP methods is given in Fig.2.b. The traffic sign is not visible, while in the defogged image, the sign and the surroundings are more clear.

In Fig.3.a, foggy road image taken in Erzurum, Turkey is demonstrated, while, the defogging result obtained by MP method is given in Fig.3.b. As it can be seen in Fig.3, the lanes are more visible in the defogged image.

CONCLUSION

Decreasing the number of traffic accidents is very important for human life. In order to increase the traffic safety, driving support systems are being developed recently. One of the causes for traffic accident is the low visibility of the traffic signs in the highways, generally caused by foggy weather conditions. Therefore, we propose to use a real time defogging algorithm to increase the visibility of the traffic signs, traffic lanes and visibility. The algorithm is a preprocessing for driving support systems. By this way, the videos obtained by the cameras used for driving support will be preprocessed by the defogging algorithm and then the video will be transferred to the driver support screen. Since, the described defogging algorithm calculates every parameter automatically, and is a fast algorithm, it makes the method to be a good candidate for driving support systems. Although being an efficient and fast algorithm, there is still some improvement to be done for further studies, such as; using different types of filters and developing a more adaptive algorithm.

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POSSIBLE WAYS OF MITIGATING THE EFFECTS OF CLIMATE CHANGE USING EFFICIENT URBAN PLANNING AND LANDSCAPE DESIGN PRINCIPLES IN TURKEY

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ABSTRACT

Although its effects are clearly seen in many parts of the country, studies on climate change only date back to nearly three decades ago in Turkey. However, many good quality and conclusive studies have been conducted to reveal the trend and extent of these changes considering the locations and time periods. Because such studies are dealt mainly with the subject from only meteorological and climatologic points of view, very little emphasis has been given on the effects of these changes on specific human occupations, e.g. urban, landscape or architectural planning or design. This study may be among the first to evaluate the effects of climate change on urban, landscape and architectural planning/design works in Turkey by reviewing the related studies, projections and their outputs and justifying their results to mention some proposals considering main principles. Present study is aimed to mention about the sizes of the regional and seasonal climatic changes by considering the projections of some climate change scenarios (RCP: Representative Concentration Pathways; RCP4.5 and RCP8.5 accepted to be used for IPCC 5th Assessment Report). Main concern in the study is to discuss the possible impacts of the changes foreseen in the scenarios on urban and landscape planning works. After gaining some concrete insights about the conditions, mitigation of these effects is also discussed considering some basic planning and design principles.

KEYWORDS: climate change, urban planning, landscape architecture, architecture

INTRODUCTION

Transformed earth surfaces due majorly to anthropogenic activities cause imbalances in heating mechanism of earth atmosphere. Among such activities as agriculture and deforestation, urbanization perhaps accounts for the largest rate of the changes in surface transformation and thus the mentioned mechanism.

According to UN [1], in 2014, 54% the world’s population lives in urban areas being expected to increase up to 66% by 2050. The number of mega-cities inhabiting more than 10 million people is increasing from 10 in 1990 (home to 153 million people) to 28 in 2014 (home to 453 million people). By 2030, the world is projected to have 41 mega-cities with 10 million inhabitants or more.

According to [2], climate is not only long term means of atmospheric features at a certain point but also the combination of temporal distribution of their frequencies, observed extremes, severe weather events and all variability types. Such an approach defends that the result of the changes and developments have been seen in nearly the last 20 years. Climate may change due to natural inner and outer processes and continuous anthropogenic changes in the combination of atmosphere and land-uses [2]. In this respect, industrial revolution is a breakthrough for climate as for several other matters since it caused gigantic anthropogenic effects never seen before in human history on earth surface (transformation of lands) and atmosphere (increase of carbon rate). Only nearly 2.7% of the earth’s surface is covered by urban areas, but their impacts on both atmosphere and climate is much larger due to their interventions with the natural heating mechanism of the atmosphere. As can be seen in Fehler! Verweisquelle konnte nicht gefunden werden., due to anthropogenic activities, cities use fossil fuels producing greenhouse gases (CO2; CH4; N2O etc.) and particles and produce waste heat causing overheating in urban atmosphere. According to [3], “the warming trend over the last 50 years (1955 to 2005) is nearly twice that for the last 100 years” [4].

This study may be among the first to evaluate the effects of climate change on urban, landscape and architectural planning/design works in Turkey by reviewing the related studies, projections and their outputs and justifying their results to mention some proposals considering main principles. Therefore, this study tries to express the extents of the regional and seasonal climatic changes based on the projections of some climate change scenarios (RCP 4.5 and 8.5) by considering their possible effects on urban and landscape planning works to mitigate these effects using basic planning and design principles.
Socioeconomic developments in Turkey. Turkey is a developing European country located between Asia and Europe in Asia Minor (majorly Anatolia Peninsula; 25.66 - 44.82E; 35.82 ± 42.10N). Its population is 79,814,871 and annual population growth rate is 13.5 and it has been consistently increasing since the foundation of modern republic in 1923. As can be seen from Fehler! Verweisquelle konnte nicht gefunden werden., Turkey is consistently growing economically but producing CO2 and GDP have always grown especially over the last 15 years and CO2 emissions (metric tons per capita) have shown the same increasing trend.

Key points of the studies on climate changes in Turkey. Studies related to climate change in Turkey started in the first half of 1990s (e.g. [5]) and their quality and quantity increased in later dates by evaluating trends in long-term temperatures [6,7,8,9]. First studies found mainly cooling trends in mean yearly temperature series but a general warming trend in minimum temperatures in especially springs [10,11]. A study [12] found a decrease in mean yearly global solar radiation in 1960 – 1994 due to lower air quality. A study [13] found an increasing trend in annual, winter and spring temperatures at 70 stations in Turkey in 1929-1999 period while [11] found a significant increase in the majority of the urbanized and urbanizing stations for the same period. Some urban heat island (UHI) studies [14,15] found increases in temperatures depending on urbanization, which concluded the main reasons of climate change in Turkey to be urbanization. In 2007, two significant reports [16, 17] were prepared and one congress [18] was held. In [16] it was announced that in 1951 ± 2004 period in Turkey, an increase in summer temperatures was seen mostly in western and southern parts of the country, especially

| TABLE 1: Some indicators of Turkey

<table>
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</thead>
<tbody>
<tr>
<td>Population(a)</td>
<td>53.9</td>
<td>63.2</td>
<td>70.4</td>
<td>71.3</td>
<td>72.3</td>
<td>73.4</td>
<td>74.6</td>
<td>75.8</td>
<td>77.0</td>
<td>78.3</td>
<td>79.5</td>
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<tr>
<td>Pop. growth (%)</td>
<td>1.74</td>
<td>1.52</td>
<td>1.20</td>
<td>1.27</td>
<td>1.38</td>
<td>1.49</td>
<td>1.57</td>
<td>1.62</td>
<td>1.63</td>
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<td>1.57</td>
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<tr>
<td>Surface area (sq. km)</td>
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<td>785350</td>
<td>785350</td>
<td>785350</td>
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<tr>
<td>Pop. density (per km)</td>
<td>70.06</td>
<td>82.17</td>
<td>91.52</td>
<td>92.69</td>
<td>93.98</td>
<td>95.38</td>
<td>96.89</td>
<td>98.47</td>
<td>100.09</td>
<td>101.70</td>
<td>103.31</td>
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<tr>
<td>Poverty (%)</td>
<td>6.80</td>
<td>4.40</td>
<td>3.70</td>
<td>2.80</td>
<td>2.30</td>
<td>2.10</td>
<td>1.60</td>
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<tr>
<td>Life expectancy</td>
<td>64.28</td>
<td>70.00</td>
<td>73.50</td>
<td>73.81</td>
<td>74.09</td>
<td>74.37</td>
<td>74.64</td>
<td>74.90</td>
<td>75.15</td>
<td>75.41</td>
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<tr>
<td>Forest area (sq. km)</td>
<td>96220</td>
<td>101830</td>
<td>109866</td>
<td>110948</td>
<td>112030</td>
<td>113054</td>
<td>114078</td>
<td>115102</td>
<td>116126</td>
<td>117150</td>
<td>..</td>
</tr>
<tr>
<td>Urban pop. (%)</td>
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<td>101830</td>
<td>109866</td>
<td>110948</td>
<td>112030</td>
<td>113054</td>
<td>114078</td>
<td>115102</td>
<td>116126</td>
<td>117150</td>
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<td>Energy use (kg)</td>
<td>121.09</td>
<td>141.35</td>
<td>1370.79</td>
<td>1474.67</td>
<td>1546.20</td>
<td>1585.40</td>
<td>1542.97</td>
<td>1577.83</td>
<td>1656.80</td>
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<td>CO2 emissions</td>
<td>2.71</td>
<td>3.42</td>
<td>4.03</td>
<td>3.89</td>
<td>4.12</td>
<td>4.37</td>
<td>4.42</td>
<td>4.29</td>
<td>4.49</td>
<td>..</td>
<td>..</td>
</tr>
<tr>
<td>Electric cons. (kWh)</td>
<td>929.70</td>
<td>1652.75</td>
<td>2421.98</td>
<td>2314.11</td>
<td>2491.63</td>
<td>2696.31</td>
<td>2772.06</td>
<td>2760.65</td>
<td>2854.57</td>
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<td>..</td>
</tr>
<tr>
<td>GDP (current US$) (b)</td>
<td>150.7</td>
<td>273.0</td>
<td>764.3</td>
<td>644.6</td>
<td>771.9</td>
<td>832.5</td>
<td>874.0</td>
<td>930.6</td>
<td>934.2</td>
<td>859.8</td>
<td>863.7</td>
</tr>
<tr>
<td>GDP growth (%)</td>
<td>9.27</td>
<td>6.64</td>
<td>0.85</td>
<td>-4.70</td>
<td>8.49</td>
<td>11.11</td>
<td>4.79</td>
<td>8.49</td>
<td>5.17</td>
<td>6.09</td>
<td>3.18</td>
</tr>
</tbody>
</table>

(a) Million, b) Billion
Mediterranean coastline due to urbanization. [19] stated that there is a general warming trend all over the country after a cold year in 1992. A study [20] using data series of temperature and rainfall in 1952 – 2006 and 1940 – 2006 showed an increase (0.121°C to 0.312°C) per decade in the southern and south-western parts of the country due to urbanization developing over nearly the past 50 years. A 30 – year average of climatic elements is accepted to be normal. From this point of view, Turkey’s normals are compared over three 30 – year periods (1961-1990; 1971-2000 and 1981 – 2010) by [21]. According to the results, temperature normal is in increasing trend and the last period exhibits larger rate of increase compared to the others. (Fehler! Verweisquelle konnte nicht gefunden werden.). As can be seen in Fehler! Verweisquelle konnte nicht gefunden werden.2b, temperature normal is larger and rainfall normal is lower than the previous periods. The risk, frequency/recurrence and intensity/severity of certain extreme weather events or record values like record temperatures over a long period of time (heatwaves), droughts, heavy downpours, flooding from intense precipitation and storms have increased and continue to increase depending on climate change [23]. In Turkey, it can be seen from Fehler! Verweisquelle konnte nicht gefunden werden.2b that the frequency of such events has always been increasing over especially the last years. In the graphic given, the number of days; with Summer daily mean temperature > 25°C in eastern part of Turkey, exceeding normal temperature and rainfall values (in 1971-2000 period), exceeding threshold values, frost, tropical characteristic, severe rainfall amount, very severe rainfall amount, excessive differences between maximum and minimum temperatures are considered.

**Scenarios of climate change and its impacts for Turkey.** As in other countries, in Turkey, various scenarios for climate change and its impacts in the future have been analyzed using various simulation and modelling studies for nearly three decades [24]. At first studies like [25], effects of global circulation were mainly investigated and temperature increases and precipitation regime changes were evaluated with their possible impacts [16]. [20] used PRECIS regional climate model for Turkey and reported 4 - 5 °C and 5-6 °C increase in mean temperatures and the finding was supported by [26,27].

Climate modelling is the study of predicting future climatic conditions using some scientific calculation and formulas [22]. Such a method has been used to forecast atmospheric conditions for nearly a century especially during and after World War II. In Turkey, Turkish State Meteorological Service (MGM) follows the new developments in climate models and tried to adapt and downscale it to determine the future projections in climate. In one of such studies carried out by MGM, new approaches (RCP: Representative Concentration Pathways; RCP4.5 and RCP8.5) accepted to be used for IPCC 5th Assessment Report were used as scenarios to evaluate the climate projections in Turkey using the data given in Table 2.

In the temperature and rainfall based projection considering RCP4.5 scenario and using HadGEM2-ES, [29] over three periods (2016 – 2040; 2041 – 2070; 2071 – 2099), Turkey is predicted to face temperature increases in 2016-2040 period up to 2°C, and decreases in annual rainfall up to 20%. In 2041-2070 period, temperature increases are estimated in spring and autumn up to 2 – 3°C while in summer this increase will reach up to 4°C. Interior and eastern parts of the country are expected to face rainfall shortage in the rate of 20 - 30%. In 2071-2099 period, temperature increase in winter and spring – autumn will be 2°C and 3°C, respectively while in summer this increase will be 4°C in hot regions, Aegean and Southeast Anatolia. For rainfall, again a decrease will be seen in especially spring precipitations up to 20% (Figure 3).
TABLE 2
Data used for the projections.

<table>
<thead>
<tr>
<th>Global Climate Model</th>
<th>HadGEM2-ES</th>
<th>MPI-ESM-MR</th>
<th>GFDL-ESM2M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution of GCM (km)</td>
<td>112.5</td>
<td>210</td>
<td>200</td>
</tr>
<tr>
<td>Scenarios adopted</td>
<td>RCP4.5-RCP8.5</td>
<td>RCP4.5-RCP8.5</td>
<td>RCP4.5-RCP8.5</td>
</tr>
<tr>
<td>Projection Period</td>
<td>2016-2099</td>
<td>2016-2099</td>
<td>2016-2099</td>
</tr>
<tr>
<td>Regional climate model</td>
<td>RegCM4.3.4</td>
<td>RegCM4.3.4</td>
<td>RegCM4.3.4</td>
</tr>
<tr>
<td>Resolution of produced projections (km)</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

According to temperature and rainfall projection based on RCP8.5 scenario using HadGEM2-ES, in 2016-2040 temperature increase is predicted to be 3°C in spring and summer and rainfall will decrease up to 40%. In 2041-2070 period, temperature increases will be 2-3°C, 3-4°C and 5°C, in winter, spring–autumn and winter, respectively. Rainfall will decrease in spring and summer 20 and 50% in especially eastern Anatolia. In 2071-2099 period, summer temperature will increase up to 6°C while rainfall will decrease up to 20 – 50% (Figure 3).

DISCUSSION AND CONCLUSION

Points to be considered for climate change in the respect of architectural disciplines in Turkey. From the reviewed literature, it can be concluded roughly for Turkey that a) climate change in Turkey has been caused by changes in land use/cover due to rapid urbanization especially over the last 70 years in addition to changes in general atmospheric circulation [11,13], b) temperatures have started to increase and are expected to increase in the projected years to certain extents (up to 6°C), c) rainfall started to decrease at a considerable rate and continues to decrease showing irregularity for seasons, d) extreme events are seen more frequently by breaking new records in mainly urban areas.

From the sides of massive architectural, spatial and landscape designs and solutions, climate is among the major factors playing important roles. Therefore, either in structural or spatial design, all the solutions and proposals should put climate or climate-related factors in the center of their approaches. It may be a good way to evaluate mitigation efforts for climate change in terms of architectural disciplines i.e. city and regional planning, landscape architecture and architecture.

In terms of urbanism/city planning, it is possible to say for Turkish cities that they grow, do not
develop. Because of the policy adopted over the last fifteen years or longer main economic activities are based strictly on land property and asset ownership in especially city centers. Therefore, a rapid, restless and devastating process on urban areas and their surroundings has been going on resulting in the transformation of larger natural/agricultural surface into impervious or paved ones triggering over-heating mechanism in Turkish cities. Main problem seen over the last years in Turkish cities is the increasing prevalence of extreme weather events each of which turns out to be destroying disasters causing human and economic loses.

Turkey is among the countries which face urban population increase and urban migration requiring larger rate of structuration and energy consumption [30]. Even though official statistics say 92.6% of Turkish population live in urban areas because of a legislation related to grand municipalities (30 most populated provinces are accepted to be urban in every part), this rate is between 75 and 80% accounting for above 60 million people [31]. Urbanization rate of population has been nearly 3% yearly over a long time. The problem in Turkish cities is to find place to live and work with suitable infrastructure for the newcomers while renewing and maintaining the present ones for the existing people. Such a condition becomes more problematic when the unfavorable effects of climate change make them sense on this development. Therefore, when renewing or newly constructing a city part, the latest climate data and future projections should be considered in the cities.

Such negative impacts (will) affect mainly well-being and prosperity of urban residents in the country. Due to unplanned and low – resistant infrastructure systems constructed without considering even climatic normal such as water and energy supply, sewage and roads. The nation’s economy, security, and culture all depend on the resilience of urban infrastructure systems [23] since large size devastation occurs during an extreme event all the governmental organs may turn out to be open to threats. Very few of the local governments (municipalities) have their adaptation plans to take action against climate change by determining their insufficient aspects in the country. Therefore, either central government institutions (e.g. Turkish Ministry of Environment and Urbanism) or local administrations (municipalities) should prepare and implement their adaptation plans as soon as possible by considering resilient infrastructure systems, public health and security and economic losses in cooperation with and with the participation of all sides of the society.

On families’ agenda, effects of climate change do not take place until they give some types of harm to them, e.g. when their house is flooded. This is a social phenomenon that awareness and adaptability of city dwellers to climate change depend largely on their social status and demographic features like age, ethnicity, gender, income, health, and (dis)ability differences [23]. At regional level, inter – or intraregional cooperation should be founded between especially local governments e.g. the unions for infrastructure in a basin or sub – regions to reduce wastes, greenhouse gases or increase resilience etc.

At national or regional scale in Turkey, changing development policies i.e. land rent-based growth (profiting from lands; urban sprawl, over valuation of land parts in urban) should be avoided. Clean energy using industry should be preferred in well-organized industrial regions. Respectful manmade structures to nature and climate should be adopted. Climate sensitive urban and landscape designs should be preferred using native construction materials and plants. Creating quality human resources (both conscious about climate and nature and earning their lives from light industry, R&D, tourism, consultancy in place of heavy industry) and decentralization of industrial even urban areas should be planned.

From landscape architecture perspective, it is a very hard work in Turkish cities to satisfy all kind of human comfort conditions (such as thermal comfort, aesthetics, well-being, economic etc.) using very limited suitable areas left for this aim. "Due to ever increasing economic value of housing areas, lands and assets demand for such investment tools is also increasing which in turn requires new areas to open for such activities or transformation of green or open city parts. Therefore, landscape / urban designers may be accepted as unarmed warriors to fight for leaving enough ecological / green corridors for dwellers in Turkish cities. Even though, legislation in Turkey brings obligation and certain standards to be considered in plans and designs but main problem is seen in the enforcement of these regulations. Today, Turkish cities are turning out to be settlements with concrete housing blocks dominating green areas and piles of buildings are constructed without considering legal regulations, scientific facts especially those related to climatic ones (e.g. prevalence wind directions, frosty days etc.). Result is the uncomfortable cities where unhappy and dissatisfied people with life live. In cities already in not so a brilliant condition for urbanism and landscape architecture requirements, effects of climate change will be very adverse on human comfort (thermal) and health. Any changes in one of the atmospheric elements can directly affect human thermal comfort conditions. In Turkey, for the last 70 years, especially since 1980s, a considerable increase has been seen in urban population, due to industrialization, tourism and terror, which compels Turkish people to live in complex, uncomfortable and torrid city environments. In studies [32,33] carried out in Erzurum, a medium sized eastern Turkish city, it was found that urban area is 1.7 °C warmer, 2.5 to 3.4% drier and 0.8 m/sec. less windy than rural while in another study [34] in Ankara capital of the country urban
area is 2.01 °C warmer than rural. In another study [35], urban open space was found to be bio-climato-
logically less comfortable than rural and urban for-
est. From this point of view, Turkish cities are
warmer, drier and less windy compared to rural areas
as in other countries.

Considering these findings, for the developed
and newly developing Turkish cities to provide more
comfortable environments with people, upper-scale
policies based on land evaluation should be avoided.
Required legal regulations should be enforced to
leave enough and efficient areas for green areas and
thus increasing ecological resilience of cities. Since
nearly whole country will be in short of water, ex-
tensive turf areas should be avoided by preferring the
use of native succulent species.

Resulting from extremely heavy precipitations
sewage systems should be reregulated to carry sud-
den water loads. As the large air masses behave dif-
differently, their movement routes and speed also
change by producing very strong winds, storms even
tunnels in Turkey which is an interior region coun-
ty. Therefore, destroying effects of wind should also
be considered and Turkey should count itself among
the countries where storms and tunnels are seen. In
contrast to what is said, in some cities and seasons
depending on street canyons, very calm urban air
facing inversion depending on the prevalent air masses (e.g. Basra low [39], Azores / Siberia Anti-
cyclones), cities are exposed to polluted, dry, hot (or
very cold) air blocks depending on the topography.
In order to prevent such cities from this conditions
production or benefitting from wind may be a good
solution even using suitable planning and greening
techniques unfavorable effects. In windless, arid,
torrid and polluted – by particles urban environ-
ments, provision of efficient air movements can be
of vital importance to supply moisture, decrease
temperature and remove particles.

In architecture, all effective climatic elements
(e.g. solar radiation, temperature, humidity and wind
[37]) on human thermal or life comfort outdoor are
also sensed indoor. Therefore, structures should be
built by considering these effects (paying attentions
on orientation, compatible materials etc.) and special
actions should be taken for the changes in these ele-
ments.

When the effects of climate change on Turkish
cities are considered, it is seen that they will become
hotter, drier, calmer (less windy) dirtier (lower air
quality) depending on the increase in temperature
and ongoing processes. Therefore, the first thing to
be mentioned may be human bioclimatic or thermal
comfort conditions (stress or discomfort from ambi-
ent in cities [38]. In the newly developing sites tra-
ditional architecture styles should be considered
since they could provide more comfortable circum-
stances in the past; modern urban planning principles
like smart city) should be adopted. The other thing
is that urban areas will become more dangerous to
dwellers for their economy and wellbeing due to sud-
den changes and extreme weather conditions. In the
newly developing areas, the use of green roofs
should be encouraged by architecture in public and
private buildings.

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CHECKING THREE – YEAR DIFFERENCES IN SOME CLIMATIC ELEMENTS BETWEEN URBAN AND RURAL AREAS AFTER A TWELVE – YEAR PERIOD CONSIDERING SOME EFFECTIVE PARAMETERS AND SOLUTIONS

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ABSTRACT

In addition to global fluctuations in climatic elements effective on the country-size mean values, developing and urbanising countries, such as Turkey, witness the changes in climatic elements through their climatic measurement stations, which were very away from urban when they were first established but have gradually been surrounded by densely structured urban areas. This study is aimed to determine the urban-rural climatic differences in temperatures and relative humidity and compare the results from two different periods 12 years after the first one (2002 – 2004 and 2014 - 2016) in urban and rural parts of the city centre of Erzurum, which is an unindustrialised middle – sized eastern Turkish city with the most important carbon emission sources of domestic heating and traffic (45.5 and 25.0%, respectively). Rural meteorological station has been operated at the airport property of the city since 1988, but urban station made measurement only between 2002 and 2004 and began measurement again in 2013 through automated weather observation system. Therefore, the present study compares the mean values of two 3-year periods. In the scope of the study, changes in climatic elements after a 12 – year period were calculated considering the possible effective factors on this change i.e. human population growth, increase in urbanisation, the number of motor vehicles and green area rate in addition to the factors stated in the previous studies. In order to monitor the possible effective factors, present study compares the 10-year change in human population, urbanisation ratio (structured area), green area rate and the number of motor vehicles.

It was found that all parameters in both urban and rural areas increased in the 2nd period compared to the 1st one. The extent of the changes in urban is 1.3°C, 0.2°C and 1.1°C for mT, maT and miT, respectively while 2.2% for relative humidity. Difference in rural between periods is seen to be 1.7 °C, 1.1 °C, 1.9 °C for mT, maT and miT, respectively and 4.7% for RH.

Based on the results above, some suggestions are proposed for the local administrations to create climatically more tolerable and favourable environments for urban people.

KEYWORDS:
Rural area, urban area, temperature, relative humidity, rainfall, urbanisation, Erzurum

INTRODUCTION

Alterations in natural heating mechanism in urban areas cause urban heat island (UHI) effect associated with various factors like industrial and residential areas as the source of excessive heating and air pollutants (including greenhouse gases) and urban surface characteristics with different albedo causing excessive heat storage and reflection of solar radiation.

Depending on the intensity of UHI effect, urban environment may exhibit higher temperature, lower humidity and weaker wind speeds than surrounding semi-urban or rural areas [1, 2, 3, 4, 5]. Density and effects of UHI have been studied for nearly two hundred years [6 in London] considering various aspects of the topics like the sizes, populations, surface characteristics etc. [7, 8, 9, 10, 11, 12, 13, 14]. Quality and quantity of Turkish studies on urban climate have begun to increase over nearly the last 30 years by considering the topic together with the studies on climate change [15, 16].

Urban climate is required to be followed for longer periods in order to understand its nature, effective factors and mitigating or removing measures to take against some harmful phenomena in urban environment like UHI, air pollution, unfavourable thermal comfort conditions. Urban climate studies are generally based on the detection of the extent of differences in climatic elements from semi - urban or rural counterparts and then the suggestion of measures to be taken for the mitigation [14]. In order to determine the size of differences in climatic elements, generally measurements taken simultaneously under the same conditions (e.g.
measurement heights, devices etc.) are evaluated in rural and urban.

Present study is related to the differences in some climatic elements (temperature °C; mean, mT, maximum, maT and minimum miT temperatures and relative humidity RH%) between rural and urban areas of the city of Erzurum over two different 3-year periods, 12 years after the first one, with the same time period length in order to follow and gain insight how much an unindustrialised, middle-sized city affects the climatic elements with developing surface areas.

MATERIALS AND METHODS

Erzurum city center is located in the east part of Turkey (39° 55’N; 41° 16’E; Figure 1) at an elevation changing between 1850m and 2100m in the skirts of Palandöken Mountain, an internationally famous ski center. Harsh continental climatic characteristics are prevalent in the city, where temperature can reach up to 36.5°C and down to -37.2°C (Table 1).

Table 1 gives average and total values of some meteorological parameters measured over a period from 1950 to 2015, where long term mean temperature is 5.6°C, annual rainfall is 403.3mm and mean relative humidity is 66.3%. Apart from the figure and table, mean yearly wind speed is 2.7m/sec and prevalent wind direction is ENE in summer and WSW in winter due to frontal systems in the city center. The city is among small–middle sized and unindustrialized Turkish cities, where more than half of the working people are in service (mainly public) sector. Population of the city center is about 417,385 according to Turkish State Statistics Institution in 2016. The first meteorological observation station was established in the city in 1929 and transferred to the city airport, nearly 7 km away, in 1988. From time to time, both in the city center and at the airport two stations were operated simultaneously.

Data and Measurement. Since aim of the study is to evaluate the urban – rural differences in some climatic elements over two different 3–year periods (2002 – 2004; 1st Period and 2014 – 2016; 2nd Period), simultaneous data were obtained throughout the mentioned years from urban and rural stations working in the city center and at the airport (Figure 4). Urban station is established in the garden of Regional Meteorological Administration Office in the city center (1856m; 39°.55’N–41°.16’E). The station reflects the effects of all urban characteristics e.g. traffic load because it is very close to main city artery, waste domestic heat and excessive solar radiation absorption since it is surrounded by 3-6-
storey buildings (Figure 2). Rural station (1758m; 39°57’N-41°10’E) is operated for the aims of aviation at the airport about 7 km bird–eye from the city center and urban station and it is in the middle of a vast plain covered with grassy plant species. The area shelters no buildings or human activities except for one – storey service buildings around the station. Each station is operated and maintained regularly by the Turkish State Meteorological Service (MGM). For the 1st Period, all measurements were conducted at manned stations but for the 2nd Period, data were taken from Automated Weather Observation Systems (AWOS). For both periods and stations temperature measurements were conducted in a shelter with louvered screen (so-called Stevenson Screen) at the height of 2m, which is the standard of measurement on the ground accepted all over the world [17].

In the 1st Period, even though AWOS worked at the airport station to obtain instant data (every 2 second), data were taken at only climatic observation times (i.e. three measurement times, 07.00, 14.00 and 21.00) in order to catch the maximum similarity and harmony between the data at both stations because of the type of the urban station. In the 2nd Period, data from hourly measurements were used to calculate daily averages for both stations. For both periods and stations, temperature (mT, maT and miT) and RH values were obtained, evaluated and compared.

RESULTS

Results of the urban (U) and rural (R) data analysis over the first and the second periods are as follows:

Differences in mean daily temperatures. Figure 3 and Table 2 can show clear differences between the periods and the areas for all months of the year. Mean U – R temperature differences over 1st and 2nd periods are 1.5°C and 1.1°C, respectively. This means that urban is always warmer than rural in both period (Figure 3). The largest differences are seen in winter months between 23°C and 3°C (January, February and March, which is also a winter month in the city and the region) while summer and fall represent the lowest differences beginning from August to the end of fall season (Table 2).

Differences in maximum temperatures. It is seen from Table 3 and Figure 3 that mean U – R difference in mean maT is 0.9°C (urban is warmer) for the 1st Period while there is no difference in the 2nd Period even though some clear differences are seen between months (especially in winter).
TABLE 3
Differences in the maximum temperatures for the periods (°C).

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
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<tbody>
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<td>First Period</td>
<td>Urban</td>
<td>-0.6</td>
<td>-0.5</td>
<td>3.6</td>
<td>11.1</td>
<td>17.1</td>
<td>22.7</td>
<td>26.7</td>
<td>28.3</td>
<td>23.4</td>
<td>16.8</td>
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<tr>
<td></td>
<td>Rural</td>
<td>-3.2</td>
<td>-2.8</td>
<td>1.5</td>
<td>10.3</td>
<td>17.4</td>
<td>22.3</td>
<td>26.7</td>
<td>28.5</td>
<td>23.1</td>
<td>17.1</td>
<td>5.2</td>
<td>-4.6</td>
</tr>
<tr>
<td>Difference</td>
<td>Urban</td>
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<td>-2.3</td>
<td>2.1</td>
<td>0.8</td>
<td>0.3</td>
<td>0.4</td>
<td>0.0</td>
<td>-0.2</td>
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<td>0.7</td>
<td>2.3</td>
<td>0.9</td>
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<tr>
<td></td>
<td>Rural</td>
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<td>-1.3</td>
<td>6.0</td>
<td>12.8</td>
<td>16.9</td>
<td>22.4</td>
<td>28.1</td>
<td>29.5</td>
<td>23.5</td>
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<td>-0.2</td>
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<td>-0.2</td>
<td>-0.6</td>
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TABLE 4
Differences in the minimum temperatures for the periods (°C).

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
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</thead>
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<td>-9.9</td>
<td>-6.4</td>
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<td>11</td>
<td>12.1</td>
<td>7.9</td>
<td>4.3</td>
<td>-3.2</td>
<td>-11.1</td>
<td>0.7</td>
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<tr>
<td>Rural</td>
<td>-13.8</td>
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<td>-6.1</td>
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<td>3.1</td>
<td>2.1</td>
<td>2.2</td>
<td>2.5</td>
<td>2.4</td>
<td>2.9</td>
<td>3.4</td>
<td>3.3</td>
<td>2.9</td>
<td>9.4</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Urban</td>
<td>-10.6</td>
<td>-8.0</td>
<td>-3.2</td>
<td>1.2</td>
<td>5.4</td>
<td>9.2</td>
<td>13.1</td>
<td>13.9</td>
<td>8.5</td>
<td>3.9</td>
<td>-3.4</td>
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<tr>
<td>Rural</td>
<td>-15.0</td>
<td>-12.6</td>
<td>-5.6</td>
<td>-1.0</td>
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<td>6.6</td>
<td>10.5</td>
<td>11.5</td>
<td>5.5</td>
<td>1.7</td>
<td>-6.4</td>
<td>-8.9</td>
<td>-0.8</td>
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</tr>
<tr>
<td>Difference</td>
<td>4.4</td>
<td>4.6</td>
<td>2.4</td>
<td>2.2</td>
<td>1.8</td>
<td>2.6</td>
<td>2.5</td>
<td>2.4</td>
<td>3.0</td>
<td>2.2</td>
<td>3.0</td>
<td>0.0</td>
<td>2.6</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 5
Differences in the relative humidity for the periods (%).

<table>
<thead>
<tr>
<th></th>
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<th></th>
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<tbody>
<tr>
<td>Urban</td>
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<td>70.9</td>
<td>67.6</td>
<td>60.7</td>
<td>60.3</td>
<td>61.0</td>
<td>45.6</td>
<td>41.8</td>
<td>45.0</td>
<td>55.5</td>
<td>63.9</td>
<td>69.8</td>
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<td>Rural</td>
<td>75.7</td>
<td>74.6</td>
<td>71.8</td>
<td>62.4</td>
<td>56.9</td>
<td>53.7</td>
<td>48.0</td>
<td>45.9</td>
<td>46.6</td>
<td>61.6</td>
<td>72.0</td>
<td>73.8</td>
<td>61.9</td>
<td></td>
</tr>
<tr>
<td>Difference</td>
<td>-4.7</td>
<td>-3.6</td>
<td>-4.2</td>
<td>-1.7</td>
<td>3.3</td>
<td>7.3</td>
<td>-2.4</td>
<td>-4.0</td>
<td>-1.6</td>
<td>-6.1</td>
<td>-8.0</td>
<td>-4.0</td>
<td>-2.5</td>
<td></td>
</tr>
<tr>
<td>Urban</td>
<td>77.4</td>
<td>76.6</td>
<td>66.7</td>
<td>58.8</td>
<td>63.9</td>
<td>54.3</td>
<td>45.0</td>
<td>41.4</td>
<td>47.4</td>
<td>65.8</td>
<td>64.1</td>
<td>78.5</td>
<td>61.7</td>
<td></td>
</tr>
<tr>
<td>Rural</td>
<td>84.0</td>
<td>84.3</td>
<td>73.4</td>
<td>64.3</td>
<td>72.2</td>
<td>59.4</td>
<td>49.2</td>
<td>42.8</td>
<td>49.7</td>
<td>69.1</td>
<td>72.3</td>
<td>84.0</td>
<td>66.6</td>
<td></td>
</tr>
<tr>
<td>Difference</td>
<td>-6.6</td>
<td>-7.7</td>
<td>-6.7</td>
<td>-5.5</td>
<td>-3.3</td>
<td>-5.1</td>
<td>-4.1</td>
<td>-1.5</td>
<td>-2.2</td>
<td>-3.3</td>
<td>-8.2</td>
<td>-5.5</td>
<td>-5.0</td>
<td></td>
</tr>
</tbody>
</table>

FIGURE 3
Urban and rural differences in all parameters

Maximum temperature differences are seen in again winter months, especially January and February, in both periods. December shows one of the largest differences in the 1st Period but it is not the same in the 2nd Period. Out of winter, the differences are very little (below 1 °C).

Differences in minimum temperatures. It is seen when considered Table 4 and Figure 3 that
average miT is always higher in urban than rural and the differences are 3.4°C and 2.6°C, for the 1st and 2nd periods, respectively.

In all months in the 1st Period, urban is seen to be warmer while in the 2nd one, only in one month there is no difference and again the largest differences are seen in winter months in both periods especially in January and February, except for December in the 2nd Period, when a difference of 9.4°C is seen (Figure 3, Table 4).

November exhibits the largest difference in miT in both periods, followed by June and February in the 1st and 2nd periods, respectively (Table 5; Figure 3).

**Differences in relative humidity.** There is a clear difference in relative humidity between rural and urban in both periods, where rural is majorly and always more humid. Difference is 2.5% and 5.0% in the 1st and 2nd periods, respectively (Table 5, Figure 6).

**Differences in parameters between the periods.** Differences of parameters evaluated between the 1st and 2nd Periods are given in Table 6. It is clearly seen that all parameters in both urban and rural areas increased in the 2nd period compared to the 1st one. The extent of the changes in urban is 1.3°C, 0.2°C and 1.1°C for mT, maT and miT, respectively while 2.2% for relative humidity. Difference in rural between periods is seen to be 1.7 °C, 1.1 °C, 1.9 °C for mT, maT and miT, respectively and 4.7% for RH.

### TABLE 6

**Differences between the periods.**

<table>
<thead>
<tr>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 Urban</td>
<td>-8.7</td>
<td>-5.3</td>
<td>0.1</td>
<td>5.9</td>
<td>8.0</td>
<td>15.5</td>
<td>19.7</td>
<td>19.7</td>
<td>14.7</td>
<td>9.5</td>
<td>2.8</td>
<td>-9.6</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>2 Urban</td>
<td>-6.3</td>
<td>-4.2</td>
<td>1.6</td>
<td>7.4</td>
<td>11.2</td>
<td>16.3</td>
<td>20.8</td>
<td>21.7</td>
<td>15.3</td>
<td>8.5</td>
<td>1.3</td>
<td>-5.4</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>Difference</td>
<td>2.4</td>
<td>1.1</td>
<td>1.5</td>
<td>1.5</td>
<td>-2.2</td>
<td>-0.8</td>
<td>-1.0</td>
<td>-1.9</td>
<td>-0.6</td>
<td>1.0</td>
<td>1.5</td>
<td>-4.2</td>
<td>-1.3</td>
<td></td>
</tr>
<tr>
<td>1 Rural</td>
<td>-10.9</td>
<td>-8.4</td>
<td>-3.1</td>
<td>4.2</td>
<td>10.4</td>
<td>14.4</td>
<td>18.4</td>
<td>18.7</td>
<td>13.7</td>
<td>8.5</td>
<td>-0.1</td>
<td>-10.9</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>2 Rural</td>
<td>-9.2</td>
<td>-7.1</td>
<td>0.6</td>
<td>6.5</td>
<td>10.6</td>
<td>15.1</td>
<td>19.9</td>
<td>21.0</td>
<td>15.0</td>
<td>8.3</td>
<td>-0.1</td>
<td>-5.9</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>Difference</td>
<td>-1.7</td>
<td>-1.3</td>
<td>-3.7</td>
<td>-2.3</td>
<td>-0.2</td>
<td>-0.7</td>
<td>-1.6</td>
<td>-2.3</td>
<td>-1.3</td>
<td>0.2</td>
<td>-0.1</td>
<td>-5.0</td>
<td>-1.7</td>
<td></td>
</tr>
</tbody>
</table>

| Period | Mean Temperature (°C) | | | | | | | | | | | | | |
| 1 Urban | -0.6 | -0.5 | 0.1 | 11.1 | 17.1 | 22.7 | 26.7 | 28.3 | 23.4 | 16.8 | 5.9 | -2.3 | 12.7 |
| 2 Urban | -2.4 | 0.0 | 6.1 | 12.5 | 16.7 | 22.3 | 27.7 | 29.2 | 22.9 | 14.6 | 6.8 | -1.0 | 12.9 |
| Difference | 1.8 | -0.5 | -2.5 | -1.4 | 0.4 | 0.4 | -1.0 | -0.9 | 0.5 | 2.2 | -0.9 | -1.3 | -0.2 |
| 1 Rural | -3.2 | -2.8 | 1.5 | 10.3 | 17.4 | 22.3 | 26.7 | 28.5 | 23.1 | 17.1 | 5.2 | -4.6 | 11.8 |
| 2 Rural | -4.1 | -1.3 | 6.0 | 12.8 | 16.9 | 22.4 | 28.1 | 29.5 | 23.5 | 15.0 | 7.0 | -0.4 | 12.9 |
| Difference | 0.9 | -1.5 | -4.5 | -2.5 | 0.5 | -0.1 | -1.4 | -1.0 | -0.4 | 2.1 | -1.8 | -4.2 | -1.1 |

| Period | Relative humidity (%) | | | | | | | | | | | | | |
| 1 Urban | 71.0 | 70.9 | 67.6 | 60.7 | 60.3 | 61.0 | 45.6 | 41.8 | 45.0 | 55.5 | 63.9 | 69.8 | 59.4 |
| 2 Urban | 77.4 | 76.6 | 66.7 | 58.8 | 63.9 | 54.3 | 45.0 | 41.4 | 47.4 | 65.8 | 64.1 | 78.5 | 61.7 |
| Difference | 6.4 | 5.7 | 9.9 | 1.9 | 3.6 | 6.7 | 0.6 | 0.5 | -2.4 | -10.3 | -0.1 | -8.7 | 22.2 |
| 1 Rural | 75.7 | 74.6 | 71.8 | 62.4 | 56.9 | 53.7 | 48.0 | 45.9 | 46.6 | 61.6 | 72.0 | 73.8 | 61.9 |
| 2 Rural | 84.0 | 84.3 | 73.4 | 64.3 | 67.2 | 59.4 | 49.2 | 42.8 | 49.7 | 69.1 | 72.3 | 84.0 | 66.6 |
| Difference | -8.3 | -9.7 | -1.6 | -1.9 | -10.3 | -5.7 | -1.1 | 3.1 | -3.0 | -7.5 | -0.3 | -10.1 | -4.7 |

**DISCUSSION**

In an urban environment, main causes of the changes in climatic elements are anthropogenic activities which produce; 1) particles and gases absorbing sunrays, 2) excessive heat emitted into atmosphere and 3) turn natural surfaces into impervious ones resulting again overheating due to albedo differences from its original forms.

In this respect, the study area, the city of Erzurum, harbors all the mentioned activities above either limited or extensively. Even though the city is not exposed to a dense industrialization to produce particles, gases and waste heat, air pollution sourcing from domestic heating and motor – vehicle traffic is largely on the scene in the city depending on the length and severity of winter weather conditions. In addition to carbon and excessive heat releasing activities, the city is also exposed to rapid and dense urbanization transforming agricultural or natural surfaces into concrete, asphalt or other artificial surfaces. Another effective factor for the city in the change of climatic elements may be the snow cover, which is regularly cleared away in urban area for transportation.

Urban was found to be warmer and drier in several studies evaluating various parameters such as urban population, surface characteristics and industrialization such as [18,4]. Present study shows clear U – R differences in all parameters evaluated e.g. mean, maximum and minimum temperatures and relative humidity in both 1st and 2nd periods and
Urban heat island is an important phenomenon for nearly all occupational disciplines from health care providers to city planners and environmental agencies to economists since its impacts are so diverse and cost much. Therefore, studies in literature are related to its every aspect from its density, causes, effects and mitigation. This study tries to follow the trend in urban – rural differences (density of UHI) in some climatic elements by comparing two

<table>
<thead>
<tr>
<th>Authors</th>
<th>Temperature differences Urban-Rural</th>
<th>Relative humidity differences Urban-Rural</th>
<th>Name of the observational area</th>
<th>Population of the area</th>
</tr>
</thead>
<tbody>
<tr>
<td>[22]</td>
<td>0.1°C (urban-suburban)</td>
<td></td>
<td>At 1221 stations in continental</td>
<td>Urban is more than 10.000</td>
</tr>
<tr>
<td>[21]</td>
<td>1.5 to 2.0°C</td>
<td></td>
<td>U.S.A</td>
<td>Rural is less than 2.000</td>
</tr>
<tr>
<td>[20]</td>
<td>2.2°C</td>
<td></td>
<td>Szeged (Hungary)</td>
<td>180.000</td>
</tr>
<tr>
<td>[18]</td>
<td>No difference</td>
<td></td>
<td>Barrow (Alaska. U.S.A)</td>
<td>More than 4600</td>
</tr>
<tr>
<td>[2]</td>
<td>8.0°C (maximum)</td>
<td></td>
<td>289 stations in Contiguous United States</td>
<td>Adjusted values were used</td>
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<tr>
<td>[4]</td>
<td>1.7°C (for the same area)</td>
<td>3.4%</td>
<td>Łódź (Poland)</td>
<td>780.000</td>
</tr>
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<td>[3]</td>
<td>2.5°C</td>
<td></td>
<td>Erzurum (Turkey)</td>
<td>366.962</td>
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<tr>
<td>[23]</td>
<td>2.5°C</td>
<td></td>
<td>Rome (Italy)</td>
<td>2.7 million</td>
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<tr>
<td>[5]</td>
<td>0.8°C</td>
<td></td>
<td>Erzincan (Turkey)</td>
<td>121.000</td>
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### TABLE 8

**Differences in the measured climatic elements between the areas**

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<tr>
<th>Climates</th>
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<th>Mean difference (Urban-Rural)</th>
<th>Maximum difference (Urban-Rural)</th>
<th>Minimum difference (Urban-Rural)</th>
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</thead>
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<td>Temperature (°C)</td>
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<td>3.2 (March)</td>
<td>-2.4 (May Rural is warmer)</td>
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</tr>
<tr>
<td>Maximum temperature (°C)</td>
<td>0.9</td>
<td>2.6 (January)</td>
<td>0.0 (July)</td>
<td></td>
</tr>
<tr>
<td>Minimum temperature (°C)</td>
<td>3.4</td>
<td>9.4 (December)</td>
<td>2.1 (April)</td>
<td></td>
</tr>
<tr>
<td>Relative humidity (%)</td>
<td>2.5 (Rural is more humid)</td>
<td>8.0 (November)</td>
<td>1.6 (September)</td>
<td></td>
</tr>
<tr>
<td>2nd Period</td>
<td>Mean difference (Urban-Rural)</td>
<td>Maximum difference (Urban-Rural)</td>
<td>Minimum difference (Urban-Rural)</td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>1.1</td>
<td>3.0 (February)</td>
<td>0.2 (October)</td>
<td></td>
</tr>
<tr>
<td>Maximum temperature (°C)</td>
<td>0.0</td>
<td>1.7 (January)</td>
<td>-0.6 (September; December)</td>
<td></td>
</tr>
<tr>
<td>Minimum temperature (°C)</td>
<td>2.6</td>
<td>4.6 (February)</td>
<td>0.0 (December)</td>
<td></td>
</tr>
<tr>
<td>Relative humidity (%)</td>
<td>5.0</td>
<td>8.2 (November)</td>
<td>1.5 (August)</td>
<td></td>
</tr>
</tbody>
</table>

Differences in parameters between the periods are seen clearly to be increased. Such differences can be seen as the result of general atmospheric circulation all over Turkey [19]. Due to only urbanization, the city faces to increased temperature values compared to rural. In addition to the increase in temperatures based on general atmospheric circulation, the city is exposed to 1.1°C higher yearly mean temperatures. Another parameter, relative humidity, is also open to discussion because it also increased in the second period in both areas. All these results show that the city is getting warmer and drier when compared to its rural counterpart. Depending on some interventions into naturally working mechanisms, e.g. large – extended transformation activities of natural and agricultural surfaces due to the construction of housing areas, increasing number of motor – vehicles, use of low quality fuels producing particles, smoke and gases and different reflectivity of snow cover in urban and rural.

### CONCLUSION

Urban heat island is an important phenomenon for nearly all occupational disciplines from health care providers to city planners and environmental agencies to economists since its impacts are so diverse and cost much. Therefore, studies in literature are related to its every aspect from its density, causes, effects and mitigation. This study tries to follow the trend in urban – rural differences (density of UHI) in some climatic elements by comparing two
different (batched) 3-year data sets belonging to rural and urban areas and two different time series (2002 – 2004 and 2014 – 2016).

Results show that as the climatic elements exhibit great changes in a short period of time even in its global circulation, urban areas are exposed to such effect nearly two fold more. In the example of Erzurum, urban climate is getting warmer and drier which is a condition that must urgently be taken under control for human health and better living environment.

Based on national economic development policies, nearly all cities of Turkey are expanding and sprawling mainly on natural lands causing larger impervious surfaces and waste heat. In order to reduce or remove such negative effects city planning principles must absolutely be followed and efficient urban green spaces must be considered in all large or small-scale projects. All the materials used in buildings as especially surface coatings and pavements must be selected from those respectful to climatic conditions e.g. not increasing temperatures.

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SESSION V
ECOTOXICITY AND BIODIVERSITY
THE ANTIBIOTIC RESISTANCE GENES IN ESCHERICHIA COLI ISOLATES FROM NARMAN LANDFILL (NL) AREA IN ERZURUM, TURKEY

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ABSTRACT

In this study, we aimed to investigate four antibiotic resistance genes (ARGs) [β-lactams resistant genes (bla\textsubscript{SIV} and bla\textsubscript{CTX-M}), and tetracycline resistant genes (tet\textsubscript{A} and tet\textsubscript{B})] in Escherichia coli isolates by PCR. For this purpose, samples were collected with refuse sampling technique (AK1, AK2, AK3, AK4) from Narman Landfill (NL, Erzurum, Narman) and from surface water of streams (D1, D2, D3, N1, N2) and around the natural environment of landfill (C1, K1), seasonally. Firstly, we used culture-dependent methods and molecular techniques to detect and quantify antibiotic-resistant bacteria (ARB) and antibiotic resistance genes (ARGs) in Escherichia coli.

Results showed that tested tet\textsubscript{A} and tet\textsubscript{B} genes have been detected in all landfill samples, suggesting that landfill served as ARGs reservoir. tet\textsubscript{A} was detected from the isolates from stations K1 and D3 in 2012; tet\textsubscript{B} were detected from stations K1 and D2 in 2012 and from D3 in 2013. bla\textsubscript{SIV} and bla\textsubscript{CTX-M} were not detected from any of the stations. Especially, antimicrobial-resistant bacteria have been detected in all landfill area (mostly in animal wastes and clinical wastes), and in surface water of streams near the landfill. The main pathways of spread of ARGs, found in and around landfill facilities, are thought to occur through environmental factors like leachate, surface waters and storms. Additional transmission vectors can be considered birds, insects and animals of the local environment.

KEYWORDS:
Landfill, Antibiotic resistance (AR), Antibiotic-resistant genes (ARGs), Narman.

INTRODUCTION

Nowadays, in order to dispose municipal solid waste (MSW) worldwide, landfills are the most used method. Because landfills include different kind of wastes, which may include sources of new pollutants, unused and/or expired antibiotics and bioactive wastes, they may also serve as a bioreactor for increased antibiotic resistance [1, 2]. Antibiotic resistance genes (ARGs) in landfill could flow into the environment through leakage of landfill leachate and pose potential risk to public health. Today, more than 65% of MSWs are not collected properly and disposed to unchecked dumpsites. As a result, MSWs in these areas are affecting approximately 64 million people. In addition during past decade, antibiotic usage of these developing countries has been increasing [3, 4]. Therefore making an assumption of antibiotic residues entering local wastes, discharge and disposal systems caused by inefficient MSW management and increased usage of antibiotics can be considered logical. Consequently, antibiotic compositions identified in landfill areas are similar to what is used by domestic population [1, 5].

In studies before, different kind of antibiotics, ARGs and antibiotic resistant bacteria (ARB) were detected in landfill leachate [1, 6, 7, 8]. For example, Wu et al. [7], detected 20 antibiotics and 6 ARGs (including sul\textsubscript{1}, sul\textsubscript{2}, tet\textsubscript{Q}, tet\textsubscript{M}, erm\textsubscript{B}, and mef\textsubscript{A}) in MSW. The landfill areas may have released large quantities of antibiotics into environment, which can cause the emergence and spread of ARBs and ARGs in different parts of environmental compartments, because of absences in disposal management [9, 10, 11, 12]. Global human health is having a recent challenge by the emergence of ARGs, which may be defined as a new emerging contaminant [12, 13, 14].

According to UNESCO, Geoparks are single, unified geographical areas where sites and landscapes of international geological significance are managed with a holistic concept of protection, education and sustainable development. Narman, the area of this study, has many long geo-routes with red fairy chimneys. Red fairy chimney-like shapes are extraordinary natural wonders formed by the erosion of sandy soil through the wind and rain over thousands of years. The geopark project for Narman, which also forms the base of this study, has started in 2012. In that time, our aim was only to complete the environmental impact assessment of this area and to get the permission of Narman.
becoming a geopark site. But determination of landfill potential effects, which is preferred as municipal solid waste in this particular area, has been identified as the other objective of the project.

In our first study [15], we identified *Escherichia coli* (*E. coli*) strains and calculated multiple antibiotic resistance index (MAR) index. Tetracycline resistance was found in 100% of *E. coli* isolates in that previous report [15]. Among all isolates, the highest resistance ratios after tetracycline were against ampicillin, followed by chloramphenicol, trimethoprim-sulfamethoxazole and nalidixic acid. The multiple antimicrobial resistance index (MAR) is useful in analysis of health risks, and is used to check antimicrobial resistance. It is expected to be lower than 0.2, but for this area, this index is found as the maximum value (0.7) in AK1, N1 and N2 stations. In addition, AK4, K1, D2 and D3 stations had the values of 0.5 and 0.6. After these results, it was necessary to investigate the ARGs in *E. coli* isolates by PCR, which formed this study.

In many studies, tetracycline resistance has been used as the key determinant to monitor resistance genes in natural environments such as rivers, lakes or seawater. For this reason, in this study, we aimed to investigate four ARGs [β-lactams resistance genes (*bla*SHV and *bla*CTX-M), and tetracycline resistance genes (*tet*A and *tet*B)] in *E. coli* isolates by PCR in and from surface water of streams and around the natural environment of landfill.

**MATERIALS AND METHODS**

**Description of Landfill and Sampling.** Sampling was performed at Narman Landfill (NL) in Erzurum, Turkey. This landfill, which is distanced from city center around 1 km, and 600 m from the closest water supply, is located in eastern semirural area of Erzurum. The area around the unsanitary dumpsite was chosen as the first station and, thereafter, other stations were selected according to the assessment on the environmental conditions and polluted areas (Figure 1).

In order to understand the effects of landfill on surface waters, eleven stations were selected for sampling in the study area. Four (AK1, AK2, AK3 and AK4) were around the main field, two (K1 and C1) were the source areas for water supply, and the last five (D1, D2, D3, N1 and N2) were further away from the sampling area, in direction on which the Narman stream flows. For a better understanding, Figure 2 presents a sketch map of sampling stations. In this figure, multiple antibiotic resistance index (MAR Index) data per stations were shown with symbols.

![FIGURE 1](image1.jpg)

**FIGURE 1**
Narman Landfill (NL) Sampling Area
FIGURE 2
The sketch map of landfill and the distribution of sampling sites with MAR index.

Bacterial collection. A total of thirty-six E. coli isolates, stored in the coliform collection of the Microbiology Research Laboratory of Veterinary Faculty of Istanbul University-Cerrahpaşa, which had been previously isolated from NL area were used in this study [15]. The antibiotic resistance results in landfill leachate and stream water samples were optimized according to our previous study [15]. The multi resistant E. coli isolates (according to the guidelines of Clinical Laboratory Standard Institute (CLSI; Clinical and Laboratory Standards Institute 2003), were evaluated in terms of the molecular characterization of four ARGs [β-lactams resistance genes (bla<sub>SHV</sub> and bla<sub>CTX-M</sub>], and tetracycline resistance genes (tetA and tetB)].

DNA Extraction and Quality Control. In our previous study, DNA extraction was performed on E. coli isolates. In this study, the yield and quality of the DNA extractions were verified again by spectrophotometry (NanoDrop<sup>®</sup> ND-1000, Thermo Scientific<sup>™</sup>, Plymouth Marine Laboratory-PML, UK). Obtained DNA extracts with the OD260/280 value between 1.8 and 2.0 were used. The DNA concentration of the samples was ranged between 39 and 1510 ng/μL. The qualified DNA extracts were stored at the -20°C for further ARGs analysis.

Examination of ARGs by PCR. In this study, two tetracycline resistance genes (tetA and tetB), and two β-lactams resistance genes (bla<sub>SHV</sub> and bla<sub>CTX-M</sub>) were screened by using the primer pairs as shown in Table 1. Polymerase chain reaction (PCR) were performed in a mixture of 25 μL containing 2.5 μL of 10x PCR Buffer (including 1.5 mM MgCl<sub>2</sub>), 0.5 μL dNTP Mixture (10 mM of each), 1 μL of each forward and reverse primer (10 pmol of each), and 0.2 μL Taq DNA polymerase (5U/μL), 2 μL template DNA and 17.8 μL nuclease free water (Bishop, Canada, WAT222.1). Taq PCR Core Kit (Qiagen, Germany, Cat No.201225) was used for PCR amplification.

The amplification of the samples were carried out by the thermocycler [Sensouquest thermal-cycler (Sensouquest, Germany)] as follows: for tet(A); initial denaturation at 94°C for 3 min followed by 25 cycles of 1 min at 94°C, 1 min at 57°C and 1 min at 72°C followed by 10 min at 72°C; for tet(B), at 94°C for 3 min followed by 30 cycles of 1 min at 94°C, 1 min at 52°C and 1 min at 72°C followed by 10 min at 72°C [16]; for bla<sub>SHV</sub> at 94°C for 5 min followed by 35 cycles of 1 min at 94°C, 1 min at 58°C and 1 min at 72°C followed by 10 min at 72°C [17]; for bla<sub>CTX-M</sub> at 94°C for 5 min followed by 36 cycles of 1 min at 94°C, 30 sec at 58°C and 1 min at 72°C followed by 10 min at 72°C [18].

Nuclease free water was used as negative control. E. coli AC76, and E. coli AC32 which were provided kindly by Prof. Dr. Osman Birol ÖZGÜMÜŞ (Microbiology & Molecular Biology Research Laboratory of RTE University), and previously confirmed field isolates from culture collection of Istanbul University- Cerrahpaşa, Faculty of Veterinary Medicine, Department of Microbiology, were used as positive controls for tet(A), tet(B), bla<sub>SHV</sub> and bla<sub>CTX-M</sub> respectively. The PCR products were visualized with UV light after electrophoresis on 1.5% agarose gel containing ethidium bromide (0.5 μg/ml, Bio Basic Inc.). The strains and their tetracycline properties are shown in Figure 3-4.
TABLE 1

Oligonucleotide primers used in the amplification of tetracycline resistance genes (tetA and tetB) and β-lactams resistance genes (blaSHV and blaCTX-M) [16, 17, 18]

<table>
<thead>
<tr>
<th>Primer name</th>
<th>Gene</th>
<th>Primer sequence</th>
<th>Amplification size (bp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tet (A)-1</td>
<td>tetA</td>
<td>5'- GTAATTCTGAGCACTGTCGC-3'</td>
<td>956</td>
</tr>
<tr>
<td>tet (A)-2</td>
<td></td>
<td>5'- CTGGCCTGGACAACATTGCTT-3'</td>
<td></td>
</tr>
<tr>
<td>tet (B)-1</td>
<td>tetB</td>
<td>5'- CTCAGTATTCCAAGCCTTG-3'</td>
<td>414</td>
</tr>
<tr>
<td>tet (B)-2</td>
<td></td>
<td>5'- ACTCCCCTGAGCTTGAGGGG-3</td>
<td></td>
</tr>
<tr>
<td>SHV-R</td>
<td>blaSHV</td>
<td>5'- GGTTATTCTTATTGGTGC-3'</td>
<td>928</td>
</tr>
<tr>
<td>SHV-F</td>
<td></td>
<td>5'- TTAGCGTTGCCAGTGCTC</td>
<td></td>
</tr>
<tr>
<td>CTX-M-R</td>
<td>blaCTX-M</td>
<td>5'- ACGCTGTTGTTAGGAAGT-3'</td>
<td>857</td>
</tr>
<tr>
<td>CTX-M-F</td>
<td></td>
<td>5'- TTGAGGCTGGGTAGAAGT -3'</td>
<td></td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Our previous study demonstrated a notable positive correlation between the abundance of *E. coli* and the amount of anions-cations, and also antibiotic wastes were detected at comparatively high abundance in both main landfill area and leachates. This area commonly contaminated with expired medicines, used baby diapers and toilet papers from home/healthcare units. When these wastes are dumped together with general wastes into a landfill, the enteric bacteria including *E. coli* originated from fecal-contaminated wastes can be exposed to many types of medicines including antibiotics. It is highly possible that *E. coli* may interchange their antibiotic resistance properties during a long incubation period inside the landfills [6, 7, 14]. The ARGs may be transferred by conjugation, transformation, and transduction into the pathogenic/ environmental bacteria living in the environment through the horizontal gene transfer mechanism. Existence of *E. coli* may be an important risk factor for the treatment of human infectious diseases caused by these microorganisms because coliform pathogens could acquire resistance genes from bacterial populations in aquatic environments by horizontal gene transfer to neutralize various groups of antibiotics. Results may suggest landfill could contribute to the enrichment of ARGs in the long-term.

In the present study, an interesting finding was that the diversity of antibiotic resistance in K1 was significantly higher than the diversity of the other stations (Figure 2). Existence of tetA and tetB genes in K1 station can be seen in Figure 3 and 4. The possible reason could be due to the location of K1 which is the basin of rain water collecting from NL.

In 2013, no ARGs were detected in any station except D3. The results suggest that different conditions could affect *E. coli* susceptibility to antibiotics in landfills. The physicochemical factors may affect antibiotic presence in landfills. Additional research must be performed to determine landfill operating conditions to minimize the development of antibiotic resistant bacteria [6].

D2 and D3 stations are in route of surface water streaming from both NL area and K1. In these stations, only tetA and tetB genes were detected in sampling years. While tetB was detected in D2 in 2012; for D3 tetA was identified in 2012 and tetB in 2013 (Figure 3,4).

With these results and considering their location, presence of ARGs in these stations are intriguing. According to Davison et al. [19] the release of bacteria into the environment, e.g. through hospital wastewater, favours the exchange of genetic materials with previously non-resistant populations thereby increasing the dispersion of resistant capacity in the environment. More studies suggesting this statement can be found [7, 14, 20, 21, 22, 23]. Both of our studies correlate with this statement.

![FIGURE 3](image_url)

*E. coli* isolates in 2012 and 2013 with tetA genes.
Characterisation has to be integrated with information from dose–response and hazard identification steps, to estimate the scope of the public health problem and to evaluate variability. To lower the concentration of ARGs in environment necessary precautions should be taken by local governments.

Prospective worldwide studies; explore co-occurrence of ARGs and related different genetic elements and identify ARGs-carrying bacteria, are encouraged for the better understanding of ARGs dissemination in landfill systems and neighboring environments. The presence of ARGs in landfill may be the result of the migration of unused and unwanted antibiotics from waste and ARGs from illegal waste (e.g., feces, activated sludge). Further studies are necessary to illuminate current situation.

**ACKNOWLEDGEMENTS**

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**REFERENCES**


**FIGURE 4**

*E. coli* isolates in 2012 and 2013 with *tetB* genes

In our previous study we found that the enteric bacteria concentrations of site N1 and N2 were different from other stations. Additionally, the best result of this study was no presence of ARGs in site N1 and N2, as these stations are used for irrigation and animal farming.

In our previous study, there were no multiple antimicrobial resistant bacteria in C1 and D1. Therefore these stations were not included in this study (Figure 3,4).

Another interesting result of the current study is that no ARGs were found in AK1, AK2, AK3, and AK4 *E. coli* isolates from those stations had high MAR index. Since we examined only four genes associated with resistance, the reason of lack of ARGs from those isolates can be caused by this situation.

Even though the sampling period was short, results of the study suggest that the surface waters in this region could be considered as a reservoir for the antibiotic resistance genes and it may result in a potential public health risk around the Narman area.

**CONCLUSIONS**

In some developing countries, uncontrolled landfill disposal is a common way to manage household wastes. However, it is difficult to reach sanitary landfills due to increasing population and distance between residential locations. Landfill composition is effected by rain and when the amount of rainfall is taken into consideration, surface and underground water sources tend to incur damage. In addition to environment, human health is also threatened.

Risk assessment studies must be carried out, including hazard identification, exposure assessment, and dose-response relationship. Also, the risk

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EFFECT OF CAPTOPRIL ON GROWTH DEVELOPMENT AND CUTICULAR SECRETION IN PUPAE OF THE MEDITERRANEAN FLOUR MOTH, *EPHESTIA KUEHNIELLA ZELLER*

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ABSTRACTS

Captopril is an inhibitor of angiotensin converting enzyme. It was tested *in vivo* by topical application on growth, development, whole body ecdysteroids and cuticular secretion in female pupae of The Mediterranean four moth *Ephestia kuehniella* Zeller (Lepidoptera: Pyralidae). The compound is diluted in acetone and applied topically to newly emerged pupae (10μg/pupa). Results show that treatment exhibited various morphological abnormalities on adult exuviation. Captopril induced precocious and lethal adult exuviations, and caused several malformations. The enzyme-immunoassay measurements of ecdysteroids in whole body extracts revealed that the drug increase the amount of ecdysteroids. Observation under a photonic microscope on the cuticle secretion showed that the captopril increase the thickness of the old and the new cuticle.

KEYWORDS: *Ephestia kuehniella*, development, growth, ecdysteroids, angiotensin converting enzyme, cuticle, captopril

INTRODUCTION

The Mediterranean flour moth, *Ephestia kuehniella* Zeller (Lepidoptera: Pyralidae), is one of the major pests in industrial flourmills in temperate climates [1]. Larvae reduce product quality by their presence and by the production of faeces and webbing, and they cause direct damage by feeding [2]. Control of these pests during storage is almost impossible and the application of various synthetic insecticides and fumigants to grain storage over the years has led to a number of problems, including the development of insecticide resistance in stored grain insect pests [3]. In order to fight against this pest it’s very important to know their physiology.

Angiotensin-converting enzyme (ACE) is a dipeptidyl carboxypeptidase and a key player in the renin angiotensin system, responsible for the removal of the C-terminal dipeptide of angiotensin I to generate the powerful vasoconstrictor, angiotensin II [4-5].

Little is known about the role of the invertebrate angiotensin converting enzyme (ECA) [6]. In several insects, a peptidyl dipeptidase similar to mammalian ACE has been found [7-9]. Captopril, a strong and specific inhibitor of ACE, is often used in the treatment of hypertension [10]. Thus, [6] reported that captopril and enalapril applied by injection into newly molted fifth instar larvae of *Spodoptera littoralis* stopped larval feeding and decreased their weight. Similarly, [11] found that lisinopril and captopril (2 μM) injected into *Manduca sexta* slowed larval growth rate. Other studies have provided data supporting the results of a study of the effects of ACE inhibitors on the development and survival of larval instars of both Aedes aegypti and Anopheles gambiae [11-13]. In Tenebrio molitor, we have shown that this compound affected the morphometric measurements of the ovary [14]. Lisinopril, another ACE inhibitor, induced a significant decrease in the whole body content of ecdysteroids in *E. kuehniella* pupae [15]. More recently [16] we have shown that captopril applied topically on newly molted pupae of *E. kuehniella* was found to decrease the duration of the oviposition period and the morphometric measurements of ovaries, the fecundity and the egg viability. Nevertheless, ACE inhibitors can be acutely toxic to insects, which contrasts with their life-span extending properties in rodents [17] and the nematode, Caenorhabditis elegans [18]. They have been useful in confirming important roles for ACE in reproduction, growth and development in several insect species [6, 13, 19-20]. ACE should be considered as a potential target for the development of newly insect growth regulators [11]. In the current study, it was evaluated the *in vivo* toxicity of captopril. The latter drug was, applied topically on newly molted pupae of *E. kuehniella*, and the effects on the, growth, development, whole body ecdysteroids and cuticular secretion in pupae were examined. The results will contribute to understand the mechanism of action of captopril.
MATERIALS AND METHODS

Insects  Ephesia kuehniella  (Zeller, 1879) was reared at 27°C and 80% relative humidity in almost continuous darkness as reported before [21]. Last instar larvae were collected from a stock colony, separated according to their sex and deposited in jars containing flour until pupation. Pupae were classified according to their age in days. Pupae were taken at various times after pupal eclosion (1, 3, 5, 7 and 9 days).

Chemical and treatment Captopril (D-3mer-capto-2-methyl-propionyl-L-proline) was purchased from Sigma Co. (98%, Bornem, Belgium). A stock solution of ACE inhibitor captopril (5 mg/ml) was prepared in acetone. Newly molted pupae (<8 h old) were topically treated (10 μg/pupa). In the control groups, pupae were treated with 2 μl of a solvent (acetone).

Morphological study Morphological analyses were conducted in order to detect possible abnormalities after captopril treatment. The morphological analyses were done on newly emerged adults (0 day). Each experiment used 60 individuals and was replicated three times. Adult aberrations were incomplete adult, emergence partially ecysed, malformed adult and total inhibition of adult [22].

Enzyme immunoassay of free ecdysteroids in whole body. In this study was used whole body extracts. Thus, female pupae were sampled from control and treated series at different times (0, 1, 3, 5, 7 and 9 days) during the pupal development. Each pupa was individually extracted with 300 μl of methanol by sonication, and after centrifugation (5000 g for 10 min), the supernatants were taken and evaporated. The extracts were suspended in phosphate buffer (0.1 M, pH 7.4). Each sample was analyzed in duplicate by enzyme immunoassay (EIA) as previously reported by [21] using a conjugate of 20 E coupled to peroxidase as the enzymatic tracer, tetramethyl benzidine as the color reagent and a rabbit B polyclonal antibody. Data are expressed in pg 20E equivalents per mg of body weight. Antibody was kindly supplied by Dr. J.P. Delbecque (University of Bordeaux I, France) and peroxidase by C. Blaise (Pierre and Marie Curie University, Paris, France).

Measurements of cuticle thickness in the integument The first 4 abdominal sternites are taken from pupae aged 0, 1, 3, 5, 7 and 9 days and were fixed according to [23] in paraformaldehyde (2%) and glutaraldehyde (3%) in cacodylate buffer (0.1 M, pH 7.4) for 12 h at 4°C, and then post-fixed with osmium tetroxide at 4% 1h dehydrated, embedded in Epon-araldite mixture Anderson and Ellis [24]. The semi-fine sections were made with ultramicrotome LKB V and stained with toluidine blue to measure the thickness of old and new cuticle.

RESULTS AND DISCUSSIONS

As a consequence of treatment with captopril disrupts nymphal development and induces early and lethal adult moults. Adult eclosion of individuals in the control group was 83.31%. The eclosion rates in treated series is significantly reduced and the value recorded is 28.76%. Several forms of morphological malformations resulted from treatment of newly ecysed pupae with captopril. There are four different morphogenetic types (Figure 1), normal adults, malformed adults, partially ecysed and blocked molt.

During pupal development the ecdysteroid titer in the control series increased from 116.45± 15 in 1 day to reach a peak of 243.50 ± 13.90 pg 20E/mg in 5 days and then decreased at day 7 (p< 0.0001). In the treated series, a similar trend was recorded. EIA measurements revealed that the captopril caused significant increases in the ecdysteroid titters (p=0.000) from the first day to the fifth day, at seventh day (p=0.016) (Figure 2). The secretion of the pupal cuticle begun from the transformation of larva to pupa and the thickness of the cuticle peaking at the third day (apolyosis) in control and treated series with captopril then started decreasing, while the secretion of the adult cuticle begun in fifth day. Captopril treatment caused a significant increase of the pupal cuticle (p<0.01). In fact, it significantly increased the thickness of the pupal cuticle in the 3rd day (p=0.001) and in fifth day (p=0.04). In addition, the captopril significantly increased (p=0.04) the thickness of the adult cuticle. (Figure 3). In the present study, we topically applied captopril on newly molted pupae. Results revealed that captopril affected moulting and induced a range of anatomical abnormalities in E. kuehniella. The pupation and eclosion rates were significantly reduced compared to controls. Pupae that did moult did not complete the process properly. The percentage of transformation of pupae to adults reduced from 83.31% to 28.73%. Several forms of morphological malformations resulted from treatment, incomplete adult, emergence partially ecysed, malformed adult and total inhibition of adult. Captopril is known to reduce pupation and eclosion rates of many insects like S. littoralis [20]. It has been reported that topical application of captopril to pupae of S. littoralis results in...
large increase in mortality, the percentage of successful adults formation was significantly reduced from 80% to 30% [20]. This effect of an ACE inhibitor on metamorphosis is evidence that the strong ACE gene expression seen during metamorphosis in holometabolous insects is important for adult development. When captopril and fosinopril two inhibitors with different modes of interaction with the ACE active site, were added to the rearing water, high levels of larval mortality were observed. This confirms the potential of insect ACE inhibitors as mosquito larvicides [25]. In insects 20-hydroxyecdysone (20E) and juvenile hormone (JH), play a central role in the regulation of growth and development [26]. 20E initiates all major developmental transitions, but it is an interaction with JH that transduces the 20E pulses into stage specific responses [26]. There is little literature on the physiological and biochemical processes related to molting and metamorphosis in insects compared to other aspects like reproduction [27]. In the present study, we demonstrated that captopril significantly increased the ecdysteroid titer during the pupal stage. Unlike our results lisinopril, another ACE inhibitor induced a significant decrease in the whole body content of ecdysteroids in E. kuehniella pupae [16]. The results concerning the effect of captopril on the secretion of the pupal and adult cuticle recorded in our experiments seems to be correlated with the increase in ecdysteroid contents with the secretion of cuticle in mealworms can be induced by 20E [29-31].

![Distribution (%) of different morphogenic types observed after treatment of females of E. kuehniella by captopril.](image1)

![Effect of captopril (10 μg/pupae), applied topically on newly molted pupae of E. kuehniella, on ecdysteroid amounts pg 20E equivalent/ mg weight during the pupal stage. Each value is the mean ± SD established on 6. Different letters indicate a significant difference (p < 0.05).](image2)
FIGURE 3
Effect of captoril (10 μg/pupa), applied topically on newly molted female pupae of *E. kuehniella*, on, the cuticles thickness during pupal development of old (A) and new cuticle (B). Each value is the mean ± SD established on 6. Different letters indicate a significant difference (p < 0.05)

CONCLUSION

In conclusion, our findings indicate that captopril negatively affects the hormonal control of metamorphosis causing perturbations in *E. kuehniella* development. Nevertheless, the precise way in which ecdysone is affected by captopril requires further research.

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THE USE OF BROADBAND VEGETATION INDICES IN CULTIVATED LAND DETECTION WITH LANDSAT 8 OLI MULTI-TEMPORAL IMAGES

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Istanbul Technical University (ITU), Faculty of Civil Engineering, Department of Geomatics Engineering, 34469, Maslak, Istanbul, Turkey

ABSTRACT

Determination of cotton and maize cultivated areas with multi-temporal satellite images using vegetation indices is the main objective of this research. Study area was located on Sanliurfa province, Turkey, which hosts huge amount of agricultural production of cotton and maize in spring-summer season with its suitable and effective irrigation system. The Landsat 8 OLI multi-temporal images acquired with 16-day interval were used to identify cultivated areas in the study area. Image acquisition dates from 30 April 2015 to 21 September 2015 completely covers the phenological development period of cultivated crop types. Terrain corrected images were radiometrically calibrated to produce Top of Atmosphere (ToA) reflectance images, in order to reduce the atmospheric and illumination effects, thus providing efficient multi-temporal analysis. ToA reflectance images were then used in vegetation index (VI) production. Normalized Difference Vegetation Index (NDVI), Transformed Difference Vegetation Index (TDVI), Enhanced Vegetation Index (EVI) and Green Normalized Difference Vegetation Index (GNDVI) were used in this research as vegetation suppression and data dimension reduction methods. Then VI image stacks were classified with pixel based Support Vector Machine (SVM) algorithm and results were compared with statistical production database to evaluate the effectiveness of broadband VIs in cultivated area and crop pattern detection. Results of the analysis provided that, GNDVI based dataset provided highest accuracies according to areal comparison and point based accuracy assessment. NDVI and TDVI based datasets were ranked as the second with similar accuracy results, while EVI based dataset was in the last place when compared to remaining VI datasets. Additionally, area determination efficiency and classification accuracy for the cotton was higher than the maize nearly in all regions.

KEYWORDS:
Cultivated area mapping, crop type identification, multi-temporal satellite image, broadband vegetation indices, support vector machine classification

INTRODUCTION

Determination of the cultivated areas and crop types is crucially important in yield estimation and gross agricultural production determination, but also considerably essential in terms of environmental monitoring as agricultural activities affect the environment directly by increasing the use of water resources and nutrient loads in soil. Moreover, vegetation development has also direct impact on carbon cycle due to photosynthesis progress [1, 2, 3].

One of the efficient methods for cultivated area and crop type determination is the satellite image based analysis. Satellite images provide timely and accurate information for environmental and agricultural monitoring with their large coverage capability and their sensitivity to surface spectral responses [4, 5, 6]. Crop types can be identified by their unique spectral reflectance characteristics in their different development stages, thus they can be effectively mapped for large spatial extends by classification of the satellite images [7].

Previous researches showed that, using a single date image classification for crop type identification may result with insufficient results if the image acquisition date is not suitable for differentiating the crops spectrally [4, 8, 9]. As single date image analysis requires a very specific acquisition time interval, most of the researches rely on multi-temporal images acquired periodically during the growing season of the crops [10, 11, 12]. At this point, using all of the image spectral bands will be time and source consuming as processing of the huge amount data is not feasible, thus a data dimension reduction strategy becomes vital. The broadband vegetation indices (VI) are proved as being one of the most effective ways to detect the vegetative situation of crops and can be used to reduce data dimension in agricultural researches [13].

This study aims to investigate the use of different VIs in determination of the cotton and maize cultivated areas with multi-temporal Landsat 8 OLI satellite images. For this purpose, VI time series were classified by use of SVM classification algorithm. Accuracy of the analysis results was determined by areal comparison with farmer registration system (FRS) and point based accuracy assessment.
MATERIALS AND METHODS

Study Area. Study area is located in Sanliurfa province, south eastern part of Turkey. Province has important contribution to cotton and maize production with its agriculturally important plains [14]. Three districts of the province namely: Eyyubiye, Harran and Akçaçale, were selected considering their high production rates according to FRS statistics. Figure 1 demonstrates the geographical location of the study area coupled with borders of the districts overlaid on VI dataset.

Satellite Images and Pre-processing. Landsat 8 OLI images were acquired with 16 day intervals were used in this research. 8 satellite images were selected according to phenological stages of the crops between 30.04.2015 and 20.08.2015. Images were downloaded as Level 1T in which radiometric calibration and orthorectification was performed. Then, images converted to Top of Atmosphere (ToA) reflectance data and results were saved as stack of 30m resolution multispectral bands. ToA images were clipped according to district boundaries for further processing.

Vegetation Indices. In this study, the performance of four VIs were evaluated for multi-temporal crop type identification. The first one is the Normalized Difference Vegetation Index (NDVI), which has been used extensively in environmental and agricultural studies for three decades. NDVI is a measure of green vegetation with use of absorption and reflectance wavelengths for vegetation [15]. Formulae is presented in Equation 1.

NDVI = (NIR — RED)/(NIR + RED)  (1)

The second index used in this study is the Transformed Difference Vegetation Index (TDVI), which asserted to be useful in monitoring vegetation in urban lands. This index does not saturate like NDVI [16]. Formulae is presented in Equation 2.

TDVI = SQRT ((0.5 + (NIR-RED)) / (NIR+RED))  (2)

The third index used in this study is Enhanced Vegetation Index (EVI), which initially developed as a standard MODIS product. This index uses the blue wavelength region for correction of soil background and atmospheric effects [17]. Formulae is presented in Equation 3.

EVI = 2.5 * (NIR-RED) / (NIR+6*RED-7.5*BLUE+1)  (3)

The last index is called as Green Normalized Difference Vegetation Index (GNDVI), which is similar to NDVI but using the green wavelength instead of red. It is more sensitive to chlorophyll concentration when compared to NDVI [18]. Formulae is given in Equation 4.

GNDVI = (NIR - GREEN) / (NIR+GREEN)  (4)

Support Vector Machine Classification. Support Vector Machine (SVM) is a machine learning based classification algorithm, which separates the data according to a decision surface that maximizes the separation between classes. The surface is called as optimal hyperplane and vectors defined by the closest points to the hyperplane are called support vectors [19]. In this study, RBF kernel based SVM classification was applied to all dataset by use of same training set for each region.

Accuracy Assessment. Accuracy assessment of the results was performed with two approaches. In the first approach, areal statistics of crop classes were compared to FRS statistics and relative errors for each data type in each region was calculated. In the second approach, 100 stratified random points were produced and error matrices were calculated with class labels and corresponding ground truth information [20]. User and producer accuracy metrics were derived from these matrices [21].
RESULTS AND DISCUSSION

Classification was performed by SVM algorithm in order to determine 5 classes namely, cotton, maize, barelands, impervious surfaces and wetlands & water bodies for each district (Figure 2-4). Areal statistics were derived from classification results belonging to 4 different index dataset in each region. This information was compared with Farmer Registration System (FRS) records (Table 1). According to comparison results, determination of cotton planted lands was more successful than maize planted lands for all regions. Area determination accuracy was over 95% for cotton in nearly all datasets. Area determination of maize planted lands were mostly satisfactory, however in Eyyubiye region, areal error reached 20 percent. GNDVI provided slightly better performance than the other indices overall. Remaining indices showed similar performance in terms of area determination. Harran region showed the highest accuracies for all datasets and for the both crop types. Accuracy assessment was performed with 100 stratified random points in each region and for four different datasets (Table 2). According to results GNDVI dataset provided comparatively best results while EVI dataset provided worst. Poor estimation of maize planted lands in Eyyubiye region also observed in point based accuracy assessment. Cotton planted lands classified more accurate in all regions and with all data types when compared to maize. Highest overall accuracy was reached in Harran region.
Classification results of Harran district.

**Table 1**
Areal comparison of classification results with farmer registration system statistics

<table>
<thead>
<tr>
<th></th>
<th>NDVI</th>
<th>TDVI</th>
<th>GNDVI</th>
<th>EVI</th>
<th>FRS</th>
<th>ESNDVI</th>
<th>ETNDVI</th>
<th>EGNDVI</th>
<th>EEVI</th>
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<tr>
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<tr>
<td>Cotton</td>
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<td>302.473</td>
<td>309.980</td>
<td>294.039</td>
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<td>0.04</td>
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<td>0.07</td>
<td>0.06</td>
<td>0.05</td>
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<tr>
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<tr>
<td>Cotton</td>
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<td>319.377</td>
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<td>317.680</td>
<td>333.400</td>
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<td>54.181</td>
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<td>53.998</td>
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<td>0.21</td>
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<tr>
<td>Cotton</td>
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<td>353.155</td>
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**Table 2**
Point based accuracy assessment of classification results

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<tr>
<th></th>
<th>NDVI</th>
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<th>GNDVI</th>
<th>EVI</th>
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<th>Prod Users</th>
<th>Prod Users</th>
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<tr>
<td>Cotton</td>
<td>87.50%</td>
<td>87.50%</td>
<td>84.62%</td>
<td>88.00%</td>
<td>91.67%</td>
<td>95.65%</td>
<td>82.14%</td>
<td>88.46%</td>
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<tr>
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<td>83.33%</td>
<td>90.91%</td>
<td>86.36%</td>
<td>95.00%</td>
<td>80.00%</td>
<td>90.91%</td>
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<tr>
<td>Overall</td>
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<td>88.00%</td>
<td>84.00%</td>
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<tr>
<td>Cotton</td>
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<td>91.30%</td>
<td>86.96%</td>
<td>90.91%</td>
<td>90.91%</td>
<td>86.96%</td>
<td>81.82%</td>
<td>85.71%</td>
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<tr>
<td>Maize</td>
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<td>71.43%</td>
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<tr>
<td>Cotton</td>
<td>88.00%</td>
<td>91.67%</td>
<td>88.00%</td>
<td>84.62%</td>
<td>92.00%</td>
<td>100.00%</td>
<td>80.00%</td>
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<tr>
<td>Maize</td>
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<td>89.47%</td>
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CONCLUSIONS

This study demonstrated the use of broadband vegetation indices for crop type and area determination with satellite image time series. Four different indices were evaluated for their effectiveness in cultivated land determination in three agriculturally active regions. GNDVI provided best results for type identification and area determination, NDVI and TDVI provided similar results, while EVI provided comparatively worst results. Additionally, cotton plant determination was comparatively better than maize according to both the areal comparison and point based accuracy assessment. Dense time series provided a good spectral response to differentiate crops. Further study is planned to reduce the image amount according to spectral profiles and to evaluate other classification algorithms including the object based classification.

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EVALUATION OF NANOSILVER ECOTOXICITY USING REPRESENTATIVES OF DISTINCT TROPHIC LEVELS

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2Department of Chemistry and Biochemistry, Mendel University, Brno, Czech Republic
3Central European institute of Technology, Brno University of Technology, Technicka 3058/10, CZ-61600 Brno, Czech Republic

ABSTRACT

Silver nanoparticles are used in a wide range of products, mainly because of their antibacterial effect. However, increasing production and utilisation of nanosilver pose risks. The aim of this study was to examine the acute toxicities of silver nitrate and four nanosilver suspensions of varying particle sizes (0.7 – 100 nm) to aquatic organisms and find out the biological effect of small and large sized nanoparticles. Nanoparticles were characterized by transmission electron microscopy (TEM) and by dynamic light scattering (DLS). Tests were conducted with representatives of different trophic levels such as producers (green freshwater algae Pseudokirchneriella subcapitata), consumers (water fleas Daphnia magna) and destruents (marine bacteria Vibrio fischeri). Experiments were carried out methodologically in accordance with the following standards: OECD 201 guideline, OECD 202 guideline and ISO 11348-2. Daphnia magna showed the highest sensitivity to the tested silver nanoparticles from all three organisms. On the other hand, the lowest toxicity of all tested samples was recorded for Vibrio fischeri.

KEYWORDS:
Silver nanoparticles, silver nitrate, Daphnia magna, Pseudokirchneriella subcapitata, Vibrio fischeri

INTRODUCTION

Silver nanoparticles (AgNPs) are used as an antimicrobial agent in various commercial products, varying from medical devices to consumer goods like clothes and personal hygiene products. The increasing production and utilisation of silver containing products will surely lead to the release of AgNPs into the environment [1]. The predicted environmental concentrations of AgNPs in the environment are in the range from 0.01–0.43 μg.L⁻¹ [2]. One of the main routes of entry of AgNPs into the environment is from washing clothes, which contain silver [4]. Despite the growing commercialization of silver containing products, little is known about the environmental effect associated with their widespread use [5]. The ionic silver is considered as the most toxic for fish and invertebrates [6].

Size has been considered as one of the characteristic that affects toxicity. Therefore, the objective of the study was to find out the biological effect of small and large sized AgNPs in comparison with AgNO₃ exposure for three aquatic species. In the research plan, we assumed that smaller AgNPs have a higher toxic effect.

MATERIALS AND METHODS

Test organisms. Daphnia magna was obtained from an in-house culture collection of the Ecotoxicological laboratory of the University of Veterinary and Pharmaceutical Sciences Brno, Czech Republic. The green algae Pseudokirchneriella subcapitata (Korshikov) Hindak comes from the collection of autotrophic organisms of the Botanical Institute of the Academy of Sciences in Trebon, Czech Republic. The liquid dried bacteria Vibrio fischeri were commercially supplied (Hach-Lange GmbH in Dusseldorf, Germany).

Inhibition of mobility of Daphnia magna. The immobilization test of D. magna was performed according to the OECD 202 guideline (CSN EN ISO 6341 – Determination of the inhibition of mobility of Daphnia magna Straus). Testing was performed with neonates (<24h), which were kept in 100 mL glass beakers with dilution water with different concentrations of AgNO₃ and AgNPs. Daphnia specimens in the control were exposed to dilution water only. Test beakers were maintained at temperature of 20–23 °C ± 2 °C inside a controlled temperature chamber with a photoperiod (16 h of light and 8 h of dark). Immobilization of daphnids was recorded after 24 and 48 hours. From the number of immobilized individuals at the test concentrations compared to control, the 48hEC50 value was determined by the probit analysis [7, 8].
Freshwater algal growth inhibition test. The growth rate inhibition of *P. subcapitata* was performed according to the guideline OECD 201 (CSN EN ISO 8692 – Fresh water algal growth inhibition test with unicellular green algae *P. subcapitata*) with adaptations to fit our experimental conditions [9, 10]. Test medium was prepared as described in the guideline. A drop of the algal inoculum was transferred to the Bürker counting chamber and under a microscope the algae were counted. The initial concentration of 25 × 10⁴ algae cells/mL was applied to 250 mL Erlenmeyer flasks in the prepared concentration ranges and controls. Flasks were incubated in a controlled chamber at 26 ± 2 °C for 72 h under continuous illumination (6000-10000 lux). The test endpoint was the algal culture growth rate inhibition after 72 ± 2 h of exposure compared to the control. The 72hErC50 value was calculated using the software program TOXICITA 3.1. For the test to be valid, we followed the criteria mentioned in the guideline [11, 12].

Inhibitory effect on the light emission by *Vibrio fischeri*. The experiment was performed under the conditions specified in ISO 11348-2 (CSN EN ISO 11348-2 – Determination of the inhibitory effect of tested substances on the light emission of *V. fischeri*). Rehydrated bacteria were exposed to varying silver nanoparticle concentrations dissolved in the dilution solution. Since *V. fischeri* is a marine organism, the test medium is a 2% NaCl solution. Bacteria and the prepared dilution were stored in glass cuvettes [13].

**Chemicals.** Silver nitrate was purchased from Sigma-Aldrich (St. Louis, MO, USA) as a crystalline powder, 99% purity CAS 7761–88–8. AgNO₃ was used as the source of silver ions. Commercial colloidal silver was supplied by Koloindri stribro s.r.o. (Zlin, Czech Republic). The declared particle size was 10–100 nm. Colloidal silver of particle size 100 nm was made by the Silver Medic Ultra generator (MANAUTIK s.r.o., Krtiny, Czech Republic). AgNPs with 0.7–2.7 nm and 6.5–18.2 nm size ranges were synthesized at Mendel University as described below.

**Silver nanoparticles.** The AgNPs with different sizes (AgNPs1: 0.7–2.7 nm) and (AgNPs2: 6.5–18.2 nm) were synthesized by aqueous chemical reduction method using gallic acid as a reducing and stabilizing agent. When preparing AgNPs1 and AgNPs2, the reduction reaction was carried out at pH 11 and 10 [14]. AgNPs were characterized by TEM (Tecnai F20, FEI, Eindhoven, Netherlands) and DLS (Zetasizer Nano ZS90, Malvern Instruments, Worcestershire, UK).

Analyzes were performed in phosphate buffered saline (pH 7.4). Prior to measurements, samples were incubated at 25 °C for 15 min.

All test solutions were prepared by dilution of the initial dispersion of AgNPs/AgNO₃ in the culture media to the desired concentration. Concentrations were selected on the basis of the range finding test. The tests were performed in three replicates at each test concentration and controls. Test concentrations and stock solutions of AgNPs and ionic form of silver are presented in Table 1.

**Statistical analysis.** The 72hErC₅₀ values were calculated using the TOXICITA 3.1 software (VUV Ostrava, Czech Republic) by means of regression analysis of data with 95% confidence interval, based on squared deviations of experimental values from the selected approximation function.

The 48hEC₃₀ values, as well as their associated 95% confidence intervals (95% CI), were determined by probit analysis using a computer program (PROBITY VURH, Vodnany, Czech Republic).

### TABLE 1

Overview of the stock solutions and test concentrations of AgNPs and AgNO₃.

<table>
<thead>
<tr>
<th>Test organisms</th>
<th>AgNO₃</th>
<th>0.7–2.7 nm</th>
<th>6.5–18.2 nm</th>
<th>10–100 nm</th>
<th>100 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>s.s.</td>
<td>10 mg.l⁻¹</td>
<td>10 mg.l⁻¹</td>
<td>10 mg.l⁻¹</td>
<td>6 mg.l⁻¹</td>
<td>4, 10, 12, 16, 20 µg.l⁻¹</td>
</tr>
<tr>
<td>Daphnia magna</td>
<td>1, 1.5, 2, 2.5, 3 µg.l⁻¹</td>
<td>0.5, 0.7, 0.9, 1.2 µg.l⁻¹</td>
<td>0.5, 1.5, 2, 2.5 µg.l⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s.s.</td>
<td>10 mg.l⁻¹</td>
<td>10 mg.l⁻¹</td>
<td>10 mg.l⁻¹</td>
<td>20 mg.l⁻¹</td>
<td></td>
</tr>
<tr>
<td>P. subcapitata</td>
<td>10, 25, 50 µg.l⁻¹</td>
<td>1.5, 2.5, 3.5, 4.5, 6.5 µg.l⁻¹</td>
<td>1, 2, 3, 4, 5 µg.l⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s.s.</td>
<td>100 mg.l⁻¹</td>
<td>66.5 mg.l⁻¹</td>
<td>10 mg.l⁻¹</td>
<td>10 mg.l⁻¹</td>
<td>8 mg.l⁻¹</td>
</tr>
<tr>
<td>Vibrio fischeri</td>
<td>100, 50, 25, 12.5, 6.25 mg.l⁻¹</td>
<td>10, 5, 2.5, 1.25, 0.63 mg.l⁻¹</td>
<td>10, 5, 2.5, 1.25, 0.63 mg.l⁻¹</td>
<td></td>
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</tr>
</tbody>
</table>

s.s.- stock solution
TABLE 2
Summary values of EC50 of AgNPs and AgNO3.

<table>
<thead>
<tr>
<th>Test organisms</th>
<th>AgNO3 0.7–2.7 nm</th>
<th>6.5–18.2 nm</th>
<th>10–100 nm</th>
<th>100 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Daphnia magna</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48hEC50 (μg.l⁻¹) 95% CI</td>
<td>1.964 (1.73-2.23)</td>
<td>23.377 (20.54-26.21)</td>
<td>1.680 (1.43-2.03)</td>
<td>1.470 (1.26-1.68)</td>
</tr>
<tr>
<td><strong>P. subcapitata</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>72hErC50 (μg.l⁻¹) 95% CI</td>
<td>36.65 (36.65-36.65)</td>
<td>43.450 (43.45-43.45)</td>
<td>4.480 (4.48-4.48)</td>
<td>95% CI</td>
</tr>
<tr>
<td><strong>Vibrio fischeri</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15’ EC20; 30’ EC50 (μg.l⁻¹)</td>
<td>5170 fk 0.99</td>
<td>16490 fk 1.10</td>
<td>723 fk 1.11</td>
<td>453 fk 1.05</td>
</tr>
<tr>
<td></td>
<td>1.08</td>
<td>9090 fk 1.22</td>
<td>1255 fk 1.25</td>
<td>2103 fk 1.10</td>
</tr>
</tbody>
</table>

*ErC20, 95% CI - 95% confidence interval; fk - correction factor for 15 or 30 min incubation must be between 0.6–1.8.

FIGURE 1
TEM micrographs and particle size histograms of investigated AgNPs: (a) AgNPs-1 (0.7–2.7 nm); (b) AgNPs-2 (6.5–18.2 nm). The representative TEM micrographs demonstrates the variety of AgNPs sizes and their oval-to-spherical morphology.

RESULTS AND DISCUSSION

To confirm the size-effect hypothesis, we produced and purchased AgNPs of different particle sizes.

Non-commercial AgNPs were characterized for their morphology and size distribution (Fig. 1). Synthesized AgNPs had oval-to-spherical morphology. From the performed particle size analysis was found that more than 65% of AgNPs-1 were within the size range 0.8–1.1 nm, while nearly 75% of AgNPs-2 were within the range 7.8–10.1 nm.

The ecotoxicity of AgNPs and silver nitrate was determined on three species representing different levels of an aquatic trophic chain. The results EC50 of AgNPs and AgNO3 on the tested organisms are shown in table 2.

The 72hErC50 value of AgNO3 for the growth inhibition of P. subcapitata was 36.65 μg.l⁻¹ and 48hEC50 for Daphnia magna was 1.96 μg.l⁻¹. Similar results were seen in other studies, e.g. the EC value of AgNO3 for P. subcapitata was 33.79 μg.l⁻¹ and for D. magna the value was 1.36 μg.l⁻¹ [1] and 2.51 μg.l⁻¹ [15] AgNO3 toxicity has been attributed to the
free silver ion Ag⁺. Ksiazyn et al. (2015) investigated the toxicity of AgNPs with the average size of particles 34 ± 18 nm to P. subcapitata and obtained LC₅₀ of 1630 μg.l⁻¹, many fold higher than our results (43.45 μg.l⁻¹). This difference could be related to the particle size – in our studies the particles were smaller (having diameter of 0.7–2.7 nm). To the best of our knowledge, this AgNPs are among the smallest AgNPs used in ecotoxicological testing. Most ecotoxicological studies evaluate nanoparticles size from 3 nm and above. Li et al. (2010) tested different sized AgNPs (33–66 nm) and observed a LC₅₀ for D. magna of 3–4 μg.l⁻¹. Our effective concentration was 1.47 μg.l⁻¹ for AgNPs (10–100nm) and 14.78 μg.l⁻¹ for size of 100 nm. The differences among EC₅₀ values are related to differences in particle characteristics and size. For commercial silver was declared size 10–100 nm without the known particles size distribution. From our results based on EC₅₀ values, it is cleared that this sample contained a higher proportion of smaller particles. The EC₅₀ and ErC₅₀ values approximate to AgNPs with particles size of (6.5–18.2 nm) than to silver with particles size of (100 nm). Testing of commercial nanoparticles is not accurate and therefore it is not suitable for ecotoxicological experiments. In our study, Daphnia magna showed the highest sensitivity to the tested AgNPs. Since Daphnia are part of the diet of other organisms (e.g. fish), there is a potential for uptake and the subsequent transfer of AgNPs to higher organisms. Toxicity of AgNPs has been found for many kinds of organisms (e.g. bacteria, algae or fish), Daphnia were the most sensitive [18].

Vibrio fischeri was the least sensitive to the silver nanoparticles. The 30 EC₅₀ value for AgNO₃ was 16490 μg.l⁻¹ and for AgNPs 1255–9090 μg.l⁻¹. In another study, the 50% effective concentration of four different surface-coated AgNPs with an average particle size of 20 nm was 1570 to 5190 μg.l⁻¹ [19]. Only few studies have measured the toxicity of AgNPs for marine organisms, which makes it difficult to determine the mechanism of toxicity. Such a low toxicity of AgNPs and AgNO₃ to marine bacteria results probably from changes in toxic effect of silver due to chloride complexation. Silver in the presence of any salt always creates silver chloride. This can have a major effect on the stability of AgNPs, as well as on their toxicity [19, 20].

CONCLUSION

The ecotoxicity of silver nanoparticles and ionic form of silver varies considerably according to the test organisms and particle size. The lowest toxicity of all tested samples was observed in bacteria while the highest toxicity was in Daphnia. The low EC₅₀ (ErC₅₀) values show high toxicity to Daphnids and confirm the strong bactericidal and algicidal effects of AgNPs. These organisms are good bioindicators for assessing the acute toxicity of environmental contaminants.

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**IN-VITRO ANTIOXIDANT, A-GLUCOSIDASE AND A-AMYLASE INHIBITORY ACTIVITIES OF CRUDE ETHANOL EXTRACT AND FRACTIONS OF ENDEMIC HYACINTHELLE ACUTILOBA K.PRESS. & WENDELBO BULBUS**

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**ABSTRACT**

In the present study, the antioxidant potential as well as the α-amylase and α-glucosidase inhibitory activity of different extracts of *Hyacinthella acutiloba* bulbus were investigated using an *in vitro* model. Antioxidant activity was assayed by the DPPH radical scavenging activity, total phenol content (TPC) and total flavonoid content (TFC), reducing power assay, ferric thiocyanate (FTC) and thiobarbituric acid method (TBA). Among the extracts, n-hexane and chloroform extract of *H. acutiloba* displayed more activity than other extracts against α-amylase and α-glucosidase.

**KEYWORDS:**
*H. acutiloba*, antioxidant, α-amylase, α-glucosidase

**INTRODUCTION**

Diabetes mellitus (DM) is a metabolic disorder direct afflicting populations of both developing and developed countries. Recent reports have estimated that there is a dramatical increase in the prevalence of diabetes year by year. More attention is drawn to herbal drugs due to they are known to cause less adverse effects compared to conventional antidiabetic drugs [1-4].

DM is characterized by abnormal increase of blood glucose level, which is regulated by α-glucosidase. α-glucosidase inhibitors (AGIs) can control the blood sugar level by competitively inhibiting glycosidase activity and preventing the fast breakdown of sugars, therefore used as a new class of anti-diabetic drugs [5]. Although many studies on the antidiabetic activity of medicinal plants have been reported up to now, there is still a need to work to characterise and identify active plant-driven natural compounds. AGIs drugs are unsatisfactory due to their advers effects related with gastro-intestinal system and lower bioavalibility [6-7]. Therefore, more effective, less side-effect and less toxic α-amylase and α-glucosidase enzyme inhibitors from natural sources have been sought for the treatment of diabetes and its complications [8].

Mainly two carbohydrate hydrolyzing enzymes (α-amylase and α-glucosidase) are responsible for postprandial hyperglycemia [9]. α-amylase joins the process of carbohydrate digestion by hydrolysis of 1,4-glycosidic linkages of polysaccharides (starch, glycogen) to disaccharides. α-glucosidase catalyzes the disaccharides to monosaccharides, which leads to postprandial hyperglycemia [10].

Oxidative stress is closely related to diabetes mellitus. In DM, high blood glucose level determines overproduction of reactive oxygen species (ROS) by the mitochondria electron transport chain. Thus, it leads to chemical changes of cellular compounds such as DNA, protein and lipid peroxidation. Therefore, oxidative stress plays a pivotal role in the development of diabetes complications [11]. Hence the use of natural antioxidants has been beneficial in alleviating the severity of diabetic symptoms [12].

*Hyacinthella acutiloba* K.Perss. & Wendelbo belongs to Asparagaceae family, an endemic plant, mainly distributed in Kayseri, Sivas, Malatya and Erzincan province in Turkey. On the Turkey map, the plant mainly located at B6 and B7 grids [13]. *Hyacinthus orientalis* L., the species systematically closest to our study material was investigated for its phytochemical compounds and more than 40 polyhydroxylated alkaloids in other name as iminosugars were isolated [14].

This study mainly focuses on the evaluation of *in vitro* antioxidant and antidiabetic activity of the endemic plant *H. acutiloba* that could be effective in the treatment of diabetes mellitus.
MATERIALS AND METHODS

Reagents and chemicals. All the chemicals used in this study were of analytical grade. 2, 2-azino-bis (3-ethyl benzothiazoline-6-sulfonic acid) di-ammonium salt (ABTS), butylated hydroxy anisole (BHA), 2, 2-diphenyl-1-picryl-hydrazyl (DPPH), linoleic acid, α-amylase and α-glucosidase enzyme were purchased from Sigma Chemicals Co (St. Louis, MO, USA).

Plant materials. Hyacinthella acutiloba was collected in March 2015 from natural habitats at Ulus-Sivas province of Turkey. Identification and collection of the endemic plant was done by botanist Dr. Mehmet Tekin.

Extraction and fractionation. The finely dried and powdered bulbus (200 g) were macerated with ethanol (2000 mL, 80% v/v aqueous ethanol) overnight at room temperature. The suspension was filtered through a filter paper and the residue was extracted with same volume of ethanol twice. The filtrates were combined and the ethanol was evaporated in vacuum with rotary-evaporator (Buchi, R-100) to give ethanol extract (13.67 %). The ethanol crude extract was suspended in 500 mL of water and fractionated successively with n-hexane (Hex), chloroform (CHCl3), ethylacetate (EtOAc), n-butanol (ButOH), and water to yield the Hexane (HAH: 1.88%), Chloroform (HAC: 1.32%), EtOAc (HAEA: 6.07%), n-Butanol (HAB: 0.31%), and water (HAW: 2.48%) fractions. Each fraction was tested by the in vitro antioxidant and antidiabetic assays in order to determine the most active fraction. All the fractions were stored in a freezer at -20°C until their use for bioassay.

In-vitro antioxidant activity. DPPH free radical scavenging effect were estimated according to Lee et al [15]. DPPH was prepared daily in 80% methanol and stored at 4°C in the dark. Stock solutions of the test samples were prepared with methanol at 2 mg/mL concentration and diluted in 96-well plates. Then 150 µL DPPH solution was added to 50 µL of different concentration of test samples on each well. After thoroughly mixing, covered with aluminium foil and stand for 30 minutes in the dark. Then optical density (OD) at a wavelength of 517 nm was read with Elisa reader. As a control, the OD value of the DPPH solution without the test sample was measured. All tests and analyzes were run in triplicate and the results were given as mean ± standard deviation. Antioxidant activity results were calculated as a percentage of DPPH inhibition according to the following equation:

\[
\text{% Inhibition} = \left( \frac{A_a - A_b}{A_a} \right) \times 100
\]

where:
- \( A_a \): The absorbance value of the control group
- \( A_b \): The absorbance value of the test group

Reducing power method. Reducing power of extracts were evaluated by Oyaizu et al. [16]. Briefly, 2.5 mL of 0.2M phosphate buffer (pH=6.0), 2.5 mL of 1% (w/v) K3Fe(CN)6 and 1 mL of test samples / BHT / α-tocopherol in various concentrations (20-1000 µg/mL) were mixed in test tubes separately. Then incubated for 20 min at 50°C. After that, 2.5 mL of 10% trichloroacetic acid (TCA) was added and centrifuged at 2500 rpm for 10 min. Then 2.5 mL of upper layer were mixed with 2.5 mL distilled water, absorbance was measured at 700 nm using a UV-VIS spectrophotometer.

Ferric thiocyanate method (FTC). The antioxidant activity of the extracts on lipid peroxidation inhibition was determined according to the ferric thiocyanate method reported by Kikuzaki [17]. 4 mL of 1 mg/mL extract / fractions /standards (BHT, Vc) in 99% ethanol, 4.1 mL of 2.52 % linoleic acid in absolute ethanol, 8 mL of 0.05 M phosphate buffer (pH=7.0) and 3.9 mL of distilled water were mixed together in falcon tubes and then were placed in dark at 40°C. Then 9.7 mL of 75% ethanol, 0.1 mL of 30% ammonium thiocyanate, 0.1 mL of 0.02 M FeCl3
(prepared in 3.5% HCl acid) was added to 0.1 mL of this mixture. Exactly 3 min later, the absorbance was measured at 500 nm for every 24h about 8 days.

**Thiobarbituric acid (TBA) method.** The method described by Zahin et al. [18] was used. To 1 mL of test samples prepared in FTC method was added 2.0 mL of 20% trichloroacetic acid and 2.0 mL of 0.67% thiobarbituric acid. The mixture was placed in boiling water for 10 min, then it was centrifuged at 3000 rpm for 20 min and absorbance was measured at 500 nm.

**Total phenolic content (TPC).** The amount of total phenolics in different fractions of *H. acutiloba* was determined with the Foin- Ciocalteau reagent using the modified method by Slinkard and Singleton [19]. Results were expressed as milligrams of gallic acid equivalent per gram of extract on dry weight (mg GAE/g dw).

**Total flavonoid content (TFC).** The amount of total flavonoids in different fractions of *H. acutiloba* was determined with Aluminum chloride colorimetric method [20]. Results were expressed as milligrams of quercetin equivalent per gram of dry weight (mg QE/g dw).

**Antidiabetic activity.**

**α-glucosidase inhibition activity.** This assay was performed using a modified procedure by Ying [21]. 120 μL of extract /Acarbose (Sigma, positive control) / distilled water (Control) in 0.01 M phosphate buffer (pH=6.8), 30 μL of α-glucosidase (0.2 U/mL) /buffer (blank) were mixed in 96 well plate, then they were incubated at 37°C for 15 min. To this, 20 μL of 5 mM p-nitrophenyl-α-D-glucopyranoside (p-NPG) was added and further incubated at 37°C for 30 min. 100 μL of 1.0 M Na2CO3 was added to stop reaction, the absorbance of the mixture was measured at 405nm.

**α-amylase inhibition activity.** This assay was performed using a modified procedure [8]. 40 μL of extract /Acarbose (positive control) in 0.01 M phosphate buffer (pH=6.8), 160 μL of distilled water, 400 μL of 0.5% starch in buffer and 200 μL of α-amylase (2 U/mL) enzyme solution (without enzyme-blank) were mixed separately in 96-well plate. After preincubating at 37°C for 5 min, reaction stopped with adding 100 μL of dinitrosalicylic acid (DNS reagent) and was incubated 85°C for 15 min. Then mixture was diluted with 900 μL of distilled water, absorbance read in 96 well plate by diluting solution 5 times, the absorbance of the mixture was measured at 540 nm. The % Inhibition was calculated with the following formula:

% Inhibition activity = \[ \frac{(A_{\text{control}} - A_{\text{blank}}) - (A_{\text{sample}} - A_{\text{blank}})}{A_{\text{control}} - A_{\text{blank}}} \times 100 \]

**RESULTS AND DISCUSSION**

In the present study, hydro-alcoholic and five fractions of *H. acutiloba* bulbus were evaluated for their antioxidant activity and inhibitory effect on α-amylase and α-glucosidase enzymes by in-vitro method.

In antioxidant activity study, the hydro-alcoholic extract and its fractions of *H. acutiloba* were evaluated for antioxidant activity with different methods such as DPPH radical scavenging, ferric reducing, ferric thiocyanate and thiobarbituric acid method, total phenol and flavonoid content method.

**DPPH radical scavenging.** The radical scavenging activity measures via intracting extract with DPPH, transfer an electron or a hydrogen atom to DPPH, naturalizing its free radical character, thus purple color of freshly prepared DPPH solution was faded or disappeared. The radical scavenging capacities as determined by DPPH is shown in Fig 3. According to the results, the hydro-alcoholic extract and its fractions were exhibited concentration dependent scavenging effect on DPPH free radical, while the n-butanol fractions showed highest scavenging activity on DPPH than other fractions.

**Reducing power assay.** Reducing power is widely used in evaluating antioxidant activity of polyphenols presented in plant extracts. In this method, the reductants in the extract reduced Fe³⁺/ferricyanid complex to Fe²⁺/ferrous form [22]. The hydro-alcoholic extract and its fractions were showed moderate reducing power, the chloroform fractions shows better reducing activity than other fractions.

**Ferric thiocyanate method.** The hydro-alcoholic extract and its fractions exhibited strong antioxidant activity, which was comparable to standard antioxidant compounds BHT and α-tocopherol.
Figure 4
Ferric reducing power of *H. acutiloba* extracts and standard compounds.

Figure 5
Antioxidant capacity of *H. acutiloba* extracts and standard compounds by FTC method.

**TBA method.** Among the tested crude extract and fractions, the n-butanol fractions showed good antioxidant activity than other fractions by the TBA method.

Figure 6
Antioxidant capacity of *H. acutiloba* extracts and standard compounds by TBA method.

**Total phenolic and flavonoid content.** The total phenol and total flavonoid content are shown in Figure 7. As determined from the spectrophotometric method, the total phenolic and flavonoid content were rich in chloroform fractions than other fractions and it was followed by hexane fractions and n-butanol fractions. The total phenolic content of the extracts were in the range of 85.75-277.02 mg gallic acid equivalents /gram of extract and the total flavonoid contents were in the range of 0.13-103.39 mg of quercetin equivalent /gram of extract.

Figure 7
Total phenol and flavonoid content of *H. acutiloba* extracts

**In-vitro anti-diabetic activity study.** The inhibitory activity of the ethanol extract and different fractions prepared from *H. acutiloba* bulb against α-glucosidase and α-amylase were determined at different concentrations between 0.1 and 2 mg/mL. Acarbose was used as standard reference drug. All of the extracts showed both enzyme inhibition activity in a dose dependant manner in the range of tested concentration (Fig 8-9).

Figure 8
α-glucosidase inhibitory of *H. acutiloba* extracts and reference compound acarbose

Figure 9
α-amylase inhibitory of *H. acutiloba* extracts and reference compound acarbose
Among all, the fractions of hexane and chloroform has shown strong α-glucosidase enzyme inhibitory activity with an IC₅₀ value 15.52 and 8.39 µg/mL, and n-butanol fractions shows highest α-amylase inhibition activity with an IC₅₀ value of 332.8 µg/mL which were higher than acarbose (IC₅₀ value are 26.51 µg/mL and 14.24 µg/mL, respectively). Many bioactive compounds from different plants have been reported to have hypoglycemic effect, in that mostly phenolics and triterpenoids such as oleane, ursane, lupane, and flavonoids have a positive correlation as anti-diabetic agents. The presence of inosinosugars and phenolics in fraction might have been attributed to the highest enzyme inhibition activity compared to other fractions. Hence, the inosinosugars of this plant may be responsible for enzyme inhibitory activity [23-25].

CONCLUSION

There was no information available in the literature about the in-vitro (α-amylase and α-gluco- sidase inhibitory activity) anti-diabetic and antioxidant studies of Turkish endemic plant, *H. acutiloba*. With the help of results in correlation with previous reports, it can be hypothesized that the significant enzyme inhibitory activity of n-butanol and chloroform fractions may interfere or delay the absorption of dietary carbohydrates as well as disaccharides in the small intestine, leading to the suppression of meal-induced increase of plasma glucose. Hence, it may useful in the management of type-2 diabetes (T2D). Based on the lead fractions obtained from in-vitro studies, we are going to plan an in-vivo study for further confirmation of the obtained results.

These results suggests that the extract of *H. acutiloba* can prevent oxidative damage due to their antioxidant characteristics and can be helpful for the treatment of DM and its related complications. However, further phytochemical and characterization studies are needed to iden tificate the extract active compounds presented in the extract by bioactivity guided isolation method.

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ESTIMATION OF IN VITRO ANTIOXIDANT AND ANTIMICROBIAL ACTIVITY OF METHANOL EXTRACTS FROM STEVIA

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ABSTRACT

In this study, the efficiency of the plant age and growth period on antioxidant and antimicrobial activity of stevia (Stevia rebaudiana Bert.) was investigated. Samples were taken from S. rebaudiana plants of three different ages (2, 3 and 4 years old) and four different growth periods (H1: 1 July, H2: 1 August, H3: 1 September and H4: 1 October). Extracts of sweet herb (S. rebaudiana) were obtained by maceration method with methanol as solvent. The experiments were carried out in completely randomized design with three replications. According to results, the highest antioxidant activity (metal chelating activity of methanol extract from stevia leaf; DPPH Free Radical Scavenging Activity of methanol extract from stevia leaves) was determined from respectively No.2 sample (3-year-old plant harvested in July) and No.1 sample (2-year-old plant harvested in July). The highest antimicrobial and antifungal activity for Escherichia coli and Staphylococcus aureus was determined from No.9, No.10, and No.11 samples (in the order of 3-year-old plant harvested in September, 3-year-old plant harvested in October, and 4-year-old plant harvested in November). All of the stevia samples harvested in different age and different periods were showing antimicrobial effect against Pseudomonas aeruginosa, E. faecalis and Candida albicans.

KEYWORDS: Stevia rebaudiana, age and growth period, antioxidant, antimicrobial

INTRODUCTION

The S. rebaudiana (Bert.) is a perennial plant and it belongs to the family of Asteraceae. Stevia leaves mainly contain glycosides such as stevioside and rebaudioside A, 300-350 times sweeter than sucrose [1-2]. Extracts obtained from sugar cane contains flavonoids, alkaloids, essential oils, watersoluble chlorophyll, xanthophyll and hydroxycinnamic acid [3]. The powder extract also contains stevioside, rebaudioside A, B, C, D, E and dulcoside-A glycosides, 300 times sweeter than sucrose [4-5]. In this context, the plant has great importance for diabetics and it has other important biological activities such as antioxidant, antimicrobial and antifungal due to the bioactive compounds [6-7].

Oxidation is a process required for the energy production of living things. However, oxygen-centric free radicals and other reactive oxygen species cause cell death and tissue damage by the time. Antioxidants have the ability to protect the body from damage caused by free radical induced oxidative stress [8-9]. Essential oils show antimicrobial action due to the phenols in their ingredients. In addition, phenolic compounds are also used in the food industry as antioxidants, anticancer agents, antiobesity, antidiabetic, and antimutagenic agents [10-11]. Therefore, natural antioxidant phenols can prevent oxidative tissue damage [12].

Studies on antioxidant and antimicrobial effects of S. rebaudiana are available. However, there are no studies on the antioxidant and antibacterial activity levels of the components of the plant in terms of age and growing period. In this study, the antioxidant and antimicrobial activity levels of methanol extracts of S. rebaudiana were evaluated in terms of plant age and growing season.

MATERIALS AND METHODS

Plant material. In 2014, the plant samples were obtained from 1-year old plant (transferred to field in 2013), 2 years-old plant (plant transferred in 2012) and 3 years-old plants (plant transferred to field in 2011) and in 4 different periods (H1: 15 July, H2: 15 August, H3: 1 September and H4: 1 October). Leaf samples were milled with a grinder after dried up to constant weight in the shade.
Preparation of the extract. The air-dried leaves of Stevia (0.5 g) were powdered and then extracted with 50 mL of methanol by maceration process. The crude extract was filtered and evaporated under reduced pressure to obtained a methanol extract. The extract was stored at 4°C for further use. This methanol leaf extract of Stevia was reconstituted in 80% methanol and used for the assessment of antioxidant and antimicrobial activity.

Antioxidant activity. The DPPH free radical scavenging activity of methanol extract of Stevia leaves was measured in terms of hydrogen donating or radical-scavenging ability using the stable radical DPPH [13]. 0.15 mM solution of DPPH in ethanol was prepared and 50 μL of this solution were mixed with 150 μL of extract solution in 96 well plate. Thirty minutes later, the absorbance was measured at 517 nm. Gallic acid was used as the reference standard compound. Lower absorbance of the reaction mixture indicated higher free radical scavenging activity. DPPH radical scavenging activity was expressed as the inhibition percentage of free radical by the sample and was calculated using the following formula:

\[
\% \text{ inhibition} = \left( \frac{A_{\text{control}} - A_{\text{sample}}}{A_{\text{control}}} \right) \times 100.
\]

where \(A_{\text{control}}\) was the absorbance of the control (blank, containing all reagents except for the test sample), and \(A_{\text{sample}}\) was the absorbance in the presence of the extract/reference. All the tests were performed in triplicate and the graph was plotted with the mean values.

The ferrous ion-chelating effect of the extracts by Fe²⁺-ferrozine test system was estimated by the Fe²⁺-Ferrozine Test System [14]. Briefly, 740 μL of methanol and the samples were incubated with 2 mM FeCl₃ solution. The reaction was initiated by adding 40 μL of 5 mM ferrozine solution into the mixture, then the mixture is allowed to stand at the appropriate temperature for 10 minutes. The absorbance of the reaction mixture was measured at 562 nm. EDTA was used as reference standard. All measurements were performed in triplicate. The ratio of inhibition of ferrozine-Fe²⁺ complex formation was calculated as follows:

\[
\% \text{ Inhibition} = \left( \frac{A_{\text{Control}} - A_{\text{Sample}}}{A_{\text{Control}}} \right) \times 100
\]

The control contained only FeCl₂ and ferrozine. Analyses were run in three replicates and expressed as average values with SD.

The amount of total soluble phenolic in the leaf methanol extract of Stevia were determined using modified Folin- Ciocalteu colorimetric method according to the method [15] with slight modification using gallic acid as a standard phenolic compound. 1.0 mL of extract solution containing 1.0 g extract in a volumetric flask was diluted with 46 mL of 75 % ethanol. 100 μL of Folin-Ciocalteu reagent was added and mixed thoroughly. 5 minutes later, 80 μL of 7.5 % sodium carbonate was added and the mixture allowed to stand for 2 h with intermittent shaking. The absorbance of the blue color was measured at 750 nm. The concentration of total phenolic content was expressed as mg/g of dry extracts. The results were expressed as milligram of gallic acid per gram extract (mg GAE/g extract).

The total flavonoid content was evaluated by aluminum chloride colorimetric method [16]. The diluted standard solutions and methanol extracts of different stevia (0.5 mL) were separately mixed with 1.5 mL of 95% ethanol, 0.1 mL of 10% aluminum chloride, 0.1 mL of 1M sodium acetate and 2.8 mL of distilled water. After incubation at room temperature for 30 min, the absorbance of the reaction mixture was measured at 415 nm with a Shimadzu UV-160A spectrophotometer (Kyoto, Japan). The amount of 10% aluminum chloride was substituted by the same amount of distilled water in blank.

Antimicrobial activity. In order to determine the MIC (minimum inhibition concentration) for the test organism using 96- well microplate serial dilution was conducted according to the method described previously [17]. The extracts were dissolved in 10 % DMSO and then diluted to the highest concentration (20 mg/mL) to be tested. Serial two-fold dilutions were made in 96-well plate. 50 μL of inocula of the bacterial strains (Staphylococcus aureus [ATCC 29213], Escherichia coli [ATCC 27853], Pseudomonas aeruginosa IATCC 25922)) grown at 37 °C in Mueller-Hinton broth [Merck chemicals] and suspensions were adjusted to 0.5 McFarland standard turbidity, then were added to each well. The final volume in each well was 100 μL. The concentration of the extract in wells ranged from 5.00 to 0.009 μg/mL. The final volume in each well was 100 μL. The 11th well was used sterility control and the last well containing Mueller Hinton broth and inocula without extract was used as growth control. The covered microplates were incubated 24 h at 37 °C. To indicate bacterial growth, 10 μL of 2,3,5-triphenyltetrazolium chloride (TTC, tetrazolium red, Sigma) dissolved in water (2 mg/mL) were added to the microplate wells and incubated at 37 °C for one hour.

Statistical Analysis. All the antioxidant activity tests were conducted in triplicates. The values are expressed as the mean ± standard deviation (SD). The statistical analysis of the data among groups was done by using Graphpad prism 7 software.
RESULTS AND DISCUSSION

Stevia extract is obtained from plant leaves and so plant’s green parts has importance. This extract has anticancer properties and biological activities like antimicrobial, antifungal and antioxidant [6, 18-20].

Antioxidant activity. There are increasing evidences that indigenous antioxidants may be useful in preventing the deleterious consequences of oxidative stress and there is a great interest in the protective biochemical functions of natural antioxidants present in spices, herbs and medicinal plants [21]. The DPPH scavenging activity was determined by the decrease in its absorbance at 517 nm, which is induced by antioxidants in extract. In the DPPH radical scavenging assay, stevia methanol extract had remarkable radical scavenging effect with increasing concentration in the range of 50-1000 μg/mL when compared with reference compound gallic acid (Figure 1).

The metal chelating activities of different stevia samples and EDTA are shown in Fig. 2. In this method, ferrozine can make complexes with Fe²⁺ quantitatively. In the presence of chelating agents such as antioxidant compounds, the formation of complex is failed and as a result the red color of the complex decreased. Therefore, metal chelating activity can be estimate by measurement of color reduction. In this study, No.1 sample showing good chelating activity than others, suggesting that the extract of this sample can competitively make complexes with ferrous ion than ferrozine. Metal chelators can reduce the concentration of the catalyzing transition metal in lipid peroxidation. In this context, metal chelating capacity was very important for antioxidant defense. It was reported that chelating agents can stabilize the oxidized form of metal ion by reducing the redox potentials [22]. The results obtained from Fig. 2 demonstrate that in stevia samples, the growing age is an important factor which is affecting metal chelating activity. This variation may be due to the fact that the secondary metabolites change depending on the age of the plant.

Phenolic compounds are the secondary metabolites in plants due to their potential natural antioxidant behaviour both as radical scavenger and metal chelator in the biological system. For this reason, the total amount of phenolic compounds was determined in our study. The total amount of phenolic content present in the methanolic leaf extract of S. rebaudiana is shown in Fig. 3. In one gram of methanolic leaf extract, 18-129 mg gallic acid equivalent of phenols was detected. In previous reports, ethanolic leaf extract of S. rebaudiana showed 61.50 mg gallic acid equivalent [7] and 130.67 mg [23] catechin equivalent of phenols. Previous results suggest that higher levels of antioxidant activity were due to the presence of phenolic components. Phenolic compounds can be retardant for oxidative degradation of lipids and thus improve quality of nutritional value and quality of foods, therefore phenolics are getting more interest nowadays in food industry [24].

Flavonoids, as phenolic compounds, have been reported to be responsible for the antioxidant activities of herbal extracts. DPPH, OH radical, and superoxide anion radical scavenging activity show correlation with amount of phenolic and flavonoid content [25-26]. Fig. 3 shows total flavonoid content decreased by harvesting period in 1-year old samples. However, it increased in last three sample in the order of harvested in September <October<November in 3-years-old plants.
Antimicrobial activity. The in vitro antimicrobial activity of methanol extracts prepared from stevia samples which are collected in different year and different growing period are shown in Table 1. Among the bacterial pathogens, E. coli exhibited higher rate of susceptibility than other tested microorganisms against stevia methanol extracts. All of the samples of stevia in different age and period have no significant differences for each other in case of microbial growth inhibition. The lowest MIC value were observed for No.1 stevia sample against E. coli and S. aureus. In previous study, among various solvent extracts of S. rebaudiana leaves, the petroleum ether extract was found to have antimicrobial activity than other solvent extracts against tested animal pathogen bacteria [27]. As the same, hexane extract showed significantly higher activity compared to methanol and ethyl acetate extracts against tested microorganisms [28]. However, in another work, acetone extract showed greater antibacterial effect than other tested solvent extracts [29]. According to reports, essential oils and methanol extracts of stevia have antimicrobial activity [30-31]. Antimicrobial activity of a plant extract is assessed as significant (MIC < 100 μg/mL), moderate (100 < MIC ≤ 625 μg/mL) or weak (MIC > 625 μg/mL) [32]. In this study, antimicrobial activity of the methanol extracts of stevia were detected as weak against the bacteria. The significant variance in antimicrobial activity in extract of different polarity may be attributed to the secondary metabolites presented in the extracts. Therefore, it requires further studies about the active compounds as to be a potential drug component as well as antimicrobial agents.
CONCLUSION

In the present study, we demonstrated the methanolic leaf extract of *S. rebaudiana* growing in Turkey contained higher level of phenolic and flavonoid compounds and have potential on quenching free radical to end up the radical chain reaction. The stevia extract can be used as widely available source of natural antioxidants and a good food preservatives or in pharmaceutical preparations not only as a sweetener but also as a natural antioxidant and antimicrobial agent. In addition, it can be used as preservative against oxidative degradation in food industry.

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COMMUNICATING MULTI-HAZARD HEALTH RISK THROUGH A WEB-GIS PLATFORM: A CASE-STUDY

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ABSTRACT

The aim of this paper is to show the potential of a web-gis platform in communicating data and results to the scientific community, stakeholders and citizens. This web-gis is a product of the EU-funded PEC Project (Post-Emergency, multi-hazard health risk assessment in Chemical disasters) and it provides a graphical interface for most of the research activities undertaken during the project. The project aims at implementing an integrated model for rapid multi-hazard health risk assessment applicable to chemical release incidents occurring during natural or man-made disasters. The web-gis developed may display input and output data used for the multi-hazard assessment. The data type showed could be different: vector maps, raster maps, tables or interactive graphs. The user can interact with the maps using the typical tools of a desktop gis such as: zoom, distance and area measure, layer visibility switch, layer order, data interrogation feature; other data are shown with different representations i.e. graph and data tables. The system architecture is flexible to allow new data and results to be added systematically during the project development. Users can access the PEC web-gis tool with different privileges, which allow them to access all or a subset of data/analyses results. The paper describes the system architecture of the web-gis platform. Due to its multi-disciplinary nature, the project may generate different type of output. The paper underlines how the web-gis system harmonises data and results of very different kind.

KEYWORDS:
Web-Gis, Data Analysis, It-Infrastructure, It-Architecture

INTRODUCTION

A Geographic Information System (GIS) is a system designed to capture, store, manipulate, analyze, manage, and present spatial or geographic data. The web-gis is an application of GIS that allows to browse and query a map through a common web browser. The web-gis is therefore the extension of the web application, born and developed to manage the digital cartography. What distinguishes a web-gis project from a GIS project are its specific purposes of communication and information sharing with other users. With web-gis, the traditionally developed GIS applications for stand-alone utilities or connected in local networks, can be uploaded to the web-server (i.e. map server), allowing interaction with cartography and associated data also through Internet network.

A web-gis platform can be very convenient to show the analysis results that have geographical connotation. Images and map view are intuitive and using a web-gis they are easily accessible through a simple Internet browser. Eucentre has developed for the Italian Department of Civil Protection several web-gis platforms such as the platform for the evaluation of the seismic risk at municipal scale in Italy [1], the one for the seismic risk of the Italian school buildings [2] and the one for the seismic risk of the road system [3]. Eucentre has also developed platforms for assessing seismic risk for some European funded projects. Within the SASPARM2.0 project (Support Action for Strengthening Palestinian capabilities for Seismic Risk Mitigation) has been developed a web-gis platform for Nablus city, in Palestine [4] and another web-gis platform has been developed in the NERA project (Network of European Research Infrastructures for Earthquake Risk Assessment and Mitigation) for the assessment of the damage scenario taking into account the progressive damage [5]. In all the projects mentioned, the web-gis platforms have been produced using Open Source code. In [6] is possible to find a list of some of the recent projects developed with Open Source code.

The PEC project aims at implementing an integrated model for rapid multi-hazard health risk assessment applicable to chemical release incidents occurring during natural (earthquake or floods) or man-made disasters and developing a composite risk matrix, considering both severity and probability of identified hazards, to prioritize disaster-related public health risks from clusters of industrial facilities handling toxic chemicals. The first objective of the project is to develop an operational approach toward the implementation of a model applicable to contamination and health risks assessment in connection to natural and man-made disasters. Then, it is
fundamental to estimate pathways, levels and time course of environmental contamination, human exposure profiles and health impacts that may result, at various time intervals after a disaster, from acute or prolonged absorption of a mixture of hazardous chemicals selected from the EU inventory of high-risk toxic industrial substances. The project is also expected to develop a series of risk mitigation guidelines for characterization of “multi-hazard and multi-event-related” health risks in chemical exposures following natural or man-made disasters. The web-gis platform described in this paper is one of the products of the PEC project.

MATERIALS AND METHODS

**IT infrastructure.** The web-gis is designed to show many data types: maps, vector or raster format, numeric data, shown as interactive graphs or thematic maps, and text documents. The data are both project input and results from elaborations. Figure 1 shows the IT infrastructure for the web-gis application. Data are saved on a database or on file system, in this way the data management has a good flexibility. In the PEC web-gis the large part of the data, including vector maps, are saved on a database. The database gives a high speed in reading and writing and all the functions that a database has: SQL queries, indexing, backup management, changes monitoring. The database is Postgres with the PostGis extension, which adds spatial capabilities such geographic SQL queries.

The main part of the IT infrastructure is the web server. In our case the web server is Apache Tomcat that has the capability of running Java Servlets (and several others Java specifications). A Java Servlet is a kind of java program that can interact with the “outside world” (i.e. external web). In this project the component that calculates the values of the graphs is a Java Servlet. Geoserver, Java Servlet and Web-App run under Apache Tomcat. Geoserver is a Java Servlet specialized in publishing maps and geographic data linked with maps. Geoserver reads the data and maps from database or filesystem and has functions to transform this data into images or tables when the client ask for a map or a data table. In this infrastructure, when a client ask for data stored in the Db, there are specific java servlet that connect to the database, run queries and give back the result.

The client (i.e. the graphic interface that the final user sees in his/her web browser) is a web site with a collection of libraries written in javascript. Some of the libraries are developed by third parties for general purposes and others are developed for this project. The client libraries work together to manage the user interaction: map navigation, tabs consulting, graph interaction and so on. Table 1 shows a list of programs and libraries used in this project.

The PEC web-gis is developed using Open Source or Free Code. The open source lets the possibility to try and to develop different alternatives and solutions without blocked code or licensing costs. The web-gis main task is to show the input data and the results of the PEC project in a synthetic, understandable and complete way. From this perspective the interface organization has a fundamental role.

![FIGURE 1](image.png)

**FIGURE 1**

IT infrastructure. On the left the server side, on the right the client side
The web-gis (Figure 2) is organized in two areas:

- Left area where there are the list of the available layers, the tool to manage the layers order and the tab that shows the legend;
- Center area where there are the main map, the tools map and the tabs for visualize all the data that are not geographic.

**Left Area.** In the left area the layers are organized in a tree view (Figure 3). The layer tree has the following groups: Overview, Data and Results. The node Overview contains the background layers. The aim of these layers is to give to the user a familiar view of the entire area. Two kinds of layers are shown:

- Third parties layers. The web-gis uses the Google physical layer that gives satellite images and Open Street Map layer the gives a precise street map.
- Layers developed for this project representing regions and municipalities. All these layers help to improve the comprehension of the entire area.

The Data-Physical group collects all the geographic data used as input for the subsequent elaborations. The Digital Elevation Model (DEM) and the contour lines are part of the inputs used in the hazard identification for floods. The land use is one of the inputs for the environmental impact assessment. In the Data-Site Plan group are collated the specific geographic data of the industrial area analyzed. The group is composed by the boundary plant and the plant layout. The group Results collects all the geographic data created during the project. In the web-gis the user can make visible or invisible each available layer. In this application the user cannot add or remove layers nor change the layer tree organization.

**FIGURE 2**
Overview of web-gis interface
A toolbar that allows changing the visibility order of the layers has been developed for the project. The toolbar includes commands that permit to move the layer up or down along the layer stack. Moving a layer up means that the layer visibility is increased. Other commands in the toolbar allow enabling/disabling all the layers or a group of them (i.e. input data layers, results layers). The possibility of change the layers order with the possibility of enable/disable the layers gives to the user a simple way to personalize the view in function of his needs.

All the layers are displayed with a legend that shows the meaning of symbols and colors used.

Tabs in the right area - Item data. The web-gis is developed to show geographic data but also other non-spatial data, that is data not relative to a specific point in the map or unique for the entire study area. Access to this data is made through tabs. When a user selects an appropriate item on the map, the relevant data (that are saved on the database) are loaded and showed in the dedicated tab. The user can then see the data of the chosen item. The diagram of operation is shown in Figure 4.

When the user selects an appropriate item on the map, the web-gis captures the click-point and transforms it in geographic coordinates (Latitude, Longitude and geographic reference system). At this point, the application chooses, as a function of the active layer, one of the two alternatives:

- Get data through Geoserver;
- Get data through a Java Servlet.

Geoserver has natively a set of function for querying geographic data (both vector and raster layers) anywhere they are saved but the resource has to be registered in Geoserver. The Geoserver answer has all the fields and values of the item(s) corresponding to the query.

The answer could be either simple text or html. When the web-gis receives the answer, it can show directly to the user or execute other operation, for example improve the readability of the result. In this project a set of Java Servlet has been developed to answer queries that are more complex.

A Java Servlet receives as input the coordinates of the selected item, the layer of the item and other parameters to improve the request. The Servlet sends a request to the database and the database can answer either geographic queries (e.g. the land use in the next 50 m near the selected point) or a standard SQL query. The Servlet can evaluate and transform the answer before sending it back to the web-gis. In this point of the IT infrastructure there are a lot of possibilities: from the simplest math operation to the most complex, i.e. it is possible to call other programs (third parties programs or ad-hoc routines) or to connect to other internet based services and so on. This structure gives a great flexibility on the type of

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**FIGURE 3**
Layer tree

- Urban Area
- Rural area
- Land Use
- Contour lines
- DEM

**FIGURE 4**
Getting data. Geoserver in blue, Java Servlet in green
queries, data manipulation and data representation. The data can be showed in tables, graphs, maps and in text documents. This architecture has been already used for other projects: for collecting data for define seismic risk in Palestine [4], for defining seismic risk of bridges in Italy [3] and for evaluating seismic risk for Italian municipalities [1]. The most complex calculation is encapsulated in the server and it is not directly accessible to the final user.

**Graph example: fragility curve.** In the PEC project two set of fragility curves have been developed: for seismic risk and for flooding risk. A seismic fragility curve shows the probability of reaching or exceeding the damage levels for a structure subjected to a ground shaking in terms of peak ground acceleration [7]. For the fragility studies the tanks have been classified in four classes depending on the ratio between diameter and height. For each class the web-gis shows:

- A graph with the plot of the curves calculated by a servlet. The user can interact with the graph moving along the curve and visualizing the graph values;
- Two tables, the first that shows the parameters used for the plot (mean and standard deviation for the lognormal distribution) and the second that shows the one-year probability to reach the two performance point (leakage of connected piping and collapse).

**Other docs (pdf).** The web-gis maintains all the characteristics of a standard internet site, so there are no specific limits on documents download or links to other web sites. For example, it is possible to link other web pages both remaining in the same site or in external sites. It is possible to provide link to download documentation, link to multimedia file and so on. By way of example in the PEC web-gis it is possible to download the project deliverables from the tab “Other Info”.

**Data preparation.** In risk studies, the input data and the results are the fundamental aspects, along with the procedures applied to derive them. Below is shown how all this different types of information can be integrated in the IT infrastructure. The data and results are grouped in three classes:

1. Geographic data (e.g. map of flooding, land use);
2. Item data (e.g. fragility curve plot);
3. General data for the entire study area (e.g. total population);

GeoServer manages all the geographic data. In GeoServer the publication of a map needs to be specified along with some parameters: the file position, the thematic for the map, the reference system. The files can be on file system, option used for raster map, or on database. The use of the database simplifies the data management (i.e. backup, spatial queries) but it is not mandatory. There are tools (some of them free such as QGis), that permit to import and export easily the layers from a database or to connect directly to the database. The map management, usually, is straightforward even if it is a good practice to harmonize some elements within the research teams, for example the reference system. The re-projection is nowadays a common operation but it has always errors [8]. An item data is a data specific for an item (on a map). The natural storing position is on database table. Many times choosing to save on database is a satisfactory solution but in some cases it can be useful another way. Looking at the fragility curve in Figure 5, each curve is fully described by its formula and by its parameters. In this case, it is suggested to save the parameters values on the database and to calculate, the different point values, only when it is requested, so as to save space storage and, if it is necessary, to change “on the fly” any of the parameters.

**FIGURE 5**

Example of graph in the web-gis
Data saving on database has no specific issues but it is recommended to manage carefully the identification codes which connect geographic items with data on tables. These operations have to be previously planned to prevent the increasing number of identifications code as this would increase the difficulty in developing and managing the entire infrastructure. The “on the fly” calculation needs time to validate the result and the interaction with the development team has to be planned.

General data, that is unique for the entire study area, is handled in the same way of the item data without the need to provide a specific identification code.

Profiling. The access to web-gis is limited to registered users. The registration encompasses the definition of the role of each user. The allowed roles are “citizen” or “researcher”.

The web-gis is customized to show data in different ways depending on the user role, for example it is possible to have a different list of layer, different tools, a specific organization of layer tree and tabs. The aim of profiling is to show the data in the most effective way to people who may have different knowledge of the study. A citizen could be more interested in a synthetic representation of the results while a researcher could be more interested in the data completeness and results replicability.

CONCLUSION

A description of PEC web-gis functionalities was presented linked with the informatics infrastructure that runs hidden to the final user. It has been shown that a web-gis could be more than a collection of maps. This paper demonstrates how using Open Source programs already available it is possible to enrich common web-gis with more information about both the entire project and single items on the map. It has been shown how, with the same informatics architecture, the web-gis could be linked to external programs and presents the results.

Further development could be done in the user experience. An interesting new function may be the saving of user view preferences. With the existing web-gis any user selection, e.g. the layer order, will be lost in the moment the user logs out. With the saving of his preferences, a user could access the webgis in the way he is more interested in.

An additional improvement could be the download of data and maps. This function might be useful for those users who need to execute their own elaborations or to check independently those presented on the webgis.

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A CASE STUDY: ECOLOGICAL QUALITY STATUS OF SUSURLUK RIVER BASIN (MARMARA SEA)

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ABSTRACT

This study was carried out with the aim of determining the Ecological Quality Status (EQS) of coastal transitional waters of Susurluk River Basin (Marmara Sea). Macrozoobenthic invertebrate material was collected in May of 2013 from six stations in triplicate by means of a van Veen grab. Shannon-Weaver Diversity Index and associated Pielou’s Evenness Index together with biotic indices AMBI and BENTIX were calculated. Some ecological variables (Secchi disc depth, temperature, salinity, dissolved oxygen, pH, total phosphorus, total nitrogen, silica, Chlorophyll-a) of the sea water and total organic carbon of the sediment were also measured. Ecological Quality Status at each station was assessed by considering individual dominancy of sensitive and tolerant species, results from univariate/biotic indexes and some ecological parameters. When EQS of the basin is evaluated as a whole, it was seen that there was not any station in “Good” or “High” EQS at the study area, stations were in “Poor” or “Bad” EQS at the stations where the River meets the sea, while the stations off the River mouth were in “Moderate” EQS. Both species pattern of macrozoobenthic invertebrate communities and ecological parameters determined in the basin such as TOC and nutrients present the negative impacts of the River over the basin and indicate the necessity of efficient precautions to be taken.

KEYWORDS:
Ecological Quality Status, Marmara Sea, Macrozoobenthos, TOC, AMBI, BENTIX

INTRODUCTION

The Marmara Sea is a small intercontinental basin, connected to the Black Sea through the Istanbul Strait and to the Aegean Sea through the Çanakkale Strait, with an approximate size of 70 x 250 km and surface area of 11500 km². Physico-chemical features of the Marmara Sea is influenced by neighboring seas. The surface water, originating from the Black Sea, is of 22-26 ppt salinity while the bottom water, originating from the Mediterranean Sea, is of 38.5 ppt salinity. Pollutants are being introduced to the Marmara Sea in considerable amounts due to high population, industrial facilities, agricultural activities and maritime transport.

Susurluk Basin is located between 39° - 40° N latitudes and 27° - 30° E longitudes in the Marmara Sea. A lot of small and large streams in the Basin drain off to the Marmara Sea together with Ulubat and Manyas Lakes. Wastes coming from domestic, dense industrial facilities including eleven organized industrial sites and mining activities including boron and marble stratum generate serious pollution pressure over the Basin.

Marine environments are recipients of pollutants and bottom sediments are final sink for those contaminants. Considerable amount of pollutants and organic matter are accumulated in sediments. Concentrated contaminants affect the composition of zoobenthic invertebrates that are dependent to the sea bottom. Amounts of organic carbon and pollutants are positively correlated very often and therefore content of organic carbon in the sediment can be used as a pollution indicator. Pattern of macrofaunal community and organic carbon quantity of sediment can provide important tools to determine ecosystem health.

The term Ecological Quality Status (EQS) was developed by European Water Framework Directive (WFD 2000/60/EC) to detect condition of any water body. The EQS is assessed in five classes as High, Good, Moderate, Poor and Bad. Since benthic invertebrates are of numerous species with different tolerance to pollution and alterations in their communities are indicator of environmental pressure for having very limited mobility, they are extensively utilized in studies to detect the level of
pollution [12, 13]. Many new methods were
determined to determine the EQS of coastal benthic
ecosystems by utilizing macrozoobenthic
communities. Among them, AMBI [14] and BENTIX [15],
both based on sensitivity/tolerance of zoobenthic
species or taxa, biotic indexes are commonly used
in the Mediterranean.

Albayrak et al., [16, 17] and Çağlar and Albayrak [18]
performed studies about EQS of many
sites in the northern part of the Marmara Sea. However,
there is not any research achieved in the
southern part. The present study was carried out to
determine the EQS of coastal transitional waters of
Susurluk River Basin located in the southern part of
the Marmara Sea by utilizing macrozoobenthic
invertebrate community structure, related biotic
indexes and environmental physico-chemical
variables.

MATERIALS AND METHODS

Material of this study was obtained in May of
2013 from six stations (Fig. 1).

FIGURE 1

Locations and Ecological Quality Status of sta-
tions at coastal transitional waters of Susurluk
River basin. “Bad” EQS , “Poor” EQS
, “Moderate” EQS

Some variables (temperature, pH and dis-
solved oxygen) of the sea water were measured in
situ using a CTD probe. Secchi Disc Depths (SDD)
were measured with a 30 cm diameter white disk.
Sea water samples for the analysis of Total Nitro-
gen (TN), Total Phosphorus (TP) and Silica were
collected with the aid of Niskin bottles and deep
frozen to -20 °C. Nutrient analysis (nitrate+nitrite
and silicate) were carried out with a Skalar Autoan-
alyzer according to colorimetric methods; SM 4500
[19]. TN content of the samples was analyzed by
the autoanalyzer after persulfate digestion. TP sam-
ple were digested with potassium persulfate to a
reactive form in an autoclave and analyzed in the
autoanalyzer [19, 20]. For Chlorophyll-a analysis,
seawater was filtered through 0.7 μm pore and 47
mm diameter GFF membrane filters and then filters
were deep frozen to -20 °C till the analysis. The Chlorophyll-a concentrations were measured with
the acetone extraction method; S.M 10200 H [19].
Total Organic Carbon (TOC) analysis at the sedi-
mant samples was carried out by Elemental Ana-
lyzer by in house method of the laboratory. For
determination of organic carbon contents of the
sediment, organic matter of the samples were oxi-
dized with HCl and later samples were dried at 50-
60 °C and grounded. After these preparation stages,
analysis was carried out by Elemental Analyzer.

Macrozoobenthic samples were collected in
triplicate by means of a van Veen grab with a sam-
pling area of 0.1 m². Samples were sieved through a
0.5 mm mesh. Macrofaunal elements were sorted
out, preserved in 4% formalin, identified in labora-
tory to the lowest possible taxon and individuals of
each species were counted per unit sample.

The Bray-Curtis Similarity Index, based on
log (x+1) transformation, was employed to deter-
mine the similarity between stations. SIMPER
analysis was performed to identify the similari-
ty/dissimilarity between groups, that were detected
by cluster analysis, and the percentage contribution
of each species to the overall similari-
ty/dissimilarity within each group [21].

On the basis of the qualitative and quantitative
composition of the macrozoobenthic fauna Shann-
on-Weaver Diversity Index (H’log2) [22] and asso-
ciated Pielou’s Evenness Index (J) [23] were calcu-
lated. Biotic indices AMBI [14] and BENTIX [15],
which are based on the relative individual percents
of species classified into groups according to
their sensitivity or tolerance to stress, were also
calculated. Mean values of biotic variables and
indexes were exhibited at each sampling station for
0.1 m².

RESULTS AND DISCUSSION

Ecological Variables. Sea water temperature
varied between 11.3 and 21.3 °C, salinity between
0.27 and 29.03 ppt, dissolved oxygen between 6.86
and 10.59 mg/l, pH between 7.65 and 8.66, total
phosphorus between <5.69 and 166.1 μg/l, total
nitrogen between 146.3 and 1618.6 μg/l, silica
between 6.51 and 4654.5 μg/l, chlorophyll-a be-
tween 0.36 and 6.17 μg/l, secchi disc depth between
0.4 and 3.8 m, total organic carbon of sediment
between 20.16 and 45.72 mg/g (Tab. 1). Secchi
disc depth and salinity increased with depth while
temperature, total phosphorus, total nitrogen, silica and
chlorophyll-a decreased with depth.

According to chlorophyll-a values, SD2P and
MD19P stations have Lower Mesotrophic (0.1-0.6
μ/l), SD1P and MD20P stations Higher Mesotrophic (0.6-2.21 μ/l), SD1G and SD2G stations
Eutrophic (>2.21 μ/l) water characters [24].

TOC content of sediment was Intermediate
(10-28 mg/g) at MD19P and MD20P stations, High
(>28 mg/g) at SD2G, SD1P and SD2P stations

770
according to thresholds of Magni et al., [25]. TOC content could not be determined at SD1G station since its sediment was coarse.

**Faunistical Analyses.** A total of 19865 individuals belonging to 64 macrozoobenthic species were obtained in this study. Polychaeta was determined as the most dominant group with 20 species (31.25%) and 18674 individuals (94%), Bivalvia followed it with 15 species (23.43%) and 593 individuals (2.98%), Amphipoda with 10 species (15.62%) and 428 individuals (2.15%), Gastropoda with 10 species (15.62%) and 114 individuals (0.57%). The most dominant species in the study area was *Capitella capitata* with 17771 individuals (89.45%), it was followed by *Spio decoratus* with 739 individuals (3.72%), *Ampelisca spinipes* with 352 individuals (1.77%), *Abra alba* with 212 individuals (1.06%) and *Corbula gibba* with 170 individuals (0.85%).

SD1G station included 10 species and 781 individuals, SD2G station included 14 species and 312 individuals, SD1P station included 8 species and 17720 individuals, SD2P station included 40 species and 823 individuals, MD19P station included 16 species and 67 individuals, MD20P station included 17 species and 162 individuals.

Cluster analysis applied to combine the grab samples revealed two distinct groups (Fig. 2). The first group included stations SD1G, SD2G and SD1P closer to river mouth, the second group included stations SD2P, MD19P and MD20P off the river mouth. Within the first group, similarity between SD2G and SD1P was 58.75%, SD1G connected them with 29.42% similarity. Within the second group, similarity between MD19P and MD20P was 41.41%, SD2P connected them with 19.91% similarity. According to SIMPER analysis, the species mostly contributing to similarity in the first group were *Capitella capitata* (79.91%), *Spio decoratus* (10.13%) and *Tritia neritea* (5.05%), while in the second group those species were *Corbula gibba* (33.08%), *Ampelisca spinipes* (14.36%), *Iphinoe serrata* (12%) and *Abra alba* (8.82%).

Average dissimilarity between two groups was 93.45% and the species with highest contribution to the dissimilarity were *Capitella capitata* (40.42%), *Spio decoratus* (23.68%), *Abra alba* (9.09%) and *Ampelisca spinipes* (8.19%).

**Assessment of Ecological Quality Status (EQS).** While reaching to final assessment of EQS at stations, information about ecological parameters and faunistical composition were considered along with information from Table 2 where univariate and biotic indexes/metrics were summarized.

### TABLE 1

<table>
<thead>
<tr>
<th>Ecological variables of stations.</th>
<th>SD1G</th>
<th>SD2G</th>
<th>SD1P</th>
<th>SD2P</th>
<th>MD19P</th>
<th>MD20P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (m)</td>
<td>0.8</td>
<td>1.6</td>
<td>7.5</td>
<td>12</td>
<td>20</td>
<td>22</td>
</tr>
<tr>
<td>SDD (m)</td>
<td>0.4</td>
<td>0.7</td>
<td>2</td>
<td>2.5</td>
<td>3.8</td>
<td>3.5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>21.3</td>
<td>17.5</td>
<td>13.8</td>
<td>12.8</td>
<td>11.7</td>
<td>11.3</td>
</tr>
<tr>
<td>Salinity (ppt)</td>
<td>0.27</td>
<td>10.97</td>
<td>23.58</td>
<td>24.4</td>
<td>26.7</td>
<td>29.03</td>
</tr>
<tr>
<td>dO (mg/l)</td>
<td>6.86</td>
<td>9.08</td>
<td>10.27</td>
<td>10.59</td>
<td>8.32</td>
<td>8.56</td>
</tr>
<tr>
<td>pH</td>
<td>8.66</td>
<td>8.16</td>
<td>8.15</td>
<td>8.14</td>
<td>7.65</td>
<td>8.01</td>
</tr>
<tr>
<td>TP (μg/l)</td>
<td>166.1</td>
<td>125.5</td>
<td>6.2</td>
<td>&lt;5.69</td>
<td>&lt;5.69</td>
<td>&lt;5.69</td>
</tr>
<tr>
<td>TN (μg/l)</td>
<td>1618.6</td>
<td>1427.8</td>
<td>151.8</td>
<td>170</td>
<td>146.3</td>
<td>180.8</td>
</tr>
<tr>
<td>Si (μg/l)</td>
<td>4654.5</td>
<td>3751.1</td>
<td>21.3</td>
<td>10.4</td>
<td>31.4</td>
<td>6.51</td>
</tr>
<tr>
<td>Chl-a (μg/l)</td>
<td>6.17</td>
<td>4.88</td>
<td>0.8</td>
<td>0.36</td>
<td>0.46</td>
<td>0.62</td>
</tr>
<tr>
<td>TOC (mg/g)</td>
<td>-</td>
<td>33.86</td>
<td>31.49</td>
<td>45.72</td>
<td>27.39</td>
<td>20.16</td>
</tr>
</tbody>
</table>

SDD: Secchi Disc Depth, dO: Dissolved Oxygen, TP: Total Phosphorus, TN: Total Nitrogen, Si: Silica, Chl-a: Chlorophyll-a, TOC: Total Organic Carbon

**FIGURE 2**

Grouping of stations based on macrozoobenthos composition produced with Bray-Curtis group average clustering technique.
TABLE 2
Mean values of species number (S), individual number (N), Evenness Index (J), Shannon-Weaver (H), AMBI and BENTIX.

<table>
<thead>
<tr>
<th></th>
<th>SD1G</th>
<th>SD2G</th>
<th>SD1P</th>
<th>SD2P</th>
<th>MD19P</th>
<th>MD20P</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>5</td>
<td>8.6</td>
<td>6.6</td>
<td>22.6</td>
<td>8.6</td>
<td>9.3</td>
</tr>
<tr>
<td>N</td>
<td>260.3</td>
<td>104</td>
<td>5906.6</td>
<td>274.3</td>
<td>22.3</td>
<td>54</td>
</tr>
<tr>
<td>J</td>
<td>0.43</td>
<td>0.69</td>
<td>0.07</td>
<td>0.68</td>
<td>0.89</td>
<td>0.66</td>
</tr>
<tr>
<td>H</td>
<td>0.82</td>
<td>2.15</td>
<td>0.19</td>
<td>3.08</td>
<td>2.77</td>
<td>2.13</td>
</tr>
<tr>
<td>AMBI</td>
<td>3.69</td>
<td>2.34</td>
<td>5.9</td>
<td>2.39</td>
<td>1.77</td>
<td>2.62</td>
</tr>
<tr>
<td>BENTIX</td>
<td>2.28</td>
<td>2.45</td>
<td>2.02</td>
<td>2.52</td>
<td>2.75</td>
<td>2.66</td>
</tr>
</tbody>
</table>

**FINAL ASSESSMENT**
BAD POOR BAD MODERATE MODERATE MODERATE

**SD1G.** A total of 10 species and 781 individuals were obtained in this station. Mean species number was 5/0.1m² and mean individual number was 260.3/0.1m². Species sensitive to organic pollution were P. maculata, T. neritea and G. auquicauca; species tolerant to organic pollution were A. succinea, A. oxycephala, P. ciliata, P. paucibranchiata, S. decoratus, C. capitata and A. diadema. Individuals belonging to sensitive species formed 0.6% of total, while individuals belonging to tolerant species formed 99.4%.

Shannon-Weaver classified this station in “Bad”, AMBI in “Moderate”, BENTIX in “Poor” EQS. Final judgement for this station is BAD. Tolerant S. decoratus contributed to 87.9% of all individuals. Total abundance of it together with another tolerant species C. capitata reached to 98.5%. Sensitive species were represented by only 5 individuals within 781 (0.6%). dO of sea water was 6.86 mg/l, TP 166.1 μg/l, TN 1618.6 μg/l, Si 4654.5 μg/l, Chl-a 6.17 μg/l, SDD 0.4 m. TOC content could not be determined since the sediment was coarse.

**SD2G.** A total of 14 species and 312 individuals were obtained in this station. Mean species number was 8.6/0.1m² and mean individual number was 104/0.1m². Species sensitive to organic pollution were Glyceria sp., M. adriaticus, S. substruncata, C. gallina, T. neritea and E. pulchra; species tolerant to organic pollution were S. tentaculata, P. paucibranchiata, S. decoratus, C. capitata, A. alba, R. philippinarum, I. serrata and A. spinespis. Individuals belonging to sensitive species formed 11.5% of total, while individuals belonging to tolerant species formed 88.5%.

Shannon-Weaver and BENTIX classified this station in “Poor”, AMBI in “Good” EQS. Final judgement for this station is POOR. Level of species richness is not high, sensitive species were lowly represented quantitatively, middling qualitatively. TOC of sediment was 33.86 mg/g (High), dO of sea water 9.08 mg/l, TP 125.5 μg/l, TN 1427.8 μg/l, Si 3751.1 μg/l, Chl-a 4.88 μg/l, SDD 0.7 m.

**SD1P.** A total of 8 species and 17720 individuals were obtained in this station. Mean species number was 6.6/0.1m² and mean individual number was 5906.6/0.1m². Species sensitive to organic pollution were M. adriaticus, S. substruncata and T. neritea; species tolerant to organic pollution were S. tentaculata, S. decoratus, C. capitata, A. alba and R. philippinarum. Individuals belonging to sensitive species formed 0.5% of total, while individuals belonging to tolerant species formed 99.5%.

Shannon-Weaver and AMBI classified this station in “Bad”, BENTIX in “Poor” EQS. Final judgement for this station is BAD. Tolerant C. capitata contributed to 98.8% of all individuals. Sensitive species were represented by only 90 individuals within 17720 (0.5%). Values of Shannon-Weaver and Evenness are extremely low. TOC of sediment was 31.49 mg/g (High), dO of sea water 10.27 mg/l, TP 6.2 μg/l, TN 151.8 μg/l, Si 21.3 μg/l, Chl-a 0.8 μg/l, SDD 2 m.

**SD2P.** A total of 40 species and 823 individuals were obtained in this station. Mean species number was 22.6/0.1m² and mean individual number was 274/0.1m². Species sensitive to organic pollution were Actinaria sp., Sipuncula sp., Glyceria sp., Onuphis sp., O. fusiformis, M. adriaticus, F. glaber, L. divaricata, S. substruncata, T. donacina, P. rudis, H. rugosa, T. papyracea, B. laterilli, C. chinensis, T. reticulata, M. conoeida, P. aperta, P. longimanus, A. gracilis, D. pugilator, L. vernalis and M. glacialis; species tolerant to organic pollution were M. picta, S. tentaculata, N. hombergii, E. vittata, P. macrolekae, C. capitata, S. triqueter, M. galloprovincialis, A. alba, C. gibba, A. laterilli, A. spinespis and M. rotundirostre. Individuals belonging to sensitive species formed 13.9% of total, while individuals belonging to tolerant species formed 85.4%.

Shannon-Weaver and BENTIX classified this station in “Moderate”, AMBI in “Good” EQS. Final judgement for this station is MODERATE. Both total and mean species number were highest here among all stations. Level of species richness is moderate, sensitive species were lowly represented quantitatively, highly qualitatively. TOC of sediment was 45.72 mg/g (High), dO of sea water 10.59 mg/l, TP ≤5.69 μg/l, TN 170 μg/l, Si 10.4 μg/l, Chl-a 0.36 μg/l, SDD 2.5 m.
MD19P. A total of 16 species and 67 individuals were obtained in this station. Mean species number was 8.6/0.1 m² and mean individual number was 22.3/0.1 m². Species sensitive to organic pollution were Actinaria sp., L. yhleni and P. aperta; species tolerant to organic pollution were N. hombergii, A. alba, I. serrata, A. diadema, A. spinipes, A. ramondi and M. rotundiroste. Individuals belonging to sensitive species formed 17.9% of total, while individuals belonging to tolerant species formed 70.1%.

Shannon-Weaver classified this station in “Poor”, AMBI in “Good”, BENTIX in “Moderate” EQS. Final judgement for this station is MODERATE. Tolerant A. alba was the most abundant species by forming 29.8% of all individuals. Abundance of sensitive species was the highest in this station. TOC of sediment was 27.39 mg/g (Intermediate), DO of sea water 8.32 mg/l, TP <5.69 μg/l, TN 146.3 μg/l, Si 31.4 μg/l, Chl-a 0.46 μg/l, SDD 3.7 m.

MD20P. A total of 17 species and 162 individuals were obtained in this station. Mean species number was 9.3/0.1 m² and mean individual number was 54.0/0.1 m². Species sensitive to organic pollution were Sipuncula sp., L. yhleni, L. divericata, A. tornatilis and M. glacialis; species tolerant to organic pollution were N. hombergii, L. latreiillii, C. gibba, I. serrata, A. diadema, A. spinipes and A. ramondi. Individuals belonging to sensitive species formed 14.8% of total, while individuals belonging to tolerant species formed 70.9%.

Shannon-Weaver classified this station in “Poor”, AMBI in “Good”, BENTIX in “Moderate” EQS. Final judgement for this station is MODERATE. Tolerant C. gibba was the most abundant species by forming 51.2% of all individuals. Abundance of sensitive species was the second highest in this station. TOC of sediment was 20.16 mg/g (Intermediate), DO of sea water 8.56 mg/l, TP <3.69 μg/l, TN 180.8 μg/l, Si 6.5 μg/l, Chl-a 0.62 μg/l, SDD 3.5 m.

CONCLUSION

A total of 19865 individuals belonging to 64 macrozoobenthic species were obtained in this study. Thirty-one (48.44%) out of determined 64 species are sensitive to organic pollution, 24 (37.50%) are tolerant, while there is no certain information about sensitivity of 9 (14.06%) species. Sensitive 31 species were represented by 282 individuals (1.4%), tolerant 24 species by 19546 individuals (98.4%), uncertain 9 species by 37 individuals (0.2%). Tolerant polychaete Capitella capitata, typical species of organically polluted waters throughout the world and hence called as global bioindicator, was the most dominant species of study with 17771 individuals (89.45%). It was followed by tolerant polychaete Spio decoratus with 739 individuals (3.72%), by tolerant amphipod Ampelisca spinipes with 352 individuals (1.77%), by tolerant bivalves Abra alba with 212 individuals (1.06%) and Corbula gibba with 170 individuals (0.85%). Species sensitive to organic pollution could not reach to high individual numbers, their most abundant species belonged to Mollusca. Bivalves Spisula subtruncata represented by total 88 individuals (0.44%) and Modiolus adriaticus by 23 individuals (0.11%), gastropods Tritia nitida by 33 individuals (0.16%) and Tritia reticulata by 20 individuals (0.10%). Even though individuals of the most abundant Capitella capitata are kept out from total, it was seen that 84.7% of remaining 2094 individuals belonged to tolerant, 13.4% to sensitive species. As it appears, coastal transitional waters of Susurluk River Basin are substantially dominated by individuals of species tolerant to organic pollution.

Global bioindicator Capitella capitata was encountered only at stations SD1G, SD2G, SD1P and SD2P which located in the direction of river flow. Tolerant species formed 98.7% of all individuals at these four stations while sensitive species formed only 1.2%. Two stations, MD19P and MD20P, located outside of the direction of river flow had a different individual distribution. Tolerant species at these two stations formed 70.7% of all individuals while sensitive species formed 15.7%. Total organic carbon (TOC) of sediment was in “Intermediate” category (10-28 mg/g) at MD19P and MD20P, in “High” category (>28 mg/g) at resting four stations. Quantitative discrepancy of this important ecological factor effected species composition at stations, as a result, different EQS were encountered.

Shannon-Weaver (H) classified SD1G and SD1P as “Bad”. The lowest mean species number and Evenness Index (J) values were obtained at these two stations. SD1G was significantly dominated by tolerant Spio decoratus, SD1P by tolerant Capitella capitata. Therefore, very low H and J values were calculated. Percentage of individuals belonging to tolerant species at two stations were 99.4% and 99.5%, respectively. BENTIX classified both of them as “Poor” since it accepts only zoic stations as “Bad”. AMBI scored SD1G as “Moderate”, SD1P as “Bad”. S. decoratus, the most dominant species of SD1G, was placed in Group III instead of Groups IV or V by AMBI, hence, it accepted this station as “Moderate”. Consequently, final assessment was “Bad” for SD1G and SD1P where tolerant species were extremely dominant and a healthy species composition was not present.

SD2G, of which final assessment was “Poor” and where sensitive species were lowly represented quantitatively, middling qualitatively, was accepted as “Poor” by H and BENTIX, as “Good” by AMBI. Ampelisca spinipes, the second dominant
(24.6%) species of this station, was placed in Group I, which includes the species sensitive to organic enrichment and present at unpolluted environments, by AMBI which overestimated the station. However, A. spinipes can be represented by high individual numbers in sediments with high TOC.

SD2P was scored as “Moderate” by H’ and BENTIX, as “Good” by AMBI. Ampelisca spinipes, the most dominant (31.7%) species of this station, was placed in Group I by AMBI and therefore it overestimated the station. However, the highest TOC content of sediment within study area was detected in this station. Other dominant species were tolerant Capitella capitata (17%), Corbula gibba (10.5%) and Spirobranchus triqueter (7.7%). This station included the highest species number and sensitive species were represented by low percentage of individual number but by high percentage of species number. Species richness is at moderate level. SD2P was assessed as “Moderate” in final judgement.

MD19P and MD20P, of which TOC content is in Intermediate category, were accepted as “Poor” by H’, as “Moderate” by BENTIX and as “Good” by AMBI. Acanthocardia paucicostata, Hyale vitrea and Iphinoe serrata, having a total dominance of 16.4% at MD19P, 15.4% at MD20P and accepted as tolerant by BENTIX, were placed in Group I by AMBI, thus, it classified these two stations in “Good” EQS. The most dominant species was Abra alba (29.8%) at MD19P, Corbula gibba (51.2%) at MD20P, both species are tolerant according to BENTIX and AMBI. Since these stations were highly dominated by one each species, H’ assessed them as “Poor”, however, J value is high especially at MD19P. Individual number percentages of sensitive species were highest (17.9% and 14.8%, respectively), of tolerant species were lowest (70.1% and 70.9%, respectively) at these stations. Final assessment for MD19P and MD20P is “Moderate”.

Comparing with final assessment of EQS, Shannon-Weaver underestimated two stations (MD19P and MD20P), AMBI overestimated 5 stations (all except SD1P). BENTIX overestimated two stations (SD1G and SD1P). BENTIX accepts only azeic stations as “Bad”, therefore, it scored SD1G and SD1P as “Poor” and overestimated them. Efforts of AMBI and BENTIX methods were reviewed by many studies such as Prado et al. [26] and Simboura and Argyrou [27]. According to Prano et al. [28], biotic indexes generally overestimate the EQS of not strictly marine ecosystems, as is Susurluk River basin, and they indicated that BENTIX discriminated the stations better than AMBI in the Venice Lagoon. Simboura and Argyrou [27] asserted that AMBI overestimated the EQS in Eastern Mediterranean areas. Çağlar and Albayrak [18] also denoted biotic indexes tended to overestimate the EQS of the stations in the Northern Marmara Sea and BENTIX was more successful in identifying the EQS. Since transitional ecosystems naturally host many tolerant and opportunistic species adapted to the natural stress of the environment, biotic indexes are not very effective in such areas [29]. However, main problem of these biotic indexes is classifying some species into different ecological groups and they are subjective at least when selecting species as sensitive or tolerant [30, 31].

Secchi Disc Depth values at stations were very low (0.4-3.8 m). Nutrient levels were very high, salinity was very low especially at SD1G and SD2G stations. According to Chlorophyll-a values, waters of SD2P and MD19P were in lower mesotrophic (0.1-0.6 μg/l), SD1P and MD20P in higher mesotrophic (0.6-2.21 μg/l), SD1G and SD2G in eutrophic (>2.21 μg/l) character, and, SD2P was in “Good”, MD19P in “Moderate”, SD1P and MD20P in “Poor”, SD1G and SD2G in “Bad” EQS [24]. This designation brings out the effect of land based sources with low salinity on primer production. Considering the factors such as dense population and industrial activities around rivers flowing into seas, it is clear that rivers considerably contribute to marine pollution. Findings of this study indicate the effect of Susurluk River over the study area.

When EQS of coastal transitional waters of Susurluk River Basin is evaluated as a whole, it was seen that there was not any station in “Good” or “High” EQS at the study area, stations were “Poor” or “Bad” at the stations where the River meets the sea, while the stations off the River mouth were “Moderate”. Both species pattern of macrozoobenthic invertebrate communities and ecological parameters determined in the basin such as TOC and nutrients present the negative impacts of the River over the basin and indicate the necessity of efficient precautions to be taken.

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PIGMENT SYNTHESIS AT EARLY STAGES OF DEVELOPMENT AT GM AND NON-GM MAIZE CULTIVARS UNDER HERBICIDE TREATMENT

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ABSTRACT

The continued need for improvement of crop’s yield has increased the categories of herbicides in use in Albania. Independently of the category, they increase the toxicity of the soils for weeks to months, which may slow photosynthesis and plant growth during the early phases of development.

The impact of most used herbicides, Afalon (linuron), Pendimex (pendimethalin), and Equip (foramsulfuron and isoxadifen-ethyl) on pigment synthesis for six cultivars of maize (Zea mays L.) were verified. The analyzed cultivars were AGS-4, AGS-83, AGS-500, MONO, Dvorani, and Floqi, the first four introduced, and the last local native. Seeds were planted in soil and kept in growth room for 7 days prior to treatment. Chlorophyll pigments were extracted following a standard DMSO protocol from leaf samples 30 days old. Cultivars were controlled for Bt-176 event, using specific PCRs for maize zein, CaMV35S, P-CDPK, CryIA(b), and for Bt-11 construct using primers specific for Intron IVS2-2/PAT-B. Results show that maize cultivars display significant differences in the rate of pigment synthesis under treatment; Local cultivars were the most affected (2X and 4.6X decrease) compared to the introduced ones (1.3-1.4X decrease); Under treatment with herbicide Equip plants reach the lowest pigment synthesis rate. Bt-176 construct was found present at four introduced cultivars, which were not labeled as such.

KEYWORDS:
GMOs, Bt crops, photosynthetic pigments.

INTRODUCTION

Albania is an agricultural country where cultivars of maize (Zea mays L.) are consumed as human food, animal feed and as nutrients in food industry. Most of the cultivars are introduced, and some are local native. At the global level, cultivars marketed with the HT trait are either transgenic varieties, or varieties developed without transgenic techniques from individual plants possessing either spontaneous or induced mutations. Nowadays, many maize hybrids are delivered to producers, coated with an insecticide or fungicide, or both, as seed dressing. Seed treatments are added to seed

a) to protect seedlings against soil, seedborne diseases and pests, b) to enhance germination and c) to promote seedling emergence during the critical first few weeks after planting [1]. The term herbicide-tolerant variety refers to cultivated varieties into which the HT trait has been intentionally introduced; it does not include a species inherent capacity to tolerate application of an herbicide [2].

However, the continued need for improvement of maize’s yield has increased the categories of herbicides in use in Albania, among which Afalon (linuron), Pendimex (pendimethalin) and Equip (foramsulfuron and isoxadifen-ethyl) were identified as the most widely used. Herbicide damage to crops is rarely due to the herbicide(s) alone, because detrimental environmental conditions (cold and wet weather during application), choice of hybrid (sensitive or tolerant to certain herbicides) as well as inaccurate dosage rates, are important factors playing a role in the severity of damage [1].

Linuron a pre, and a post-emergent herbicide causes peroxidative breakdown of the membrane lipids, that leads to destruction of the pigments, changes in the energy transfer, disorganization of the chloroplast membranes, and accumulation of toxic organic peroxides [3]. The second herbicide considered here, pendimethalin prevents plant cell division and elongation in susceptible species, while Equip is made up of foramsulfuron and isoxadifen-ethyl (the first inhibits the synthesis of amino acid in plants through inhibition of acetolactate synthase-ALS, and isoxadifen-ethyl serves as a crop safener).

The major mechanism by which currently developed safeners protect crops from herbicidal injury is through enhancement of the activity of degradative enzymes, such as cytochrome P-450 monooxygenases,glutathione S-transferases (GSTs), and UDP-dependent glycosyltransferases [4]. Interestingly, a strong correlation was observed between the efficacy of a safener and its ability to induce GST activity, suggesting that herbicide tolerance in safener-treated plants is a result of the induced ability to detoxify the herbicide via GSH conjugation [5]. Because herbicide use presents phytotoxicity issues
for crop plants, the agro-chemical industry has traditionally sought to develop selective herbicide molecules, intended to have a maximal effect on weeds while exerting a minimal effect on the crop. In other cases, rather than searching for new herbicide molecules and families, companies seek to create crop varieties genetically adapted to existing active ingredients.

MATERIALS AND METHODS

Growth and treatment of plants. Maize cultivars AGS-4, AGS-83, AGS-500, MONO, Dvorani, and Floqi were donated from Local Authority for Seed Resources of Korca region. They were planted in soil and kept in growth room for 7 days prior to treatment with herbicides Afaloni (linuron), Pendimex (pendimethalin) and Equip (formamsulfuron and isoxadifen-ethyl), following the manufacturer’s instructions.

Pigment extraction and measurement. Thirty days old plantlets were used to extract photosynthetic pigments following a standard DMSO protocol from leaf samples [6], [7]. Calculations were made based on Arnon’s equations:
Chlorophyll A (mg/g fresh weight)=(12.7*A663) - (2.69*A645)/(V/1000*W)
Chlorophyll B (mg/g fresh weight)=(22.9*A645) - (4.68*A663)/(V/1000*W)Tot.Chlorophylls=(20.08*A645+8.02*A663)/(V/1000*W) Carotenoids+xanthophylls (mg/g fresh weight) = (1000*A470 - 1.90ChlA63.14ChlB/214)/(V/1000*W).

Control for GM constructs. Cultivars were controlled for BT-176 and BT-11 events using specific PCRs. For zein, CaMV35S and Intron IVS2-2/PAT-B (event BT-11) primers were designed following [8]. Primers for BT-176 transgenic construct CDPK-cry-03/cry-04 and Cry1A(b)-1/A(b)-2 were designed according to [9]. DNA was extracted from leaves following CTAB based protocol [10].

RESULTS AND DISCUSSION

Amount of pigments was used to understand differences in photosynthesis rate among six maize cultivars non-treated or treated with herbicides.

The measurement of chla, chlb, total chl, and carotenoids showed considerable differences among controls from each cultivar, which were considered during the further analysis of the impact of herbicide treatment (Fig.1). Chla, chlb, and carotenoids synthesis is reduced under herbicide treatments. For cultivars AGS-4, AGS-83, AGS-500 and Floqi the AFALON-45 had the lowest impact; for Dvorani and MONO the herbicide of choice should be PENDIMEX; Dvorani and Floqi are the most affected cultivars (2X and 4.6X decrease) compared to the rest (1.3–1.4X decrease);
the herbicide of choice should be PENDIMEX; Dvorani and Floqi are the most affected cultivars (2X and 4.6X decrease) compared to the rest (1.3-1.4X decrease); The lowest pigment synthesis values for all cultivars were reached during treatment with the herbicide Equip.

Control for GM constructs. In order to use PCR based methodology for the control of the presence of GMO constructs at the six maize cultivars under study, first the quality of the genomic DNA was verified through the amplification of a fragment of the zein coding gene (Fig.2).

**FIGURE 2**  
Control for zein gene fragment (139bp).  

It was amplified from samples representing the six maize cultivars, meaning the work could be continued for the detection of GMO constructs. First was controlled for the CaMV promoter, which is reported to be present at more than 85% of the commercialized GMOs (Fig. 3).

The presence of CaMV fragment at most of the samples shows that they are modified, however the category of the construct had to be further verified. As reported the event Bt-176 construct containscry1Ab gene (insect resistance: lepidoptera), bar gene (herbicide tolerance: glufosinate), and bla gene (antibiotic resistance: ampicillin).

**FIGURE 3**  
Control for CaMV promoter region (195bp).  
From right to left the sample order is: Molecular marker 0.1-10kbp; ½. Dvorani; ¾. Floqi; 5/6. AGS-83; 7/8. AGS-4; 9/10. AGS-500; 11/12.

We controlled for cry1Ab gene. The amplification of Cry1 A(b) coding gene fragment (Fig.4) showed that samples 1, 3, 4, 5, 6 and 7, which represent the four foreign introduced cultivars, do have the required fragment.

The presence of Bt-176 construct was further explored using another primer pair, which could amplify the gene fragment of P-CDPK promoter from maize (Fig.5).

**FIGURE 5**  
Control for CDPK (211bp) gene fragment.  
Order of samples from right to left: ½. AGS-83; ¾. AGS-4; 5/6. AGS-500; 7/8. MONO; Marker 0.1-10kbp.

It was amplified from all the samples, proving that they were GM with Bt-176 construct. Introduced cultivars do have Bt-176 constructs, while local cultivars Dvorani and Floqi do not;

The control for Event Bt-11, which carries cry1Ab, cry1Fa2 and vip3Aa20 genes (insect resistance: lepidoptera), pat gene (herbicide tolerance: glufosinate), cp4epsps gene (herbicide tolerance: glyphosate), and pmi gene (marker: mannose isomerase), proved unsuccessful, meaning this construct was not present at the analyzed samples.

Based on our results, the local cultivars (Dvorani and Floqi) were more susceptible to herbicide treatment than the introduced ones, which contain the Bt-176 construct. The last, except from being capable of producing Cry proteins are supposed to be resistant toward glufosinate ammonium. Since none of maize cultivars under study amplified the Bt-11 construct, we could not correlate the herbicide impact on pigments synthesis with its specific construct-mediated tolerance.

**CONCLUSIONS**

Four out of six maize cultivars in use in Korca region are GM with Bt-176 construct for resistance toward insects and glufosinate, and they are not labeled as such.

From two native local cultivars, namely Dvorani and Floqi, no GM constructs were amplified for events Bt-176 and Bt-11.

Their pigment synthesis was most affected by herbicide treatment compared to the GM-cultivars;

Following the results of this work, local authorities and farmers could be advised on the proper HB treatment of different maize cultivars.
REFERENCES


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HERBICIDES IN THE CAVE ENVIRONMENT: ECOTOXICOLOGICAL RISKS

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ABSTRACT

This study aimed to detect triazine pesticides and their metabolites in the drip water of the Amaterska cave system (Moravian karst, Czech Republic). Ecotoxicological tests were used to assess the risk of selected herbicides (i.e. atrazine and terbutylazine) and their metabolites (atrazine-desethyl, atrazine-disisopropyl, terbutylazine-desethyl) in the drip water by means of bioassays with selected bioindicators. Tests were conducted on organisms representing all trophic levels of the aquatic ecosystem: producer algae *Pseudokirchneriella subcapitata* and macrophyte duckweed *Lemna minor*, a consumer water flea *Daphnia magna*, and decomposer bacterium *Vibrio fischeri*. Effects of herbicides on edaphon representatives were measured by testing the reproductive inhibition of enchytraeids *Enchytraeus crypticus*.

Triazines and their metabolites were analysed in the drip water of the Amaterska cave system sampled at a site under agricultural cropland. Standard methods were used for testing procedures: OECD 201 (Freshwater algal growth inhibition test), OECD 221 (*Lemna* sp. Growth Inhibition Test), OECD 202 (Inhibition of the mobility of *Daphnia magna*), ISO 11348-2 (Inhibitory effect of water samples on the light emission of *Vibrio fischeri*) and OECD 220 (Enchytraeid Reproduction Test).

Drip water samples were examined for 350 substances. Six pesticides above the limit of quantification were identified; all of these substances belong to the triazine pesticide group. The performed experiments showed no evidence of acute toxicity of the drip water. However, accumulation in the environment and chronic toxicity could not be ruled out. The ecotoxicity of selected herbicides and their metabolites differed significantly depending on the test organism and testing conditions.

KEYWORDS:
pesticides, ecotoxicity, bioindicators, bioassay, drip water.

INTRODUCTION

Residues of commonly used pesticides can remain at detectable levels in the environment for years. Metabolites are usually more polar than the parent pesticide and thus pose a greater potential risk of groundwater contamination. Regarding the widespread pollution of aquatic ecosystems, atrazine has been banned in EU countries and replaced with the structurally analogous terbutylazaine [1].

The karst vadose zone consisting of the soil, epikarst, and transmission zone can hold large amounts of water as well as potential contaminants. This unsaturated zone of karst aquifers allows for the biodegradation of contaminants and other attenuation processes to operate, but the efficacy of these processes depends on the rate of transportation downward to the active conduit network often via vertical shafts [2, 3]. Different types of substances originating from human activities at the land surface, such as agriculture or wastewater, can be transported through karst systems and can potentially accumulate in cave sediments [3]. Cave drip water is water infiltrated through soil pores on the cave surface during/after rainfall into the karstic profile [4]. The composition and volume of drip water are influenced by many environmental factors [2]. Drip water is a useful tool for the monitoring of surface environmental contamination [5].

Some of the pesticides found most commonly in ground water are triazine, terbutylazaine and their metabolites that belong to triazine herbicides. The residence times of the water within a karst vadose zone, which is several tens of meters thick, were estimated to range from several months to several years [6].

The aim of this study was to 1) detect triazine pesticides and their metabolites in the drip water of the Amaterska cave system, 2) determine the ecotoxicity of drip water by means of bioassay with selected bioindicators and 3) define the effects of herbicides (atrazine and terbutylazaine) and their metabolites on selected bioindicators.
MATERIALS AND METHODS

To assess the impact of the selected herbicides and their metabolites on the representatives of the aquatic and soil biocoenosis, acute toxicity tests on aquatic organisms (\textit{Pseudokirchneriella subcapitata}, \textit{Daphnia magna}, \textit{Vibrio fischeri} and \textit{Lemna minor}) were employed. A chronic toxicity test of the studied herbicides and their metabolites was performed on the representative of the soil edaphon (\textit{Enchytraeus crypticus}). Methodologically, relevant OECD standards were followed. In addition, biological testing of drip water toxicity was carried out with samples collected in the Amaterska cave, Moravian Karst, Czech Republic (Rozlehlá Corridor), situated under farmed land. Samples of drip water were immediately transferred for chemical analysis at the ALS Czech Republic Laboratory in Brno and the Ecotoxicology Laboratory of the Department of Ecology and Diseases of Game, Fish and Bees, Faculty Hygiene and Ecology, University of Veterinary and Pharmaceutical Sciences Brno where the bioassays and the determination of selected analytes (Aquamerck$^\text{®}$, Merck, Germany) were performed.

![FIGURE 1](image)

\textbf{FIGURE 1}

\begin{enumerate}
\item Location of the Moravian Karst within Central Europe;
\item North-eastern part of the Moravian Karst with the studied cave systems;
\item Amaterska Cave with drip eater sampled (Rozlehlá corridor).
\end{enumerate}

The map was taken over and adjusted according to our needs [5].

Site of study. The Moravian Karst is the largest and best-developed karst area in the Bohemian Massif (Czech Republic). The Moravian Karst with an area of over 92 km$^2$ and more than 1600 known caves was declared a protected landscape area in 1956. The Moravian Karst is a moderately warm (average annual temperature 7–8 °C) and moderately humid (average annual rainfall 550–650mm) climatic region with the drier and warmer sites in its southern part [4]. The longest cave system is the Amaterska cave with an underground corridor measuring more than 35 km in length. The sampling site of drip water was below arable land (Rozlehlá corridor) (Fig. 1).

Sampling method and chemical analyses. Triazines and their metabolites were analysed in drip water from the Amaterska cave system area from a site (Rozlehlá corridor) which was situated beneath agriculture cropland. Sampling was carried out during spring, summer and autumn 2017. The drip water was sampled into 500 ml polyethylene plastic laboratory bottles and immediately decanted to polyethylene bottles according to following analyses, inserted into a cooling box/bag, and transported to laboratory. The analyses were performed in the laboratories ALS Czech Republic, according to the methods CSN EN 15637, US EPA 1694. Measurements were performed by ultra-performance liquid chromatography coupled with triple quadrupole tandem mass spectrometry.

Two samples of drip water were prepared for the bio-test with autotrophic organisms. One sample was enriched with nutrients in the same amount as is normally added to a nutritional solution, and the other sample was free of nutrients. The sample was enriched with nutrients in order to prevent the inhibition of growth due to the absence of nutrients.

The Aquamerck testing laboratory (The MColortest$^\text{TM}$ Compact Laboratory for Water Testing) was used to determine: ammonium, total hardness, nitrate, nitrite, pH, phosphate, oxygen and oxygen consumption, and temperature. The tests are based on colorimetric and titrimetric methods.

Test organisms. The test organisms (\textit{Daphnia magna}, \textit{Lemna minor}, \textit{Enchytraeus crypticus}) originated in cultures from the Ecotoxicological laboratory of the University of Veterinary and Pharmaceutical Sciences Brno (Czech Republic), except for the liquid-dried bacteria \textit{Vibrio fischeri} which were obtained from producer Hach-Lange GmbH (Düsseldorf, Germany) and a culture of green algae \textit{Pseudokirchneriella subcapitata} (Korshikov) Hindak, which was obtained from the collection of autotrophic organisms of the Botanical Institute of the Academy of Sciences (Trebon, Czech Republic).

Experimental design. Testing procedures were carried out in accordance with the following standards with minor changes to fit our experimental conditions: OECD 201 (Freshwater algal growth inhibition test), OECD 221 (\textit{Lemna} sp. Growth Inhibition Test), OECD 202 (Inhibition of the mobility of \textit{Daphnia magna}), ISO 11348-2 (Inhibitory effect of water samples on the light emission of \textit{Vibrio fischeri}) and OECD 220 (Enchytraeid Reproduction Test).

Pesticides. The effects of Atrazine, Atrazine-desethyl, Atrazine-desisopropyl, Terbuthylazine and Terbuthylazine-desethyl were examined. All
chemicals (PESTANAL®, analytical standard) were purchased from Sigma-Aldrich Corporation (USA).

All the tested pesticides are water soluble. Therefore, for the preparation of the stock solutions, dilution water of composition described in the relevant standards was used. In the test with *Vibrio fischeri* the dilution water was 2% NaCl solution; in the test with *Lemma* minor the dilution water was Swedish standard medium; in the algal test standard nutrient solution and in the test with *Daphnia magna* dilution water (CSN EN ISO 6341) were used. In tests with *Enchytraeus crypticus* the soil was contaminated by dissolved pesticides in an adequate amount of deionised water to achieve soil moisture equal to 50% of maximum water-holding capacity.

The concentration ranges of selected pesticides and their derivatives was determined by analysis of the real samples of drip water. The concentration ranges of selected pesticides (Atrazine, Terbutylazine) and their metabolites (Atrazine-desethyl, Atrazine-desisopropyl, Terbutylazine-desethyl) were the following for duckweed and algae (0.1; 1; 10; 25; 50 and 100 μg L⁻¹), for daphnia (5; 50; 125; 250, 375 and 500 μg L⁻¹) and bacteria (0.195, 0.391, 0.78, 1.563, 3.125, 6.25, 12.5, 25 and 50 mg L⁻¹).

**Statistical analysis.** The test results were evaluated using the TOXICITA 3.1 (VUV Ostrava, Czech Republic) software, by means of a regression analysis of the data with 95% confidence interval (CI), based on squared deviations of experimental values from the selected approximation function.

**RESULTS AND DISCUSSION**

Drip water samples were examined for 350 substances (active substances and selected metabolites). By means of chemical analysis using ultrapure liquid chromatography with tandem mass spectrophotometry carried out in an accredited laboratory of the ALS Czech Republic in Brno, 6 pesticides (herbicides atrazine and terbutylazine and their metabolites) were found in drip water (Table 1). The detection limit for aqueous samples is 0.001–0.01 μg L⁻¹. Atrazine preparations containing the active substance have been prohibited in the Czech Republic since 2005. The analysis shows that the concentration of triazine herbicides did not exceed the maximum contaminant level (MCL) either for the total of pesticides (MCL 0.5 μg L⁻¹) or for the individual pesticides including metabolites (MCL 0.1 μg L⁻¹) in the drinking water (Decree No. 252/2004 Coll., Council Directive 98/83 / EC).

The results of our study (the presence of triazines in drip water from the Amaterska cave in the depth of approximately 120 m) are contradictory to the statement that „Due to the low solubility of triazine substances in water, they usually do not penetrate down to the deeper levels of soil and thus have little effect on deep-rooted plants, which is one of the factors governing their selective application“ [7, 8]. Modra et al. (2017) state that concentrations of atrazine in the Amaterska cave sediment ranged from 0.7 to 7.3 μg L⁻¹, which means that concentrations of atrazine in the cave sediment were 16 to 70 times higher than in those in the drip water. The biodegradability of these pesticides in cave sediments is limited due to the lack of photolysis and thermal decomposition [2].

The presence of atrazine in water has long been studied, and, generally, residual levels of these pesticides are detected at the low ng L⁻¹ level. However, some reported concentrations exceed values of μg L⁻¹ because of extensive agricultural activity (for example from 0.001 μg L⁻¹ up to values exceeding 100 μg L⁻¹ in the US “corn belt” and Canada [7, 9].

One of the major degradation pathways of atrazine in surface soils is hydrolysis to atrazine-2-hydroxy, and the reported half-life of atrazine-2-hydroxy is 121 days. The maximum concentration of atrazine-2-hydroxy detected in Czech rivers was 0.657 μg L⁻¹. Due to persistence, water solubility and mobility, these metabolites are frequently detected in rivers and lakes, posing potential cumulative risks to aquatic organisms [1].

Terbutylazine concentrations in surface and ground waters range from 0.01 to 4.50 μg L⁻¹ and terbutylazin-desethyl at 0.008 to 1.80 μg L⁻¹ [1, 7, 10]. The highest reported environmental concentration of terbutylazine in Czech rivers was 2.6 μg L⁻¹ [11]. The degradation products of pesticides are usually more polar and thus pose a greater potential risk of ground water contamination, often with considerably higher toxicity than in the parent compound [12, 13].

In most studies, the triazine concentrations reported in water did not exceed the level of micrograms per litre and these have usually been regarded to be of low ecological risk [7]. The most important parts of the aquatic food chain are freshwater invertebrates that serve as a food source for juvenile or adult fish. A reduction in a single species of zooplankton might affect the food supply for fish and thus the whole aquatic ecosystem [14].

The next stage of our study was the acute toxicity tests with selected pesticides (Tab. 2). Although *D. magna* is one of the aquatic organisms most sensitive to foreign substances, especially to organophosphate residues, the acute toxicity of the studied pesticides was not established. Low toxicity of pesticides and their metabolites was detected for bacteria. The tests performed did not show the inhibition of the light emission of bacteria to exceed 20% at exposure periods of 15 or 30 minutes. Terbutylazine pesticide was proven to have inhibitory effects on algae and duckweed. Acute toxicity, expressed by the value of 72 hEC50 and 168 h EC50, was 99.99 μg L⁻¹ for both. The results found for *P.*
The acute toxicity values detected in the present study with pesticides and their metabolites were many times higher than the real environmental concentrations found.

The result of the biological test of the drip water toxicity (using D. magna, V. fischeri, E. crypticus) was negative, i.e. there was no change in behaviour and in the state of organisms compared to the control. In the study by Wang et al. (2016) evaluating the acute toxicity test with *Eisenia fetida*, 14dEC50 was detected at 190.4 mg kg⁻¹ of artificial soil. This is again many times higher than any real environmental concentrations found [17].

By bioassay with autotrophic organisms (*P. subcapitata, L. minor*), an overlimit (≥30%) inhibition of growth was detected over the control, probably due to the absence of nutrients (Table 3). This was confirmed by strong growth stimulation following the nutrient enrichment. This marked stimulation is likely to be due to the presence of nitrate in the sample (140 mg L⁻¹, on average) (Table 4). The summary results of the chemical analysis performed using the compact Aquamerek® laboratory in Tab. 4.

In another study, nitrate concentration was analysed from 60 drips in the Amaterska Cave, sampled in June, 2007. The mean nitrate concentration in the drips from never fertilized areas was 10 mg L⁻¹ in the area originally fertilized but converted to grassland in 1998 it was 78 mg L⁻¹; and in presently-fertilized land it was 80 mg L⁻¹. The mean concentration in the drips below fertilized lands was 61–105 mg L⁻¹. At the same time, the mean residence time of nitrate is <10 years in the 25–30 m thick vadose zone, but >16 years in the 105–120 m thick vadose zone (which is the case with the Amaterska Cave) [5].

**TABLE 1**

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>May, 2017</th>
<th>July, 2017</th>
<th>October, 2017</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine (µg L⁻¹)</td>
<td>0.011</td>
<td>0.01</td>
<td>0.014</td>
</tr>
<tr>
<td>Atrazine-2-hydroxy (µg L⁻¹)</td>
<td>0.013</td>
<td>0.01</td>
<td>0.015</td>
</tr>
<tr>
<td>Atrazine-desethyl (µg L⁻¹)</td>
<td>0.02</td>
<td>0.02</td>
<td>0.034</td>
</tr>
<tr>
<td>Atrazine-desisopropyl (µg L⁻¹)</td>
<td>&lt; 0.010</td>
<td>&lt; 0.010</td>
<td>&lt; 0.010</td>
</tr>
<tr>
<td>Terbuthylazine (µg L⁻¹)</td>
<td>&lt; 0.010</td>
<td>&lt; 0.010</td>
<td>&lt; 0.010</td>
</tr>
<tr>
<td>Terbuthylazine-desethyl (µg L⁻¹)</td>
<td>&lt; 0.010</td>
<td>&lt; 0.010</td>
<td>&lt; 0.010</td>
</tr>
<tr>
<td>Total pesticides and metabolites (µg L⁻¹)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**TABLE 2**

<table>
<thead>
<tr>
<th>Pesticides</th>
<th>Test organisms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><em>Pseudokirchneriella subcapitata</em></td>
</tr>
<tr>
<td></td>
<td>72hEC20 (µg L⁻¹) (95% CI)</td>
</tr>
<tr>
<td>Atrazine</td>
<td>98 (86.5–109.5)</td>
</tr>
<tr>
<td>Atrazine-desethyl</td>
<td>a</td>
</tr>
<tr>
<td>Atrazine-desisopropyl</td>
<td>a</td>
</tr>
<tr>
<td>Terbuthylazine</td>
<td>a</td>
</tr>
<tr>
<td>Terbuthylazine-desethyl</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>(91.37–108.62)</td>
</tr>
<tr>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>a</td>
</tr>
</tbody>
</table>

95% CI – 95% confidence interval, fkt – correction factor for 15 or 30 min incubation must be between 0.6–1.3, a Not obtainable
TABLE 3
Results of drip water bioassay without and with nutrient enrichment (Iµ - inhibition of algae/duckweed growth compared to the control, IB - inhibition of duckweed biomass compared to the control).

<table>
<thead>
<tr>
<th>Test organisms</th>
<th>May, 2017</th>
<th>July, 2017</th>
<th>October, 2017</th>
</tr>
</thead>
<tbody>
<tr>
<td>P. subcapitata</td>
<td>Iµ</td>
<td>Iµ</td>
<td>Iµ</td>
</tr>
<tr>
<td>Drip water sample</td>
<td>36.05%</td>
<td>30.37%</td>
<td>26.83%</td>
</tr>
<tr>
<td>Drip water sample + nutrients</td>
<td>-47.62%</td>
<td>-26.75%</td>
<td>-6.36%</td>
</tr>
<tr>
<td>Lemma minor</td>
<td>Iµ</td>
<td>IB</td>
<td>Iµ</td>
</tr>
<tr>
<td>Drip water sample</td>
<td>38.59%</td>
<td>46.30%</td>
<td>32.63%</td>
</tr>
<tr>
<td>drip water sample + nutrients</td>
<td>8.85%</td>
<td>12.14%</td>
<td>0.73%</td>
</tr>
</tbody>
</table>

TABLE 4
Summary of the results of chemical analysis of drip water by Aquamerck compact laboratory.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.77</td>
<td>7.23</td>
<td>7.11</td>
</tr>
<tr>
<td>temperature (°C)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>O₂</td>
<td>9.9</td>
<td>9.19</td>
<td>9.23</td>
</tr>
<tr>
<td>NH₄⁺ (mg.L⁻¹)</td>
<td>0</td>
<td>1.75</td>
<td>0</td>
</tr>
<tr>
<td>NO₃⁻ (mg.L⁻¹)</td>
<td>112.5</td>
<td>135</td>
<td>146</td>
</tr>
<tr>
<td>NO₂⁻ (mg.L⁻¹)</td>
<td>0.025</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PO₄³⁻ (mg.L⁻¹)</td>
<td>0.25</td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td>ammoniacal nitrogen (mg.L⁻¹)</td>
<td>0</td>
<td>1.36</td>
<td>0</td>
</tr>
<tr>
<td>nitrate nitrogen (mg.L⁻¹)</td>
<td>25.5</td>
<td>3.6</td>
<td>33</td>
</tr>
<tr>
<td>chlorides (mg.L⁻¹)</td>
<td>5.3</td>
<td>6.08</td>
<td>8.46</td>
</tr>
<tr>
<td>Total hardness (mg.L⁻¹)</td>
<td>310</td>
<td>360</td>
<td>340</td>
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</tbody>
</table>

CONCLUSION

The application of pesticides is currently very widespread and, as can be seen from our results, the pesticides can also be detected in specially protected areas where the long-term use/application of pesticides leads to their persistence in the environment and subsequent contamination of groundwater. Although the values we set out for the acute toxicity of the pesticides and their metabolites are many times higher than the real environmental concentrations found, due to the need to preserve vulnerable cave ecosystems it is necessary to eliminate sources of pollution and continue to monitor the trend in the occurrence and transformation of pesticides.

In view of the importance of preserving vulnerable cave ecosystems, it is necessary to eliminate sources of pollution to protect the organisms that are bound to the karst environment. Pesticides do not only contaminate karst water, which serves as a source of drinking water, but can also have a negative impact on animals bound to this unique environment. The question remains whether the current amount of applied pesticides is reasonable and whether it would not be appropriate to find an alternative solution.

ACKNOWLEDGEMENTS

The authors are indebted to M. Kotyzová from the Nature Conservation Agency for her support of the cave drip water research. The study was supported by the Internal Grant Agency of the University of Veterinary and Pharmaceutical Sciences Brno (No. 228/2017/FVHE).

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REFERENCES


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SESSION VI
WATER AND SOIL POLLUTION
SEASONAL CHANGES IN PHYTOPLANKTON COMMUNITY STRUCTURE OF SOUTHWESTERN COAST OF THE BLACK SEA

Neslihan Balkis-Ozdelice1,*, Merve Anda Peynirci2

1Istanbul University, Faculty of Science, Department of Biology, Istanbul, Turkey
2Istanbul University, Institute of Science, Istanbul, Turkey

ABSTRACT

In order to determine the phytoplankton species of southwestern coast of the Black Sea, and the environmental factors that affect the distributions of the species, the water samples were collected vertically and horizontally with a plankton net at different depths at 5 stations between December 2012-November 2013. From the examination of the samples, 83 phytoplankton species belonging to 4 classes were identified. The majority of the species composition was represented by dinoflagellates (56%) and diatoms (41%) respectively. The highest cell numbers of phytoplankton were recorded in December (28730 cell/L) and August (35490 cell/L) in this study. Primary ecological variables, such as temperature (7.97-26.17 °C), salinity (13.58-17.75%), dissolved oxygen (3.63-16.65 mg/L) and pH (4.8-9.94), were recorded on each sampling occasion. In addition, nitrite+nitrate-N (0.01-3.24 µg-at N/L), ammonium-N (0.01-16.5 µg-at N/L), phosphate-P (0.01-6.7 µg-at P/L) and silicate-Si (0.71-72.7 µg-at Si/L) concentrations were measured, and also chlorophyll-a and suspended solid material values ranged between 0.05-3.31 µg/L and 0.007-0.042 g/L, respectively. Spearman’s rank correlation analysis was used to determine the relation between phytoplankton species and ecological variables, and Bray-Curtis analysis was applied to bring out the similarity between stations. The percentage of the similarity was 85% between stations.

KEYWORDS:
Phytoplankton, abundance, ecological variables, Black Sea.

INTRODUCTION

Connected to the Mediterranean Sea through the Straits system, and located between 41°-46° north latitude and 28°-41.5° east longitude, Black Sea is an almost isolated inland sea; and, with its 423000 km² surface area, it constitutes approximately one fifth of the Mediterranean. Having 547000 km³ water volume in total, Black Sea’s maximum depth is 2200 m [1]. Apart from the northwest of Black Sea, shallow areas are limited; and generally, areas that have 200 m depth at maximum are mostly located in northwestern parts [2]. Also, three biggest rivers of the Europe such as Danube, Dnieper, and Dniester Rivers affect the northwestern part. With the effect of these rivers, there are plenty of nutritional element inputs in the sea. Black Sea has faced several ecological problems since 1960s [3]. However, in recent years, with the increase of the concentration of nutritional elements such as NO₃, PO₄ and SiO₂ which were carried through these big rivers in the northwest of Black Sea, ecosystem of Black Sea has changed in a negative way [1, 4]. These changes have become apparent especially in northwestern coasts of Black Sea with eutrophic and hypoxic conditions; and with the improper use of the sources in recent years, there has been a significant decrease in the fish stock [5, 6]. Especially in less deep coastal waters, mass mortality of hypoxia/anoxia and benthic organisms has become common because of red-tide events [7].

Between 1886 and 1917, while the most important and first basic study on phytoplankton species in Black Sea was carried out by Reinhard [8], the second study carried out in Turkish territorial waters of Black Sea was conducted by Benli [9]. Later, many researchers have carried out studies on the distribution of phytoplankton species found especially in the middle and eastern parts of Black Sea [10-33].

When the above given studies are analysed in detail, it is seen that the relevant researches have generally focused on especially in the middle and eastern parts of Black Sea, and there have been less studies carried out in the western part. For this reason, in this study, the aim is to identify the environmental conditions that have effect on phytoplankton species and their distribution in the southwestern coasts of Black Sea.

MATERIALS AND METHODS

Sampling and analysis. The water samples were collected vertically and horizontally with a
plankton net at different depths (0.5, 5, 10, 15, 20 and 30 m) at 5 stations between December 2012 and November 2013 in the southwestern coast of the Black Sea (Fig. 1). Water samples for ecological variables and quantitative phytoplankton analyses were collected using a 5 l Ruttner bottle with a thermometer. pH of the sampled waters were measured using YSI 556 model multiparameter probes connected to a YSI datalogger (Ohio, USA). The Mohr-Knudsen method [34] was used for measuring the salinity values, and the Winkler [35] method was used for dissolved oxygen (DO).

Nitrate+Nitrite-N (NO$_3$-N) concentrations were measured by the cadmium reduction method using the Seal AA3 HR Auto/Analyser (Norderstedt, Germany). Phosphate-P (PO$_4$-P), Silicate (SiO$_4$-Si) and Chlorophyll-a (Chl-a) were analyzed according to Parsons et al. [36] and ammonium (NH$_4$-N) determination was performed with the indophenol blue method [37]. In addition, suspended solid materials (SSM) of water samples were calculated according to the gravimetric 2540-D standard method [38].

For phytoplankton taxonomic identification, horizontal and vertical samples from each sampling station were gathered using a plankton net with a 40 μm mesh size. Material was fixed with neutral 4% formaldehyde solution and observed by using an Olympus CK2 inverted phase-contrast microscope with a Motic MC1000 model camera attachment. References used to identify the phytoplankton species can be found in previous work [39]. Phytoplankton cell counts were obtained from 10-50 ml subsamples, preserved with acid Lugol’s iodine solution, allowed to settle from 1 l sample for 24-48 hours [40]. Then, neutral formaldehyde which has a concentration of 4% was added to preserve the cells [41] and counted in a Sedgewick-Rafter cell under an Olympus CK2 model inverted phase-contrast microscope and results were reported as cell numbers per liter [42].

**Statistical analysis.** Spearman’s rank correlation coefficient [43] was used to correlate the species number of phytoplankton and ecological variables. The Bray-Curtis similarity index in Primer v6 software, based on log(x+1) transformation, was calculated to detect the similarity between sampling stations [44].

**RESULTS**

**Environmental variables.** Primary ecological variables, such as temperature (7.97-26.17 °C), salinity (13.58-17.75‰), dissolved oxygen (3.63-16.65 mg/L) and pH (4.8-9.94), were recorded on each sampling occasion (Fig. 2). With regard to the temperature, big changes were observed in August, from the surface to the bottom. It was identified that in parallel with the increase in river intakes and rains, there was a decrease in salinity values in April. In addition, nitrite+nitrate-N (0.01-3.24 μg-at N/L), ammonium-N (0.01-16.5 μg-at N/L), phosphate-P (0.01-6.47 μg-at P/L) and silicate-Si (0.71-72.42 μg-at Si/L) concentrations were measured, and also chlorophyll-a and suspended solid material values ranged between 0.05-3.31 μg/L and 0.007-0.042 g/L, respectively (Fig. 2).

**Phytoplankton species diversity and abundance.** From the analysis of phytoplankton community composition, 83 taxa of four different algal groups were identified: 46 dinoflagellates (56%), 34 diatoms (41%), 2 dictyochophyceans (2%) and 1 chrysophycean (1%). The highest species numbers (65 taxa) were recorded in December 2012, whereas August was the month with the fewest species (52 taxa). The highest cell numbers of phytoplankton were recorded in December (28730 cell/L) and August (35490 cell/L) in this study. In addition, potentially harmful phytoplankton species were identified (dinoflagellates *A. sanguinea*, *A. minutum*, *D. acuminata*, *D. acuta*, *D. caudata*, *D. fortii*, *G. polygramma*, *L. polyedrum*, *N. scintillans*, *P. rotundatum*, *P. micans*, *S. trochoideae*, *T. furca* and *T. fusus*, diatoms *C. pelagica*, *C. closterium*, *L. danicus*, *P. pseudodelicatissima*, *P. pungens*, *S. costatum* and *T. nitzschioides* and dictyochophycean *D. fibula*) but none of them reached a level high enough to cause any negative effect.
FIGURE 2
Seasonal variations of ecological variables along the water column. Data are reported as averages of the sampling stations.
### TABLE 1

List and frequency distribution of phytoplanktonic taxa of southwestern coast of the Black Sea

<table>
<thead>
<tr>
<th>Taxa</th>
<th>Dec.12</th>
<th>Apr.13</th>
<th>Aug.13</th>
<th>Nov.13</th>
</tr>
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<tr>
<td>Akashiwo sanguinea (K.Hirasuka) G.Hansen and O.Monestrup, 2000</td>
<td>-</td>
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<td>Dinophysis fortii Pavillard, 1923</td>
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<td>Pleurosigma sp.</td>
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37 34 38 35
**Statistical data.** In order to reveal the relationship between phytoplankton species and cell numbers obtained from 5 stations and 6 different depth points in southwestern coasts of Black Sea and the ecological variables, Spearman’s rank correlation method was used; and, it was identified that as long as temperature, pH, and PO₄₃⁻ amount increased, species and cell numbers of phytoplankton increased as well; and in parallel with the increase of NO₂⁻ and SS, they decreased. Also, it was found out that the number of species had a negative relationship with SiO₂ and had a positive relationship with chl-a while the number of cells had a positive relationship with NH₄ and had a negative relationship with depth. It was also observed that as an indicator of productivity, the amount of chl-a had negative relationships with all variables, apart from NO₂⁻ and depth. The results of Bray-Curtis similarity index, which was carried out to identify the similarity between stations with regard to the diversity and abundance of species, are shown in Figure 3 (a, b); and, it was observed that the similarity between stations are at the rate of 85% with respect to both diversity and abundance of species; and the station number 4 is different from other stations in terms of the diversity, and the station number 2 is different from other stations in terms of the abundance of species.

**DISCUSSION**

Conducted in the southwestern coasts of Black Sea, in this study, Dinophyceae classis constituted 56% of the species acquired in this study with 46 taxa it included. In the studies containing Dinophyceae group and carried out by the researchers of the countries that are neighbour to Black Sea, Krakhlmalny [45] identified 193 species, and Gomez and Boicenco [46] identified 267 dinoflagellate species in the compilation study they carried out. The most comprehensive compilation study recently conducted in Black Sea reported the existence of 456 dinoflagellate species [47]. It was reported that there are 1400-1800 dinoflagellate species around the seas in the world [48, 49]. The reason why dinoflagellate species are less in Black Sea compared to 673 dinoflagellate species known in the Mediterranean is that diversity in brackish waters, which have a more stressed structure compared to sea waters, is generally less. Particularly it is reflected by the situation that visibility in Black Sea is low, the bottom layer has no oxygen, and the life is limited only with the upper level [46]. 46 dinoflagellate species found in this study comprise 10% of the known species in Black Sea. This rate is pretty low. One of the reasons of this is that 456 species were found as a result of many studies carried out through a long period and from the coastal waters of different countries; and the other reason is that this study includes only 4 sampling periods and it was carried out in 5 stations located only in southwestern coasts of Black Sea. If weekly or monthly sampling were taken, more species could be found. Also, it is known that if there is an over-nutritious element loading in an environment, there can be a decrease in the number of phytoplankton species as an indication of stress, and a proportional differentiation between taxonomic groups can occur [17]; and, in recent years, the increase in the amount of nutrional elements is pretty high.

When the studies carried out in Turkish coastal waters of Black Sea are compared, Benli [9] reported 93 (53% dinoflagellate, 47% diatom), Karaçam and Düzgünes [12] reported 29 (41% dinoflagellate, 59% diatom), Eker et al. [18] reported 142 (53-55% dinoflagellate, 23-25% diatom), Türkoglu and Koray [20] reported 191 (47% dinoflagellate,
49% diatom), Koray et al. [22] reported 173 (45% dinoflagellate, 50% diatom), Türkoğlu and Koray [23] reported 179 (46% dinoflagellate, 49% diatom), Uysal [50] reported 86 (22% dinoflagellate, 65% diatom), Taş and Okçu [30] reported 129 (36% dinoflagellate, 53% diatom), Feyziəğlu and Seyhan [31] reported 115 (34% dinoflagellate, 54% diatom), Bat et al. [33] reported 401 (43% dinoflagellate, 20% diatom), and Ağırbaş et al. [51] reported 89 taxa (71% dinoflagellate, 23% diatom); it is observed that compared to diatom species, dinoflagellate species have recently shown an increase in terms of diversity. This situation indicates the negative change taking place in Black Sea day by day. Eker et al. [18] stated that depending on the increasing amount of the nutritional elements, species and abundance of myxo- and heterotrophic dinoflagellate showed an increase compared to autotrophic diatoms. Kideys [14] also reported that passing from 1960s to 1990s, as a result of eutrophication, dinoflagellates showed increase compared to diatoms, new species began to be observed in the environment, and the formation of red-tide increased.

It has also been observed by other researchers that because of the over-accumulation of nutritional elements coming from especially the northwestern parts of Black Sea through rivers such as Danube, Dnieper, and Dniester, especially after 1960s, pico- and nanoplankton species and dinoflagellate species have become dominant compared to diatom species by reproducing both in qualitative and quantitative terms. In 1960s and 1970s, Bacillariophyceae constituted 67% of the population and Dinophyceae constituted 19% of the population [52]; in 1980s, the rate of Dinophyceae increased up to 55% [53]; and, in 1990s, the contribution of diatoms to the total mass decreased in also quantitative terms by dropping to 38% from 92.3% [54]. In this study, it was found out that the rate of Dinophyceae classis com- pared to Bacillariophyceae classis was higher in all sampling periods, and it was identified that 46 of the 83 obtained taxa were Dinophyceae (56%), and 34 of them were Bacillariophyceae (41%). It was re- ported that Protoperidinium genera was represented with the highest number of species with 41 species [46] and 67 species [47] among the dinoflagellate species that have recently shown increase both in number of species and abundance; a similar result was obtained from this study, and the highest number of species (13 species) was identified to belong to this genera.

Belogorskaya and Kondratyeva [55] reported that while diatoms generally show increase in Black Sea in winter and early spring, coccolithophorids and dinoflagellates show increase in late autumn and early winter. In this study, less amount of phytoplankton abundance was observed in the sample of April compared to the other samples; the highest numbers of cell were found in December representing the cold period, and in August representing the warm period. Especially the dinoflagellates that love warm waters were effective in the increase observed in August. According to Sorokin [56], algal bloom in

**FIGURE 3**

Bray–Curtis similarity dendogram of the sampling stations a) species diversity b) abundance.
Black Sea creates two peaks; the highest of these peaks was observed in the end of winter and in the beginning of spring while the other peak was observed in the end of summer and in the beginning of autumn. Also, Eker et al. [18] reported in their studies that the lowest amount of abundance was observed in March-April period and the average amount of abundance was about 129000 cell/L; they identified that *H. triquetra*, *S. trochoidea*, *P. calcisialis* and *E. huxleyi* were the species that showed a significant decrease. In this study, during all sampling periods, significantly low values under 5x10^4 cell/L were acquired in terms of abundance. However, in a study comprising the years between 1977 and 1986 [57], phytoplankton community in Mamata Gulf was found to be 2.5-12x10^6 cell/L. In this study, apart from the above-mentioned species, species belonging to *Prorocentrum* also showed a similar increase. Especially in the August sampling, in number 3 station and in 15 m depth, *P. calcisialis*, as a boreal origined diatom, showed increase (1.3x10^6 cell/L). Similar to this finding, although many diatoms prefer cold waters, in a study carried out in the coast of Sinop Peninsula by Türköglu [16], it was reported that some diatoms such as *P. calcisialis* and *C. closterium* excessively reproduced in summer months, and *P. calcisialis* reached the highest cell density with 1.7x10^6 cell/L.

Although it was observed that as a diatom *S. costatum* reached to 100x10^6 cell/L in spring in the coasts of Romania [58], and in 1984, this species reached to 8.3x10^6 cell/L in the northwestern part of Black Sea [59], and they were observed in the coasts of Sinop Peninsula throughout the whole year, they reached to 1.0x10^6 cell/L only in March, 1996 [16]; an excessive increase of *S. costatum* was not observed in this study. It was known that with the increase in the temperature of sea water, there might be an increase in the cell densities of diatoms and dinoflagellates [60]. Also, daily temperature change in the coastal shallow waters was 2 °C at maximum [61]. In this study, no significant difference between the surface water temperatures of the stations; and sea water temperature showed a positive relationship both with the number of species and the abundance. In addition to this, it is known that temperature has varied in accordance with seasons and depths, and the most important factor that affects the temperature of surface water is weather conditions [62]. In this study, although some differences were observed between sampling periods, it was determined that especially in the sampling periods of August and November, when the change in the upper water level was rare, the temperature showed sudden decrease in the depths under 20 m. Results of the conducted correlation analysis also showed that as the depth increases, temperature decreases (p<0.01).

In Black Sea, with the effect of rivers, salinity rate in the coastal areas can drop to 8-14%, and especially under 50 m, it shows sudden increase [63]. In a study carried out in the coastal waters of Sinop Peninsula, similar findings were acquired; it was reported that salinity rate increases under 50 m, and there is halocline layer at about 75 m [16]. Although lower values were measured in the April sampling of this study, it was observed that in the layer down to 30 m, there was not a significant level of change in the salinity rate and there was an approximately 3% difference.

The increase observed recently in the amount of nutritional elements in Black Sea caused changes in the number of phytoplankton species and their abundance. Passing from 1960s to 1980s, in the northwestern region of Black Sea, where rivers such as Dumble, Dnieper, and Dniester are effective, the amount of PO₄ increased from 10 µg/L to 200 µg/L, the amount of NO₃ increased from 20 µg/L to 200 µg/L, and the amount of SiO₂-Si increased from 1.029 µg/L to 857 µg/L [64-68]. It caused some dinoflagellate species to show excessive increase, and it made the ecosystem structure in this sea irregular and unbalanced [17]. In this study, the amount of NO₂-N was measured as 3.24 µg-at/ L at maximum; the amount of PO₄-P was measured as 6.47 µg-at/L and, the amount of SiO₂-Si was measured as 72.41 µg-at/L. These values are lower than the values measured in the northwestern region where 3 big rivers are effective. When it was compared in terms of the abundance of phytoplankton, it was determined that although the individual number of phytoplankton had been reported as 10^5-10^6 cell/L [66, 69], it was measured as 10^6 cell/L at maximum in this study. Dense anthropogenic inputs in the northwestern region caused an increase in the amount of phytoplankton in this region. When these values are considered, it can be said that west part of the Turkish territorial waters of Black Sea are less affected by these rivers than the ones in northwestern region. Also in a study carried out in the coasts of Trabzon in eastern Black Sea, it was reported that the abundance of phytoplankton similarly reached to the level of 10^6 cell/L only in the period when excessive reproduction was observed; apart from this period, it varied between 10^5-10^6 cell/L [15].

Overgrown species have been reported in high nutrient quantities in the environment [70]. In this study, the highest number of cells was obtained during the August sampling period, when the nutrient element contents were maximum. Silicate is known to be an essential element for the development of diatoms [71]. The reason for measuring the amount of silica needed for the cell wall of the diatoms at the highest level during the November sampling period may be that these organisms are represented by few cells during this period. The results of Spearman's rank correlation method showed that the number of phytoplankton was negative with NO₂-N and positive with NH₄. This may be due to the suppression of NO₃ use even if NH₄ is present in very low amounts in the environment. Conway [72] revealed this finding in a
culture study of *S. costatum*. It has also been reported that NH₄ is preferred because phytoplankton uses NH₄ as a nutrient element and consumes less energy than NO₃ [73]. In addition to these findings, the fact that NH₄, PO₄ and SiO₂ are negatively related with the amount of chl-a indicates that the nutrients are used by these organisms during phytoplankton increase periods. However, there is no relationship between chl-a and species abundance. Travers [74] also stated that there will not always be a fit between the amount of chl-a and phytoplankton abundance. The reason is that the number of chlorophyll contained in the species and the size of the chlorophyll varies from species to species.

It has been reported that the chl-a values change depending on the hydro-chemical conditions such as nutrients, temperature, light and water mixtures [75]. Classification according to chl-a values; <0.5 μg / L oligotrophic, 0.5-1.0 μg / L mesotrophic and >1.0 μg / L eutrophic [76]. Considering chl-a values in this study, mesotrophic/eutrophic species were generally observed in December and April sampling periods, and oligotrophic species were observed in August and November sampling periods. Prior to eutrophication, there was a decrease in abundance of large volume species such as L. danicus, D. brightwellii and *P. calcare-avis* from diatoms, and an increase in the abundance of smaller volume species such as *P. balticum*, *P. cordatum*, and *P. micans* from dinoflagellates [5].

However, in this study, it was determined that *P. micans* increased in the December sampling period reflecting the mesotrophic/eutrophic state and that the cells belonging to this genus reached the highest abundance in the August sampling period which reflects the oligotrophic condition. Likewise, Türkoğlu [16] found in his study that *P. micans* increased in the summer season.

It has been suggested that one of the important factors affecting increases in dinoflagellate in coastal areas is pH and positive correlation with dinoflagellate abundance [77]. In this study, pH values were observed especially during December and April sampling periods and a positive relationship was found between phytoplankton abundance. Seasonal pH changes in the environment are due to carbon exchange between CO₂ and organic matter in seawater.

**CONCLUSION**

Consequently, this study aims to identify phytoplankton species and their abundance in southwestern parts of Black Sea where very limited studies were carried out about phytoplankton, and to reveal their relationship with ecological variables. This study can be used as a source especially for the studies to be conducted towards the observation and identification of the possible future effects of 3 big-


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METHYLMERCURY AND TOTAL MERCURY IN SQUALIUS CEPHALUS FISH TISSUES: EFFECT OF MUNICIPAL WASTEWATER TREATMENT

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ABSTRACT

The aim of this study was to determine the concentrations of mercury in tissues of the European chub (Squalius cephalus) which is used as a bioindicator of pollution of aquatic ecosystems. Levels of methylmercury and total mercury were determined in muscle and skin of twenty fishes caught at two sampling sites in the Svatka River, near the Brno City, Czech Republic. The effect of municipal wastewater treatment plant (WWTP), which is located between these two sampling sites, was considered. Determination of methylmercury was carried out by optimized extraction method and gas chromatography with electron capture detector. Total mercury concentrations were determined using the technique of direct combustion. The same methodology was applied to certified reference material. Concentrations of methylmercury ranged from 124.25 to 255.32 μg·kg⁻¹ in the muscle and from 34.18 to 103.98 μg·kg⁻¹ in skin samples of fishes caught upstream to the WWTP. Downstream to the WWTP, concentrations of methylmercury ranged from 59.74 to 183.50 μg·kg⁻¹ in the muscle and from 13.62 to 76.88 μg·kg⁻¹ in the skin. Concentrations of total mercury in muscle and skin of fishes caught upstream and downstream to the WWTP showed a similar pattern. Differences between levels of mercury in different fish tissues were compared, and the impact of WWTP was assessed.

KEYWORDS:
Chub, muscle, skin, mercury, wastewater-treatment-plant, Svatka River

INTRODUCTION

Mercury is a hazardous element that can be found in all components of ecosystem. Nowadays, it is considered to be a global pollutant of the environment and there is a growing interest in determination of mercury levels in all components of the aquatic ecosystem including water, sediment or fish tissues [1-5]. Behaviour of mercury in the environment depends on its chemical form and on the matrix in which it is situated [6].

Methylmercury is considered to be the most toxic form of mercury, especially due to its bioaccumulation and persistence. It is produced by biomethylation or abiotic methylation from inorganic forms of mercury by specific bacteria living in water sediment [7, 8]. The total content of mercury and methylmercury in aquatic organisms increases with the trophic level of the food chain [9].

Fish belong to the group of bioindicating organisms which accumulate mercury compounds from the aquatic environment. More than 90 % of mercury in muscle of predatory fishes is in the form of methylmercury [9, 10]. European chub (Squalius cephalus) is usually 30 – 50 cm long fish living in fresh waters of almost all Europe. It is omnivorous fish with the widest food web (algae, aquatic plants, terrestrial seeds, insect, larvae, small fishes, frogs or molluscs and crustaceans animals). Thus it is very suitable for monitoring of water ecosystems [11, 12]. Consumption of contaminated fishes is a way of human exposure to methylmercury, which is related especially to neurological adverse effects. Prenatal exposure to methylmercury results in mental retardation of children [13-15].

MATERIALS AND METHODS

Sampling. In this study, levels of total mercury and methylmercury were determined in muscle and skin tissues of 20 fish (species Squalius cephalus). Fish were caught at two localities situated at the Svatka River downstream the Brno City, which is the second largest city of the Czech Republic (approximately 400,000 inhabitants). Sampling site A was situated at the confluence of the Svatka and the Svitava rivers, sampling site B near the town of Rajhradice. Municipal wastewater treatment plant (WWTP) is located between these two sampling localities (Figure 1). The health condition and body proportions of each fish were assessed (Table 1),
samples were prepared and stored in a freezer (-18 °C) until they were processed further.

**FIGURE 1**

Map of the Czech Republic with the sampling sites (A: 49°8’34.643”N, 16°37’41.364”E; B: 49°5’27.748”N, 16°37’11.381”E)

The WWTP Brno-Modrice receives waste-water from the Brno City and from its broad surroundings, and discharges its effluent into the Svrataka River. Its permissible volume of discharged wastewater is 4 222 l/s and 61 520 m³/year. It performs mechanical and biological treatment [16].

**TABLE 1**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Length [mm]</th>
<th>Weight [g]</th>
<th>Gender [Male/Female]</th>
<th>Age [years]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>245</td>
<td>160</td>
<td>M</td>
<td>5+</td>
</tr>
<tr>
<td>2</td>
<td>290</td>
<td>290</td>
<td>F</td>
<td>3+</td>
</tr>
<tr>
<td>3</td>
<td>255</td>
<td>180</td>
<td>F</td>
<td>4+</td>
</tr>
<tr>
<td>4</td>
<td>225</td>
<td>110</td>
<td>M</td>
<td>3+</td>
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<td>3+</td>
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<td>140</td>
<td>M</td>
<td>4+</td>
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<td>3+</td>
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<td>F</td>
<td>4+</td>
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<td>15</td>
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<td>M</td>
<td>4+</td>
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<td>19</td>
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<td>250</td>
<td>M</td>
<td>5+</td>
</tr>
<tr>
<td>20</td>
<td>269</td>
<td>270</td>
<td>M</td>
<td>4+</td>
</tr>
</tbody>
</table>

Chemicals and materials. All organic solvents, sorbents and other chemicals used for the analysis were of high purity for the residual analysis. Toluene p.a., acetone for gas chromatography, concentrated hydrochloric acid (30%, Suprapur) and anhydrous sodium sulphate p.a. were obtained from Merck (Darmstadt, Germany). Certified reference material ERM-CE464 “Total and methylmercury in tuna fish” was purchased from IRMM (Geel, Belgium). Methylmercury chloride standard was purchased from Sigma-Aldrich (Steinheim, Germany).

Stock standard solution of methylmercury at concentration of 1000 ng·mL⁻¹ was prepared in toluene and stored in the dark at 4 °C. Helium 6.0 (purity of 99.999%) was used as a carrier gas with flow rate of 1 mL/min. High-purity nitrogen (99.996%) was used as a make-up gas; both supplied by Messer Technegas (Prague, Czech Republic).

The centrifuge EBA 20 from Hettich (Tuttlingen, Germany) was used for sample preparation. The Hewlett Packard 6890 Series II (Agilent Technologies, Santa Clara, CA, USA) gas chromatograph with the electron capture detector (GCμECD) and capillary column DB 17 (30 m × 250 μm i.D., 0.25 μm film; J&W Scientific, Folsom, CA, USA) were used for analyses. Evaluation was made using HP ChemStation software (Agilent Technologies, Santa Clara, CA, USA). Total mercury content was determined using the AMA 254 system purchased from Altec Ltd. (Prague, Czech Republic).

**Analytical procedures. Methylmercury.** Determination of methylmercury was carried out by optimized extraction method [17]. Exactly 0.2 g of each sample was taken for analysis and homogenized. For pre-cleaning, 5 mL of acetone was added to the sample in a test tube and shaken vigorously for 30 s. After 5 minutes of centrifugation at 3500 rpm, 4 mL of supernatant have been removed. Another 4 mL of pure acetone were added, and the whole procedure was repeated. After removing the last 4 mL of supernatant, 4 mL of pure toluene (instead of acetone) were added to the test tube following by centrifugation. Again 4 mL of supernatant have been removed and 0.7 mL of concentrated hydrochloric acid (30% HCl) was added, and the whole content of the test tube has been transformed to a paste condition using a glass rod. The following extraction step was performed by two consequent additions of 4 mL of toluene. After each addition of solvent the test tube was shaken, centrifuged and 4 mL of extract were removed and stored in a dry clean test tube containing 2 g of anhydrous sodium sulphate (Na₂SO₄) to remove the moisture. Finally the test tube containing 8 mL of extract was stored in the refrigerator for one hour. One mL of such prepared extract was further used for analyses as a analytical sample that was measured by GCμECD. The same methodology was applied to prepare extracts from both muscle and skin tissues, as well as to certified reference material (CRM). Each sample was processes in two parallel determinations.

Used chromatographic conditions were set as follows [18]: column temperature was programmed from 80 °C, held for 1 min, increased at 15 °C/min to 180 °C, followed by a second increase at 5 °C/min to 220 °C. Samples were injected in splitless mode at 250 °C. The detector temperature was held at 280 °C. Helium was used as a carrier gas at a linear flow rate of 30 cm³/s. Nitrogen was used as a make-up gas at flow rate of 28 mL/min. The column was adjusted...
TABLE 2
Analytical parameters of methylmercury and total mercury contents in the Certified Reference Material (CRM)

<table>
<thead>
<tr>
<th></th>
<th>Methylmercury [µg kg⁻¹]</th>
<th>Total mercury [µg kg⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Certified value</td>
<td>Measured 95% CI</td>
</tr>
<tr>
<td></td>
<td>5.50 ± 0.17</td>
<td>5.18 ± 0.21</td>
</tr>
</tbody>
</table>

CI – confidence interval; SD – standard deviation

by 10 sprayings 0.3 mM HBr before the actual measurement of calibration solutions or samples.

**Total mercury.** Total mercury concentrations were determined using the technique of direct combustion by a single purpose instrument AMA 254 (Advanced Mercury Analyser). Instrumental conditions for the determination were as follows: 90 s drying time, 210 s decomposition time and 55 s waiting time. The instrumental concentration range used for the determination of total mercury content was adjusted to 0.05 – 600 ng Hg in compliance with data found in literature. The same methodology was applied to both muscle and skin tissues, as well as to certified reference material (CRM). Each sample was performed in two parallel determinations.

**Methodology optimization.** For the methylmercury determination, calibration line from standard stock solution of methylmercury chloride was constructed. The coefficient of determination expressing the reliability (R²) was higher than 0.999. All results were processed in mean values (n = 2) with standard deviation (SD) and confidence interval (CI). The values of limit of detection (LODₘ₅₉₉₉ = 2.87 µg·kg⁻¹) and limit of quantification (LOQₘ₅₉₉₉ = 9.57 µg·kg⁻¹) were calculated by Eq. (1) and (2), respectively. The height of the noise presents hₙ, the slope of the pertinent calibration line presents m.

\[ \text{LOD} = \frac{3 \times h_n}{m} \]  \hspace{1cm} (1)

\[ \text{LOQ} = \frac{10 \times h_n}{m} \]  \hspace{1cm} (2)

Concentrations of methylmercury and total mercury measured in CRM proving the accuracy of the methodology are shown in Table 2. Results of both methylmercury and total mercury did not show any statistically significant differences between the certified and our measured values at the confidence level α = 0.95.

**RESULTS AND DISCUSSION**

Mercury contamination of all components of the environment could come either from natural or anthropogenic sources. Natural resources include volcanic activity, rock weathering, forest fires or evaporation from oceans and wetlands [6, 9]. The main anthropogenic sources of mercury in the environment are leaching at sites with active and also finished mercury mining, combustion of coal and other fossil fuels (average content of mercury in coal is 0.01 – 3.30 mg·kg⁻¹), incineration of waste and waste sludge, or crematoriums [19, 20]. Other industrial mercury sources are extraction, treatment and processing of ores and metals, chemicals and manufacturing processes (mercury compounds, paints, batteries, thermometers, or starters and catalysts for various chemical products); further chemical industry waste or leaching from wastes containing mercury compounds in landfills, discharge of contaminated municipal wastewater, cement production, or use of agricultural stains [9, 19, 21]. Volatile mercury compounds primarily reach the upper layer of atmosphere and due to their relatively high stability and long conversion cycles, in a favorable weather situation they can contaminate areas that are very distant from the point of origin [9].

Concentrations of methylmercury (MetHg) and total mercury (THg) in muscle and skin of fishes caught at the sampling site A (upstream to the WWTP; samples No. 1 - 10) can be found in Table 3. At this locality, the minimal concentration of MetHg 124.25 µg·kg⁻¹ was found in the muscle of sample No. 6; the maximal concentration of 255.32 µg·kg⁻¹ (sample No. 10) was measured in the muscle tissue too. Order-of-magnitude lower concentrations of MetHg were determined in the skin tissues of fish samples with the range from 34.18 µg·kg⁻¹ (sample No. 5) to 103.98 µg·kg⁻¹ (sample No. 4). Concentrations of MetHg and THg in muscle and skin of fishes caught at the sampling site B (downstream to the WWTP; samples No. 11 - 20) can be seen in Table 4. At this site the minimal concentration of MetHg 59.74 µg·kg⁻¹ was found in muscle of sample No. 13; the maximal content of 183.50 µg·kg⁻¹ (sample No. 16) was measured again in muscle tissue. Concentrations of MetHg in skin samples from this sampling site were usually lower than in muscle tissue and they ranged from 13.62 µg·kg⁻¹ (sample No. 19) to 76.88 µg·kg⁻¹ (sample No. 15). Data in Table 3 and Table 4 are expressed in form of 95% confidence interval.
TABLE 3

Concentrations of methylmercury (MeHg) and total mercury (THg) in muscle and skin of Squalius cephalus upstream to the wastewater treatment plant (Sampling site A)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>MeHg [µg·kg⁻¹]</th>
<th>SD</th>
<th>THg [µg·kg⁻¹]</th>
<th>SD</th>
<th>MeHg [µg·kg⁻¹]</th>
<th>SD</th>
<th>THg [µg·kg⁻¹]</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>251.46 ± 5.75</td>
<td>4.42</td>
<td>207.05 ± 11.89</td>
<td>9.15</td>
<td>41.17 ± 1.17</td>
<td>1.62</td>
<td>43.59 ± 11.89</td>
<td>9.15</td>
</tr>
<tr>
<td>2</td>
<td>187.77 ± 17.31</td>
<td>13.31</td>
<td>197.10 ± 9.22</td>
<td>7.10</td>
<td>77.41 ± 3.65</td>
<td>0.57</td>
<td>42.06 ± 8.58</td>
<td>6.60</td>
</tr>
<tr>
<td>3</td>
<td>192.25 ± 10.86</td>
<td>15.09</td>
<td>186.54 ± 3.62</td>
<td>0.56</td>
<td>84.59 ± 8.27</td>
<td>6.36</td>
<td>68.49 ± 3.91</td>
<td>3.01</td>
</tr>
<tr>
<td>4</td>
<td>224.70 ± 5.55</td>
<td>4.27</td>
<td>158.85 ± 11.46</td>
<td>8.82</td>
<td>103.98 ± 3.42</td>
<td>4.75</td>
<td>100.20 ± 7.93</td>
<td>6.10</td>
</tr>
<tr>
<td>5</td>
<td>133.15 ± 10.65</td>
<td>8.20</td>
<td>119.37 ± 6.05</td>
<td>4.66</td>
<td>34.18 ± 9.29</td>
<td>7.15</td>
<td>67.33 ± 7.17</td>
<td>1.12</td>
</tr>
<tr>
<td>6</td>
<td>124.25 ± 8.24</td>
<td>6.34</td>
<td>109.86 ± 4.28</td>
<td>0.67</td>
<td>50.74 ± 4.45</td>
<td>6.18</td>
<td>45.83 ± 6.72</td>
<td>1.05</td>
</tr>
<tr>
<td>7</td>
<td>157.63 ± 12.46</td>
<td>9.58</td>
<td>160.95 ± 9.83</td>
<td>7.56</td>
<td>74.51 ± 2.78</td>
<td>2.14</td>
<td>66.96 ± 0.79</td>
<td>0.12</td>
</tr>
<tr>
<td>8</td>
<td>189.87 ± 3.51</td>
<td>2.70</td>
<td>153.24 ± 8.30</td>
<td>6.39</td>
<td>43.47 ± 5.22</td>
<td>7.25</td>
<td>67.90 ± 8.70</td>
<td>6.69</td>
</tr>
<tr>
<td>9</td>
<td>228.24 ± 5.19</td>
<td>3.99</td>
<td>132.21 ± 10.16</td>
<td>7.81</td>
<td>51.32 ± 10.70</td>
<td>1.67</td>
<td>61.78 ± 5.91</td>
<td>4.54</td>
</tr>
<tr>
<td>10</td>
<td>255.32 ± 10.23</td>
<td>7.87</td>
<td>197.10 ± 7.92</td>
<td>6.09</td>
<td>75.02 ± 4.53</td>
<td>3.49</td>
<td>65.10 ± 7.72</td>
<td>5.93</td>
</tr>
</tbody>
</table>

SD – standard deviation

TABLE 4

Concentrations of methylmercury (MeHg) and total mercury (THg) in muscle and skin of Squalius cephalus downstream to the wastewater treatment plant (Sampling site B)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>MeHg [µg·kg⁻¹]</th>
<th>SD</th>
<th>THg [µg·kg⁻¹]</th>
<th>SD</th>
<th>MeHg [µg·kg⁻¹]</th>
<th>SD</th>
<th>THg [µg·kg⁻¹]</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>93.36 ± 3.46</td>
<td>2.66</td>
<td>150.51 ± 3.37</td>
<td>2.59</td>
<td>69.01 ± 8.34</td>
<td>6.42</td>
<td>67.34 ± 0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>12</td>
<td>75.79 ± 8.40</td>
<td>6.46</td>
<td>107.31 ± 1.80</td>
<td>1.39</td>
<td>38.99 ± 4.02</td>
<td>5.58</td>
<td>42.28 ± 2.77</td>
<td>2.13</td>
</tr>
<tr>
<td>13</td>
<td>59.74 ± 11.20</td>
<td>8.61</td>
<td>107.75 ± 4.23</td>
<td>3.26</td>
<td>56.70 ± 5.41</td>
<td>4.16</td>
<td>48.51 ± 6.41</td>
<td>1.00</td>
</tr>
<tr>
<td>14</td>
<td>151.58 ± 3.70</td>
<td>5.14</td>
<td>109.83 ± 2.61</td>
<td>2.01</td>
<td>65.04 ± 14.99</td>
<td>11.53</td>
<td>38.14 ± 4.32</td>
<td>3.33</td>
</tr>
<tr>
<td>15</td>
<td>67.72 ± 6.96</td>
<td>5.35</td>
<td>102.08 ± 3.05</td>
<td>2.34</td>
<td>76.88 ± 3.66</td>
<td>2.82</td>
<td>46.60 ± 2.01</td>
<td>1.55</td>
</tr>
<tr>
<td>16</td>
<td>183.50 ± 10.34</td>
<td>7.95</td>
<td>131.79 ± 2.10</td>
<td>1.62</td>
<td>35.64 ± 6.18</td>
<td>4.75</td>
<td>44.94 ± 4.46</td>
<td>3.43</td>
</tr>
<tr>
<td>17</td>
<td>176.06 ± 2.27</td>
<td>0.36</td>
<td>113.45 ± 3.83</td>
<td>2.95</td>
<td>47.17 ± 3.67</td>
<td>0.57</td>
<td>44.92 ± 7.71</td>
<td>3.56</td>
</tr>
<tr>
<td>18</td>
<td>146.12 ± 8.88</td>
<td>6.83</td>
<td>160.20 ± 2.36</td>
<td>1.81</td>
<td>19.66 ± 2.67</td>
<td>0.42</td>
<td>38.44 ± 2.77</td>
<td>2.13</td>
</tr>
<tr>
<td>19</td>
<td>148.95 ± 3.78</td>
<td>2.91</td>
<td>122.98 ± 1.76</td>
<td>1.36</td>
<td>13.62 ± 2.92</td>
<td>2.25</td>
<td>34.93 ± 10.63</td>
<td>1.66</td>
</tr>
<tr>
<td>20</td>
<td>109.16 ± 9.30</td>
<td>7.15</td>
<td>123.67 ± 1.04</td>
<td>0.80</td>
<td>14.08 ± 3.13</td>
<td>2.40</td>
<td>23.29 ± 3.06</td>
<td>2.35</td>
</tr>
</tbody>
</table>

SD – standard deviation

From Tables 3 and 4 it is obvious that concentrations in muscle tissue compared to skin tissue are higher at all fish samples. This fact confirms that mercury compounds including methylmercury are ingested by aquatic organisms, including fishes, either directly from water or sediment through food, and its content then apparently increases with the trophic level of food chain. In this way it finally gets in the muscle of omnivorous and predatory fishes [7, 9]. Solubility of mercury in water differs according to its form. Methylmercury is the most significant and the most toxic organic form of mercury whether there are two forms – monomethylmercury and dimethylmercury. Monomethylmercury (CH₃Hg⁺) is soluble in water where it is relatively stable. Dimethylmercury (CH₃₂Hg) is less stable compared to monomethylmercury, and is volatile and less soluble in water [6]. Dissolved mercury compounds are then accepted by aquatic organisms by adsorption or absorption through the body surface or respiratory organs. In this way it can contact and transfer over the fish skin but its permeation is not as high (compared to transfer via food) [9].

According to the literature, more than 90 % of mercury in muscle of predatory fishes could be in the form of methylmercury [9, 10]. Similar data about content of methylmercury and total mercury in fishes from the Czech rivers and water reservoirs are interpreted in following studies. Houserová et al. (2006) have found average concentration of 0.732 ± 0.228 mg·kg⁻¹ of total mercury in fish (European chub) caught in the Dyje River. They have appointed that 83.6 - 92.0 % of this value should be present in form of methylmercury [11]. In another study, Houserová et al. (2007) have found concentration of 0.735 ± 0.266 mg·kg⁻¹ of total mercury in fish (Common carp) from the region Záhlinec and the portion of methylmercury was estimated to be 65 - 83 % [22]. Maršálek et al. (2005) analysed the content of methylmercury and total mercury in samples of common carp from the Skalka reservoir. They have found 0.83 ± 0.21 mg·kg⁻¹ of methylmercury and 0.90 ± 0.28 mg·kg⁻¹ of total mercury in average [23]. In our study, the results of methylmercury are at some samples higher than concentrations of total mercury, especially at muscle samples of fishes caught upstream to the WWTP (sampling site A). Anyway, in average percentage of methylmercury in content of total mercury is always about 100 %. This deviation can be caused by lower accuracy of the methodology for the determination of total mercury (89.1 %) compared to the methodology for methylmercury (94.2 %) proven by measuring of CRM (Table 2).
Comparison of methylmercury content found at the different sampling sites located up- and downstream to the WWTP in both muscle and skin of fishes can be seen in Figure 2. Two graphs illustrate that the concentrations of MetHg in muscle tissue were order-of-magnitude higher compared to skin tissue, no matter what sampling site is considered. From the graphs it is also apparent that concentrations of MetHg were generally higher at sampling site A located upstream to the WWTP compared to location downstream to the WWTP (sampling site B). Therefore we could say that the WWTP Brno-Modřice is not a significant source of contamination of water ecosystem of the Svatka River by methylmercury. There are either none or very low sources of mercury in the influent wastewater, or the mercury contamination is trapped in the WWTP mechanisms. The purified wastewater from the effluent of WWTP rather dilutes the river water which would explain lower concentrations of MetHg in fishes caught downstream to the WWTP. Water environment downstream to the WWTP (water, sediment, phytoplankton, zooplankton) is not exposed to high contamination by methylmercury and thus the content of MetHg in fish tissues is also not significant. (Note: Fishes caught for this study could not migrate between sampling site A and B because of high water weir located between these two localities). Sources of contamination of water ecosystem of the Svatka River by mercury seem to be primarily the Brno City and its industrial pollution.

The highest values of both MetHg (255.32 μg·kg⁻¹; fish No. 10) and THg (207.05 μg·kg⁻¹; fish No. 1) were observed in muscle tissue of fish caught upstream to the WWTP, which seems to be the most contaminated matrix evaluated in this study. Compared to that, the lowest values of both mercury compounds were observed in skin tissue of fish caught downstream to the WWTP (MetHg: 13.62 μg·kg⁻¹ at fish No. 19; THg: 23.29 μg·kg⁻¹ at fish No. 20).

Commission Regulation (No. 1881/2006/ES) sets the maximum limit of mercury in fish muscle to 0.5 mg·kg⁻¹. For some selected fish species (especially marine fishes and sea food) the accepted maximum limit of mercury in muscle is 1.0 mg·kg⁻¹ [24]. None of the fish samples examined for this study exceeded this limit.

CONCLUSION

Differences between levels of mercury in different fish tissues were compared, and the impact of the WWTP was discussed. The muscle tissue of fishes from this study contained significantly higher concentrations of methylmercury than skin, no matter what sampling site was considered. Therefore, the main source of mercury compounds occurring in fish tissues seems to be primarily their food through the food chain. There is a considerable difference between two sampling sites situated up- and downstream to the municipal WWTP Brno-Modřice. Concentrations of methylmercury were lower at sampling site B situated downstream to the WWTP and thus we can say that this WWTP does not have any negative impact on pollution of water ecosystem of the Svatka River by mercury compounds. Fish body parameters such as length, weight, gender and age seem to have no significant effect on the level of contamination by mercury compounds. None of the samples exceeded the limit for total mercury in fish muscle tissue required by legislation in the Czech Republic.

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USING SATELLITE IMAGERIES AND ORTHOPHOTO TO QUANTIFY ENVIRONMENTAL IMPACT OF MINING ACTIVITIES IN FOREST AREA

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³Yildiz Technical University, Faculty of Civil Engineering, Department of Geomatics Engineering, Istanbul, Turkey

ABSTRACT

In this study, monitoring and investigating the mining activities located in the forestry area and quantifying the environmental effect of these activities were carried out by means of orthophotos and satellite imageries. The study area consists of 4 open pit mines surrounded by forestry area located in the Antalya province which is nearby the Mediterranean Sea known as one of the most popular holiday destinations in Turkey. Opposite to the expansion of the mine areas forestry area decreases in this region. To quantify the decrease in the forestry area multi-temporal satellite imageries were used for 4 open pit mines. Used data were Spot 5 and Spot 6 satellite images with spatial resolution of 5 m and 6 m respectively. Spatial change was determined by applying object-based classification method for all satellite images. Accuracy analyses were made by means of overall accuracy and kappa statistic values. The overall accuracy values of the classified imageries of 2011, 2014 and 2017 were respectively 94.81%, 94.0% and 97.1% with the kappa statistical values of 0.9212, 0.9070 and 0.9538. According to the results of these classifications, the area values covered by the mines in the study area were respectively 55.06, 77.02 and 103.10 hectares in 2011, 2014 and 2017. Additionally, an unmanned aerial vehicle (UAV) was used in one of the mine areas in order to realistic evaluation of an area by using orthophotos. Two orthophotos with the pixel sizes of 4 cm and 7 cm were produced from multi-temporal aerial photographs. As a result of the study, it can be said that remotely sensed imageries are the main data to temporal follow-up of the mine areas. In this context, UAVs have been shown to be a better option for monitoring the environmental effects of mining areas when criteria such as acquisition of the data, accuracy, speed and time are evaluated. The difficulty of finding an optimal satellite image in terms of cost and different types of resolutions such as spatial, spectral, radiometric and temporal make the use of UAVs more prominent.

KEYWORDS:
Change Detection, Classification, Forest, Mine, Photogrammetry, Spot, Uav

INTRODUCTION

The existence of natural resources such as mines is very important for the economic development of a country and continuation of this. The fact that the raw materials obtained from the mines are used in many sectors from industry to agriculture increases the importance of the works carried out in these regions [1]. There are approximately 11000 mines operating in Turkey [2], which is very rich country in terms of natural resources due to its geographical location. Licenses and permits required for the operation of minefields in Turkey are arranged according to the Mining Law and the Mining Activity Regulations. Necessary and compulsory permissions are taken from the Ministry of Energy and Natural Resources of Turkey for the mining area to be operated within the forest area and excavation works are carried out under the specified legal restrictions [3].

Mines can be operated as open system like quarry, marble pit etc. and open mines have dynamic structure exposed to people’s interventions and thus resulting in a change around them. Works continually performed in a mine area such as excavations for extraction of raw materials and accumulation of the obtained products in and around the field cause the expansion of the mine. In addition to all these, transportation of obtained materials from a place to another one also contributes to the relationship between mine and environment [4]. For a mine in forested area, loss of forest does not mean only a numerical decrease of trees. At the same time, it means interfering with the order of ecosystem. An open mine also causes the surrounding area to be exposed to negative conditions such as dust, haze, noise pollution, and waste matter. As noted by Gazi et al. [5] 70% the mineral quantity is emerged as waste during the extraction and processing of a marble mine. The constantly increasing relationship between the natural environment and human activities must be
FIGURE 1
4 open pit mines and their surroundings

properly assessed and interpreted to protect the environment. Temporal detection of land cover/land use change in the region is an important option for use in strategies to be implemented [6]. For this reason, it is necessary to make temporal follow-up of the spatial change that takes place in the mine area. The expansion of the area covered by the mine represents a spatial change and this causes the shrinkage of the area covered by other facts in environment. The expansions of the mines in the forest area are legally restricted to prevent loss of forest areas and disruption of the existing habitat system. The determination of whether this legal restriction is violated plays an important role in inspection to be made for mine area. In this study, it was investigated whether the temporal evaluation of the spatial change in the mine areas located in forested area could be determined with the help of remotely sensed data in the desired quality and quantity.

STUDY AREA

The study area indicated in Fig.1 is located in the Antalya province which is nearby the Mediterranean Sea known as one of the most popular holiday destinations in Turkey. Study area consists of 4 open pit mines surrounded by forestry area. Study area covers an area of approximately 1700 hectares (ha). Mining operations in the region began in the last quarter of 2009 and continues. Marble is extracted as raw material from different sized mines. There are also mines in other areas besides the study area limits. Opposite to the expansion of the mine area forestry area decreases in this region.

DATA AND METHODOLOGY

Multi-temporal satellite imageries provide the possibility of transformation from image to information due to classification methods and algorithms. Remote sensing for the detection of change and integration of remote sensing and geographical information system (GIS) for the interpretation of the change are among the most preferred methods [7]. In this study, two types of remotely sensed data presented in Table 1 were used to determine the effect of mining activities. Orthophotos generated from aerial photographs obtained by UAV were used for one of the mines to evaluate the data in terms of acquisition and different types of resolution such as spatial and temporal. Both data are multi-temporal and were used for change detection analysis. Satellite imageries covers 6 years and there is 1-year difference between the acquisition dates of the aerial photographs.
TABLE 1

<table>
<thead>
<tr>
<th>Data</th>
<th>Year</th>
<th>Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthophoto</td>
<td>08.12.2016</td>
<td>4 cm</td>
</tr>
<tr>
<td>Orthophoto</td>
<td>15.12.2017</td>
<td>7 cm</td>
</tr>
<tr>
<td>Spot 5 Image</td>
<td>19.08.2011</td>
<td>5 m</td>
</tr>
<tr>
<td>Spot 5 Image</td>
<td>05.09.2014</td>
<td>5 m</td>
</tr>
<tr>
<td>Spot 6 Image</td>
<td>26.07.2017</td>
<td>6 m</td>
</tr>
</tbody>
</table>

Used UAV platform in photogrammetric application has weight of 2.6 kg without payload and 4 kg with the equipment loaded on it. This tool has the ability to automatically take-off and landing vertically. The vehicle with a hexa-shaped platform can autonomously fly according to the programmable flight plan. Canon IXUS 160 for the flight of 2016 and Sony a6000 for the flight of 2017 which both of them are digital compact camera, were used during the flights. Small dimensions that make them compact and lower weight including battery compared to mirrored digital single lens reflex cameras (DSLR) ensure that the UAV remains in the air for a maximum period of time. Also, the absence of mirror mechanism provides that the incoming light directly reaches the sensor. In this way, the image appears on the screen and in the electronic viewfinder at the same time, which this increases the continuous shutter speed. This is the main theoretical difference between the mirrorless and mirrored systems [8]. Despite being amateur cameras, they are sufficient for obtaining desired and sufficient quality photographs for the mine area and its surrounding. The high texture in the region also positively contributes to the number of points to be formed after the photographs are matched to each other.

For the mine, the orthophotos were produced from aerial photographs obtained according to the flight plans. Both flights were carried out on a larger area than the excavation area. In this way, the forest area was also within the orthophotos. Two flight tasks in 2016 and one flight task in 2017 were performed to obtain photographs of the mine sites. The reason why the number of flights in the previous mission is more than 1 was inadequacy of existing battery. For the flight in 2016, 13 ground control points were used on the field to scale the mine model. In the flight mission in 2017, 8 control points were used. The ground control points were distributed homogeneously both around the excavation area and close to the outer boundary of the region. Pix4D commercial software was used to manipulate the photographs during the production of orthophotos depending on the structure from motion process. Generated orthophotos are indicated in Fig. 2.

With the advancing technology, high-resolution satellite images can be obtained, but the use of only spectral features in the process of classification brings about some limitations. In the object-based classification method, example based-or rule-based classifications can be performed by adding features such as shape and texture as well as the spectral information of the pixels [9]. Another advantage of object-based classification is that it forms segments by grouping neighbouring pixels with similar spectral

FIGURE 2

The orthophotos belonging to 2016 (left) and 2017 (right)
characteristics representing the earth surface objects. So, it is possible to work with meaningful image objects consisting of pixels instead of working with single pixels. In this study, two Spot 5 images concerning 2011 and 2014 and one Spot 6 image for 2017 were used. Spot 5 and Spot 6 operate with the altitudes of 822 km and 694 km from the earth surface, which increases spatial resolution. Detailed features of the satellite images used are presented in Table 2.

In order to classify satellite images and to evaluate change detection, all data to be used must be in the same coordinate system, have the same datum and have the same pixel size. All the satellite images were referenced in the Universal Transverse Mercator projection coordinate system, in WGS84 datum and in the northern hemisphere with the slice number 35 but pixel sizes of them were different from each other. Thus, resampling operations were applied to the images to eliminate this difference. There are three resampling methods in the literature as nearest neighbour, bilinear and cubic convolution from simple to complex [10]. In this application, two Spot 5 images with the resolution of 5 meter were resampled to Spot 6 image with the resolution of 6 m by using nearest neighbour method. If the reverse was preferred, loss of information in the image of 2017 was likely possible.

<table>
<thead>
<tr>
<th>Specification</th>
<th>SPOT 5</th>
<th>SPOT 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Bands</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Band 1</td>
<td>G: 500-590 nm</td>
<td>B: 450-520 nm</td>
</tr>
<tr>
<td>Band 2</td>
<td>R: 610-680 nm</td>
<td>G: 530-590 nm</td>
</tr>
<tr>
<td>Band 3</td>
<td>NIR: 780-890 nm</td>
<td>R: 625-695 nm</td>
</tr>
<tr>
<td>Band 4</td>
<td>-</td>
<td>NIR: 760-890 nm</td>
</tr>
<tr>
<td>Pixel Size</td>
<td>5 m</td>
<td>6 m</td>
</tr>
</tbody>
</table>

**FIGURE 3**
Classified images (a) 2011, (b) 2014 and (c) 2017
FIGURE 4
Spatial changes within 6 years (2011 to 2017) for 3 classes

TABLE 3
Accuracy assessments for object-based classifications

<table>
<thead>
<tr>
<th>Classified Image</th>
<th>Overall Accuracy (%)</th>
<th>Kappa Statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot 5 (2011)</td>
<td>94.81</td>
<td>0.9213</td>
</tr>
<tr>
<td>Spot 5 (2014)</td>
<td>94.0</td>
<td>0.9070</td>
</tr>
<tr>
<td>Spot 6 (2017)</td>
<td>97.1</td>
<td>0.9538</td>
</tr>
</tbody>
</table>

Object-based classification method was applied to classify satellite images. At this step, eCognition software was preferred. In segmentation which is the first step of object-based classification, multi-resolution segmentation was employed, and images were segmented with the help of appropriate scale, shape and compactness parameters. In this stage, the pixels with similar reflection characteristics were grouped with each other [11]. During the segmentation step, it was aimed that pixel groups representing sparse forest, dense forest and mine areas do not interfere with each other. Since there is no clear boundary between sparse and dense forest classes, in fact the mining areas were taken into consideration in the implementation of parameters. Then, the identified sample areas were specified on the images and the classification process was completed. The classified images are indicated in Fig. 3 and Fig. 4 represents the area-based changes statistically.

RESULTS AND CONCLUSIONS

In this study, the spatial enlargement of 4 mine sites within the forest area from 2011 to 2017 was observed by processing satellite images. Based on the object-based classification results, the mining areas constitute 3.31% in 2011, 4.63% in 2014 and 6.2% in 2017 in a study area of approximately 1700 ha. These percentages correspond to 55.06 ha for the 2011, 77.02 ha for the 2014 and 103.10 ha for the 2017. These increases indicate the amount of decline in the forest area, as well. The accuracy analyses of the applied classifications depending on the ground truths obtained from other datasets such as orthophotos are shown in Table 3. When classified images are examined, it is seen that spatial growth is valid for every mine. The area where the mine-4 is located was entirely forested in 2011 and it can be clearly identified in the images of other years given it was started to be operated later.

The purpose of classifying the satellite images is to make interpretation about interest of area based on image processing techniques. Spatial, spectral and radiometric resolution values of the image can directly affect the resulting product. Although there is a direct correlation between the levels of these resolution types and quality and correctness of the classified image, the restrictive interrelation between them may be a problem. The fact that spatial resolution and spectral resolution mostly are not at high level together constitutes a trade-off for an optimal satellite image data [12] At this point, interpretation has an important status in the final evaluation of satellite imagery. That is, classification workflow is applied for objects that cannot be distinguished clearly and sharply by the human eye. In other words, detailed classification process may not need to be applied if the target object (open pit mine in this study) can be clearly discriminated. Therefore, it was not necessary to use an extraction algorithm or to classify the orthophotos because the resolutions of these data sets were in order of cm. A reliable vector data can be also obtained via digitization on the orthophoto. In fact, the preference here also depends on the number of target object in the study area, as time required for the evaluation of the data will be an important factor. Fig.5 represents the monitoring made on orthophoto data.

Mine-1 was also analysed by means of orthophotos created from aerial photographs obtained by UAV. On the orthophoto of the year 2017, a polygonal outer frame covering only the outer boundary of the mine was determined by digitizing. When this outer boundary was integrated on the orthophoto of the year 2016, it was determined that region coloured
by red in Fig. 5 which corresponds to area of approximately 0.48 hectare is the place where the enlargement of the mine area was realized within 1 year.

FIGURE 5
Region where spatial change occurred in mine-1 from 2016 to 2017

As a result of the study, UAVs have been shown to be a better option for monitoring the environmental effects and spatial changes of mining areas when evaluated in terms of acquisition, accuracy, speed and time. The difficulty of finding an optimal satellite image in terms of spatial, spectral, radiometric and temporal resolution makes the use of UAVs more prominent. Since the data required for such studies to be made in open pit mines must be continuous, cost for the data is also an important criterion. Data with high spatial resolution are needed to reach reliably change detection results, which is directly proportional to the cost of the satellite images. The use of UAVs is more reasonable in this regard too. However, usage of UAVs in mining sites for a purpose like in this study may not be realistic due to non-technical reasons. The size of the study area and the degree to which the legal permissions and limitations are also important in selecting the data and method to be preferred.

ACKNOWLEDGEMENTS

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CONTINUOUS SOME METALS REMOVAL FROM AQUEOUS SOLUTIONS BY BIOMASS IN PACKED-BED COLUMN

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ABSTRACT

The aim of our study was to evaluate the potential of a white rot fungi (Phanerochaete chrysosporium) immobilized on sepiolite, in a continuous flow removal of trace heavy metals. The present work proposes the use of a white rot fungi (Phanerochaete chrysosporium) immobilized on sepiolite as a new sorbent in trace metal determination. The procedure is based on the biosorption of Cr(III), Ni(II) and Cd(II) ions on a column of sepiolite loaded with dried, dead fungi components prior to their determination by atomic absorption spectrophotometry. The effects of pH, amount of solid phase, eluent type and volume of the sample solution, flow rate of solution on the retention of the metal ions have been studied. The optimum pH value of quantitative sorption for Cr(III), Ni(II) and Cd(II) was found to be 5. These metal ions can be desorbed with 1 M HCl (recovery 95-100 %). The effects of some interfering ions were also studied. The optimum experimental parameters were determined to be pH 5, concentration of 10 mg/L, contact time of 30 min and 0.2 g of adsorbent for a quantitative adsorption of the metals. Each column can be used up to 20 successive analyses without considerable change in recoveries of metal ions.

This procedure was applied to Cr(III), Ni(II) and Cd(II) determination in aqueous solutions, including tap water system. These metal ions can be desorbed with 1 M HCl (recovery 95-100 %). The results indicate advantages of high metal biosorption capacity and satisfactory recovery of Cr(III), Ni(II) and Cd(II).

The proposed method is very good as regards simplicity, sensitivity, selectivity, precision, accuracy and column stability.

KEYWORDS:
Cr(III), Ni(II), Cd(II), Solid Phase Extraction, Biomass, Sepiolite

INTRODUCTION

Heavy metal ions have lethal effects on all forms of life and can enter the food chain through the disposal of solid and liquid wastes in water. Heavy metals are non-biodegradable and can accumulate in living organisms. The stricter environment regulations on the discharge of heavy metals make it necessary to develop various technologies for the removal.

Therefore, alternative treatment processes for the removal and recovery of toxic metals have to be applied. Many methods, such as extraction, co-precipitation, electrodeposition and ion exchange have been used for preconcentration of trace metals [1-7].

Studies carried out to look for new and innovative treatment technologies have focused their attention on the metal binding qualities of various types of biomass. The utilization of biosorption technology for the treatment of heavy metal contaminated wastewaters and for the recovery of precious metals from mining wastes or in metallurgical effluents are very important [8-12]. The use of microorganisms as a biosorbent for metals has become a good alternative to the other preconcentration methods as regards higher recovery, economical advantages, simplicity and environmental protection [13-15].

MATERIALS AND METHODS

Analytical reagent grade CrCl₃, 6H₂O, NiCl₂, CdCl₂, HCl, NaOH, chemicals from Merck (Germany), Cr(III), Ni(II) and Cd(II) atomic absorption spectrometry standard solutions (1000 mg/L) (Fluka Chemicals) were used for experiments. The stock solutions of Cr(III), Ni(II) and Cd(II) (1000 mg/L) were prepared in double distilled water using their salts, CrCl₃, 6 H₂O and NiCl₂ and CdCl₂ 0.1 M HNO₃ and 0.1 M NH₃ solutions were used for pH adjustments.

Phanerochaete chrysosporium was used in the experiments. 200 mg of dry P. chrysosporium was mixed with 2 g of sepiolite. The mixture was wetted with 2 mL of doubly distilled deionized water and thoroughly mixed. After mixing, the paste was
heated in an oven at 80 °C for 24 h to dry the mixture. The wetting and drying step were repeated 4 times to maximize the contact between fungi and clay, thereby improving the immobilization efficiency. Then, fungi immobilized resin (0.2 g) was packed in a glass column (10 mm i.d and 200 mm length). Before use, 1 mol/L HCl solution and doubly distilled water were passed through the column in order to condition and clean it. Then, the column was conditioned to study the effect of pH.

The effects of experimental parameters, such as pH and flow rate of sample solution, amount of solid phase, eluent type, and concentration on the recovery of the metal ions were investigated.

A low cost sorbent, sepiolite was used for the removal of Cr(III), Ni(II) and Cd(II) ions from aqueous solutions. A natural sepiolite [MgSi0.32(OH)-6H2O] was obtained from Eskisehir region of Turkey. Characterization of the sample was first identified by X-ray diffraction, differential thermal and IR spectrophotometric analysis. Chemical analysis of the sample was carried-out on a GESPG 7, X-ray fluorescence spectrophotometer. The results are summarized in Table 1.

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Chemical analysis of natural sepiolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td>%</td>
</tr>
<tr>
<td>SiO2</td>
<td>58.7</td>
</tr>
<tr>
<td>MgO</td>
<td>25.0</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.5</td>
</tr>
<tr>
<td>CaO</td>
<td>0.5</td>
</tr>
<tr>
<td>(FeO+ Fe2O3)</td>
<td>0.05</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.05</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.005</td>
</tr>
<tr>
<td>MnO</td>
<td>n.d.</td>
</tr>
<tr>
<td>P2O5</td>
<td>n.d.</td>
</tr>
<tr>
<td>L.O.I.a</td>
<td>14.8</td>
</tr>
</tbody>
</table>

a; not detected , b; loss of ignition

RESULTS AND DISCUSSION

The effect of pH. Biosorption of metal ions in the column is attributed to the ionic attraction between the metal ions and functional groups of the biomass. Therefore, the pH of the metal solution is an important parameter to study in this system. The influence of pH of the aqueous solution on the retentions of the metal ions on P.chrysosporium immobilized on sepiolite is strongly dependent on hydronium (or hydroxide) ion concentration in the media. The pH value of the sample solutions was adjusted to a range of 1-7 with HCl or NaOH. The solutions were passed through the column at a flow rate of 2 mL/min. The results are given in Figure 1. The uptake values were increased with increasing pH for all metals. In order to avoid the precipitation of metals, high pH values were not tested. The optimum pH was chosen as pH 5 for all metals. The degree of sorption for metal ions was between 85-90 % in this pH value. The decrease in the recoveries of the analytes at the lower pH values could be due to the competition between protons and the analytes for the adsorption sites of the biomass. This situation was proposed by several authors [16-18].

![FIGURE 1](image1.png)

**FIGURE 1**
Effect of pH on the recovery of chromium, nickel and cadmium by P. chrysosporium immobilized on sepiolite

The effect of the amount of adsorbent. The removal of the metals studied was examined in relation to the amount of P.chrysosporium immobilized on sepiolite, which was varied from 0.05 to 0.4 g. The results are given in Figure 2. It was found that the retention of metal ions increased with increasing the amount of the adsorbent up to 0.2 g. This result can be explained by the fact that for optimum biosorption, extra binding sites are available for biosorption reaction, whereas by increasing the biomass concentration, number of binding sites available for biosorption also increases [19-21]. Thus, better performance in metals removal was observed at a higher biomass concentration.

![FIGURE 2](image2.png)

**FIGURE 2**
Effect of amount of adsorbent on the recovery of chromium, nickel and cadmium by P. chrysosporium immobilized on sepiolite

The effect of flow rates of sample solutions. Sample and eluent flow rates are important parame-
ters to obtain quantitative retention and elution, respectively. Therefore, the effect of the flow rate of the sample and eluent solutions was examined under optimum conditions (pH, eluent type, etc.) by using a peristaltic pump. The solutions were passed through the column with the flow rates adjusted in a range of 1-7.5 mL/min. As shown in Fig. 3, the optimum flow rate was found as 2.5 mL/min for all metal ions. The adsorption of Cr(III), Ni(II) and Cd(II) ions decreased with increasing flow rate as expected. At higher flow rates, the contact time of these ions with the column material is shorter. It appears that mass transport of the -Cr(III), Ni(II) and Cd(II) ions binding to the binding sites may limit the effective capacity observed at these flow rates.

![FIGURE 3](image)

**FIGURE 3**
Effect of flow rate on the recovery of chromium, nickel and cadmium by *P. chrysosporium* immobilized on sepiolite

The effect of the type and volume of eluent. The regeneration of the adsorbent (*P. chrysosporium*-immobilized on sepiolite) for the reuse in multiple biosorption-desorption cycles is important for the non-destructive recovery. For that reason, the concentration of acid solution used for the stripping metals bound to the cell surface must be as low as possible. To obtain a higher preconcentration factor, the volume of the eluent must be as small as possible. The elution studies were performed with 0.5 and 1 M HCl and HNO₃ solutions. The eluent volume was 5, 10 and 15 mL. The results are given in Table 2. For both elements studied 10 mL of 1 M HCl solution was found to be satisfactory.

The effect of column reuse Accuracy and reproducibility in analytical data is challenging task with the reuse of the same column. In order to study these effects, the metal ions were sorbed and desorbed on 0.2 g of the sepiolite loaded with *P. chrysosporium* several times using a solution (100 mL) having a concentration of 2.5-25 µg/L Cr(III), Ni(II) and Cd(II) under experimental conditions. The columns seem to be relatively stable up to 20 cycles. Therefore, repeated use of the column is possible.

**Precision of the method.** For evaluation of the precision of the method, the optimum conditions mentioned above were used, and successive retention and elution cycles (with 25 µg of Cr(III), Ni(II) and Cd(II)) were performed. As can be seen in Table 3, the precision of the method is very good, and the recoveries of analytes are quantitative (above 95 %).

**TABLE 2**
Effect of the type and volume of elution solutions on the recovery of metals

<table>
<thead>
<tr>
<th>Element</th>
<th>Type of eluent</th>
<th>Volume (mL)</th>
<th>Conc. (M)</th>
<th>Rec. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(III)</td>
<td>HCl</td>
<td>5</td>
<td>1</td>
<td>94.50</td>
</tr>
<tr>
<td></td>
<td>HCl</td>
<td>10</td>
<td>1</td>
<td>97.87</td>
</tr>
<tr>
<td></td>
<td>HCl</td>
<td>15</td>
<td>1</td>
<td>98.80</td>
</tr>
<tr>
<td></td>
<td>HNO₃</td>
<td>5</td>
<td>1</td>
<td>85.45</td>
</tr>
<tr>
<td></td>
<td>HNO₃</td>
<td>10</td>
<td>1</td>
<td>87.98</td>
</tr>
<tr>
<td></td>
<td>HNO₃</td>
<td>15</td>
<td>1</td>
<td>90.40</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>HCl</td>
<td>5</td>
<td>1</td>
<td>85.67</td>
</tr>
<tr>
<td></td>
<td>HNO₃</td>
<td>10</td>
<td>1</td>
<td>87.90</td>
</tr>
<tr>
<td></td>
<td>HNO₃</td>
<td>15</td>
<td>1</td>
<td>89.14</td>
</tr>
<tr>
<td></td>
<td>HCl</td>
<td>5</td>
<td>1</td>
<td>88.25</td>
</tr>
<tr>
<td></td>
<td>HCl</td>
<td>10</td>
<td>1</td>
<td>95.60</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>HCl</td>
<td>15</td>
<td>1</td>
<td>90.80</td>
</tr>
<tr>
<td></td>
<td>HNO₃</td>
<td>5</td>
<td>1</td>
<td>80.50</td>
</tr>
<tr>
<td></td>
<td>HNO₃</td>
<td>10</td>
<td>1</td>
<td>84.45</td>
</tr>
<tr>
<td></td>
<td>HNO₃</td>
<td>15</td>
<td>1</td>
<td>86.60</td>
</tr>
</tbody>
</table>

**TABLE 3**
Precision of the method

<table>
<thead>
<tr>
<th>Element</th>
<th>Recovery⁹</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(III)</td>
<td>98.5 ± 0.4</td>
<td>5</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>96.2 ± 0.5</td>
<td>5</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>97.8 ± 0.3</td>
<td>5</td>
</tr>
</tbody>
</table>

³D$YHUDJH RI 1 GHWHUPLQDWLRQV ZLWK   FRQILGHQFH OHYHOZLWKVWGGHY´

The effect of electrolytes and foreign ions. To investigate the effect of the interference of elements to each other on biosorption, the recoveries of elements were examined when they existed together in the same medium. In this study, the influences of some ions such as "NaCl, KBr, KI, NaNO₃, Na₂SO₄, Na₃PO₄, Ca(II) and Mg(II)", which are known as interfering ions in the AAS determination, on the sorption of Cr(III), Ni(II) and Cd(II) metal ions by *P. chrysosporium* loaded onto sepiolite in the column were investigated. The concentrations of interfering metal ions were adjusted in the range of 0.5-10 µg/mL. The tolerance limits of the electrolytes or cations are given in Table 4. The reported tolerance limit is defined as the electrolyte ion concentration causing a relative std. error of ± 5 %.

Effect of electrolyte ions on the recovery of Cr(III), Ni(II) and Cd(II) from a sepiolite column.
that the proposed pre-concentration method could be applied to natural water samples that contain such ions at the tolerable levels given in Table 4.

**TABLE 4**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Electrolytes or metal ions (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaCl</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>0.12</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>0.15</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>0.14</td>
</tr>
</tbody>
</table>

**Application.** The proposed method was applied to the determination of Cr(III), Ni(II) and Cd(II) in tap water, employing standard addition. An appropriate volume of sample solutions was adjusted to the optimum pH and subjected to the recommended column procedure for the preconcentration and determination of metal ions.

The results reported in Table 5, with a confidence interval for the 95% confidence level, show the applicability of the proposed method to water analysis. The analytes were determined with a relative error lower than 10% in all samples. When the results compared to permissible limits of these metals in tap water, it shows that the method is very convenient for determination of Cr(III), Ni(II) and Cd(II).

**TABLE 5**

<table>
<thead>
<tr>
<th>Element</th>
<th>Added (µg)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(III)</td>
<td>10</td>
<td>96.4 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>96.8 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>97.3 ± 0.3</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>10</td>
<td>95.6 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>95.3 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>96.5 ± 0.5</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>10</td>
<td>96.6 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>96.8 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>97.5 ± 0.3</td>
</tr>
</tbody>
</table>

*Mean of 5 determinations with 95% confidence level*

**CONCLUSION**

The method proposed by the use of *P. chrysosporium* immobilized on sepiolite for the preconcentration of chromium, nickel and cadmium is simple, sensitive and accurate. The recoveries of analytes studied were nearly quantitative (≥ 95%). The relative standard deviations for 5 experiments were < 5%. The analytes could be preconcentrated directly by using the proposed method without using any chelating or complexing agent which usually used to increase retention. Only 0.2 g of the adsorbent is needed and repeated use is possible. The optimum pH was chosen as pH 5 for all metals. The optimum flow rate was found as 2.5 mL/min for all metal ions. Each column can be used up to 20 successive analyses without considerable change in recoveries of metal ions. The matrix effects were reasonably tolerable. The method is relatively rapid as compared with previously reported solid phase extraction procedures for the enrichment of metal ions at trace levels. The use of *P. chrysosporium* immobilized on sepiolite as an adsorbent may be an alternative to more costly materials such as activated carbon for the treatment of liquid wastes containing metal ions. Moreover, the rapid uptake allows to consider carrying out the sorption of heavy metals on columns filled with this adsorbent because the contact time between the metal solution and the adsorbent is generally short in this process.

In conclusion, the proposed method is very good as regards simplicity, sensitivity, selectivity, precision, accuracy and column stability.

**REFERENCES**


INVESTIGATION OF DETERGENT ADSORPTION ON MICROPLASTICS IN LABORATORY CONDITIONS

Nurtac Oz*, Yasin Erol, Meral Yurtsever

Sakarya University Engineering Faculty Environmental Engineering Department Esentepe Campus 54187 Sakarya, Turkey

ABSTRACT

The adsorption of linear alkyl benzene sulphonate (LAS) onto microplastics has been investigated under laboratory conditions. In order to investigate the efficiency of adsorption on polypropylene (PP) and polyethylene (PE) micropellets have been used as adsorbent in the experiment. Temperature (°C) and adsorption equilibrium kinetics were compared in PP and effect of contact time on the adsorption of LAS was compared for PP against PE. In addition, adsorption isotherms and adsorption kinetic models have been investigated. It was observed that the adsorption rate did not change much at the two different temperature values, the adsorption reached equilibrium at the end of 2 hours at both temperatures, the adsorption capacity of PP increased and the adsorption rate of PP was better than PE. Experimental results showed that the pseudo-second kinetic model is more appropriate than the pseudo-first kinetic model. Adsorption isotherms indicate that the Langmuir model is more appropriate than the Freundlich model.

KEYWORDS: Adsorption, anionic surfactants, LAS, microplastics

INTRODUCTION

LAS which is anionic surfactants, has recently been used as a cleaning agent in the industrial detergent industry and in the textile industry. LAS which is used as a raw material for liquid detergents which are widely used in everyday life, constitutes a big industrial field. The detergent foams in the wastewater are not decomposable at the treatment plants and cause pollution in the rivers and seas where these waters are drained. Anionic surfactants can form a film layer beneath the water surface through the interaction with the hydrophilic and hydrophobic properties of the water. This causes a decrease in the amount of dissolved oxygen in the water. Secondly, detergent toxicity makes aquatic flora and fauna danger [1, 2]. Therefore, it is not desirable to find overloaded anionic surfactants in the water because detergents disrupt the ecological balance of water. Despite the many techniques for removing detergents from water, adsorption is considered to be the most suitable technique for purification, due to its high efficiency in treatment, simple operations and commercial convenience in supplying chemicals [3].

Although there is a lot of scientific research on surfactants, the investigation of surfactant adsorption on micropellet pellets is scarce. Microplastics come from a wide variety of sources, including the disintegration of larger plastic parts, synthetic fibers cut from laundry washed at home, and small plastic beads used for a range of consumer products and abrasive or other properties in industrial products. In this study, as an adsorbent, polypropylene and polypropylene were used in granular form which is a microplastic type. Polyethylene is a thermoplastic used in a wide variety of products [4]. The nominal monomer is taken from the existing ethyl, polyethylene is produced by using ethylene. Polyethylene granules are used in the production of washing water, shampoo, detergent and many products. Polypropylene is used in the automotive sector, plastic case production, construction sector, bucket, flowerpot, table, chair and various plastic toy industry [5].

The polypropylene obtained by polymerizing the monomer propylene is extremely resistant to chemical solvents (acids and bases). Materials such as detergent canisters, margarine vessels are produced from the material type. With this recycling, synthetic carpet floor, various plastic toys, stationery materials and similar products can be manufactured. It is an indispensable raw material of injection and textile industry. It is seen from the wide usage areas of microplastics that pollution loads caused by this industry should also be taken seriously [6]. These plastics, degraded in the aquatic environment after centuries, can cause harm to the digestive system of the water creatures as well as ecological pollution [7, 8, 9, 10].

In this study, the adsorption of anionic surfactant LAS onto microplastics was investigated depending on the temperature and contact time.

MATERIALS AND METHODS

Chemicals. The chemical LAS, which can be sold for commercial purpose, is 96% pure, has a high viscosity liquid and is supplied from polyvinyl chloride chemical industry. All solutions have been prepared with de-ionized water.
Preparation of Stock Solution. The reference material was weighed to be equal to 1 g LAS in 96% purity and dissolved in distilled water to complete 1 L. 1 mL of this solution contains 1 mg LAS. To prevent biodegradation, the solution was prepared weekly and stored in the refrigerator.

Adsorbates. In this study, it has been studied with PE and PP which are obtained after recycling process. These products are commercially available from the market and have diameters of 0.5-1 mm.

Experimental Procedure. The chemicals used were selected in the standard methods according to detergent analysis method. The prepared stock solution was diluted to 1 L with distilled water, and a standard LAS solution was prepared.

Adsorption Experiments. Adsorption of LAS from aqueous media using PP and PE was studied at various time intervals (15, 30, 45, 60, 75, 90, 105, 120, 135, 150, 165 and 180 min.) under experimental conditions such as solution pH and temperature. The concentration of 2 mg/L from the standard LAS solution was diluted to 100 mL and 10 g PP and PE were added separately to the solution and mixed with heating magnetic stirrers and the measurements were carried out every 15 minutes and this process was continued for 3 hours. 1N NaOH and 1N H2SO4 solutions were prepared for neutralization. Extraction was carried out by adding methylene blue and CHCl3 to the separation funnels used for the density difference. The bottom liquid was taken in a separate vessel and the glass wool was passed through filter paper and the adsorption results were measured by UV-spectrophotometer at 652 nm. The percentage removal efficiency (R %) were calculated using Equation (1).

\[
R\% = \frac{C_0 - C_e}{C_0} \times 100
\]  

(1)

Where \(C_0\) and \(C_e\) are initial and equilibrium phenol concentrations, respectively (mg/L), \(V\) is LAS solution volume.

RESULT AND DISCUSSION

Effect of Contact Time. The change in PP and PE removal rates with the same initial concentrations is shown in Figure 1 depending on the contact time. The results show that the equilibrium has been reached at the end of about 110 minutes. Therefore, according to the experimentally result, the obtained data has been plotted according to the mixing result of 180 minutes. After 105 minutes, the removal rates for both microplastics were 50% and the adsorption started to stabilize. When working under the same ambient conditions, the removal rates of PP were found to be higher than those of PE.

Effect of Temperature. LAS was studied at 2 different temperatures to investigate the adsorption onto PE and PP. It is known that the increase in adsorption rate is directly proportional to the increase in temperature [11]. Regardless of the detergent analyzed, it was observed that up to this time the adsorption rate increased 1.5-3 times at 15°C. Despite the fact that the total absorption capacity is temperature independent, absorption rates are strongly dependent on temperature [12, 13].

![FIGURE 1](Effect of Contact Time on the Adsorption of LAS (Initial pH 6.0, T=20-40°C))
When the effect of temperature on adsorption is examined in this experimental study, it has been observed that the adsorption rate obtained at 40°C and PP are better than the adsorption rate obtained at 20°C. Removal efficiency (R %) obtained as a result of 180 minutes of mixing were 60% and 79% for T = 20°C and T = 40°C, respectively.

Adsorption Isotherm Models. In this work, Langmuir and Freundlich isotherms were used to examine LAS adsorption upon microplastics.

Bulut et al. mentioned that adsorption about Langmuir isotherm increases linearly with initial adsorbate concentration [14]. And they found that the surface is covered with a single layer and the amount of adsorbate adsorbed to the surface remains constant at the maximum saturation point. The linear forms of Langmuir isotherm are shown in equations 2, 3 and 4; [14].

\[ q_e = \frac{Q_{\text{max}} a_L C_e}{1 + a_L C_e} \]  
\[ q_e = \frac{k_L C_e}{1 + k_L C_e} \]  
\[ \frac{1}{q_e} = \left( \frac{1}{k_L} \right) \frac{1}{C_e} + \frac{a_L}{k_L} \]  

If we write in a linear form:

\[ \frac{1}{q_e} = \left( \frac{1}{k_L} \right) \frac{1}{C_e} + \frac{a_L}{k_L} \]  

Ce : Concentration of the remaining material in solution after adsorption (mg/L)
q_e : Amount of adsorbed material on the unit adsorbent (mg/g)
K_L : Constant dependent on the adsorption capacity of the adsorbate (L/g)
a_L : Constant dependent on adsorption energy (L/mg)
Q_{\text{max}} : Maximum adsorption capacity of the adsorbent (mg/g)

The linear forms of Freundlich isotherm has been shown in equation 5 and 6.

\[ q_e = K_F C_e^{1/n} \]  
\[ q_e = \log K_F + \frac{1}{n} \log C_e \]  

Ce: Concentration of the remaining material in solution after adsorption (mg/L)
q_e: Amount of adsorbed material on the unit adsorbent (mg/g)
K_F: It is calculated experimentally. Adsorption capacity (L/g)
n: Adsorption density (unitless)

In the Freundlich isotherm, the logarithm of both sides of equation 5 is taken and linearized.

\[ q_e = \log K_F + \frac{1}{n} \log C_e \]  

K_F and n constants are found by plotting the value change of log q_e relative to the log C_e. The cutoff point of y-axis of the line obtained from the graph gives log K_F and its slope gives 1/n. n > 1 indicates that the adsorption process is convenient [16].

To find out which adsorption is better explained with which isotherm, the experimentally obtained data is applied to all isotherm equations and poured into the graph. The isotherm type of data forms a linear graph. The linear graph helps to find the correlation coefficient and is the most suitable for that adsorption.

However, the adsorption may also be suitable to one or more isotherm [17].

Isotherms for LAS Adsorption upon PP. The PP adsorption was investigated at low concentrations and at different temperature and pH ranges. At the result of the studies which were completed at 2 different conditions, it was observed that the adsorption conditions suitable for PP were pH = 6, T = 40°C and Langmuir isotherm has been poured by obtained data as shown Table 1. The R² constant indicating suitability for adsorption indicated that the Langmuir isotherm was appropriate (Figure 2). In order to determine the suitability of Langmuir isotherm, the results were tabulated with values read on the graph. At the result of studies, it has been observed that PP has greater adsorption capacity than PE under these conditions.

<table>
<thead>
<tr>
<th>Terms</th>
<th>Parameters</th>
<th>K_L</th>
<th>a_L</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH=6,T=20°C</td>
<td>PP</td>
<td>3.22</td>
<td>-1.65</td>
<td>0.9869</td>
</tr>
<tr>
<td>pH=6,T=40°C</td>
<td>PP</td>
<td>0.3</td>
<td>-1.01</td>
<td>0.9915</td>
</tr>
<tr>
<td>pH=6,T=20°C</td>
<td>PE</td>
<td>0.083</td>
<td>1.1</td>
<td>0.9799</td>
</tr>
</tbody>
</table>
AdSORBON Kinetics. There are various kinetic models that characterize the adsorption process and plays a role in the adsorption of LAS onto PP and PE depend. These models can be examined in three classes, namely pseudo first-order kinetic model, pseudo second-order kinetic model and intraparticle diffusion model.

Pseudo First-Order Model or Lagergren’s Equation. The pseudo first-order kinetic model was developed by Lagergren and is expressed in the following equation. Lagergren has developed a first-order rate equation to describe the kinetic process of oxalic acid and malonic acid in liquid-solid phase adsorption on coal, which is believed to be the first model of adsorption rate based on adsorption capacity.

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$$  \hspace{1cm} (7)$$

Here, \( q_e \) is the amount of adsorbed material (mg/g) per gram of adsorbent at equilibrium, \( q_t \) is the amount of adsorbed material (mg/g) per gram of any adsorbent, \( k_1 \) is the rate constant (1/min), and \( t \) is the contact time.

The rate constant \( k_1 \) is calculated from the slope of \( \log(q_e - q_t) \) plotted against \( t \), and the theoretical \( q_e \) value is calculated from the graph's cutoff point. Lagergren's pseudo-first-order rate equation is used to distinguish kinetic equations based on adsorption capacity from solution concentration [18]. Recently it has become a widely used model for determining the adsorption of pollution in wastewaters in different areas [19].

Pseudo-second-order rate equation. The pseudo-second-order kinetic model was developed and is expressed in the following equation [20].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (8)$$

*FIGURE 2*
Langmuir adsorption isotherm for LAS upon PP on conditions pH=6, T=40°C

*TABLE 2*
The PFO and PSO kinetic parameters for the adsorption of LAS onto PP and PE

<table>
<thead>
<tr>
<th>Parameters</th>
<th>T (°C)</th>
<th>C_o (mg/L)</th>
<th>qe exp (mg/g)</th>
<th>k_1 (1/min)</th>
<th>qe cal (mg/g)</th>
<th>R^2</th>
<th>k_2 (g/mg.min)</th>
<th>qe cal (mg/g)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>20</td>
<td>2</td>
<td>0.15</td>
<td>0.01</td>
<td>0.147</td>
<td>0.9708</td>
<td>5.22</td>
<td>0.155</td>
<td>0.9938</td>
</tr>
<tr>
<td>PP</td>
<td>40</td>
<td>2</td>
<td>0.11</td>
<td>0.01</td>
<td>0.105</td>
<td>0.9759</td>
<td>6.26</td>
<td>0.11</td>
<td>0.997</td>
</tr>
<tr>
<td>PE</td>
<td>20</td>
<td>2</td>
<td>0.10</td>
<td>0.01</td>
<td>0.094</td>
<td>0.9584</td>
<td>5.66</td>
<td>0.099</td>
<td>0.9947</td>
</tr>
</tbody>
</table>
Where; $k_2$ is the second order kinetic rate constant is (g/mg.min). When a graph is drawn between $t/q_t$ and $t$, a straight line is obtained. The curve of this line gives the $1/q_e$ value and the point where it cuts the y axis gives the $1/k_2.q_e^2$ value.

The PSO kinetic model obtained under different conditions is given in Table 2. According to this result, it is seen that the PSO kinetic model is compatible with the high correlation coefficient ($R^2$) as a result of the experimental data obtained. On the other hand, it was observed that the theoretical $q_e$ value obtained from the PSO kinetic model gives the closest result to the experimental $q_e$ value.

CONCLUSIONS

In this study, LAS adsorption on microplastics was investigated. It was observed that PP and PE can adsorb LAS under different temperature conditions and the adsorption capacity increases as the temperature increases. It was investigated that the amount of adsorbed LAS at 40°C is higher than the one at 20°C. The LAS removal rate was 80% when working with PP at 40°C, while the rate on PP and PE at 20°C was 60% and 51%, respectively. Equilibrium studies show that Langmuir isotherm is highly suitable. According to the LAS adsorption, the adsorption up to 50 minutes was performed rapidly, then decreased slower to 110 minutes and the result was observed to be stabilized after 110 minutes. When the $R^2$ values of the kinetic models were compared, it was observed that the pseudo second order kinetic model was the most suitable model for the adsorption process.

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THE SEDIMENTARY INFILL OF THE PERTUSILLO FRESHWATER RESERVOIR (VAL D'AGRI, SOUTHERN ITALY)

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ABSTRACT

Freshwater reservoirs fed by multiple tributaries supplying water and sediments from different catchment areas are poorly known, notwithstanding their worldwide diffusion and environmental value.

The purpose of this study, focused on the sedimentary infill of the Pertusillo freshwater reservoir in Southern Italy, was to illustrate the complex sedimentary pattern that can develop in these water bodies, characterized by multiple point sources of sediments, complex hydrodynamics and dramatic water-level fluctuations. The environmental studies of such reservoirs must necessarily take into account the complexity of the sedimentary processes and the variability of bottom sediments where pollutant accumulate, in order to understand the complex geochemical pattern of these basins, that play an important role for the human life.

15 sediment cores, up to ~2 m long, were collected to study the sedimentologic and lithostratigraphic characteristics of the sedimentary infill of the Pertusillo reservoir, in Val d’Agri (Southern Italy). 11 lithofacies were identified, whose areal variability is the result of the complex sedimentary processes in the reservoir, related to its complex morphology and hydrology with dramatic seasonal fluctuations of the water level, and to the presence of multiple tributaries.

Two main different depositional areas separated by a transition zone were identified in the reservoir: a proximal coarser-grained deltaic area, characterized by high hydrodynamics and sediment variability, with multiple longitudinal and lateral deltas, and a distal quiet and muddy "lacustrine" area, where black anoxic beds also occur. The latter are common in eutrophicated waters, due to the abundance of nitrogen and phosphorous produced mainly by agricultural and industrial activities, both present in the study area, where the large Val d’Agri oil field occurs.

KEYWORDS:
Freshwater reservoir, sediment cores, anoxic beds, Val d’Agri, Pertusillo, Southern Apennines.

INTRODUCTION

Freshwater reservoirs have an important role, since they supply water for drinking, domestic, irrigation and industrial use, regulate discharges, prevent floods, generate energy [1-2]. They have also a relevant environmental value, since they act as effective traps for fluvial material and can thus record natural and artificial events occurring in the watersheds during the past [3]. Due to their rapid sedimentation rates, reservoir sediments may represent a continuous record of deposition of recent sediments and preserved historical pollutant inputs, and can be a valuable archive for the evaluation of the contamination caused by natural and anthropic events [3]. Moreover, many reservoirs provide waters for human use and consequently the knowledge and control of the water quality represent a relevant environmental challenge. However, geochemical studies investigating the pollutant dispersal in these complex basins need, as a necessary background, the knowledge of their hydrodynamics and sediment distribution.

Although the use of lake sediments as environmental archives is well established, reservoir sediments have less frequently been used as temporal records, and there is a lack of information on the matter. Besides, the knowledge of sediments in natural lakes may not apply to reservoirs. The variety of reservoir functions, such as water supply, power generation, discharge regulation, flood control, produce fluctuations in water level larger than in most natural lakes. Furthermore, a component of riverine hydrodynamics that lakes tend to lack, multiple source of sediment input with consequent faster sedimentation rates, differences in geometrical characteristics and drainage area to surface area ratios, imply the impossibility of applying to reservoirs the knowledge on the sediment type distribution in natural lakes [4-6].

The aim of this study is to reconstruct type and geometry of the sediment infill, lithofacies, sediment provenance and sedimentary processes of the modern Pertusillo freshwater reservoir, located in Val d’Agri (Basilicata, Italy; Fig. 1). Several anthropic activities occur in the surrounding areas of this reservoir, that provides waters for human use to Puglia, Basilicata and Calabria regions; they are mainly
related to oil and gas production, waste-water treatment, agriculture, landfills, plastics.

This anthropogenic pressure may thus represent an impact factor on the environmental equilibrium of this system, and a monitoring framework needs to be properly assessed. This study provided the necessary background for the successive geochemical and mineralogical study [7].

STUDY AREA

The Val d’Agri (VDA) is a NW-elongated Quaternary basin of Southern Italy (Fig. 1), occurring in the axial part of the Southern Apennines thrust-and-fold belt [8-12], and filled by fluvio-lacustrine sediments [13-15]. The VDA is mostly occupied by an elongated alluvial plain (140 km²), drained by the Agri River and its tributaries, and filled by up to 500 m of coarse- and fine-grained lacustrine and alluvial sediments, where minor porous aquifers occur. Important karstified and fractured aquifers are present in the pre-Quaternary bedrock of the valley margins.

The VDA hosts abundant ground and superficial water with 23 streams, about 650 springs [16-17] and the Marsisco Nuovo and Pertusillo freshwater reservoirs (Fig. 1). The latter is the largest and was realized in the period 1957-1963 by a dam wall across the Agri River; it is a long and narrow water body with two main arms on its southern margin (Vella and Maglia arms), and is mainly fed by the Agri River which enters longitudinally the reservoir from the northwest. Other minor lateral tributaries occur on both the northern (Spartifave, Rifreddo, Spetruzzone, Scazzzero and Grumentino) and the southern (Maglia, Vella and Sciaura) margins, mainly with a torrential-type discharge regime (Fig. 1).

In the VDA the largest exploited oil field of western onshore Europe occurs, and since 90’s oil extraction, treatment and wastewater injection are performed. The ~660 km² large Val d’Agri oil concession actually hosts 37 wells (24 in production [18]), located mainly in the northeastern margin of the valley and of the Pertusillo reservoir, the Centro Olio Val d’Agri (COVA) treatment plant and the Costa Molina 2 injection well.

The Pertusillo reservoir is affected by strong seasonal fluctuations of water level as high as 40 m (Figs. 2, 3), which correspond to a variation in the reservoir storage of about 80 million m³ (i.e. about half of the reservoir storage), mainly due to the seasonal rainfall/discharge.

The extent of drawdown during the last 51 years (i.e. 1964-2015) is illustrated in Fig. 2A. The lake level shows an annual cycle, decreasing in late autumn (October-November), and increasing from November to March, as documented by data on the period 2001-2015 [19] (Fig. 2B).

FIGURE 1
Location of the Val d’Agri, the Agri River drainage basin and the tributaries of the Pertusillo freshwater reservoir [21].

FIGURE 2
B, right: seasonal changes in the reservoir capacity during the period 2001-2015 [19].
FIGURE 3
The dramatic water-level fluctuations of the proximal part of the reservoir.

FIGURE 4
A, left: sediment thickness of the Pertusillo freshwater reservoir in September 2007 [20].
B, right: original bathymetry related to 533 m a.s.l. in 2007 [20].

The sediment volume accumulated in the reservoir is about 7420000 m³ from 1963 to 2007 [20]. The pachymetrical map [20] shows the highest sediment thickness along the axis of the reservoir, coinciding with the pre-reservoir Agri channel, and gradually increases towards the dam to the SE (Fig. 4A). The maximum sediment thickness is about 8.7 m, measured in the deepest area near the dam. It is then possible to calculate the approximate sedimentation rate, that ranges from a value of 4.5 cm/yr near the first islet, to a maximum value of about 19.7 cm/yr in the distal area near the dam.

The sediment distribution in the reservoir is controlled by the Agri River and its tributaries. Among them the largest sediment input is due to the northern Rifreddo and Grumentino streams, and to the southern Sciaura, Vella and Maglia streams. The suspended sediment yield (Tsd) was > 700 T/km²/yr for the Vella basin [21-22] and > 900 T/km²/yr for the Rifreddo basin [23].

Basinwards of the first islet, sediment thickness increases with the increasing water depth, as it appears if we compare them with the original bathymetry calculated by CRA-ABP in September 2007 [20] (Fig. 4B).

METHODS

The sediment sampling of the Pertusillo reservoir was carried out in May 2014. 15 cores, up to ~2 m long (Fig. 5), were collected in selected points, using a motorized platform and a UWITEC gravity corer. On the basis of the national and international guidelines, a gravity corer was selected for sampling soft fine-grained sediments (silt and clay) at limited depths, in order to minimize the disturbance.

Cores were sampled along the reservoir axis (A, B, F, F1, L, N, P, S, T, V), in each of the two arms (I = Maglia; M = Vella), and at the confluence of two tributaries (H = Rifreddo; Q, R = Spetrizzare-Scazzero). Cores were stored in lab at 4°C; after splitting, a detailed bed-by-bed sedimentological description of each core was performed on the basis of lithology, grain size, color, sedimentary and biogenic structures, other organic and inorganic
FIGURE 5
The map shows core location and lithostratigraphic logs summarizing the upper 2 m of the Pertusillo sediment infill.

components; sediment color was determined using the Munsell comparative tables [24]. The data of each core were plotted into logs and lithofacies were identified. These operations allowed us to identify the horizons to be sampled (147 samples) for the successive geochemical and mineralogical study.

RESULTS

Figure 5 shows the location and lithostratigraphic logs of the 15 cores distributed across the whole Pertusillo reservoir, in order to provide a first reconstruction of the depositional setting.

A very detailed sedimentological study allowed us to identify 11 lithofacies in core sediments, on the basis of the macroscopic features as described below.

**Facies A: cm- to dm-bedded massive mud.** This is the most abundant facies in the reservoir sediments. It mostly consists of mud varying in colour from ocher, reddish and greenish in the proximal cores, to gray in the distal cores (Fig. 6). Near the mouth of tributaries this facies becomes siltier, whereas in core Q rounded and angular granules and sandstone pebbles occur. Except for core B and Q, this facies occurs at the top of each core. In the proximal cores, red and black spherules and organic matter (branches, leaves) are widespread; frustules decrease in the other cores.

**Facies B: cm-bedded, massive mud with organic matter.** This facies, a few centimeters thick, was found only in cores A and I, and is represented by clayey silt with abundant frustules, leaves and roots, intercalated to mud of facies A. Beds have irregular contacts.

**Facies C: variegated cm- to dm-bedded mud.** It consists of disturbed poorly laminated mud with a variegated colour, changing from ocher-orange in the proximal cores to gray in the distal ones. This mud was found in several cores, from F to T, with thickness increasing in the center of the reservoir (cores I, P, R) and decreasing up to few centimetres and disappearing at the reservoir margins. In cores L and P thick black laminae were found at different depths.

**Facies D: finely laminated mud.** This facies occurs in cores B, F1, I, L, N, P and S. From proximal to distal cores laminae become progressively sharper, thicker and darker. In cores B and N laminae become siltier; branches and leaves are also present. This facies reaches its maximum thickness (29 cm) in core I and is always associated to facies C.

**Facies E: dark gray to black cm- to mm-bedded mud.** This facies (Fig. 6), that becomes increasingly abundant basinward from core F1, is represented by dark gray to black anoxic beds, whose thickness, number and colour intensity increase basinward, becoming progressively darker. The maximum number of beds (14) occurs in the distal core V.

**Facies F: graded mud.** This facies, that occurs in cores B, F, I, M, N, is represented by beds of (sandy) silt grading upwards into clayey silt, reaching the maximum thickness of 13 cm in core M. In the proximal cores B and F beds show frequently erosional bases.
Facies G: cm-bedded massive sandy mud. This facies is mainly developed in cores collected in the central portion of the lake, H, I and M. It consists of beds of sandy mud up to 6 cm thick; in core H several branches, leaves and black-purple powdery agglomerates are widespread.

Facies H: dm-bedded graded silty sand. This facies occurs at the bottom of cores F and I, and is represented by two beds, 15 and 11,5 cm thick respectively, of fine sand (with rare granules), becoming muddier upwards. In core R sand becomes coarser with rare frustules.

Facies I: cm-bedded massive sand. It is found in the proximal core A, in the central core I, in core Q and in the distal core R. This facies consists of medium to coarse well-selected sand, often with granules. In proximal core A beds locally have erosional bases.

Facies J: granules. It is represented by a 3 cm thick bed of rounded red-brown and subangular white clasts, occurring at the bottom of core N.

Facies M: massive breccia. It is well developed in core S where large angular sandstone clasts, up to 5 cm in diameter, occur in a sandy-muddy matrix. The thickness reaches 24 cm in core S, while it decreases to 6 cm in core Q.

DISCUSSION AND CONCLUSIONS

Core analysis of the uppermost ~2 m of the Pertusillo sediment infill shows a large vertical and lateral sediment variability, with 11 lithofacies ranging from muddy to sandy-pebbly sediments of different composition. Such variability is the result of the complex sedimentary processes related to the morphology and idrology of the Pertusillo reservoir, fed by the main Agri River and laterally by 7 main tributaries, and to dramatic seasonal fluctuations of the water level.

According to the data of core analysis, two different depositional areas have been recognized in the Pertusillo freshwater reservoir, from the Agri River mouth to the dam: a complex and coarser proximal deltaic area, characterized by high hydrodynamics and sediment variability, and a distal quiet, monotonous and muddier "lacustrine" area.

The deltaic area that occupies the northwestern half of the reservoir (cores A, B, F, Fl, H, I, L, M, N), is the site where the velocity of the sediment-laden Agri River and main tributaries drops abruptly, forming small deltas as coarse material is deposited at the stream mouths. This area is influenced by a highly dynamic fluvial behaviour, with the torrential regime of several tributaries, episodes of flooding, channel migration, changes in the position of the tributary mouths, of their morphologies and deltaic deposits, and with alternating episodes of deposition and erosion. In addition, this area is also dramatically influenced by seasonal fluctuations of the water level, that cause alternating episodes of emersion and submersion of large areas of the reservoir. Consequently, the multiple tributaries in the area between the mouth of the Agri River and the first islet, and the input of coarse-grained sediments cause a complex relationship between the spatial distribution of sediment types and water depth.

The textural characteristics and composition of the Pertusillo deltaic deposits are highly variable vertically and laterally, resulting in the alternation and intersecting of high-energy silty-sand and sand deposits (facies G, H, I, L, M), locally showing pedogenic horizons due to episodes of reservoir floor emersion, with muds typical of low-energy environments (facies A and F).

In the deltaic areas (cores A, B, F, Fl, H, I, L, M, N, R + Q, R) muddy sediments are quite homogeneous, lamination is always absent or disturbed (facies C), due to mud deposition in oxic conditions at the bottom, that favours bioturbation. Episodes of emersion of the reservoir floor are documented by the occurrence of erosional surfaces and pedogenic levels with abundant roots and frustules (facies B). Red and black spherules may suggest the migration of Fe and Mn along the sediment column during the water level fluctuations. The coarser sediment beds (facies G, H, I, L, M) have often erosional basal surfaces and include rounded fluvial granules in cores A and F, and angular granules in cores Q and R, where detrital material from the shore (core Q) and from the islet interrupts the lacustrine deposition.

In the distal deltaic area (cores F1, L, I, M, N) muddy sediments are largely prevalent to the sandy ones. In this area the disturbed laminated muddy sediments (facies C) are always associated to undisturbed laminated sediments (facies D); thin black laminae start to appear, testifying the progressive deepening of the area and the establishment of redox conditions. Erosional surfaces are lacking.

The "lacustrine" zone s.s. (cores P, S, T, V) coincides with the southeastern and deeper area of the reservoir, where sediments turn completely muddy, with the exception of the river mouths of two lateral tributaries on the northeastern margin (cores Q, R). In this low-energy sector, hardly affected by water level fluctuations, sediments are represented by grayish laminated muds (facies D) with light color differences and with intercalated cm-bedded black beds (facies E), that increase towards the dam in quantity, thickness and color intensity.
Completely black thin beds have been found in cores R, T and V. These beds show the highest total organic contents: most likely they were deposited under anoxia conditions of the hypolimnion. At the bottom of core S a massive coarse-grained deposit was found, probably related to the erosion of the upstream islet.

Sedimentation in this area of the reservoir is due to dispersal of plumes of stream water laden with suspended sediment load, and it settling to the floor to form a layer of mud. The abundance of organic matter and the lack of mixing of the oxygenated surface water with the lower part of the water column, result in anaerobic conditions at the bottom of the stratified lake. Oxygen-consuming organisms are unable to tolerate the anaerobic conditions, so the lake floor is devoid of life, and therefore there is no biogenic activity, and sediment lamination is not disrupted by such activity. The anoxia also prevents the aerobic breakdown of organic material that settles on the lake floor, allowing the accumulation of organic rich sediments, forming anoxic black beds.

The higher water level and sediment thickness, the presence of anoxic beds and the scarcity of sand fraction, lead us to identify this portion of the lake as the accumulation zone, whose sediment properties are replicable over the whole area.

In conclusion, this study provided the basic knowledge on the sedimentary processes and sediment distribution in the Pertusillo freshwater reservoir, essential for the successive geochemical and mineralogical study, in order to evaluate the contamination caused by natural and anthropic events in such a complex reservoir, that provides water for the human use of millions of people.

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USE OF ADVANCED OXIDATION PROCESSES FOR WATER TREATMENT

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ABSTRACT

This paper investigates removal efficiencies of ozone and hydrogen peroxide based advanced oxidation processes (AOPs) on pharmaceuticals (antibiotics and non-steroidal anti-inflammatory drugs) in water solution, which are commonly presented in outflow of wastewater treatment plant. It is proved that AOPs are able to satisfy remove these substances from water and interrupt its entrance to aquatic environment. Balance between removal efficiencies and costs is the main issue of current research into removing xenobiotics from wastewaters. To investigate justification of using costlier processes for reaching higher effectivity, sets of trials were performed. Artificially contaminated drinking water matrix was treated by various combinations of AOPs (O₃, H₂O₂, UV, O₃/UV, H₂O₂/UV, O₃/H₂O₂) in flow through AOPs pilot unit. Evaluation of removal efficiencies for each AOPs combination was made. Study proves that AOPs are capable of pharmaceuticals removal, especially ozone-based processes which showed very high rate in removal of studied substances in comparison to hydrogen peroxide-based processes. However, coupling ozone with UV or hydrogen peroxide did not result in significant increase of pollutant removal and justification of higher costs is debatable.

KEYWORDS:
Advanced oxidation processes, macrolide antibiotics, sulfonamides antibiotics, non-steroidal anti-inflammatory drugs, water matrix

INTRODUCTION

Pharmaceuticals, an important group of worldwide emerging contaminants in the environment which attracted world-wide attention. They might cause a potential threat of irreversible changes in the environment. The source of these pollutants is anthropogenic activities connected with human and veterinary medicine. The usage and consumption are increasing. Pharmaceuticals can enter the aquatic environment as parent compounds, metabolites or conjugates of both. These substances are excreted from human and animal bodies via urine and feces, which enter the environment in wastewaters or via agricultural use – usage of manure and sludge on fields [1, 2]. Conventional wastewater treatment plants are insufficient to removing these low bio-degradable pharmaceuticals [3]. Additionally, other problem is contamination of groundwater through surface water and landfill leakage. Presence of pharmaceuticals in drinking water should be considered as important for human health safety [4]. Therefore, it is necessary to monitor and identify the occurrence of pharmaceuticals in environment. On the other hand, it is important to find some new technologies, which can reduce micropollutants from water. Advanced oxidation processes are the promising technology for effective elimination of these substances [3, 5].

In general, pharmaceuticals in wastewater are usually presented in low concentrations from ng/l to µg/l [6]. Despite minute amounts in water, these micropolutants are toxic on living organisms [1, 3], interfere with endogenous hormonal signaling system [7] or cause changes in bacterial DNA [2].

Our study was focused on the removal of widespread and wide-used non-steroidal inflammatory drugs (NSAID) – ibuprofen (IBU), naproxen (NAX), ketoprofen (KET), diclofenac (DIC), sulfonamide antibiotics - sulfamethazine (SMZ), sulfamethoxazole (SMX), sulfathiazole (STZ) and macrolide antibiotics – azithromycin (AZI), clarithromycin (CLA), erythromycin (ERY), roxithromycin (ROX), which are included in the decision 2015/495/EU as substances potentially posing a significant risk [8, 9]. Main health risk of antibiotics for human is antibiotics resistance [10].

MATERIALS AND METHODS

Chemicals and materials. Regarding optimization method for determination of our target compounds (Table 1), high purity grade pharmaceuticals standards were used. The solvents, HPLC grade
methanol, acetonitrile (both J. T. Baker), Milli-Q water (Millipore QGARD, Academic, Germany), nitrogen for drying (4.7, SIAD Czech spol. s r.o.), formic acid (≥ 98 %, Sigma-Aldrich), helium (6.0, Linde, gas a. s.). The cartridges used for solid phase extraction were Supel™ Select HLB (200 mg, 6mL) from Sigma-Aldrich.

The individual standard solution was prepared in methanol. After preparation, standards were stored in fridge at 4 °C. A mixture of all pharmaceuticals was prepared through appropriate dilution of individual standard solutions in methanol-water (50:50, v/v).

**AOPS pilot unit.** A flow-through prototype unit for advanced oxidation processes studies, illustrated in Fig.1, was used for all conducted experiments during this study. The unit contains ozone generator (WEDECO EFFIZONE GSO 10) generating max. 30g O₃/h with ozone analyzer (WEDECO MC 400plus), hydrogen peroxide dosing pump (GrundfosAlldos DDA 7.5-16) and a pair of UV reactors with single LP UV-C lamp (WEDECO AQUADA Proxima 7, 80W). In addition, the prototype is equipped with flow measuring (Sika VVX 25) at the inlet, ozone injector, static mixing after ozone and hydrogen peroxide dosage.

**Experimental procedure.** Raw water (a mixture of drinking water and added chemicals; pH=7) was pumped from accumulation tank to the system in constant flow 3.024 m³/h through pipes with inner diameter 25 mm. This created turbulent flow (Reynolds number approx. 42.000) and the mixture was permanently mixed not only in static mixer, but also in the pipes. In this study, following AOPs combinations were tested: O₃, H₂O₂, O₃ + UV, H₂O₂ + UV, O₃ + H₂O₂. Every combination was also tested with different concentration of oxidants (O₃, H₂O₂) to determine the dosage required for satisfactory micropollutants removal. In case of O₃ + H₂O₂ combination, molar ratio O₃ : H₂O₂ - 2:1 was applied due to avoiding of generating HO₂⁻ scavengers [11]. Samples were taken at the outlet from the unit.

**Samples and samples collections.** All experiments were conducted with artificially contaminated water. This water was prepared by dissolution of commercially used drug pills which contained target compounds (ibuprofen, naproxen, azithromycin) or analytical standards (diclofenac, ketoprofen, sulfamethazine, sulfamethoxazole, sulfathiazole, clarithromycin, erythromycin and roxithromycin) in drinking water in concentrations ranging from ng/L to µg/L similar to real wastewaters.

<table>
<thead>
<tr>
<th>Therapeutic group</th>
<th>Compounds</th>
<th>CAS number</th>
</tr>
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<tr>
<td>Non-steroidal anti-inflammatory drugs</td>
<td>Ibuprofen</td>
<td>15687-27-1</td>
</tr>
<tr>
<td></td>
<td>Naproxen</td>
<td>22204-53-1</td>
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<tr>
<td></td>
<td>Ketoprofen</td>
<td>22071-15-4</td>
</tr>
<tr>
<td></td>
<td>Diclofenac</td>
<td>15307-79-6</td>
</tr>
<tr>
<td>Sulfonamides antibiotics</td>
<td>Sulfamethazine</td>
<td>57-68-1</td>
</tr>
<tr>
<td></td>
<td>Sulfamethoxazole</td>
<td>723-46-6</td>
</tr>
<tr>
<td></td>
<td>Sulfathiazole</td>
<td>72-14-0</td>
</tr>
<tr>
<td>Macrolide antibiotics</td>
<td>Azithromycin</td>
<td>83905-01-5</td>
</tr>
<tr>
<td></td>
<td>Clarithromycin</td>
<td>81103-11-9</td>
</tr>
<tr>
<td></td>
<td>Erythromycin</td>
<td>59319-72-1</td>
</tr>
<tr>
<td></td>
<td>Roxithromycin</td>
<td>80214-83-1</td>
</tr>
</tbody>
</table>

**FIGURE 1**

Scheme of pilot unit for advanced oxidation processes studies
TABLE 2
Limit of detection and quantification for target compounds

<table>
<thead>
<tr>
<th>Therapeutic group</th>
<th>Compounds</th>
<th>LOD [ng/mL]</th>
<th>LOQ [ng/mL]</th>
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</thead>
<tbody>
<tr>
<td>Non-steroidal anti-inflammatory drugs</td>
<td>Ibuprofen</td>
<td>0.5945</td>
<td>1.982</td>
</tr>
<tr>
<td></td>
<td>Naproxen</td>
<td>0.0652</td>
<td>0.2173</td>
</tr>
<tr>
<td></td>
<td>Ketoprofen</td>
<td>0.3325</td>
<td>1.108</td>
</tr>
<tr>
<td></td>
<td>Diclofenac</td>
<td>0.2235</td>
<td>0.7451</td>
</tr>
<tr>
<td>Sulfonamides antibiotics</td>
<td>Sulfamethazine</td>
<td>1.487</td>
<td>4.957</td>
</tr>
<tr>
<td></td>
<td>Sulfamethoxazole</td>
<td>2.953</td>
<td>9.842</td>
</tr>
<tr>
<td></td>
<td>Sulfathiazole</td>
<td>4.285</td>
<td>14.28</td>
</tr>
<tr>
<td>Macrolide antibiotics</td>
<td>Azithromycin</td>
<td>13.39</td>
<td>44.62</td>
</tr>
<tr>
<td></td>
<td>Clarithromycin</td>
<td>6.733</td>
<td>22.44</td>
</tr>
<tr>
<td></td>
<td>Erythromycin</td>
<td>1.463</td>
<td>4.878</td>
</tr>
<tr>
<td></td>
<td>Roxithromycin</td>
<td>4.595</td>
<td>15.32</td>
</tr>
</tbody>
</table>

Samples were collected from the outflow of AOP unit. For each combination used, 1 L of sample were taken into glass bottles, previously rinsed by ultrapure water. The collected samples were stored in fridge at 4 °C until processing (max. 24 h).

Sample preparation. Target compounds were extracted from raw water samples by solid-phase extraction (SPE) by SupelcoTM-Select HLB, 200 mg, 6 mL (Supelco, Sigma-Aldrich) using a Baker vacuum system (J.T. Baker, Deventer, The Netherlands). Briefly, SPE cartridges were conditioned with 6 mL of HPLC grade acetonitrile followed by 6 mL of Milli-Q water (pH = 5.5). 200 mL of water sample was then processed through the cartridge, dried under vacuum for 20 min and eluted with 3 × 4 mL of mixture 50:50 HPLC-grade methanol-acetonitrile, dried under the gentle stream of nitrogen and after dissolved in 1 mL of HPLC-grade methanol-water (50:50, v/v).

Instrumental analysis. Final analysis, identification and quantification, were done by high-performance liquid chromatography with DAD detector and mass spectrometry detector with ion trap analyzer and electrospray ionization (HPLC-DAD-MS; HPLC Agilent 1100 Series; Mass spectrometer Agilent 6320 Series, Ion Trap LC/MS). Chromatographic separation was achieved with the Kinetex C18 (150 x 3.0 mm, 2.6 μm) column. The optimum column temperature was adjusted on 40 °C. For the analysis eluent A was methanol and eluent B was 10 mM formic acid (pH = 2.4) at a flow rate 0.3 mL/min. The sample injection volume was set at 2 μL. The gradient program of A eluent (%): t0 = 40, t5 = 60, t6 = 80, t10 = 80, t15 = 90, t16 = 90, t18 = 40.

RESULTS

Developed analytical method was applied for 11 pharmaceuticals from three therapeautic groups, non-steroidal anti-inflammatory drugs, macrolide and sulfonamides antibiotics for the evaluation of pharmaceuticals removal by different possibilities of advanced oxidation processes. Experiments has shown that ozone-based processes were more effective for degradation of investigated micropollutants than hydrogen peroxide-based processes. A simple ozonation was able to remove all ERY, AZI, CLA, ROX, STZ, SMX, NAP at very low concentration of ozone (0.024 mmol/L). On the other side, IBU and KET removal was just slightly increasing with O3 dose and the removal was approximately 83% at 0.116 mmol O3/L.

Application of hydrogen peroxide alone, at concentration 3 mmol/L, had only margin effect on studied pollutants and practically all remained untouched. From all studied pharmaceuticals, 4 has been found to be reduced by simple UV irradiation – sulfathiazole 82%, sulfamethoxazole 50%, ketoprofen 95% and diclofenac 84%.

Coupling ozone with hydrogen peroxide in ratio H2O2/O3 = 0.5 noticeably increased the removal of SMZ, IBU by 9% in average, KET 12% in average. Experiment with ozonation combined with UV did not show any significant improvement (except KET due to UV irradiation) in removal compared to the simple ozonation.

On the other hand, removal efficiencies were considerably affected by coupling hydrogen peroxide with UV irradiation. Removal rates from 48% (AZI, CLA) to 100% (STZ) were observed at 3 mmol/L.

Operational costs of simple ozonation were calculated for approx. 0.22 €/m³ in average for concentration range of 0.024-0.116 mmol O3/L. In full scale operation, costs could be decreased by using more effective ozone generator or by operating the system with higher O3/O2 ratio in dosed gas, which had the main impact on the costs. Coupling ozonation with UV irradiation or H2O2 resulted only in marginal increase of costs to 0.23 €/m³.

Lower removal rates and high operational costs (0.82 €/m³ for concentration 3 mmol H2O2/L) of H2O2/UV determines this process as inefficient.
FIGURE 2
Removal of target compounds by ozone based AOPs

DISCUSSION AND CONCLUSION

The analyzed pharmaceuticals are shown in Table 1. They are separated into three therapeutic groups: non-steroidal anti-inflammatory drugs, sulfonamides antibiotics and macrolide antibiotics.

Artificially contaminated drinking water by target pharmaceuticals were used for the oxidation experiments. For oxidation, a flow-through prototype unit for advanced processes, which is shown in Figure 1, was used.

As results show, sufficient removal rate of studied pollutants was reached only by using ozone-
based processes. Hydrogen peroxide processes at 24 times higher dosage of H2O2 against O3 have not reached comparable results. From tested combinations of oxidation processes, the O3/ H2O2 combination in ratio 2:1 was the most efficient at removing of studied pollutants, where removal rate of all pollutants was above 90% and most of them were removed completely.

Sulfonamides antibiotics were the best group for the removal by all tested combinations. On the other hand, non-steroidal anti-inflammatory drugs was the worst group for removal. Ibuprofen has the worst removal by each used combination. Ibuprofen, from NSAID group, is one of the most frequently prescribed pharmaceuticals which is detected around word in all types of water.

Public awareness and policy attention have recently increased the studies about removal of pharmaceuticals in water. Advanced oxidation processes are promising technologies to oxidize these compounds. The most studied oxidation reaction is ozonation, which gives good expectative to be applied with success. Our result shows practical implications for the removal of organic micropollutants, especially for antibiotics.

The chemical oxidation has been proved to be an effective treatment process for wide spectrum of residues of micropollutants from water matrices. Published articles are especially focused on removal of residues pharmaceuticals and personal care products. The articles are coinciding with used doses of oxidizing agents. The most effective one was ozone-based reactions with ozone ranging from 2 to 5 mg/L. O3, 2-2.5 mg/L was also found as lowest dose to be highly effective to remove 90 – 99 % contamination in drinking water across published literature [3, 12]. Our results are comparable with other published literature.

**FIGURE 3**
Removal of target compounds by hydrogen peroxide and UV radiation combination

**FIGURE 4**
Removal of target compounds by UVC radiation
ACKNOWLEDGEMENTS

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VARIATION OF MICROBIAL ACTIVITY AND PERMEABILITY OF COMPACTED CLAYS PERMEATED WITH LEACHATE

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2 Nevsehir Haci Bektas Veli University, Department of Environmental Engineering, Faculty of Engineering-Architecture, Nevsehir, 50300, Turkey
3 Istanbul University-Cerrahpaşa, Faculty of Engineering, Department of Environmental Engineering, 34320 Avcilar-Istanbul-Turkey
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ABSTRACT

In this paper, the effects of microbial activity on permeability and the treatment capability of compacted clay soil have been determined. Soil samples and leachates were obtained from the Şile-Kömürçüoda Organized Landfill Area on the Asia side of Istanbul. Standard and modified proctor compaction tests were applied to the clay soil. The leachate sample has been passed through the reactors prepared with the clay samples taken from the same facility and subjected to the standard and modified compaction tests. The effects of microbial activity on the permeability of compacted clay soil samples have been analyzed. Microbial activities of influent and effluent samples have been also measured to determine the treatment capability of the compacted clay soil. Microbial activities i.e., microorganisms including total heterotrophic bacteria, fecal coliforms, total coliforms, fecal streptococci and fungi have been monitored and tested. Based on the findings, initially some decrease has been observed in the clay permeability associated with the contamination. The suspended solid matters of leachate have filled the spaces between the particles and the clay soil. The growth of microorganisms inside the soil pores caused pore clogging which have led to a decrease in the permeability. In the length of time, these results show that leachates may cause increase in the permeability.

KEYWORDS:
Permeability, leachate, compacted clay soil, removal efficiency, microbial activity.

INTRODUCTION

Rapid growing of world’s population and unplanned urbanization in parallel with technological development and industrialization is increasing the human impact on environment. While the growth in production, wastes produced due to growing trend in consumption. On this account, wastes have reached dangerous levels due to their quantity and hazardous composition. Currently, world cities generate about 1.3 billion tonnes of solid waste per year and are expected to increase to approximately 2.2 billion tonnes per year by 2025 [1].

Municipal solid waste (MSW) is a major problem in Turkey, as in many world cities. Istanbul is the largest city in Turkey with a population of 15 million. According to the Turkish State Institute’s 2016 database, 1.3 kg/person-day waste water is collected in Istanbul. One being in the European side and the other in Asian side there are two Sanitary Landfill Facilities in Istanbul in which domestic wastes are disposed. Kömürçüoda Solid Waste Landfill Facility on the Asian side is established on a total acreage of 233 Ha in Kömürçüoda location of Karakiraz Village in Şile country. Odayeri and Kömürçüoda Sanitary Landfill Facilities were commissioned by completing construction works in 1995. 10,500 tonnes of wastes are disposed in the European side of the city, whereas 5,500 tonnes of it is collected on the Asian side and this garbage is brought to sanitary landfill areas and disposed.

Leachate generation is a major problem for municipal solid waste (MSW) and causes significant threat to groundwater and surface water. The burial of MSW in landfills is the most common disposal practice in most countries [2]. Leachates contained in most modern waste-containing facilities are aqueous solutions containing complex mixture of organic and inorganic contaminants [3, 4]. Leachate may also have a high concentration of metals and contain some organic chemicals [5]. The volume and chemical composition of leachate depends on the water that infiltrates in the landfill, and the chemical reactions between the solid and liquid phases, including dissolution, precipitation, ion exchange and biochemical processes [6]. Composite liner systems, which are consisted of a layer of compacted clay liner or a geosynthetic clay liner, are used in landfills to isolate waste components from the...
environment and, therefore, to protect the soil and groundwater from pollution originating in landfills [7]. Compacted clay soils are widely used in solid waste landfills due to their cost effectiveness and large capacity of attenuation [8]. Through the compacted clay soils possess many advantages include low hydraulic conductivity (<10^-9 m/s), they have high potential of shrinkage and instability problems [9]. The liner component is compacted to achieve a hydraulic conductivity no greater than 10^-8 m/s [10]. The ability of compacted soil liners to restrict the movement of water and contaminants depend on particle size, void ratio, specific surface, degree of saturation and fluid properties [6]. Although the hydraulic conductivity of clay soils is normally considered to be low, hydraulic conductivity of compacted clays can vary enormously depending on the soil composition and the conditions under which they are compacted [11]. Landfill leachate exposure may also cause changes in the soils’ chemical composition, mineral composition, and physical properties of clay liners. Hydraulic performance of the treated clay may change on account of these changes [7]. Benson and Trast reported that hydraulic conductivity is sensitive to the Atterberg limits and particle size distribution [11]. Soils with higher liquid limit or contain better quality of minute particles have lower hydraulic conductivity. Sivapullaiah P. et al. determined the hydraulic conductivity of soils decrease with increasing fine particle content [12]. Cation Exchange Capacity (CEC), thickness of the double layer, and mineral composition were the parameters used to assess the effect of landfill leachate on the hydraulic performance of clay barriers [7]. Griffin R. A. et al., demonstrated a decrease in hydraulic conductivity of clay soils upon exposure to domestic waste leachate due to bacterial clogging, double layer expansion, and Na+ adsorption [13]. Microorganism and bacterial biomass cause e bio-clogging in landfill liners. Tang, Q., et al. were conducted a long term hydraulic conductivities of compacted clay and fine sand with distilled water, landfill leachate and one type of nutrient solution, and they found such a significant difference that attributed to the effect of bio-clogging “the microorganism and bacterial biomass reduced the hydraulic conductivity up to one order of magnitude” [14]. Also, Franciscia F. M. and Glatstein D. A. measured the long term hydraulic conductivity of compacted silt-bentonite mixtures with distilled water, landfill leachate and a nutrient solution [6]. They found that the hydraulic conductivity decreased significantly with time when the permeating liquid microorganism growth inside the soil pores and causes pore clogging.

The purpose of this study is to evaluate removal rate of microorganisms (microbial activity) and their effects on the permeability of landfill leachate by compacted clays used as liners in Turkish landfill sites.

MATERIALS AND METHODS

Properties of the clay soil and the leachate. The clay soil was taken from Şile-Kömürçüoda Organized Landfill Area on the Asia side of Istanbul which is situated in partially or totally abandoned mine quarry areas with damaged native soil surfaces. The site is in a slightly sloped valley covered with Neogene aged layers of clay soil, sand, gravel and coal lenses. The clay soil is chemically compatible with the fill area. Typical clay liners have been constructed with natural soils having low permeability and they have been built up with heavy soil compaction equipment or cylinders. The clay liner underlying domestic solid wastes stored in the Kömürçüoda solid waste landfill site is 60 cm thick with a permeability coefficient from 1x10^-7 to 1x10^-8 m/s [15, 16]. The properties of the leachate and the clay soil have been determined. The results of the chemical analysis of the clay soil and the characterization studies conducted on the leachate from the Şile-Kömürçüoda Landfill Site are presented in Table 1 and Figure 1. The results of sieve analyses are given in Figure 2 [15]. Leachate have dark brown color and very small granules and also contain large amounts of organic, inorganic contaminants and a high concentration of metals.

The Şile-Kömürçüoda Landfill Site soil samples have contained 68 to71 % kaolinite, 6 to 9 % free quartz, 15 to18 % illite, and 2 to 5 % others. Their color was brownish-gray. The kaolinite and illite have been considered to be true clay soil minerals. The soil samples had a coefficient of permeability k=1x10^-8 m/s a discharge loss of 8.5 to 9 %, and a water absorption of 0.2 to 0.4% [15].

Chemical Analysis

![Soil minerals](image)

**FIGURE 1**

The Chemical Analysis of the Clay Soil Used in Kömürçüoda Solid Waste Landfill [15].

Permeability tests. Standard (ASTM D698/AASHTO T99) and Modified Proctor (ASTM D1557/AASHTO T180) methods are commonly applied in the laboratory at different water contents in a module (0.102m. ID X 0.117m. H) and vary only in the amount of applied energy to determine the
maximum dry density-water content relationship. Standard Proctor involves 25 drops of a 24.5 kN hammer from a height of 0.305 meters and three soil layers. The Modified Proctor uses a 45 kN hammer, a fall of 0.45 meters on five layers of soil, i.e., a higher compactive energy [17].

The reactor tests performed by flowing the liquid downwards through 100 mm diameter compacted specimens. The height of the compacted clay soil was 110 mm. The soil was constrained against swelling. The clay soil has been saturated under a 0.3 bar pressure [18, 19] (Figure 3).

![Sieve Analysis](image)

**Figure 2**
Sieve Analysis [15].

![Experimental Setup](image)

**Figure 3**
Experimental Setup.

### TABLE 1
Properties of the Leachate

<table>
<thead>
<tr>
<th>Parameter/Averages</th>
<th>pH</th>
<th>COD (mg/L)</th>
<th>BOD (mg/L)</th>
<th>TKN (mg/L)</th>
<th>Total P (mg/L)</th>
<th>SS (mg/L)</th>
<th>VSS (mg/L)</th>
</tr>
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<tr>
<td>[15]</td>
<td>6.5</td>
<td>9500</td>
<td>3500</td>
<td>3000</td>
<td>5</td>
<td>1159</td>
<td></td>
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<tr>
<td>[16]</td>
<td>6.8</td>
<td>10000</td>
<td>1010</td>
<td>1635</td>
<td>5</td>
<td>1010</td>
<td>855</td>
</tr>
<tr>
<td>This Study</td>
<td>6.7</td>
<td>13526</td>
<td>6235</td>
<td>2876</td>
<td>7</td>
<td>1283</td>
<td>987</td>
</tr>
</tbody>
</table>

Microbial Activity Analysis. Microbial activity (Total Heterotrophic Bacteria, Total Coliform, Fecal Coliform, Fecal Streptococcus, Fungi) have been measured according to Standard APHA Methods both in the influent and effluent of the continuous reactor [20]. These analyses have been conducted on the samples taken from the influent of the solid waste leachate and effluent of the reactors treating the leachate, using membrane filtration technique. Membrane filtration method has been applied to detect microorganisms under aseptic techniques. Results were reported as colony forming unit (CFU) per 100 ml of sample. The media and 0.45 μm membrane filter papers were commercially purchased. TTC medium for total heterotrophic bacteria, endo medium for total coliforms, medium for fecal coliforms (MFC), azide medium for fecal streptococci and sabouroud medium for fungi have been used in the microbiological analyses. Plates for total bacteria, total coliforms and fecal streptococci tests were incubated at 37 °C for 24 hours and then counted under the colony counter. Fecal coliform medium plates were incubated at 44.5 °C for 24 hours and then counted under the colony counter. Fungi plates have been incubated at 25 °C for 48 hours and then counted under the colony counter.

**Scanning Electron Microscope (SEM) analysis.** SEM analyses have been performed on the clean and contaminated soil samples. The specimens photographed were formed from the soil in the form of large clods. The high-magnification photographs have been taken with a SEM equipped with a camera. The specimens have been prepared for this practice in the following manner: (1) A small piece of soil was removed from the large compacted specimen with a sharp knife; (2) This small piece was oven-dried at 105 °C; and (3) The oven-dried soil was plated with gold in a very low-pressure atmosphere of argon gas. Constant Head Tests, using the following equation, have been performed to find the coefficient of permeability of the clay soil:

\[
K = \frac{QL}{At(h_1 - h_2)}
\]

(2.1)
where, k: Coefficient of permeability, cm/s; A: Surface area of the specimen, cm²; L: Distance between the manometers, cm; (h₁-h₂): Differential head across the sample, cm; Q: Total discharge, cm³/s; t: elapsed time, s.

RESULTS AND DISCUSSION

Compaction and permeability tests. The variation of the densification degree to be obtained with a compaction energy applied with the water content has been determined experimentally for the soil to be used in the landfill. Two different Proctor Tests, standard and modified, are extensively used which differ in the total energy applied in sample preparation. Permeability tests have been carried out on the samples obtained from the Standard and Modified Proctor tests. The samples have been prepared at the optimum water content and at the water contents 3% above and below this value. Then, leachate has been passed through these prepared samples and the permeability coefficients have been determined. The results obtained during this process are given in Figure 3. In Figure 4A, the variation in the permeability of the clay sample as the result of contamination is observed. These variations show that the permeability somewhat decreases. It has been seen that the growth of microorganisms inside the soil pores caused pore clogging; and suspended materials in the leachate fill the spaces between the particles of the clay hence the coefficient of permeability decreases. The permeability of the current clay liner in the Şile Kömürücüoda landfill site was measured between k=5.2x10⁻⁴ and 6.45x10⁻⁸ m/s the permeability was decreased (opt.modify compacted; k=2.53x10⁻⁹ m/s) when clay soil samples were leached with leachate, which clearly can be seen from Figure 4A. In the long term, a reversed variation, in other words, increase in the permeability was seen (Figure 4B). The initial permeability values are 2.56x10⁻⁴ and 1.1x10⁻⁹ m/s; the observed lowest values are 1.1x10⁻⁸ and 5.28x10⁻¹¹ m/s; the values in the end day of experiments were found 2.78x10⁻⁴ and 2.11x10⁻⁹ m/s for clay soils that were performed with standard and modified proctor compaction, respectively. It is thought that the chemical and physical deteriorations due to the contaminant in the soil would result in such an alteration.

Microbial activity analysis. Removal efficiencies of the microorganisms were studied in 4 separate reactors with standard and modified compacted clayey soil samples with different moisture ratios. Four different reactors filled with clayey soil samples compacted using standard and modified Proctor methods were used to monitor the removal rate of microorganisms. The results are shown below in Figures 5-9.

Total heterotrophic bacteria. The initial total heterotrophic bacteria value of the leachate was measured as 2400000 CFU/100ml. As the first transition of the leachate through the clayey soil has taken 31 days for the clay performed standard compaction, for the clay performed modified compaction it has taken 44 days. For the samples with the water contents of 25 % (opt.) and 28 % in the standard compacted reactors, in the day 182, the total heterotrophic bacteria effluent values of 12000 CFU/100ml and 11000 CFU/100ml and removal rates of 100 % and 100 % have been obtained respectively. In the modified compacted reactor with the water content of 21 % on the day 75, a total heterotrophic bacteria effluent value of 1400000 CFU/100ml and a removal rate of 42 % have been obtained. Similarly, on the day 192, at the water content of 18 % (opt.) a removal rate of 100 % and at the water content of 21 % a removal rate of 100 % has been obtained in the reactors compacted modified methods. Adsorption was observed for a period of 246 days for reactors that compacted standard method and 255 days for reactors that compacted modified method. For the soils compacted with the modified compaction method, the average removal rate at the water content of 18 % (opt.) has been 85 % and for the soils which were
compacted with standard compaction method, the removal rate of water content of 25% (opt.) has been 68%.

**Total Coliform.** The initial total coliform value of the leachate was measured as 110000 CFU/100ml. As seen from the figure, in the reactor where the sample has been compacted with the water content of 25% (opt.), in the day 31, a total coliform effluent value of 820000 CFU/100ml and a removal rate of 26%, and in the day 62, a total coliform effluent value of 5 CFU/100ml, and a removal rate of 100% have been obtained. For the samples with the water contents of 25% (opt.) and 28%, in the day 182, the total coliform effluent values of 0 CFU/100ml and 5000 CFU/100ml and removal rates of 100% in both cases have been obtained. As seen from the figure, the removal rate of the total coliform in the compacted soil is quite high. For the clay performed under modified compaction, the first transition of the leachate through the clay soil has taken 44 days. In the reactor with the water content of 18% (opt.), on the day 75, a total coliform effluent value of 5 CFU/100ml and a removal rate of 100% have been obtained. In the reactor with the water content of 21% on the day 75, a total coliform effluent value of 130 CFU/100ml and a removal rate of 100% have been obtained. Similarly, on the day 192, at the water content of 18% (opt.) a removal rate of 100% and at the water content of 21% a removal rate of 100% have been obtained. As observed from the results, rate at the optimum water content has been greater. For the soils compacted with the modified compaction method, the average removal been 100% and for the soils compacted with standard compaction method, the removal rate at the water content rate at the water content of 18% (opt.) has of 25% (opt.) has been 87%.

**FIGURE 4B**
Permeability and Time Relation

**Fecal coliform.** The beginning fecal coliform value of the leachate has been measured as 480000 CFU/100ml. As seen from the figure, in the reactor where the sample has been compacted standard method with the water contents of 25% (opt.) and 28%, in the day 182, the fecal coliform effluent values of 0 CFU/100ml and 0 CFU/100ml and removal rates of 100% and 100% have been obtained respectively. For the clay performed modified compaction, in the reactor with the water content of 18% (opt.), on the day 75, a fecal coliform effluent value of 5 CFU/100ml and a removal rate of 100% have been obtained. In the reactor with the water content of 21% on the day 75, a fecal coliform effluent value of 5 CFU/100ml and a removal rate of 100% have been obtained. Similarly, on the day 192, at the water content of 18% (opt.) a removal rate of 100% and at the water content of 21% a removal rate of 100% have been obtained. As observed from the results, rate at the optimum water contents have been major. For the soils compacted with the modified compaction method, the average removal rate at the water content of 18% (opt.) has been 100% and for the soils compacted with standard compaction method, the removal rate at the water content of 25% (opt.) has been 86%.

**FIGURE 5**
Variation and removal rate of total heterotrophic bacteria

**FIGURE 6**
Variation and removal rate of total coliform

**Fecal streptococcus.** The initial fecal streptococcus value of the leachate has been measured as 27000 CFU/100ml. For the samples performed standard compaction with the water contents of 25% (opt.) and 28%, in the day 182, the fecal streptococcus effluent values of 0 CFU/100ml and 0 CFU/100ml and removal rates of 100% and 100% have been obtained respectively. Adsorption has been observed for a period of 246 days. As seen from the figures, the removal rate of the fecal streptococcus in the compacted soil is high level. For the clay performed modified compaction, in the
reactor with the water content of 18 % (opt.), on the day 75, a fecal streptococcus effluent value of 5 CFU/100ml and a removal rate of 100 % have been obtained. In the reactor with the water content of 21 % on the day 75, a fecal streptococcus effluent value of 17 CFU/100ml and a removal rate of 100 % have been obtained. Similarly, on the day 192, at the water content of 18 % (opt.) a removal rate of 100 % and at the water content of 21 % a removal rate of 100 % have been obtained (Figure 8). As observed from the results, rate at the optimum water contents have been greater.

Variation and removal rate of fecal coliform

![Graph showing variation and removal rate of fecal coliform](image1)

Variation and removal rate of fecal streptococcus

![Graph showing variation and removal rate of fecal streptococcus](image2)

Fungi. The beginning fungi value of the leachate has been measured as 500000 CFU/100ml. As seen from the figure, in the reactor where the sample has been compacted standard method with the water content of 25 % (opt.), in the day 31, a fungi effluent value of 110000 CFU/100ml and a removal rate of 78 %, and in the day 62, a fungi effluent value of 2000 CFU/100ml, and a removal rate of 100 % have been obtained. For the samples performed standard compaction with the water contents of 25 % (opt.) and 28 %, in the day 182, the fungi effluent values of 220000 CFU/100ml and 200000 CFU/100ml and removal rates of 56 % and 60 % have been obtained respectively. For the clay performed modified compaction, the first transition of the leachate through the clay soil has taken 44 days. In the reactor with the water content of 18 % (opt.), on the day 75, a fecal streptococcus effluent value of 350 CFU/100ml and a removal rate of 100 % have been obtained. In the reactor with the water content of 21 % on the day 75, a fecal streptococcus effluent value of 400 CFU/100ml and a removal rate of 100 % have been obtained. Similarly, on the day 192, at the water content of 18 % (opt.) a removal rate of 96 % and at the water content of 21 % a removal rate of 100 % have been obtained (Figure 9). As observed from the results, rate at the optimum water content has been greater. For the soils compacted with the modified compaction method, the average removal rate at the water content of 18 % (opt.) has been 71 % and for the soils compacted with standard compaction method, the removal rate at the water content of 25 % (opt.) has been 62 %. In general, there is a removal for all of the parameters where bacterial cell numbers have decreased in the effluent wastewater compared to those in influent wastewater. Especially the numbers of total coliform, fecal coliform and fecal streptococci is decreased to undetectable levels. However, in spite of reduced numbers, fungi and total bacteria numbers were still detectable in the effluent wastewaters. The effluent water of the reactor which contains a clay compacted with modified Proctor at a water content of 21% (opt.+3) especially gave poor results (Figure 24). However, it can be concluded that some of the microorganism are affected by the change in the leachate properties and/or time-dependent increase in the concentration of toxic matter within the reactor.

SEM analysis. The images obtained from the SEM with a magnification factor of 2,500 of the clean and contaminated clay specimens have been presented in Figures 10 to 13. It is seen from the clean clay images (Fig. 10,12) that the texture of the clay particles is amorphous. It is also evidently observed from the photographs that the leachate is accumulated between and on the surface of the clay flocs (the dark parts between the flocs) in the specimens contaminated with the leachate (Fig. 11, 13). Together with the fact that the leachate changes the coefficient of permeability while it passes through the clay soil, several mechanisms are effectual in removing the contamination in the leachate. These can be listed as the mechanical...
filtration, sedimentation, adsorption, chemical reactions and biological activities. Filtration as a mechanical process is the procedure of catching some of the contaminative components while the waste water passes through the filter layer. Because the dimensions of the suspended solid matters are greater than the mesh of the filter material, they are hold. On the other hand, as a result of the fact that some of the particles come into contact with each other during the filtration, greater flocs take shape; hence, the contaminative components cannot pass through the filter layer and cannot interfere the effluent. The sediments taken place during the filtration decrease the volume of the mesh of the filter layer and as a result, the cross-section through which the water passes decreases and the velocity of the water increases. Adsorption is one of the most important processes in the removal of the colloids and the small suspended particles. The adsorption forces are affective for very small distances like maximum 0.01-1 μm; whereas the thickness of the film layer wrapping the clay particles is much greater than this distance. In case this point is taken into consideration, it could be thought that adsorption would not play any role in the catching of the particles; however, the fact is not so. The particles in the water which are present by the removal mechanisms and which help the adsorption process, are approached to the clay particles constituting the filter material, hence the distance is decreased and the particles are held. The transport mechanisms can be classified as overlapping, inertia, gravity, and diffusion and hydrodynamic affects. Certain reactions take place during the filtration process; hence, the dissolved contaminative matters decompose, convert either to less hazardous components or to under compressable components and move away from the water by sedimentation and adsorption. The microorganisms living in and on the clay soil layer show biological activity. A certain amount of the nutrients in the water are consumed in order to provide the energy required for the life of these microorganisms and for their growth. A certain amount of these microorganisms are kept on the surface of the clay particles by filtration, sedimentation and adsorption.

**Discussion.** The coefficient of permeability decreases during this study as a result of suspended materials in the leachate fill the spaces between the particles of the clay and the growth of microorganisms inside the soil pores caused pore clogging is observed. In general, microorganisms groups were effectively treated in the system and high removal rates for microorganisms in the effluent were reached comparing to influent concentration. Especially high removal rates of total coliforms, total fecal coliforms and fecal streptococci were reached in the effluents of the reactors. These high microbiological removal rates were obtained after the leachate were filtered through clay material. It can be stated that clay can be used effectively for the treatment of microorganisms including eukaryotic and prokaryotic species. Microorganisms are naturally adsorbed on the soil because of negatively charged clay materials which have high mechanical removal rate (adsorption) for positively charged microorganisms. Also in the system, variety of microorganisms were controlled and some species were eliminated and some species were dominated in the acclimation period of the microorganisms because of the wastewater characterization and the reactors’ operating conditions. This fact is supported by the fact that some species of microorganisms especially those that are positively charged species have been hold while negatively charged species were passed through from the clayed filtration system. Some other parameters also affect the removal rate of microorganisms by adsorption mechanism of clayey soil such as, species of microorganisms, cell wall and capsule characteristics, cell shape and type, cell organelles, soil texture, structure and characteristics. This is one of the reasons for fungi and other total heterotrophic bacteria numbers. There are also some reluctant escapes from the reactor which have been detected in higher concentrations compared to total coliforms, total fecal coliforms and fecal streptococci concentrations. In this study, test results and observations indicated that clay has a natural treatment capacity.

![FIGURE 10 SEM images](image-url)

(a) Clean Clay Standard Compaction, water content 25 % (opt.); (b) Contaminated clay Standard Compaction, Water Content 25 % (opt.); (c) Clean Clay Modified Compaction, Water Content 18 % (opt.); (d) Contaminated Clay Modified Compaction, Water Content 18 % (opt.).
CONCLUSION

In this study, high removal efficiencies have been obtained in the microbiological parameters after leachate passes through clay samples and it has been observed that the clay has a natural purification capacity. As a result of the permeability tests performed with the leachate and of the electron microscope, due to the structural deterioration, variations in the permeability of the clay specimen contaminated with leachate has been observed.

These variations have shown that permeability has decreased to a certain extent. It has been observed that the suspended matter in the leachate filled the spaces between the clay particles and the growth of microorganisms inside the soil pores caused pore clogging led to the permeability to decrease. In the long term, it can be seen that this variation would take place in the reverse direction, in other words the permeability would increase. It is considered that this variation would be the result of the certain chemical and physical deteriorations produced by the contaminative components in the leachate.

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REMOVAL OF IRON IN THE PRESENCE OF HUMIC ACID, SULPHATE AND NITRATE FROM DRINKING WATER BY ATMOSPHERIC OXYGEN

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ABSTRACT

Iron which is among the most common heavy metals in water supply can be a nuisance despite it is non-hazardous elements. Because ferrous iron in the water sources reacts with air causing turbidity and turns reddish-brown color and it cannot be used as drinking water according to TSE (Turkish Standards Institute) legislations. Ferrous iron concentrations in the ground waters and some surface waters which are used as drinking water sources in Turkey exceed the limit values recommended by EPA (Environmental Protection Agency) legislations. Also iron in waters causes stains in the fabrics and accumulates on pipe walls which cause head loss.

The aim of this paper is to establish the effects of inorganic and organic substances which are chosen as the humic acid and SO42−, NO32− ions on the oxidation of low concentration of Fe2+ with atmospheric oxygen by using synthetic water.

For this purpose, first the calibration curve was obtained from specific concentration of Fe2+ by using a spectrometer, then the oxidation of Fe2+ with atmospheric oxygen was investigated in batch reactor with and without organic and inorganic compounds. Experiments were conducted under the conditions of Fe2+:1mg/L, pH:6.7, temperature:25°C and alkalinity:2x10−2 eq/L.

The experimental results show that the oxidation rate of Fe2+ decreases in the presence of sulphate and nitrate. Humic acid increases the oxidation rate of Fe2+ in the beginning of the experiment, then decreases. The increase in the humic acid concentrations accelerates the oxidation rate.

KEYWORDS:
Ferrous iron, oxidation, organic material, sulphate, nitrate, humic acid.

INTRODUCTION

Iron is the fourth most abundant element by weight in the earth’s crust [1]. The chemistry of aqueous iron primarily involves the ferrous iron and ferric iron oxidation states and is of interest in water supplies and wastewaters. Consequently, the presence of iron is probably the most common water problem faced by consumers and water treatment professionals. Soluble ferrous iron is usually present in ground waters by contact with rocks and minerals, either in dissolved mineral form, Fe(II), or associated with various organic, mineral or chelating agents. Occasionally, iron pipes also may be a source of iron in water [2, 3]. Although iron does not present a health hazard, contrary to heavy metals, it brings unpleasantness of an aesthetic and organoleptic nature. Indeed, iron gives a rust color to water, which can stain plumbing and sanitary facilities or even food industry products [4]. For example, iron will cause reddish-brown staining of porcelain, dishes, utensils and even glassware. Similarly, clothing may become stained a brownish color; soaps and detergents do not remove these stains and the use of chlorine bleach and alkaline builders can actually intensify the stains [5]. Iron also gives a metallic taste to water, making it unpleasant for consumption; the taste of beverages, such as tea, may also be affected [6]. Additionally, iron deposits can build up in pipelines, tanks or water heaters and softeners, which reduce water flow rates by increasing pressure drops in the water distribution network. This problem is also associated to increased energy costs, like pumping water through constricted pipes or heating water with heating rods coated with iron minerals, but also to equipment cost when water supply or softening equipment must be replaced. Iron can also be at the origin of corrosion in drains and sewers due to the development of microorganisms, the ferrobacteries [4]. Additionally, when these die and slough off, this usually causes unpleasant odors and tastes. More generally, biofilms in iron pipelines are known to increase the iron(II) content in water [7].
High concentrations of iron are often associated with organic matter of natural origin in many natural aquatic systems. Previous investigators have indicated that the oxidation of ferrous iron is severely retarded in many natural waters which contain humic substances, including ground waters, surface waters, and municipal wastewaters [8,9]. When Ferrous iron (Fe(II)) meets with atmospheric oxygen, iron oxides occurs [10] and thus an autocatalytic effect is obtained with the help of iron oxides[11, 12]. But in the presence of humic acid, sulphate and nitrate, the formation of iron oxides were prevented by iron complexations with these substances [13]. To these respect, extensive studies of removing Fe(II) from drinking waters have been made, but the effect of sulphate (SO₄²⁻), nitrate(NO₃⁻) which reside in ground waters as minerals and humic acid on removal rate of Fe(II) have not been thoroughly investigated.

In this study, the effects of organic and inorganic substances which were chosen as the humic acid and SO₄²⁻, NO₃⁻ ions on the oxidation of low concentration of Fe(II) with atmospheric oxygen by using synthetic water were investigated. For that purpose, firstly calibration curve was obtained from specific concentration of Fe(II) by using a spectrometer, afterward the oxidation of Fe(II) with atmospheric oxygen was investigated in batch reactor with and without organic and inorganic compounds.

**MATERIALS AND METHODS**

**Materials.** Fe(II) stock solution was prepared by dissolving ferroammonium sulfate in 1 liter de-mineralized water containing 2 ml of concentrated H₂SO₄. Sulphate and nitrate were prepared with Na₂SO₄ and KNO₃ respectively. Also Aldhric humic acid was used for this study.

**Method.** The oxidation of Fe(II) was studied in batch reactors of 1,5 liters volume under the constant pH, 6.7, temperature, 25°C and O₂ concentration. The experimental set up is illustrated in Figure 1.

The reaction vessel was intensely mixed using Wise Stir Direct Driven Stirrer HS-50A model of mixer. NaHCO₃ was added into the distilled water in order to obtain a solution with an alkalinity equal to 2x10⁻² eq/L. The pH of the solution was controlled by adjusting the flow of CO₂ gas. The pH of the solution was measured by Schott Instruments Lab 850 type of pH meter with sensitivity of ± 0,001 pH unit. The dissolved oxygen levels were monitored using a WTW oxygen meter. Constant temperature was maintained by immersing the reaction vessel into the water bath.

The samples taken at pre-decided times as measured from the start of the experiments were transferred into the 25 mL flasks containing 1 mL of (1+4) H₂SO₄ (25% H₂SO₄ + 75% demineralized water). In the presence of high concentrations of Fe(III) 1,10 phenanthroline method as given by Tamura et.al. was followed [2]. In other cases the phenanthroline method as described in the standard methods was used [14]. T80 model UV/VIS spectrometer was used to determine Fe(II) and prepare a calibration curve and at 510 nm wavelength.

**FIGURE 1**
Experimental set up.

In this study, Fe(II) concentration was kept constant and choosen as 1 mg/L and the concentrations of sulphate, nitrate and humic acid were varied between 0.5-250 mg/L, 0.5-40 mg/L and 0.5-40 mg/L, respectively.

All experiments were repeated three times at least. In the same conditions, the results were generally found to be very close to each other. This shows that experimental conditions have been kept constant and the experiments are iterated. In the study, only one experiment was used for each set as a representative.

**RESULTS AND DISCUSSION**

All the experiments for this study were conducted under the conditions of Fe(II): 1 mg/L, pH: 6.7, temperature:25°C and alkalinity: 2x10⁻² eq/L.

**FIGURE 2**
Calibration curve for Fe(II)

**Determination of calibration curve.** In this study, since the concentration of Fe(II) was chosen
as 1 mg/L, the calibration curve for Fe(II) was plotted between the values 0.1 and 0.5 mg/L. The experiments were repeated three times to obtain the best fit and determination coefficient ($R^2$). The used calibration curve was given in Figure 2.

The Effect of Sulphate. Sulphate is one of the chosen compounds to show the effect of inorganic compounds on the oxidation rate of Fe(II). The results of the oxidation of Fe(II) were given in Figure 3. In these graphs, zero concentration of sulphate was marked as filled diamond to distinguish and compare with others easily.

Rate constants, $k$, were calculated from the slopes of the lines on arithmetical plots of Fe(II) and time. It is evident from Figure 3 that the Fe(II) oxidation in the presence of sulphate ions is in accordance with the first order kinetics. Rate constants were found as 0.0141 min$^{-1}$, 0.0103 min$^{-1}$ and 0.0118 min$^{-1}$ when concentrations of sulphate were 0 mg/L, 15 mg/L and 250 mg/L in the reactor respectively. Reaction time was calculated as 71 min in the absence of sulphate ions in the reactor. Whereas reaction times were increased up to about 93 min for the concentration of sulphate 15 mg/L and 84 min for the concentration of sulphate 250 mg/L. Also all of the rate constants and reaction times were given in Table 2. As it can be seen in Figure 3, adding sulphate into the solutions was decelerated the oxidation rate of Fe(II). When Fe(II) contact atmospheric oxygen, Fe(OH)$_3$ occures, thus the oxidation accelerates. But according to these results, existence of sulphate ions redoubles the solubility of Fe(II). Because formation of Fe(OH)$_3$ was prevented, the oxidation rate of Fe(II) slowed down. All of these results show that even though existence of sulphate was decreased the oxidation rate of Fe(II), this decrease was not a systematic decrement.

The Effect of Nitrate. Nitrate was chosen as a second compound to investigate the effect of inorganic compounds on oxidation of Fe(II) and the results which were obtained from the concentration mentioned before were given in Figure 4. In these graphs, zero concentration of nitrate ion was marked as filled diamond to distinguish and compare with others easily.

As it can be seen from Figure 4 and Table 2, nitrate ions prevented the oxidation of Fe(II) with atmospheric oxygen like sulphate ions did. When there was no nitrate ions, the rate constant and reaction time were found as 0.0128 min$^{-1}$ and 78 min. respectively. Whereas, if nitrate ions were added into the reactor, the rate constant was decreased to 0.0077 and reaction time was increased to about 129 min. with the maximum concentration of nitrate, 40 mg/L. When the effects of nitrate ions and sulphate ions were compared to each others, it was found that nitrate ions had more negative effect on oxidation rate of Fe(II) than sulphate ions and the decrease of the oxidation rate of Fe(II) was observed more clearly in the presence of nitrate ions rather than sulphate ions.
FIGURE 4
The effect of nitrate acids on Fe(II) oxidation ([Fe(II)]_o: 1 mg/l, pH: 6.7, temperature: 25°C, alkalinity: 2x10⁻² eq/L)

The Effect of Humic Acid. The final experiments were conducted to investigate the effect of an organic compounds on oxidation of Fe(II) with atmospheric oxygen and, humic acid was chosen for this investigation. The results of the effect of humic acid (HA) were given in Figure 5. In these graphs, zero concentration of HA was marked as filled diamond to distinguish and compare with others easily.

FIGURE 5
The effect of humic acid on Fe(II) oxidation ([Fe(II)]_o: 1 mg/l, pH: 6.7, temperature: 25°C, alkalinity: 2x10⁻² eq/L)

As it can be seen from Figure 5 and Table 2, the oxidation rate of Fe(II) was increased by adding humic acid up to 2 mg/L, but after this concentration,
the oxidation rate was decreased significantly. When there was no humic acid, the rate constant and reaction time were found as 0.0141 min\(^{-1}\) and 71 min. respectively. Whereas, if humic acid was added, the rate constant was decreased to 0.0045 and reaction time was increased to about 222 min. with the maximum concentration of nitrate, 15 mg/L.

In the absence of appreciable quantities of dissolved organic mater such as humic acid, Fe(II) was oxidized quite rapidly upon the introduction of oxygen to ferric iron which precipitate as Fe(OH)\(_3\) and is removed from the drinking water. If significant concentrations of humic acid were present, the complexation reaction with Fe(II) will compete with the oxygenation reaction [9, 15]. This consideration was confirmed with these results.

CONCLUSION

This study was proposed to find the effect of nitrate, sulphate and humic acid on the oxidation rate of Fe(II). Sulphate and nitrate ions were decreased the oxidation rate of Fe(II), but nitrate ions were more notable. It was found from the experiments which were made with humic acid that Fe(II) was capable of forming complexes with humic acid and as such, was resistant to oxidation even in the present dissolved oxygen. Thus in the present of humic acid was decreased the oxidation rate of Fe(II).

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NUTRIENT REMOVAL FROM HUMAN URINE BY CHEMICAL PRECIPITATION

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ABSTRACT

Several physico-chemical treatment methods such as membrane processes, air stripping, ion exchange, and electrochemical oxidation are addressed for the recovery of nutrients from source separated human urine, among them, chemical precipitation is a promising one since the nutrients are effectively transformed into solid phase which can directly be used as a fertilizer. Additionally, chemical precipitation for nutrient control using conventional precipitation agents such as iron, aluminum and calcium salts has been fully proven and commercially used treatment method for domestic and industrial wastewater. This method has also a potential to be used for separated human urine for nutrients, particularly phosphate removal. In the present study, the capabilities of conventional agents such as alum, ferric chloride and lime for the phosphate removal via chemical precipitation from human urine are experimentally investigated. Almost complete phosphorus removals were obtained at optimized operation conditions in the case of alum, ferric chloride and lime. All three precipitation agents yielded final phosphate concentrations less than 10 mgP/L.

KEYWORDS: Alum, Phosphate Precipitation, Ferric Iron, Human Urine, Calcium

INTRODUCTION

The sustainable development has encouraged reuse and recovery applications. Within this context one of the promising applications is recovery of the nutrients from domestic wastewaters. The studies concerning the utilization of domestic wastewater have found a common acceptance in Europe and in some other countries and considerable theoretical and practical work has been realized. The main approach is to segregate the domestic wastewaters at the source, namely in houses, into three flows as greywater (kitchen and washing), brownwater (faces) and yellowwater (human urine) [1-3]. Among them yellowwater or human urine is of prime importance because it contains majority of the nutrients as 75% of nitrogen and 50% of phosphorus of the total domestic flow.

Within the last two decades, considerable research has been devoted to recovery of nitrogen from human urine and a great spectrum of the methods such as struvite (MgNH4PO4·6H2O) precipitation, ion exchange, membrane process, freeze and thaw, distillation etc. has been tested [4-6]. Precipitation of nitrogen in the form of struvite seemed to be a favorable method due to its relative ease of application, high recovery efficiency, and direct use advantage of struvite as a slow release fertilizer [1, 3, 7-10]. Treatment and recovery of phosphate, however, is critical since phosphate is the limiting element to trigger the eutrophication process. Despite this fact, the studies specifically targeting phosphate removal and recovery from human urine are limited and mostly rely on struvite precipitation which removes phosphate together with ammonia [11]. On the other hand, there is a wide range of technologies to remove and recover the nutrients from domestic wastewaters including chemical precipitation, crystallization, ion exchange, and magnetic methods. Among these technologies, chemical precipitation and crystallization serve recovery of phosphates. Chemical precipitation is realized through the formation of sparingly soluble phosphate salts such as ferric calcium and aluminum phosphates. These applications have long been used under the name of tertiary treatment for phosphate control therefore there is a significant accumulation about phosphate treatment by chemical precipitation as far as the theory, design basis as well as operation are concerned. Application of these processes to human urine is expected to benefit from all these basic information and practice.

In the present study, application of conventional phosphate precipitation methods to human urine was experimentally investigated. Different forms of calcium phosphate, aluminum phosphate and ferric phosphate precipitation have been tested to find out optimized operation conditions and the best obtainable process performances.

MATERIALS AND METHODS

Samples. Human urine samples were separately collected using a waterless urinal from men’s toilet at Environmental Engineering Department building at Istanbul Technical University Campus. The urinal was connected to a 300 L storage tank
(polyethylene) placed on downstairs of the toilet by means of a pipe. This urinal was cleansed without using detergents. The collected samples were stored at least for 3 weeks to ensure complete hydrolysis of urea into ammonia. The characterization of the samples used in our experimental study is given in Table 1. The general character of the samples was consistent with the relevant literature [7–9, 12] and almost complete hydrolysis of urea was achieved.

**Experimental procedure.** Precipitation experiments were performed using Jar-Test apparatus with 5 minutes flash-mixing at 100 rpm, 30 minutes slow mixing at 30 rpm and 30 minutes settling sequence in 500 mL sample volume. During all precipitation experiments, chemical additions and initial pH adjustments (using NaOH or HCl) were made under flash-mixing conditions. All experiments were run in a temperature controlled laboratory room section (at 23±0.1°C). Al₂(SO₄)₃·18H₂O (alum), FeCl₃·6H₂O, CaCl₂·2H₂O, and Ca(OH)₂ were used as precipitation agents.

The analyses were made on filtered samples. Millipore membrane filters with a pore size of 0.45 μm were used for this purpose. pH measurements were made with Thermo Orion 920A pH meter. All chemicals used were analytical grade. All analyses were performed as defined in the Standard Methods [13].

**RESULTS AND DISCUSSION**

**Precipitation with calcium salts.** Precipitation with calcium salts was realized using both lime (Ca(OH)₂) and calcium chloride (CaCl₂·2H₂O) [14]. In these experiments, calcium was dosed at three different Ca:P ratios of 1:1, 3:2 and 5:3 (on the molar basis) corresponding to formation of CaHPO₄, Ca₃(PO₄)₂, and Ca₅(PO₄)₃OH solid phases, respectively. Table 2 shows the results obtained from these precipitation experiments using calcium salts at original pH of the Sample I.

Phosphate removal efficiencies were very low and limited to 13 % when precipitation performed using lime at the original pH of the sample. In the first instance, this insufficient process performance was attributed to dissolution problem of lime since the measured sludge concentrations were close to the lime added. To overcome this difficulty lime was replaced with calcium chloride being a soluble calcium salts. Similar phosphate abatement performances as well as sludge productions were also obtained in this case as can be seen from Table 2. Therefore, it was decided that this was not a dissolution problem of lime and performing precipitation experiment at elevated pH values could result in higher phosphate abatements than those of original pH values. In the experiment carried out using calcium chloride (on the molar basis of Ca:P/3:2) at pH 11.10, phosphate was reduced to 180 mg P/L corresponding to about 43 % of removal efficiency (shown in Table 3). In this experiment, pH was adjusted to 11.1 with NaOH solution. On the other hand, when pH adjustment was made with lime, almost complete phosphate abatements were achieved at pH values higher than 10.5 as shown in Table 3. In this application high lime requirement as well as high amount of sludge production are likely due to carbon dioxide absorption of the urine during hydrolysis.

**TABLE 1**

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<th>Parameter</th>
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D.L: Detection limit

**TABLE 2**

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<td>279</td>
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<tr>
<td>Mg</td>
<td>mg/L</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>K</td>
<td>mg/L</td>
<td>1718</td>
<td>1728</td>
<td>1695</td>
<td>1747</td>
<td>1530</td>
<td>1716</td>
</tr>
<tr>
<td>Sludge</td>
<td>mg TSS/L</td>
<td>1245</td>
<td>1840</td>
<td>2075</td>
<td>1710</td>
<td>1840</td>
<td>1880</td>
</tr>
</tbody>
</table>
TABLE 3
Calcium phosphate precipitation at elevated pH values (Sample I)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Initial</th>
<th>pH = 10.02</th>
<th>pH = 10.50</th>
<th>pH = 10.96</th>
<th>pH = 11.10*</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃-N</td>
<td>mg N/L</td>
<td>7000</td>
<td>6435</td>
<td>6630</td>
<td>5840</td>
<td>6410</td>
</tr>
<tr>
<td>PO₄-P</td>
<td>mg P/L</td>
<td>312</td>
<td>126</td>
<td>12.5</td>
<td>7.5</td>
<td>180</td>
</tr>
<tr>
<td>Mg</td>
<td>mg/L</td>
<td>12</td>
<td>9.6</td>
<td>9.6</td>
<td>48</td>
<td>16</td>
</tr>
<tr>
<td>K</td>
<td>mg/L</td>
<td>2279</td>
<td>1576</td>
<td>1542</td>
<td>1551</td>
<td>1535</td>
</tr>
<tr>
<td>Sludge</td>
<td>g TSS/L</td>
<td>-</td>
<td>20.6</td>
<td>26.6</td>
<td>28.9</td>
<td>2.1</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>g/L</td>
<td>-</td>
<td>15.3</td>
<td>19.4</td>
<td>20.1</td>
<td>2.2*</td>
</tr>
</tbody>
</table>

*using CaCl₂·2H₂O; ** dosage

TABLE 4
Precipitation with alum (Sample I)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Al:P/1 mole:1 mole</th>
<th>Al:P/1.3 mole:1 mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH*</td>
<td>-</td>
<td>4.0</td>
<td>4.5</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>mg N/L</td>
<td>6840</td>
<td>6835</td>
</tr>
<tr>
<td>PO₄-P</td>
<td>mg P/L</td>
<td>44</td>
<td>27</td>
</tr>
<tr>
<td>Ca</td>
<td>mg/L</td>
<td>17</td>
<td>32</td>
</tr>
<tr>
<td>Mg</td>
<td>mg/L</td>
<td>11</td>
<td>&lt;D.L</td>
</tr>
<tr>
<td>K</td>
<td>mg/L</td>
<td>1516</td>
<td>1542</td>
</tr>
<tr>
<td>Sludge</td>
<td>g TSS/L</td>
<td>2175</td>
<td>2000</td>
</tr>
</tbody>
</table>

*precipitation pH

TABLE 5
Precipitation with FeCl₃ (Sample I)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Fe:P/1 mole:1 mole</th>
<th>Fe:P/2.5 mole:1 mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH*</td>
<td>4.5</td>
<td>5.0</td>
<td>6.0</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>mg N/L</td>
<td>6200</td>
<td>6395</td>
</tr>
<tr>
<td>PO₄-P</td>
<td>mg P/L</td>
<td>46</td>
<td>45</td>
</tr>
<tr>
<td>Ca</td>
<td>mg/L</td>
<td>17</td>
<td>25</td>
</tr>
<tr>
<td>Mg</td>
<td>mg/L</td>
<td>&lt;D.L</td>
<td>&lt;D.L</td>
</tr>
<tr>
<td>Sludge</td>
<td>g TSS/L</td>
<td>2395</td>
<td>2390</td>
</tr>
</tbody>
</table>

*precipitation pH

Precipitation with alum. By applying alum, phosphate is removed via either precipitation of insoluble metal phosphate solid phases, or adsorption and/or entrapment of the phosphate on freshly produced aluminum hydroxide flocs depending on precipitation pH [14-16]. Beyond neutral pH values, mechanisms of adsorption and/or entrapment on freshly generated Al(OH)₃ flocs are responsible for phosphate removal [15]. Therefore, precipitation with alum was realized at acidic and near neutral pH values to ensure formation of AlPO₄ phases at stoichiometric and 30% excess aluminum doses. As shown in Table 4, the lowest remaining phosphate concentration corresponding to a removal efficiency of 91% was achieved at pH of 4.0 for stoichiometric aluminum dose. An increase of 30% in aluminum dose improved phosphate abatement efficiencies and the lowest remaining phosphate concentration was obtained as 9 mg P/L at pH 5.0. The results indicated that there were optimum pH values to obtain minimum solubilities for both aluminum doses tested. Beyond these optimum pH values, the remaining phosphate concentrations increased with increasing pH values. The highest remaining phosphate concentration was measured as 107 mg P/L in the effluent obtained from the precipitation run at pH 7.5. This deterioration in phosphate abatement can be attributed to change in the removal mechanism. At lower pH values than 7.5 the phosphate removal mechanism seems to be precipitation of insoluble AlPO₄. On the other hand, adsorption and/or entrapment on freshly generated Al(OH)₃ flocs which required excess alum doses to reach high process efficiency, begins to dominate at pH 7.5.

Precipitation with FeCl₃. Depending on ferric iron dosage, phosphate is precipitated as either FePO₄ or Fe₂.₅PO₄(OH)₄.₅ at slightly acidic pH conditions [14, 17]. Therefore, two ferric iron dosages of 1:1 and 2.5:1(Fe/P; in molar basis) corresponding to FePO₄ or Fe₂.₅PO₄(OH)₄.₅, respectively were applied to Sample I. As shown in Table 5, the stoichiometric dose of 1:1 yielded almost equal phosphate concentrations corresponding to 85% abatement at pH 4.5 and 5.0 seemed to be optimum values. On the other hand, as optimum pH values were shifted to 6.0 and 6.5, the remaining phosphate concentrations were minimum in the case of the dose of 2.5:1. Together with these highest abatement efficiencies (up to 98%), sludge generation was proportional to dose of ferric iron. Comparison of Table 4 and 5 indicated that usage of alum and ferric chloride exhibited similar process performance.
Calcium phosphate precipitation without a need of pH change did not prove to be efficient by any degree partly as expected, since calcium phosphates, particularly hydroxyapatite requires a higher pH for effective phosphate removal. As the pH reached 11 however, the best effluent quality of 7.5 mg P/L obtained with this method. Phosphate precipitation using alum and ferric chloride has optimum pH between 4.0 and 6.0, flocculation of aluminium is also between 6.0 and 8.0 [18, 19]. Their excess is generally useful to enhance process performance through varying stoichiometric of precipitating salts as well as formation of flocculation aids such as Al(OH)₃(amorphous). The results obtained by use of alum and ferric chloride fit well to this picture. For the aluminum, optimum pH was determined as 5.0 with AL/P of 1.3/1 mole ratio. Ferric iron precipitation yielded optimum results at pH 6.0 with Fe/P:2.5/1 molar ratio. The performances of these three methods were very close to one another and they were all satisfactory particularly as they are compared to the struvite precipitation which yields at least several times higher effluent phosphate concentrations [8, 9, 12]. Therefore, these all three precipitation methods being all simple economical and easy to apply proved to be viable for the control and recovery of phosphate from urine.

CONCLUSION

In the present study, phosphate removal from human urine was experimentally evaluated by using chemical precipitation. Conventional phosphate precipitation methods of calcium, aluminum and ferric iron precipitation were used. Precipitation applied to urea-hydrolyzed undiluted urine. Calcium phosphate precipitation worked at pH 11.0. Aluminum dose 30% excess of stoichiometric and pH 5 were the optimum conditions for aluminum phosphate precipitation. The best performance was obtained at Fe/P:2.5:1 dose on a molar basis and pH 6 for ferric iron. All three methods provided final phosphate concentrations less than 10 mgP/L. Phosphate control by chemical precipitation, a proven, cheap and easy-to-operate method, worked well for human urine which has a complex matrix as well as a high ionic strength. The method can be used for urine treatment after struvite precipitation or can be combined with an ammonia removal method such as ion exchange.

REFERENCES


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ECOLOGICAL STATUS ASSESSMENT USING DIATOM INDICES OF WATER ECOSYSTEMS IN GJIROKAstra, ALBANIA

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3Department of Sciences and Plant Technology, Agricultural University of Tirana, Tirana, Albania

ABSTRACT

Diatoms are an important part of microscopic algae that populate considerable water spaces. They reflect very well the natural qualities, geology, climate and physico-chemical conditions. Analyzing of diatoms as important indicators of water quality had also the advantage to compare the chemical parameters with the biological ones. The aim of this study was to evaluate two water ecosystems in the south part of Albania, Viroi lake and Drino river, using chemical parameters and biomonitoring based on diatoms population. Obtained results indicated that two ecosystems were in mesotrophic status according to measured average values of total phosphorus concentration in water. Also, in these two water ecosystems 78 species of diatoms (Bacillariophyceae) were identified, from which 7 belong to the order Centric diatoms (Centrales), whereas the rest belongs to the order Penate diatoms (Pennales). According to the saprobic classes, they vary from oligosaprob to β-mesosaprob in these two investigated water ecosystems. These results showed a good relationship between water quality assessment using chemical parameters and diatoms indices. Thus, biomonitoring by using diatoms indices can be an effective and useful tool for the evaluation of the ecological status of water ecosystems.

KEYWORDS:
Biomonitoring, Diatoms, Water ecosystems, Ecological status.

INTRODUCTION

Algae are the base of the food chain and essential to the life in the rivers and lakes. They can play a crucial role in the ability of an ecosystem to absorb nutrients and heavy metals. The most commonly group of freshwater algae is the group of diatoms [1]. Diatoms respond quickly to changes in environmental variables as light, moisture conditions, temperature, current velocity, salinity, pH, nutrients, thus are considered for assessment of general water quality, as well as acidification and eutrophication, climatic changes, both in neo and paleolimnological studies [2]. Diatoms are distributed throughout the world in nearly all types of aquatic systems and are one of the most important food resources in marine and freshwater ecosystems [3]. Diatom communities are a popular tool for monitoring environment conditions, past and present, and are commonly used in studies of water quality. Also using diatoms, we can evaluate historical pollution of water ecosystems [4]. Benthic diatom species composition responds directly to nutrients [5] and can be a more stable indicator of trophic state than measurements of nutrient concentrations [6]. To quantify water quality conditions, various indices have been calculated on the basis of nutrients and relative frequencies of the full range of diatoms species present, such as Trophic diatom index [7-8], the Saprobic index [9], Shannon Index (H') [10]. Diatoms have been used as indicators of rivers and lake pollution in Albania [3, 11-13] Some studies have been summarized by Kupe and Miho in 2006 [13]. Few data were available for Drino river, thus about 92 species were found in this river [14], but not relationship with environmental conditions were investigated. Thus, the objective of this study was to evaluate water quality in two water ecosystems by using chemical parameters as total phosphorus and bio assessment using diatom species.
MATERIALS AND METHODS

The study area. The monitoring activity was carried out in two water ecosystems in Gjirokastra district, in Viroi lake and Drino river. The two ecosystems join together because the lake's waters flow into the river. Viroi lake has a surface area of 17 ha. It has a NDUVWLFZDWHUVRXUFHFDOOHG³0RWKHURI9L URL´ZLWKDIORZRIP 3/second, and its yearly average temperature is 13-14°C [4, 15]. Drino river comes from the village called Delvinaq (in Greece) and is about 85 km long (Fig. 1).

Sample collection and preparation. Water samples for analysis were collected in two sampling stations in Viroi lake and four sampling stations in Drino river during the years 2011-2013. Samples were taken in 1.5 L plastic containers and transported in a cool box at a temperature of 4ºC. The water analyses were performed within 24h at the scientific laboratory of the Department of Agro-Environment and Ecology, Agricultural University of Tirana. Water samples were analyzed for total phosphorus using standard methods [16]. The biological investigation was based on a microscopic examination of diatom communities growing over stones, during June 2013. Algal material was collected from the surface of stones by scrubbing with a toothbrush and rinsing into a collected bottle with 4% formaldehyde [3, 12-13]. The cleaning of diatom frustules was done boiling the material, first with HClcc and then, after washing, boiling them again with H2SO4 cc, adding during the last procedure some crystals of KNO3, as described by Krammer et al. [17].

Microscopic slides were prepared using Naphrax (index 1.69) and were examined using the optic microscope. Diatoms were identified using standard literature. To get reliable 95%, more than 500 valves per slide were counted.

Data Analysis. The diversity index (H’) was calculated according [10] using following equation:

\[ H' = - \sum_{i=1}^{n} p_i \log_2 p_i \]

Where \( p_i \) is the frequency of each type to the entire population.

Trophic index (TI_DIA) and Saprobic index (SI) for the diatoms were calculated using the following formulas given by [8-9].

\[ TI_{DIA} = \frac{\sum_{i=1}^{n} TW_i G_i p_i}{\sum_{i=1}^{n} G_i p_i} \]

\[ SI = \frac{\sum_{i=1}^{n} S_i G_i p_i}{\sum_{i=1}^{n} G_i p_i} \]

Where \( TW_i \) is saprobic value of species \( i \) (varies from 1-5), \( G_i \) is the indicative weight that has any species determined by the frequency of distribution in different environments (varies from 1-3), \( p_i \) is the relative quantitative frequency of the species \( i \) (in %), \( n \) is the total number of numbered species.

According to Rott et al. [8], the classification of trophic classes of water samples was based on trophic index values and the concentration of total phosphor (Table 1). Saprobic classes of analyzed samples were determine based on saprobic values according to Rott et al. [9] (Table 2).

### TABLE 1
Relationship between trophic values, trophic classes and phosphorus concentration

<table>
<thead>
<tr>
<th>Trophic values</th>
<th>Trophic classes</th>
<th>Total phosphor (mg/l)</th>
<th>Average values</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤ 1,0</td>
<td>ultraoligotroph</td>
<td>&lt; 0,005</td>
<td></td>
</tr>
<tr>
<td>1,1 - 1,3</td>
<td>oligotroph</td>
<td>&lt; 0,010</td>
<td></td>
</tr>
<tr>
<td>1,4 - 1,5</td>
<td>oligo-mesotroph</td>
<td>0,010 - 0,020</td>
<td>0,015</td>
</tr>
<tr>
<td>1,6 - 1,8</td>
<td>mesotroph</td>
<td>&lt; 0,030</td>
<td></td>
</tr>
<tr>
<td>1,9 - 2,2</td>
<td>meso-eutroph</td>
<td>0,030 - 0,050</td>
<td>0,040</td>
</tr>
<tr>
<td>2,3 - 2,6</td>
<td>eutroph</td>
<td>0,030 - 0,100</td>
<td>0,065</td>
</tr>
<tr>
<td>2,7 - 3,1</td>
<td>eu-polytroph</td>
<td>&gt; 0,100</td>
<td></td>
</tr>
<tr>
<td>3,2 - 3,4</td>
<td>polytroph</td>
<td>0,250 - 0,650</td>
<td>0,550</td>
</tr>
<tr>
<td>&gt; 3,4</td>
<td>poly-hypertroph</td>
<td>&gt; 0,650</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 2
Relationship between saprobic values and saprobic classes

<table>
<thead>
<tr>
<th>Saprobic values</th>
<th>Saprobic classes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,0 - &lt;1,5</td>
<td>Oligosaprob</td>
</tr>
<tr>
<td>1,5 - &lt;1,8</td>
<td>Oligosaprob - β mesosaprob</td>
</tr>
<tr>
<td>1,8 - &lt;2,3</td>
<td>β mesosaprob</td>
</tr>
<tr>
<td>2,3 - &lt;2,7</td>
<td>β mesosaprob - α mesosaprob</td>
</tr>
<tr>
<td>2,7 - &lt;3,2</td>
<td>α mesosaprob</td>
</tr>
<tr>
<td>3,2 - &lt;3,5</td>
<td>α mesosaprob - polisaprob</td>
</tr>
<tr>
<td>3,5 - &lt;4,0</td>
<td>polisaprob</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

The obtained average values of total phosphorus in two water ecosystems varied from 0.003 mg/l in S1 (Drino river) to 0.07 mg/l in S3 (Drino river). These values compared with average values of total phosphorus according to Rott et al. [8], showed trophic classes that vary from ultraoligotroph in S1 to eutroph in S3. The station S1 is part of the river with clean waters while the station S3 have polluted waters due to the sewage discharge and human activities in this area. Compared to WFD (Water Framework Directive 2000/60/EC) [18], the waters of Drino river for average and maximal values of total phosphorus range from high to poor quality. Viroi lake have a moderate situation. The values of phosphorus showed a trophic classes from meso-eutroph in V1 to meso-eutroph in V2 (Table 3). The status of river waters differed from eutroph to mesotroph after the S3 station, when the waters of Viroi lake flow into the river and they join together and this status remain across the entire length of the river. This situation is also influenced from the tributaries of other rivers.

### Table 3

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Stations</th>
<th>TP mg/l ± SDerv</th>
<th>Trophic classes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>V1</td>
<td>0.026 ± 0.029</td>
<td>Mesotroph</td>
</tr>
<tr>
<td>2</td>
<td>V2</td>
<td>0.037 ± 0.049</td>
<td>Meso-eutroph</td>
</tr>
<tr>
<td>3</td>
<td>S1</td>
<td>0.003±0.004</td>
<td>Ultraoligotroph</td>
</tr>
<tr>
<td>4</td>
<td>S2</td>
<td>0.017±0.014</td>
<td>Oligo-mesotroph</td>
</tr>
<tr>
<td>5</td>
<td>S3</td>
<td>0.07±0.10</td>
<td>Eutroph</td>
</tr>
<tr>
<td>6</td>
<td>S4</td>
<td>0.017±0.011</td>
<td>Oligo-mesotroph</td>
</tr>
</tbody>
</table>

78 diatom species were present in Drino river and Viroi lake, from which 7 belong to the order Centric (Centrales), whereas the rest belongs to the order Penate diatoms (Pennales) (Table 4). Compare with the study of Gjini et. al. [14]; we have diversity in species and taxonomic varieties among which the most important are Cyclotella with 5 species, Cymbella with 10 species, Achnanthes 3, Amphora 3, Diatoma 4, Diploneis 3, Fragilaria 8, Gomphonema 7, Navicula 15 and Nitzschia with 8 species.

### Table 4

Diatoms species in sampling stations

<table>
<thead>
<tr>
<th>Species/stations</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>V1</th>
<th>V2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Centrales diatoms</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Asteromella formosa Hasall</td>
<td>0,2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclotella cyclopuncta</td>
<td>0,2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclotella delicata Hustedt</td>
<td>0,2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclotella meneghiniana Kützing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclotella ocellata Pantocsek</td>
<td>2,9</td>
<td>2,9</td>
<td>1,3</td>
<td>0,8</td>
<td>6,6</td>
<td>7,4</td>
</tr>
<tr>
<td>Cyclotella species (aff. quadrijuncte)</td>
<td>0,2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melosira varians Agardh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0,3</td>
</tr>
<tr>
<td><strong>Pennales diatoms</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Achnanthes bissolettiana</td>
<td>2,3</td>
<td>2,0</td>
<td>3,6</td>
<td>4,4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Achnanthes minutissima Kützing agg.</td>
<td>27,0</td>
<td>48,6</td>
<td>26,5</td>
<td>22,9</td>
<td>24,5</td>
<td></td>
</tr>
<tr>
<td>Achnanthes microcephala</td>
<td>0,2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amphipleura pelliculoides Kützing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amphora inariensis Krammer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0,2</td>
</tr>
<tr>
<td>Amphora pediculus (Kützing) Grunow</td>
<td>0,7</td>
<td>0,3</td>
<td>0,5</td>
<td>0,9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amphora poggenpohlii Krammer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0,2</td>
</tr>
<tr>
<td>Caloneis bacillum (Gronow) Cleve</td>
<td>0,2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cocconeis pediculus Ehrenberg</td>
<td>1,6</td>
<td>29,5</td>
<td>0,3</td>
<td>0,8</td>
<td>3,3</td>
<td></td>
</tr>
<tr>
<td>Cocconeis placentula Ehrenberg agg.</td>
<td>2,9</td>
<td>6,5</td>
<td>0,2</td>
<td>12,0</td>
<td>14,2</td>
<td></td>
</tr>
<tr>
<td>Cymbella affinis Kützing agg.</td>
<td>9,8</td>
<td>3,8</td>
<td>3,8</td>
<td>10,0</td>
<td>0,2</td>
<td></td>
</tr>
<tr>
<td>Cymbella amphicephala Naegeli</td>
<td>0,2</td>
<td></td>
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<tr>
<td>Cymbella aspera Ehrenberg</td>
<td>0,3</td>
<td>0,2</td>
<td>0,4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cymbella cymbiformis Agardh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0,4</td>
</tr>
<tr>
<td>Cymbella descrita (Husted) Krammer &amp; Lange-Bertalot</td>
<td>0,2</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Cymbella microcephala Gronow gr.</td>
<td>0,2</td>
<td>0,2</td>
<td></td>
<td></td>
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<tr>
<td>Cymbella minuta Hilde</td>
<td>0,7</td>
<td>0,2</td>
<td>2,6</td>
<td>1,1</td>
<td>2,2</td>
<td>0,2</td>
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<tr>
<td>Cymbella silestriaca Bleisch</td>
<td>0,7</td>
<td>0,2</td>
<td>0,3</td>
<td>0,4</td>
<td></td>
<td></td>
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<tr>
<td>Cymbella simulata Gregory</td>
<td>0,7</td>
<td>0,2</td>
<td>0,3</td>
<td>0,2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cymbella tumida (Brebissoni) Van Heurck</td>
<td></td>
<td></td>
<td>0,3</td>
<td>0,3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diatoma euharenbergii Kützing</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Diatoma mesodon (Ehrenberg) Kützing</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1,7</td>
</tr>
<tr>
<td>Diatoma moniliformis Kützing</td>
<td>2,6</td>
<td>1,5</td>
<td>0,2</td>
<td>0,2</td>
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<tr>
<td>Diatoma physcia Ehrenbergi</td>
<td>0,8</td>
<td>0,2</td>
<td>0,2</td>
<td>0,8</td>
<td>0,9</td>
<td>0,2</td>
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<tr>
<td>Diploneis pseudovalvis</td>
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<tr>
<td>Diploneis ovalis</td>
<td>0,3</td>
<td></td>
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<td>0,2</td>
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<td></td>
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<tr>
<td>Diploneis obtusifolia</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0,2</td>
<td></td>
</tr>
<tr>
<td>Denticula kuetzingi</td>
<td>0,2</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Fragilaria acus Kützing</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Fragilaria capucina var. capucina</td>
<td>5,6</td>
<td>0,2</td>
<td>1,7</td>
<td>2,2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fragilaria capucina var. gracilis</td>
<td>0,2</td>
<td>0,9</td>
<td>0,9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fragilaria capucina var. vanhorei (Kützing) Lange-Bertalot</td>
<td>1,3</td>
<td>0,2</td>
<td></td>
<td>0,2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The number of species varies from 30 in V2 (Virua) to 41 in S4 (Drino) and V1 (Virua). In general the two water ecosystems were rich in species but with the tendency to decrease the number in the polluted stations. Achnanthes minutissima which is considered as tolerant species [19] has been found in almost all stations. The higher percentage was in S2 station with 48.6%. This species was absent in S3 station, due to the high pollution of waters. A. minutissima is characteristic species for clean waters and with scarce nutrients. It is often accompanied with Cocconeis pediculus (29.5 % in S2), Gomphonema tergesinum, Frugilariula capucina etc.

TABLE 5
Some indexes of Diatoms in Drino river and Viroi lake

<table>
<thead>
<tr>
<th>Sampling stations</th>
<th>Number of species</th>
<th>Diversity index, H’</th>
<th>Trophic diatom index, TDiMA</th>
<th>Saprobiic index, SI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S1</td>
<td>S2</td>
<td>S3</td>
<td>S4</td>
</tr>
<tr>
<td></td>
<td>39</td>
<td>40</td>
<td>37</td>
<td>41</td>
</tr>
<tr>
<td>Number of species</td>
<td>2.77</td>
<td>1.68</td>
<td>2.47</td>
<td>2.92</td>
</tr>
<tr>
<td>Diversity index, H’</td>
<td>1.4</td>
<td>2.1</td>
<td>3.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Trophic classes</td>
<td>Oligo-</td>
<td>Meso-</td>
<td>Eur-</td>
<td>Meso-</td>
</tr>
<tr>
<td></td>
<td>mesotroph</td>
<td>eutroph</td>
<td>polutroph</td>
<td>eutroph</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>1.9</td>
<td>1.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>
this species in S3 station was about 29.5 % and 33.6% in Viroi lake in V2 station. *N. palea* was accompanied with others saprotrophic or tolerant species, like *Navicula accomoda*, *Gomphonema parvulum*, *Navicula cryptotenella*, *Fragilaria ulna* etc. This station has also the high level of phosphorus classified as eutroph part of Drino river. In this station discharged not only the sewage outlet but also the wastes from the private activities occurring along the river. Diversity index have high values in V1, S1 and S4 stations about 3.58, 2.77 and 2.92 (Table 5). In S2 and S3 stations diversity index were in lower values respectively 1.68 and 2.47. The higher values of diversity index show more variation in species. [8-9].

Trophic diatom index, *TIDIA* varied from 1.4 in S1 to 3 in S3. The stations that have lower values of this index are S1 in Drino river and V1 in Viroi lake. High values of trophic index are reflection of high pollution, especially phosphates and nitrates. So the trophic classes differ from oligo-mesotroph in S1 to eu-politroph in S3 and V2. Saprobic index varied from 1.6 in S1 and V1 to 1.9 in S2. These values correspond with saprobic classes from oligosaprob to β mesosaprob. This classification showed that these ecosystems range from no polluted to moderate polluted.

**CONCLUSIONS**

The existence of biocorridor between Drino river and Viroi lake, determine the situation of trophic status and also the kind of microscopic algae. The waters flow in one direction, from lake into the river and not in the opposite was reflected in trophic status of these ecosystems. The trophic status of investigated ecosystems Drino river and Viroi lake based on chemical analysis were from ultraoligotroph to eutroph in Drino river and mainly mesotroph in Viroi lake. Diatoms are an important group of microscopic algae in water ecosystems and using them we can evaluate ecological status of ecosystems. This group has an advantage because they can be found in every water surface and at any time can be compared with chemical monitoring. Also, the biological analysis of water samples in these ecosystems indicated about the same eutrophic status. A good correlation was observed between assessment of trophic status based on chemical and biological water analysis. The found diatoms species in these water ecosystems were of a special composition. Thus, the species like *Nitzschia palea* var. *Palea* saprotroph specie was found with higher percentage in S3 and V2 stations, which were heavily polluted habitats with organic matter. *N. palea* was accompanied with others saprotrophic or tolerant species, like *Navicula accomoda*, *Gomphonema parvulum*, *Navicula cryptotenella*, *Fragilaria ulna* etc. In all sam-

**REFERENCES**


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THE EFFECTS OF MARINE TOURISM ON WATER POLLUTION

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ABSTRACT

The tourism sector, which is one of the largest sectors in the world, has a close relationship with the environment. When tourism creates negative effects on the environment, it also puts its own existence in danger. If it takes a responsibility that protects the environment and values environmental factors, it will also provide its own continuity. Especially, tourism types such as ecotourism, rural tourism and marine tourism have more interaction with the physical environment. Since antiquity, seas have become an important means of transportation in tourism and a natural attraction for tourism activities. In general, maritime tourism is a kind of tourism that will be attended by those who want to participate in maritime activities. In recent years, sea tourism, sea-sand-sun tourism, yachts, cruise ships, daily tour boats and tourism-oriented water sports began to develop. However, while this development of marine tourism creates positive economic, social and environmental effects, it also causes adverse effects in terms of water pollution. Especially unplanned tourist enterprises in the coastal areas, waste / refuse problems, marine vehicles' effects on the ecosystem lead to serious environmental problems.

In this study, the relationship between tourism and the environment will be examined and the environmental pollution created by marine tourism will be emphasized. The aim of the work is to bring sustainable maritime tourism proposals by demonstrating the impact of marine tourism on water pollution.

KEYWORDS:
Tourism, environment, marine tourism, water pollution

INTRODUCTION

Tourism product is a mixture of natural, cultural and social amenities that are presented to the taste of tourists as a result of evaluating the services and activities that stimulate the desire to consume and which will increase this desire [1]. In tourism, the product appears in two forms. First, all natural, historical and touristic resources that a country or region has a tourism product. The second is the whole of tourist services, which makes package tours that allow consumers to make their trips and vacations. [2]. Taking these expressions into account, it is understood that one of the most important components of the tourist product is the natural resources that a destination has. These natural resources include vegetation, wildlife, physical resources [3], seas, oceans and seas, rivers, lakes, water-based resources [4].

Marina tourism is all the activities that maritime and coastal regions do, including vacation or sightseeing that tourists participate actively or passively in their free time [5]. The region where sea tourism is most concentrated is seen as the Mediterranean. According to UN World Tourism Organization, the Mediterranean is the world's leading tourism destination in terms of both domestic and international tourism [6]. The region accepts more than 300 million international tourist arrivals representing 30% of total world tourism, and half of these arrivals are in coastal regions [7].

135 million tourists who visited the Mediterranean region in 1996 are expected to rise to 235-300 million per year over the next 20 years [8]. For this reason, the impact of marine tourism on the environment in the Mediterranean also manifests itself in this region. Environmental problems in the region, excessive water use, desertification, water pollution; erosion, crooked urbanization, loss of biodiversity and deterioration of coastal areas; pollution from transportation; urban waste growth; and a decrease in biodiversity [9].

In particular, Egypt, Croatia, Cyprus, Libya, Malta, Serbia, Montenegro, Syria, Turkey, Bosnia and Herzegovina and Tunisia, Spain, Morocco, Monaco Italy have problems such as population growth, urban waste, concrete pollution, water pollution. For this reason, in the Mediterranean region, the effects of marine tourism on water pollution will be presented and recommendations on the subject will be presented.
MATERIALS AND METHODS

Literature studies have been carried out to determine the environmental issues related to marine tourism, Google Scholar, Web of Science and Science Direct, search engines are used in this study. The first researches were conducted using key words such as tourism, environmental pollution, marine pollution, water pollution, sustainable tourism, marine tourism, marine ecotourism, coastal tourism, Mediterranean, marine wildlife tourism, cruise tourism, and combinations of these words. This preliminary study yielded a lot of results, the publication summaries were read and the publications concentrated on the direct research topic.

RESULTS AND DISCUSSION

Marine Tourism. According to Orams (1999: 9), marine tourism is a type of tourism that encompasses recreational activities (which define the marine environment as salty and tidal waters) that house the marine environment or focus on the marine environment [10]. This can be described as a whole consisting of marine tourism, cruise tourism, yacht management, yacht harbor management, daily boat tours, recreational extreme water and underwater activities, and diving sports [11].

In Europe (European Commission, 2014), coastal and marine tourism is estimated to be the largest maritime activity, employing approximately 3.2 million people and representing over one third (1/3) of the maritime European economy. At the same time, more than four out of nine (4/9) nights spent in accommodation facilities in E.U. countries are spent within coastal municipalities. Similarly, cruise tourism employed 330,000 people in 2012 and generated a direct turnover of V 15.5 billion. The same year, European ports had 29.3 million passenger visits, recording a 75% increase compared to 2006 [12]. In Europe where more than 6 million technicians are involved, there are 4,500 marinas and 1.75 million yachting capacity [13].

The Effects of Marine Tourism on Water Pollution. Among the different impacts of marine tourism on the environment, the effect of tourism on public health has importance. Tourism development can put pressure on natural resources when it increases consumption in areas where resources are already scarce. Water, and especially fresh water, is one of the most important natural resources. The large increase in population during the high season results usually for the sea is polluted, causing serious problems. Numerous sewage outfalls associated with rapid tourism development affect coastal water quality. The accommodation facilities discharging the generated wastewater into the sea without any treatment, the summer resorts of the coastal areas also deteriorate the coastal waters. Since most of the summer resorts do not have any sewage system, it is difficult to control these non-point sources. The tourism industry generally overuses water resources for hotels, swimming pools, golf courses and personal use of water by tourists. This can result in water shortages and degradation of water supplies, as well as generating a greater volume of waste water. The water pollution problem in the sea is also harmful to the tourists. The people especially at risk of getting infections as a result of being exposed to the polluted water. Ingesting the water may also result in stomach aches and diarrhea, among other health problems.

One of the biggest problems threatening the coastline of the Mediterranean region is the problems caused by concrete. Uncontrolled development, especially in tourism infrastructure, is irreparably changing the natural structure of the Mediterranean coastline. The pressure that creates the ever-increasing population in the region is increasing with tourism. The Mediterranean attracts many tourists thanks to its mild climate and natural and historical heritage. About one third of the world's tourists thanks to its mild climate and natural and historical heritage. About one third of the world's tourists is traveling to the Mediterranean. Tourism is traveling to the Mediterranean. Tourism development can put pressure on natural resources. The large number of tourists has often have negative consequences for the sustainable use of the available resources, which in turn has had an effect on the integrity of the ecosystems. Tourism in the area has grown rapidly in recent years and is expected to further increase in the future. This development is put additional pressure on the resources of the marine coast, which show already signs of over-use. The consequences of overexploitation can include the lowering of the groundwater table, land subsidence, deteriorating groundwater quality, and saltwater intrusion. These, in turn, determine the living conditions in coastal areas and the effects will be felt both by the local populations and the tourist industry.

Marine tourism is an important tourism issue due to the fact that it is a type of tourism related to the environment. Sea tourism, which needs a natural environment for its formation, also has negative effects on the environment. These effects can be listed as follows [14].

- Damage to the underwater coral
- The garbage problem
- Damage to marine ecosystem by construction of marine and other water-based structures (breakwater, pier, etc.)
- Harming / hunting animals
• Damages caused by the hulls of the vessels on the sea bed
• Exposure of live fish to physical stress
• Biological effects of environmental pollutants
• Details of broken pieces, parts of surf boards and other equipment
• The use of technology during fishing causes negative effects being
• Damage to marine life of boat propellers
• pollution / degradation caused by the construction of the coastal areas

Environmental Problems Due to Marine Tourism in the Mediterranean. Mediterranean Region World can be expressed as the center of tourism. The most popular coastal destinations generally Mediterranean coastline. However, due to touristic concentration, it is also one of the most destructed areas of nature. The large coastal areas in this region have been urbanized due to tourism activities. As a result, there have been major changes in nature. In particular, seals and sea turtles in coastal areas are destined to disappear in this area due to the construction of living environments. One of the biggest problems threatening the coastline of the Mediterranean region is the problems caused by concrete. Uncontrolled development, especially in tourism infrastructure, is irreparably changing the natural structure of the Mediterranean coastline. The pressure that creates the ever-increasing population in the region is increasing with tourism. The Mediterranean attracts many tourists thanks to its mild climate and natural and historical heritage. About one third of the world's tourism is traveling to the Mediterranean. Tourism concentrates seasonally on the coastal areas, especially in the northwest coastal areas.

According to the UN World Tourism Organization (UNWTO), the Mediterranean is the world’s leading tourism destination, in terms of domestic and international tourism. This situation leads to the intensification of time and space. For this reason, the destruction in coastal areas is very high. The large increase in population during the high season results usually in an increase in the amount of waste water produced [6].

International tourist arrivals have grown from 58 million in 1970 to nearly 314 million in 2014. The number of 35 million tourist visited the Mediterranean region in 1996, with a forecasted of 500 million by 2030 [7]. Of the 637 million international tourist arrivals worldwide in 1998, over 197 million (almost one third) visited Mediterranean region [15]. According to this, Coastal tourism is the largest sea-related economic activity in the Mediterranean, with 11.3 of the regional GDP. It is evident therefore that tourism represents an important source of revenues and employment in the Mediterranean area. At the same time it implicates enormous negative impacts for nature and society [7]. One of the environmental impacts of tourism is water pollution. Water pollution has continuously increase. In particular, the amount of wastewater from tourism increases year by year. The mixing of the wastewater into the sea disrupts both the sea and the natural equilibrium.

Coastal areas often host unique ecosystems in deltas estuaries and lagoons, where birds, fish and other aquatic and terrestrial species dwell and breed. More than 50% of the 25,000 plant species in the Mediterranean are endemic to the region [8]. Mediterranean wetlands are also critical areas for migratory birds: it is estimated that about 2 billion migratory birds of 150 species use the Mediterranean wetlands as seasonal sites or as a stopover before crossing the sea or the Sahara Desert in their Africa-Palearctic flyway [8]. Particularly countries such as Egypt, Croatia, Cyprus, Libya, Malta, Serbia and Montenegro, Syria, Turkey, Bosnia and Herzegovina and Tunisian, Spain, Morocco, Monaco, Italy, have serious environmental problems such as population increase, urban waste, concrete pollution and water pollution due to tourism. In areas where sea tourism is not well managed and concentrated, exotic species are decreasing or disappearing, harmful algal blooms, ecosystem changes, and so on. This situation also causes serious health problems in humans. In particularly, Health problems such as infections of the ear, nose and throat, hepatitis and dysentery can result from swimming in polluted sea waters.

CONCLUSION

The data obtained in the study shows that marine tourism is (including cruise tourism, yacht operation, daily boat tours, leisure-oriented extreme water and underwater activities, and even diving sports, including coastal tourism) especially concentrated in the Mediterranean coast and develops.

Specially with the development of technology, environmental pressures are increasing in these regions due to factors such as the construction of bigger cruise ships, the construction of bigger marinas, the increasing number of tourists in these regions, the opening of numerous accommodation and entertainment establishments and the increase of the number of summer resorts. Contamination of marine waters due to wastes from boats, vessels, businesses and people left by people is polluting sea waters, thus affecting marine life and human health negatively. Concentration of tourists in certain destinations, however, causes distorted urbanization, deterioration and pollution of nature. The following suggestions can be presented to remove all these negative effects or to download the most auctions.
First of all, it is necessary to analyze the environmental problems that marine tourism has emerged correctly.

Determination of applicable sustainable marine tourism policies compatible with other types of tourism and development

Making spatial arrangements especially on the coastline

Increase and encourage recycling practices

For increasing environmental awareness, new integrated projects must be created and these projects should be supported by national administrations.

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ENVIRONMENTAL POLLUTION OF THE MEDITERRANEAN SEA: EVALUATION OF RESEARCH ACTIVITIES IN THE MEDITERRANEAN SEA COUNTRIES

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ABSTRACT

The Mediterranean Sea (Med-Sea) is home to 21 countries on three continents. Sustainable management of environmental issues in the Med-Sea countries has become more crucial as the population of those countries bordering the Med-Sea reached around 500 million in 2016, which increases the pressure on environment. This study is aimed to evaluate scientific publications related to major environmental problems of the Med-Sea countries. For this purpose, a bibliometric analysis was carried out and a set of 17 keywords referring to major environmental problems of the Med-Sea countries was chosen and searched in the Web of Science (WoS) core collection database, and Scopus database between 1970 and 2016. The bibliometric analysis is aimed to provide a quantitative analysis of publications using mathematical and/or statistical methods. In this study, publications from each country were identified by the country of the affiliation of at least one author of publication and numbers of publications were used as the indicator of scientific contribution for each country. The study showed that there is an increasing trend in numbers of publications starting from 2000 due to increasing environmental awareness. France, Spain, Italy, Turkey and Greece are the five most productive countries considering the numbers of publications retrieved from WoS and Scopus databases using the selected keywords referring to major environmental problems of the Med-Sea countries.

KEYWORDS:
Bibliometric analysis, environmental pollution, Mediterranean Sea, research activities, water quality, urban effluents.

INTRODUCTION

The Mediterranean Sea (Med-Sea), which is the largest semi-enclosed European sea, is bordered by 21 countries, given in Figure 1, located on three continents with a total population of around 500 million in 2016 [1,2]. 601 cities with a population of more than 10 thousand inhabitants were reported and 131 “pollution hot spots” were identified by those countries bordering the Med-Sea. [3, 4]. Furthermore, more than 100 million tourists visit Mediterranean beaches and cities each year [1]. Intensive human activities along the coastlines of the Med-Sea increase pressure on environment and results in degradation of marine environment. The Mediterranean Sea, as a home of very diverse habitats and rich biodiversity, has a highly stressed ecosystem which requires particular attention to protect the unique marine genetic resources. On the other hand, the Mediterranean is one of the most polluted sea environments in the world.

Each year, 650 million tons of sewage and a total of around 230 thousand tons of mineral oil, mercury, lead and phosphates are discharged to the Med-Sea, according to the United Nations Environment Program (UNEP). Preventing pollution is vital in the Med-Sea basin as the Med-Sea is a semi-enclosed sea with a retention time of around a century [5]. Therefore, renewing process of the Med-Sea takes around 100 years.

The major environmental problems along the coastline of the Med-Sea are urbanization, sewage and urban run-off, waste management, industrial effluents, marine transport, sand erosion and eutrophication [6,7]. Around one-third of the Med-Sea population lives in coastal regions whereas 65% of the population (around 120 million inhabitants) resides in coastal hydrological basins of the southern region of the Med-Sea, where environmental pressure is in an increasing trend [8]. Social, economic and environmental challenges have an increasing trend in Mediterranean basin due to uncontrolled and rapid urbanization. Around 70% of coastal cities with a population of more than 10 thousand in the region operate wastewater treatment plants. However, the efficiency of the plants is rather low or inadequate and it leads to sewage pollution, as one of the major problems. Solid waste with minimal or no sanitary treatment is another problem in the region whereas many coastal regions along the Med-Sea are home to chemical and mining industries producing industrial wastes including heavy metals, persistent organic pollutants (POPs) that might reach the Med-Sea environment directly or indirectly [6]. Although the
Med-Sea is characterized with low nutrient levels, eutrophication in coastal and/or lagoon areas might be experienced due to untreated wastewater and/or runoff from agricultural areas [7]. Oil pollution caused by marine transport and oil-related sites along the coastlines is one of the main sources of polycyclic aromatic hydrocarbons (PAHs) and petroleum hydrocarbons [6,7]. The major environmental problems of the countries bordering the Med-Sea, based on the studies conducted by the European Environmental Agency, are summarized in Table 1 [6].

Over the years, many research activities related to environmental problems in the Mediterranean region have been conducted by many scientists [9-12]. Bibliometric analysis, which is defined as mathematical and/or statistical methods aimed to provide quantitative analysis of publications, have been performed for evaluation of publications covering a broad range of research fields such as water pollution, waste management etc. [13-16]. Bibliometric analyses of publications are performed by extracting and evaluating publications from databases such as Web of Science (WoS), Scopus and Google Scholar [17]. WoS core collection has coverage of more than 68 million records [18], whereas the database Scopus, launched in 2004, has over 69 million core records [19]. Detailed information about Scopus can be found in the literature [17,20,21].

Google Scholar is freely available to allow researchers locating literature on the Web [17]. Numerous studies have been conducted to compare WoS, Scopus and Google Scholar for assessing the number of citations from a set of documents in each of three databases [20,22,23]. General characteristics and coverage of WoS and Scopus have been studied by many researchers [24-27]. Bibliometric analysis has also been performed to analyze research trends, distribution patterns of publication on a topic, research field and/or country [28]. Bibliometric analyses have many advantages for evaluation of research trends, results, citations etc. However, bibliometric analyses have also some limitations. Bibliometric analysis can only be performed for research fields that literature and citations can be retrieved from appropriate databases [29]. Local journals are rarely covered in WoS and Scopus databases and citations do not always represent the quality. However, all major journals are indexed by WoS and Scopus databases [30].

The main aim of this study is to evaluate research activities related to major environmental problems of the Med-Sea countries. In order to reach this aim, major environmental problems that directly and/or indirectly cause the pollution of the Mediterranean Sea are introduced and scientific responses of the Med-Sea countries against those environmental problems are examined.

**METHODOLOGY**

Scientific publications are considered as an indicator for evaluation of scientific responses on major environmental problems of the Med-Sea countries. Major environmental problems of the Med-Sea countries are summarized in Table 1 [6]. For this purpose, a bibliometric analysis, based on scientific publications between 1970 and 2016, was conducted using Web of Science (WoS) and Scopus databases for evaluation of scientific responses of the Med-Sea countries. The topic search, which can trace related information in the title, abstract, and keywords at once, was used to search publications in the WoS database whereas the selected keywords were used to search in the title, abstract and keywords in the Scopus database.

The most related keywords to major environmental problems of the Med-Sea countries were chosen to retrieve publications from each country. The keywords that are to find related publications are the “Mediterranean Sea”; “water management”; “water quality”; “water treatment”; “wastewater”; “water pollution”; “wastewater treatment”; “ballast water”; “solid waste”; “waste management”; “environmental pollution”; “eutrophication”; “ecological risk”;
RESULTS

Distribution of document types for scientific responses of the Med-Sea countries for each keyword was analyzed by the WoS and Scopus. Between 1970 and 2016, article was the most frequent publication type for all keywords and followed by proceedings papers, reviews, editorial material, meeting abstract and others including news item, letters etc. Scientific responses of each country for major environmental problems represented by the most related keyword were identified. The contribution of each country was identified by the country of the affiliation of at least one author of publication.

A summary of findings retrieved from both WoS and Scopus databases is given in Table 2. The keyword “Mediterranean Sea” has 18773 records in WoS database and 93.5% of publications were published by scientists from the Med-Sea countries whereas Scopus has 30578 records for keyword “Mediterranean Sea” and 97.9% of those publications were published by the scientists from the Med-Sea countries. As a general comparison of both databases for the selected keywords, Scopus database has more records than WoS database. Total number of publications for each country retrieved from both Scopus and WoS databases are compared in Figure 2.

Urban solid waste management is one of the major environmental problems especially for the southern Med-Sea countries. On the other hand, the most productive countries, considering the total numbers of publications retrieved from both Scopus and WoS databases using keywords “solid waste” and “waste management”, are Spain, Italy, France, Turkey and Greece where solid waste management is less important comparing to other Med-Sea countries. Although Scopus database has more records than WoS database, the most and the less productive countries for the selected keywords are same.

One of the common major environmental problems of the Med-Sea countries is resulted from urban effluents. Scientific publications of each country related to urban effluents were gathered from Scopus and WoS databases. The keywords “water treatment”, “wastewater”, “water pollution” and “wastewater treatment” are used to represent the scientific responses of each country. Spain, France, Italy, Turkey and Greece are the leading countries considering their number of publications as the indicator. The Med-Sea region is home to industrial and agricultural sites that directly and/or indirectly cause pollution. Furthermore, sea transport in the regions plays an important role. Therefore, polycyclic aromatic hydrocarbons (“PAHs”), “heavy metal”, persistent organic pollutants (“POPs”) and “pesticide” were used as keywords for evaluation of scientific responses of each country. Spain, France, Italy, Turkey and Greece are the five most scientific productive countries considering their number of publications.

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<th>Country</th>
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+: Highly important; +/-: Important; -: Less important
### Table 2
Numbers of publications between 1970 and 2016

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Nutrient levels are relatively low in the Mediterranean Sea. However, eutrophication of coastal areas and/or lagoons may be experienced due to urban, industrial and/or runoff from agricultural areas. Publications from each country using keywords “ecological risk”, “eutrophication” and “water quality” were retrieved from Scopus and WoS databases. The results showed that France, Spain, Italy, Turkey and Greece are the leading countries for given keywords.

Most of the publications retrieved from the selected keywords are in English. Trend analysis in numbers of publications showed that there is a great increase in numbers of the publications after 2000 that might be resulted from increasing attention to environmental issues, public awareness of sustainable development, and increasing demand for resources. For the selected keywords, France, Spain, Italy, Turkey and Greece are the most productive countries. Since countries Montenegro (2006), Bosnia and Herzegovina (1992), Croatia (1991) and Slovenia (1991) were recently established, numbers of the publications for the selected keywords are relatively few. On the other hand, numbers of publications are not evaluated for Libya and Syria due to current situations of these countries.

**CONCLUSIONS**

The major environmental problems and scientific responses to these problems of the Med-Sea countries were presented in this study. A bibliometric analysis was conducted using Scopus and WoS databases to evaluate the scientific responses of the Med-Sea countries. The most related keywords to major environmental problems of the Med-Sea countries were chosen to extract publications from both Scopus and WoS databases. For the selected keywords; 553823 records were retrieved from WoS database whereas 1225788 records were extracted from Scopus database.

The contribution of each country was identified by the country of the affiliation of at least one author of publication. As a result of increasing environmental awareness, there is an increasing trend in total number of publications starting from 2000. Spain, France, Italy, Turkey and Greece are the most productive countries considering the total number of publications for each keyword, respectively.

**ACKNOWLEDGEMENTS**

Authors acknowledge the support of Akdeniz University, Antalya, Turkey.

**REFERENCES**


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ENVIRONMENTAL ASPECTS AND COAL QUALITY PARAMETERS OF SOMA, KARAPINAR AND SAHINALI COALS IN TURKEY

Selin Karadirek*, Orhan Ozcelik, Mehmet Altunsoy

Akdeniz University, Department of Geological Engineering, Antalya, 07058, Turkey

ABSTRACT

Sustainable use of resources has become more crucial due to increasing global demand for energy. Coal’s share of total world energy supply has increased from 24.5% to 28.6% between 1973 and 2014, whereas the share of coal in electricity generation in Turkey was around 29% in 2015. Turkey has relatively rich lignite deposits. However, lignite deposits of Turkey have low calorific value, high contents of ash, and total sulphur and contain significant trace elements which pose adverse health and environmental affects during combustion of coal. Many health problems such as arsenism, fluorosis that are associated with coal combustion have been reported. Due to environmental and public health problems, cleaner coal technologies have attracted a worldwide attention.

Turkey has a total 15 gigaton lignite reserve and 8.5 gigaton of total lignite reserve is ready to be extracted. Western and Central part of Anatolia is home to important lignite fields. Soma-Eynez (Manisa), Sahinali (Aydın) and Karapinar (Konya) coal fields are some of those important lignite fields.

This study is aimed to evaluate the hazardous trace elements in Soma-Eynez (Manisa), Sahinali (Aydın) and Karapinar (Konya) coal fields. For this purpose, geological evolution, reserve, ultimate analysis parameters (C, H, O, N and S), proximate analysis parameters (sulphur, moisture, volatile matter, ash and fixed carbon) and trace elements of study areas were evaluated and the results were presented.

KEYWORDS:
Coal, coal quality parameters, environmental aspects, hazardous trace elements, sulphur.

INTRODUCTION

Coal is the most abundant fossil fuel and one of the most significant energy sources in many countries such as Turkey. The share of coal in electricity generation in Turkey was around 29% in 2015 [1]. Total lignite reserve of Turkey is around 15 gigaton and 8.5 gigaton of total lignite reserve is ready to be extracted [2]. In Turkey, approximately 68% of lignite/sub-bituminous coal reserves has lower calorific value (<2000 kcal/kg) whereas 23.5% has a calorific value of 2000-3000 kcal/kg and 8.5% of lignite/sub-bituminous coal reserves has a calorific value of higher than 3000 kcal/kg. It might be concluded that calorific values of Turkish lignite are relatively low. Although Turkey is one of the richest countries in terms of lignite reserves, Turkish lignite has high amount of sulphur, ash and trace elements content. Coal combustion leads air pollution that causes a variety of environmental and health problems. Carbon dioxide (CO₂), nitrogen oxides (NOₓ), particulate matter (PM) and sulphur dioxide (SO₂) are the main hazardous air pollutants associated with coal combustion. Furthermore, potentially hazardous trace elements such as arsenic (As), beryllium (Be), cadmium (Cd), chlorine (Cl), chromium (Cr), cobalt (Co), fluoride (F), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), thorium (Th) and uranium (U) are also released from coal combustion. Ash, particle material (PM), trace elements, SOₓ, NOₓ, CO₂ and inert carbon resulting from coal combustion affects environmental health in many ways [3,4]. Pollution effects of a coal-fired thermal power plant with a power of 100 megawatts are given in Table 1.

Geological locations of coals, inefficient production due to coal quality parameters and harmful effects of coal to the environment have caused the development of cleaner coal technologies. Coal gasification process is one of the cleaner coal technologies. Underground coal gasification (UCG) that minimizes air pollution is usually carried out in unmineable coal seams and/or coal reserves with lower calorific value [5, 6]. Gasification of lignite coals with lower calorific value and high amount of hazardous content seems to be viable option considering air pollution and raw material demand. Coal quality parameters (coal rank, ash content, sulphur, volatile material and moisture content, fixed carbon, calorific value, trace element content, ultimate analysis results, thickness and depth of coal seams) effect gasification process. Low ranked
coals and sub bituminous lignite should be used for UCG process, as underground gasification of high rank coals is difficult due to reactivity and low content of volatile material [7].

TABLE 1
Pollutant effects of a coal-fired power plant [3]

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>Emissions (tonnes/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>45000</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>26000</td>
</tr>
<tr>
<td>CO</td>
<td>750</td>
</tr>
<tr>
<td>PM</td>
<td>32500</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>250</td>
</tr>
<tr>
<td>Ash</td>
<td>5660</td>
</tr>
</tbody>
</table>

Sulphur in coal facilitates self-ignition of coal and it causes operational problems of coal. Coal with high content of sulphur has lower calorific value and product gas from these coals emits higher H$_2$S emissions. Therefore, lower H$_2$S content in coals is desired. CO as a result of UCG process might be stored in-situ and there is no need for controlling of NOx emissions as they are usually below limit values. Particle material, which is identified as substances found in atmosphere in solid/liquid form, plays an important role in air pollution. Ash is the mineral residue resulting from coal combustion. Chemical components of ash resulting from combustion of coal are silicon (Si), aluminum (Al), iron (Fe), calcium (Ca), magnesium (Mg), potassium (K), titanium (Ti) and phosphorus (P). Ash also contains trace elements. UCG process might be considered to minimize environmental and health effects of coal combustion as coal is one of the primary energy sources.

Environmental and health impacts of coal combustion depend on concentration and toxicity of trace elements in the coal [8]. Some elements, such as Se, Ni and Mn are required for humans at low concentrations. On the other hand, higher concentrations of those elements are toxic for human and ecosystem [9, 10, 11]. Trace elements in coal only exist in low concentrations. However, high amount of trace elements are released from combustion of tons of coal [12]. Many health problems such as arsenism, fluorosis, selenosis, mercurialism and berylliosis, which are related to coal combustion, have been reported in many developing countries [11, 13, 14, 15, 16]. Trace elements in coals and their environmental effects have been studied by many scientists [17, 18].

This study is aimed to evaluate hazardous trace elements in Soma-Eynez (Manisa), Konya-Karapinar and Aydin-Sahinali coal basins of Turkey.
MATERIALS AND METHODS

Selected coal basins within the scope of this study are Soma-Eynez (Manisa), Sahinali (Aydın) and Karapinar (Konya). Soma-Eynez (Manisa) coal basin is characterized by numerous E–W grabens and NNE-trending basins, and located within Western Anatolian extensional province. The lower coal seam (KM2) of Soma formation is of lower Miocene age and these lignite basins contain sedimentary and volcanic rock assemblages. Roof rocks and seam floor consist of claystone, sandstone, conglomerate and marl [19, 20, 21]. Sahinali (Aydın) coal basin, where the stratigraphy of the region is characterized by Precambrian-Mesozoic basement rocks and unconformably overlying Miocene, Pliocene and Holocene units, is located in the Büyük Menderes Graben (Western Anatolia, Turkey). Miocene unit begins with an alternation of conglomerate and sandstone. The other part of this unit consists of claystone, coal, and siltstone, clayey limestone and silicalimestone [22, 23]. Karapinar (Konya) coal basin is located within the Central Anatolian (Turkey). In Central Anatolia, a series of fault-controlled basins was developed due to regional tectonic movements during the Neogene period and many of them have economic coal deposits. Hotamıs Formation of Karapinar coal basin consists of two coal seams and the thickness of inorganic intercalations varies between 0.20 cm and 13.00 m. Roof rocks and seam floor consist of primarily claystone and organic mudstone. [24, 25, 26, 27]. Figure 1 depicts geological setting of Western Anatolia and selected coal basins.

Thirty coal samples from Soma-Eynez (Manisa), 25 coal samples from Sahinalı (Aydın) and 21 coal samples from Karapinar (Konya) were analyzed for determination of trace elements contents. The concentrations of elements were determined using Inductively Coupled Plasma Atomic Emission Spectrometry-Mass Spectrometry (ICP/AES-MS) methods. In this study, environmentally hazardous element contents of the coals were evaluated. Arithmetic mean was used for evaluation of potential air pollutant trace elements and enrichments of trace elements were determined according to upper continental crust (UCC), World and Turkey.

RESULTS AND DISCUSSION

Although coal is one of the primary sources of energy, environmental impacts of coal should be considered. Coal quality and characteristics should be identified. A comparison of trace element contents of coals in studied coal fields with the average values of UCC, world and Turkish coals was provided. Average concentrations of trace elements in studied coal fields and average concentrations of trace elements in UCC, world and Turkish coals are given in Table 2. As, Hg, U concentrations of Soma-Eynez coals exceed the average values of UCC, World, Turkish coals whereas Cd and Ni concentrations in Karapinar coals are higher than the average values of UCC, World, Turkish coals. Average U concentration in Karapinar coals is higher than the average concentrations of UCC and world coals and lower than Turkish coals. Average concentrations of As, Cd, Hg, Pb, Th and U in Sahinalı coals are higher than the average values of UCC, World and Turkish coals. Figure 2 depicts the concentrations of trace elements in coal samples of studied areas.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>4.80</td>
<td>8.30</td>
<td>65.00</td>
<td>77.92</td>
<td>16.06</td>
<td>107.88</td>
</tr>
<tr>
<td>Be</td>
<td>2.10</td>
<td>1.60</td>
<td>1.30</td>
<td>-</td>
<td>-</td>
<td>1.67</td>
</tr>
<tr>
<td>Cd</td>
<td>0.09</td>
<td>0.22</td>
<td>-</td>
<td>-</td>
<td>0.34</td>
<td>0.37</td>
</tr>
<tr>
<td>Co</td>
<td>17.30</td>
<td>5.10</td>
<td>10.00</td>
<td>3.04</td>
<td>13.45</td>
<td>7.48</td>
</tr>
<tr>
<td>Cr</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
<td>-</td>
</tr>
<tr>
<td>Hg</td>
<td>0.05</td>
<td>0.10</td>
<td>0.11</td>
<td>0.12</td>
<td>0.02</td>
<td>0.19</td>
</tr>
<tr>
<td>Mn</td>
<td>0.08</td>
<td>0.05</td>
<td>-</td>
<td>0.02</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni</td>
<td>47.00</td>
<td>13.00</td>
<td>150.00</td>
<td>10.72</td>
<td>112.02</td>
<td>25.93</td>
</tr>
<tr>
<td>Pb</td>
<td>17.00</td>
<td>7.80</td>
<td>9.30</td>
<td>11.05</td>
<td>31.02</td>
<td>17.92</td>
</tr>
<tr>
<td>Sb</td>
<td>0.40</td>
<td>0.92</td>
<td>2.70</td>
<td>-</td>
<td>0.30</td>
<td>1.65</td>
</tr>
<tr>
<td>Se</td>
<td>0.09</td>
<td>1.30</td>
<td>-</td>
<td>-</td>
<td>2.20</td>
<td>0.96</td>
</tr>
<tr>
<td>Th</td>
<td>10.50</td>
<td>3.30</td>
<td>-</td>
<td>4.06</td>
<td>4.53</td>
<td>16.78</td>
</tr>
<tr>
<td>Tl</td>
<td>0.90</td>
<td>0.63</td>
<td>-</td>
<td>0.23</td>
<td>0.87</td>
<td>0.29</td>
</tr>
<tr>
<td>U</td>
<td>2.70</td>
<td>2.40</td>
<td>13.00</td>
<td>20.36</td>
<td>4.55</td>
<td>17.23</td>
</tr>
<tr>
<td>S</td>
<td>1.80</td>
<td>2.00</td>
<td>3.70</td>
<td>1.19</td>
<td>0.87</td>
<td>0.97</td>
</tr>
</tbody>
</table>
Considering trace elements concentrations of selected coal fields, coal quality parameters were also evaluated, and results are given in Table 3. Applicability of UCG process in selected coal fields was also evaluated. Moisture contents of Soma-Eynez (Manisa) and Sahinali (Aydn) coal fields are appropriate for UCG process while Karapinar (Konya) coal field has a relatively high moisture content that is determined as 47%. High content of volatile material in coal is desired as it facilitates gasification process. Karapinar coal field is appropriate for UCG process as the field has a moisture content of 47%, volatile material of 24%, and caloric value of 1375 kcal/kg.

Sulphur content in coals with a caloric value of more than 3000 kcal/kg should be in the range of 0.34-0.80% according to US-Environmental Protection Agency (EPA) standards [32]. Sulphur contents in the selected coal fields were determined between 0.98-2.78%.

---

**TABLE 3**

Coal quality parameters in study areas [19, 21, 22, 24, 25]

<table>
<thead>
<tr>
<th>Coal quality parameters</th>
<th>Soma-Eynez (Manisa) (lignite)</th>
<th>Karapinar (Konya) (subbituminous coal)</th>
<th>Sahinali (Aydn) (lignite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reserve</td>
<td>148065064 ton</td>
<td>1805000000 ton</td>
<td>20650000 ton</td>
</tr>
<tr>
<td>Thickness (m)</td>
<td>~2-30</td>
<td>~21</td>
<td>~10</td>
</tr>
<tr>
<td>Depth (m)</td>
<td>537-1056</td>
<td>138</td>
<td>100</td>
</tr>
</tbody>
</table>

**Coal seam geology**

<table>
<thead>
<tr>
<th>Ultimate analysis parameters (dry, ash-free basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (%)</td>
</tr>
<tr>
<td>H (%)</td>
</tr>
<tr>
<td>O (%)</td>
</tr>
<tr>
<td>N (%)</td>
</tr>
<tr>
<td>S (%)</td>
</tr>
</tbody>
</table>

**Proximate analysis parameters**

| Moisture (%)      | 10.09-22.42 | 47          | 20.46        |
| Volatile matter (%)| 38.89-58.15 | 24          | N/A          |
| Ash (%)           | 14          | 20          | 27.24        |
| Fixed carbon (%)  | 73.09-80.79 | 10          | N/A          |
| Calorific value (kcal/kg) | 3600-6490 | 1375        | 3120         |

N/A: Not available
CONCLUSION

According to the results, Soma-Eynez coals have higher As, Hg, U concentrations than average concentrations of UCC, world and Turkish coals whereas Cd and Ni concentrations in Karapinar coals are higher than the average concentrations of UCC, World, Turkish coals. Average U concentration in Karapinar coals is higher than the average concentrations of UCC and world coals and lower than Turkish coals. In Sahinali coals, average concentrations of As, Cd, Hg, Pb, Th and U are higher than the average concentrations of UCC, World, Turkish coals.

Turkish coals have usually high ash yield and total sulphur contents. As, Cd, Hg, Ni, Pb, Sb, Se, Th and U concentration in Soma, Karapinar, Sahinali coals are found to be relatively high. Combustion of coals with higher trace element concentrations may pose environmental and health risks. Trace elements in coal cannot be totally eliminated by physical methods. Therefore, coal quality parameters and environmental aspects of coals are important for sustainability of environment. Trace elements in coal should be controlled and reduced to safe levels. For this purpose, selective mining, coal cleaning, emission control measures or cleaner coal technologies might be used. UCG in some Turkish lignite fields might enable the use of Turkish coals in an environmental friendly way. Considering the evaluations of coal quality parameters and environmental aspects of selected coal fields, UCG process might be a viable option in Soma-Eynez coal field.

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AN ASSESSMENT OF TRACE METAL CONTAMINATION IN SURFACE SEDIMENTS OF THE MONTENEGRIN COAST BY USING POLLUTION INDEXES AND STATISTICAL ANALYSIS

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1University of Montenegro, Institute of marine biology, P. Box 69, Dobrota bb, 85 330 Kotor, Montenegro
2BIO-ICT Centre of Excellence in Bioinformatics, 81 000 Podgorica, Montenegro

ABSTRACT

The concentrations of ten elements and trace metals, iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), cobalt (Co), nickel (Ni), lead (Pb), cadmium (Cd), arsenic (As) and mercury (Hg) were determined in the surface sediment collected from the coastal area of Montenegro. The metal content in the sediment collected from ten locations over two different years were analyzed using the Pearson correlation coefficient (r) and cluster analysis (CA). A correlation between the metal levels found in the sediments, for both years 2005 and 2006, was established. The metal pollution indexes (MPI) for the sediment were compared, confirming that the most polluted were locations S-9 and S-10. The geo-accumulation index (Igeo) was calculated using soil values as the background or pristine values. Extreme Igeo values (strongly polluted) were found only for Ni, Cd and Hg, each at a different single location.

KEYWORDS:
Trace metals, MPI, Igeo, Montenegrin coast

INTRODUCTION

Trace metals from natural and anthropogenic sources continuously enter the aquatic ecosystem where they pose a serious threat because of their toxicity, long time persistence and bioaccumulation [1-2]. The impact of anthropogenic perturbation is strongly felt in the estuarine and coastal environments adjacent to urban areas.

Accumulation of trace metals occurs in the upper sediment in aquatic environment by biological and geochemical mechanisms [3]. Different authors [4-6] opine that sediments are the ultimate sink of contaminants that enter in the aquatic environment [7]. They serve as a pool that can retain metals or release metals to the water column and may act as a source of exposure to aquatic organisms [8]. In addition, sediments composition reflects the long term quality situation independent of the current inputs [9]. Therefore, the knowledge of their chemical characterization is vital for assessing the quality of total ecosystem, as well as for the understanding of natural processes and human influence on these processes [9-10].

The Mediterranean Sea is an area where sediments have different geochemical composition: metal concentrations vary according to the area and different inputs from the coastal environment. Montenegro coast (Southern Adriatic Sea) is also under a great impact of anthropogenic factors and the activities on the shore. So, the aim of this study was to determine the spatial and temporal variations of trace metal contamination in the Montenegrin coast and to evaluate the influence of anthropogenic activity on the composition of the surface sediments by using metal pollution index (MPI) and geo-accumulation index (Igeo) of the metals [11-16]. These indices are often used to screen the potential of contaminants within the sediment. In this work the total concentrations of Fe, Mn, Zn, Cu, Co, Ni, Pb, Cd, As and Hg were determined in fraction (<63 μm) of ten surface sediments from the Montenegrin coast, in order to increase the knowledge on metal levels in this area, which has not been studied very much.

MATERIALS AND METHODS

The sediment samples were collected at ten different sites along the Montenegrin coastline during the autumn of 2005 and 2006 as it is shown in Figure 1. The sites Sveta Stasija (S-1), Kukuljina (S-2) and Herceg Novi (S-3) in the semi-enclosed Boka Kotorska Bay, as well as sites on the coastline of open sea, Žanjice (S-4), Mamula (S-5), Bigova (S-6), Budva (S-7), Bar (S-8), Rt Deran (S-9) and Ada Bojana (S-10), are situated in the proximity of different geochemical, hydrological and human impacts. All these sampling sites had in common long-standing exposure to different levels and sources of anthropogenic impact, such as marine ports, the airport, industrial effluents and sewage, and domestic and agricultural waste [17]. Collected sediment samples were homogenized, frozen at -18 °C, freeze-
dried at -40 °C for 48 h (CHRIST, Alpha 2-4 LD plus, Germany), ground to a fine powder and sieved through a less than 63 μm stainless steel mesh wire, for trace element analysis.

Prepared samples (0.5g) were digested with 2 mL of HNO3 (65%, Merck, Suprapur) and 6 mL of HCl (37%, Merck, Suprapur) in a microwave digestion system (CEM Corporation, MDS-2100) for 30 min at 200 °C. The digested samples were diluted (25mL) using Milli-Q water and for each batch of analysis two blank digests were performed in the same way.

The mineralized samples were analyzed for Co, Ni, Cd, Fe, Cu, Mn, Pb and Zn content by a graphite-furnace atomic absorption spectrometer (Perkin-Elmer AAAnalyst 200 model), while Hg and As were measured following a CV-AAS procedure by using a Perkin-Elmer Hydride System coupled to an atomic absorption spectrometer (AAS). The obtained results of the investigated elements in sediment are expressed in mg/kg of sample dry weight (dw). To ensure the quality control and the accuracy of the applied analytical procedure for the determination of trace metals in the sediment, the certified reference material, IAEA 158 (Marine sediment), was also digested and analyzed in a similar manner as the samples. The recovery values of metals in the standard reference material were in the range of 90–113 % of the certified total concentrations.

**Statistical analysis.** Cluster analysis (CA) was performed to classify the samples of surface sediments. All the samples were grouped in a multidimensional factor space and a dendrogram was plotted, representing the similarities and/or dissimilarities of the surface sediments in terms of their chemical composition. The data were analyzed by Statistica software (Data Analysis Software System, v.10.0, StatSoft, Inc, Tulsa, OK, USA). To track the possible source of the elements in the sediment, correlation coefficients between the average levels of the investigated elements in the surface sediments were calculated by Pearson correlations analysis in Microsoft Excel.

**Metal pollution index (MPI).** To compare the total content of metals at the different sampling stations, the metal pollution index (MPI) was used. The MPI was obtained using the equation: MPI = (Mi/M1 × M2 × M3 ×···× Mn)1/n, where: Mi is the concentration value of the first metal; M1 is the concentration value of the second metal; and Mn is the concentration of the metal n expressed in mg kg⁻¹. In this case, the number of metals (n)=10. Any MPI>1 indicates that the investigated site is polluted whereas any MPI<1 indicates no pollution [18 - 20].

The concentrations of trace metals (Fe, Mn, Zn, Cu, Co, Ni, Pb, Cd, As and Hg) investigated in sediment samples collected during 2005 and 2006 from the Montenegrin coast are summarized in Table 1. The results showed that there were significant differences in the concentrations of metals in sediments of the investigated locations. The mean concentrations of trace metals in sediment decreased in the following order Fe > Mn > Ni > Zn > Cu > Co > As > Pb > Cd > Hg, for both seasons. Stations S-9 and S-10 were locations with the highest concentrations of metals in sediments. At these locations the concentration of some elements was significantly higher compared to the other locations, in both seasons. For example, at the location S-9 (2006), concentrations of Fe and Zn had a maximum recorded values of 40.86 (10³) mg/kg and 67.2 mg/kg, respectively. High values of metals at these locations can be explained by the wastewaters and industrial waters which through a system of Skadar Lake, the Bojana River and the Drim River bring large amounts of sediment laden with many pollutants. Also, many stationary industrial facilities and hospitals on the coast contribute to quite adverse anthropogenic influence to this area [24-25].

Comparing the concentrations of the elements, the metal contents in sediment samples in autumn 2005 were generally higher than in the samples in autumn 2006. The concentrations of trace elements in the sediments from Boka Kotorska Bay were higher in relation to certain locations that are under the influence of the open sea, but not greater than

**Geo-accumulation index (Igeo).** Igeo was also calculated for analyzed metals. It was originally defined by Müller, 1981 [21] in order to determine and define metals contamination in sediments, by comparing current concentrations with pre-industrial levels [22]. It can be calculated by the following equation:

\[
I_{geo} = \log_{2} \left( \frac{C}{B} \right)
\]

where \( C \) is the measured concentration of the examined metal “n” in the sediment and \( B \) is the geochemical background concentration of the metal “n” [23]. Müller has distinguished seven classes of Igeo values [21]: 0-unpolluted, 0 to 1 unpolluted to moderately polluted, 1 to 2 moderately polluted, 2 to 3 moderately to strongly polluted, 3 to 4 strongly polluted, 4 to 5 strongly to extremely polluted, and >5 extremely polluted. This classification is a methodological approach based on the geochemical data. It allows mapping of a study area and discriminating different sub-areas according to their degree of contamination. In addition, it is feasible to obtain a proper comparison between various marine areas in terms of their heavy metal quality.

**RESULTS AND DISCUSSION**

The concentrations of trace metals (Fe, Mn, Zn, Cu, Co, Ni, Pb, Cd, As and Hg) investigated in sediment samples collected during 2005 and 2006 from the Montenegrin coast are summarized in Table 1. The results showed that there were significant differences in the concentrations of metals in sediments of the investigated locations. The mean concentrations of trace metals in sediment decreased in the following order Fe > Mn > Ni > Zn > Cu > Co > As > Pb > Cd > Hg, for both seasons. Stations S-9 and S-10 were locations with the highest concentrations of metals in sediments. At these locations the concentration of some elements was significantly higher compared to the other locations, in both seasons. For example, at the location S-9 (2006), concentrations of Fe and Zn had a maximum recorded values of 40.86 (10³) mg/kg and 67.2 mg/kg, respectively. High values of metals at these locations can be explained by the wastewaters and industrial waters which through a system of Skadar Lake, the Bojana River and the Drim River bring large amounts of sediment laden with many pollutants. Also, many stationary industrial facilities and hospitals on the coast contribute to quite adverse anthropogenic influence to this area [24-25].

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the concentrations in sediments obtained from the locations S-9 and S-10 in both seasons [24-25].
In comparison to the results of previous research conducted in the same area of the Montenegrin coast, we can conclude that the concentrations of Fe, Mn, Zn, Ni, Cu and Cd were lower [26], while concentrations of Co, As and Hg were in the range of previously obtained results [24]. Comparing with the results obtained for the sediments along the Albanian [27-29], Croatian [30-33], Slovenian [34], as well as along Italian Adriatic coast [35-38], the Montenegrin sediments had lower or similar levels of the investigated metals.
A certain degree of sediment contamination by metals was recorded at all sites in the present study. Comparing the seasons 2005 and 2006, MPI was higher at all locations in 2005 (1.39 to 3.04) than in 2006 (1.46 to 2.63). Locations with the highest MPI values in both studied seasons were S-9 and S-10 (open sea), and S-2 (Boka Kotorska Bay), which is in complete agreement with the earlier claims, because these are locations with the highest content of trace elements in sediment. Although MPI values indicated that the pollution was present, comparing with the countries of the Mediterranean Sea [18 - 20], the Montenegrin coast is the least polluted area in terms of trace elements in sediment.

**TABLE 2**

<table>
<thead>
<tr>
<th>Correlation between the metals in the sediments from both years</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Marked correlations are significant at p &lt; .05000</strong></td>
</tr>
<tr>
<td><strong>Fe</strong></td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>Mn</td>
</tr>
<tr>
<td>Zn</td>
</tr>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>Co</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>Pb</td>
</tr>
<tr>
<td>Cd</td>
</tr>
<tr>
<td>As</td>
</tr>
<tr>
<td>Hg</td>
</tr>
</tbody>
</table>

The relationship between parameters in this study is shown on Pearson’s correlation coefficient matrix in Table 2. It can be seen that the concentrations of the investigated metals in sediment were significantly correlated (p<0.05; Pearson’s test) with each other (especially Fe, Mn, Zn, Cu, Ni and Co with each other, and Cd-Pb), which may indicate that the spatial distributions of these pairs of metals are regulated by common local inputs and similar dispersion processes in the study area. Slightly negative correlations were found only for Ni with Pb, Cd, As and Hg, as well as for Hg-Co (Table 2).

Bray Curtis similarity was applied to samples. Variables were normalized by fourth root to make data more stable. The higher the value on the similarity cluster, the more significant the association is. CA presented by dendrogram (Fig. 2), shows all elements grouped into three statistically significant clusters according to the concentration values of elements in the sediment. Cluster 1 contains elements with the highest concentration values in the samples (Mn and Fe), then cluster 2 is the largest aggregation of elements with the most similar concentration (Zn and Ni, Cu and Co and Pb and As) while cluster 3 contains elements with the lowest concentration (Cd and Hg).

**FIGURE 2**

Metals cluster analysis dendrogram of sediment samples

**FIGURE 3**

Box plot for the geo-accumulation index of surface sediments

$Igeo$ values suggest that the investigated sites were mainly grouped as unpolluted or unpolluted to moderately polluted. Extreme values were found only for Ni, Cd and Hg. According to this, the locations S-9 (3.28 and 3.27) for Ni, S-2 (3.79) for Cd, and S-8 (3.21) for Hg were characterized as strongly polluted (Fig. 3). However, $Igeo$ values for Hg at other locations, as well as for toxic Pb and As, and essential Cu, Zn and Fe at all locations, classified the investigated area as practically unpolluted. According to $Igeo$ values for Ni and Cd, the location S-2 was moderately polluted and S-10 moderately to strongly polluted with Ni, while S-1, S-3, S-4 and S-8 were moderately polluted with Cd. High Cd contamination in these areas is due to the anthropogenic impacts from land, including waste water, port activities, the use of anti-corrosive paints for ships and boats [39]. Toxic metals associated with deterioration include Pb, Hg and Cd. Metals can be found in many products onboard a ship in varying quantities. Metal compounds are also present in anodes, insulation, batteries and electrical compounds [40]. Comparing the results of geo-accumulation index with other authors [15, 22], we can conclude that the obtained values were significantly lower than those quoted in the literature and connected generally with the locations where the metal concentrations were increased.
CONCLUSION

A comparison of the investigated metal concentrations in sediments along the Montenegrin coast for ten locations and two years, showed differences clearly associated with anthropogenic impact and geographical location. The metal contents in sediment samples in autumn 2005 were generally higher than in autumn 2006. The concentrations of the trace elements in sediment of Boka Kotorska Bay were higher in relation to certain open sea locations, but not greater than the concentration in sediments at two southernmost locations in both seasons, which may point out the same or similar source of these contaminants. From the point of MPI, a certain degree of metal contamination in the sediment was recorded at all sites in the present study. However, the extreme Igeo values (strongly polluted) were found only for Ni, Cd and Hg, each at a different single location. Higher concentrations of metals found near urban areas, point the strong anthropogenic influences. Thus, the only possible conclusion was that the concentration of metals in sediment was elevated due to the direct discharge of untreated municipal industrial waste into the sea. In general, the metal concentrations found in the sediments sampled from the Montenegrin coast are within the range of the mean values reported in the literature.

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VARIATION OF PERMEABILITY OF CLAY SOILS WITH DIFFERENT CONDITIONS PERMEATED WITH LEACHATE

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ABSTRACT

Solid waste landfills are a major problem and causes significant threat to groundwater and surface water. Municipal solid waste (MSW) is also a major problem in Turkey, as in many other countries. Istanbul, with a population of 14.2 million, is the crowded city in Turkey and approximately 14,000 tonnes of MSW are collected daily.

In this study, the effects of leachates on permeability and the treatment capability of clay soils with different conditions (the natural clay, compacted clay, compacted and consolidated clay soil, compacted clay soil with nanomaterial(s)) have been investigated. Clay soil samples and leachate were obtained from the Şile-Kömürçüoda landfill area on the Asian side of Istanbul.

In the experimental studies, standard proctor compaction tests and consolidation tests were applied to the clay soil. In addition, the permeability of the clay soil has been investigated by adding nanomaterial’s to the clay soil compacted by the standard method. The nanomaterial obtained from Erzurum oltu clay was used. The soil samples have a permeability k between 1.10^{-5}-1.10^{-9} m/s. In order to determine the removal rate and permeability of clay soils with different conditions and COD, SS are measured in the influent and effluent of the lab-scale reactor.

It is concluded that in the beginning some decrease has been observed in permeability of the clay soil, associated with the contamination. In the beginning, a decrease in the permeability caused by the suspended solids matters in the leachate filling the spaces between the particles of the clay soil pores. After some time, these results show that leachates may cause increase in the permeability. The treatment capabilities of natural clay, compacted clay, compacted and consolidated clay soil, compacted clay soil with nanomaterials samples were quite high. The highest removal rates and the lowest permeability are obtained in natural clay, compacted clay soil with nanomaterials, compacted and consolidated clay, compacted clay, respectively.

KEYWORDS:
Permeability, natural clay, compacted clay, consolidated clay, nano materials, leachate, and chemical parameters.

INTRODUCTION

Compacted clay soils that prevent leaching from municipal solid waste in the landfills, into the groundwater or surface water, lies below the municipal solid waste [1]. The compacted clay liner is expected to conduct less in order to decrease leachate from the waste. The permeability has to be insensitive to biological and chemical effects and changes landfill leachate [2]. Also the design of compacted clay have to be done appropriately to the landfill settlement and have satisfactory shear strength to resist slope failures and bearing capacity [3].

Former studies showed that diluted organic waste liquids do not lead to any noticeable change of permeability of compacted clay soil [4]. The other studies have also claimed that pure organic chemicals can cause dramatic rise increases in permeability of compacted clay soil [5-6]. Other study investigated the long-term permeability of compacted bentonite-silt mixtures permeated distilled water, nutrient solution and leachate. Fall of permeability while liquid-contained microorganisms permeating, point out, liquid displacement through the soil pores were controlled by some other mechanisms [7]. The other study, landfill leachate contamination lead to increase in the hydraulic conductivity [8]. Increased fine particle content decreases the permeability of compacted clay soils [9]. Landfill temperature decreases leachate viscosity that affects the permeability of compacted clay soils while leachate dissolves the clay minerals. This also affects the permeability of the compacted clay soils. Little attention is paid to the waste biodegradation, on compacted clay soils performance causing combined effect of chemical exposure and high temperature [10]. In a past study of the author k is measured as k=5.2x10^{-5} and 6.45x10^{-4} m/s where k is the permeability of compacted clay permeated with DI water. Permeability fell (k=2.53x10^{-3} m/s) in the case where compacted clay permeated with leachate [11]. In a former study, Fe(II) and Mn(II) presence do not affect the permeability values of compacted clay soil measured. Any significant change in permeability coefficient, that caused by the compacted clay soil structure, have not been observed [12]. Standard proctor compaction and consolidation tests are performed using the clay soil obtained from the Şile-Kömürçüoda landfill.
The methods and procedures fall into two stages: (1) Clay soil obtained from the Şile-Kömürçüoda landfill area has been compacted, consolidated and the permeability of the leachate has been investigated. (2) COD, SS have been performed in order to determine the treatment capacity of the clay soils with different conditions (the natural clay soil, compacted clay soil, compacted and consolidated clay soil, compacted clay soil with nanomaterials). Chemical, physicochemical and sieve analyses of clay soil have been taken from previous studies [12].

**Experimental Setup and Tests.** The mold reactor tests were performed by letting the liquid flow downward through the 100 mm diameter compacted specimens (Fig.1). Height of the clay soil specimens were 110 mm. Clay soil specimens were saturated under 0.3 bar pressure. Permeability tests were performed with water. After 3-4 weeks, water was replaced by leachate [13,14]. Experimental setup figure and photograph were given Fig.1-2.

**FIGURE 1**
Experimental set up.

In order to determine the removal capacity of the natural clay, compacted clay, compacted and consolidated clay soil, compacted clay soil with nanomaterials, COD, SS have been measured according to Standart APHA Methods both in the influent and effluent of the continuous reactor [15]. Standard Proctor Compaction Testing can be performed in the lab. The experiment of compaction is done using clay from Kömürçüoda taken in large pieces with the method ASTM D 698/ AASHTO T99 [16]. Consolidation Test Procedures have been developed to correct for the effects of sampling disturbance. The consolidation test is based on the standard method (ASTM D2435-04) [17].

All the experiments for this study were conducted under the conditions of Fe(II): 1 mg/L, pH: 6.7, temperature:25°C and alkalinity: 2x10⁻² eq/L.

**FIGURE 2**
Experimental setup photographs.

**Permeability Tests.** Constant – head tests have been performed to find the permeability of the clay soil which is calculated using the following equation:

\[ k = \frac{QL}{A(t_1 - t_2)} \]

where k is the permeability coefficient (cm/s), A is the surface area of specimen (cm²), L is the distance between the manometers (cm), Q is the total discharge (cm³/s), and t is the elapsed time (s).

**Nanomaterial’s obtained from natural clay.** In the experimental studies nano material obtained from Erzurum’s oltu clays was used. The clay used is of the high plasticity clay (CH) class according to the Unified Soil Classification (USCS) system. The characteristics of the used clay are listed in Table 1.
TABLE 1
Nanomaterial’s obtained from natural clay

<table>
<thead>
<tr>
<th>Properties</th>
<th>(%)</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay content</td>
<td>&lt;0.002 mm</td>
<td>56</td>
</tr>
<tr>
<td>Density</td>
<td>Gi</td>
<td>2.62</td>
</tr>
<tr>
<td>Liquid Limit</td>
<td>Wli</td>
<td>(%)</td>
</tr>
<tr>
<td>Plasticity</td>
<td>Ir</td>
<td>(%)</td>
</tr>
<tr>
<td>Contact angle</td>
<td></td>
<td>(%)</td>
</tr>
<tr>
<td>Cation exchange capacity</td>
<td>Mayo 100 g of dry soil</td>
<td>26.25</td>
</tr>
<tr>
<td>Optimum moisture content</td>
<td>Wopt</td>
<td>(%)</td>
</tr>
<tr>
<td>Max. Dry density</td>
<td>Ydmax</td>
<td>(kN/m²)</td>
</tr>
<tr>
<td>Free pressure test</td>
<td>qmin</td>
<td>(kPa)</td>
</tr>
<tr>
<td>BET surface area</td>
<td>(USCS)</td>
<td>(m²/g)</td>
</tr>
<tr>
<td>Ground class</td>
<td>D</td>
<td>CH</td>
</tr>
<tr>
<td>Fading rate</td>
<td>Cacr</td>
<td>(%)</td>
</tr>
<tr>
<td>Secant shift module</td>
<td></td>
<td>(%)</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

In this research, permeability and the removal rate for the COD, SS have been investigated for the leachate taken from the Şile Kömürçüoda Organized Landfill Site and the natural samples and the disturbed samples taken from the same place and natural soil samples, compacted with the standard compaction methods, compacted clay soil with nanomaterials and compacted and consolidation soil samples. The results obtained are presented below. Chemical, physicochemical and sieve analyses of clay soil have been taken from previous studies [12].

Properties of the Leachate. The properties of the leachate have been determined. The results of the characterization studies conducted on the leachate from the Şile-Kömürçüoda Landfill Site are presented in Tables 2. Leachate have dark brown color and very small granules and also contain large amounts of organic, inorganic contaminants and a high concentration of metals.

TABLE 2
Properties of the Leachate

<table>
<thead>
<tr>
<th>Parameter/Averages</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.9</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>18725</td>
</tr>
<tr>
<td>SS (mg/L)</td>
<td>1878</td>
</tr>
<tr>
<td>TKN (mg/L)</td>
<td>2752</td>
</tr>
<tr>
<td>NH₄-N (mg/L)</td>
<td>2310</td>
</tr>
<tr>
<td>Org-N (mg/L)</td>
<td>325</td>
</tr>
<tr>
<td>TP (mg/L)</td>
<td>18</td>
</tr>
</tbody>
</table>

Results of the Compaction, Consolidation and Permeability Tests. The compaction in the laboratory determines experimentally the change fullness of dry unit weight with the content of water and indicates the packing degree under certain compaction energy. The compaction experiments were conducted for the clay soil used in filling. Standard and modified compaction tests are the two most common used methods of compaction tests. The results of the experiment performed to obtain the correlation between the water content of the soil and compacted dry density are given in Table 3 and Fig. 3.

FIGURE 3
Moisture Content and Dry Density Relationship

TABLE 3
Compaction Study Results

<table>
<thead>
<tr>
<th>Sample Place</th>
<th>Kömürçüoda</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of container (cm³)</td>
<td>1000 cm³</td>
</tr>
<tr>
<td>Diameter (cm)</td>
<td>10.47 cm</td>
</tr>
<tr>
<td>Height (cm)</td>
<td>11.56 cm</td>
</tr>
<tr>
<td>Number of layers</td>
<td>3</td>
</tr>
<tr>
<td>Weight of hammer</td>
<td>2.5</td>
</tr>
<tr>
<td>Height of drop</td>
<td>30.5</td>
</tr>
<tr>
<td>Number of strike</td>
<td>25 strikes for every layer</td>
</tr>
</tbody>
</table>

Fig. 4 shows the stress and strain curves of the samples, in which consolidation was applied.

FIGURE 4
Oedometer Stress and Strain Test Relation

The experiments performed in the laboratory to determine the effects of COD and SS on permeability of clay soil. Permeabilities are determined by performing the experiments on compacted clay, compacted-consolidated clay and compacted clay with nanomaterial’s samples by different energy applications in the laboratory. Permeability experiments were performed on the samples that were prepared at the optimum water content, over 3% and under 3%
of the optimum water content, obtained as a result of the standard compaction application. Then permeability measurements were carried out, where leachate was passed through the samples. The same procedures were repeated on the samples prepared by applying natural clay soil.

Permeability Test Results of the Landfill Leachate in The Clay Soil

As seen in Fig. 5, changes were observed in the permeability of the natural clay, compacted clay, compacted and consolidated clay soil, compacted clay soil with nanomaterials. Initially, the suspended solids within leachate, was seen to decrease the permeability by filling the void spaces among the particles of the clay soil. It is well known that the metal ions and the microorganisms in the leachate cause the same effect. The permeability decreased significantly with time approximately one month, since suspended solids in the permeating liquid fill the void spaces among the particles of the compacted clay soils. However, some deformations occur in the structure of clay soil due to the presence of very high concentration and variety of pollutants in leachate. These deformations lead to an increase in the permeability of clay soils over time approximately one month. Ho Young Jo (2005) reported that hydraulic conductivity increased in the long term [18].

Effluent Analysis Results of the Landfill Leachate in The Clay Soil. Effluent analysis results for COD and SS are shown below in Figures 6, 7.

The influent COD value of leachate obtained experimentally was 18725 mg/L. For the natural clay soil at the end of the 51th day, removal efficiency and COD effluent values were 59% and 7612 mg/L, respectively. For compacted clay soil in the 30th day, the removal efficiency was found as 28% and the COD effluent value as 13425 mg/L.

The experimentally obtained influent SS value of leachate was 1878 mg/L. SS effluent value was obtained as 428 mg/L and removal efficiency as 77% on the 90 the day in the reactor for natural clay. For compacted with nano material soil samples, the SS effluent value was measured as 505 mg/L and removal efficiency as 73% on the 90th day. For compacted-consolidated clay soil samples, the SS effluent value was measured as 532 mg/L and removal efficiency as 72% on the 90th day. 583 mg/L is the determined SS effluent value and 69 % is the removal efficiency on the 90th day in the the samples compacted by standard compaction.
However, as it can be seen in Fig. 7, the removal efficiency of SS was seen to increase generally until the 90th day and it began to decrease in the following days. This change can be explained so that adsorption turns to desorption after the 90th day. SS removal efficiency was observed to be quite high for natural clay. The reason for this variation can be the adsorption until the turning point, then desorption begins. SS removal efficiency was observed to be quite high for natural clay.

The removal of contaminants in a landfill area usually involves one or more of the following processes: advection, diffusion and interactions between the leachate and the compacted clay soil, such as adsorption, ion exchange, mechanical filtration, sedimentation, chemical reaction and biological activities. These processes are complex and depend on the pH of the medium, the mineralogy and the density of the materials. In other words, if the contaminant has an acidic property, this can degrade the compacted clay soil and increases the hydraulic conductivity [19, 20, 21].

CONCLUSION

In this study, the removal rate and permeability of the natural clay, compacted clay, compacted and consolidated clay, compacted clay soil with nanomaterials were investigated. COD, SS in the influent and effluent of the lab-scale reactors were measured. Following the leachate passes through of clay soils under various conditions high removal efficiencies are yielded in the COD and SS parameters. On the 90th day, the removal efficiency value of COD is 76%, 74%, 72%, 70% for the natural clay, compacted clay soil with nanomaterials, compacted and consolidated clay soil, compacted clay respectively. On the same day of the experiments the efficiency value of SS is 77%, 73% 72%, 69% for the natural clay, compacted clay soil with nanomaterials, compacted and consolidated clay soil, compacted clay respectively. Since high removal efficiencies were obtained in the COD and SS parameters, a natural purification capacity of the clay has been observed.

More on permeability, it is observed how the permeability of the natural clay, compacted clay, compacted and consolidated clay, compacted clay soil with nanomaterials changes. In the beginning, the voids in the soil are filled by the suspended solids in the leachate. So the permeability decreased noticeably for the following month because of that reason. On the other hand, structure of the clay soil deformed because of the various existing pollutants with high concentrations. After one month, these deformed structure lead an increase of permeability of the clay soil. In order to compare the methods of compaction and sorts of inclusions, the lowest values of permeability are presented as, in natural clay (k=1.12x10^{-8} m/s), in compacted and consolidated clay (k=6.2x10^{-8} m/s), in compacted clay (k=5.2x10^{-7} m/s).

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SHIPYARD WELDING EMISSION ESTIMATION FOR DIFFERENT ELECTRODE AND SHIP TYPES

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ABSTRACT

Although welding is an essential process in shipbuilding, welding related air emissions cause remarkable problems for worker health and environment. A great number of different electrodes are used during an ordinary ship building or repairing process. Shielded Metal Arc Welding (SMAW) and Gas Metal Arc Welding (GMAW) are most frequently used welding methods in shipyards and it is well known that gaseous emissions and fumes formed during welding processes may have effect on global climate change and may cause various diseases on workers. In this study, the total amount of covered electrodes used during chemical manufacturing process is obtained and the amount of the emissions to air is estimated with the help of fume formation rate experiments. Emission amount/deadweight ton ratios are also calculated in order to investigate the efficiency of manufacturing per load.

KEYWORDS: Shipbuilding, welding, emission estimation

INTRODUCTION

Welding is the main joining process in ship manufacturing. Shielded Metal Arc Welding (SMAW), Gas Metal Arc Welding (GMAW) and Submerged Arc Welding (SAW) are the most used welding techniques in ship manufacturing [1]. During welding, heated electrode or wire tip melts and liquid drops are formed. 90% of the evaporation is formed by welding electrode and wire drops [2]. Various types of toxic gases, fume, plume and metal particles are formed during welding.

Welding processes are responsible for many different types of contaminants, which may have adverse effects on human health and environment [3]. The potential hazards of welding processes to the workers include metal fumes, toxic gases, ultraviolet and infrared radiation [4]. Toxic gases consist of Mn, Ni, Cr, Co and Pb, which are formed during welding and have extremely adverse effects on human health [5]. These effects are well-investigated and determined in the literature. Malgorzata et al. (2015) [6] indicated that the contaminants of welding fume can be linked to diseases such as bronchitis, cancer and functional changes in the lung. Sriram et al. (2010) [7] examined the effects of welding fume particulates on rats. Taylor et al. (2003) [8] studied on the effects of welding fume on solubility, acute lung damage and inflammation on rats. Lu et al, (2005) [9] realized studies on determining of gaseous form of manganese levels formed during welding processes. Ireland and Morris, (2013) [10] indicated that while particles smaller than 30 μm are inhalable through nose and throat and particles smaller than 10 μm are held by trachea, bronchi and bronchioli; particles smaller than 2-3 μm stick onto pulmonary alveoli. Chuang et al, (2018) [11] investigated the relationship between pulmonary exposure of metal fume particulate matter and sleep disturbances in shipyard welders. The authors concluded that exposure to heavy metals in metal fume PM2.5 may disrupt sleep quality in welding workers.


Celebi, (2014) [17] studied on welding emission estimation in shipyards for different ship types. He estimated the welding emissions for 4 chemical tankers, 3 container ships and 2 fishing boats. He
concluded the average welding emissions are 0.046 kg/DWT, 0.033 kg/DWT and 0.143 kg/DWT for tankers, container ships and fishing boats, respectively. DWT is the abbreviation for deadweight tonnage, which describes the movable loads, i.e. the total weight of cargo, fresh water, provision and crew, of the ship. The researcher calculated these values by using regression analysis for real electrode consumptions of ships. Abdullah et al., (2013) studied on ship breaking sector in which welding and cutting processes are used commonly. According to the latest report of United Nations Conference on Trade and Development (UNCTAD) released on 1 January 2017, there are 93,161 vessels, which have a combined tonnage of 1.86 billion DWT. Figure 1 presents the total world fleet by principal vessel type between the years 1980-2017.

Turkish shipyards delivered 609 ships, which have 3,887,000 DWT capacities between the years of 1995-2007. In 2016, the number and capacity of delivered ships are 19 and 73,384 DWT, respectively. The total repair and maintenance capacity of the sector reached 21,000,000 DWT at the end of 2016. Welding is the most common joining process used during these manufacturing and repair/maintenance activities.

In this study, actual welding electrode consumptions for a 7,100 DWT (deadweight ton) chemical tanker with 120 m length, 17 m width and 8 m height, was gathered from one of the shipyards. Mainly shielded metal arc welding (SMAW) and flux cored arc welding (FCAW) methods were utilized to build this ship and roughly 84,800 (~3,816 kg), 49,200 (~2,214 kg) and 1,200 (~54 kg) pcs of E6013 rutile, E7018 basic and E6010 cellulosic type electrodes were consumed, respectively along with 6,667 spools (~100 tons) of E71-T1 cored wire and 3,276 pcs (~119 kg) of E309Mo electrode. Electrode consumption data for a 26,200 DWT container ship with 183 m length, 28 m width and 11 m height is as follows: 192,500 (~6,213 kg), 92,400 (~2,245 kg) and 8800 (~233 kg) pcs of E6013 rutile, E7018 basic and E6010 cellulosic type electrodes, respectively. 4,250 pcs (~418 kg) of E7024 type electrodes were consumed as well as 8,000 spools (~120 tons) of E71-T1 cored wire.

Emissions per DWT are calculated by the emission estimation approaches and a sectoral manufacturing projection is realized to estimate the total emissions.

MATERIALS AND METHODS

Fume emission experiments were realized inside a fume chamber, which had been designed according to EN ISO 15011-1:2009 [20], in order to find emissions rates and factors of the electrodes. Welding power sources were Lincoln Electric Inver-tec V260-S for SMAW and Expressweld Master-MIG 501W for FCAW. In experiments, AH-36 and Grade A round shipbuilding steel plates with a 290 mm diameter were used as a base metal and rutile (E6013), basic (E7018) and cellulosic (E6010) electrodes and E71-T1 flux cored wire as filler metals. Shielding gas was 100 % CO₂ for FCAW. Before the experiments, glass fiber filters were dried in an oven at 120°C for 1 hour and weighed with an electronic balance with 1.10⁻³ g precision. Inside a fume chamber, welding was carried out for 30 seconds for rutile and basic and 15 seconds for cellulosic electrodes and 30 seconds for FCAW. Welding currents were decided to be the average values in operating range given by the electrode manufacturer. Therefore, 120 A, 120 A and 105 A current values were set during the welding with rutile, basic and cellulosic electrodes, respectively. 185 A current was selected for FCAW with 1.2 mm diameter. Fan of the chamber worked for a total of 5 minutes. After welding was finished, total suspending particulate (TSP), which was captured on glass fiber filters, were weighed.
again. Experiments were repeated five times and average fume formation rate (FFR) were measured. In addition, emission factors for covered electrodes and flux cored welding wire used in experiments were calculated.

RESULTS AND DISCUSSION

Average fume formation rates were calculated as 0.166 g.min⁻¹, 0.285 g.min⁻¹ and 0.617 g.min⁻¹ for rutile, basic and cellulosic electrodes, respectively. FFR for FCAW was calculated as 0.413 g.min⁻¹. In addition, emission factors for rutile, basic and cellulosic electrodes were calculated as 7.03 g.kg⁻¹, 10.5 g.kg⁻¹ and 26 g.kg⁻¹, respectively. Emission factor for FCAW was calculated as 17.2 g.kg⁻¹. Based on these experimental emission factors, total suspending particulate emissions were calculated as 19.11 kg, 12.55 kg and 0.83 kg for rutile, basic and cellulosic electrodes, respectively. Similarly, TSP for FCAW method was calculated as 1,720 kg. As a result, TSP emission for shipbuilding of a 7,100 DWT chemical tanker was found to be 1,752.5 kg. In a similar manner, TSP emissions for a container ship were calculated as 43.68 kg, 23.58 kg and 6.06 kg for rutile, basic and cellulosic electrodes, respectively. TSP for FCAW was calculated as 2064 kg and total TSP for 26,200 DWT container ship was obtained as 2,137 kg. TSP fume emissions per DWT were calculated approximately to be 0.247 kg/DWT and 0.082 kg/DWT for chemical tanker and container ship, respectively. According to these results, the total amount of TSP fume emissions is calculated for chemical tankers and container ships. Global total carrying capacities of chemical tankers and container ships are 43,225,000 and 245,609,000 DWT, respectively [19]. The results are given in Table 1.

TABLE 1
The total amount of TSP fume emissions for chemical tankers and container ships

<table>
<thead>
<tr>
<th>Ship Type</th>
<th>TSP Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Tanker</td>
<td>10,676.58 t</td>
</tr>
<tr>
<td>Container Ships</td>
<td>20,139.94 t</td>
</tr>
</tbody>
</table>

It should be noted some of electrodes (i.e. E309Mo and E7024 rutile) used in manufacturing of these two ships were not available during the experiments. Therefore, these electrodes couldn’t be tested and they were not included in total emission calculations, which mean actual TSP fume emissions expected should be higher. Since the consumption of E309Mo and E7024 electrodes are not high compared with other electrodes, grand total of emissions would not be affected considerably.

CONCLUSION

Emission estimates for selected ships, a chemical tanker and a container, were calculated based on fume formation rate experiments and actual electrode consumption data from one shipyard. It could be concluded that roughly 1.92 tons of TSP welding emissions were released during the manufacturing of 7,100 DWT chemical tanker and 2.14 tons during the building of a 26,200 DWT container ship. When annual average shipbuilding capacity around the world, which is estimated to be 65 million gross tons [19], is taken into account, it could be comprehended that ten thousand tons of welding fume, as well as CO₂, CO and criteria pollutants are emitted to the environment.

Welding fume and gases formed during welding cause various types of acute and chronic occupational diseases. Furthermore, welding fume has adverse effects not only for workers but also for public health. Risk maps must be prepared by the help of risk analysis approaches for places at which the welding process is realized and measurements must be taken in order to reduce the exposure to the welding fume. Besides, further studies focusing on in vivo and in vitro methods are needed to understand welder exposure better and assess the risks. Thereafter, regional investigations on the effects of welding fume on the public health must be carried out.

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QUALITY ASSESSMENT AND CHEMICAL COMPOSITION OF SURFACE WATER IN THE AKCADAG BASIN (MALATYA), TURKEY: A CASE STUDY FOR IRRIGATION AND DRINKING PURPOSES

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ABSTRACT

The quality of irrigation water has a considerable impact on what plants can be successfully grown, the productivity of these plants, and water infiltration and other soil physical conditions. Irrigated agriculture is dependent on an adequate water supply of usable quality. To avoid problems when using poor quality water supplies, there must be sound planning to ensure that the quality of water available is put to the best use.

The usage of irrigation water by Polat and Sürğü Streams is one of the most important factors in respect to the intensification of agricultural activities in the Akcadag Basin. Responsible and accurate use of these factors by means of GIS is of vital importance. This study aims to visualize waters defined to be qualified to be used for irrigation or drinking purposes with the aid of GIS and to ensure the sustainable use of surface waters in the Akcadag Basin.

The most common measure to assess irrigation water is called the Sodium Adsorption Ratio (SAR). The SAR defines sodicity in terms of the relative concentration of sodium (Na) compared to the sum of calcium (Ca) and magnesium (Mg) ions in a sample. The SAR assesses the potential for infiltration problems due to a sodium imbalance in irrigation water. The highest value was found in SAR station 2 (0.473) while the lowest value (0.027) was calculated in the station 7. The selected stations should be monitored in wet and dry seasons in order to provide a more accurate interpretation of the area and to ensure proper use. It is possible to aim to protect water resources and make people reach these resources in a healthy way, to create a sustainable water management policy by means of different monitoring tools to be used for the monitoring of the area.

KEYWORDS:
Surface water quality, irrigation water, Geographic Information System (GIS), ion balance, Sodium Adsorption Rate (SAR), Turkey

INTRODUCTION

Water quality is determined not only by natural processes but also by anthropogenic activities such as industry, agriculture, pollution discharge, and water exploitation which alter the hydrological cycle [1, 2]. One of the water quality parameters, the increase in nitrate and sulphate, especially in agricultural areas, is largely attributed to chemical fertilizer leaching. The irrational irrigation and development of intensive agriculture have resulted in salinization and alkalization [3]. Akcadag Basin is a region where large-scale agricultural activities take place and the current surface waters are used for irrigation purposes.

Malatya is located on the upper Firat River Basin in the Eastern region of Anatolia. Akcadag is a district of Malatya province and important for agricultural activities [4]. The Sürğü Stream, which rises from the southern slopes of the Karakaya hill located in the western parts of the Malatya region, is a special water area that collects the surface waters of the region. The Sürğü Stream is an important reach of the Göksu river. Following the Sürğü town, the stream that flows westward to Kapidere returns to the south. Here, the river merging with Göksu and named after Göksu as well, turns to the east and reaches the provincial border of Adiyaman and merges with Firat. The Sürğü dam is set on the Sürğü river and irrigates a large area. The rivers discharging in the Sürğü Stream such as Agçapınar (Pinarbaşı), Sürmeli-pınar, Çayırpınar, Takaz and Reşadiye are the water reaches [5]. The entire Akcadag basin, defined by this area, is where vegetable and fruit growing is carried out by the people. Because the surface waters are intensively used for irrigation purposes in agricultural areas by the people of the region.
The irrigation by the Polat and Sürğü Streams and the usage of groundwater are the most important factors in respect to the intensification of agricultural activities, increase of agricultural output and agricultural product range, density of population and habitation in the Akcadag Basin. Responsible and accurate use of these factors by means of GIS is of vital importance. This study aims to visualize waters defined to be qualified to be used for irrigation or drinking purposes with the aid of GIS and to ensure the sustainable use of surface waters in the Akcadag Basin.

MATERIALS AND METHODS

Study area. The 7 sample stations were selected as represent of the nature of the stream ecosystems which has been close to the main road with the consideration of the water sources relationship between dry and wet seasons. The general view of the streams and sample stations were shown at the Figure 1.

The study area is an agricultural territory. Due to different physical geography features of the territory, agricultural policies may be made in accordance with the characteristics of the land using with GIS and the territorial potential can be benefitted ideally. Therefore, the irrigation by Sürğü and Polat Stream is the most important factor in respect to the agricultural activities, increase of agricultural output and agricultural product range on Akcadag Basin. The characteristics of the stations selected for their structures can be explained as follows: The station 1 has water used for agricultural activities with vineyards, almonds and pear trees. Similarly, a small settlement of people around the station 2 is engaged in vegetable farming, which can be a source of livelihood. The stations 3 and 4 contain waters taken from a region close to the area that can be defined as source water. The sampling area close to both apricot farming and the trout plant is located in the station 5. The stations 6 and 7 stations, which are the follow-ups of the stream, can be defined as relatively good quality waters used only for irrigation purposes.

12% of the areas cultivated in the Akcadag basin consist of dry agricultural land and 13.15% are composed of irrigated agricultural areas. The water resources necessary for agricultural irrigation are sufficient and the existing water resources can be transported through the channels all the way to the basin due to the slope and sagged structure of the terrain as a result of the geological and geomorphological structure of the region; therefore, dry agricultural areas are very limited [6]. Although the raining is insufficient, the number of the irrigated agricultural lands has considerably increased since the Polat basin is rich in rivers, particularly in hydrographic terms. The surface waters are small, but the flow rates are rapid, which positively affects irrigation. Apple, cherry and particularly apricot trees are the main products that bring economic benefits in the specific type of agriculture, which is generally defined as vegetable and fruit growing activities. Other small-scale gardens are used by people to meet their own needs. Trout breeding started and brought economic contribution to local people in the study area where not only agricultural activities, but also local-based aquaculture activities are carried out. The water quality parameters have been measured in dry period of the year as determination of instant impacts on the river ecosystems. Physicochemical properties of the water samples, such as temperature, pH, Dissolved Oxygen (DO), electrical conductivity, were measured in situ with the SigmaProbe (EC).

Water Quality Parameters. In addition, the concentrations of changes in main parameters of anions and cations were observed. The ionic properties of the water samples were determined by Dionex ion chromatography ICS 1100 with Degas and Chromeleon SE for anions and cations respectively. An analytical AS9-HC (4 x 250 mm) column and AG9 guard column (4 x 50 mm) with ASRS-300 (4 mm) suppressor was used in ion-exchange mode in order to determine the water-soluble anions (sulphate-SO_4^{2-}, phosphate-PO_4^{3-}, nitrate-NO_3^{-}, nitrite-NO_2^{-}, chloride-Cl^{-}, fluoride-F^{-}, bromide-Br^{-}). The eluent was 9mmol Na_2CO_3 and the flow rate of the eluent was 1.0 mL/min. For the determination of water-soluble cations (lithium-Li^{+}, sodium-Na^{+}, potassium-K^{+}, magnesium-Mg^{2+}, calcium-Ca^{2+}, ammonium-NH_4^{+}), an analytical CS16 column and a CG16 guard column (both 3 x 50 mm) with CSRS-I (2 mm) suppressor was used in a chemical mode. An eluent of 10 mM methane sulfonic acid was used at flow rate of 1.0 mL/min. The eluent volume was 25 µL for all detection runs. Peak identification was confirmed based on a match of the ion chromatograph retention times with the chromatographs of the standard samples. The limit of
TABLE 1
Physical and chemical analysis results (mEq/L) and the measured Sodium Adsorption Ratio (SAR), Percent Sodium (%Na) and Hardness (HD-mg/L as CaCO3) values of the water samples.

<table>
<thead>
<tr>
<th>Stations</th>
<th>pH</th>
<th>EC</th>
<th>Ca&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>Mg&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>K&lt;sup&gt;+&lt;/sup&gt;</th>
<th>Na&lt;sup&gt;+&lt;/sup&gt;</th>
<th>HCO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</th>
<th>Cl&lt;sup&gt;-&lt;/sup&gt;</th>
<th>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;</th>
<th>NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</th>
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<td>248</td>
<td>7.93</td>
<td>3.17</td>
<td>0.31</td>
<td>0.21</td>
<td>3.24</td>
<td>0.07</td>
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<td>0.09</td>
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<tr>
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<td>2.30</td>
<td>1.01</td>
<td>0.32</td>
<td>0.61</td>
<td>3.31</td>
<td>0.27</td>
<td>0.65</td>
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<td>0.47</td>
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<td>0.34</td>
<td>0.04</td>
<td>2.54</td>
<td>0.01</td>
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<td>0.04</td>
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<td>0.01</td>
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<td>0.02</td>
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<td>0.30</td>
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<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>1.30</td>
<td>73.13</td>
</tr>
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</table>

The results and discussion

The results of the samples taken during the sampling period are presented in Table 1 under the titles of pH, EC, cations and anions. Soluble salts in natural waters are measured by electrical conductivity (EC); and the values differ from 215 to 188 micromhos / cm in this study area. In the instant samples taken without regard to station difference, the Ca concentrations are between 1.32-7.93 mEq/L, the Mg concentrations are between 0.14 and 3.17 mEq/L, while the Na concentrations differ between 0.02-0.60 mEq/L. In order to make the results of physical and chemical analysis of the water samples taken from the stations more understandable, the field was visualized using GIS. Figure 2 shows the changes in the anions while Figure 3 shows the changes in the cations.

When evaluated on station basis (Figure 2), it can be seen that the stations 1 and 2 have peak values compared to other stations. Accordingly, when the cation results are examined; Ca<sup>2+</sup> and Mg<sup>2+</sup> were recorded as the highest value in the station 1 among all other stations with the values of 7.93 and 3.17 mEq/L, respectively.

It can be considered that the peak values of the anions and cations detected in the station 1 might result from the fertilization that occurs due to the vineyards (Vitis euvitis), almond (Prunus dulcis), pear (Pyrus communis) and apricot (Prunus armeniaca) cultivation concentrated around the region. This is because of the fact that the use of potassium sulphate fertilizer and magnesium nitrate fertilizer is common for the vineyards while the use of calcium nitrate fertilizer is common for pear cultivation, and magnesium nitrate and potassium sulphate fertilizers are commonly used for apricot cultivation [10,11]. It is known that fertilizers and pesticides used in agriculture reach aquatic areas by means of irrigation waters. Irrigation water, depending on the use of fertilizer, can discharge in the active area of Ca<sup>2+</sup>, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions and can cause an increase in current concentrations. In addition, there are various amounts of sulphates in all natural waters; sulphate can more easily pass through the
waters by filtration, especially from gypsum and other salts.

Total hardness was calculated as 554.82 mg/L CaCO₃, which indicates very hard water. In addition, SO₄ concentration obtained from the anions was measured to be 8.31 mEq/L, which is approximately 400 times higher than the station 7 where the SO₄ concentration was measured to be the lowest. In the same station; alkalinity was found to be 163.59 mg/L CaCO₃.

In the station 2; Ca concentration decreased to 2.30 mEq/L and Mg concentration decreased to 1.01 mEq/L, while Na concentration reached to 0.61 mEq/L, which is the highest value among all stations. Similarly, the chloride concentration from the anions was recorded as the highest value among all the stations with the value 0.27 mEq/L. SO₄ concentration decreased about 90% compared to the previous station. However, it was still detected to be higher than other stations. Alkalinity was found to be close to the previous station (165.71 mg/L CaCO₃). In the station 2; the EC value also increased compared to the previous station, depending on the concentrations of Na and Cl in the water. Chlorides discharge in waters as a result of being dissolved from chloride rocks and soils, industrial and residential wastewaters such as salty water pollution in seacoast wells, chemical fertilizers used for agricultural purposes, water softening facilities, oil wells and refineries, paper production [12]. It is known that active vegetable cultivation is also conducted in this in addition to remarkable settlements. However, the reason for the sudden chlorine elevation in this station must be studied in further research in detail.

When other stations are evaluated; Ca, Mg and Na (1.32, 0.14 and 0.02 mEq/L) cations and SO₄ concentration (0.02 mEq/L) from the anions were found to be in the lowest values in the station 7. Alkalinity was calculated as 87.81 mg/L CaCO₃, total hardness was found as 73.13 mg/L CaCO₃ and the station no. 7 was determined to have the lowest value of both parameters.

Furthermore, NH₄, NO₂ and NO₃ concentrations were measured in the stations. The concentrations of NH₄, NO₂ and NO₃ measured in the stations before the station 5 were found to be close to each other. NH₄ concentration in the station no. 5 was found 0.65 mg; NO₃ was found to be the highest with a value of 2.89 mg/L. Feeds and oysters that are not consumed by fish-breeding species cause undesirable changes in the water column and sediment [13]. However, 85% of the phosphorus penetrating into the culture medium with the feed, 80-88% of the carbon and 52-95% of the nitrogen are distributed in the aquatic environment via feed debris, fish excreta and faeces [13, 14]. The increase in the nitrate concentration in the station 5 is thought to be due to fish farms located in that region to a large extent. In the stations 6 and 7; NH₄ and NO₃ concentrations decrease by 50% and 60%, respectively.

Piper diagram of the stations is presented in Figure 5. A Piper trilinear diagram displays that all the surface waters are characterized by the dominance of anion-cation. The samples show that various chemical compositions and waters are generally in Na-SO₄, Na-HCO₃, Na-Cl, Ca-SO₄, Ca-HCO₃ types. The piper diagram presents that the relative concentrations of six to seven ions in solutions including the cations; Ca, Mg, and Na, K, and the anions; Cl, SO₄, CO₃ and HCO₃. In most natural waters, these ions make up 95 to 100% of the ions in solution. As shown in Figure 2, there are no dominant cations and anions for most water samples, except for 2 samples that are dominated by Na⁺ and 2 samples dominated by HCO₃⁻. The ion balance (% balance error = (Σcations-Σanions) / (Σcations+Σanions) concentrations in milliequivalents) was calculated and the error was found within normal range (should be <10%) for surface waters. The data obtained for all stations are below this value.
CONCLUSION

Salinity is at the top of the parameters that adversely affect plant development. However, along with problem of salinity, the toxicity effect can also be observed due to the difference of water deficiency or water availability. This case may differ by exposure time, concentration, plant resistance and water use. When toxic ion effect on plants is mentioned, sodium, chlorine and boron elements are the first to come to mind. However, it is not always possible to mention the toxic effect of a single element. It is also known that elements interact with each other agnostically (e.g. nitrogen (N) and potassium (K), copper (Cu) and boron (B)) and synergistically (e.g. nitrogen (N) and magnesium (Mg)) [15].

Sufficient levels of Ca and Mg concentrations in irrigation waters for plant development are reported as 40-100 ppm and 30-50 ppm intervals, respectively [16]. For Mg concentration, three stations could not provide this value range while only one station can reach this value range for Ca concentration. For potassium; while there are found in very low levels in natural waters; their values which are a few ppm more in irrigation waters indicate that they are fed from fertilizers or other sources [17]. The most important cation having a direct effect on irrigation water quality is sodium. It is known that the excess of sodium, which is actually required in very small quantities, is toxic for the growth of plants [18]. The direct effect of salinity of irrigation water is their reducing or ending effect on plant growth as a result of the accumulation of some elements such as Cl, Na, HCO₃ and B at high concentration in the plant. Thus, plant yield and quality are adversely affected [19].

According to irrigation water quality criteria for the reuse of used water; salinity, electrical conductivity, TDS, SAR, specific ion toxicity (sodium, chloride and boron), nitrate, total pesticide, bicarbonate and pH parameters are emphasized. Ion toxicity, solely may be insufficient to give an idea of the toxicity of the chemical interaction that pesticides, nitrates and other anion-cations may bring into play. Apart from these chemical analyzes, biological criteria must be definitely applied in order to be able to identify toxic effects. The simplest way to solve the toxicity problem is to not use irrigation water, which has the potential to have toxic properties. However, this method is not always effective. Instead, it may be considered to reduce toxicity in the existing irrigation water. In addition, plant selection, mixing of the source with an alternative

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**FIGURE 4**
SAR and %Na values in Akcadag Basin

**FIGURE 5**
Piper diagram of Akcadag Basin

Figure 5 presents the GIS visual of the SAR values. Sodium adsorption ratio (SAR) (SAR = Na⁺/√(Ca²⁺ + Mg²⁺)/2) is used as the primary indicator for evaluating irrigation, where the concentrations of all ions are in mEq/L. According to the International SAR standards classification; SAR < 3: suitable for irrigation; SAR 3 - 9: use may be restricted and SAR > 9 unsuitable for irrigation. When the samples taken for irrigation purposes were analyzed; the SAR parameter was found to be the highest value (0.473) in the station 2 while the lowest value (0.027) was found in the station 7. Since the calculated SAR parameter is lower than the value of 3 as presented in Figure 5, it seems that the stations are suitable for irrigation water. However, in order to reach a more accurate judgment on the samples taken, sampling frequency should be increased in the study area and water quality monitoring studies in the region should be conducted by means of different monitoring tools. The sodium percentage (%Na = Na⁺ / (Na⁺ + K⁺ + Ca²⁺ + Mg²⁺) x 100) expressed as the ratio of Na⁺ concentration to Na⁺, K⁺, Ca²⁺ and Mg²⁺ concentration is another indicator which is widely used, where the concentrations of all ions are in mEq/L. The %Na values calculated for all of the stations were found lower than “60” (Figure 5).
higher quality water source, and different irrigation methods can be used to reduce toxicity and / or increase yields [20].

In addition to all this information, selected stations can be tracked by GIS in wet and dry seasons in order to ensure the proper use of water resources. It is possible to aim to protect water resources and make people reach these resources in a healthy way, to create a sustainable water management policy by means of different monitoring tools to be used for the monitoring of the area.

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EFFECTS OF WAVES ON LEVELS OF STABLE DISSOLVED OXYGEN CONCENTRATION IN COASTAL AREAS

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ABSTRACT

Coastal organisms need dissolved oxygen (DO) to live. Waters also accommodate plenty of living organisms. Accordingly, oxygen dissolution in water becomes essential in coastal life. The coast is separated into dry, wet and saturated areas in horizontal lines and from the water surface to underneath the sediment in vertical lines. Changes in the DO concentration were investigated at those lines. Experiments were performed in a wave channel that was 24-m long, 1-m wide and 1-m high. In the channel, the coast model had an average sediment diameter of 0.3 mm, a slope of 1/5 and a water depth of 60 cm. The static probe consistently measured the first and the last values as the same for certain levels in each experiment. This refers to no effect of waves on the concentration levels. After the static probe measurements, the DO concentrations were measured on seven vertical lines by moving vehicle at the coast model. Four of the vertical lines were out to sea, two were inland and one was at the shoreline. The DO concentrations in the water were measured above the sea bed and in the sediments on each vertical line. In each experiment, the probe was moved on a vertical line from the bottom towards the water surface for a wave height of H = 11 cm and a wave period of T = 1 s. Measurements made with a static probe and a moving probe were compared, and similar concentrations were found at a given level. All these trials indicated the significant relationship of wave breaks and oxygen dissolutions. We found three vertical lines sufficient in number for additional experiments to observe the different wave parameters.

The DO concentration was stable at the following depths below the sea bed (the distance in brackets is that out to sea from the shoreline; the negative value is an inland distance): 10 cm (1 m), 10 cm (0.75 m), 15 cm (0.5 m), 20 cm (0.25 m), 15 cm (0 m) and 20 cm (~0.25 m). Measurements made 0.25 m inland from the shoreline showed that the wave effect did not reach that far. By analysing different wave parameters, the measured wave breaks with constant T and increased H signified their displacement away from shoreline through the open sea. Furthermore, the sand bar’s offshore migration occurred with both increased T and H.

KEYWORDS:
Dissolved oxygen, Coastal ecosystem, Wave.

INTRODUCTION

A dissolved oxygen (DO) concentration of at least 5 mg/l is essential for a healthy aquatic ecosystem [1]. Because living organisms that need higher DO concentrations than this cannot live, few living organisms with high tolerance can continue to live there but not all competitive species can live [1]. Thus, if the ambient conditions deteriorate, the number of viable species can decrease but the number of adapted species can increase. Deteriorated conditions—in other words, conditions that are characterised by pessimism—are called pessimistic law. According to this law, deteriorated conditions decrease the number of species in that place and increase the number of adapted species [1].

Coastal ecosystems may be adversely affected if wastewater containing low levels of oxygen is discharged into coastal waters. Therefore, the effect of waves increasing the DO level in water is extremely important for coastal ecological life. Most attention is paid to DO levels in water because the DO level is the main indicator of organic pollution and biological variability in natural water resources [2].

Mild weather and eutrophication pose a risk of decreased DO levels in bottom waters, which is a dangerous situation for benthic communities. Normally, water is mixed by winds and tides. However, too much organic matter in the bottom water decreases the DO level and the number of species living there. When the DO concentration in the German Bight dropped below 4 mg/l in 1981, the macrofauna were initially unaffected but a number of deaths were observed in 1982 and 1983. With the decline of DO in 1983, the predominant species Amphipura filiformis died out and was replaced by the adapted species Amphipura filiformis and N. nifidosa. The drop in oxygen level that decreased the number of bottom living organisms was due to a phytoplankton explosion [3].

By contrast, any increase in oxygen on the sediment surface increases the diversity in benthic communities [4]. Small-diameter sediment inhibits oxygen penetration [5]. The depth to which DO penetrates sediment depends on the sediment diameter, the amount of organic matter and the amount of oxygen in the seawater. Oxygen can reach deeper into coarse-grained sediments than it can into sandy coasts such as those comprising silt and clay. Too much organic matter decreases the oxygen concentration because...
bacteria consume oxygen rapidly with organic substance [6]. As the depth to which oxygen is present in seawater decreases, the probability of oxygen at depth is also reduced. With increasing depth, the oxygen level (%) and the number of species decrease and the organic content of the sediment increases for N. Baltic supra-halocline (20–30 m) [6]. The intra-sediment oxygen levels at a depth of 10 m in the Aarhus Bight in Denmark are shown in Fig. 1.

Bubbles can transport oxygen from shallow sediments [7]. The water depth and barometric pressure may effect ebullition of gases from the sediment to the atmosphere [8]. Chipman et al. [9] noted that oxygen fluxes on a bottom surface are caused by turbulence.

FIGURE 1
Oxygen levels in deep-sea benthic layers [10].

In the present study, we used measured oxygen changes to determine the effect of wave depth along the slope to investigate the dynamic structure of the intra-sediment water under coasts that living organisms affect in combination with waves.

MATERIALS AND METHODS

Laboratory equipment. We used a wave channel that was 24-m long, 1-m wide and 1-m tall. It had glass sidewalls and a horizontal concrete floor. Irregular and regular wave series were formed in the wave channel by means of a wave generator driven by a hydraulic piston.

We used a DO measurement system in the experiments. An oxygen micro-sensor (Unisense, Denmark) was the negative electrode and a reduced Clark-type oxygen sensor (Fig. 2(a)). The OX500 sensor (an oxygen micro-sensor) has a tip diameter of 400–600 μm and can make accurate time-dependent DO measurements. As shown in Fig. 2(a), the oxygen sensor was mounted on the moving limb before measurements were made. To measure the wave height and period, we used a wave monitor and a computer-connected A/D converter card as shown in Fig. 2(b). Temperature and salinity were measured using a salinity and temperature meter comprising a TetraCon 325 probe connected to a WTW Multiline P4 universal metre.

Figure 2(c) shows the oxygen micro-sensor and the transducer to which the air-bubble device used to calibrate the micro-sensor was connected during the oxygen measurements. Calibration of the micro-sensor that measured the oxygen concentration in the intra-sediment water was performed by standard two-point calibration. The calibration process could be completed within 24 h, and so was performed before each measurement. Shown in Fig. 2(d)–(f) are the hood, the weighing scale (AG245; Mettler-Toledo, USA) with ±0.1g precision and the water-deionised device (Purelab UHQ II; Elga) that were used to prepare a zero-oxygen solution.

FIGURE 2
(a) Dissolved oxygen (DO) micro-sensor and transducer connected to limnimeter in wave channel; (b) wave monitor, A/D converter card and computer; (c) parts of oxygen micro-sensors; (d) hood; (e) weighing instrument; (f) device for deionising water.
Properties of sand. Sieve analysis was done in the hydraulic laboratory of Istanbul Technical University according to the Udden–Wentworth grain size classification [11]. In the experiments, the average grain diameter of the sediment in the channel was 0.3 mm [12].

Experimental setup. We determined the values of the wave height and period affecting the formation of the dynamic equilibrium profile under regular wave conditions. Waves were produced until their profile reached a dynamic balance (20 min). At the same time, the characteristics of the waves were determined by taking wave recordings.

At the end of each experiment, the channel was evacuated and the changes in slope profile, which was initially a flat surface, were drawn individually on transparent paper placed on the side window of the channel. The bar formation and erosion area were recorded, and the profiles were transferred to the computer. The volume and displacement of the bar were measured using the AutoCAD software [12]. The distance between the centre of the formed bar and the shoreline showed the breaking of the wave. The volume of the bar and erosion indicated the movement of solid matter. For the subsequent experiment, the slope was made smooth again.

The depth of the experimental setup for the channel was determined by the distance at which the wave no longer affected the oxygen concentration. The origin was the point 75 cm from the shoreline on the calm-water level. Measurements were taken at an average grain diameter of 0.3 mm, 1/5 slope (Fig. 2(a)). The calm-water level was set at 60 cm for all measurements.

Figure 3 shows the measurement positions located along seven vertical lines. The D5 vertical line was at the shoreline as designated by the calm-water level; the D6 and D7 vertical lines were farther inland from the shoreline. The distance between adjacent vertical lines was 25 cm and the measurement positions on each vertical line were separated by depth intervals of 5 cm. The first two characters in the name of each measurement position give the vertical-line number and the last two give the depth position, where ‘K’ means in the sediment and ‘S’ means in the water. Position K0 is on the sand surface (i.e. the sea floor), K5 is 5 cm below the sea floor and K10 is 10 cm below the sea floor. Position S5 is in the water 5 cm above the sea floor and S10 is 10 cm above the sea floor [13]. For each vertical line, the measurement positions to the water surface and to the deep are defined. For example, the completed measurements in water is 15 cm above the sea floor on vertical line D1. The reference numbers of the experiments carried out in the water and in the sediment are shown in Fig. 3.

RESULTS AND DISCUSSION

We collected wave-height data at 0.05-s intervals. Series of regular waves of height 10.9 cm and mean period 0.94 s were applied (Fig. 4). Vertical line D1 was 1 m out to sea from the shoreline. We buried the DO probe, waited approximately 2 h for a stable reading of DO concentration and then ran the wave generator for 20 min to form the beach profile. We then moved the probe upwards by 1 cm every 20 s and recorded the DO concentrations. Because of the waves, the DO concentration at the calm-water level differed from that at a depth of 30 cm (Table 1).

At 0.75 m out to sea from the shoreline, experiment D2 was started with the probe 10 cm below the slope surface and then moved upwards to the calm-water level. We measured the DO concentrations in 15 vertical increments over a time of 300 s. The probe recorded the DO concentration.
every 1 s, so 300 DO measurements were made over a distance of 150 mm. Thus, from ~100 mm to 50 mm, the DO was measured once per second at intervals of 0.5 mm. Figure 4 shows the variations of DO concentration with depth.

Experiments D1K10, D2K10, D3K15, D4K20, D5K15, D6K20, D7K15 and D7K20 were performed at depths of 10 cm, 10 cm, 15 cm, 20 cm, 15 cm, 20 cm, 15 cm and 20 cm, respectively, below the slope surface. Because the initial and final values of DO concentration were very close to each other, we reasoned that the measured depth was not affected by the waves. To confirm this, we performed experiment D5K20 (recall that vertical line D5 was on the shoreline) and observed no wave effect 20 cm below the slope surface [13].

Different wave parameters. The investigated values of wave height (H), wave period (T), wavelength (L) and wave height divided wavelength (wave steepness) and the derived values of Iribarren number (ζ), accumulated solids (D), movement of solid particles (S) and distance from the crest of the sand bar to the shoreline are given in Table 2. For waves with T = 1 s and H = 2.9, 8.3 and 11 cm, the distance of the crest from the shoreline was 39, 51 and 55 cm, respectively. For waves with T = 0.8 s and H = 9.7 and 10.1 cm, the distance of the crest from the shoreline was 44 and 45 cm, respectively. For waves with T = 1.2 s and H = 4.6, 12.8 and 13.1 cm, the distance of the crest from the shoreline was 8, 30 and 88 cm, respectively. Therefore, the wave breaks with the same T value moved through deep sea as H values increased.

We observed offshore migration of the sand bar as H and T values increased. The crest for H = 4.6 cm and T = 1.2 s was located 80 cm farther offshore from the crest for H = 13.1 cm and T = 1.2 s. In the latter case (H=13.1cm and T=1.2s) is shown in Fig. 5, the wave broke at D2 and the largest increases in DO levels were recorded at D3 and D4. Sediment deposition and transport were greater for this wave than for any other wave.

For waves with T = 1 s and H = 2.9, 8.3 and 11 cm, the distance of the crest from the shoreline was 39, 51 and 55 cm, respectively. For waves with T = 0.8 s and H = 9.7 and 10.1 cm, the distance of the crest from the shoreline was 44 and 45 cm, respectively. For waves with T = 1.2 s and H = 4.6, 12.8 and 13.1 cm, the distance of the crest from the shoreline was 8, 30 and 88 cm, respectively. Therefore, the wave breaks with the same T value moved through deep sea as H values increased.

**FIGURE 4**
Experiments performed by moving the probe along the vertical lines.

**TABLE 1**
Comparing DO (μg/l) experimental results obtained with a moving probe (M) and a static probe (S)

<table>
<thead>
<tr>
<th>Vertical line</th>
<th>D1</th>
<th>D2</th>
<th>D3</th>
<th>D4</th>
<th>D5</th>
<th>D6</th>
<th>D7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (m)</td>
<td>M</td>
<td>S</td>
<td>M</td>
<td>S</td>
<td>M</td>
<td>S</td>
<td>M</td>
</tr>
<tr>
<td>0.05</td>
<td>9.86</td>
<td>9.6</td>
<td>10.49</td>
<td>10.3</td>
<td>10.32</td>
<td>10.16</td>
<td>9.25</td>
</tr>
<tr>
<td>0.15</td>
<td>9.63</td>
<td>8.86</td>
<td>10.09</td>
<td>9.46</td>
<td>9.01</td>
<td>9.54</td>
<td>8.75</td>
</tr>
<tr>
<td>0.20</td>
<td>8.82</td>
<td>8.65</td>
<td>9.25</td>
<td>9.23</td>
<td>8.44</td>
<td>9.47</td>
<td>8.58</td>
</tr>
<tr>
<td>0.25</td>
<td>8.58</td>
<td>8.5</td>
<td>8.97</td>
<td>9</td>
<td>8.25</td>
<td>8.95</td>
<td>8.34</td>
</tr>
<tr>
<td>0.30</td>
<td>8.45</td>
<td>8.45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**FIGURE 5**
Air bubbles in the plunging wave.
CONCLUSION

We determined the depths at which the DO concentration was no longer affected by the waves. Experiments were performed down to the depth at which the initial and final concentrations of DO remained the same and were carried out at predetermined positions with a static probe. The relevant unaffected depths were as follows (the distance in brackets was the distance out to sea from the shoreline; the negative value means a distance inland): 10 cm (1 m), 10 cm (0.75 m), 15 cm (0.5 m), 10 cm (0.25 m), 15 cm (0 m) and 1 m. The DO values recorded 0.5 m inland from the shoreline showed that wave effect did not reach that far. By analyzing different wave parameters, we found that wave break displaced through the open sea when T was constant and H was increased. Moreover, when H and T were greater, we observed offshore bar migration from the experimental results.

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EVALUATION OF THE IMPACT OF POLLUTION IN THE GULF OF ANNABA (ALGERIA) BY MEASUREMENT OF ENVIRONMENTAL STRESS BIOMARKERS IN AN EDIBLE MOLLUSK BIVALVE DONAX TRUNCULUS

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ABSTRACT

Our study was aimed to assess the responses of three biomarkers, Acetylcholinesterase (AChE), Glutathione S-transferase (GST) and Malondialdehyde (MDA) in various tissues (gonad, mantle, digestive gland) of Donax trunculus (Bivalvia, Donacidae), a Mollusk Bivalve bioindicator of pollution in the Gulf of Annaba (Algeria). The samples were collected during the four seasons (winter, spring, summer, autumn) of 2016 year in three sites of Annaba gulf; Sidi Salem, site exposed to various sources of industrial and harbor pollution; Echatt, site subject to urban and agricultural wastes; and El Battah site distant from any source of pollution. The results showed a significant inhibition of AChE and induction of GST and MDA in individuals of Sidi Salem and Echatt as compared to El Battah with significant effects of both site and season. Indeed, the season effect was showed an inhibition of AChE and an induction of GST and MDA more pronounced during summer and spring compared to the other seasons. In addition, the comparison between tissues revealed a more marked response in gonad than mantle and digestive gland.

KEYWORDS: Donax trunculus, Gulf of Annaba, Biomonitoring, Biomarkers, Pollution.

INTRODUCTION

Marine environment and especially coastal zones receive a large amount of contaminants from urban, agricultural, harbor and industrial activities [1]. These contaminants cause increased pollution of marine ecosystems and have a significant toxic impact on the health of living organisms [2]. Thus, the environmental monitoring or biomonitoring, is an important tool to determine the link between the current levels of pollution and the effects observed in the field [3]. To monitor the health of coastal systems, sentinel organisms such as mussels (bivalves) have been identified as suitable candidates to indicate levels of contaminants in the coastal environment and were proposed to be bioindicator species of pollution [4]. Among those mussels, Donax trunculus, is a sentinel organism that is widely distributed in Mediterranean Sea and used in ecotoxicology studies for the assessment of marine Mediterranean environment [5, 6]. Their characteristics such as bioaccumulation capacity, adequate body size, continuous availability throughout the year, ease of sampling and high longevity, make D. trunculus particularly useful as bioindicator of contamination changes [7, 5]. In addition, D. trunculus is an economically important species that is consumed by local population of Annaba (Algeria) [8]. Annaba city, coastal zone located in the extreme Northeast of Algeria has been known these last years a development of industry, advances in agriculture, and important demography leading to an increase a sea water and littoral contaminations, which are coming from industrial, harbor, agricultural and domestic activities [8, 9].

The use of biological markers or biomarkers measured at different levels of the biological organization is an important tool to understand the possible biological adverse effects of pollutants on organisms [10]. Biomarkers contributed to the development of the effective early warning systems of environmental pollution [11]. While some biomarkers are believed to demonstrate exposure to a specific group of contaminants (e.g. Acetylcholinesterase) [12], others can be used to indicate the cumulative effects of exposure to complex mixtures of contaminants such as a Glutathione S-transferase [13], and also a biomarker of oxidative stress like Malondialdehyde [14].

The aim of this study was to evaluate the seasonal responses of three biomarkers of environmental stress, the biomarker of neurotoxicity, Acetylcholinesterase; the Phase II detoxification enzyme, the Glutathione S-transferase; and the Malondialdehyde, a biomarker of lipid peroxidation of cell membranes during an oxidative stress. The biomarkers were
determined in gonad, mantle and digestive gland of *D. trunculus*, collected from three sites of Annaba gulf (Algeria); El Battah, site considered to be a relatively clean, Echatt, site subjected to urban and agricultural wastes, and Sidi Salem, site located near several sources of pollution.

**MATERIALS AND METHODS**

**Presentation of sampling sites.** The gulf of Annaba is located in the Northeast of Algeria. It is limited by the Cap Rosa (8° 15' E and 36° 58' N) in the East and by the Cap Garde (7° 16' E and 36° 58' N) in the West. El Battah site (7° 56' E and 36°50' N), is located about 30 km to the East of Annaba far away from major human and industrial activities, and is considered to be a relatively clean site. Echatt (7° 52' E and 36° 49' N), is a site subjected to urban and agricultural pollution. However, Sidi Salem site (7° 47' E and 36° 50' N), which is located about 1 km to the East of Annaba city, is considered as a polluted area because it receives urban, harbor and industrial wastes (Fig. 1).

**Biological material.** Specimens of *D. trunculus* of standardized shell size (length 27 ± 1 mm) were collected during four seasons (winter, spring, summer, autumn) in 2016, from the three selected sites in the Annaba gulf. After sampling, *D. trunculus* were transported alive to the laboratory, and each species was quickly dissected and the tissues were removed (gonad, mantle, digestive gland) for biomarkers analysis.

**Acetylcholinesterase analysis.** The specific activity of AChE was determined according to the method described by [15]. The method is based on a coupled enzyme reaction involving acetylthiocholine as the specific substrate for AChE and 5,5'-dithio-bis-2-nitrobenzoic acid (DTNB) as an indicator for the enzyme reaction at 412 nm. Results are expressed as millimoles of thiocholine produced per minute per milligram of protein (mmol.min⁻¹.mg⁻¹ protein).

**Glutathione S-transferase analysis.** The GST activity was determined using the method described by [16] based on the GST catalyzing conjugation of reduced glutathione (GSH) with 1-chloro-2,4-dinitrobenzene (CDNB) as substrate. The increase in CDNB conjugate was monitored at 340 nm and the enzyme activity was expressed in millimoles CDNB conjugate per minute per milligram of protein (mmol.min⁻¹.mg⁻¹ protein).

**Malondialdehyde analysis.** The lipid peroxidation was estimated by quantification of MDA rates using method of [17]. The principle of the method was based on a measurement of the color produced during the reaction of thiobarbituric acid (TBA) with MDA. The rate of MDA was measured at 532 nm and expressed as mmol·mg⁻¹ protein.

**Protein quantification.** Protein concentrations in the supernatants were measured according to [18] by using bovine serum albumin as standard. Absorbances were measured at 595 nm wavelength.

**Statistical analysis.** The results were expressed as mean ± standard deviation (SD). Data were tested for normality and homogeneity of variance using Kolmogorov-Smirnoff and Levene's tests, respectively. The variation of each parameter among sites and between seasons and tissues was tested by a two-way analysis of variance (ANOVA), followed by Tukey's post-hoc test. All statistical analysis was performed using GraphPad Prism v6. The significant difference was defined at p<0.05.

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**FIGURE 1**
Location of sampling sites in the gulf of Annaba (Northeast of Algeria)
RESULTS AND DISCUSSION

Acetylcholinesterase activity. The results of seasonal variations of AChE in different tissues of D. trunculus are represented in Figure 2. The comparison between the three sites revealed a significant (p < 0.001) inhibition of AChE activities in individuals of Sidi Salem, then Echatt as compared to El Battah for the three tissues. The significant effect (p < 0.001) of season was observed with an inhibition of AChE more marked in summer and spring than autumn and winter seasons. The comparison between the tissues with ANOVA and Tukey's post-hoc test showed a significant (p < 0.001) inhibition of AChE at the gonad as compared to mantle and digestive gland (Table 1).

Acetylcholinesterase (AChE) is essential for the normal functioning of the central and peripheral nervous system. It is well known as a modulator to regulation of acetylcholine release from synaptic system. The AChE activity is used as biomarker of neurotoxic compounds in aquatic organisms. It is a target site of inhibition by organophosphate and carbamate pesticides [12] and other chemical compounds like heavy metals and hydrocarbons [19]. In our results, we reported the inhibition of AChE in D. trunculus of polluted sites compared to reference site. The inhibition of AChE was reported in the same species collected in polluted site in Tunis gulf as compared to reference site [5]. [20] have reported an inhibition of AChE in bivalve Scrobicularia plana, in polluted site as compared to reference site in France. In the other studies, AChE was reported to be inhibited in bivalve exposed to acute and subacute environmental contaminants including metals [1]; PAHs [13] and pesticides [21].

Glutathione S-transferase activity. The activities of GST (Fig. 3) recorded in D. trunculus, were increased significantly (p < 0.001) in organisms collected from polluted site of Sidi Salem, followed by Echatt as compared with El Battah site, this in all tissues. The season effect revealed a significant increase (p < 0.001) of GST activities more marked in summer and spring as compared with autumn and winter. Indeed, significant effects (p < 0.001) of both site and season were determined by ANOVA test. The activity of GST in tissues revealed a significant (p < 0.01) higher activities in gonad as compared with mantle and digestive gland tissues (Table 1).

The glutathione S-transferase (GST), a phase II detoxifying enzymes, represents one of the most basic mechanisms for detoxification system in marine organisms against a broad range of xenobiotics found in their environment [22]. Besides GST presents peroxidase activity, it is considered an indirect antioxidant, since it can eliminate a products of reactive oxygen species (ROS) generated during an oxidative stress [13]. Our results are agreeing with [23] and [7] who have reported an induction of GST in D. trunculus collected in polluted sites as compared to reference site. [13] have showed a significant induction of GST in mussels transplanted in harbor areas. An induction of GST has been reported in Mytilus galloprovincialis caged in impacted polluted areas in Sicily (Italy) as compared to reference site [24]. [25] have observed an induction of GST in gills of zebra mussels collected in sites along the Seine river (France) compared to reference site and a clear relationship between GST activities and amounts of bioaccumulated metals and PAHs was established. Induction of GST has been reported by recent studies in bivalves exposed to chemicals compounds like M. galloprovincialis, exposed to nickel [1]; Venerupis decussata, affected by permethrin and
FIGURE 3
Seasonal specific activity of Glutathione S-transferase (mmol.min⁻¹.mg⁻¹ protein) in mantle (M), gonad (G) and digestive gland (DG) of D. trunculus, sampled in three sites of Annaba gulf during 2016 (mean ± SD; n= 5). Means followed by same small case letters are not significantly different at p > 0.05 between sites in each tissue and season; while means followed by same capital letters are not significantly different at p > 0.05 across seasons within each tissue and site (Tukey’s post hoc test, p < 0.05).

FIGURE 4
Seasonal rates of Malondialdehyde (mmol.mg⁻¹ protein) in mantle (M), gonad (G) and digestive gland (DG) of D. trunculus, sampled in three sites of Annaba gulf during 2016 (mean ± SD; n= 5). Means followed by same small case letters are not significantly different at p > 0.05 between sites in each tissue and season; while means followed by same capital letters are not significantly different at p > 0.05 across seasons within each tissue and site (Tukey’s post hoc test, p < 0.05).

anthracene [26]; Ruditapes philippinarum exposed to benzo-a-pyrene [27] and Dreissena polymorpha treated by the cocaine metabolite benzoylcegonine [28].

Malondialdehyde rates. The site effect showed that rates of MDA were significantly increased (p < 0.001) in D. trunculus, from polluted sites of Sidi Salem and Echatt compared to El Battah site (Fig. 4). The results of MDA revealed a significant effect (p < 0.001) of season with higher rates in spring and summer than in winter and autumn (Fig. 4). Furthermore, the tissue effect showed a significant (p < 0.001) higher values in gonad followed by digestive gland, then mantle (Table 1).

Oxidative stress is one of the most significant effects caused by xenobiotics and can be estimated by measuring the concentration of biomarkers of antioxidant activity or a products of damages like malondialdehyde (MDA) a biomarker of lipid peroxidation of polyunsaturated fatty acids of cell membranes [29]. Oxidative stress reflects an imbalance between pro-oxidants and antioxidants who favor a production of reactive oxygen species (ROS) responsible of cellular and/or molecular damages like deterioration of cell membranes (lipid peroxidation), DNA damage and enzyme inactivation [30]. The present study showed an increase of MDA levels in D. trunculus from the polluted sites of Sidi Salem and Echatt as compared to El Battah. Increased in MDA concentrations were also detected in bivalve Unio tenuis exposed to polycyclic aromatic hydrocarbons [31], Unio gibbus exposed to insecticide cypermethrin [32] and Corbicula fluminea submitted to
herbicides Atrazine and Roundup [33]. Other studies have reported an increase of MDA in mussels subjected to environmental stress such as M. galloprovincialis exposed to nickel and thermal stress [1]; Elphidium complanatum exposed to zinc oxide nanoparticles [34]; Aulacomya atra under the effect of several metals [35] and Lasmigona costata submitted to wastewater effluents [14].

Season and tissues effects. Seasonal cyclic changes are well known to influence mussel’s physiology [36]. Due to their intertidal region habitat, mollusks bivalve can be sensitive to seasonal variations of temperature. Thus, a change in seasonal abiotic factors can affect the bioavailability of pollutants to living organisms [37]. The differences between seasons revealed in our study were probably triggered by the seasonal variation of environmental factors in seawater, such as, elevated temperature [38]. This may explain our results as we noted a strong inhibition of AChE and a significant induction of GST and MDA in the summer and spring seasons where temperatures are high and may contribute to the concentration of pollutants. [39] were reported that higher reproductive activity and seasonal temperature can modulate and cause an increase in the antioxidant defenses in the digestive gland of Perna perna, with higher levels of GST. The same result has been reported in Mytilus edulis exposed to seasonal effect of temperature [37].

### TABLE 1

Tissues effect of biomarkers response (AChE, GST, MDA): two-way analysis of variance (significantly difference at p< 0.05)

<table>
<thead>
<tr>
<th>Biomarkers</th>
<th>Tissues</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>AChE</td>
<td>Gonad</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mantle</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td></td>
<td>Digestive Gland</td>
<td></td>
</tr>
<tr>
<td>GST</td>
<td>Gonad</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mantle</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td></td>
<td>Digestive Gland</td>
<td></td>
</tr>
<tr>
<td>MDA</td>
<td>Gonad</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Digestive Gland</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td></td>
<td>Mantle</td>
<td></td>
</tr>
</tbody>
</table>

In most cases, the chemical substances enter organism tissues and subsequently induce the toxic effects. Stress syndrome in bivalve mollusks can lead to shell defects, recession of the mantle and deterioration of the epithelium in the digestive gland and gonad [40]. Some studies have reported that contaminants in polluted water enter mollusks mainly through the epidermal cells of the gill and mantle, then transported by circulatory system to other organs within the mollusk, such as digestive gland, adductor muscle and gonad [41]. These tissues have been used as a target for studying the biomarker responses to several environmental stressors [36]. We have been found in our study a tissues effect with an AChE inhibition and an induction of GST and MDA more marked in gonad than mantle and digestive gland. The gonad appear more sensitive because it ensures the reproduction of the species and it is more sensitive during the spring and summer, seasons of sexual activity of D. trunculus [42].

**CONCLUSION**

The results of the present investigation suggest that D. trunculus is a suitable organism for use as bioindicator species. In addition, it is a sensitive non-target species that could be used in biomonitoring of Annaba gulf in Algeria based on biomarkers assays. The difference recorded between the sites is related to their level of exposition to pollution in the gulf of Annaba. Indeed, Echatt site receives waste of urban and agricultural origin while the Sidi Salem site is located near a factory that produces pesticides. Furthermore, this site receives heavy metals and other pollutants from harbor activities and urban discharges.

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DETERMINATION OF CHEMICAL CHARACTERISTICS AND QUALITY ASSESSMENTS OF STREAMS BY GIS IN TUNCELI REGION, TURKEY

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ABSTRACT

The optimal use of a stream water is mainly depend on its physical and chemical characteristics which are play a significant role in classifying and assessing the water quality. Anion and cation balance are the most important parameter of these processes.

Aim of this study is the evaluation of the physical and chemical features of surface waters located in the eastern part of Turkey. The physical and chemical parameters measured in collected water samples from 23 stations which are distributed along the streams in the province of Tunceli were used as the main data sources. Some of the measured parameters in the samples are; temperature, pH, EC, DO, anions, cations and then calculated Na% and SAR.

In results, while the temperature is changing from 18 to 25°C, the pH values are changed between 6.1-8.7. Piper trilinear was also conducted indicating that all the surface waters, which are high quality and unpolluted fresh water, contain various physicochemical compositions of natural fresh waters. Especially, Sodium Adsorption Ratio (SAR meq/L) was indicated that these waters can be easily used for irrigation and agricultural activities, except 6 sampling stations. It has been determined that the there is a connection between mineral composition of the surface waters and geological formations found at the depth of origin. In addition, the Munzur and Pulumur Streams are special ecological areas. These areas and their endemic species should be protected under the national and international conventions with together flora- fauna and special water resources for natural ecological balance.

KEYWORDS:
Pulumur Stream, Munzur Stream, irrigation indicators, SAR, Tunceli, Turkey.

INTRODUCTION

Natural freshwater rivers are used particularly to meet the water requirements and needs of people in their daily lives [1-2]. The quality of water, river soils and basins is the most important factor that affects all the creatures living in the same ecosystems. Considerable amount of polluting matters, which influence aquatic environments, discharges into the fresh water environments because of anthropogenic activities. Therefore, the river ecosystem is among the most affected areas where agricultural and domestic wastes discharge directly or indirect into the water body. Nowadays, the anthropogenic pollution effects can be observed from the bottom sediment to the surface water at different levels, and water quality parameters can be used to assess the monitoring of this pollution [3]. Likewise, all over the world, freshwater resources and their water quality are among the most important issues for drinkable water resources and their irrigation.

The sampling area of this study has a specific natural quality not only for Turkey, but also for the Earth ecosystems. The Munzur Stream is the primary resource for drinking, agricultural activities, irrigation and fishing in the province of Tunceli. The Munzur Stream is particularly the living area for many unique life forms such as endemic plants and fishes species (e.g. trout with red spotted) [4-5]. The Munzur National Park, which is also a part of the Munzur Stream, was declared a “national park” in 1971 and with its area of 42,000 hectares. “The Munzur Valley National Park", which is one of the biggest national parks in Turkey, is located 8 km far from Tunceli city center and extends over the valley to the Munzur Mountains [6]. The Munzur Mountains rising to 3300 meters in the north are surrounded by the Mercan Stream and the Munzur Stream valleys [7]. It is very important to understand the human impact on the water resources in order to be able to detect the water quality ecological status of this protected area and its rich biodiversity of both flora and fauna. Although the management of the water sources is classified under a single title, it contains a wide scope of issues such
as water use for agricultural, civil and industrial areas, water quality, water usage regulations, and international law and health regulations. This study aims to evaluate the physical and chemical characteristics of the surface waters located in the province of Tunceli, the eastern part of Turkey, via statistical tools and geographic information systems (GIS) as well as to detect the irrigation potentials of the surface waters. It is well known that, the use of geographic information systems (GIS), remote sensing and related mapping techniques for spatial planning is one of the most popular methods to help decision makers to plan, implement and regulate issue related to water resources management such as zoning and multi sectoral development of a water resource.

MATERIALS AND METHODS

Study area. This study was carried out on the Munzur and Pulumur Streams and their many tributaries. The Pulumur Stream, which is about 70 km long, has its origin near the district of Pulumur in Tunceli. The Munzur Stream and Pulumur Stream merge in the city center of Tunceli and create the Uzuncayır reservoir. The Munzur Stream takes its source from the Ziyaret Hill on the Munzur Mountains and flows in the west-east direction in the middle of the Ovacık plains [7].

The Munzur Stream, which collects the waters of Havaçor, Mamasuğaşı, Şamusuğaşı, Kabușağı, Nakościği, Haçılı, Mercan, Merho and Kalan flowing through various directions, merges with the Pulumur Stream in the central district and then flows into south, the Keban Dam Lake. Tunceli has 3114 hm³ water potential annually since it receives an annual average of 1000 mm rainfall covering 80% of its territory with oak and various herbs. A large portion of this water flows through the Munzur, Pulumur and the Peri Streams. The Munzur and the Pulumur Streams reach 86 thousands m³ flow rate in average per second after merging in the city center [4].

The general view of the streams and sample stations is presented in Figure 1. The point 23 among the sample stations was selected to represent the nature of the river ecosystems since it is close to the main road in consideration of the relationship between the water sources dry and wet seasons.

The characteristics of the selected stations can be defined as follows. The stations numbered 1-4 are the streams that discharge into the Munzur Stream in an area where the settlement is more limited compared to the other stations. The required agricultural irrigation for the income of the people is mostly met from the stream water. In the areas of the stations 1 and 2, mostly walnut and mulberry trees prevail. The stations 6-9 constitute the Pulumur Stream into which the stations 10-13 discharge. In this area, the region of the station 6 is defined by beekeeping activities. In the stations 7-8, grain-based agricultural activities prevail. The station 9, on the other hand, is a touristic area which is used as a "beach" by local people

FIGURE 1
The sampling stations of the Munzur and Pulumur Stream in in the province of Tunceli.
during summer. The stations 10-11-12-13 take place in an area where the settlement is fewer and agriculture near the water resource is very limited (Figure 1). The area between the stations 14-23 is defined as the Munzur Stream. The stations 14-17 take place in an area where the settlement engaged in stockbreeding is intense. The area of the station 18 can be defined as a picnic area which is very popular for people during summer. The stations 19-23 take place in an area which includes intense thermal springs and is claimed to have fossil beds by people. The station 21 is out of use due to military reasons, yet a special station about which people rumor that "mining" activities can be carried out.

**Water Quality Parameters.** The water quality parameters have been measured in dry period of the year as determination of instant impacts on the river ecosystems. Physicochemical properties of the water samples, such as temperature, pH, Dissolved Oxygen (DO), electrical conductivity (EC), were measured in situ with the SigmaProbe. In addition, the concentrations of changes in main parameters of anions and cations were observed. The ionic properties of the water samples were determined by Dionex ion chromatography ICS 1100 with Degas and Chromelone SE for anions and cations respectively. An analytical AS9-HC (4 x 250 mm) column and AG9 guard column (4 x 50 mm) with ASRS-300 (4 mm) suppressor was used in ion-exchange mode in order to determine the water-soluble anions (sulphate-SO$_4^{2-}$, phosphate-PO$_4^{3-}$, nitrate-NO$_3^{-}$, nitrite-NO$_2^{-}$, chloride-Cl$^-$, fluoride-F$^-$, bromide-Br$^-$). The eluent was 9mmol Na$_2$CO$_3$ and the flow rate of the eluent was 1.0 mL/min. For the determination of water-soluble cations (lithium-Li$^+$, sodium-Na$^+$, potassium-K$^+$, magnesium-Mg$^{2+}$, calcium-Ca$^{2+}$, ammonium-NH$_4^+$), an analytical CS16 column and a CG16 guard column (both 3 x 50 mm) with CSRS-1 (2 mm) suppressor was used in a chemical mode. An eluent of 10 mM methane sulfonic acid was used at flow rate of 1.0 mL/min. The injection volume was 25 µL for all detection runs. Peak identification was confirmed based on a match of the ion chromatograph retention times with the chromatographs of the standard samples. The limit of detection was determined as mean equal to 3 times standard deviation of the field blank value, corresponding to a range of 0.008 to 0.023 ng/L for the anions and to a range of 0.021 to 0.083 ng/L for the cations. The limit of quantification was between 0.028 and 0.078 ng/L for the anions and between 0.063 and 0.252 ng/L for the cations.

**Geographic Information Systems (GIS).** Many different definitions are done for GIS, most agree that GIS is computer-based systems whose incorporated software are capable of using georeferenced data for a range of spatial analyses and outputs. Most of the GIS software have been designed to answer different types of spatially related queries and analysis, such as network analysis, temporal analysis, modeling etc. [3,8-10]. All kinds of measurements and analysis can be performed and stored in GIS. In this study, selected stations and measured parameters were visualized by means of GIS and maps were produced. Obtained results related to stations were presented in Figure 2, 3, and Figure 4.

**Statistical Analysis Tools.** Statistical analysis of some parameters was carried out to describe the general physicochemical characteristics preliminarily, and the results are used for calculation of SAR and %Na index. After that the Piper diagram was plotted for understandable of irrigation quality of stream water. The Piper diagram includes two trilinear diagrams, one for anions (on the lower right) and one for cations (on the lower left) [11-12]. For each sample, the information from each trilinear diagram is projected up into the central quadrilateral. Therefore, each sample will plot in each frame of the Piper, once representing cations, once representing anions, and once representing the combination. Sample points with similar hydrochemistry tend to cluster together in the diagram [13]. Hydrochemical facies were distinguished by equal 25% increments.

**RESULTS AND DISCUSSION**

This article touches upon the physical and chemical characteristics of stream waters located in the province of Tunceli, the east part of Turkey. Sample results taken during the sampling period are presented in Table 1.

The pH values of the streams vary between 6.1 and 8.7 and DO concentrations vary between 5.8-11.4 mg/L. The highest dissolved oxygen values measured during the whole sampling period (9.8-11.4 mg/L) belong to the stations 10-11 and 13 where the waters discharge into the stream. Similarly, the area of these stations is a water area which can be defined as "the 1st class water quality" in terms of the other measured parameters since the pH values are between 7.6 and 8.2. In the stations 8 and 9, on the other hand, the pressure felt particularly during summer due to the intense usage and the grain-based agriculture explain the DO values measured between 5.2 and 7.0. The lowest DO (5.2-6.1 mg/L) and pH (6.1-6.9) values measured during the sampling period belong to the stations 15-16-17 where settlement, agricultural and stockbreeding activities are extensive (Table 1). The findings of previous studies results report that additional agriculture and stockbreeding might have apparent effects on the fresh waters of streams as contaminated waters. These effects particularly include
TABLE 1

Physical and chemical analysis results (mg/L) and the measured Sodium Adsorption Ratio (SAR). Percent Sodium (%Na) and Hardness (HD) values of the water samples.

<table>
<thead>
<tr>
<th>Stations</th>
<th>pH</th>
<th>EC</th>
<th>Cations (mg/L)</th>
<th>Anions (mg/L)</th>
<th>SAR</th>
<th>%Na</th>
<th>HD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ca$^{2+}$</td>
<td>Na$^{+}$</td>
<td>Cl$^{-}$</td>
<td>SO$^{2-}$</td>
<td>NO$^{3-}$</td>
</tr>
<tr>
<td>1</td>
<td>7.3</td>
<td>218.0</td>
<td>26.23</td>
<td>11.94</td>
<td>45</td>
<td>97.7</td>
<td>0.27</td>
</tr>
<tr>
<td>2</td>
<td>7.3</td>
<td>413.0</td>
<td>24.16</td>
<td>10.94</td>
<td>56</td>
<td>109.6</td>
<td>0.36</td>
</tr>
<tr>
<td>3</td>
<td>7.9</td>
<td>352.5</td>
<td>30.20</td>
<td>12.71</td>
<td>35</td>
<td>436.5</td>
<td>0.22</td>
</tr>
<tr>
<td>4</td>
<td>7.3</td>
<td>318.9</td>
<td>46.88</td>
<td>13.72</td>
<td>56</td>
<td>114.8</td>
<td>0.30</td>
</tr>
<tr>
<td>5</td>
<td>8.5</td>
<td>340.2</td>
<td>50.87</td>
<td>12.49</td>
<td>47</td>
<td>1659.6</td>
<td>0.29</td>
</tr>
<tr>
<td>6</td>
<td>7.5</td>
<td>493.0</td>
<td>43.46</td>
<td>12.17</td>
<td>98</td>
<td>186.2</td>
<td>0.54</td>
</tr>
<tr>
<td>7</td>
<td>7.0</td>
<td>468.2</td>
<td>43.21</td>
<td>11.75</td>
<td>109</td>
<td>55.0</td>
<td>0.54</td>
</tr>
<tr>
<td>8</td>
<td>8.0</td>
<td>397.1</td>
<td>36.75</td>
<td>14.77</td>
<td>84.6</td>
<td>57.5</td>
<td>3.18</td>
</tr>
<tr>
<td>9</td>
<td>7.0</td>
<td>383.2</td>
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<td>15.27</td>
<td>83.4</td>
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<tr>
<td>10</td>
<td>8.2</td>
<td>207.0</td>
<td>36.26</td>
<td>5.88</td>
<td>0.97</td>
<td>776.2</td>
<td>0.49</td>
</tr>
<tr>
<td>11</td>
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<td>310.3</td>
<td>35.82</td>
<td>5.63</td>
<td>12.44</td>
<td>0.96</td>
<td>645.7</td>
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<tr>
<td>12</td>
<td>7.6</td>
<td>205.0</td>
<td>69.31</td>
<td>16.22</td>
<td>14.21</td>
<td>239.9</td>
<td>2.83</td>
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<tr>
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<td>317.6</td>
<td>61.79</td>
<td>6.53</td>
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</tr>
<tr>
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<td>136.9</td>
<td>59.22</td>
<td>6.54</td>
<td>12.74</td>
<td>2.11</td>
<td>446.7</td>
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<tr>
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<td>413.5</td>
<td>64.31</td>
<td>6.68</td>
<td>10.60</td>
<td>2.12</td>
<td>776.2</td>
</tr>
<tr>
<td>18</td>
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<td>385.3</td>
<td>52.69</td>
<td>6.72</td>
<td>11.96</td>
<td>2.14</td>
<td>467.7</td>
</tr>
<tr>
<td>19</td>
<td>7.8</td>
<td>299.6</td>
<td>69.04</td>
<td>16.04</td>
<td>12.76</td>
<td>27.37</td>
<td>354.8</td>
</tr>
<tr>
<td>20</td>
<td>8.2</td>
<td>315.7</td>
<td>43.83</td>
<td>8.46</td>
<td>16.94</td>
<td>1.21</td>
<td>871.0</td>
</tr>
<tr>
<td>21</td>
<td>7.6</td>
<td>249.7</td>
<td>63.22</td>
<td>27.33</td>
<td>12.07</td>
<td>4.92</td>
<td>218.8</td>
</tr>
<tr>
<td>22</td>
<td>8.7</td>
<td>233.1</td>
<td>36.98</td>
<td>5.93</td>
<td>13.77</td>
<td>0.58</td>
<td>2570.4</td>
</tr>
<tr>
<td>23</td>
<td>8.6</td>
<td>270.0</td>
<td>70.11</td>
<td>16.64</td>
<td>12.63</td>
<td>27.48</td>
<td>2138.0</td>
</tr>
</tbody>
</table>

HD : Hardness (mg/L as CaCO$^3$)  H: High  M: Middle  S: Soft

physicochemical parameter changes such as decreased dissolved oxygen and increased biochemical oxygen demand and nutrient concentrations. The DO value 5.9 mg/L and the pH value 7.1 pH in the station 18 define the use of this area as a special and sacred meeting point and picnic area for people.

Nitrite, nitrate and ammonium nitrogen-containing compounds were found to be appropriate in the Pulumur and Munzur Streams in terms of the water quality criteria levels. Sulfate is an indicator of pollution caused by industrial wastes, agricultural activities and domestic waste in various aquatic environments. A higher value of sulfate content than 250 mg/L indicates higher contamination [13].

The studies conducted in the same field emphasize that the area is under the threat of contamination particularly due to domestic wastes [3, 8, 10]. Some prospective and negative changes were observed in the water quality of the Munzur River especially due to domestic waste, directly discharged into the Munzur River and pollution threat due to the absence of a treatment facility [14]. On the other hand, it is hard to have an opinion about the future projection of the quality water resources since the geographic structure and current status of the research area prevent long-term sampling.

According to the hardness (mg/L as CaCO$_3$) results calculated at the equivalence of CaCO$_3$ regarding the parameters measured at the stations; the station 11 was found to have very hard water (H: 150-300). The frequent finding of the Mollusca

The data are visualized via GIS in order to better comprehend the physical and chemical analysis results of the water samples taken from the stations. Figure 2 and 3 present the change in anion and cation visuals. Sodium adsorption ratio (SAR = Na$^+$ / (Ca$^{2+}$ + Mg$^{2+}$) / 2) is used as the primary indicator for the evaluation of irrigation, where the concentrations of all ions are in meq/L. According to the “International SAR Standards” classification; SAR < 3: suitable for irrigation; SAR 3 – 9: use may be restricted and SAR > 9 unsuitable for irriga-
tion. Figure 4 presents the GIS visual of the SAR values.

According to the values of the stations, it was found that the values in the stations 8, 9, 12, 14, 19 and 23 are too high for irrigation. It can be seen that irrigation is possible in 11 stations where SAR parameter is lower than 3. The sodium percentage (%Na = Na+ / (Na+ + K+ + Ca2+ + Mg2+)× 100) expressed as the ratio of Na+ concentration to Na+, K+, Ca2+, and Mg2+ concentrations is another indicator widely used, where the concentrations of all ions are in mEq/L. The %Na values calculated for all stations were found lower than “60” [16].

A Piper trilinear diagram presents that all the surface waters are characterized by the dominance of anion-cation (Figure 5). The samples display that various chemical compositions and water samples generally are in Na-SO4, Na-HCO3, Na-Cl, Ca-SO4, Ca-HCO3 type [11-13]. The piper diagram shows the relative concentrations of six to seven ions in solutions, in this case, the cations are Ca, Mg, and Na+K, and the anions are Cl, SO4, CO3, and HCO3.

In most of the natural waters, these ions make up 95 to 100% of the ions in a solution. As presented in Figure 4, there are no dominant cations and anions for most water samples, except for the 7 samples that are dominated by Na+ and 9 samples dominated by HCO3-. The ion balance (% balance error = (Σcations-Σanions)/(Σcations+Σanions) in mEq/L) was calculated between 0.19 and 0.91, which refers to the normal range. The error should be <10% for surface waters, and the calculations for all stations are below this value [11].
Munzur- Pulumur Streams

FIGURE 5
Piper diagram of the Munzur and Pulumur Streams

The bioindicator species and water quality parameters of the stations were studied. Makrozoobenthos are bioindicators for water quality, and streams can be classified by the presence of these bioindicators. Regarding the benthic community as a whole number of taxa, the proportion of sensitive taxa and the presence of them in both streams indicate a good to very good ecological quality [18]. According to Gültekin et al. [19], the mean abundance of EPT-Taxa amounts to 87% of the total benthic abundance in the Munzur Stream, and it is 50% in the Pulumur Stream. Prosobranchs are often sensitive indicators of water quality due to widespread geographic distribution and require contact with the aquatic environment [20-21]. Dissolved oxygen levels in the water are among significant parameters for the abundance of especially Prosobranchia species [14]. *Anatolodrominacola gloeri*, *Bithynia tentaculata* were collected from both streams.

In various studies carried out by different researchers, endemic species and their tissues were determined, with a view to using them as potential future biomarkers of fresh waters quality. Fish are largely being used for the assessment of aquatic environment quality and as such can serve as bioindicators of environmental pollution [22]. In both streams, it is an important finding that oxidative stress biomarkers didn't reach a significant value in fish [23].

CONCLUSION

In the present study, three principal results were found and interpreted in parallel with the previous studies. These results can be suggested for the further researches to be carried out in the research.

In this study, the lack of industrial facilities nearby the agricultural and residential area is considered to have a great positive contribution to the sustained water quality. The high quality irrigation water by the Munzur and Pulumur Streams and the usage of groundwater are the most important factors in respect to the intensification of agricultural activities, increase of agricultural output and agricultural product range, density of population and habitation on the Munzur Basin. However, if the current anions and cations balance continues with the same trend, it may pose a threat for fresh water reservoirs in the future.

In addition, the Munzur and Pulumur Streams are special ecological areas. These areas and their endemic species should be protected by means of national and international conventions along with their flora- fauna and special water resources for natural ecological balance.

The standardization of methodologies to access water quality studies should be the next step for comparing results of the different studies. In addition, technology improvement is also necessary for increasing the water resources management.

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SESSION VII
NEW AND EMERGENCY TECHNOLOGIES FOR ENVIRONMENTAL AND HEALTH APPLICATION
INTRODUCTION

Ionic liquids (ILs) have many potential applications in diverse fields because of their distinctive properties. The increasing interest in ILs in industrial and academic sectors is mainly due to recent demonstration of the close relationship between the compound structure and their properties, which could be modified for different purposes. ILs contain an inorganic anion and an organic cation, and different cations and anions could potentially be combined to create ILs for specific applications as, for example, bioseparation agents of active compounds (with special importance in petroleum industry), drug delivery systems, lithium ion batteries, paint additives, lubricants for high temperatures and low pressures and absorbents for heat pump devices [1-5]. More than 30000 imidazolium-based ILs have already been included in the CAS database, and it has been estimated that more than $10^{12}$ different ILs could be synthesized [4]. The vapour pressure of ILs is very low [4], and in some contexts ILs are considered innocuous because they are not harmful to the atmosphere. They are often referred to as "green fluids". However, their innocuousness has still to be proven, as the fact that they do not act as atmospheric toxins does not mean they are also harmless to aquatic and terrestrial environments. Furthermore, in case of accidental spillage, water-soluble ILs would quickly reach the soil surface in the surrounding area, as well as the deeper layers of soil and surface and subsurface waters. Moreover, given the large number of combinations of anions and cations and the lack of knowledge about the effects of IL structure on toxicity, it is not possible to generalize about the potential impact of ILs on the environment.

The ionic liquid 1,3-dimethylimidazolium dimethylphosphate ([C$_1$C$_1$Im][DMP]) has many potential applications and is already used as, e.g., a lubricant-hydraulic fluid, an absorbent in heat pumps, a heat transfer fluid (in heaters or freezers) and a surfactant [3,5-6]. However, the toxicity of this IL to the soil remains to be investigated. This is especially important as soils with different characteristics, particularly in relation to organic matter (OM) and pH, may react differently to the presence of any exogenous compound [7].

Ecotoxicology testing is often carried out with agricultural plants because these are sensitive to environmental stress and pollution [8-9]. Seed germination and seedling development are crucial and particularly sensitive stages of plant development. If plants are grown in contaminated soil, the seeds and roots will be in direct contact with the pollutants, thus potentially affecting germination and/or plant development [10-11]. Moreover, toxicity tests based on seed germination and elongation can be carried out with a wide variety of plant species that are readily available and also germinate and grow rapidly [8-9].

The aim of this study was to investigate the toxicity of [C$_1$C$_1$Im][DMP] in soil by analyzing the germination and early development of seeds of one forest and one agricultural plant species in two different types of soil spiked in different compound concentrations.

KEYWORDS:
Ionic liquids, 1,3-dimethylimidazolium dimethylphosphate, ecotoxicity, soils, seed germination, seedling development

MATERIALS AND METHODS

The ionic liquid 1,3-dimethylimidazolium dimethylphosphate, [C$_1$C$_1$Im][DMP], (99% pure, analytical grade) was purchased from IOLITEC (Heilbronn, Germany). The main chemical and structural characteristics of this IL are summarized in Table 1. The plant species selected for the study were garden cress (Lepidium sativum L.) and eucalyptus (Eucalyptus globulus Labill.). Both plants are suitable for use in ecotoxicity studies because of their abundance, high rate of germination and rapid, early development [8, 12-13].
### TABLE 1
Main characteristics of the ionic liquid [C1C1Im][DMP]: CAS identification number, structure, molecular mass and purity

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Short Name</th>
<th>[CAS Number Id.]</th>
<th>Structure</th>
<th>Mn (g mol⁻¹)</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-dimethylimidazolium dimethylphosphate</td>
<td>[C1C1Im][DMP]</td>
<td>[654058-04-5]</td>
<td><img src="image" alt="Structure" /></td>
<td>222.18</td>
<td>&gt; 0.99</td>
</tr>
</tbody>
</table>

### TABLE 2
Main characteristics of the soils used in the study

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH H₂O</th>
<th>pH KCl</th>
<th>C₄ (%)</th>
<th>N₄ (%)</th>
<th>C/N</th>
<th>Fe₂O₃ (%)</th>
<th>Al₂O₃ (%)</th>
<th>Texture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agricultural</td>
<td>5.44±0.05</td>
<td>4.23±0.06</td>
<td>2.22±0.03</td>
<td>0.20±0.00</td>
<td>11</td>
<td>0.89±0.02</td>
<td>0.46±0.01</td>
<td>Loamy</td>
</tr>
<tr>
<td>Forest</td>
<td>4.45±0.02</td>
<td>3.51±0.03</td>
<td>11.91±0.08</td>
<td>0.58±0.00</td>
<td>21</td>
<td>0.95±0.01</td>
<td>1.08±0.01</td>
<td>Sandy-loam</td>
</tr>
</tbody>
</table>

Two soils destined for different use (agricultural and forest), containing different amounts of OM of different quality, were selected for the study. At each site, 10-15 subsamples of the A horizon (0-10 cm) were obtained at random points and pooled in the field to produce a composite sample. The samples were transported in isothermal bags to the laboratory where they were sieved (< 4 mm). A sub-sample of each soil was air-dried for determination of general soil properties, and the remainder was stored at 4 °C until required for the germination and early seed development tests.

Spiked soil samples were prepared from different solutions of [C1C1Im][DMP] by diluting the compound in water, to yield final concentrations of 0, 1, 2.5, 5, 10, 25, 50, 75 and 100%. The soils were spiked with 0.1 ml of each of these solutions per gram of soil (equivalent to doses of 0, 0.47, 1.2, 2.4, 4.7, 11.7, 23.3, 35 and 46.7 g of [C1C1Im][DMP] kg⁻¹ dry soil), and water was added to reach 80% of the water holding capacity of the soil. The spiked soils were maintained at 20 °C for three days before the start of the planting experiment to maximize the contact between the soil and the IL. Quadruplicate samples were prepared in plastic pots for each treatment and plant species. Nine seeds of each plant species were placed on the surface of each replicate spiked soil. The pots containing soil were placed for 16 days in a growth chamber at 25 °C, ambient humidity of 60% and light/dark cycles of 16/8 h. Water was added daily to replace the water lost by evaporation. Seed germination (%) was determined during the incubation period. Diverse plant growth parameters (length, number of leaves and dry weight) were measured 16 days after the seeds were sown.

An air-dried sub-sample of each soil was analyzed to determine the following physical and chemical soil properties, by previously described methods [14]: pH in water (1:2.5 w:v, soil:water ratio), pH in 1 M KCl (1:2.5 w:v, soil:solution ratio), total carbon (dichromate oxidation in acid medium), total nitrogen content (Kjeldahl procedure), amorphous Al₂O₃ and Fe₂O₃ [15], particle size distribution (Robinson pipette, with Calgon® as dispersant) and texture. The mean values and standard deviations of these properties in the agricultural and forest soils are shown in Table 2.

### RESULTS AND DISCUSSION

**General soil data.** Both the agricultural and the forest soil were strongly acidic, with pHs in KCl of respectively 4.23 and 3.51. As expected, the total organic carbon content was lower in the agricultural soil (2.22% C₄) than in the forest soil (11.91% C₄). The total nitrogen content was also different in the agricultural soil (0.20% N₄) and in the forest soil (0.58% N₄). The amorphous Fe₂O₃ and Al₂O₃ contents of the agricultural soil were respectively 0.89 and 0.46, and the corresponding values in the forest soil were 0.95 and 1.08%. The texture of the agricultural soil was loamy while the forest soil was sandy-loam (Table 2).

**Plant parameters.** [C1C1Im][DMP] had a negative effect on the germination of garden cress and eucalyptus seeds. Thus, for doses of 11.7 (11.7 g of [C1C1Im][DMP] kg⁻¹ dry soil) and higher the germination percentage for seeds of both species in both soils was zero, except for garden cress in the forest soil (20% germination) (Figs. 1 and 2). In general, for doses lower than 11.7 g of [C1C1Im][DMP] kg⁻¹ soil the germination percentage (%) for both garden cress and eucalyptus was higher in the forest soil than in the agricultural soil (Fig. 1 and 2).
Germination of both species was very variable, depending on the type of soil and dose of IL, and was the same, higher or lower than in the control (non-spiked) soil. Thus, in some samples spiked with doses of up to 2.4 g of [C1C1Im][DMP] kg\(^{-1}\) or eucalyptus in the agricultural soil spiked with 0.47 g of [C1C1Im][DMP] kg\(^{-1}\) (almost 15% higher). On the other hand, the response of the samples of garden cress in the forest soil spiked with doses of 0.47, 1.2 and 2.4 g of [C1C1Im][DMP] kg\(^{-1}\) was very similar to that of the control sample, and germination was only lower in the soil spiked with 4.7 and 11.7 g of [C1C1Im][DMP] kg\(^{-1}\). In previous studies, large reductions in germination were also observed in response to the presence of other imidazolium-based ILs such as [C4C1Im][BF4], [C3C1Im][NTf2] and [C4C1Im][OTf] [16-17], although in these cases the seeds were in direct contact with the IL solutions. Germination of the cress seeds also tended to take longer as the dose of [C1C1Im][DMP] increased. This effect was not observed for eucalyptus seeds, probably because germination is slower (Figs. 1 and 2).

As germination of both species was inhibited in soils spiked with doses of 11.7 g of [C1C1Im][DMP] kg\(^{-1}\) soil and higher, seedling elongation at these doses was also zero. For doses of 4.7 g of [C1C1Im][DMP] kg\(^{-1}\) or lower, and although the germination was stimulated in some samples, there were no differences in the pattern of elongation between the two soils or the two species. Thus, for doses of between 0 and 4.7 g [C1C1Im][DMP] kg\(^{-1}\) soil, the elongation of garden cress and eucalyptus seedlings decreased as the dose of the IL increased (Fig. 3). The [C1C1Im][DMP] had a stronger effect on the elongation of eucalyptus compared to that
garden cress, especially in the forest soil; elongation of both plant species, especially garden cress, was higher in the agricultural than in the forest soil (Fig. 3).

Studzinska and Buszewski [12] also observed that the development of garden cress in soils spiked with three different 1-alkyl-3-methylimidazolium chloride ILs was hindered above a certain concentration of IL, and the effect was dose-dependent. The highest doses of IL killed the plants. The authors attributed the effect to the uptake of IL by plants via the primary cell wall, which is semipermeable and thus allows the passage of small molecules. They attributed the toxic effect to the salts that formed inside the plants. A similar process may have occurred in the present study, as [C₃H₇Im][DMP] should be able to pass through the cell wall pores in both garden cress and eucalyptus (pores of diameter between 5 and 10 nm) [18]. However, it is difficult to explain the stimulatory effect of doses of IL up to 2.4 g kg⁻¹ soil on germination of both garden cress and eucalyptus. The addition of nutrients such as N or P with non-toxic doses of the IL might be expected to have a stimulatory effect; however, this should affect elongation rather than germination and is unlikely to explain the enhanced germination.

Other researchers have also observed that the effects of ILs vary depending on the type of soil, attributing this to the OM content and suggesting that the OM will adsorb the IL and thus prevent it appearing in the soil solution and thereby reducing its toxicity [12]. A similar relationship between OM content and toxicity has also been observed in Galician soils contaminated with different organic compounds, such as chlorophenols [19]. However, the pH and OM also interact, exerting an effect that is regulated by the pK of the chlorophenol [7]. Likewise, in the present study, the OM content did not appear to be the only factor regulating the negative effects on plant development. If this was the case, the elongation would be greater in the forest soil than in the agricultural soil, which is the opposite to what was observed. It is impossible to clarify which factors determine the toxicity with the data available, and further studies should be carried out with different types of soil in order to clarify this point.

The presence of [C₃H₇Im][DMP] reduced the number of leaves in the garden cress and eucalyptus plants in both soils. This effect increased with the dose of [C₃H₇Im][DMP] (Fig. 4). The garden cress grown in the agricultural soil had statistically significant higher number of leaves than the garden cress grown in the forest soil, whereas the eucalyptus plants grown in both types of soil had very similar numbers of leaves.

Taking into account that the presence of [C₃H₇Im][DMP] reduced the elongation and the number of leaves of both plants species, the different doses of [C₃H₇Im][DMP] were also expected to
cause a decrease in the dry weight of the plants, as was observed. Thus, the decrease in dry weight increased with the dose of [C$_3$C$_1$I][DMP] (Fig. 5). The decrease in the dry weight of garden cress was greater in the forest soil, while the effect on eucalyptus was similar in both types of soil (Fig. 5).

The [C$_3$C$_1$I][DMP] also caused chromatosis, i.e. the leaves and stems of the garden cress and eucalyptus plants grown in both agricultural and forest soils spiked with doses above 1.2 g of [C$_3$C$_1$I][DMP] kg$^{-1}$ soil underwent a colour change. The colour of some of the leaves of the garden cress gradually changed to violet, while the colour of the eucalyptus plants changed to light green or dark yellow (Image 1). This phenomenon, like the reduction in seedling size at the highest doses of IL, has been related to chlorosis [12], a plant disease caused by a lack of chlorophyll and/or macronutrient deficiency. It was suggested that the ILs present in the soil solution may block nutrient transport to the plant, or that ILs are preferentially absorbed by the plants, thus causing a deficit of macronutrients in the plants [12].

The results of the present study demonstrate that the presence of [C$_3$C$_1$I][DMP] has harmful effects on the germination of *L. sativum* and *E. globulus* seeds and on the early development of these plants.

Although ILs are often considered to be less toxic than other chemical substances and even non toxic to the atmosphere, the findings of this study show that the IL [C$_3$C$_1$I][DMP] strongly affects the early development of plants and that the effect depends on both the dose of IL and on the soil characteristics. Therefore, before this compound can be used as lubricant-hydraulic fluid, absorbent in heat pumps, heat transfer fluid, surfactant, and/or other purposes, further studies should be carried out to investigate its toxicity to soils and plants and, if necessary, its presence in the environment should be regulated.

**CONCLUSIONS**

Doses of 4.7 g of [C$_3$C$_1$I][DMP] kg$^{-1}$ soil and higher had a negative effect on the germination and development of both garden cress and eucalyptus, regardless of the soil type.

Doses up to 2.4 g of [C$_3$C$_1$I][DMP] kg$^{-1}$ soil stimulated the germination of *L. sativum* and *E. globulus* seeds.

The reduction in elongation, dry weight and number of leaves of *L. sativum* and *E. globulus* plants increased with the dose of [C$_3$C$_1$I][DMP] added to the soil.

Doses of [C$_3$C$_1$I][DMP] above 1.2 g kg$^{-1}$ caused chromatosis in garden cress and eucalyptus plants, a phenomenon resembling chlorosis and probably caused by blockage of nutrient transport or the preferential absorption of ILs by plants, and the consequent reduction of macronutrients in the plant tissues.

**ACKNOWLEDGEMENTS**

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SESSION VIII
ENVIROMENTAL ECONOMIC POLICY AND EDUCATION
DETERMINING PHARMACEUTICAL WASTE GENERATION CAPACITY IN ISTANBUL AND THE HABITS RELATING TO PHARMACEUTICAL WASTE DISPOSAL

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Department of Environmental Engineering, Faculty of Civil Engineering, Yıldız Technical University, Istanbul 34220, Turkey

ABSTRACT

It has been known today that the increase in medicine consumption has been causing certain environmental and economic problems. To solve these problems, it is useful to know the amount of waste medicine generation and the volunteerism of users in removing waste medicines.

In this study, habits of people living in Istanbul relating to the use of medicine and pharmaceutical waste generation and their willingness to the efforts aiming reducing pharmaceutical waste, which might accordingly be generated, as soon as it has emerged. As a result of the survey, drug usage was determined to be 6.14 boxes per year per person, while unused drugs were found to be very high at an annual average of 5.40 boxes. 60% of unused medicines were discarded while 24% of these were stored at home and only 7.7% were returned to pharmacies.

KEYWORDS: Pharmaceuticals disposal, Istanbul, wastewater

INTRODUCTION

Turkish pharmaceutical industry has been growing fast in parallel with increasing health necessities. It reached 9.1 billion $ with the annual growth of 5.4% in 2011 while it was 6.64 billion $ in 2005. According to the data of 2010, Turkey accounts for 11% of the world medicine market along with South Korea, Australia and Poland [1]. In Turkey and in the world, both human and animal drugs have mostly been thrown away without being used due to many reasons as for past expiration date or for being left unfinished. Unused medicine amounts are increasing day by day depending on the increase in medicine consumption. It is known that pharmaceutical waste has been spread over a wide range [2-4]. Medicines, which have been thrown away without being used and accumulated in the environment, indicate insufficient medical services and an action in the disposal of medicines that is improper for the environment. Then, this evidences a risk of living in an unhealthy environment for people and natural life. The most important unknown issue about medicines is the rate of accumulation and sediment production when they interfere the environment as a pollutant. The medicine disposal and the relevant amount is important for two aspects. Firstly, it is important for the use of more accurate and comprehensive data modeling for being able to predict concentrations or amounts of active pharmaceutical ingredients (APIs) introduced into the environment. Secondly, understanding the proper medicine prescription is important for correct medicine use, changing the habits of using wrong or unnecessary medicines and therefore, the decrease of intoxication causing disease and death [5]. There are two basic reasons for not disposing of unused drugs immediately: medicines piled up at home beyond control of household and intentional storage. The consumers, who accumulate the medicines willingly, for wait sufficient reasons for their opinions before discarding them.

The essential objective of this study is to determine the amount of the medicines disposed without being used in Istanbul. Other objectives of the study include determining level of the users’ awareness relating to adverse effects caused by the disposal of pharmaceutical waste to the environment, finding preference of the users relating to the medicine recall locations and learning figures relating to willingness to pay for the relevant surcharge, which might be levied. In general, data collected in Istanbul could be used for the prediction of the pharmaceutical waste in Turkey.

MATERIALS AND METHODS

A survey including 19 questions was prepared to determine the amounts of used and discarded unused medicines; the change of these amounts depending on the socio-economic conditions like age, education and income and the formation of such a program all across Istanbul. Questions, which aim to determine respondents’ habits relating to medicine consumption like how much medicine they use, what they do with unused medicines, the amount of used medicines and prediction about the amounts of disposed medicines, were asked to the respondents in
addition to the socio-economic questions. Furthermore, the degree of participation to a program, which may be established for collection of unused medicines, and the degree of willingness to pay for such programs were determined. Awareness and willingness were analyzed by using the obtained data.

Contingent valuation (CV) surveys consisting of such type of questions do not produce certain data but they are used in making predictions. Therefore, this should be kept in mind that only estimated figures can be found and assumptions can be made by using the data obtained here.

Study Area. The population of Istanbul, with individuals of 12,915,158, accounts for approximately 17.8% of population of Turkey. It consists of approximately 6,292,000 males and 6,283,000 females [6]. Gonullu and Arslankaya [7] reported the amount of pharmaceutical waste as 1.2 kg per person/day in general across Istanbul. There are 200 hospitals, 15,291 doctors in Istanbul. 1 doctor is available for 817 patients. The number of pharmacies in Istanbul is approximately 550.

Survey design and data collection. The survey study was conducted with 496 persons in total. The survey questions were printed and delivered to 418 persons and recorded as written documents. The rest 78 persons received the same survey questions, via e-mail. Support was provided by the website under the name of www.anketix.com for this survey conducted over the internet. The surveys were conducted between the dates of November 16, and December 30, 2009 and in different districts of Istanbul to ensure diversification. The youngest respondent was 15-year old.

Statistical analysis. The data collected via the survey were entered into SPSS statistics program one by one to create a dataset. SPSS statistics program was chosen because it is a practical and useful program professionalized on statistical analyzing methods being able to produce the required graphics and to conduct the required analyses. The obtained data was analyzed through the SPSS Statistics program and comparisons were made in the form of graphics and cross-tables.

RESULTS AND DISCUSSION

Socio-economic results. Socio-economic status of the respondents (Table 1) shows age average, distribution according to gender, average educational status and average monthly income, and minimum and maximum values are figures of the variables, which have been previously defined for the statistics program. According to Table 1, numbers of male and female respondents are almost equal. This ratio includes the same values for demographic structure in Istanbul in general [6]. The average age of the respondents is around 32.7-year. Average salary was determined as around 2,100 Turkish lira (TL) per month. Salary of almost 50% of the respondents was determined as 1,000-2,000 TL while it was determined that approximately 30% of them received 1,000 TL or less in a month. Average educational status reached up to university level and 46% of the respondents were university graduates while educational level was high school or less for 40% of them. Only 14% of the respondents had a master degree or a higher degree.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Mean</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gender (Male = 1)</td>
<td>0.512%</td>
<td>0.501</td>
</tr>
<tr>
<td>Age (years)</td>
<td>32.700</td>
<td>14.100</td>
</tr>
<tr>
<td>Income (annual-TL)</td>
<td>2,100,000</td>
<td>1,195,000</td>
</tr>
<tr>
<td>Education:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elementary or High school</td>
<td>0.400%</td>
<td>0.490</td>
</tr>
<tr>
<td>Undergraduate or Graduate</td>
<td>0.600%</td>
<td>0.490</td>
</tr>
</tbody>
</table>

Pharmaceutical waste generation depending on its causes. Certain reasons, which have been defined as major for disposing unused medicines, were added to the survey due to possible benefits for medical staff. Many medicines become waste due to the reasons like improper medicine prescription and improper medicine use as mentioned before. The most effective way to prevent it would be to investigate the issue from all aspects to find medicines, which has been improperly prescribed and consequently, thrown away without being used, along with the relevant reasons. If doctors write their prescriptions by considering the medicines disposed without being used and prefer more effective medicine curing, disposed medicine amounts would decrease automatically. The most rational solution for settling pharmaceutical waste problem would be to prevent the problem before it emerges. According to the present study, the users are aware of the fact that waste medicines are harmful even though they do not have detailed knowledge about the harms of waste medicines. Approximately, 62% of the respondents stated that they had heard previously that waste medicines were harmful for human health and the environment; however, 38% of them said that they had never heard about anything about pharmaceutical waste.

This study results indicate that major reason for medicine disposal is expired medicines with a rate of 42.1% (Table 2). Although some parts of these expired medicines have been used, medicines in significant number have been disposed in a completely unused form. Partially used or unused medicines are the ones that are usually quit depending upon the re-
cupation of the patients in the sequence of treatment. Especially doctors, pharmacists and other medical staff should recommend effective medical treatment for their patients and should warn the patient that medicines must be used in a way that is required. However, the present practice consists of only writing how many times the relevant medicine should be taken on the prescription or the box. It can be possible to ensure more effective medicine use if medical staff are trained on this matter to improve their approach to patients. Then, the amount of medicine disposal would automatically be reduced.

**TABLE 2**

**Reasons for pharmaceutical waste generation**

<table>
<thead>
<tr>
<th>Reasons for pharmaceutical waste generation</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expired medicines</td>
<td>42.11</td>
</tr>
<tr>
<td>Patients healed up</td>
<td>33.01</td>
</tr>
<tr>
<td>Unwillingness of the patient to use the medicine</td>
<td>8.13</td>
</tr>
<tr>
<td>Ineffective medicines</td>
<td>8.13</td>
</tr>
<tr>
<td>Doctor's decision for replacing a medicine with another one</td>
<td>7.18</td>
</tr>
<tr>
<td>Death of the patient</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Other reasons for medicine disposal are the medicines failing in achieving the expected result, doctor’s decision for replacing a medicine with another one, incorrect diagnosis or ineffective medicine prescription. These reasons accounting for 15.31% (Ineffective medicines + Doctor’s decision for replacing a medicine with another one) cause the fact that medicines become waste due to incorrect diagnosis although they are functional. Therefore, correct diagnosis is very important. More diligent behaviors of medical staff would ensure that this waste disposal potential of 15.31% become usable.

Those who participated in the survey were asked about the types of medicines they had disposed without using them and the answers were summarized in Figure 1. According to Figure 1, mostly disposed of medicine group consists of pills, which are generally antibiotics. These pills have a high usage ratio like 52%. Medicines in the form of spray and mouthwash have a usage ratio of 20% while the ratio is 10% for ointments and creams. A study conducted in Izmir indicated that most frequently disposed medicines are antibiotics, painkillers and rheumatic medicines respective [8].

These studies conducted on types of pharmaceutical waste indicate that there are an extravagance and irregularity in the use of antibiotics in Turkey. The data for 2007 shows that the amount of antibiotic emission used in Turkey in a year is approximately 700 tons [9]. Antibiotics which are life saving when they are used in the required amount and in the required form, threaten public health and the environment in our country. Such high usage ratio for antibiotics in our nation, especially in comparison with other countries, points out the incidences needing more detailed further studies. Action should be taken by investigating such incidences and the relevant data to improve usage of antibiotics and other pills.

Participants in the questionnaire were asked to answer some questions such as; how many boxes of medicines were purchased in a year, where medicines were removed, general awareness about medicine pollution, the maximum amount they would pay for a medicine disposal program, and volunteering for participation in such a program. The answers given for the question (On average, how many boxes of medicines do you use per year?) are shown in Table 3. Table 3 shows medicine use per person (as purchased medicine) are averagely 6.14 boxes in a year. This generation rate to almost 5 boxes for young people while it increases for old people depending on chronic and persistent diseases.

![FIGURE 1](image)

**TABLE 3**

**Medicine amounts in box purchased by the age groups**

<table>
<thead>
<tr>
<th>Age interval</th>
<th>Purchased medicines (box)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15-24</td>
<td>5.02</td>
</tr>
<tr>
<td>25-34</td>
<td>4.92</td>
</tr>
<tr>
<td>35-44</td>
<td>7.21</td>
</tr>
<tr>
<td>45-54</td>
<td>6.46</td>
</tr>
<tr>
<td>55-64</td>
<td>7.00</td>
</tr>
<tr>
<td>&gt; 65</td>
<td>14.00</td>
</tr>
<tr>
<td>Total</td>
<td>6.14</td>
</tr>
</tbody>
</table>

The answers to the question (Can you give a number about the yearly figure for medicines that are not used in your home / family?) are given in Table 4. According to the present study, 5.40 unused or partially used boxes of medicine are disposed annually per person. An interesting point, when the two data
are compared, is the actual medicine usage amount, briefly 6.14 are purchased but only 0.74 box of medicine is used. The results of the survey show that waste generation ratio is very high in medicine usage. This may be interpreted as the fact that patients never use the purchased medicines and dispose them or dispose them after they use some of the medicine. The young population has a higher share in pharmaceutical waste generation while this production rate decreases in the age group older than 65-years but never be minimized (Table 4).

Pharmaceutical waste generation ratio is very higher in young people compared with old people. This may be interpreted in two ways. The first one is the fact that young people is not sufficiently careful in the use of medicine. The other reason may be the medicine amounts in boxes higher than the required.

TABLE 4
Disposed unused medicine amounts in box by the age groups

<table>
<thead>
<tr>
<th>Age interval</th>
<th>Unused and/or expired medicines</th>
</tr>
</thead>
<tbody>
<tr>
<td>15-24</td>
<td>5.70</td>
</tr>
<tr>
<td>25-34</td>
<td>5.43</td>
</tr>
<tr>
<td>35-44</td>
<td>4.39</td>
</tr>
<tr>
<td>45-54</td>
<td>6.34</td>
</tr>
<tr>
<td>55-64</td>
<td>4.88</td>
</tr>
<tr>
<td>&gt; 65</td>
<td>4.31</td>
</tr>
<tr>
<td>Total</td>
<td>5.40</td>
</tr>
</tbody>
</table>

Habits relating to medicine disposal and sensitivity/awareness for a collection system. Waste medicines are generally disposed in various ways by users without caring potential hazards. Whereas expired medicines must be collected and destroyed as dangerous waste in a way as specified in the Regulation on Control of Medical Wastes. But the regulations cover only expired medicines existing in pharmacies and medicine storages. The regulations have no sanction to be imposed on people or other bodies. However, it is explicitly seen that expired medicines are required to be classified and destroyed as hazardous waste. Traditional methods in disposal of these pharmaceutical wastes classified as hazardous waste containing many risks are seen in Figure 2. As seen explicitly in Figure 2, the most frequently preferred disposal method is to throw medicines into the trash. These medicines in the trash are dissolved in a mixture with other wastes in solid garbage storage fields after a while and enter into surface or groundwater through leachate. Unused medicines are thrown into trash enter waterways through the same way with those excreted out of the body after used. These data show that, medicine concentrations encountered in receiving aquatic environments are sourced from medicines excreted out of the body after used and thrown into sewage or trash without being used.

More effective medicine use may prevent medicine pollution, more or less, caused by medicines excreted out of the body after used; however, it is possible to prevent pollution by 100% caused by unused medicines thrown into trash/sewage. As seen in Figure 2, almost 60% of medicines are thrown into trash.

FIGURE 2
Methods used in disposal of unused pharmaceutics

Unused medicines are piled up at homes of 24% of the respondents while just 7.7% of the respondents prefer the only proper way in disposal of unused medicines by returning their unused medicines to pharmacies. Another approach is to throw medicines stored at home in trash when they are expired. The ratio for stored at homes intentionally or unintentionally is 24%. Considering that these medicines are thrown into trash in the future when they are expired, it is seen that 84% of the purchased medicines become waste. Therefore, the amount of waste medicines required to be taken back has a vital importance for the environment.

Due to lack of any recall campaign or an event for raising awareness is not available in Istanbul in general or any location across the country, it cannot be hoped medicine users return unused medicines to pharmacies. Although there is a campaign, which has been held in Izmir [10], naturally, it has local effects. First of all, events should be held across the nation for advertising and raising awareness. Then, it may be hoped users return unused medicines to pharmacies. Thus, it may be ensured that this waste, which is very harmful for the environment, is treated as a hazardous waste.

In this study, the respondents were asked to recommend alternatively suitable fields for pharmaceutical wastes so that they do not cause damages on the environment. Thus, the recall location, which has been considered most practical by the users and consequently, might produce highest efficiency, was determined. The results of the survey that pharmacies are the most preferred locations for waste medicine collection with a ratio of 67%. The respondents’ choice is an expected status. The simplest reason for
it is the fact that pharmacies in high numbers are available in every district in Turkey. Furthermore, considering continuous contact with pharmacies, programs intended for raising awareness and advertising may be implemented by pharmacies easily and a recall action can be sustained in these locations with high efficiency. In case of establishment of a center for waste medicines, the most important factor would be willingness of users for participating in such a campaign. It was found that support to be provided by the respondents to such a program would be high. As seen in Figure 3, 63% of the respondents agreed to bring unused medicines to medicine recall locations.

![Figure 3](image-url)

**FIGURE 3**
Willingness to participate in a program relating to pharmaceutical waste recall

32.5% of the respondents, who were uncertain, may be convinced through campaigns aiming to raise awareness. Therefore, advertising and training are important as much as projects for waste collection. It has been mentioned above that medicines become useless due to inefficient or incorrect use. To resolve this issue, other methods in addition to proper prescription and use should be produced. Refill practice and reducing amounts inside medicine packages are the methods seen across the world. A study conducted according to the available models in practice may ensure that patients purchase the required amount and pay less for them and moreover, medicine pollution is prevented before it emerges. Accordingly, 63% of the respondents gave positive answers to our question about refill or less medicine amount in packages. A majority of people would welcome practice of such system if it is demanded.

**Willingness to Pay for Environmentally Pharmaceuticals Waste Management.** Recall programs are necessary for human health and the environment; however, it needs a benefit-cost analysis like all environmental programs. Although such benefit-cost analysis cannot be conducted herein, some comparisons were made to optimize the benefit to be achieved and willingness of the respondents to pay a surcharge for establishment of such program was researched to find an average amount.

Surcharge that the respondents might be willing to pay for a medicine recall program was defined as 0.10 TL, 0.25 TL, 0.50 TL,” and 1 TL. Willingness to pay for each prescription was found as 0.22 TL (Figure 4). Assuming that 75% of users use prescribed medicines and minimum two prescriptions are written for each one in a year, if a surcharge of 0.22 TL is taken for each prescription after second one, total amount is predicted as minimum 2.13 million TL for Istanbul. Considering that this amount is collected to be spent on recycling services across Turkey, contribution to Turkish economy would be minimum of 12 million TL.

![Figure 4](image-url)

**FIGURE 4**
Surcharge- willing to pay

A project similar to our study is in practice in Izmir City of our nation. According to the data obtained through the interviews conducted with the managers of the project in practice relating to collection and disposal of waste medicine in Izmir, a budget of 240,000 TL is enough for disposal cost of waste medicine collected from one third of Izmir (1.75 million people). Thus, the surcharge of 0.14 TL per person was enough to execute the project. It was determined that the total sum to be obtained through a surcharge of 0.22 TL per person would be enough for the budget required for recycling services.

**CONCLUSION**

By means of this present study, with a data set provided from 496 individuals, it was provided to estimate many topics such as the perception of waste medicines throughout Istanbul, medicine consumption, participation and willingness to pay for waste medicine disposal program.

In consequence of the survey, average annual medicine use per person is 6.14 boxes. While this rate is lower in young people, it is increasing due to permanent and chronic diseases in the elders. Another remarkable data in the analysis of annual medicine use is the amount of unused medicines. Accordingly, the unused or partially used medicine amount is approximately 5.40 boxes per year.

Other important data obtained from this study was the willingness of the individuals to pay the sur-
charge for the waste medicine program. It was determined from the survey data that the average amount is 0.22 TL for each prescription beginning from the second prescription. Consequently, this amount would provide a sufficient participation value in discarding waste medicine.

Disposal of wastes that may be included in natural environments and recycle of them in appropriate conditions is important in terms of the environment. Raising awareness of the public about the disposal of unused medicines, making the public understand the harm to nature and living beings should be applied as government policy.

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ESTIMATION OF HOUSING SALES PRICES BY MULTIPLE LINEAR REGRESSION ANALYSIS (MLRA) FOR THE DETERMINATION OF ECONOMICALLY EFFECTIVE EARTHQUAKE BASED URBAN TRANSFORMATION LOCATIONS

Busra Kartal¹, Hayri Hakan Denli

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ABSTRACT

The aim of the study was to examine both physical and locational variables that might affect the house prices and estimate a price function using a multiple linear regression analysis and visualize the results by thematic maps. This study utilizes a large data set representing 390 home sales in Umraniye County in Istanbul/Turkey, which are researched with their physical and locational variables. The identification of the variable affecting the price of houses in the district with a population of approximately 600000 is expected to provide a significant contribution to the house marketing. Physical variables are chosen as the age, number of rooms, size, floor number of the apartment and the floor that the house is positioned in. Locational variables are chosen as to the nearest hospital, school, park and the police station distances to the house. The effects of the variables on the house prices are examined both by multiple linear regression analysis and hedonic regression analysis models, which are both stochastically analysis methods. The regression parameters found from both models leads almost to the same results.

KEYWORDS:
Urban transformation, regression analysis, value map

INTRODUCTION

In Turkey, although the first study of the estimating house sales prices has been investigated in 1981, there isn’t satisfying study in this area until now. A house may be valued for a certain price based on quantitative characteristics such as the age of the house, the number of rooms, and the garage space or qualitative factors such as the geographical location, school districts, environmental quality etc. Therefore, the price of a house relative to another will differ with various quantity native for one house against to another [1]. The fact that if the house is old, it effects the price of the house negatively. Among the reasons that the age of the house may have an adverse effect are; having an old appearance, facing the danger of demolition or having an unaesthetical pleasing. Valuation of the property and reflecting the actual value of the property to the tax is one of the most important economic resources of the developed countries [2]. In this manner, the resulted variables adopted from the regression analysis will provide approximate real and actual house prices. After the regression analysis, thematic maps are composed of the variables which are; age, price and price per square meter for the county. Because that the locational variables may also affect the real value of the property such as the physical characteristics, the most significant of the thematic maps is the price per square meter map. A different practice has been developed from the thematic maps by searching the ability of using price per square meter map in urban transformation practices. Marking old buildings in the price per square meter map made a different and new interpretation to determine the buildings to which should be given priority during an urban transformation in the county. This area is under the risk of earthquakes disaster because of the North Anatolian Fault. Houses older than 15 years are marked on the price per square meter map to gather a list of both old and expensive square meter apartments. With the help of this list, the priority should then be given to the selected (expensive) ones to support the economy of the country by reason of an earthquake loss. As this action has been performed for the prevention of the economy we might call this urban transformation as earthquake based urban transformation.

MATERIALS AND METHODS

The identification of factors affecting the price of houses in the county (Figure 1) with a population of approximately 600000 on an area of about 4500 hm² is expected to provide a significant contribution to the house market.
Due to the North Anatolian Fault, Istanbul had many destructive earthquakes throughout its history. The last earthquake struck Kocaeli in 1999 where nearly 17000 people died and 66000 houses damaged. After the earthquake, investigations of the damaged structures showed that the houses built before 1999 are of poor quality and poor performance [3]. The Turkish government published a new guide for Earthquake regulation in 2007, to prevent buildings with poor performance concrete structure. There exists no report about the structures, which are under the threat of the earthquakes. Therefore an earthquake based urban transformation should be performed in order to rebuild them into stronger structures. According to the Figure 2, there are five degrees of earthquake zones in Istanbul. Umraniye is situated in first and second degree earthquake zones.

When the age range of houses in Umraniye county is examined (Figure 3), it is seen that 67% of the buildings in the study area are new, whereas 17% are old and they were built before the new Earthquake regulation guide has been published [4]. There were no value maps made for the house prices in the county so far. New approaches have been developed for creating the value maps. Price per square meter map has been created additionally (Figure 4).

From Figure 4, now a list for both older and expensive houses can be gathered. Using this list, the priority could be given to the selected higher valued old houses to support the economy of the country during an earthquake loss. We may call this urban transformation as an earthquake-based urban transformation.

Additions to natural disasters, another problem affecting the human life are the environmental problems after earthquakes. The primary environmental problems that arise due to the destructions by earthquakes are construction waste induced by the demolished houses, chemical leakage occurring due to the damage of factories which are making chemical production and medical waste occurring due to the damage of hospitals; these problems threaten life of alive people significantly. Environmental pollution differs due to the affecting activities, besides its importance, it depends on the type, amount and area where they are disposed. During ordinary times solid waste problem catches attention of the public as well as all other environmental problems, but because of its important environmental effects, it gains currency after earthquakes which are extraordinary situations [5].

RESULTS AND DISCUSSION

The data used for analysis in this study is provided from www.hurriyetemlak.com website and totally 390 houses around Umraniye are evaluated due to the physical and locational factors [6]. The examined variables for all houses are listed below:

- House Price (Y) (Dependent variable)
• Size in m² (X₁)
• Age (X₂)
• Number of floors (X₃)
• Floor number of house positioned in (X₄)
• Number of rooms (X₅)
• Distance to the nearest school (X₆)
• Distance to the nearest hospital (X₇)
• Distance to the nearest police station (X₈)
• Distance to the nearest park (X₉)

The impact of these parameters on the price derived from the current real estates in sales was achieved by performing the Excel Packet - Multiple Linear Regression Analysis (MLRA) Tool.

**TABLE 1**

<table>
<thead>
<tr>
<th>Regression Statistics</th>
<th>Multiple R</th>
<th>0.778</th>
</tr>
</thead>
<tbody>
<tr>
<td>R Square</td>
<td>0.605</td>
<td></td>
</tr>
<tr>
<td>Adjusted R Square</td>
<td>0.596</td>
<td></td>
</tr>
<tr>
<td>Standard Error</td>
<td>8.890</td>
<td></td>
</tr>
<tr>
<td>Observations</td>
<td>390</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 explains the model summary. The R square is the ratio of the total variation that explains how Y values are affected by the X variables and must be between zero and one, with a higher value indicating more explanatory power by the independent variables [7]. Since the adjusted R-square value is 0.60, the formulated model has a fairly high explanatory power as a primitive model. The R square value is 0.60 and it shows that there is a secondary relationship between the house price and the independent parameters, that are used in the multiple linear regression analysis.

The general regression equation formula is: \( Y_i = \beta_0 + \beta_1 X_{i1} + \beta_2 X_{i2} + \ldots + \beta_n X_{in} \)  

(1)

The resulting general regression equation from linear regression analysis is:

\[
Y = 1.405 + 0.909 X_1 - 0.075 X_2 + 0.468 X_3 - 0.015 X_4 + 0.253 X_5 + 0.001 X_6 - 0.054 X_7 + 0.025 X_8 - 0.046 X_9
\]

(2)

The hedonic approach explores the effect of the product characteristics on its price. The structure of the hedonic model is same as the multiple regression model. However, different functional structures can be used in the hedonic approach [8]. The most commonly used functional structures are logarithmic linear form, natural logarithm and root transformation [9]. The impact of the same parameters to the price achieved by performing the hedonic - logarithmic linear regression was nearly the same as achieved with Equation (2).

The general hedonic - logarithmic linear regression equation formula is:

\[
\ln Y_i = \beta_0 + \beta_1 \ln X_{i1} + \beta_2 \ln X_{i2} + \ldots + \beta_n \ln X_{in}
\]

(3)

The resulting logarithmic linear regression equation is:

\[
\ln Y = -85.292 + 32.381 \ln X_1 - 0.650 \ln X_2 + 12.288 \ln X_3 + 0.120 \ln X_4 - 7.884 \ln X_5 + 0.539 \ln X_6 - 1.878 \ln X_7 + 0.419 \ln X_8 - 1.093 \ln X_9
\]

(4)

The results to be achieved from Equation (2) and Equation (4) are as follows:

• The most important factor affecting the house price (Y) is the house size.
• Another important factor affecting Y is the number of floors having the house.
• The relation between Y and locational parameters (X₆, X₇, X₈, X₉) is scarcely any.
• The relation between Y and physical parameters (X₁, X₂, X₃, X₄, X₅) is in the medium level.

**CONCLUSION**

While the house prices in Umraniye county can be expressed by physical qualities of the houses at the ratio of 60%, the remaining 40% part should be investigated by using the parameters other than the ones used in this model.

The current building stock should be analyzed urgently and urban transformation of buildings which are risky for security should be ensured by taking into consideration that Istanbul carries earthquake risk and the effects of 1999 earthquake happened in soon history has not been forgotten. Price and age maps should be composed and precautions should be taken by determining where the old houses piles. Every county should have its own specific building stock structure and this should be kept under control. However, a data stock was not found for the houses which are at the end of their economic life or under earthquake risk. Once the house stock has once been determined, pre - etude studies can easily be made for mitigation of economic damage. In order not to be caught unprepared and to prevent the increase in earthquake damage due to the environmental risks and to reduce loss of life, natural disaster risk plans should be done before and after earthquakes happen.

**REFERENCES**


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CONSERVATION OF AHLAT TOMBSTONES BY USING NANOTECHNOLOGY

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ABSTRACT

The deterioration of historical monuments is a well-known problem especially established as an open air museum. From the engineering perspective, deterioration of monuments can be studied both theoretically and experimentally by focusing on materials which were used to build monuments and by developing suitable solutions to conserve monuments from environmental effects. The main reasons of deterioration are investigated and classified during the literature survey and supported by field observations. Moreover, these observations are supported by experimental tests to show that properties of ignimbrite and porosity are determined as main deterioration factor onto stone surface. Then, commercial deterioration dispersion is implemented onto stones to dispose the porosity which is designated as important factor of deterioration. Results are evaluated by eye view and supported by high definition closer photographs from drop and stone surface to see angle between them.

KEYWORDS:

Ahlat, tombstones, conservation, preservation, deterioration, historical monuments

INTRODUCTION

Ahlat is the town which is located in the Eastern Anatolia of Turkey. The location of the town is close to Lake Van, which is the largest lake of Turkey. Ahlat played an important role in the Anatolian history in many eras [1]. According to the archaeological digs, there were serious settlements at the first Bronze Age, almost 3000 B.C. [2].

There are many myths about the name of Ahlat. This name is closer to Arabic statement, ‘ahlatuin min’nas’ [1] that means ‘hybrid community’ in Arabic [3].

Because of the migration problems in Seljuk Empire, Turkmenians were sent to Anatolia by Seljuk leaders to find new wide grasses [4-5].

In the archaeological area of Ahlat, there were ceramics in red-black color emerging from tombs [6]. Turan quoted from Josef Strzygowski, that Turks had their own art which was original and independent. This was supported by the digs that were performed between Orhon and Selenga Rivers, cairns contained historic artefact by Turks [7]. Taşağıl indicates that, Turks constructed these kinds of monument areas in Central Asia during Gotk Turks era [8]. Their construction plans have also similarity according to digs and researches [9]. According to Kuban, new rulers of these lands used Christian artists and craftsmen to construct their monuments [10]. Ahlat Seljuk tombstones were ornamented by Koran, hadiths, literary texts about corpse by using rumi pattern and animal motives that were stylized by Anatolian Seljuk motives. Sprout and leaf were also used. These are arabesque geometrical lapse intricate grids, so called hetai convoluted branches by stylizing flowers, kandil and tulip as a Seljuk immortality figures. Two head dragons and a wolf were connected with Turkish sagas symbolizing the infinity of the universe [11]. In the Orkhon monuments, dragoon motive symbolizes protection [12]. There are three types of tombs in Ahlat that are listed by Karamagrali as follows [11];

- Framework Tomb
- Tomb without Shaide
- Tomb with Shaide

Ahlat stone is a volcanic rock and its petrographic name is ignimbrite. It can be easily shaped and easily processed as other subsurface stones. There are four different colors ignimbrite that are observed in Ahlat which are reddish brown, dark brown, yellowish gray and black ignimbrite. Reddish one was mostly used in monuments and tombstones [13].Ahlat stone is commonly used as a construction material [14]. Ignimbrites are pyroclastic flow rocks, composed of volcanic glass, high amount of pumice and a small amount of lithic particles and they flow under gravity and high temperature. Thickness of ignimbrite is generally limited because of its high flow velocity. As the distance to source increases, the thickness of ignimbrite decreases to 10-100 cm. Some pyroclastic sediments, which are rich in pumice, are described as high flow ignimbrites. It is also defined that, when Ahlat stone is prevented from absorption of water, it can show some degree of
heat isolation [15]. Chemical properties of Ahlat ignimbrite and Mexico Morelia ignimbrites are very similar to each other. Morelia is the historic city, where most of the monuments were built by using ignimbrite rocks of this region [16].

**TABLE 1**

Properties of Nemrut Ignimbrites [17].

<table>
<thead>
<tr>
<th>Samples</th>
<th>Reddish Brown</th>
<th>Dark Brown</th>
<th>Yellowish Gray</th>
<th>Black</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry unit weight (kN/m²)</td>
<td>15.13</td>
<td>15.77</td>
<td>16.82</td>
<td>14.85</td>
</tr>
<tr>
<td>Saturated unit weight (kN/m³)</td>
<td>17.89</td>
<td>18.60</td>
<td>18.59</td>
<td>18.00</td>
</tr>
<tr>
<td>Apparent porosity (%)</td>
<td>28.89</td>
<td>27.40</td>
<td>30.35</td>
<td>31.53</td>
</tr>
<tr>
<td>Water absorption by weight (%)</td>
<td>18.68</td>
<td>16.92</td>
<td>12.03</td>
<td>20.80</td>
</tr>
<tr>
<td>Uniaxial compressive strength (MPa)</td>
<td>15.78</td>
<td>12.10</td>
<td>28.92</td>
<td>12.43</td>
</tr>
<tr>
<td>P-wave velocity (m/s)</td>
<td>1709</td>
<td>2378</td>
<td>2623</td>
<td>1491</td>
</tr>
</tbody>
</table>

Ahlat tombstones are in the candidates of the tentative lists of UNESCO’S Human Heritage sites. There is serious structural deterioration, erosion, and deformations which can be observed on the surface of the stones easily along with excessive lichen colonization which starts from the top and partly penetrates the mid-sections of the stelae causing extensive deterioration and discoloration on the surface of the tombstones [18].

**FIGURE 1**

Ahlat Tombstone

Lake Van is the fourth largest endorheic lake and the largest soda lake on earth. The climate of this region is very harsh and there are temperature differences between winter and summer [18]. Based on the meteorological data, an arid climate was dominant in this region [17]. This saline soda lake could be responsible for the deterioration of the exposed tombstones and it could also be enhanced by salt and ice crystallization due to the water freezing in the stone and its pores and capillary structure in long winter seasons [18]. As a result of chemical weathering of volcanic rocks and evaporation processes, the lake water is saline (21.4%) and alkaline (155 mmEq-l, pH 9.81) [19]. It is very important because of the fact that there is roughly 50% decrease in percentage Na₂O amount in recently extracted Ahlat stones and the historical tombstone samples [18]. The moisture effect is also important, as it deteriorates the rock [17]. Condensation or capillary rise plays a key role in degradation of porous materials that is responsible for many decay processes such as freeze-thaw cycles, soluble salts crystallization, biological growth, chemical attack by rain and wind erosion. A proper understanding of the role of moisture and salts in the structural performance of porous materials is of fundamental importance in the design of conservation procedures and strategies for safeguarding of cultural heritage [20]. There is a significant correlation between porosity level and capillary water absorption by causing extensive moisture expansion into stone and it affects the structure of stone by internal weathering [18].

Salts can enter and move through porous bodies only when they are dissolved in water. Salt and rock react with each other because of water and this situation accelerates the deterioration in stone. There is also dehydration and hydration process. Salt also created volume changes. Then, some micro-cracks can be occurred due to the volume changes that can induce water movement into stone and accelerate the deterioration of the stones. These salts that stick to moisturized parts of stone is a good place for biological lives [21]. For low welding rates, deterioration due to the effect of humidity was more apparent [20]. Middle section of the tombstones is inside the capillarity zone, thus salt crystallization is more effective than other sections of the stone. Effective water capillary suction is through the pores and channels in the structure and main mechanism of physical degradation from the bottom part to the middle section. Salt crystallization is always more effective in the capillary zone than in the immersion zone. It is clear that many tombstones cracked to their middle point and most of the broken tombstones were about 10 to 70 cm in terms of their height [17-18]. In areas where freezing-thawing is more effective because of minimum exposure to the sun and/or type of surface drainage pattern, fairy chimney erosion increases [22]. Cycling freezing and melting of water carrying soluble substances through the pores, voids and capillaries causes efflorescence on the surface [18]. There is another decay process on Ahlat tombstones along with the chemical action of the surface lichens that
occur due to typical chemical weathering that induces the mineral dissolution in rock content [18].

![FIGURE 2](image)

**Ahlat tombstones covered by lichens**

Lichen colonization on Ahlat stones like thallus, act as a binding fiber, holds the finely fragmented soft matrix together and protects the structure [18]. Ozvan et al. (2015) also support the idea about decelerating the penetration rate of surface water into rock by biofilms originating from lichens and it results to higher resistance surface to deterioration [17]. In addition, elimination of lichens and removal of thallus leave the surface in a more porous condition due to its past movements into rocks, and then, the structure has to face more chemical attacks. This means that lichens create further decay on the stone [18].

For conservation of monuments and especially stone conservation, there are several properties that must be controlled. These are penetration depth, resistance properties such as pressure, elastic modulus, bending resistance and weathering resistance, absorption of water, vapor resistance, chemical attacks resistance, salt crystallization resistance and changes into the appearance of stones [23]. In the area of the conservation, the products that are used to deal with damages are generally names as silane. Silane includes at least one alkyd group attached to silicon atom. It should be marked that alkyd groups attached to the silicon atoms provide hydrophobicity to the compound. Environmental conditions are also important to gain success for conservation applications of this material such as humidity and temperature. There is one more thing about stored salts into voids and pores of stone, they directly affect the condensation rate of the implanted chemicals which increases due to Sodium Sulfate and decreases due to Sodium Chloride. These crystallized salts can damage the polymer films that cover the stone surface in long time period [23-24]. Silanes are preferred since they do not degrade in long term and they are more viscous than water, which provides them with better impregnation ability. These materials are colorless and have low toxicity. After they are stored in stone, they will polymerize, hydrolyze and condense. This process ends after the formation of Si-O-Si bond, which makes the material more resistant. Alkoxy silane creates alcohol as a by-product after hydrolysis reaction and it easily evaporates by abandoning the solid polymers into stone. The color of the stone can change due to implanted solution which can also create white points on the stone surface before hydrolysis and this can be irreversible for these kind of materials. Polymerization rate is very important for using Alkoxy silane since polymerization affects the quality of the product. If this happens slowly, chemicals evaporate from the surface before penetrating, in high rate, gel formation is observed, which provides external preservation to stone. These chemicals are implanted onto stone generally spraying in low pressure or using brushing again and again onto surface [23]. For the Ahlat tombstone, there is a parliamentary research commission report. According to the report, monuments in Ahlat need to be preserved because of deteriorations. However, the most important thing in the report is that past restoration and preservation works gave serious damages to stone. The report also shows that cement was used during the restoration for the stone instead of using natural stone that is quarried from Ahlat [25]. Solution-gelation (sol-gel) method is a ceramic production method that has been improved during the last twenty years. Sol-gel method was defined as synthesis of inorganic polymers such as ceramic or glasses by using colloidal phases in the solution. This has improved to serve the purpose of producing high-tech ceramics. It is mostly used in fiber, coatings and powder productions. It is considered as a good method as it decreases the distance between particles in the solution. Sol-gel method is also used in conservation of the stones as consolidation material. For the ideal consolidation, there are seven rules from 1921 by Heaton [26].

- Deeply penetration into stone and stays after drying
- Resist against erosion but there is no crusting on the surface
- Avoid humidity inside, but let it outside from stone
- Natural appearance and color must be same after implementation
- It should not expand or shrink with stone to provide spalling/ flaking
- It should not be corrosive and harmful
- Its material and application must be economical

This solution can be implemented on the surface by using brush or spraying for historical monuments. First one created particular forms in nm. Lastly, the consolidation process creates a barrier against water inlet on the stone surface [26].
### TABLE 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>Dry Weight (g)</th>
<th>Inside water weight (g)</th>
<th>Saturated weight (g)</th>
<th>Water absorption (%)</th>
<th>Effective porosity (%)</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reddish brown (1)</td>
<td>313</td>
<td>166</td>
<td>395</td>
<td>26.20</td>
<td>35.81</td>
<td>2.13</td>
</tr>
<tr>
<td>Reddish brown (2)</td>
<td>443</td>
<td>233</td>
<td>559</td>
<td>26.19</td>
<td>35.58</td>
<td>2.11</td>
</tr>
<tr>
<td>Black (3)</td>
<td>108</td>
<td>59</td>
<td>135</td>
<td>25.00</td>
<td>35.53</td>
<td>2.20</td>
</tr>
<tr>
<td>Black (4)</td>
<td>71</td>
<td>121</td>
<td>298</td>
<td>25.35</td>
<td>36.00</td>
<td>2.22</td>
</tr>
<tr>
<td>Yellowish gray (5)</td>
<td>240</td>
<td>121</td>
<td>298</td>
<td>24.17</td>
<td>32.77</td>
<td>2.02</td>
</tr>
<tr>
<td>Yellowish gray (6)</td>
<td>36</td>
<td>18</td>
<td>45</td>
<td>25.00</td>
<td>33.33</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Materials and Methods

Conservation method was tested in this study to conserve Ahlat tombstones which are reported by parliamentary commissions to preserve. Ignimbrites were examined to determine their properties that can be related to deterioration. The mineralogical and porosity analysis was performed to determine differences between minerals of stone according to their color and to see their effects on the stone deterioration. In the XRD analysis, mineralogical distribution of the stone content was determined. Then, in order to determine the effective performance of the solution used by sol-gel method, closer photographs of drop impact which are related to spreading angle of the drops on the stone surface were used.

In this study, mineralogical analysis was performed by using GNR APD 2000PRO X-RAY DIFFRACTOMETER in laboratory of the Department of Geological Engineering in Istanbul University. Samples were dried in twenty-four-hour time period by using YKM-F120 laboratory type incubator. This given equipment was used to determine total porosity and effective porosity by using specific calculations. In this study, effective porosity and density of the stone was calculated by using Archimedes method.

For the implementation of the commercial product which includes ethanol, water and effective silane, brushing covering method was performed. These specimens were eluirated by using distilled water. Then, samples are made dry and they were cleaned by using ethanol. Commercial consolidation product (Effective silane included Hydrophobic oleophobic dispersion, probably contains TEOS, supplied by ARITEK) was taken and poured into the beaker in addition to this, process was not quantitatively performed. Samples which were washed by alcohol were dried by using Firework Station CYBER-803. Then, by using brush, ignimbrites were coated with consolidation solution. After coating was performed, specimens were stayed to dry for at least one day in room temperature. For observing the effectivity of the consolidation solution, water drops were dropped onto samples surfaces. Then, these drops were examined by using high definition camera because contact angle between drop and stone surface must be observed.

It was important to understand that consolidation dispersion worked or not.

Results and Discussion

In this study, ignimbrites which are used as a raw material to build Ahlat tombstones are coated by effective consolidation solution. These are the historical tombstones that are placed in the Eastern Anatolia region. Ahlat ignimbrites are very porous stones which can be affected from environmental effects easily and also these effects can reach inner points of stone or weathering because of the channels between pores. Consolidation material was used to decrease the effects of pores onto stone surface.

Drop impact determination was performed to see spreading of the drop onto stone surface which is important for the effective work of the implemented dispersion. Capillary recessions which occur due to filling of pores by nanoparticles of dispersion probably containing TEOS, can also be observed. It is clear that coated Ahlat stones can be protected by water absorption and moisture effects. Capillary effect which is prevented by implementing dispersion is clearly observed after coating processes. This consolidation solution decreases capillarity by preventing porosity effect and absorption by avoiding of water which can penetrate into stone.

Determination of effective porosity for Ahlat stone. Porosity is one the most important properties that deteriorates the Ahlat stone and it is used as an insulator construction material. For all color stones, this procedure was performed twice and the results are listed in Table 2.

Ahlat stones are very porous materials. Porosity induced their water absorption amount. Effective porosity and water absorption amount changes directly proportionally, when porosity is less, water absorption amount also declines. Moreover, effective porosity shows the amount of water that can penetrate the rock. XRD analysis was also performed to see mineralogical distribution.
For black color ignimbrites, analysis is done and as it can be seen, there are unmatched results between samples for black ignimbrites. Sanidine is the common mineral for both of them. Most important varying is related to Albite and Hematite, as it is shown, for the outside part, there is Hematite and there is no Albite. Albite-Hematite changes can also define color changes for ignimbrites which can be altered easily during the alteration color changes between the new surface and the dusted surface.

Dispersion implemented Ahlat stone test & drop impact of porosity. Dispersion implementation into Ahlat stone surface is tested by dropping water, saturated water and dirty water. This implementation must preserve water penetration into rock body by filling pores of stone. As it can be seen in Figure 5, coated stone surfaces are tested by dropping water and comparing with un-coated surfaces of same stone sample as it follows.

Stone sample number one is covered twice by using dispersion and specimen and the second sample is coated only once by dispersion. As it can be seen, both covering processes work to preserve penetration of water into rocks.

To investigate the drop impact in detail and more clearly, position of the drop with its spreading and making angle with rock surface must be observed. In Figure 6, spreading of drop and angle between surface and drop due to capillary effects can be observed as it follows.
creasing capillary effect and preventing water absorption into rock. Figure 7 shows the angle between drop and surface.

To increase the density of the water drop, solute is added into it and density is changed which directly affect the capillary effect. Therefore, angle between surface and saturated water drop is highest for the front drop as it can be seen. Raining or snowing which create water onto tombstones probably act as saturated water drop as it can be Figure 8.

FIGURE 8
Saturated, pure and dirty water drops (listed as front to back) on Ahlat tombstone

CONCLUSION

Ahlat tombstones are aged almost 800-900 years ago and they have been affected by the whole climate conditions in Ahlat. The alkaline character of the Ahlat region is very effective on deteriorations of Ahlat tombstones. This is one of the most important deterioration processes due to the fact that it puts salts into rock pores by rain or snow. This shows that porous character of rock must be decreased or completely prevented to preserve these monuments. Lichen colonization is the other reason of deterioration. It is clear that, lichens are not acceptable onto these tombstones due to the fact that they prevent the ornaments on stone surface and destroy their meanings. These coated stones show that Ahlat tombstones can be conserved by using some nano-tech materials. As it can be seen above, the main problem of the Ahlat stones is porosity. This porous character induces some problems which are lichen colonization, salt crystallization and moisture affects. These problems are also related to harsh climate conditions. In this study, some properties of Ahlat stones are determined. Then, the figures presented how capillary effect was changed. The main purpose of the conservation process for Ahlat stone is against the porosity.

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SESSION IX
NATURAL AND MEN MADE DISASTERS
MULTITEMPORAL ANALYSIS OF COASTAL DYNAMICS BY HIGH-RESOLUTION RECONSTRUCTION OF TOPOGRAPHY USING UAVs

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ABSTRACT

Dynamic networks of Unmanned Aerial Vehicles (UAVs) can be used in a broad range of missions like monitoring and surveillance of the coastal environments to detect shoreline changes. The aim of this study is to evaluate topographic changes along a stretch of coastline in the Silivri, which is outside metropolitan Istanbul (along the Sea of Marmara) in Turkey, by means of an UAV coupled with Structure from Motion (SfM) and multi-view stereo techniques. This region was surveyed over 11 months from September 2016 to July 2017 in order to produce digital elevation models and orthophotos of the coastal area by using dense point clouds. Changes in the shore topography associated with usual tide and human activities were assessed in terms of sediment activity and wet–dry boundary shifting that defines the shoreline. The results showed that UAVs can be used for regular coastal monitoring purposes and that they can provide new insights into the processes related to natural and/or human-related topographic coastal changes.

KEYWORDS:
Shoreline, Coastal change, Silivri, Point cloud, Multitemporal analysis, Structure from Motion

INTRODUCTION

Coastal environments are dependent on the prevailing coastal processes and geological structures, which are sensitive to sediment transport due to erosional and depositional processes with the actions of waves, littoral current, wind and certain anthropogenic activities [1]. Coastal geomorphology requires an accurate topographic information to perform trustworthy simulation of coastal erosion/deposition following the assessment of the coastal sediment budget. Coastal vulnerability can be analysed with the help of coastal change assessment [2,3].

Recent advances in remote sensing provides adequate information on spatial distribution of changes in coastal environment enabling us to analyse coastal dynamics with higher spatial resolution [4-6]. Previous studies have highlighted advantages of using Digital Elevation Model (DEM) and Light Detection and Ranging (Lidar) datasets for geomorphic detection and volumetric change of sediment load along the coastal area [7-10]. The topographical changes of the sediment load in the coastal environments has been investigated from the temporal DEMs using the extracted cross and along shore profile analysis that provide geomorphic change information in vertical scale [2, 11]. The volumetric change of sediment load estimated using DEMs are capable of generating significant results on loss and gain that are relatively closer to the field based measurements [8]. Many researchers observed relatively high accuracy between the DEM derived geomorphic changes and field measurements for coastal areas [10, 12, 13].

Unmanned aerial vehicles (UAV) based solution produces Digital Surface Model (DSM) with a similar accuracy compared to Lidar or Terrestrial Laser Scanning (TLS) [14, 15]. In recent years, with several advantages result from the use of integrated GPS direct georeferencing, automatic triangulation and dense stereo matching methods allowing the generation of 3D point clouds and digital surface models, digital photogrammetry has become a more affordable solution for coastal monitoring [16].

In order to overcome the limitations of the Lidar and TLS methods, the UAV-based survey for 3D reconstruction of coastal environments is being currently investigated. The Structure-from-Motion technique is derived by the integration of computer vision and image analysis [17,18], which automatically solves the geometry of the scene, the camera positions and orientation, which have known 3-D positions [19-21].

The aim of the study is to map coastal environments and assess the volumetric change of sediment load along the part of the west coast of Istanbul by high-resolution reconstruction of topography using UAVs. Therefore, in the study, cross-shore and along-shore profile change analysis with geomorphic change detection have been analysed by using UAV-derived DSMs along the coastal stretch. Further, the volumetric change assessment of the coastal site has been done using UAV-generated point clouds.
TABLE 1
Characteristics of the acquisitions.

<table>
<thead>
<tr>
<th>Acquisition Date</th>
<th>Flying time (min)</th>
<th>Lat./lon. overlap (%)</th>
<th>Average GSD (cm)</th>
<th># of photo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sept. 2016</td>
<td>12</td>
<td></td>
<td>2.38</td>
<td>303</td>
</tr>
<tr>
<td>Nov. 2016</td>
<td>12</td>
<td></td>
<td>1.72</td>
<td>323</td>
</tr>
<tr>
<td>Jan. 2017</td>
<td>13</td>
<td></td>
<td>1.85</td>
<td>305</td>
</tr>
<tr>
<td>Feb. 2017</td>
<td>12</td>
<td></td>
<td>1.77</td>
<td>314</td>
</tr>
<tr>
<td>Mar. 2017</td>
<td>12</td>
<td>85/80</td>
<td>1.77</td>
<td>290</td>
</tr>
<tr>
<td>Apr. 2017</td>
<td>13</td>
<td></td>
<td>1.75</td>
<td>308</td>
</tr>
<tr>
<td>May 2017</td>
<td>11</td>
<td></td>
<td>1.80</td>
<td>260</td>
</tr>
<tr>
<td>Jun. 2017</td>
<td>16</td>
<td></td>
<td>1.92</td>
<td>387</td>
</tr>
<tr>
<td>Jul. 2017</td>
<td>13</td>
<td></td>
<td>1.85</td>
<td>342</td>
</tr>
</tbody>
</table>

FIGURE 1
The study area.

THE STUDY AREA

The study area corresponds to the Silivri region, located on the European side of Istanbul bordering Tekirdağ province. Because of having 45 km long coast, Silivri becomes one of the most populated districts of Istanbul especially during summer season (Fig. 1). Coastal vulnerability assessment of this area is currently of great interest because of the importance of the coast for tourism-generated economy, a significant resource for the local community during the summer season.

The area is exposed to semi-annual tides ranging from 1 to 3 meters. This hydrodynamic circumstance drives fast morphological changes at the shore. The dynamics of coastal topography, its geometric properties and estimates of eroded and deposited sand volumes were determined by monthly monitoring of the shore in the region.
DATA AND METHODOLOGY

Data acquisition. The study area was surveyed over 11 months from September 2016 to July 2017. In the study, an autonomous quadcopter (Phantom 3 Pro) with on-board artificial intelligence, which analyses data from Inertial Measurement Unit (IMU), and equipped with an integrated GPS and camera was used to optimize every aspect of the flights. To acquire the images with ground sampling distance (GSD) approximately 2 cm, an average flight altitude was fixed at 40 meters and acquisition was automatic set on an overlap percentage of 85% and 80% for latitudinal and longitudinal overlap, respectively. Flight time varied between around 11 and 16, depending on the wind condition on the acquisition date. The characteristics of the acquisitions were given in Table 1.

Further, the Pix4D software was used to orientate the images, extract point clouds, build a DSM and produce orthomosaics. The processing including triangulation with camera calibration and subsequent model generation, was mostly automated.

Reconstruction of topography. In the study, 3D reconstruction of coastal topography was done by SfM algorithm, which is based on a multi view of the scene, and the redundancy of the information allows the success of this process [22-25]. This algorithm allows reconstructing a 3D scene geometry from a set of images of a static scene by matching features on multiple images. SfM incorporates multi-view stereopsis (MSV) techniques, which derives 3D structure from overlapping photography acquired from multiples angles [26]. D-GPS based six ground control points (GCPs) were used in order to georeference the orthomosaics and the sparse DSMs. The location of the GCPs were represented in Fig. 2.

After each acquisition, the alignment of the acquired images was performed. Following with the aligned dataset, a pixel-based dense stereo reconstruction was implemented. Afterwards, fine topographic details available on the original images were meshed and a texturing was applied to the mesh. The point cloud was then derived and referenced to UTM coordinate system applying the bundle adjustment procedure to produce accurate results. The point clouds extracted by UAV-SfM methodology represented different point densities depending on the images textural properties. DSMs were therefore generated from UAV.

All these automated processing steps for each acquisition were time consuming and the computations has been limited by both the amount of RAM available and the number of images acquired. Consequently, the SfM technique applied to images acquired by a low-altitude UAV system produced a point cloud and derived DSM representing coastal environment with high topographic quality. The mean vertical and horizontal accuracies were acquired as 0.065 and 0.076 meters, respectively. In addition, during the UAV measurements, the achieved mean ground sampling distance was approximately 2 centimeters within a total covered area of about 6.7 ha.

Cross-shore and along-shore profile analyses. The extracted cross-shore and along-shore profile analysis using the DSM datasets provide information on geomorphic change of the coastal environment in vertical scale [11, 27, 28]. In the study, along-track and across-track profile locations have been chosen from the south-west coast of the study area where the sediment load change was maximum (Fig. 2). The profiles were separately extracted using UAV-derived DSM datasets over seven months.

Coastal volumetric change analysis. The assessment of geomorphic features is usually based on multi-temporal surfaces analysis, where an interpolation process is required. The analysis has been done by calculating the volumes from point clouds derived from UAV-SfM methodology. The volumetric changes of sediment loads discloses in the cross-shore fluxes are summarised in Table 2, in which the negative and positive values represent the rate of erosion and deposition of sediment load respectively.

TABLE 2 Assessment of sand volume changes.

<table>
<thead>
<tr>
<th>Acquisition Date</th>
<th>Cut ( m^3 )</th>
<th>Fill ( m^3 )</th>
<th>Difference ( m^3 )</th>
<th>Total ( m^3 )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>-1815.6</td>
<td>384.4</td>
<td>-1467.1</td>
<td>2200.0</td>
</tr>
<tr>
<td>Nov. 2016</td>
<td>-2329.2</td>
<td>570.8</td>
<td>-1758.4</td>
<td>2900.0</td>
</tr>
<tr>
<td>Jan. 2017</td>
<td>-623.1</td>
<td>1878.8</td>
<td>1255.7</td>
<td>2501.9</td>
</tr>
<tr>
<td>Feb. 2017</td>
<td>-1576.9</td>
<td>2501</td>
<td>924.1</td>
<td>4077.9</td>
</tr>
<tr>
<td>Mar. 2017</td>
<td>-621.7</td>
<td>2816.7</td>
<td>2195.0</td>
<td>3428.4</td>
</tr>
<tr>
<td>Apr. 2017</td>
<td>-1368.2</td>
<td>588.3</td>
<td>-780.0</td>
<td>1956.5</td>
</tr>
<tr>
<td>May 2017</td>
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<td>2120.7</td>
<td>473.0</td>
<td>3768.4</td>
</tr>
<tr>
<td>Jun. 2017</td>
<td>-2838.2</td>
<td>648.5</td>
<td>-2189.7</td>
<td>3486.7</td>
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<tr>
<td>Jul. 2017</td>
<td>-2802</td>
<td>1029</td>
<td>-1773</td>
<td>3831</td>
</tr>
</tbody>
</table>

RESULTS

Along-track and across-track profile change detection and assessment. The results of vertical differences between these cross-shore and along-shore profiles denotes eroded and deposited sediment loads in the coastal environment along the seven months during 2016–2017 (Fig. 3). In November 2016, the profile depicts decrease of sediment loads at a rate of about 0.85 m within a distance of 80 m along the shoreline. Along the coastal plain
FIGURE 2
UAV-derived DSM of the study area with along-track and across-track profile locations with GCPs (red stars)

FIGURE 3
Extracted profiles from UAV-derived DSMs over seven months.
within a distance of 320 m shows minor change in sediment load between January 2016 and May 2017. However, the maximum eroded sediment volume can be clearly seen on April 2017. Besides, across-track profiles illustrate similar patterns. Across the coastal plain within a distance of 10-20 m from the shoreline illustrates the erosion process due to waves especially after January 2017. It should be noted that, the distortion on the profiles within a distance of 20-25 m from the shoreline is due to the DSM derivation process of the occurrence of the water surface.

**Volumetric change assessment of the coastal site.** Fig. 4 shows the volumetric changes of sediment load on each acquisition date for a specific site of the study area.

The sea conditions induced a cycle of morphologic change on the study swath. Volumetric changes of sediment load in the study area using Cut and Fill method over seven months is shown in Fig. 5. When the detailed surveys commenced in early September 2016, the beach was recovering from an eroded state induced from the rough weather and wave conditions in May 2017. Volumetric calculations have shown that the erosion and deposition of sand in the specific region is more likely to occur in the bay side. The maximum erosion and deposition have been observed in March 2017 and November 2016, respectively. The mixed state was seen in April 2017, in which the eroded and the deposited sand volumes were most likely the same.

**FIGURE 4**
Point cloud derived volumetric changes during 2016-2017.

**FIGURE 5**
Volumetric changes of sediment load of coastal environment in the study area using Cut and Fill method over seven months.
As an overall result, the pattern of the volumetric change assessment of the coastal site by UAV-generated point clouds supports the along-track and across-track profile change detection analysis using UAV-derived DSMs.

CONCLUSIONS

This study analyses the use of unmanned aerial vehicles to analyse the coastal dynamics with mapping and monitoring the specific beach area. To monitor coastal environments, UAV is a low-cost and easy to use solution to enable data acquisition with very high spatial and temporal resolution.

Coastal areas suffer degradation due to the action of the sea and other natural and human-induced causes. Topographical changes and coastal dynamics need to be investigated, both after severe events and on a regular basis, to observe the evolution of these natural environments. Accurate data and a better understanding of coastal topographic change can significantly improve the success rate of such coastal environmental projects. On coastal environments, the water surfaces are problematical to DSM construction. Areas classified by smooth surfaces, like beach sand, snow or backwater surface, may be failure-prone because of possible difficulties by the matching algorithms to extract corresponding features from over smooth surfaces [15, 29]. However, the very high spatial resolution of images acquired at 40 meters altitude have been facilitated the recognition of textures at the ground. SfM proves to be a powerful tool to process many of high-resolution aerial images. The high degree of automation of the workflow suggests possible uses in the fields of high-resolution terrain analysis, coastal hydrodynamic modeling and natural disaster assessment.

Ultimately, UAVs can replace many of the conventional flights for coastal monitoring, since they are one of the simple and cheapest equipment in image acquisition. Moreover, the outputs of this study can form primary information source for coastal vulnerability and would help preparation against any possible natural disasters and recreational plans that likely to affect the coastal region.

REFERENCES


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EFFECT OF HYDROGEOMORPHOLOGICAL CHANGES IN FLOOD PLAIN ON BRIDGE MULTI-HAZARD PERFORMANCE

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ABSTRACT

Unmanned Aerial Systems (UASs) are widely used for various applications, especially for large-scale mapping of flood plains. The Unmanned Aerial Vehicles (UAVs) act as a bridge to fill the gap between the satellite and the field scale, as they provide an alternative to temporal and spatial resolution to the satellite imagery and can be directly linked to the terrestrial measurements. In the study, UAV-derived point clouds are used to create very high-resolution surface models based on Structure from Motion (SfM) technique, which is applied for the creation of 3-D models from unstructured imagery and frequently used in conjunction with UAVs. Thus, seasonal hydrogeomorphological changes in the Boğçay River floodplain in Antalya Province have been evaluated by using fine resolution UAV-derived orthophotos and Digital Surface Models (DSMs). The monitored landscape changes were determined to have the utmost influence on the multihazard performance of the bridges, which are located on the study region. Further, in the light of this information, the seismic performance of reinforced concrete (RC) bridge infrastructure was determined via static pushover methods. In the study region, the scour depths were determined to reach maximum of 2.2 meters under the bridge piers. The scour-induced reduction in pile lateral displacement capacities was detected to deteriorate the seismic performance of the bridges.

KEYWORDS:
Bridge piers, Multi-hazard, Scouring, UAV, Hydrogeomorphology.

INTRODUCTION

Determination of multi-hazard performance of RC bridges located in flood plain has major importance in establishing the economic life and planning required retrofitting of engineering structures. Since pile scouring in bridge substructures was observed to be one of the major cause of failure in RC bridges [1-3], seasonal determination of scour depth is essential in predicting the multi-hazard bridge performance. Thus, the reliability of scour depth measurements is crucial in bridge performance evaluation. In this scope, in previous studies scour depth were designated majorly by experimental [4, 5], sonar [6-8], ground-penetrating radar (GPR) [9-11], radio frequency identification (RFID) [12, 13] and accelerometer [14-16] based methods. The specified techniques for measuring scour depth incorporate implementation difficulties as well as uneconomic measurement expenditure. Thus, UAV based measurement methods can be regarded as an economic alternative for scour depth monitoring at bridge piers located in flood plain due to its ease of use. The geographical information system (GIS) based flood risk analysis was conducted by using satellite information and numerical high precision modeling in the previous studies [17-19]. Herein, current research on UAV based measurement comprises flood analysis [20, 21] however there were no studies regarding UAV based scour monitoring. Consequently, using the UAV based monitoring methods, the scour depth at bridge piers was measured seasonally and the lateral capacity of the RC bridge was determined for varying scour depths. The alterations in bridge multi-hazard performance were determined by pushover analysis for the bridge under investigation.

For designating the time based variations in earth surface topography, high resolution digital surface models (DSMs) was implemented by using classical topographic surveys (RTK, GNSS, TLS, Lidar etc.) or by current image processing techniques as Structure from Motion (SfM). Structures having three dimensions such as terrain, buildings and landforms can be modeled using SfM methods that provides motion integrated two dimensional image clusters [22]. SfM photogrammetry is a low cost user-friendly technique that enables broad scale implementation of high-resolution data clusters. The SfM algorithm consists of four steps in generating three-dimensional (3D) surfaces [23, 24]: i. Camera alignment by bundle adjustment in which common nodes on overlapping maps are matched. ii. Dense point cloud generation by calculating the location of each node by stereo-photogrammetric equations using camera locations and photos. iii. Three dimensional polygon mesh constitution that represents surface depending on dense point cloud. iv. Mesh model regeneration that is used for orthophoto generation.
For aerial photogrammetry, while frontal overlapping ratio in direction of motion is at least 75%, the lateral overlapping ratio is at least 60%. However, for surfaces covered with mud or having shallow water, which have minor visual contents, the overlapping ratios were determined as 85 and 70%, respectively [25].

**METHODOLOGY**

In this study, the scour depth at bridge piers was determined reliably by UAV based measurements. Herein, the transverse and longitudinal cross sections that were obtained along the investigated bridge were determined in three dimensions while providing the input for earthquake performance analysis. In addition, horizontal and vertical accuracy of models that represent surface morphology were acquired by precise ground control points (GCPs) that were obtained by differential global positioning system (DGPS). In order for scour analysis, 3D model of the surface at bridge piers was obtained by images taken at various camera angles at manually adjusted camera altitudes. The overlapping ratios for aerial images were optimized as 85% both in direction of motion and in lateral direction. For the images obtained at these altitudes, ground-sampling distance (GSD) was obtained as 1-2 cm/pixel while satisfying high spatial resolution. Although the accuracy of DSM was increased by increased resolution, the vertical accuracy was controlled by DGPS sensitivity [21]. In the study, the accuracy of the multitemporal measurement data was acquired using 17 GCPs as shown in Fig. 1. In all seasonal measurements, the accuracies of UAV-derived orthomosaics were found not to exceed 0.055 and 0.082 meters in the horizontal and vertical, respectively. Within these UAV-based measurement accuracies, the seasonal change analysis could be made by high reliability. Thus, the scour depth at bridge piers was determined by acquired high-resolution orthophotos and point clouds for measurements in clear and shallow water.

Pix4D [25] software was implemented for processing images taken by UAV and for generation of 3D dense point clouds, mesh models and high-resolution DSMs. The generated 3D point clouds and the mesh models were rearranged, referenced and the artifacts were resolved by open source software VisualSFM that uses SfM algorithm for resizing the model. In 3D data processing, for the volumetric calculations from TIN and closed mesh models, eroded geomorphology generally occurs from highly complicated open and hollow earth surfaces.

In order to obtain volumetric information for this type of earth surfaces, the generated mesh structure was transformed into closed mesh model by positioning a plane at the top of generated mesh structure [26]. For minimizing the effect of resolution differences in generated models, the scale of the SfM generated point clouds were reduced and resampled according to the data with minimum resolution. The error statistics in generated point clouds were obtained as compared to the DGPS measurements. The diachronic generation of high-resolution DSMs for the study region enabled scour monitoring, mapping and volumetric change calculations. The seasonal difference between latter and former generated DSMs demonstrated erosion and accumulation for negative and positive values, respectively. The seasonal trend of the morphological changes in the study region was acquired by calculating the seasonal DSM differences.

Multi-hazard bridge performance was assessed using the UAV based scour measurements. The scour data were implemented in the 3D finite element model (FEM) of the RC bridge that was constructed by SAP2000 software [27]. For modeling the bridge piles that were interacting with the surrounding soils, nonlinear springs were used in bridge FEM. The p-y curves [28, 29] were introduced in order to characterize the lateral resistance developed at the piles due to the surrounding soils. The characteristics of the p-y curves depend on the soil type. The t-z curves [30, 31] identify the soil reaction provided by axially loaded pile (frictional side and end resistance) corresponding to vertical displacements. The lateral response of the bridge was assessed in terms of lateral load and displacement capacities and the effect of scour depth on bridge lateral response was assessed in terms of lateral load capacity, displacement capacity and ductility.

**THE CASE STUDY – BOĞAÇAY BRIDGE**

The Boğaçay Bridge that is located on the Antalya Boğaçay River was selected as the case study (Fig. 1). The bridge has 12 piers including three columns per pier in addition to two abutments having cross section dimensions of 1×2 m and 1.2×14 m, respectively.

The 4.5 m tall piles were spaced at 20.3 m that were measured between the top of pile cap and superstructure deck. Bridge superstructure consists eight prestressed (PC) girders spaced at 1.7 m and connected to 22 cm thick RC deck. PC girders were placed on two 60 durometer elastomeric bearings with dimensions of 0.25x0.45 m with 9 cm thickness at each girder end. The pile system includes 12 m tall 12 piles with 1 m diameter that were connected to a 1.5 m thick strong pile cap having dimensions of 3x15 m. C25 and C40 concrete were implemented for RC and PC, respectively. For the bridge under investigation, the maximum scour depth was determined to reach 2.2 m at the middle piers by UAV based seasonal scour measurements in summer season as shown in Figs. 2a-2d. In the summer season at when the surface runoff was the minimum (Fig. 2d), clearest scour measurements were carried out.
In addition, maximum, minimum and average transverse and longitudinal cross sections were obtained across the bridge piers as shown in Figs. 3a and 3b, respectively. It can be observed from the seasonal scour measurements that the scouring was almost concentrated at the middle piers at where the maximum scour depth was measured. Considering the drilled bridge piles into soil layers of sand and limestone, two types of p-y and t-z curves were used in 3D FEM of the bridge. Thus, soil-structure interaction was modeled using nonlinear springs that were distributed along bridge piers and piles considering the water table. Herein, the alterations in nonlinear soil spring characteristics with the depth were reflected in modeling by modifying the characteristics of p-y and t-z curves with depth. The curves for sand layers had greater lateral and vertical load capacity with increasing depth. However, the curves remained unchanged with depth for limestone layers. The lateral capacity of the nonlinear soil springs were defined regarding the relative height of the centroid of the soil layer to the top soil elevation. As the scour depth increases, the nonlinear springs that were defined along the piles were removed. Since the lateral and vertical load capacity of each layer were computed relative to the top of the scoured topmost soil layer, the adverse effect of scouring was reflected in the bridge modeling by diminishing the nonlinear spring load capacities of the soil layers (Figs. 4a and 4b).
In the case study, the case without scouring was termed as the condition with zero scour. The seasonal UAV based scour measurements at the middle piers reached 2.2 m relative to condition without scour that denoted the current condition in calculations. Besides, four additional scour depths were defined as 1.5, 2.75, 4 and 5.25 m relative to the current condition with 2.2 m of scour. As a result, total scour depths relative to the initial condition without scour were 2.2, 3.7, 4.95, 6.2 and 7.45 m. Further, p-multipliers were introduced in the pile and pier nonlinear spring modeling [32]. Regarding the pile group efficiencies, the nonlinear spring resistances for closely spaced piers and piles (spacing lower than three pile diameters) were decreased to 0.7, 0.5 and 0.35 of considered lateral load (p) for the leading pile, the following row and the other rows, respectively. Thus, the lateral load capacities (p) of the nonlinear p-y springs were reduced according to the p-multipliers.

For multi-hazard performance assessment of the investigated bridge, six pushover analyses were implemented considering different scour depths along the piles. In order to represent the failure mechanism of the bridge, plastic hinge locations were predetermined as consistent with the maximum bending moment locations of pier columns and the piles. For the pier columns, the plastic hinge locations were considered as the top and bottom locations at where the pile cap and pier caps were connected. The plastic hinge locations for piles were determined in a stepwise manner by means of systematic pushover analysis and tracking the maximum moment locations along pier and pile lengths. First plastic hinge locations were monitored to form at the pile cap to pile connection since the piles were observed to have the maximum value at the connections to the strong pile cap.

After the formation of the first plastic hinge, second hinge location was determined to be at 3 m below the bottom of the pile cap before scouring occurred. Since the pile scouring altered the locations at where the plastic hinges formed, a similar plastic hinge location tracking method was implemented for varying scour depths. Hereby, the plastic hinge locations for four scour depths of 3.7, 4.95, 6.2 and 7.45 m were observed to occur at 3, 3, 5.5 and 6.75 m relative to the pile top, respectively. It can be observed that the plastic hinge locations migrate towards the topmost scoured soil layer. The lateral load and curvature capacities of the plastic hinges were computed by standard section analysis without considering confinement effects regarding the most unfavorable bridge conditions were considered in the multi-hazard performance analyses.

RESULTS

The maximum scour depth monitored at the bridge piers under investigation was 2.2 m that was acquired by UAV based spring season measurements. Additional scour depths were considered to predict the safety of the bridge under various heights of scour concentrated in the bridge piers and piles for more reliable bridge performance assessment.

Preliminary modal analysis was carried out and results revealed that the scour depth had an insignificant influence on the natural vibration characteristics.
of the bridge. Herein, the increase in scour depths was observed to have insignificant influence on the natural vibration periods and mode shapes since the scour was concentrated only at the middle piers (Fig. 2d, Fig. 5).

![FIGURE 5](image)

**FIGURE 5**
Bridge modal shapes and corresponding natural periods.

The failure mechanisms of the bridge in longitudinal and transverse directions are shown in Figs. 6a and 6b, respectively.

The failure in longitudinal directions initiated by the plastic hinges that formed at the bridge piers instead of piles due to the higher stiffness of piers rather than the piles in loading direction. Thus, the lateral load and displacement capacities in longitudinal direction were monitored to respond irrespective of the scour depth (Fig. 6a). The response of the bridge in longitudinal direction was linear up to the failure load with no ductility. However, in transverse direction the major difference in bridge performance was observed in terms of lateral load and displacement capacities with varying depth of scour (Fig. 6b). The augmented levels of scour at the piles induced diminished lateral stiffness and load capacities while inducing higher displacement ductility ratios. Herein, for higher scour depths, the surrounding soil layers around piers and piles receded and consequently the piles tended to respond with lower stiffness and lateral load capacities due to the enhancement in the unsupported pile lengths. As consistently, the displacement capacity and ductility tended to increase with increasing scour depth.

**CONCLUSIONS**

In this study, the effect of scouring on bridge multi-hazard performance was assessed by using UAV based scour measurement techniques. The scour depth at bridge piers or piles were monitored by newly implemented UAV based SfM measurement method. This method was applied to the case study bridge on Boğaçay River in Antalya Province. It was demonstrated that UAV based scour monitoring methods could be successfully implemented with a good measurement accuracy. The multi-hazard performance of the bridge was assessed by numerous pushover analyses for varying scour depths.

![FIGURE 6](image)

**FIGURE 6**
The failure mechanism and pushover curves of the bridge in a) longitudinal and b) transverse direction.

For the lateral response of the piles, various nonlinear soil spring models were used both in lateral and vertical direction for sand and limestone layers that were varying with depth. Herein, the lateral and vertical properties of the soil layers were represented by nonlinear springs and the spring properties were updated for varying scour depths. In addition,
the p-multipliers were applied both in piers and in piles in order to represent the group efficiency. The modal characteristics of the bridge were determined to be independent on the scour depths considered in the scope of this case study. Ultimately, the lateral performance of the bridge was monitored to be independent upon scour depths in the longitudinal direction. However, for the transverse direction, the lateral load capacity and the stiffness tended to decrease. The lateral displacement capacity and displacement ductility were monitored to improve with increasing scour depth. Regarding the enhancement in unsupported pier or pile lengths due to scour, the lateral response of the bridge exhibited a softening type of behavior as the scour depth increased. Therefore, the scour depth along bridge piers and piles can be seasonally monitored by UAV based measurement methods considering its economy and ease of implementation. Further, the multi-hazard performance of bridges should be monitored continuously in order to prevent unnecessary losses due to multi-hazard scenarios including scouring and earthquake.

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VULNERABILITY ANALYSIS FOR AIR TRANSPORTATION NETWORK: A NATURAL DISASTER SCENARIO FOR TURKEY

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ABSTRACT

Natural disasters have an adverse impact on transportation activities, where this could return have environmental, social and economical impacts. This study examines the Turkish airtransport network in case of an possible disruption. According to the designed scenario, after a possible earthquake in Marmara region, the Istanbul Atatürk Airport is highly damaged and transport activity is disrupted. In order to detect the vulnerability towards that disruption, connectivity indicators are utilized, namely; closeness, betweenness and straightness. According to the results, even disruption of one airport may cause crucial performance issues in the airtransport network. In case of a possible disruption of the selected airport; the betweenness of all airports in the network will decrease 3%, straightness value will decrease 9% and the closeness values increase 9%. This sample scenario could aid decision makers to prioritize their investments, where the performance of the current network is quantitatively assessed.

KEYWORDS:
Geographic Information Systems (GIS), Natural Disaster, Air-Transport Network, Vulnerability, Connectivity

INTRODUCTION

Disaster, such as earthquake, flood, hurricane, or volcanic eruptions, can happen anytime, anywhere and this could cause devastating affects, where among them it could disrupt and/or delay transportation activities that is vital for economy. Air transportation holds a significant place among other transport modes due to its advantages such as, being free from geographical constraints, time saving, accessibility, safety, comfort, etc. Hence, the vulnerability and robustness of the system should be analyzed.

The Turkish air transport network has been evolving over the last decade. The network has undergone many alterations with new, renewed airports, where several new domestic/international routes are lately introduced. However, such impacts due to natural disasters, has not been fully investigated. Hence, Turkey’s domestic air traffic network is analyzed in this study via using abilities of Geographic Information Systems (GIS).

For performing the vulnerability analyses, connectivity indicators including betweenness, straightness and closeness are generally utilized. Beyond, vulnerability analyses, connectivity could be in order to assess the performance of airports under congestion and delays. According to the study about US airport network held in 2013, connectivity analyses aid the authorities to prioritize their airport infrastructure investments. [1]. Another study for European air transport network, explores the fastest indirect connections are not operated by the flight network via flight times and waiting times including connectivity [2].

This paper outlines a spatial analysis methodology, to detect vulnerability of air-transport network towards a possible disruption scenario. The current air-transport network is compared with the disrupted network, where the Istanbul Atatürk Airport is omitted from the current network. Hence, the performance of the air-transport network is tested without the disrupted airport.

MATERIALS AND METHODS

Turkey is a large peninsula that bridges the continents of Europe and Asia. Turkey is surrounded on three sides by the Black Sea, the Mediterranean Sea, and the Aegean Sea. Istanbul, the largest city in Turkey, is built on land in the Bosphorus seaway. The study area is given in Figure 1.

Within the scope of the study, 35 of the 55 airports in Turkey were evaluated because of operational reasons (modification, capacity increase, and seasonal variations). Among the airports evaluated, the 10 busiest airports containing almost 95 percent of the passenger traffic in Turkey’s flight network are given in Table 1.
FIGURE 1
Study area.

TABLE 1
Annual number of passengers and change rate.

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<tbody>
<tr>
<td>İstanbul Atatürk</td>
<td>18,542,295</td>
<td>56,695,166</td>
<td>19,333,873</td>
<td>61,332,124</td>
<td>4%</td>
</tr>
<tr>
<td>İstanbul Sabiha Gökçen</td>
<td>14,955,571</td>
<td>23,494,646</td>
<td>18,525,649</td>
<td>28,108,738</td>
<td>24%</td>
</tr>
<tr>
<td>Antalya</td>
<td>6,230,885</td>
<td>28,303,192</td>
<td>6,906,364</td>
<td>27,769,404</td>
<td>11%</td>
</tr>
<tr>
<td>İzmir Adnan Menderes</td>
<td>8,390,425</td>
<td>10,970,663</td>
<td>9,545,443</td>
<td>12,178,100</td>
<td>14%</td>
</tr>
<tr>
<td>Ankara Esenboğa</td>
<td>9,591,350</td>
<td>11,035,606</td>
<td>10,562,282</td>
<td>12,113,439</td>
<td>10%</td>
</tr>
<tr>
<td>Adana</td>
<td>4,057,291</td>
<td>4,687,494</td>
<td>4,582,185</td>
<td>5,309,706</td>
<td>13%</td>
</tr>
<tr>
<td>Muğla Dalaman</td>
<td>1,012,396</td>
<td>4,309,480</td>
<td>1,229,318</td>
<td>4,382,083</td>
<td>21%</td>
</tr>
<tr>
<td>Muğla Milas-Bodrum</td>
<td>2,011,444</td>
<td>3,846,547</td>
<td>2,309,115</td>
<td>3,877,873</td>
<td>15%</td>
</tr>
<tr>
<td>Trabzon</td>
<td>2,668,349</td>
<td>2,777,536</td>
<td>3,249,120</td>
<td>3,362,799</td>
<td>22%</td>
</tr>
<tr>
<td>Gaziantep</td>
<td>1,889,937</td>
<td>2,082,821</td>
<td>2,136,123</td>
<td>2,331,227</td>
<td>13%</td>
</tr>
</tbody>
</table>

Centrality Indexes. Centrality indexes are used for characterizing the network for analysis in the Multiple Centrality Assessment (MCA). There are numerous indexes including betweenness, closeness or straightness [3].

Closeness Centrality. The closeness is one of the most distinguishing property of corresponding nodes. Closeness defined as the inverse of cumulative distance to arrive from one node to other nodes within the search radius. Higher closeness value represents more connections within shorter distances.

Closeness centrality, CiC, indicates to which extent a node i is near to other nodes within the shortest path, and is defined as in the formula below, where $d_{ij}$ is the shortest path distance between nodes i and j [4]:

$$C_i^C = \frac{N-1}{\sum_{j \in G, j \neq i} d_{ij}}$$

Betweenness Centrality. In addition to closeness index, the connectivity of two nodes relies on the path bridging them. This index is used for discovering the potential for different nodes of the network.

Betweenness index, CiB, deals whether if the node is in between many other nodes, and is defined as in the formula below. In the formula $n_{jk}$ is the total number of shortest paths between nodes j and k, and $n_{jk}(i)$ is the total number of shortest paths between nodes j and k containing the node i [4];
\[ C_i^B = \frac{1}{(N-1)(N-2)} \sum_{j,k=\neq i} n_{jk}(i) / n_{jk} \]  

(2)

**Straightness Centrality.** This index is based on the theory; if the path is straight between two nodes, then, the connection between them is better. Therefore, Straightness centrality, \( C_i^S \), is calculated with regard to the inverse of the shortest path distance (\( d_{ij} \)) between two nodes (\( i \) and \( j \)), and it is calculated as in the formula below. In the formula below, \( d_{ij}^{Eucl} \) is the Euclidean distance between nodes \( i \) and \( j \) [4];

\[ C_i^S = \frac{1}{N-1} \sum_{j \in G, j \neq i} \frac{d_{ij}^{Eucl}}{d_{ij}} \]  

(3)

The inverse of cumulative distance to arrive from one node to others is described as closeness index. The other nodes cannot be further than the search radius. The higher the closeness value, the more connections the node has with the closer nodes. Lower closeness values represent fewer connections with the closer nodes.

Betweenness index is used for calculating visitor potential for nodes. This is computed by considering how many surrounding nodes are linked to the node. Straightness index value is based on theory that two nodes have a better link between them if the path connecting them are straight. Straightness index value is higher if the Euclidean distance between two nodes is closer to the path distance of the network.

Calculating a new vulnerability index is require to examine properly the consequences of a link closure. Disregarding the impacts has consequences of link closures and misidentify the most critical links [5]. As the first step towards disaster-resilient societies; characterization of vulnerabilities has vital importance [6]. Detection of airports which has the potential of closure may help the development of contingency plans to develop an appropriate response to any airport closure. Most critical airports can be detected with an adaptive strategy based on betweenness centrality [7].

In addition to air transport network analysis, network analysis itself is another challenging area. There are many different ready-to-use tools for such kind of analysis, also one may create a tool, as well. However, in this study, Urban Network Analysis Toolbox for ArcGIS is used, which is developed by City Form Lab [8]. The toolbox was originally developed to analyze urban design, planning, and real-estate research. However, centrality analysis for any network calculated with the same approach. Therefore, this tool is employed for the analysis, and it performed well.

**RESULTS AND DISCUSSION**

Flight network of Turkey is mainly based on Istanbul. There are two large airports in Istanbul, named, Atatürk Airport and Sabiha Gökçen Airport. After these two important airports, Ankara Esenboğa and İzmir Adnan Menderes Airports follows the airports in Istanbul. Adana, Antalya, Trabzon, Diyarbakır and Van Ferit Melen Airports are other busy airports in Turkey. Visualization of flight network in Turkey is given in Figure 2, additionally flight network excluding Istanbul Atatürk Airport is given in Figure 3.

The results of betweenness, straightness and closeness analysis for all airports in Turkey, and same analysis for all airports in Turkey except Istanbul Atatürk Airport is given in Table 2.
The effects of the scenario can be seen in the table above. Betweenness of Ankara Esenboga, Istanbul Sabiha Gokcen, Trabzon, and Izmir Adnan Menderes Airports are affected from closure of Istanbul Ataturk Airport. According to the results, straightness values decreased 8.5% and closeness values increased 8.9% on average.

As the distance travelled between two airports, those without direct flights, increased, the straightness values decreased. This increase in travel distances, also increases the closeness values. This is because, the excluded airport provided a shorter distance for most of the minor airports. Many major airports served as a transfer station to other airports. However, due to the exclusion, such major airports caused decrease in betweenness values.

CONCLUSION

The study shows us that even disruption of one airport may cause performance issues in the network. This can be seen with the comparison of the betweenness, straightness, and closeness centrality values. One should mind that these analyses were held for domestic flights only. In case of addition of international flights, the differences between these values would be higher, which refers to a worse scenario. Moreover, such scenario would be realized with the publicly awaiting great Istanbul earthquake, which might affect Istanbul Ataturk, and/or Sabiha Gökçen Airports. It may also affect the airports close the Istanbul such as; Kocaeli, Tekirdağ and Bursa. Authorities should be working on such scenarios for disability of any airports including the mostly used ones.
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THE USAGE OF UNMANNED AERIAL VEHICLES (UAVs) FOR 3D MAPPING OF ARCHAEOLOGICAL SITES

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ABSTRACT

In archaeological sites, mapping, documentation, registration, and visualization of cultural heritage is very important for both cultural heritage’s conservation, understanding of the historical importance and to transmit future generations. Traditionally, mapping and documentation studies are carried out through terrestrial measurements performed during excavation or at the end of each workday. Together with the improvements in image acquisition and processing techniques, Unmanned Aerial Vehicles (UAVs) have become an alternative for many applications including archaeological areas, historic sites, and cultural heritage buildings with accurately and efficiently. The UAVs provide the user low cost, fast data collection even in real-time, and application flexibility for mapping especially of small areas. This study aimed to investigate the usability of UAVs for 3D mapping of archaeological sites. For this purpose, two measurement campaigns were carried out in two different archaeological sites, Alacahöyük and Şapınova. From the outcome of this study, it is clear that aerial maps and 3D models of the studied sites were produced with UAV measurements within a cm to dm level of accuracy in a fast and cost-effective manner. In general, the results show that UAVs can be used for many archaeological mapping and documentation studies as a strong alternative to high cost and labor conventional terrestrial and photogrammetric surveying methods.

KEYWORDS:
Unmanned Aerial Vehicle (UAV), archaeology, cultural heritage, 3D model, mapping.

INTRODUCTION

Restoration, restitution and archaeological mapping studies are required to protect, strengthen and document all archaeological areas, historic sites, and cultural heritage buildings and their neighborhood. The main aims of these studies are the documentation of these structures, determining their problems, preparing drawings and producing archaeological site maps with a report for potential decisions to be made for repairment, if needed. The excavation activities are dynamic phenomena and open to the outside environment and most of the sites are at risk of being physically altered. Digital recording, documentation and protection ensure that the heritage (natural, cultural or both) is protected against attrition, war, natural disaster, weather, urbanization damage, climate change and human neglect throughout history [1, 2, 3]. Therefore, detailed documentation and mapping studies should be performed with great care, accurately and as quickly as possible in all parts of the archaeological/heritage sites. Generally, it is necessary to establish the excavation process of archaeological sites by producing maps at certain intervals during the excavation, both for evaluating the current situation and for the planning of future works. In addition, digitally documentation and evaluation are extremely important for the archaeological findings.

The architectural survey and restitution studies are documentation methods and basic preliminary stages for the preparation of a restoration project. These studies are usually prepared two-dimensionally in a 2D format with traditional methods. Over the last years, the three-dimensional (3D) applications have emerged, using modern measuring equipment and techniques (such as laser scanning and aerial photogrammetry or alike) all over the world. Although such practices have not yet spread in Turkey, they have been used in different archaeological studies for documentation and mapping of archaeological sites from aerial images and laser scanner [1, 4, 5, 6]. 3D data acquisition methods mainly provide three-dimensional visualization and reconstruction. The findings with potential to be used successfully in many different areas. Producing of high-quality digital replicas of cultural heritage assets and creating digital 3D representations of artifacts could be done by using this digital technology [7, 8].

Acquired 3D data can be used to prevent damage to archaeological objects and provide digital documentation and visualization of volumetric geometries [5]. The three-dimensional studies give more detailed information of standard information to researchers, and also provide additional features such as depth, texture and spatial perspective that conven-
tional methods cannot offer. In this way, multi-layered, multi-dimensional, interrogable 3D models open new research areas. 3D measurement studies made at certain intervals can be used to more precisely determine the deformations that occur in the monitored structures and, if necessary, the intervention processes can be planned more quickly and effectively. 3D reconstruction of archeological sites allows an easy and rapid intellectual access to heritage [9]. This technology can be used for the generation of a virtual model which is necessary for a more realistic representation of archeological sites and for access to web-based systems via virtual reality applications. Nowadays, web-based publishing and visualization of 3D models are consolidating and becoming a de-facto standard for many applications [8].

UNMANNED AERIAL VEHICLE (UAV) FOR ARCHAEOLOGICAL MAPPING

There are numerous acquisition techniques and methods for documentation and mapping of archeological sites all over the world with different equipment and surveying methods including terrestrial measurement systems, Global Navigation Satellite System (GNSS), ground-based laser scanning, aerial photogrammetry, and remote sensing [10]. Although the conventional methods used for documentation have been widely used for a long time, the obtained products are sometimes not satisfactory except for taking standard information, because these products are generally shown in 2D. In 3D applications, archeological sites and especially architectural structures and findings can be obtained digitally as point clouds in detail.

Recently, in archaeology, Unmanned Aerial Vehicle (UAVs) have mainly been used for providing digital surface and digital terrain models with the photogrammetric survey of landscapes and for the 3D recordings and documentation of excavations and historical monuments. UAVs can be operated in hazardous or temporarily inaccessible locations [3, 11, 12]. By using UAVs, it is possible to collect digital data that will take the place of traditional research methods [2]. Archaeologists have already begun to use UAVs in several ways including reconnaissance, site documentation, mapping, site preservation, monitoring. Research using UAVs for archeological monuments and historical buildings are among the most common practices in archeology and heritage management from the earliest days [10]. Furthermore, the UAVs have been used to determine excavation plans, perspective drawings, and maps. In general, documentation, observation, monitoring, mapping, 3D modeling and 3D reconstruction are the most applicable features of UAVs in cultural heritage areas besides digital maps, digital orthophotos, Digital Elevation Models (DEM) and Digital Surface Models (DSM) [13].

UAVs provide detailed and effective observation at low altitudes. It has a data collection capacity from less than one hectare to 300 hectares per day in a wide coverage at an altitude of about 20 to 200 m [10]. Naturally, they are safe since they are unmanned and can reach places that are difficult or dangerous to reach by a manned flight. There are different types of maps produced by UAVs such as geographically accurate orthorectified two-dimensional maps, elevation models, thermal maps, and 3D maps or models [14].

Within the last few years, UAVs have been widely used in many applications such as producing large-scale maps, environmental surveying, forestry, urban planning, agriculture, film, search and rescue, energy, real-estate, public safety, monitoring naturally protected areas, locating coastal lines, traffic monitoring, water quality estimates since they provide very fast, flexible, accurate and cost-effective solution. More detailed information about the UAVs (or drones) usability in different archeological application areas can be found in [10, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23].

MATERIALS AND METHODS

Description of the Study Area. In this study, usability and accuracy performance of UAV derived maps in archaeological documentation and monitoring studies was investigated. For this aim, two different archeological excavation sites i.e. Alaca Höyük and Şapinuva were selected. These sites belong to the Hittite civilization, the large states established in Anatolia within the borders of the Çorum Province, in Turkey (Figure 1).

Alaca Höyük is located 45 km from Čorum and 36 km northeast of Hattusa (Boğazköy). This site was first identified in 1835, and since then, several excavation campaigns have been brought to light, but regular research has been started by the Turkish Historical Society by the order of Mustafa Kemal Atatürk in 1935. Alaca Höyük is one of the important cities of the pre-Hittite period. It dates back to 4500 BC to the Chalcolithic period and was one of the most important centers for the Hittites. The artifacts that are exhumed from the kings’ tombs in the pre-Hittite period going back to 2500 BC are the most valuable findings. It covers an area of about 20 hectares.

Şapinuva is located approximately 3 km southwest of the Ortaköy district of Čorum. It is one of the most important Hittite cities during the empire period. The remains of the city in which many building foundations are located spread over an area of 900 hectares. In this study, initially, approximately 6.3
 hectares of the area were selected for the test study in Şapinuva archeologic site.

**FIGURE 1**
Study area.

**Archaeological Mapping with Unmanned Aerial Vehicle.** Two different Unmanned Aerial Vehicles were used in the sites of the study. In Alahahöyük, the first site, we used Multirotor G4 Eagle octocopter, which is powered by eight electrical motors. This UAV has the ability to vertical takeoff and land. This octocopter was equipped with a Sony A7R RGB sensor camera and effective megapixel of this RGB camera is 36.4 M. The study was conducted at 120 m altitude above ground level. The front and side overlap ratios were set to 70% and 40%, respectively. It should be noted that quality of the photos taken will closely affect the results. The Ground Sample Distance (GSD) was 1.81 cm/pixel.

In Şapinuva, DJI Phantom 4 PRO quadcopter was used. This UAV has the ability for a vertical takeoff and land. This UAV has a steady camera equipped with a 1” CMOS sensor and three-axis gimbal system. The effective pixel of the RGB camera is 20 megapixel. Moreover, this UAV uses GPS and GLONASS satellite systems for positioning. The front and side overlap ratios were set to 65% and 60%, respectively. The GSD was 1.38 cm/pixel.

In order to calculate scale, orientation, and absolute position of the photos taken by the UAV's, 8 for first measurement and 9 for second Ground Control Points (GCPs) were established in favorable locations homogeneously in the study area by following general photogrammetric measurement criterion. These points were marked before starting the UAV flight using easy-to-see targets. These GCPs were used for geo-referencing of all the measurement in ITRF96 datum. The coordinates of the GCPs were determined using multi-constellation and multi-frequency Trimble R10 GNSS receivers with Turkish Network RTK GNSS system called as TUSAGA-Aktif. Network RTK accuracy performance of used GNSS receivers are given as 8 mm + 0.5 ppm RMS for horizontal and 15 mm + 0.5 ppm RMS for vertical components [24]. TUSAGA-Aktif Network covers Turkey almost entirely and the Turkish Republic of Northern Cyprus with its 2 Control and 146 Reference Stations with an average spacing of about 70-100 km. In this system, VRS, FKP, and MAC correction techniques are used. The positioning accuracy of the TUSAGA-Aktif system in real-time measurements is given as under 3 cm for 2D position and 5 cm for height. More information about Network RTK and Turkish RTK CORS can be found in [25, 26, 27].

**3D Map of Archaeological Sites.** After the image acquisition stage obtained from the archaeological sites, the photographs taken were processed with the Pix4D Mapper software that is especially designed for UAV mapping. Firstly, a new project was created and photos were imported to this project. Moreover, in this step, projection settings of the output products were defined. In the initial processing step, key-point extraction and sparse point cloud were generated from the existing coordinate system of the photographs. In addition, the camera calibration parameters were also calculated at this stage. At the end of the initial step, GCPs were included in the project to obtain highly accurate position output products. GCPs were matched from as many photos as possible and the necessary coordinate transformations were performed. Then, the output products named as densified point cloud and 3D textured mesh were obtained. In the final step, the raster DSM and orthomosaic map obtained are given in Figure 2 for Alahahöyük and Figure 3 for the Şapinuva archeological sites.

**Assessment of the Positioning Accuracy.** In order to make the positioning accuracy assessment of the models obtained using UAV, some sharp, well defined, and clearly identified points on photos were coordinated from the produced 3D Model and in the field. For this purpose, 122 and 75 checkpoints were determined at the Alahahöyük and Şapinuva sites, respectively (Figure 4).
FIGURE 2
Produced orthophoto map and digital surface model for the Alacahöyük archeological site.

FIGURE 3
Produced orthophoto map and digital surface model for Şapinuva archeological site.

FIGURE 4
The distribution of ground checkpoints; (left) Alacahöyük, (right) Şapinuva archeologic sites.
FIGURE 5
Differences between the models coordinates and the reference coordinates

The checkpoints were coordinated with Trimble R10 GNSS receivers using TUSAGA-Aktif Network. The coordinates of the points having different characteristics in the archaeological areas were then compared with those obtained from the model. The obtained differences in position and heights are given in Figure 5.

Some statistical information about the obtained differences are summarized in Table 1.

<table>
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<td>The statistics of obtained differences.</td>
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<tr>
<td>Alacahöyük</td>
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<td>Position (m)</td>
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<td>Min.</td>
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<td>Mean</td>
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<td>RMSE</td>
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When the results given in Figure 5 and Table 1 are examined, it is seen that the maximum differences were found 15 cm (with 4 cm RMSE) for 2D position and 27 cm (with 8 cm RMSE) for height component for Alacahöyük site. For the Şapinuva site, the maximum differences were found 10 cm (with 3 cm RMSE) for 2D position and 15 cm (with 6 cm RMSE) for height. After a general interpretation of the results, it is seen that position accuracy is achieved with an accuracy of a few cm levels for both Alacahöyük and Şapinuva. For height component, the accuracy is found a bit worse for both sites. However, the accuracy of the 2D position, as well as the height, is relatively low in the measurements made on the Alacahöyük archaeological site. It is estimated that the sudden elevation differences in the excavation area of Alacahöyük caused especially the height error to be higher than the error of Şapinuva excavation area. When the points are examined in detail, it is seen that the height of small objects on land cannot be modeled exactly, and these objects have the same height values as the ground they are on. This situation is thought to cause the height error to increase. The overall results imply that 3D map with a UAV can be achieved with a dm level of accuracy. This accuracy fulfills most mapping requirements including archaeology.

CONCLUSION

In this study, the usability of an inexpensive UAV for archaeological site surveying is investigated. The results show that aerial maps and 3D model of the Alacahöyük and Şapinuva archaeological sites were produced by using the UAV measurement with a centimeter to decimeter level of accuracy. From the outcome of this study it is clear that, the high-resolution data collection skills of UAVs offer accurate, cost-effective, efficient, and reliable and a simple solution to map the area of the studied archeological sites when the archaeological site is not covered by trees or when the sites are not protected by a roof, shelter, etc. These data can be used in a number of areas including the environment, documentation of cultural heritage, monitoring and recording the changes in archaeological sites, and risk analysis and management processes.
The results also prove that UAVs can be used in many types of archaeological projects including surveying, mapping, documentation, and 3D modeling applications for archaeological and heritage sites in open areas as a strong alternative to high cost and labor traditional photogrammetric and ground surveying methods. Depending on these advantages, UAVs are becoming increasingly common surveying method in archaeology.

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USING EXPLORATORY FACTOR ANALYSIS TO IMPROVE THE CALIBRATION OF SLEUTH URBAN GROWTH MODELS

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ABSTRACT

Simulation models based on cellular automata (CA) are often used to track changes in land cover caused by urban growth. The main program for these models is the SLEUTH Urban Growth Model, which is open source and free. This program uses Monte Carlo (MC) iteration in three phases: testing, calibration, and prediction. Calibration is based on 13 variables. The goal of this study is to test the effectiveness of exploratory factor analysis (EFA), a previously untested method, to improve the calibration of CA-based urban growth models. EFA was evaluated against two commonly-used methods, Lee-Sallee and Optimum SLEUTH Metrics (OSM), using synthetic test data from the Project Gigalopolis website. The results show that EFA had highest regression scores for six of the 13 metrics, performing better than OSM with high scores in four variables and Lee-Sallee with high scores in just three variables. Improving calibration with EFA will result in more accurate models and predictions of urban growth.

KEYWORDS:
Exploratory Factor Analysis, SLEUTH, Cellular Automata Model Calibration, Urban Growth Simulation Models,

INTRODUCTION

Urban population are increasing daily. This leads to growth on the edges of urban areas and significant changes in land cover. One of the most important global problems, in terms of sustainable development policies, is the inefficient use of natural and environmental resources by rapidly growing cities [1-3]. Urban decision makers would like to control urban growth to improve living conditions and better utilize natural and environmental resources [4]. To facilitate these goals, a number of urban growth simulation models have been created [5-8]. They predict the direction and speed of urbanization so this growth can be managed.

Cellular automata (CA) modeling is the simplest and most popular approach. It is generally used to create urban growth simulation models (UGSM) which describe and predict the impact of urbanization on land cover. CA models have five basic elements: space, state, neighborhood, transition rules, and time [9-10]. They allow the user to divide a state into cells and to predict the future state of each cell according to the state of neighboring cells [9, 11]. Information can be exchanged between cells or dispersed to neighboring cells; in this sense, these models track spatial spread of information [9].

Various CA-based simulation models have been created to monitor urban growth; SLEUTH is one of the best-known and has been used in several projects worldwide [12-18]. Models are created in three phases: testing, calibration, and prediction [19]. During the testing phase, data are checked for calibration readiness. In the calibration phase, five coefficients from four growth rules are evaluated with Monte Carlo (MC) iteration, which determines the best fit values [19]. In the final phase, the model uses the best fit values to predict urban growth [5].

SLEUTH contains 13 variables, each of which include Pearson’s product-moment correlation coefficient $r^2$ score. They have separate impacts on the calculation of urban growth during the calibration process, which has three steps: coarse, fine, and final [19]. Brute Force Calibration is used to execute a best fit value for each coefficient [20]. Coefficient ranges are initially set between 0 and 100. In MC iteration, the interval is narrowed after every calibration and the best fit values are calculated [19]. The main problem is selecting the best range to narrow the interval of coefficients. Lee-Sallee and OSM are generally used to do this. However, there is no consensus on which method is more effective. The Lee-Sallee method has been frequently used [19]. Jantz et. al. (2004) used “Compare, Population, and Lee-Sallee” metrics [14] for the Washington–Baltimore area and Dietzel and Clarke (2007) developed the Optimal SLEUTH Metric (OSM) technique [20] that does not require best fit values in the forecast step. However, neither Lee-Sallee nor OSM can assess all 13 SLEUTH variables. The main purpose of this study is to evaluate the ability of exploratory factor analysis (EFA) to identify which variables to use by grouping correlated SLEUTH variables. This makes it possible to remove some variables and calculate...
the remaining ones. EFA was used to obtain unique variables for model calibration.

EFA is a multivariate statistical method that reduces the number of variables by combining correlated variables into factors [21]. The aim is to specify the underlying dimensions behind a set of factors [22]. This statistical method has wide-ranging applications, for example in statistics, geography, urbanization, economy, medicine, etc.

Before implementing the EFA, the suitability of dataset used was evaluated. Sample size is an important criterion. Comrey and Lee (2013) suggested the following ranges of sample size for dataset quality: 50 is very poor; 100 is poor, 200 is fair, 300 is good, 500 is very good, and 1000 is excellent [23]. However, the generally accepted minimum sample size for acceptable samples could be below 100 [24]. However, for each calibration step: coarse, fine and final.

The results show that EFA identified six inter-correlated variables, more than the other two methods, that could be used for calibration.

MATERIALS AND METHODS

Calibration Phase of SLEUTH. The MC simulation technique is used to calibrate [5]. The initial interval of the coefficients should be set to between 0 and 100. The calibration results in five model parameters with best fit values for each coefficient.

Lee-Sallee Metric. This metric is defined as “…the ratio of the intersection and union of the simulated and actual urban areas” [20]. It has been used in a number of projects [19].

OSM. The OSM was developed by Dietzel and Clarke (2017). Growth coefficients can be calculated from “Compare, Pop, Edges, Clusters, Slope, X-Mean and Y-Mean” metrics plus “F-match,” if land cover data is used [20].

EFA. EFA attempts to identify inter-correlated variables as well as the underlying structure of the variables. These factors explain the pattern of correlations within a set of variables [21]. EFA is often used to reduce the number of variables to those that explain most of the variance in the data [22][25].

When using EFA, it is important to evaluate the Kaiser-Meyer-Olkin (KMO) measure of sampling adequacy and Bartlett’s test of sphericity. The KMO value indicates the proportion of variance in variables that might be caused by underlying factors and the Bartlett’s test of sphericity uses a correlation matrix to evaluate the hypothesis that the variables are uncorrelated [24]. If the KMO value is greater than 0.45 [22] and Bartlett’s test of sphericity’s p-value is less than 0.05 [24], sample size is adequate for EFA.

The second step is to calculate the Total Variance Explained (TVE) based on the eigenvalues for each factor [22, 26].

The final step is to generate a Rotated Component Matrix (RCM), a factor loading matrix. Since our data have a multi-factor structure, we used orthogonal rotation with the varimax rotation method [21, 24].

RESULTS AND DISCUSSION

This section compares the results of UGSMs created with three different calibration techniques. In all three methods, calibration was done in three steps. Synthetic data were downloaded from the Project Gigalopolis website and used for testing the calibration methods. The top three scores for all these methods were used to select the coefficient ranges. Arithmetic averages were calculated for each variable. KMO and Bartlett’s tests showed that the sample size was adequate (Table 1).

<table>
<thead>
<tr>
<th>Calibration Step</th>
<th>Coarse</th>
<th>Fine</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>KMO values</td>
<td>0.780</td>
<td>0.815</td>
<td>0.599</td>
</tr>
<tr>
<td>Bartlett’s test of sphericity’s p-value</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

The first method was the Lee-Sallee metric; the top three scores were used for calibration. The second one was OSM, and the final one was EFA. These methods were implemented with SPSS software.

For the coarse calibration, TVE identified three factors that explained 77.65% of the total variance. For the fine calibration, two factors explained 86.21% of the variance. For the final calibration, three factors explained 87.17% of the variance.

In the coarse calibration, the Monte Carlo iteration number was set to 100 for all three calibration methods and the ranges were successively narrowed (Table 2).

In the fine calibration, the Monte Carlo Iteration number was set to 100, and all three methods were compared (Table 3). In the final calibration, the Monte Carlo Iteration number was set to 150 to find more precise best fit values. Regression scores were compared for all three methods (Table 4). The results show that of the 13 metrics, EFA identified six with high regression scores in coarse calibration, five in fine calibration, and seven in final calibration. With the OSM, the number of scores in the three calibration steps were four, five, and three, respectively. The Lee-Salle method identified three scores in each calibration step.
The study’s goal was to evaluate EFA as a method to calibrate SLEUTH models and compare it to Lee-Sallee and OSM methods, which have both been used for a long time. This study is the first use of EFA for SLEUTH calibration.

In the EFA method, all SLEUTH variables were handled at the same time. The correlation of metrics was investigated and coefficient intervals were narrowed using highly correlated variables. As shown in Tables 2-4, promising results were obtained from EFA. Compared to the other two methods, the highest regression scores were obtained from EFA with the synthetic test data. However, other datasets should also be tested.

### TABLE 2
Comparisons of calibration methods for coarse calibration

<table>
<thead>
<tr>
<th>Product</th>
<th>Compare</th>
<th>Population</th>
<th>Edges</th>
<th>Clusters</th>
<th>Size</th>
<th>Lee-Sallee</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lee-Sallee</td>
<td>0.00444</td>
<td>0.36036</td>
<td>0.94784</td>
<td>0.95807</td>
<td>0.98393</td>
<td>0.84089</td>
</tr>
<tr>
<td>Mean</td>
<td>0.00444</td>
<td>0.36036</td>
<td>0.94784</td>
<td>0.95807</td>
<td>0.98393</td>
<td>0.84089</td>
</tr>
<tr>
<td>OSM</td>
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<td>0.98123</td>
<td>0.99985</td>
<td>0.98386</td>
</tr>
<tr>
<td>Mean</td>
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<td>0.55981</td>
<td>0.94650</td>
<td>0.95840</td>
<td>0.99710</td>
<td>0.82245</td>
</tr>
<tr>
<td>EFA</td>
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<td>0.97567</td>
<td>0.28248</td>
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<td>0.97363</td>
</tr>
<tr>
<td>Mean</td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Slope</th>
<th>%Urban</th>
<th>X-mean</th>
<th>Y-mean</th>
<th>Radius</th>
<th>F-match</th>
<th>Lee-Sallee</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6171</td>
<td>0.92963</td>
<td>0.23744</td>
<td>0.53979</td>
<td>0.97196</td>
<td>0.71520</td>
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<td>0.92963</td>
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<td>0.85753</td>
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<td>0.21480</td>
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### TABLE 3
Comparisons of calibration methods for fine calibration

<table>
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<th>Product</th>
<th>Compare</th>
<th>Population</th>
<th>Edges</th>
<th>Clusters</th>
<th>Size</th>
<th>Lee-Sallee</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.99398</td>
<td>0.97176</td>
<td>0.81766</td>
<td>0.90551</td>
</tr>
<tr>
<td>Mean</td>
<td>0.00018</td>
<td>0.93415</td>
<td>0.99398</td>
<td>0.97176</td>
<td>0.81766</td>
<td>0.90551</td>
</tr>
<tr>
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<tr>
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<td>0.36603</td>
<td>0.99975</td>
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</table>

<table>
<thead>
<tr>
<th>Slope</th>
<th>%Urban</th>
<th>X-mean</th>
<th>Y-mean</th>
<th>Radius</th>
<th>F-match</th>
<th>Lee-Sallee</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.96547</td>
<td>0.98461</td>
<td>0.00013</td>
<td>0.99982</td>
<td>0.99573</td>
<td>0.69400</td>
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</tr>
<tr>
<td>0.96547</td>
<td>0.98461</td>
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<td>0.99982</td>
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### CONCLUSION

In the EFA method, all SLEUTH variables were handled at the same time. The correlation of metrics was investigated and coefficient intervals were narrowed using highly correlated variables. As shown in Tables 2-4, promising results were obtained from EFA. Compared to the other two methods, the highest regression scores were obtained from EFA with the synthetic test data. However, other datasets should also be tested.
### TABLE 4
Comparisons of calibration methods for final calibration

<table>
<thead>
<tr>
<th>Product</th>
<th>Compare</th>
<th>Population</th>
<th>Edges</th>
<th>Clusters</th>
<th>Size</th>
<th>Lee-Sallee</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lee-Sallee</td>
<td>0.11795</td>
<td>0.76372</td>
<td>0.99471</td>
<td>0.99889</td>
<td>0.64059</td>
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<td>Lee-Sallee</td>
<td>0.11795</td>
<td>0.76372</td>
<td>0.99471</td>
<td>0.99889</td>
<td>0.64059</td>
<td>0.90643</td>
</tr>
<tr>
<td>Mean</td>
<td>0.11795</td>
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<tr>
<th>Slope</th>
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<th>X-mean</th>
<th>Y-mean</th>
<th>Radius</th>
<th>F-match</th>
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### ACKNOWLEDGEMENTS

The authors would like to thank Cumhuriyet University because of support the study under CUBAP project numbered M 673.

### REFERENCES


ANALYZING THE IMPACT OF AN EARTHQUAKE ON THE SHORELINE USING SAR IMAGES AS ALTERNATIVE DATA SET

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1Akdeniz University, Space Science and Technologies, 07058, Antalya, Turkey.
2Yildiz Technical University, Department of Geomatics Engineering, Davutpasa Campus, Esenler, 34220, Istanbul, Turkey
3Istanbul Technical University, Department of Geomatics Engineering, 80626 Maslak, Istanbul, Turkey

ABSTRACT

Shorelines change rapidly, and the natural disasters such as earthquakes may destroy their morphologies. Therefore, shoreline monitoring is vital for preservation. Traditional methods, such as field surveys, are inefficient for monitoring coastal regions in terms of both time and cost. Alternatively, remote sensing technologies and image processing techniques can be used to derive such information effectively. The objective of this study is to investigate shoreline changes before and after an earthquake in Christchurch city from Canterbury region of New Zealand by non-parametrically processing of SAR imagery. The segmentation parameters were determined using optical SENTINEL 2A images and changes in the shoreline were determined using SAR data. The main motivation of the study is to use Optic SAR as a replacement for LiDAR data to analyze the shoreline changes. Experiments were performed to evaluate the proposed method by comparing the obtained results with the reference data. It was observed that the proposed method was effective in determining the changes in the shoreline with high accuracy.

KEYWORDS:
Sar, Lidar, Multispectral, Sentinel, Shoreline Detection, Earthquake

INTRODUCTION

Shorelines need rapid and up-to-date information for the environmental management [1]. Shoreline monitoring has become more important as many human induced and natural phenomena such as climate change, erosion and earthquakes etc., are creating more threat to the living beings along shorelines [1-2]. Compared to traditional methods, remote sensing and LiDAR systems are cost effective and usually produce more accurate results [3]. A number of studies have investigated remote sensing and LiDAR data with image processing techniques for shoreline detection. For instance, in [4] authors proposed edge-tracing method to detect shorelines from low resolution radar imagery. Similarly, [5] applied Canny edge detection to derive the shorelines from SAR data. Active contour model was applied in [6] on ERS-1 SAR images. [7] also proposed active contour models to detect shorelines from polarimetric SAR data. [8] utilized a method which applies diffusion on the polarimetric SAR imagery. [9] developed a method based on morphology, [10] combined geometric active contour models with quad-tree segmentation to extract the shorelines. In [11] K-means segmentation method is integrated with Canny edge detection for shoreline extraction. [12] also used K-means algorithm with an object-based region growing method for delineation of shorelines. [13] applied fuzzy clustering and active contour model to detect shorelines.

The spectral capabilities of many passive remote sensing systems allow to obtain useful data. SAR data can be used also as an active system for data collection. Although, SAR technology usually capture single channel, yet, the data can be collected independently from atmospheric conditions and sunlight. Beside the active and passive remote sensing systems, LiDAR systems collect high resolution 3D data of the earth surface as an active data source which become very popular for many different applications.

Beside SAR data, optical imageries were also used for shoreline detection [14-16]. Some studies presented that terrestrial laser scanners can be used for determination of shoreline profile changes [17].

The main objective of this study is to extract shoreline changes before and after an earthquake. Christchurch city from Canterbury region of New Zealand was selected as the study area was hit by several earthquakes between 2011 and 2016. Mean shift method was employed for segmentation and the SAR data was used as an alternative for LiDAR data.
MATERIALS AND METHODS

In this study, Christchurch city from Canterbury region of New Zealand was selected as the study area. Several earthquakes hit the city in the years 2011, 2013, 2015 and 2016. The last earthquake, which occurred on 14th of November, 2016, had magnitude of 7.8 [18] in which two people lost their lives and fifty seven were injured [19].

In this study, LiDAR point cloud, SENTINELp-1A and SENTINEL-2A images were used to analyze post-quake shoreline changes. Sentinel-1A images were selected which were taken before and after the earthquake. The LiDAR dataset was only available for May 2015 which belongs to pre-earthquake period. The study area, the properties of LiDAR, Sentinel 1A and 2A images are shown in Figure 1 and listed in Table 1 respectively. The shoreline of the pre-earthquake period from LiDAR dataset was extracted by using Mean-Shift method. Thus, the fuzzy membership parameters were calculated for clustering of SENTINEL-1A imagery. Manually digitized images of shoreline were taken as reference data for evaluation. Experiments were performed to test if the SAR dataset could be used as an alternative to the LiDAR data.

SAR images were clustered using segmentation results from SENTINEL-2A multispectral images by applying Mean-Shift method. The results were evaluated to test the possibility to replace LiDAR data with SENTINEL-2A image for deriving the used parameters in SAR clustering. Then, the shorelines from the post-earthquake period were extracted from SENTINEL-1A imagery using the parameters derived from SENTINEL-2A imagery.

Processing of LiDAR and SENTINEL-2A MS image. In this study, the Mean-shift algorithm [20] has been used for image segmentation. The method is based on the non-parametrically estimation of the density function known as Parzen window technique [21]. According to [21] the gradient of the density estimator is given in equation (1).

$$\nabla f(x) = \frac{2c_k d}{n h^d} \left[ \sum_{i=1}^{n} g \left( \frac{\|x - x_i\|^2}{h^2} \right) \left[ \sum_{j=1}^{n} \frac{c_j d_j}{\left( \|x - x_j\|^2 \right)^{(d+1)/2}} \right] - x \right]$$

(1)

Where $g(x)$ is the kernel function ($g(x) = c_k d_k \left( \|x\|^2 \right)$), $x_i$ is a data point, $x$ is the data center, $h$ is the bandwidth parameter, $c$ is the normalization
constant. The first term is related to density estimation of \( x \) by Kernel \( g(x) \), the second term is the Mean-shift.

<table>
<thead>
<tr>
<th>TABLE 2 Mean-shift parameters</th>
<th>LiDAR</th>
<th>Sentinel 2A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spatial Window Radius</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Color Window Radius</td>
<td>15</td>
<td>1</td>
</tr>
<tr>
<td>Minimum Segment Size</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Maximum Iteration</td>
<td>200</td>
<td>100</td>
</tr>
</tbody>
</table>

To use LiDAR data, first it has been converted to image by using minimum height values and interpolating to the grid in 1m size. As a result image from point cloud data has been created in 1.41m spatial resolution. The Mean-shift parameters have been given in Table 2. These parameters were calculated empirically that produced optimal results. The Mean-shift algorithm has been implemented using Emgu CV library in the .NET environment as applied in [22].

Shoreline extraction method is divided into five main steps for both LiDAR and Sentinel-2 imagery: (i) segmenting images using Mean-shift algorithm, (ii) thresholding, (iii) editing of erroneous segments, (iv) noise elimination and (v) obtaining final binary land/water classes. Figure 2 shows the results obtained for each stage applied on LiDAR and the Sentinel-2 images.

An optional editing step has been added to remove falsely classified or to add miss-classified segments manually. This step, which has been coded using MATLAB© environment, improved the overall accuracy of the proposed method.

The empirically defined threshold values for LiDAR data are Red: 137 – 148 and 150 – 175; Green: 170 – 198; Blue: 0 – 255 and for SENTINEL 2A image NIR: 0 – 255; Red: 0 – 255; Blue: 149 – 255. Noise removal step is based on blob analysis. For this purpose, the first maximum area of white pixel blob is calculated and the rest of the blobs that their area is less than calculated value are deleted. So final land/water classes for LiDAR data and SENTINEL 2A image have been obtained. Results from LiDAR and SENTINEL 2A multispectral image were evaluated with manually created reference datasets. The statistics are shown in Table 3.

SENTINEL 1A fuzzy clustering. The extraction of shorelines from SENTINEL 1A image carried out in three steps: pre-processing, fuzzy clustering and post-processing. The workflow of processing is shown in Figure 3.
Regarding to post-processing, a speckle of SAR image is needed to be eliminated [23]. Lee filter [24] is applied to reduce the speckle since it preserves the sharpness of the image while eliminating the speckle. The geometric correction of the image was done with SRTM terrain model. Opposite to commonly used parametric methods, land and water classes were segmented by non-parametric approach provided by the authors of this study. Therefore, the mostly used classification methods such as maximum likelihood and minimum distance do not work efficiently with SAR datasets [25]. In the fuzzy clustering step of the study, membership values were defined as in equation 2. Defuzzification was realized for generation of land and water classes. Mean standard deviation function method was selected as membership function.

As applied by [26], the membership values were calculated with following equations:

For land class and water class,

\[
\begin{align*}
\text{Land Class} & : \mu(x) = 1 - \frac{a}{(x - \alpha) + b}\ldots (b) \\
\text{Water Class} & : \mu(x) = 0
\end{align*}
\]

\[
\begin{align*}
\text{Land Class} & : \mu(x) = 1 - \frac{a}{(x - \alpha) + b}\ldots (2) \\
\text{Water Class} & : \mu(x) = 0
\end{align*}
\]

Where \(m\) is the mean, \(\sigma\) is the standard deviation, and \(a\) and \(b\) are multiplier parameters. The parameters \(a, b, \sigma\) and \(m\) were created with use of segmentation results of LiDAR image and SENTINEL 2A as a mask. Once the fuzzy membership values were defined for SENTINEL 1A image then the computed mean and standard deviation values are used to calculate the multipliers of \(a\) and \(b\). It was supposed that the land and water classes from LiDAR data give the membership value of 1 with the calculated mean and standard deviations for the equation 2. Since its performance is the best among the others, the centroid method is selected as defuzzication method [27].

### RESULTS

The abstract of shorelines detection method, quality assessment results and calculated thresholds for defuzzification are given in Table 3. The validation process was realized by taking into account perpendicular distance between reference and obtained data in each 10 meters of segment length. Since the results of case 5 in Table 3 were used only for change analyses (before and after earthquake periods), therefore statistics analysis were not available. The obtained shorelines of before and after earthquake periods are shown in Figure 4.

The detected changes along the shoreline between the periods October -2015, September 2016, and December 2016 are given in Table 4.

### TABLE 3

<table>
<thead>
<tr>
<th>Case</th>
<th>Period</th>
<th>Main dataset</th>
<th>Parameter Estimation</th>
<th>Method</th>
<th>Threshold (mean // median// std dev(m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pre-earthquake</td>
<td>LiDAR dataset</td>
<td>empirical</td>
<td>Mean-Shift</td>
<td>N/A 18.88/20.39/16.92</td>
</tr>
<tr>
<td>2</td>
<td>Pre-earthquake</td>
<td>Sentinel 2A MS</td>
<td>empirical</td>
<td>Mean-Shift</td>
<td>N/A 21.51/22.39/16.00</td>
</tr>
<tr>
<td>3</td>
<td>Pre-earthquake (September 2016)</td>
<td>Sentinel 1A SAR</td>
<td>LiDAR</td>
<td>Fuzzy MSLarge</td>
<td>38.62 21.88/21.31/17.03</td>
</tr>
<tr>
<td>4</td>
<td>Pre-earthquake (September 2016)</td>
<td>Sentinel 1A SAR</td>
<td>Sentinel 2A MS</td>
<td>Fuzzy MSLarge</td>
<td>36.13 8.86/17.85/4.45</td>
</tr>
<tr>
<td>5</td>
<td>Post-earthquake (December 2016)</td>
<td>Sentinel 1A SAR</td>
<td>Sentinel 2A MS</td>
<td>Fuzzy MSLarge</td>
<td>36.62 5.79/3.05/12.4</td>
</tr>
</tbody>
</table>

### FIGURE 4

Detected shoreline of the date, a: September 2016, b: December 2016
TABLE 4
Change analysis along the shorelines

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>11.85 m</td>
<td>9.46 m</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>16.16 m</td>
<td>12.46 m</td>
</tr>
<tr>
<td>Median</td>
<td>6.04 m</td>
<td>5.58 m</td>
</tr>
</tbody>
</table>

CONCLUSIONS

In this study, the effects of an earthquake along the shorelines were analyzed using SENTRY-1A, SENTRY-2A and LiDAR data. LiDAR data was used to detect the shorelines for the period of pre-earthquake, and the result was used to estimate fuzzy membership values to extract shorelines from SENTRY-1A image. Instead of LiDAR data, SENTRY-2A MS image was used to segment of land and water classes which were used for determining of fuzzy membership values to extract shoreline from SENTRY-1A which was taken pre-earthquake period. The results from pre- and post-earthquake were compared to find the changes in the shoreline caused by the earthquake.

In the presented study, a non-parametric approach has been proposed which also can be used for high resolution LiDAR intensity data. The performance of object based mean shift segmentation and additionally utilized editing module increased the precision of the parameter estimation for fuzzy clustering. As shown in Table 4, the difference between the shorelines of two epochs (pre-and post-earthquake periods) is not significant since it is about 1 pixel distance of Sentinel 1A which is 10 m. Therefore any shift along the shoreline cannot be reported in this study.

As a conclusion, open datasets SENTRY 1A and SENTRY 2A MS images can be used to investigate the effects of the earthquakes to analyze the shoreline changes in medium scale studies. The quality assessment shows that the use of Sentinel datasets provide an accuracy below one pixel in average. On the other hand, LiDAR datasets are not always available and are usually expensive to acquire. In addition, the results are not satisfactory (as shown in Table 3) due to the noise intensity and lacking the radiometry when converting heights to the legend colors. On the other hand, SENTRY-1A and SENTRY-2A datasets are useful for shoreline extraction to monitor general characteristics of shorelines with an accuracy below 1 pixel in average.

In the future projects the proposed shoreline extraction framework will be implemented on the UAV – LiDAR derived data.

ACKNOWLEDGEMENTS

This study has been supported by TUBITAK (The Scientific and Technological Research Council of Turkey) with project number 115Y718. Authors acknowledge Mr. Akhtar Jamil’s useful comments.

REFERENCES


COMPARING TWO DIFFERENT SPATIAL INTERPOLATION APPROACHES TO CHARACTERIZE SPATIAL VARIABILITY OF SOIL PROPERTIES IN TUZ LAKE BASIN - TURKEY

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ABSTRACT

The main objective of this study is to compare the performance of two interpolation approaches, namely Inverse Distance Weighting (IDW) and Ordinary Kriging (OK) methods, for mapping spatial distribution of soil characteristics including electrical conductivity (EC), organic matter, phosphorus, lime and boron in the Tuz Lake Basin of Turkey. A total number of 312 soil samples were used for analyses, in which 80% of the data was employed to generate interpolation models; whereas, the rest 20% was engaged for validation of the estimated outputs. Additionally, linear regression analysis was performed for further comparative evaluation. The results demonstrate that OK provided better results than IDW in estimating lime and EC parameters. On the other hand, IDW provided better results in estimating phosphorus, organic matter and boron. Both methods are useful to produce areal maps of the related soil parameters by using discrete number of point observations.

KEYWORDS:
Spatial interpolation, Soil properties, Inverse Distance Weighting, Ordinary Kriging, Tuz Lake, Turkey.

INTRODUCTION

Maintaining soil quality is significantly critical for sustainable management of ecosystems. Therefore, utilizing spatial interpolation methods can be highly supportive especially when point based field measurements are available [1,2]. Interpolation approaches have so far drawn attention of scientists due to their suitable and cost-effective estimation of unsampled locations and creation of areal surface maps from limited point-wise observations [3, 4, 5, 6].

The most appropriate interpolation method for a specific application should be carefully selected considering the distribution, behavior and variability of observed data. In addition, several factors influence the estimating supremacy of the methods. Data quality, sampling approach and correlation among primary and secondary variables are the main parameters influencing the performance of interpolation methods [7]. The most appropriate method may be selected for estimating the values at un-sampled locations from the surface generated by the measured sampling points in each study area [8, 9].

Recently, many studies have been carried out for modeling the soil parameters using geo-statistical methods and evaluating their performance. Karydas et al. [10] examined three interpolation methods for predicting soil characteristics; namely clay content, Fe, EC, organic matter and total CaCO₃ in the southern part of Heraklion city in Greece. In the study, Inverse Distance Weighting (IDW), Ordinary Kriging (OK) methods and Radial Basis Functions (RBF) approaches were applied for producing prediction maps. The Goodness of prediction (G) was calculated for each method and it demonstrated positive values for Fe content and total CaCO₃ considering all the three approaches. Likewise, slightly positive values were obtained only for organic matter applying IDW. Despite of this finding, analysis of all interpolation approaches resulted in negative values for EC and clay content. Positive values revealed that the estimations have more reliability than employing the sample mean and negative values.

Another study was conducted for estimating the spatial variation of lead, cadmium and copper in the mid Tong Zhou district in Beijing-China by utilizing several interpolation approaches containing RBF, local polynomial (LP1), OK and IDW. The outcomes demonstrated that all the interpolation methods have capability for estimating the pollution area; but OK and RBF interpolations provided higher accuracies with minimum RMSE [11].

OK method was evaluated for estimating soil properties including soil organic carbon and nitrogen in the northern part of Nile Delta in Egypt. The results showed that OK produced accurate maps by estimating and interpolating the unknown locations [12].

In a more recent study, researchers conducted OK method for modeling the spatial distribution of soil organic carbon (SOC) in Lusaka province of
Zambia. The results showed that the root mean square error (RMSE) of the estimations was 0.64 and the generated maps can be utilized as guides for different applications including optimization of soil sampling [13].

The main objective of this research is to compare the performance of IDW and OK interpolation methods for predicting spatial distribution of soil properties including soil organic matter, phosphorus, lime, boron and EC in the Tuz Lake Basin of Turkey by utilizing the soil analysis data obtained from the Ministry of Food, Agriculture and Livestock of Turkey.

**MATERIALS AND METHODS**

**Study Area and Data.** Tuz Lake Basin, bearing the second largest lake in Turkey, is located in the Central Anatolian region of the country with a surface area of 1500 km² [14, 15]. Studies on the land-use/cover changes by use of CORINE data showed only slight alteration by anthropogenic causes between years 2000–2012 [16]. In terms of ecological importance, Tuz Lake is a significant location for 279 kinds of halophytic plants and it supports approximately 6000 nesting and breeding areas for migrating birds. In the sense of economic significance, it is the main salt production area of Turkey [17]. Figure 1 demonstrates the geographical location of the study area coupled with a Landsat satellite image of the Tuz Lake that was acquired in 2017.

A total number of 312 soil samples were collected and analyzed through a comprehensive field study within the scope of a national project conducted by the Ministry of Food, Agriculture and Livestock of Turkey [18]. The 50 out of 312 homogeneously distributed samples representing the vicinity of the lake were chosen as validation points for examining the validity of each interpolation method; whereas, the remaining 262 samples were utilized for generating the prediction maps by applying IDW and OK interpolation approaches.

**Description of Soil Parameters.** Several soil parameters were investigated in this study. Soil salinization was measured as electrical conductivity (EC). In general, as it increases, the capability of plant roots to absorb water and nutrient elements from soil decreases. It occurs mostly due to presence of parent materials including salt in soil, excessive use of groundwater, soil structure, poor quality irrigation water and water table depth [19]. In that sense, it is one of the important soil parameters regarding agricultural activities. Soil organic matter is the main component for soil productivity, since it supplies essential nutrients for plants and enhances soil fertility. Presence of excessive organic matter in soil, contributes to balancing of metal concentration in soil [20]. Phosphorus is another significant soil parameter that using proper amount in soil enhances plant root growth and cell division. Regarding to importance of lime, it is examined that sufficient amount of this soil property increases water penetration and provides optimum water uptake of
Inverse Distance Weighting (IDW). IDW interpolation method assumes that points close to each other have more similarity than those which are far away from one another. Therefore, points in the near target value are given higher weights; whereas, points at a far distance are given lower weights [22]. In this study, IDW approach was applied to generate a model for estimating the values of unknown locations by the aid of 262 known samples and to produce prediction maps of five soil parameters.

Ordinary Kriging (OK). One of the most frequently used geo-statistical interpolation method is OK, known as the best linear unbiased estimator, since it is a proper method for minimizing the variance of errors. OK method is unbiased as it considers having the error or the mean residual equal to zero [23]. In this study, OK method was applied to develop a model for estimating the soil property value of unknown location by the aid of 262 known samples and to produce prediction maps of five soil parameters.

Linear regression analysis was conducted to evaluate the relationship between the known/measured validation points and the prediction maps that were produced with two methods for each soil parameter.

RESULTS AND DISCUSSION

As shown in Table 1, accuracy of IDW and OK interpolation methods for estimating EC, organic matter, phosphorus, lime, and boron were compared by utilizing RMSE and R-squared ($R^2$) as the two general statistical measures. $R^2$ depicts the degree of closeness of the predicted data to the measured validation points. RMSE was applied for calculating the error of estimation. The lowest RMSE value shows the most accurate prediction [24]. Although RMSE is a good quantitative metric for presenting the accuracy of a single parameter derived from several measurements or comparing the accuracy of different methods for a single parameter, variations in magnitude of errors can be confusing while performing a comparative analysis for several parameters with different methods. At this point, normalization of RMSE errors could provide valuable information for interpretation of the results. In this study, RMSE were normalized by dividing them to the range of the related parameter (NRMSE). Range for each parameter was calculated from the minimum and maximum values of the whole dataset consisted 312 points. Figure 2 (a, b, c, d, e) illustrates prediction maps produced by conducting IDW and OK interpolation methods for boron, lime, organic matter, phosphorus and EC, respectively.

The results of this study indicate that, the IDW method provided comparatively better results in prediction of phosphorus, organic matter and boron. On the other hand, OK was comparatively better in predicting lime and EC. More specifically, both methods showed good linear relationships with $R^2$ value of 0.90 for lime; however, OK provided slightly lower RMSE. For phosphorus, IDW was better with higher $R^2$ and lower RMSE. For organic matter, results were almost similar with same $R^2$ and RMSE. For boron, IDW provided slightly better results in terms of $R^2$ and RMSE. For EC, OK provided slightly better results in terms of $R^2$ and RMSE. In general, lime showed highly satisfactory relationship with 0.90 $R^2$ value exceeding all other parameters that are providing $R^2$ of around 0.70. According to NRMSE comparison; lime, phosphorus and organic matter parameters provided similar results around 0.10, while smaller errors observed for boron and EC that were around 0.03.

Table 2 illustrates various case studies from different parts of the world, which applied IDW and OK methods for predicting soil lime, organic carbon, phosphorus and EC. In this research, RMSE and $R^2$ values can be considered as satisfactory for all the concerned soil properties since most of the $R^2$ values were above 0.70, providing higher correlation between observed and estimated values when compared to results derived from the other referred studies. OK and IDW methods showed the highest performance for predicting soil lime with $R^2$ value of 0.90 when compared to other studies.

When the studies within similar geographic zones are investigated, it can be also asserted that current study provided similar or better results. In Karatasbagi Stream catchment of Turkey, scientists applied IDW and Kriging interpolation methods for estimating organic carbon, and they reached $R^2$ value of 0.74 similar to this study. In another study, OK method was used for predicting organic carbon in Telangana, India and the corresponding results showed comparatively lower $R^2$ of 0.59. A different study in Medinipur district in West Bengal, India demonstrated higher $R^2$ value for both OK and IDW methods compared to this study.

In addition, the results attained for the other soil properties were so close to those studies that had best estimations. Selecting homogeneously distributed sampling points around the lake with considering various data ranges for each soil property resulted in producing more accurate models for this study.
2. IDW and OK are among the common spatial interpolation approaches utilized for analyzing, predicting and mapping soil properties. Characteristics of each specific dataset, such as spatial distribution and value range of samples, should be considered during the selection of a proper interpolation method.

Therefore, it is hard to suggest the best and common spatial interpolation method for the majority of the applications. Prediction maps that were produced in this study by applying IDW and OK for boron, EC, phosphorous, lime and organic matter demonstrated promising results with high R-squared and acceptable NRMSE values.

As a final remark it can be stated that these maps can be supportive for decision makers, especially in charge of agricultural industry, during dealing with proper agreements for tree plantation and for managing the proper amount of required fertilizers.

### Table 1
Linear regression analysis results - R square and RMSE - NRMSE values that are calculated for different soil parameters using IDW and OK methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Lime</th>
<th>Phosphorus</th>
<th>Organic matter</th>
<th>Boron</th>
<th>EC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>RMSE</td>
<td>NRMSE</td>
<td>$R^2$</td>
<td>RMSE</td>
</tr>
<tr>
<td>IDW</td>
<td>0.90</td>
<td>7.12</td>
<td>0.10</td>
<td>0.78</td>
<td>5.72</td>
</tr>
<tr>
<td>OK</td>
<td>0.90</td>
<td>6.85</td>
<td>0.09</td>
<td>0.71</td>
<td>7.06</td>
</tr>
</tbody>
</table>

### Table 2
Case studies which applied IDW and OK methods for predicting soil lime, organic carbon, phosphorous and EC

<table>
<thead>
<tr>
<th>Study Area</th>
<th>Soil property</th>
<th>Method</th>
<th>RMSE</th>
<th>$R^2$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>London, United Kingdom</td>
<td>phosphorus</td>
<td>IDW</td>
<td>-</td>
<td>-</td>
<td>[25]</td>
</tr>
<tr>
<td>Podlasie, Poland</td>
<td>organic carbon</td>
<td>IDW</td>
<td>-</td>
<td>-</td>
<td>[26]</td>
</tr>
<tr>
<td>Karatashbag Stream Catchment, Turkey</td>
<td>organic carbon</td>
<td>IDW</td>
<td>0.29</td>
<td>0.74</td>
<td>Block Krigging</td>
</tr>
<tr>
<td>Andhra Pradesh, India</td>
<td>EC</td>
<td>phosphorous</td>
<td>IDW</td>
<td>0.014</td>
<td>0.4</td>
</tr>
<tr>
<td>Moso Bamboo Forests, China</td>
<td>phosphorus</td>
<td>OK</td>
<td>0.015</td>
<td>0.38</td>
<td>[29]</td>
</tr>
<tr>
<td>Vukovar-Srijem Croatia</td>
<td>organic matter</td>
<td>OK</td>
<td>0.04</td>
<td>0.27</td>
<td>[30]</td>
</tr>
<tr>
<td>Sri Lanka</td>
<td>organic carbon</td>
<td>OK</td>
<td>0.09</td>
<td>0.59</td>
<td>[31]</td>
</tr>
<tr>
<td>Telangana, India</td>
<td>organic carbon</td>
<td>OK</td>
<td>0.31</td>
<td>0.59</td>
<td>[32]</td>
</tr>
<tr>
<td>Central Amazon, Brazil</td>
<td>Carbon Stock</td>
<td>OK</td>
<td>1.79</td>
<td>0.58</td>
<td>[33]</td>
</tr>
<tr>
<td>Languedoc-Roussillon, France</td>
<td>organic carbon</td>
<td>Kriging</td>
<td>18.64</td>
<td>0.51</td>
<td>[34]</td>
</tr>
<tr>
<td>Xinjiang, China</td>
<td>EC</td>
<td>universal kriging</td>
<td>0.51</td>
<td>0.64</td>
<td>[35]</td>
</tr>
<tr>
<td>Madhya Pradesh, Central India</td>
<td>soil organic carbon</td>
<td>regression kriging</td>
<td>0.23</td>
<td>-</td>
<td>[36]</td>
</tr>
<tr>
<td>New South Wales, Australia</td>
<td>soil organic carbon</td>
<td>local regression kriging</td>
<td>-</td>
<td>-</td>
<td>[37]</td>
</tr>
<tr>
<td>La Peyne, South of France</td>
<td>lime</td>
<td>OK</td>
<td>0.45</td>
<td>-</td>
<td>[38]</td>
</tr>
<tr>
<td>Ismailia Province, Egypt</td>
<td>EC</td>
<td>OK</td>
<td>0.91</td>
<td>-</td>
<td>[39]</td>
</tr>
<tr>
<td>CaCO3</td>
<td>OK</td>
<td>IDW</td>
<td>0.86</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Gabrovo, Bulgaria</td>
<td>OK</td>
<td>IDW</td>
<td>1.19</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Madrid, Spain</td>
<td>OK</td>
<td>IDW</td>
<td>1.65</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Tabriz, Iran</td>
<td>organic carbon</td>
<td>OK</td>
<td>0.13</td>
<td>0.51</td>
<td>[40]</td>
</tr>
<tr>
<td>Chisinau, Moldova</td>
<td>organic carbon</td>
<td>IDW</td>
<td>7.18</td>
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<tr>
<td>Mediniup district in West Bengal, India</td>
<td>organic carbon</td>
<td>IDW</td>
<td>0.11</td>
<td>0.92</td>
<td>[41]</td>
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<tr>
<td>Cairo, Egypt</td>
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<td>OK</td>
<td>152.11</td>
<td>-</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>IDW</td>
<td>305.05</td>
<td>-</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td>OK</td>
<td>0.62</td>
<td>-</td>
<td>[42]</td>
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<tr>
<td></td>
<td></td>
<td>IDW</td>
<td>0.64</td>
<td>-</td>
<td></td>
</tr>
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ACKNOWLEDGEMENTS

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EXPLORATION OF A FAST PATHWAY TO NUCLEAR FUSION: FIRST THERMO MECHANICAL CONSIDERATIONS FOR THE ARC REACTOR

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ABSTRACT

The recent progress in fields such as High Temperature Superconductors (HTS), Additive manufacturing, new diagnostics, and innovative materials, has led to new scenarios and to a second generation of Nuclear Fusion Reactor designs. A new Affordable Robust Compact (ARC) Fusion Reactor, could be a power reactor connected to the electrical grid as a load-following reactor, capable to cover peak requests and other plant shutdowns. In order to investigate this interesting potential of ARC, its more sensitive component has been analyzed: ARC vacuum vessel. The study has been split in two parts: a steady state simulation and a transient one. The steady state study has dealt with temperature, displacements and stress calculations by means of a model set up with the COMSOL software. The transient study has dealt with temperature calculations with the same model, however during a simulation of a start-up transient, quite useful to describe a load-following scenario for ARC. The results show that, in the Inconel layers, temperature does not necessarily decrease as the distance from the plasma increases. This is because neutrons have a deep penetration into matter, and their energy deposition, however, radially decreasing with distance from plasma, might cause temperature peaks in structural materials, in points far from the refrigerating fluid. Hence, it is necessary to optimize the heat exchange, geometry and thickness of the components, in order to avoid hotspots. Nonetheless, no concerning hotspots have been detected in this simulation.

KEYWORDS:
Nuclear Fusion, Tokamak, ARC, COMSOL, Energy, Thermomechanical

INTRODUCTION

A new keystone for fusion energy has been achieved, namely high temperature superconductors (HTS). They are now available on industrial scale, and are able to tear down one of the most concerning issues of this research field: it is possible indeed to shrink the size of a tokamak without undermine its power, this would lead to relevantly cheaper reactors and therefore cheaper electricity.

The design of the Affordable Robust Compact (ARC) reactor (Fig. 1), a Tokamak concept proposed by MIT and PSFC (Plasma Science and Fusion Center at MIT) scientists, relies on these premises. In a research field that needs huge and expensive machines, each device shows several features that are unique, compared to the previous ones. This means that every little aspect of the project has to be accurately designed and analyzed from the very beginning.

FIGURE 1
ARC Reactor design

The ARC Reactor design, in particular, shows a high number of distinctive features.

Magnets composed by tapes of HTS is one of the most important features, as mentioned previously. Secondly ARC has been designed following a new concept, bringing to a layout that allows fast assembly, maintenance, and dismantling of the machine. The third important innovation is a single piece vacuum vessel, which relies on new 3-D printing technologies, and that is immersed in a molten salt tank. The fluid is able to work as both blanket and coolant for the vessel. Furthermore, the fluid and the vessel both have to provide the possibility of a fast plant power change in order to guarantee a versatility never seen before in nuclear plants, the former by promptly changing flow rate and then the heat removal capability, the latter by enduring variable thermal loads.
All of the mentioned features are put together in a small, fast-to-build fusion device, able to produce energy and provide electricity to the grid.

This paper is interested in pointing out some of the main thermo-mechanical issues concerning the vacuum vessel and investigating the feasibility of its configuration and design.

In order to do that, a model of a small portion of the vessel will be built and finite elements simulations using COMSOL will be done, studying the model in both steady state and transient circumstances.

The final aim of the study is to build and validate the model, prove the integrity of the structure, and set the basis for a further study of thermal fatigue and creep life of the vessel, which are necessary for proving the feasibility for ARC of power variation and load-following plant's condition. That would complete the thermo-mechanical analysis of the component and allow the reactor to move to a next step in its design.

MATERIALS AND METHODS

We mentioned above that this machine needs the study to begin from the most relevant components: the most critical tokamak's component has been determined, considering the issues tackled in this paper. First, a 3-D model of the tokamak has been designed and built. A second phase was to simulate a steady state scenario, in order to validate the model and meanwhile to provide the prerequisites for the feasibility of an ARC-like tokamak. The third phase was to set up and run time dependent simulations, to test how this device will behave during several types of transient: not only the occasional shutdowns and turn-ons, but also a daily scheduled power change, necessary for a more versatile, capable of following the power request, power plant.

In this context, the vacuum vessel is supposed to be the most vulnerable component and one of the key pieces of the machine, both for its dimensions and tasks. First, it has to provide an optimal environment for the plasma, namely an almost perfectly free-from-impurities vacuum. Furthermore, it has to shield the other components from radiations and, finally, it has to get thermal energy deposition from the plasma and transmit it to the coolant. The vessel is literally the first heat exchanger of the device: this is a passive task but important as well.

In short, from a thermo-mechanical viewpoint, this component is the box where a hundred million Kelvin plasma runs, and it is then exposed to extremely high heat fluxes. Therefore, it has to be well designed and analyzed in order to ensure its integrity and effectiveness.

The vessel is actually one of the several innovations that ARC proposes. Indeed, it is designed to be built using additive manufacturing technology, which allows the design to adopt complex geometries without any problem, and the structure to be single-piece, which is a good feature for shorter demounting times.

Moreover, the vessel is immersed in a tank filled of a molten salt called FLiBe, which is a mixture of Fluorine, Lithium and Beryllium [1]. This is another originality, compared to other recent tokamaks designed so far. The blanket indeed, composed by this fluid, is completely liquid. FLiBe works as tritium breeder, neutron shield and coolant, drawing from the chamber all the thermal energy produced by the fusion reaction.

Vessel dimensions, configuration, materials and thermal load are key features to design the vessel and to model its thermomechanical performance and feasibility.

ARC’s vacuum vessel has a toroidal symmetry, with a major radius of 3.3 m. Its section is 2.6 m high and 4.6 m wide. The component is relatively small if compared to the vessel of other tokamaks with a similar fusion power (e.g. ITER), indeed ARC’s plasma, able to reach 0.5-1 GW of fusion power is compressed in a very small volume, thanks to the intense magnetic field that can be reached by means of HTS magnets.

A main chamber, where the plasma runs, and the divertor area, where a considerable fraction of the heat flux is exhausted, compose the vessel. In particular, ARC shows two long-legged divertors (Fig.2), able to increase the surface of heat exchange while avoiding deposition of most of the neutron flux, and its related complications [2].

FIGURE 2
Slice of ARC’s vacuum vessel and blanket tank.

This study is focused on the main chamber, as it will have to deal with both a high heat flux and a high neutron flux.

The piece is designed to be double walled, and composed by several layers of material. Beginning from the plasma-facing layer up to the blanket, the materials are the following: 1 mm of Tungsten and 10 mm of Inconel 718 compose the inner wall while 10 mm of Beryllium and 30 mm of Inconel 718 make
up the outer wall [1], as depicted in Figure 3. Tungsten serves as the first wall, Inconel, which is a Nickel-based superalloy, works as structural material while Beryllium is needed in order to multiply the incident neutrons and thus help to raise the tritium breeding ratio (TBR) [1].

Channels of flowing FLiBe divide the two walls. This molten salt has the tasks of draw the heat from the vessel, multiply neutrons, breed Tritium for the fusion cycle and finally shield the main magnets from detrimental neutron fluxes and radiation damage.

![Main chamber layers scheme](image)

**FIGURE 3**
Main chamber layers scheme

**TABLE 1**
Fluid dynamic and thermal properties of FLiBe at 800 K [4]

<table>
<thead>
<tr>
<th>Property</th>
<th>FLiBe (2LiF-BeF₂)</th>
<th>W</th>
<th>Inconel 718</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ [kg/m³]</td>
<td>2000</td>
<td>110</td>
<td>220</td>
</tr>
<tr>
<td>Tₘ [K]</td>
<td>733</td>
<td>19300</td>
<td>8190</td>
</tr>
<tr>
<td>Cₚ [J/kg/K]</td>
<td>2414</td>
<td>1570</td>
<td>1844</td>
</tr>
<tr>
<td>k [W/m/K]</td>
<td>1</td>
<td>150.6</td>
<td>2852</td>
</tr>
<tr>
<td>µ [Pa·s]</td>
<td>0.0056</td>
<td>1.53</td>
<td>105</td>
</tr>
</tbody>
</table>

LiBe flows poloidally in the chamber being injected from the upper side, then it runs through the walls along the entire main chamber, and finally it flows into the blanket tank - which is filled with the same fluid - from the bottom of the vessel, carrying out the heat [3].

Since the component is immersed in the tank and has to be withdrawn from top of the reactor during demounting phases, its supports are just on its upper part; they are sliding supports able to allow thermal expansion of the chamber without provoking further, avoidable stress to the structure [1].

The main thermo-mechanical properties of the involved materials are listed in tables 1 and 2.

**RESULTS AND DISCUSSION**

In order to carry out a complete thermo-mechanical analysis, it has been decided to begin the study building a model of a main chamber’s small portion (Fig. 4). This would lead to accurate results concerning each material layer behavior.

A little portion of the vessel has then been modeled, using Solidworks, a 3-D CAD software.

**TABLE 2**
Mechanical and thermal properties of vessel’s materials [5-7]

<table>
<thead>
<tr>
<th>Property</th>
<th>Tungsten</th>
<th>Inconel 718</th>
<th>Beryllium</th>
</tr>
</thead>
<tbody>
<tr>
<td>σₛ [MPa]</td>
<td>600</td>
<td>110</td>
<td>370</td>
</tr>
<tr>
<td>σₗ [MPa]</td>
<td>550</td>
<td>970</td>
<td>220</td>
</tr>
<tr>
<td>E [GPa]</td>
<td>386</td>
<td>179</td>
<td>268</td>
</tr>
<tr>
<td>p [kg/m³]</td>
<td>19300</td>
<td>8190</td>
<td>1844</td>
</tr>
<tr>
<td>Tₘ [K]</td>
<td>3680</td>
<td>1570</td>
<td>1550</td>
</tr>
<tr>
<td>α [μm²/m²]</td>
<td>5.533</td>
<td>15</td>
<td>15.697</td>
</tr>
<tr>
<td>Cₚ [J/kg/K]</td>
<td>145</td>
<td>435</td>
<td>2852</td>
</tr>
<tr>
<td>k [W/m/K]</td>
<td>125</td>
<td>20</td>
<td>105</td>
</tr>
</tbody>
</table>

It is important to point out that a double symmetry has been chosen.

![Vessel slice and particular of the CAD designed part](image)

**FIGURE 4**
Vessel slice and particular of the CAD designed part.

Preliminarily, a rigid connection between the two walls has been assumed in the model. This is a double simplification: there should be just a circular symmetry in the toroidal direction, while the poloidal symmetry is an acceptable assumption since the piece studied is very small with respect the entire vessel geometry and there is actually a poloidal curvature. Furthermore, connections between walls have not been decided yet, and they had to be simply modelled here, nonetheless the actual connections will be investigated in further studies and design activities. In fact, they are likely to be flexible connections able to let expand the structure during the frequent transients.

Subsequently, thermal loads have been modelled and split into three different types. Electromagnetic radiations due to plasma’s photons have been modelled as superficial heating on the tungsten first wall. For the FLiBe, it was sufficient to opt for turbulent films for both channels and tank, each of them...
with its respective convection coefficient. Finally, neutrons able to escape the plasma and cross all the mentioned materials up to the bulk tank, needed computations in order to find out their heating power with respect each vessel’s layer (Table 3, for 500 MW of plasma power). Figure 5 shows a qualitative 2-D sample of the modelled loads for the inner wall. In transients, while neutrons heat flux has a linear scale with fusion power, electromagnetic radiations follow a law that takes into account of the Bremsstrahlung effect.

![Image](image_url)

**FIGURE 5**
Scheme of the heat exchange model.

**TABLE 3**
Model’s thermal load for 500 MW of plasma fusion power, steady state condition [3].

<table>
<thead>
<tr>
<th>Material</th>
<th>avg radiative heating [MW/m²]</th>
<th>avg neutron heating [MW/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten PFC</td>
<td>0.5</td>
<td>34.5</td>
</tr>
<tr>
<td>Inconel 718</td>
<td>-</td>
<td>16.5</td>
</tr>
<tr>
<td>FLiBe Channel</td>
<td>-</td>
<td>15.8</td>
</tr>
<tr>
<td>Beryllium</td>
<td>-</td>
<td>9.8</td>
</tr>
<tr>
<td>FLiBe Tank</td>
<td>-</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 1 shows us that the coolant is a mixture that melts at about 730 K [4]. Then it must be secured that the system cannot reach lower temperatures. A high temperature is a good point for the thermodynamic efficiency of the cycle, but it is a drawback for the integrity of the structure, since it might cause issues like creep and thermal fatigue.

A second important note is that ARC is supposed to be able to change its fusion power in a range that goes from zero power to 1 GW [3]. However, ARC is more likely to run in a way shorter range, in the order of hundreds of megawatts, centered roughly around 500 MW. Thus, the following simulations have been run for the nominal plasma power of half a GW, for beginning the vessel study.

In thermo-mechanical simulations, the main expected issues consist of high temperature, above the material melting point or creep limit, temperature and stress hotspots due to a non-optimized design and thermal expansion troubles such as constraining stress and unacceptable displacement of components.

For the thermal problem, COMSOL considers the geometric model as a discretized continuum and it solves the two following well-known 3-D equations in order to come up to the simulation’s solution:

\[
\frac{\partial T}{\partial t} + \rho c_p \cdot \nabla T + \nabla \cdot q = Q + Q_{ted} \tag{1}
\]

\[
q = -k \nabla T \tag{2}
\]

While the law dominating thermal expansion issues is the following:

\[
\sigma = \alpha \cdot \Delta \cdot E \tag{3}
\]

Steady state: A first simulation was interested in a steady state condition, as how plasma reached constant fusion power while coolant flows steadily in channels and tank (Figures 6-9).

![Image](image_url)

**FIGURE 6**
Model: particular of the mesh quality.

**FIGURE 7**
Temperature distribution in vessel layers [K]. Steady state scenario.

In a turn-on transient it is supposed that all the system within the tank will be kept at around 300 K, in order to avoid FLiBe solidification, pumps will make the fluid flowing firstly, and then fuel will be heated up to fusion conditions, producing power.
load-following power plant, which relies on a cool-
ant pumps' power change as the plasma power
changes.

In this simulation, temperature time evolution
has been determined, in seven different points, along
the radial direction of the studied component and in
the bulk tank very close to the vessel, as it can be
seen in Figure 10.  

Solution of the above-mentioned calculations, for
each point, are shown in the graphic below.

FIGURE 11
Component's temperature evolution in seven
different points.

CONCLUSION

The study has been split in two parts. A steady
state simulation and a transient one. The steady state
shows no concerning issues about temperature: all
the materials are widely below their melting point
while the molten salt is hot enough to guarantee no
solidification (Fig. 7). Displacement stands in an ac-
ceptable range, no more than 30 mm (Fig. 8), and
way lower than 10% of the dimensions of the whole
structure.

Stress on the other hand shows an issue. Indeed,
for Tungsten it is almost five times higher than the
rupture limit [5]. This because Tungsten, Inconel and
Beryllium have very different thermal expansion co-
efficients, and while Inconel expands, tungsten does
not, experiencing a tensile strength due to Inconel’s
displacement (Fig. 9).

There are viable solutions that however need to
be investigated, the most interesting ones are:
• tiles and other type of connections
• graduated materials
• new and more ductile alloys.
Nevertheless, tiles and connections will not be
adopted so far, since they do not match ARC design
criteria, such as a small number of components.

This issue should be verified with a complete
model of the vessel.
The second part of the study is about a sort of turn-on transient, which is simulated by a worst-case assumption, i.e., a stepwise increase.

The results show that, in the Inconel layers, temperature does not necessarily decrease as the distance from the plasma increases. Point “Inconel 4” is a clear example of that (Fig. 11), if compared with “Inconel 3”. This is because neutrons have a deep penetration into matter, and their energy deposition, however radially decreasing with distance from plasma, might cause temperature peaks in structural materials, in points far from the refrigerating fluid. Hence, it is necessary to optimize the heat exchange, geometry and thickness of the components, in order to avoid hotspots.

Nonetheless, no concerning hotspots have been detected in this simulation, and it has been noticed that the fluid reaches the steady state conditions after roughly 30 seconds, both in the channels and in the tank. The neutron heat deposition helps speeding up this process.

In a load-following scenario, coolant’s pump have to behave accordingly to this timescale, while plasma changes must do the same, in order to be able to draw a new heating power by changing mass flow rate.

Further assessments are to follow in the near future: for instance, safety assessments, with activation calculations, accidental scenarios, etc.

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MAPPING ISTANBUL QUARRY MINING REGION USING LANDSAT 8 OLI&TIRs DATA

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ABSTRACT

Open mining operations have brought number of environmental challenges, which may result in soil erosion, dust, noise, water pollution, and severe impacts on biodiversity. Determination of the mining activities and its surrounding environment is a major issue in sustainable resource management. Many remote sensing indices have been developed and widely applied as an effective tool to determine different land surface types. The main objective of this study was to determine quarry mines and its surroundings land use and land cover (LULC) categories in the selected study area of Istanbul using different remote sensing indices including Tasseled Cap Transformation (Brightness, Greenness and Wetness) and Normalized Difference Bareness Index (NDBals). In this study, an open mining area in the northern Black Sea coastal part of Istanbul was selected as study area. Freely available Landsat 8 OLI & TIRs image was used to determine quarries and land cover/land use categories in the concerned area. By using original bands of Landsat 8 OLI, TCT components and NDBal, three different data sets were created. Each image was then separately subjected to support vector machine classification and processed to identify and quantify LULC categories. The accuracy of classification results were evaluated in a comparative manner using error matrix. Data set C had the highest overall accuracy and Kappa statistics that were calculated as 83.00 and 0.80, respectively.

KEYWORDS:
Open mining area, Landsat 8 OLI & TIRs, classification, support vector machine, mapping.

INTRODUCTION

Mining activities have brought number of environmental problems. Potential impacts of these activities are land degradation, changes in topography, ground vibration, air blast, fly rock, soil erosion, soil and water pollution, dust, noise and ecological deterioration [1, 2, 3, 4]. Accurately determination of the mining activities and its surrounding environment is an important issue in sustainable resource management [5]. Satellite based remote sensing is widely accepted and utilized by different disciplines. Remote sensing techniques are useful tools for extracting accurate and reliable thematic information. Many studies have reported the urgent need to acquire up-to-date spatial information on land use-land cover and to quantify of its change for sustainable use of the Earth’s natural resources [6, 7, 8, 9]. Especially, land cover and land use determination provides significant information for natural resource managers, policy and decision makers. On the other hand, to create thematic maps of heterogeneous areas are really difficult because of similar spectral characteristics of different objects. In order to solve this problem many remote sensing indices and transformation methods were developed and applied [10]. These methods have been used as ancillary data with advanced classification methods such as Support Vector Machine Classification Method [11] to improve the classification accuracy results to determine LULC categories such as artificial surfaces, crop types and forest biomass.

The main objective of this study is to determine open quarry mine area of Istanbul using different remote sensing indices and advanced supervised classification method. Therefore, potential of using free-of-charge Landsat 8 OLI & TIRs imagery was tested for quarry mining area mapping in heterogeneous area.

MATERIALS AND METHODS

In this study, one of the huge open mining area of Istanbul in Turkey (Figure 1) were selected as study area. Istanbul is one of the most important cities in the world due to its industrial importance along with its natural characteristics. Istanbul lies between the continents of Europe and Asia and has an area of approximately 5,757 ha. The selected open mining area is located on the Asian side of the Istanbul in Omerli Region and not far from away from the Black Sea Coast of the city. The mining area was in rural part of the mega city and it is located in the heart of forest areas of the city. Therefore, the open mining area is located in fresh water basin (Ömerli Water...
Because of this reason, it is very important to determine land cover/use categories of the region for sustainable management activities.

New generation medium resolution Landsat 8 data was used in the study. 2016 dated Landsat 8 carries two instruments: the Operational Land Imager (OLI) and the Thermal Infrared Sensor (TIRS). OLI collects image data for nine shortwave bands (Band1, 433-453 nm; Band2, 450-515 nm; Band3 525-600 nm; Band4, 630-680 nm; Band5, 845-885 nm; Band6, 1560-1660); Band7, 2100-2300 nm; Band8, 500-680 nm; Band9, 1360-1390 nm. The pixel size of Bands 1-7 and 9 is 30 meters and the pixel size of Band 8 is 15 meters (Table 1). For the thermal infrared bands (Band 10 and Band 11) spatial resolution is 100m and resampled to 30m.

Free distribution of its archive digital dataset with a wider swath-width of 185-km and a 16-day temporal resolution makes the Landsat 8 sensor one of the key primary data sources highly suitable and practical for land cover/use studies. Improved radiometric resolution from 8 bits to 12 bits, which is critical in determining the characterization of different land cover/use categories. Additionally, the changes in the sensor design have also resulted in substantial improvements in signal to noise ratios (SNR) [12, 13].

The study was performed mainly in four stages; i) Three different data sets were created in the first step using Landsat 8 OLI & TIRS data a) Landsat 8 OLI data with 8 bands were used for data set (A) b) Tasseled Cap Transformation were applied to create data set B (Landsat 8 OLI data (8bands) + 3 components of TCT c) Normalized Difference Bare Index was calculated for data set C (Landsat 8 OLI data (8 bands) + NDBI) ii) Support vector classification applied to created three different data sets to produce open mining area and its’ surrounding area mapping iii) Classification accuracy assessment applied using error matrix to determine the best performance (Figure 3).

### Figure 3
Flowchart of the methodology

In the first stage of the study Tasseled Cap Transformation method was used to create brightness, greenness and wetness components. The Tasseled Cap Transformation (TCT) has been widely applied in the remote sensing community to produce accurate and reliable thematic maps. In this method, Brightness gives to the physical properties that influence total reflectance, Greenness is responsive to the properties of green vegetation that includes the combination of high absorption of chrophyll in the visible bands and high reflectance of leaf structure in the near-infrared band (14). Wetness shows the amount of moisture of vegetation or soil. Therefore, to test the mining area mapping

### Table 1
Landsat OLI/TIRS spectral bands.

<table>
<thead>
<tr>
<th>Spectral Band</th>
<th>Wavelength (μm)</th>
<th>Resolution (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band1 - Coastal /Aerosol</td>
<td>0.433-0.453</td>
<td>30</td>
</tr>
<tr>
<td>Band2-Blue</td>
<td>0.450-0.515</td>
<td>30</td>
</tr>
<tr>
<td>Band 3 – Green</td>
<td>0.533-0.590</td>
<td>30</td>
</tr>
<tr>
<td>Band 4 – Red</td>
<td>0.636-0.673</td>
<td>30</td>
</tr>
<tr>
<td>Band 5 - Near Infrared (NIR)</td>
<td>0.851-0.879</td>
<td>30</td>
</tr>
<tr>
<td>Band 6 - Shortwave Infrared (SWIR) 1</td>
<td>1.566-1.651</td>
<td>30</td>
</tr>
<tr>
<td>Band 7 - Shortwave Infrared (SWIR) 2</td>
<td>2.107-2.294</td>
<td>30</td>
</tr>
<tr>
<td>Band 8 – Panchromatic</td>
<td>0.503-0.676</td>
<td>15</td>
</tr>
<tr>
<td>Band 9 – Cirrus</td>
<td>1.363-1.384</td>
<td>30</td>
</tr>
<tr>
<td>Band 10 - Thermal Infrared (TIRS) 1</td>
<td>10.60-11.19</td>
<td>100</td>
</tr>
<tr>
<td>Band 11 - Thermal Infrared (TIRS) 2</td>
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<td>100</td>
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<td>Index</td>
<td>Equation</td>
<td>Source</td>
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<tr>
<td>---------</td>
<td>---------------------------------------------------------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>Landsat Brightness</td>
<td>$0.3029 \times \text{OLI}_2 + 0.2786 \times \text{OLI}_3 + 0.4733 \times \text{OLI}_4 + 0.5599 \times \text{OLI}_5 + 0.508 \times \text{OLI}_6 + 0.1872 \times \text{OLI}_7$</td>
<td>[15]</td>
</tr>
<tr>
<td>Landsat Greenness</td>
<td>$-0.2941 \times \text{OLI}_2 + 0.5424 \times \text{OLI}_4 + 0.0713 \times \text{OLI}_5 + 0.1608 \times \text{OLI}_7$</td>
<td>[15]</td>
</tr>
<tr>
<td>Landsat Wetness</td>
<td>$0.1511 \times \text{OLI}_2 + 0.1973 \times \text{OLI}_3 + 0.3283 \times \text{OLI}_4 + 0.3407 \times \text{OLI}_5 - 0.7117 \times \text{OLI}_6 - 0.4559 \times \text{OLI}_7$</td>
<td>[15]</td>
</tr>
<tr>
<td>NDBal</td>
<td>$\frac{\text{OLI}_6 - \text{TIRs}_10}{\text{OLI}_6 + \text{TIRs}_10}$</td>
<td>[16]</td>
</tr>
</tbody>
</table>

In remote sensing, the most commonly used classification methods are unsupervised classification and supervised classification. In the second stage of the study supervised classification was applied to produce thematic maps of the selected region. Supervised classification is a technique that based on the statistics of training areas representing different ground objects selected subjectively by users on the basis of their own knowledge and/or experiences [17]. In this study, Support Vector Machine (SVM), classification method was used to derive land use/cover categories. The Support Vector Machine (SVM) that is the non-parametric supervised machine learning algorithm and based on statistical learning theory has been applied for the classification. The significant point of the SVM is to able to perform the classification in high-dimensional feature spaces with small number of training dataset [18, 19]. SVMs do not attempt to model the distribution of the training data, but try to separate the different classes by directly searching for adequate boundaries between them [19]. Like other supervised classifiers, training data is a prerequisite to define the decision boundaries within the feature space, based upon which classification decision rules are made. Kernel functions could construct the optimal hyperplane for the complex data classification [18]. Radial Basis Function (RBF), which is widely used for SVM classification, has been selected as a kernel type. First, the RBF kernel non-linearly mapped samples into a higher dimensional space so the RBF could handle the case when the relationship between class types and attributes was not linear.

Second, the RBF kernel has fewer numerical computational difficulties. In this study, optimal parameter values for the selected kernel function determined based on literature review. The parameters for the RBF kernel were set to 0, 125 and 100 for pyramid parameter, $\gamma$ (gamma = 1/number of the band) and for C (error penalty), respectively for image classification. The pyramid parameter was set to a value of zero to process the satellite data at full resolution (30 m). Each image was then separately subjected to support vector machine classification and processed to identify and quantify LULC categories.

Classification accuracy is the basic measure of the quality of thematic maps that produced as a result of classification [20, 21]. Error matrix was created to calculate the two most popular metrics such as overall accuracy and Kappa statistic in accuracy assessment [22]. For this purpose, firstly a reference data set including a total of 140 points was created. These points were selected over different locations representing different land cover classes. Same reference data was used for the accuracy assessment of three data sets.

FIGURE 4
Classification results for three test data (A; Landsat 8 OLI data with 8 bands, B; Landsat 8 OLI data with 8 bands and 3 components of TCT, C; Landsat 8 OLI data with 8 bands and NDBal)
RESULTS AND DISCUSSION

In this research, the applicability and potential of TCT and NDBal of Landsat 8 OLI & TIRs imagery for land use/cover mapping of quarry mining area has been examined using support vector machine classification. In the classification, at the first stage, training and test data were prepared to classify satellite image that is covering the study area. For the classification same training and test data were used for three data set. Totally, 3 classification results were obtained and results shown in Figure 4.

As a result of the classification, seven LULC categories were distinguished in the selected region: quarry mining, sand dune, bare land, road, forest, water surfaces and others that includes agricultural fields and built up areas.

To determine the accuracy of each classification result, thematic accuracy assessment was performed. Error matrix of each classification was created and overall accuracy and Kappa statistics were calculated to evaluate classification accuracies. Results are as shown in the following tables (Table 3 A, B and C).

Overall accuracy of classified images for the data set A and data set B is found 78.00 %, and 83.00% for data set C. The evaluation results demonstrated that data C has higher Kappa statistics in comparison with data B and data A. Classification results indicated that quarry mining areas were mixed with bare and urban lands. They had very similar spectral characteristics. Another mixing problem occurred between sand dune and mining areas in the selected area.

CONCLUSION

Classification of Landsat 8 OLI & TIRs data created three different data set using support vector machine classification method were evaluated and compared. The overall classification accuracy showed that test 3 data (Original 8 bands + NDBal) was higher than the other two data set. Therefore, freely available Landsat 8 OLI and TIRs data had a satisfactory performance in land cover classification that includes open mining areas and semi-natural environments. In order to keep sustainable management under control, producing accurate and reliable LULC maps of quarry mining area has huge importance.

Future work would test the classification potential of using the different band composites of Landsat 8 OLI & TIRs images. Different transformations and remote sensing indices and pan sharpening methods would test.

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TEMPORAL ASSESSMENT OF NATURAL WETLANDS VIA REMOTELY SENSED DATA: A CASE STUDY FROM TURKEY

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ABSTRACT

Lakes and wetlands have a variety of uses in keeping the ecological balance and the well-being of a basin. Turkey has almost 303 water bodies among which Konya Closed Basin bears 29 of those where two of them have been registered as Ramsar sites. In this study, one of these sites, Meke Lake, and its nearby Akgol Wetland and Acigol Lake that are of international value are temporally assessed by means of satellite images regarding their water surfaces. Meke Lake has been declared as a Ramsar site in 2005, whereas Acigol is one of the volcanic lakes of the world with a depth of 300 m. Akgol has been registered as 1st level Natural Site and Natural Protection Area. Four classified images belonging to years 1990, 2000, 2010 and 2016 are further correlated with the ground truth measurements to assess the temporal variation of the sites. Producing such scientific data and conducting similar analyses are important for especially the local, regional and national authorities and planners in charge of the rehabilitation and restoration of natural sites that have lost a significant amount of land and water in the past years.

KEYWORDS:
Landsat, natural wetlands, Ramsar Sites, remote sensing, temporal change, Turkey.

INTRODUCTION

Inland and coastal wetlands covering a surface area of 12.8 million km² contribute to 12% of the global carbon pool highlighting their significant role in the global carbon cycle [1]. Estimates suggest that since 1900s, the entire world has lost around 50% of its wetlands [2, 3]. Europe experienced 60% loss on the average [4], and USA lost overall 54% since the 18th century [5] and a further 5% loss of both inland and coastal wetlands is recorded during years 1998-2004 [6]. Remarkable rates of loss in these countries have been observed basically in 1950-1980 period. In Europe, a further 2.7% of inland vegetated wetlands were lost between 1990 and 2006 while open waters increased by 4.4%, and coastal wetland areas remained almost stable [4]. In China, natural inland wetlands decreased by 33% and coastal wetlands by 31% between 1978 and 2008, whereas artificial inland wetlands increased by 122% over the same period [7].

Wetlands still continue to face severe pressures, despite many benefits they provide to people and the environment. Many conservation/restoration successes from recent efforts ranging from local to national and global scales are observed [4]. Wetlands which have either been disturbed or irreversibly destroyed in Turkey throughout the last century resulting from various interferences like draining and agricultural irrigation projects account to 1.3 million ha [8]. While the wetlands were being dried out with the purpose of fight against malaria disease until 1950’s, development-oriented practices starting from 1950’s have increased the damages caused to wetlands. Draining of wetlands has accelerated in line with the capability to cultivate vast areas due to mechanized agriculture and to increase in the construction of dams and roads in these years [9].

As known, lakes and wetlands have a variety of uses in keeping the ecological balance and the well-being of a watershed. For their effective monitoring and protection, researchers have to analyse the trends and causes of landscape pattern change temporally. Since 1970s, satellite images have been successfully used to obtain data on wetlands to be further utilized in producing more data for their management, and finally for modelling of both the water quality and the terrain. Free remote sensing data is an important data source for these studies on land-use/cover changes. Mapping wetland areas, classifying the corresponding vegetation, and detecting change are the most common research themes using Landsat data on a regional scale; not only because of the advantages in terms of spatial and temporal resolution, but also because of free accessibility to data [10].

There are numerous studies conducted on the wetlands all over the world that examined and monitored their various aspects via remote sensing methods. Wetlands database for the Koshi Basin in Nepal was developed by using Landsat data of 1990 and 2010 through knowledge-based image classification [11]. The hydrological and ecological change in Rawal Watershed located in Pakistan is determined through utilization of satellite data for the years 1992
to 2012 [12]. In China, the Poyang Lake, which has been declared as a Protection Area since 1983, was observed for the potentially rapid water level changes in addition to annual and seasonal monitoring for any deviation in the trends via images [13]. Suitability of habitat for water birds in the West Songnen Plain in China was analysed by developing an object-oriented segmentation approach in conjunction with GIS spatial analysis and remote sensing image data [14]. Another study referred to the utility of remote sensing methods in the wetlands of USA. One of the suggestions mentioned in the study was the use of medium-resolution sensors in the large wetlands [15]. Wetlands in the Lower Mekong River Basin in Asia were mapped using Landsat 7 ETM+ images and field survey data, and the maps produced were used both at provincial and national levels in Thailand, Cambodia and Vietnam for resource and conservation planning, and for management applications [16].

Similarly, quantifying the condition of wetlands along the western coastline of Sri Lanka was described and trends in land-use pattern were outlined in another study from Asia [17]. Furthermore, in Greece, the methodology for creating baseline data for wetland monitoring by keeping fieldwork at a minimum was practiced. The automated image analysis techniques were preferred against traditional surveys on the wetland delta, Axios-Loudas-Aliakmonas [18]. A group of scientists used Landsat 7 ETM+ satellite images to make change detection for the Spanish wetland, La Mancha Húmeda, designated as a Biosphere Reserve for the period of 2013–2015 [19]. A more recent study was conducted in the two wetlands of Europe; one in Southern Spain and the other in South of France by using Sentinel 1 imagery for short term change detection [20]. A Turkish scientist investigated the effects of climate change in the Tuz (Salt) Lake- Turkey, by evaluating salt and water reserve changes through seasonal and multi-temporal SPOT imagery collected in 1987 and 2005 [21]. In another study from Turkey, coastline changes on water reservoirs located in the Konya Basin were examined using Landsat TM and ETM+ during 1987–2006 and 1990–2000 periods [22]. Moreover, temporal changes of sensitive areas such as shorelines, wetlands, and rivers of Beyşehir Lake which is also located in Konya Basin were determined by means of 1987 and 2000 Landsat 5 TM satellite data [23]. Finally, the authors of this article have already analysed the land-use changes that had occurred in the Akgol Wetland and its surrounding area along years 1987 and 2015 through classifying Landsat images [24].

In this study, 3 nearby water bodies; namely Meke Lake, Akgol Wetland and Acigol Lake located in the Konya Basin of Turkey are assessed by means of satellite images regarding their water surfaces at 4 different times within a time scale of 26 years (1990-2016). The basin situated in an arid region owns 29 natural lakes and wetlands among which 2 of them are registered as Ramsar sites [25].

**STUDY AREA**

Turkey bears 25 watersheds among which Konya Closed Basin covers approximately 7% of the entire area of the country (Figure 1). The basin consisting of volcanic rocks and limestone is surrounded by high mountains indicating that it has an inadequate drainage [26]. Resultantly, basin soil is in general salty. As the basin is enclosed by high mountains, there exists no drainage to the sea. Therefore, it is the largest closed basin of Turkey. Continental climate type dominates the basin; hot and dry summers, cold and rainy winters.

FIGURE 1
The geographical location of the Konya Basin and the examined water bodies

Meke Lake (Ramsar site) and its nearby Akgol Wetland and Acigol Lake of international value located in the Konya Basin of the country are temporally assessed regarding changes in water surfaces. The neighbourhood water bodies are important in terms of their benefits.

Meke Lake is one of the most important heritage sites of Turkey and of the world in terms of its appearance and geological structure. However, it is entirely opposed to danger of dryness. It is a volcanic eruption pit known as Maar and has become a lake filled with water. The water of Meke Lake is rich in K, Mg, Na, Ca, sulphate and chlorides, and salt has been produced from the lake for many years [27]. As it houses a variety of endemic species and acts as a shelter for many migrating birds, it has been declared as a Ramsar site in 2005. It is about 981 m above sea level and the depth of the lake is not more than 12 m.

Acigol is one of the world’s most important volcanic lakes with a depth of 300 m and almost 70 m below the ground level. Due to the presence of sulphate salts in the water body, microbiological species are not available in the aquatic environment like
the Meke Lake. The detection of volcanic gas outcrops at the edge of the lake indicates that the volcanic activity has not yet reached its end [26]. Another feature of the lake is that the water level never changes. Acigol, of scientific importance and rarity, is also a geological structure in which the properties such as visual aesthetics and landscape are also of high value. It is an important area that hosts many bird species. In 2005, Acigol was declared as a Wildlife Protection Area.

Akgol is one of the most important wetlands of Konya Closed Basin known as Eregli Reeds. It has been a habitat for many species, especially the aquatic species. A large number of migratory bird species have opportunities for nesting, sheltering, feeding and reproduction at Akgol. The wide range of reeds and wide water holding area together with the steppe character around it allows a high biological diversity in comparison with many similar areas. Akgol was declared as the 1st level Natural Site by the Ministry of Culture in 1992 and as a Nature Conservation Area in 1995.

### MATERIALS AND METHODS

Landsat 4-5 TM and Landsat 8 OLI satellite images have been used to determine the temporal changes in the Akgol Wetland, Acigol and Meke. General characteristics of the Landsat images are given in Table 1. These images are downloaded from the USGS website [28]. Pixel based image classification method, the process of grouping pixels of images into patterns of varying grey tones or assigned colours that have similar spectral values to transform data into information for determining various earth resources, was used to obtain land-use/cover information. Multispectral image classification is one of the most frequently used methods for information extraction [29]. Supervised classification method is applied by using Maximum Likelihood Algorithm to obtain water bodies and others. The overall accuracy assessment of the images for 4 images was above 95% and the Kappa statistics were calculated above 0.95 for the images. As the study area had 3 different wetlands, they were cropped into sub-areas and the water-covered areas were obtained separately as shown in Figure 2 and Figure 3.

There are no rivers or streams feeding the 3 water bodies; only a significant amount of precipitation and superficial flow from the north of the Taurus Mountains and drains from these mountains feed the wetlands. For that reason, meteorological data including precipitation and evaporation values were considered in the evaluation of the results obtained from the satellite images. Data obtained from the Eregli Meteorological Station that is located in the vicinity of the study area have been used. The results showed that the average rainfall of the area which was determined as 303.6 mm is almost half of the average rainfall of Turkey which is 628.9 mm (Table 2) [30]. Table 3 shows the monthly precipitation values for the respective years covering the same dates as satellite images. Precipitation in the region usually starts in October and continues until the end of May. Months with precipitation are marked up based on the date of the image and the total precipitation amounts of these months are associated with the surface area of water in the wetlands determined by classification of the images.

### TABLE 1

<table>
<thead>
<tr>
<th>Image Date</th>
<th>Satellite</th>
<th>Path</th>
<th>Row</th>
<th>Spectral Resolution, μm</th>
<th>Spatial Resolution</th>
<th>Radiometric Resolution</th>
<th>Temporal Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>May 08, 1990</td>
<td>Landsat 4 Tm</td>
<td>176</td>
<td>34</td>
<td>7 Band (0.45-2.35)</td>
<td>B1, B2, B3, B4, B5, B7:30 m</td>
<td>8 bit</td>
<td>16 days</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>B6:120m</td>
<td></td>
</tr>
<tr>
<td>May 11, 2000</td>
<td>Landsat 5 Tm</td>
<td>176</td>
<td>34</td>
<td>7 Band (0.45-2.35)</td>
<td>B1, B2, B3, B4, B5, B7:30 m</td>
<td>8 bit</td>
<td>16 days</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>B6:120m</td>
<td></td>
</tr>
<tr>
<td>May 07, 2010</td>
<td>Landsat 5 Tm</td>
<td>176</td>
<td>34</td>
<td>7 Band (0.45-2.35)</td>
<td>B1, B2, B3, B4, B5, B7:30 m</td>
<td>8 bit</td>
<td>16 days</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>B6:120m</td>
<td></td>
</tr>
<tr>
<td>April 05, 2016</td>
<td>Landsat 8 Oli</td>
<td>176</td>
<td>34</td>
<td>9 Bands (0.433-2.30)</td>
<td>B1, B2, B3, B4, B5, B7, B9:30 m</td>
<td>16 bit</td>
<td>16 days</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>B6:60m B8:15m</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 2

<table>
<thead>
<tr>
<th>Station</th>
<th>Annual precipitation averages (mm)</th>
<th>Long Term Average(mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turkey</td>
<td>609.4</td>
<td>637.6</td>
</tr>
<tr>
<td>Eregli</td>
<td>282.4</td>
<td>277.2</td>
</tr>
</tbody>
</table>
Table 3 shows the monthly evaporation data obtained from Eregli Meteorological Station. It is observed that there is no evaporation from November till the end of April except for 2016. It can be stated that one of the reasons for drying of the shallow wetlands, which are fed by rainwater in spring, is the high evaporation in summer.
RESULTS AND DISCUSSION

In this study, temporal changes of water surfaces in Akgol Wetland, Acigol and Meke lakes were successfully determined via remotely sensed data (Table 5) between years 1990-2000, 1990-2010 and 1990-2016. According to the classification results, the most remarkable and drastic change occurred in Akgol Wetland. It is clearly observed that Akgol Wetland has been lost by 66% within the decade of 1990-2000, and almost disappeared in year 2010. Although around 100 ha are gained back in 2016, the overall decrease in its area in 26 years period is 98% (Figure 2). It can be seen from the results of classification that there is almost no change in the 4 inspection years in Acigol Lake, and even the surface area increased by 7% with the precipitation in 2000. The situation in Meke Lake is similar to Akgol (Figure 3).

Meke Maar was showing lake characteristics till 2010, but nowadays, it is about to lose this feature.

As shown in Figure 3, the surface area of the lake, which was 41.76 ha in 1990, reached to 62 ha in 2000 and then decreased to 2.61 ha in 2016 indicating 94% loss within 1990-2016. This huge reduction in the water surface was observed in the field survey conducted in November 2017. The highly remarkable water surface changes in both Akgol Wetland and Meke Lake need further investigation at the region.

CONCLUSIONS

It is known that irrigated agriculture is the dominating sector in the region; thus, farmers provide their water need from the aquifers either legally or illegally, and frequently withdraw surface water leading to both wetland and lake especially in case the groundwater level decreases in dry periods. This fact seems to be the main cause of significant water loss within years both in Akgol Wetland and Meke Lake. Therefore, it is necessary to establish applicable management plans for these sensitive water bodies of international attraction. In recent years, a considerable decline has occurred in the groundwater table of the region as a result of excessive water withdrawal; where the majority is used for irrigating crops that require high water like sugar beet. Management plans need to be developed for the region and in that sense, temporal change detection is important for the preparation of the plans.

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OBJECT BASED CLASSIFICATION OF UNMANNED AERIAL VEHICLE (UAV) IMAGERY FOR FOREST FIRES MONITORING

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ABSTRACT

In case of fire, determination of burned trees and fire direction is very important. Until now, satellite images and aerial photographs have been widely used in forest fire studies. However, these data can be ineffective in terms of temporal and spatial resolution. In recent years, due to high resolution of provided images, use of Unmanned Aerial Vehicle (UAV) rapidly increased in forest related monitoring studies. Images obtained soon after the forest fires by means of UAVs became the most important data to evaluate the damage level in the forestry area using different classification techniques. Conventional image classification methods are inefficient for evaluation of high resolution images. However, object-based classification is more accurate than conventional methods. Because, this method uses spectral, neighborhood, texture, hierarchy and size based relationships. In this study, forest fires occurred in Camburnu Natural Park in Sürmene District of Trabzon Province located in the Black Sea Region of Turkey was selected as the study area. To determine the destroyed area, high resolution UAV images of the study area were obtained and image pre-processing steps were employed. Object-based classification and pixel-based classification have applied to these images. The boundaries of destroyed forest have been extracted by means of two classification methods. Additionally, combining of these two classification results was investigated to improve the results of the burned area.

KEYWORDS: Object Based Classification, Unmanned Aerial Vehicle, Digital Photogrammetry, Computer Vision, Forest Fires.

INTRODUCTION

Determining the areas that are changing over time due to natural or human-induced reasons has great importance for future planning and making decisions. For this purpose, there is a need for up-to-date data that will reveal the current situation. These regions must be monitored at specific time intervals in order to identify these changes. In determining the areas that have been damaged; aerial photos, classical measuring methods (such as electronic distance meter, GNSS), LIDAR (Light Detection and Ranging), Unmanned Aerial Vehicles (UAVs) and satellite images (high or medium resolution) can be used [1]. Recently, the evaluation of the images (obtained by UAVs) using digital photogrammetry techniques has started to be widely used.

UAV technology has significant advantages in terms of speed, cost and accuracy. There has been an increase in the studies on the availability of UAVs in disaster studies. Automatic image extraction with electronic systems has been carried out and these images were used to produce Digital Terrain Models (DTM) and orthophoto map. Measurements and interpretation processes were performed on digital images to execute volume calculations and emergency response studies of the affected areas. Some studies have been carried out on obtaining high-resolution landslide images, coastal management [2], determination of land-use changes [3], disaster management and monitoring [4], management of search and rescue operations [5] and collecting landslide inventory information using by UAV [6].

Forest fire is a natural disaster that has a negative impact on the environment and affects the economic state. Forest fires lead to the destruction of forest and the wildlife and have a disastrous social, economic and environmental impact [7]. Hundreds of thousands of hectares are devastated by forest fires each year. Nonetheless, real-time fire monitoring has always been important to protect forests. With the development of the UAV, remote sensing and processing technology, it has been possible to real-time process and analysis of images. UAVs can also be applied for forest-fire detection, confirmation, localization and monitoring. UAVs are also useful for the evaluation of the fire effects and particularly for the estimation of the burnt area. Therefore, the use of UAV to detect fires becomes exceptionally significance.

Interpretation of the photogrammetric data produced by visual interpretation or similar methods requires too much time and operator work. It’s almost impossible to interpret the damage that occurred in
the big diameter areas from this point of view. For this reason, satellite images or orthophotos can be interpreted using classification techniques. In addition, work can be carried out quickly and automatically to determine how much area was damaged after the fire and what operations need to be done. Basically, classification is the process of aggregating objects with similar spectral reflectance values under the same class. In other words, it is the process of comparison the values of all pixels on each band to the pixels of the image and classifying the similar pixels into the classes or class numbers that the user has identified [8].

The purpose of the classification process is to increase the discriminability of data groups with the same spectral characteristics by collecting them under the same group. The desired classes to be extracted from an image can be determined by the user or can be done randomly by selecting only the number of the class [9]. In this context, considering the basic unit and the structure used in classification, it is possible to mention two types of classification as pixel-based classification and object-based classification.

In this study, the most commonly used image pair algorithms were used. Afterwards, high resolution orthophoto of the area was produced using the photogrammetric evaluation methods using high spectral resolution images of forest fire area taken with the UAV. Using these images, burned areas were determined accurately by means of pixel-based and object-based classification methods (with E-Cognition software). Using the bands of the orthophoto, different index images in greyscale were produced. Additionally, intersection of object-based and pixel-based classification results was examined to determine burned areas. Burned areas were extracted from these images to demonstrate the usability of UAV images in forest fires.

**FIGURE 1**
The Study Area (Trabzon-Turkey).

**STUDY AREA**

In this study, a natural park named Çamburnu which is located in Trabzon Province located in the Black Sea Region was selected as the study area (Figure 1). This area where yellow pine forests can land at sea level is unique in the world. On January 8, 2017, an unpredicted forest fire happened and about 20 hectares were destroyed. Approximately 8 hectares were selected as the test area. 511 high resolution images were taken from UAV from 80 meters altitude has been used for evaluation.

**DATA AND METHODOLOGY USED**

Recent advances of the computer science have introduced computer vision technology to the engineering discipline. Methods and tools developed in computer vision prove to be useful for increasing the degree of automation in digital photogrammetry. Image pairs are needed to be matched in order to generate 3D data (such as Digital Surface Model (DSM) or depth map). This task is generally handled with alignment of image pairs with matching features or establishing a set of correspondences between them (i.e. epi-polar geometry) and both approaches take advantage of features in image pairs.

These features are mostly unique points (or key points) in images, those can be corners, doorways or some other local regions of interest. Such features are detected and described using patches, which are formed with feature point’s surrounding pixels’ grey values and provide uniqueness. [10].

Feature detection task is about if a pixel could form a feature or not with respect to the surrounding pixels (i.e. if a pixel and its surroundings share the same gray value, the pixel could not form a feature). Feature description is a completing task which deals with identification of the detected features with respect to neighbor pixels that helps matching the same features in image pairs.

There are some challenges that feature detection and description algorithms should deal with. These difficulties can be listed as: being invariant to scale and rotation, being repeatable and working fast. Furthermore, features also need to be unique, easily traceable and comparable. To achieve these goals, many feature detection, description and both of them algorithms have been developed.

In this study, the most commonly used image pair algorithms were determined. BRIEF, FAST, BRISK, SIFT have resulted in fast, accurate and large data sets with algorithms that can perform photogrammetric process. SIFT is advantageous to perform scale independent, detail and high accuracy image pairing and to produce high-accurate result products compared to other algorithms. In addition, SIFT is an algorithm for both detection and description. Therefore, a SIFT based computer vision software was used (Agisoft Photoscan) in this study. SIFT algorithms used in computer vision-based digital photogrammetric software can achieve more accurate image matching with 80% overlap and 60% side lap. For this reason, all flights made in the study area were made considering this coverage ratio. These
images were obtained using DJI Phantom 4 UAV. General features of used UAV;

- Image size 4000*3000 pixels
- 1/2.3" CMOS sensor
- 35 mm focal length
- Pixel size 6 μm x 4 μm

Agisoft Photoscan software was used for photogrammetric evaluation of the images. Digital photogrammetric technique was applied through this computer vision-based software to produce approximately 4 cm resolution orthophoto-map from the images. A high production type has been chosen for the production of orthophoto-map in order to be able to perform the classification of the orthophoto, the main aim of this study, more precisely and correctly.

Pixel-based classification (PBC) is a classification method that classifies all pixels in an image using multispectral classification techniques by comparing their spectral proximity with the class to be assigned. Unlike pixel-based classification, object-based classification does not work on directly a single pixel. These methods work on objects that are composed of many pixels, grouped in a meaningful way by the segmentation process. Then these objects are used instead of pixels as a classification object [11, 12].

Maximum likelihood classification (MLC) algorithm was used for pixel-based classification of UAV images. The maximum likelihood algorithm is based on the possibility that a pixel belongs to a specific class. The basic equation supposes that these possibilities are equal for all classes, and that the input bands have normal distributions [14]. The details to be extracted in this study were determined as damaged forest areas and undamaged areas. Undamaged areas are union of building, road, water, soil and agriculture area class sets. Training data were created with the help of data collected from both the existing maps and with field work. After then UAV image is classified using by this sample data.

The object-based classification (OBC) method consists of two stages as segmentation and classification of segments. In the first stage, neighboring pixels are combined until the desired details are extracted and appropriate segments are created for the classification process in the second step. Segmentation is the process of separating images into objects or areas that reflect the same characteristics. Segmentation is the main element for creating objects from image pixels [14]. The quality of objects created by segmentation directly affects the accuracy of classification [15]. The selection of these objects is usually determined by trial and error method [16]. However, there have been recent attempts to automate this process [17]. Scale parameter estimation (ESP) tool that calculates the scale parameter quickly and easily have developed using the local variances of the image on Cognition Network Language (CNL) environment of eCognition Developer [18]. ESP tool is the most preferred one [19]. Drăgut et al. improve this tool in 2014 to develop an ESP2 based tool with statistical analysis of local variance [20]. The ESP2 tool can be determine the segmentation parameters by defining eleven parameters. These parameters are; 3 types of scale parameters start number, 3 increase amount of scale parameter, cycle count, shape, compactness, hierarchy usage approval and hierarchy type. Once these parameters are defined, the appropriate segments for the image are determined at 3 different levels. (Figure 2).

Segmentation was also determined with trial and error method. There are three parameters in the segmentation process which are: scale parameter, shape parameter and compactness parameter. For this reason, the compactness parameter was taken 0.5 and the scale and shape parameters were tested. Firstly, we tried to find the most appropriate scale parameter for the orthophoto by giving the values of compactness parameter 0.5, shape parameter 0.1 and scale parameter between 10 and 200. Experiments made for the scale parameter in the orthophoto are shown in Figure 3a and the experiments made for the shape parameter are shown in Figure 3b.
(a) Scale Parameter Levels, (b) Shape Parameter Levels.

FIGURE 3

Segments created with inappropriate parameters (missegmentation).

FIGURE 4

In the first step, 10 scale parameters were used to determine the scale parameter. The scale parameters (20, 30, 40, 50, 60, 70, 80, 90, 100, 120) determined by keeping the compactness and shape parameters constant have been tested one by one. Every detail has its own scale parameter. For this reason, it is important to select segments according to the desired detail. For example, the ideal scale parameter for extraction of forest detail is 70 while the ideal scale parameter for extraction of road detail is 120. If we extract the forest detail with the scale parameter set for the road, the wrong segments will appear as shown in figure 4, so the classification process will be incorrect. The second step is to determine the target shape parameter. For this purpose, trial and error method was applied to find the ideal shape parameter while keeping the scale and compactness parameter constant. For this purpose, 9 shape parameters (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9) were applied and tested one by one.

FIGURE 5

The indexed values of the classes specified (burned forest (black), other details (blue)).

In order to apply object-based classification to the orthophoto, band combinations in the literature
have been investigated. Classification has been performed according to these band combinations, Green-Red Vegetation Index (GRVI), Red Ratio Index (RRI), Green Ratio Index (GRI) (Figure 5).

In these 3 band combinations (GRVI, RRI, GRI) overlap of the values of burnt forests was taken to eliminate both the confusion between the details and to obtain a better classification result (Figure 7). Thus, burned forest extracted from image without any mixed pixel.

RESULTS

In the object-based classification method, the first process is segmentation. Segmentation results directly affect the accuracy of the classification result. In this study, accepted ESP and trial-and-error methods were used and the most appropriate segments were created. As a result of the researches, it is seen that segmentation can be made faster by ESP method, but it is also seen that better segments are created by trial and error method because the creation of segments by trial and error method is directly connected to the user.

The second step in object-based classification is to assign the created segments to classes. For this purpose, images were converted into gray scale images using band combinations. The purpose of this process is to extract the properties of the desired class using the properties in the image. In this study, 3 different band combinations (GRVI, RRI, GRI) were used to separate burned forest areas from other details and burned forest areas were obtained. Classification results are shown in figure 6. Burned areas in the study area were digitized to determine the accuracy of classification results (Figure 7), also intersection of two methods.

The purpose of intersection of results is to increase the accuracy result in burned area which is determined both pixel and object-based classification result. Approximately 8 ha of forest areas were digitized as burned areas by on the screen digitizing method. Classification results show that PBC results have 5.5 ha burned areas and it contain 69% of digitized burned areas, additionally, OBC results have 7 hectares burned areas and it contain 87% of digitized burned areas. Although OBC is more accurate than PBC, in some objects there are misclassification in OBC when it’s truly extracted in PBC. OBC and PBC classification results are given in figure 8.

To determine burned areas which are not contain misclassification, intersection of two classification results (OBC and PBC) are created using intersect tool in GIS (Figure 9).

CONCLUSIONS

As a result of this study, the use of 3-band orthophoto map obtained by UAV was investigated and found sufficient for rapid determination of sudden changes in forest areas (due to landslide, fire etc.). It has been observed that the object and pixel-based classification method used for the classification of orthophoto map with very high resolution results in a more accurate and faster manner than the other.
classical methods with the hierarchical and automatic (semi-automatic) classification structure. However, if more detailed information is requested (tree species, healthy plant cover, etc.), the near infrared band defect in the orthophoto is seen as a disadvantage.

FIGURE 9
Intersection of two classification results (green), Digitized burned areas (pink).

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SEISMIC VULNERABILITY ASSESSMENT OF STORAGE STEEL TANKS IN INDUSTRIAL AREAS: A CASE-STUDY

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ABSTRACT

In urban and rural areas near to an industrial plant it is fundamental the analysis of health impacts associated with accidental release of chemicals in the environment, as an accident could produce a huge number of casualties resulting from exposure to the toxic cloud. Furthermore, a cascading spill of hazardous chemicals contaminating the soil and the water supply would affect the local population with health changes that may become clinically evident even months or years after the disaster. These are crucial aspects taken into account within the framework of PEC (Post-Emergency, multi-hazard health risk assessment in Chemical disasters), a prevention and preparedness project aimed at developing a multi-hazard risk assessment toolkit applicable to chemical disasters.

The proposed model was assessed on the basis of a case-study represented by two chemical plants located in the Priolo Gargallo area, on the West coast of Sicily (Italy). Although the project considers the effects of natural and man-made disasters, such as earthquake, flood and terroristic attack, on plant structures and infrastructures, the work described in this paper is chiefly concerned with the seismic vulnerability of tanks, owing to the huge amount of chemicals stored by them and also to the fact that several earthquakes in the past have demonstrated the susceptibility of storage tanks to earthquake-induced damage.

In the vulnerability assessment of storage steel tanks, the definition of their structural properties is relatively straightforward since items of this type are highly standardised in terms of construction and design. It is noted that design criteria for these plant structures evolved very slowly over the past decades, as confirmed by a brief overview of international codes and standards provided in the paper. For this reason, tanks are very similar around the world and their vulnerability is uncorrelated with the construction period. Thus, in order to quantify the seismic vulnerability of these storage structures, fragility curves, describing the probability of reaching or exceeding a certain damage limit condition for a given severity of the ground shaking, have been calculated by means of a mechanics-based model that assumes the peak ground acceleration (PGA) to represent the ground motion severity. Noteworthy is that the set of fragility models proposed in this study has been validated by the results of detailed high-definition finite element (FE) models and by the comparison with other curves available in the literature.

KEYWORDS:
Steel Tanks, Fragility Models, Finite Element Models, Buckling, Toppling.

INTRODUCTION

To evaluate the amount of material stored in a tank that may spill into the environment after a seismic event, fragility models are the foremost tool because they describe the physical vulnerability of a structure or of a class of structures. In other words, they describe the probability of reaching or exceeding a certain damage limit condition for a given severity of the ground shaking. Thus, this paper discusses the main steps towards the derivation of fragility curves that can be applied for seismic risk assessment and management of tanks, the latter being common storage items of a plant.

The set of fragility curves presented in this study are mechanics-based and have been calculated through a simplified model, which describes the population of structures by means of random variables. Fragility curves have been derived by selecting the PGA of an earthquake as the most representative parameter of the ground motion severity and have been calculated for different types of storage tanks, each of which classified according to its geometric characteristics. Therefore, a type and a set of fragility curves can be associated with each storage tank of the area of interest, as discussed in what follows.

MATERIALS AND METHODS

Damage typologies in past and recent earthquakes. As described in [1-3], numerous seismic events occurred in the United States of America, Japan, Turkey and Italy have shown the susceptibility
of storage steel tanks to damage due to earthquake-induced actions. The most common occurrences are depicted in Figure 1 and also listed below:

a) Elastic-plastic buckling of the tank wall;
b) Elastic buckling of the tank wall;
c) Failure of pipes connected to the tank;
d) Roof damage due to convective waves;
e) Secondary buckling at the top of the shell;
f) Settlement of the foundations;
g) Toppling around a corner at the base.

As far as the 2012 Emilia, Italy, earthquakes are concerned, the most damaged structures were precast industrial facilities [3, 4] and nearby storage steel tanks, the poor seismic performance of which confirmed a disproportionately high vulnerability of these structures compared to the severity of the seismic events. Furthermore, damage and failure mechanisms were in close agreement with those shown by destructive earthquakes in other areas [5-8], given that the affected tanks were designed in accordance with early methods. In detail, the most common types of failure were (i) fracture of base anchors as well as (ii) elephant foot buckling near the base of the tank. Generally, the latter damage mode was experienced in squat tanks, whilst some of the slender tanks developed diamond-shaped buckling. Total and partial collapse of legged tanks was also observed because of either shear failure or buckling of their legs due to axial forces resulting from tank overturning moment. In some cases, flat-bottomed steel cylindrical tanks, typically larger than legged tanks, failed in tension at the bottom of the tank wall, in correspondence of the anchor rods or massive concrete pads.

**International codes.** For what concerns the vulnerability assessment of storage tanks, it can be inferred that the identification of key structural properties is quite trivial since tanks and vessels are highly standardised in terms of construction and design. The analysis of international codes confirms this and also points out that the criteria assumed to design these structures evolved very slowly over the course of the past decades. For this reason, tanks are very similar around the world and their vulnerability is almost independent from the construction period.

For the structural design of steel storage tanks, reference can be made to four guidelines/standards: two American codes [9, 10] and two European codes [11, 12]. Although the use of US standards is much more consolidated in practice since they were originally released in the 30’s, the Eurocodes can be considered as more appealing because they rely upon the shell theory and fall within the framework of performance-based approaches. By contrast, the American codes provide crude rules, often based on empirical expressions, that can be used to easily design the thickness of the tank components. In this case, admissible stress criteria are adopted instead of methods that identify limit state conditions.

**Fragility curves.** First of all, the storage tanks of the two plants have been classified as a function of the ratio between diameter (D) and height (H), as such ratio (D/H) was proven to have the highest influence on the seismic performance of this type of structures according to field observations collected in the aftermath of past earthquakes [13]. In light of this, the storage tanks of the industrial plants herein considered have been categorised as follows:

- class 1: \(0.7 \leq D/H \leq 1.0\);
- class 2: \(1.0 < D/H \leq 1.5\);
- class 3: \(1.5 < D/H \leq 2.0\);
- class 4: \(D/H > 2.0\).

Moreover, it can be inferred that the following damage mechanisms were taken into account for vulnerability assessment: (i) buckling of the wall, and (ii) toppling of the storage tank. It is also noted that damage modes due to relative displacements between the wall and the pipes were not accounted for. This damage mechanism/condition has to be neglected because it is strongly dependent on the relative stiffness of the wall-pipe connection, which does not follow a standard, and therefore a suitable distribution through a random variable cannot be found. The fragility curves have been produced for both anchored and unanchored tanks as well as for tanks on both soil (considering the characteristics of the site of interest) and rock, namely without soil-structure interaction.
For what concerns the comparison with curves coming from the literature, fragility models on rock are selected. Figure 2 shows a comparison between the ones calculated in this study and those proposed in HAZUS (HAZard in the US [14]) for the limit state of moderate damage (MD) and of severe damage (SD), that here corresponds to the activation of buckling of the tank wall. It can be observed that there is a good agreement between the fragility curves produced in this study and the ones suggested by [14]. A further validation of the results of this study is that the fragility increases when the ratio D/H reduces. Such a trend, which implies that higher levels of damage can be associated with slender tanks, has been confirmed by past earthquakes.

For the sake of clarity, it is worth specifying that the mechanical model used for nonlinear dynamic analyses of tanks and hence for derivation of the curves presented in this study allows only the calculation of curves for moderate and severe damage conditions, since mechanisms other than those cannot be explicitly recognised by numerical simulations. Accordingly, the curves corresponding to the other damage limit states have been obtained calculating the mean and the standard deviation of the lognormal function as specified below:

- The calculated curve is assumed to be corresponding to the limit state of severe damage;
- The average of the curves relative to other limit states was calculated preserving the ratio between the average values of the curves proposed in [14];
- The standard deviation was calculated assuming for each limit state the same dispersion of the curve really calculated.

As an example for the case of not anchored tanks, Figure 3 shows the fragility curves produced for each limit state and tank class. It is noted that the abovementioned curves refer to non-anchored storage tanks on soil. The information on the anchor conditions is not known, therefore the tanks are assumed as not anchored, which corresponds to the most common practice for similar structures.

**Mechanical model validation.** Several computational strategies can be easily used to reproduce the complex response of industrial storage structures, whose behaviour is governed by a combination of many interacting phenomena. High-fidelity FE models were thus developed to predict the dynamic response of the case-study structures. Comparisons between experimental and numerical estimates may serve as a validation of this modelling approach, which was then used to perform a set of nonlinear dynamic analyses aimed at exploring behavioural changes in the seismic response of similar structures as a consequence of parametric variations in their geometry. Those findings were finally used to correlate estimates resulting from detailed and simplified modelling approaches, which implies on-spot validation of the trends shown by the proposed fragility models.

Needless to say that FE analyses are able to capture stress/strain concentrations, which are crucial in interpreting damage patterns and failure modes. Therefore, a wide set of high-fidelity FE models has been developed to reproduce the seismic response of flat-bottomed steel tanks featuring different geometrical properties. Geometrically and materially nonlinear explicit dynamic analyses have been carried out by making use of a general purpose finite element package with fluid-structure interaction capabilities. The FE software LS-DYNA has been adopted to perform the numerical analyses described in what follows. The Arbitrary Lagrangian Eulerian (ALE) method has been used to allow for large structural and liquid deformation. The numerical technique proposed herein is able to account for many sources of nonlinearity, such as large amplitude nonlinear sloshing of free surface liquid and yielding/buckling mechanisms of the tank wall. Such a detailed finite element approach has been applied to predict the experimental response of two case-study tanks [15, 16].
Comparisons between numerical and test results. The first case-study structure is the one tested in the pioneering experimental research carried out by Manos and Clough [15]. In particular, an open-top, anchored tank resting on rigid foundation was analysed numerically. The tank prototype used in the experiments was a 1/3 scaled structure having radius of about 1.83 m and height of 1.83 m. The system was filled with water up to a height of 1.53 m. The tank was made of aluminium with a density of 2700 kg/m³. The thickness of the base plate was 2 mm. The same thickness was used for the tank wall, which however has a second course with a thickness equal to 1.3 mm. An L-shaped steel girder was placed onto the top of the second shell course. In the experimental shake-table test, the input motion was derived from the horizontal component of the El Centro 1940 earthquake assuming a peak ground acceleration (PGA) of 0.50 g. The input was then scaled with respect to time by a factor equal to 1/3 because of similitude requirements.

A comparison between numerical predictions and experimental data is given in terms of pressure time histories at different locations up to the height of the tank wall, as shown in Figure 4. Numerical predictions were found to be in close correlation with experimental results, as almost negligible differences can be observed. Response graphs revealed that peak pressures were predicted in a very consistent and accurate manner, and the same applies to the post-peak behaviour. Similar considerations can be drawn for the shape and amplitude of sloshing wave, as small discrepancies (<5%) were determined from the comparison between numerical and experimental data.

The aforementioned numerical techniques were considered to predict the experimental response of another reference tank, namely case-study 2. In particular, the cylindrical tank tested by Haroun [16] is an open-top, anchored prototype filled with water. The tank wall is made of aluminum with density of 2600 kg/m³. The radius of the tank is 1.18 m; its total height is 4.57 m, whilst the height of the water free surface was 3.96 m. The 1994 El Centro earthquake, scaled to a PGA equal to 0.5 g, was assumed by Haroun [16] to perform the shake table test considered here for validation purposes. Figure 5 collects the prevailing results obtained numerically. Also in this case, numerical predictions were proven to be in close agreement with experimental results, as a difference of about 2% was indeed obtained in terms of maximum base shear. Similar discrepancies can be observed as far as the maximum meridional compressive force and the peak radial displacement are concerned.

Parametric simulation of representative storage systems. Once the aforementioned numerical procedures were validated in compliance with experimental data, a set of parametric FE analyses was performed to explore the seismic vulnerability...
of these systems. Predictions were collected to point out behavioral changes in the seismic response of storage tanks as a consequence of variations in their geometrical characteristics. The analysis results may thus serve as a cross-validation of the trends emerged from the set fragility curves presented in the previous Sections. The prototype tanks were characterized by different height-to-radius (H/R) and radius-to-thickness (R/t) ratios. Numerically predicted and analytically computed hydrostatic pressure profiles were compared for tanks having different height-to-radius ratios, thus showing an almost perfect match also in this case (see Figure 6a). Explicit nonlinear dynamic analyses were then performed. For instance, Figure 6b shows the pressure distributions obtained for tanks with H/R = 3 and different R/t. Severe concentrations can be observed in the set of pressure peak profiles determined for tanks having H/R equal to or higher than 3, whilst the other case-study tanks under consideration are less vulnerable to earthquake excitation. Such trends are in close agreement with those shown by fragility models.

FIGURE 4
Case-study 1 [15] – Comparison between experimental and numerical pressure time histories.

FIGURE 5
Case-study 2 [16] – Base shear time history and maximum radial displacement profile.

FIGURE 6
a) Hydrostatic and hydrodynamic pressure: a) comparison between analytical estimates and FE predictions, and b) parametric simulations of slender case-study tanks.
CONCLUSION

This study has dealt with the seismic vulnerability assessment of existing tanks that are typical items of petro-chemical plants for storage of contaminant fluids. For this reason, a great attention has been paid to the analysis and inventory of frequent damage mechanisms observed for such shell structures in past and recent earthquakes. The observed failure mechanisms, in addition to the indications provided by international codes and standards, have represented a useful guide for the definition of damage limit states. The main aim has been the identification of damages that could lead to the spilling of contaminant fluids contained in this type of structures. The steel tanks under study were assumed to be characterised by two possible configurations of base connection (i.e. anchored and not-anchored tanks) and to be distinguished in four classes according to their D/H ratio. A simulated design has been performed following the design prescriptions provided by codes available at the time of construction. Then, simplified numerical models have been developed using FE procedures. These models have been submitted to a series of nonlinear dynamic analyses in order to evaluate the seismic capacity of each model and to derive sets of fragility models at multiple damage conditions. A careful validation of the abovementioned fragility curves has been carried out by comparison with (i) other curves published in the scientific literature and (ii) the results of high-definition FE models able to account for fluid-structure interaction in an explicit manner. The latter numerical models were first validated by using experimental results and then used to predict the trends of mechanics-based fragility curves. It should be noted that the obtained fragility models/cases are applicable for seismic risk assessment and management of storage tanks of industrial plants.

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SEISMIC RISK ANALYSIS OF PRESSURE VESSELS

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ABSTRACT

In the context of seismic risk analysis of chemical plants, pressure vessels are one of the most sensitive equipment to be considered because of the quantity of hazardous products contained and the large number of vessels present in a single plant. For these reasons, this equipment must be designed to ensure safety against any low probability-high consequence event that may occur in the lifetime of a plant, and earthquakes are one of the most vivid examples of this type of occurrence.

Among the possible geometrical configurations, the present study addresses the seismic risk analysis of two kinds of pressure vessels: (i) horizontal vessels supported on steel saddles and vertical rigid supports, and (ii) slender vertical vessels supported by a skirt.

To identify deterministic and epistemic parameters of interest, a simulated design is first developed by considering the indications provided in the Italian seismic code applicable in the 90’s for what concerns the characterization of the seismic input. Then, fragility curves are derived by means of simplified and reliable methods. Finally, the seismic risk, evaluated in terms of frequency of event per year, is related to consequence in terms of chemical release quantity, in such way that the input for further loss and emergency analysis can be defined.

KEYWORDS:
Seismic Risk, Fragility Curves, Pressure Vessels.

INTRODUCTION

Pressure vessels represent one of the most widespread equipment included in industrial plants. In particular, their presence is even more recurrent in sectors of paramount industrial importance, such as the nuclear, oil, petrochemical, and chemical sectors. In addition to vessel’s widespread use, it is important to notice their recurrent use for containing the large quantity of hazardous and polluting material. The main objective of the present study was to propose a simplified procedure for the estimation of the seismic risk, hence the estimation of the frequencies of occurrence of specific damage states and the relative consequences in terms of content release.

One of the criteria for classifying vertical and horizontal pressure vessels is the kind of support whose stiffness strongly influences the global geometry. In the case of vertical vessels, the most recurrent typologies of supports are legs, skirt and lugs. In the case of horizontal vessels, the supports can be distinguished in short or rigid and flexible piers. The present study focuses only on vertical vessels supported by skirts and horizontal pressure vessels supported by steel saddles with vertical rigid supports.

Even if numerous references can be found in the scientific literature about the design of pressure vessels, the majority of them regard only the static and functional design [1]. More limited is the number of references dealing with the seismic design, the majority of which are concentrated on the analysis of specific case studies [2,3], and even more about the estimation of fragility curves.

With the aim to cover this gap, fragility curves were derived considering simplified models. The properties of the vessels discussed herein were defined through Montecarlo simulations. The study is then devoted to the estimation of seismic risk for the specific case of existing industrial equipment for which the design process mainly considered functionality requirements (pressure and temperature). This assumption affects more the support properties than the vessel walls that are indeed governed by internal pressure and temperature and not by the seismic action.

MATERIALS AND METHODS

The seismic risk procedure starts with the derivation of the fragility curves, referring to as the probability of reaching or exceeding a certain damage state for a given seismic intensity (assumed as the Peak Ground Acceleration PGA).

The representativeness of the vessels seismic performance was guaranteed by referring both to the direct observation of damages occurred in past earthquakes [4-5-6] and to the data provided by international standards [7]. The mentioned references allowed the identification of connections and foundations as the most critical components in pressure vessels (Figure 1). The majority of observed failure mechanisms involved the anchor bolts, the connections between piping and vessels.
and the supporting skirt, while rare was the failure of the vessel walls as first collapse mechanism.

The design criteria provided by specific international standards [8-11], even if mainly focused on the static and operational behaviour, were also considered to improve the reliability of the modelling assumptions and represented the reference for the simulated design of vessels. Concerning the estimation of seismic actions, the indications provided by Eurocode 8 part 4 [11] were applied to account for the hydrodynamic forces due to a seismic event, while ASCE 7-10 [12], FEMA P750 [13] and FEMA P751 [14] provided indications for the estimation of the fundamental period of vibration, seismic base shear and overturning moments. Finally, the characterization of seismic input was performed by following the Italian seismic standard applicable in the 90's [15], which was valid in the assumed period of construction.

**Fragility Curves for Horizontal Vessels.** Referring to horizontal pressure vessels supported by rigid saddles, the determination of seismic fragility curves followed a simplified procedure based on the selection of deterministic parameters (structural materials, geotechnical data, geometrical properties of foundation and vessels length to radius ratio), epistemic parameters (the vessel radius, the number of connections and the moment/rotation curve of the foundation) and aleatory parameters (the seismic input).

The random variability of the epistemic parameters, performed by Monte Carlo simulations, provided a sample of 90 statistically independent case studies. More specifically, the case studies derived assume: 10 different cross-section radius uniformly distributed with an average value of 1 m and a variation of ±25% and a fixed length to radius ratio equal to 3; 3 connection configurations; 3 moment/rotation curves for the characterization of the foundation behaviour considered as lower/medium/best estimate of the soil parameters.

Once defined the sample of case studies, a simulated design was initially performed for deriving realistic geometrical properties for both the pressure vessels and their supports. This leads to the estimation of the wall vessel thickness. The resulting vessels were characterized by a mass varying from 537 kg to 1917 kg, while the mass of the contained fluid varied from 3998 kg to 19164 kg.

Due to the relative high stiffness of the horizontal vessel with respect to soil, the soil-structure interaction is accounted by means of a simplified iterative procedure and assuming an equivalent linear model.

With the aim to account the foundation non linearity, the initial rotational stiffness was reduced as a function of the foundation rotation and the axial load ratio v (ratio between the foundation bearing capacity and the applied vertical load) [17]. In the present study, the axial load ratio was assumed to 7.50 for all the vessels and three levels of uncertainty was accounted for the soil parameters (lower, medium and high estimation).

With the modelling assumption described above, incremental equivalent linear static analyses were performed for all the vessels and with reference to response spectra defined for different return periods of the seismic intensity (variable from $T_1 = 30$ years to $T_r = 2475$ years). The seismic action associated to each seismic intensity was estimated with reference to the equivalent single degree of freedom (SDOF) model submitted to a spectral acceleration, and hence to the corresponding base shear and overturning moment, defined as a function of the fundamental period of vibration [16] and the radiation damping [11].

For the estimation of the fragility curves, the following *engineering demand parameters* (EDPs) were assumed: foundation rotation, vessel rotation, base shear and the corresponding overturning moment.

The base shear and overturning moment represent the actions with respect to which were checked the performance levels (PLs). The following performance levels were assumed in the vulnerability analyses: -PL1, corresponding to the first leakage of the fluid content and minor damage in the vessel; -PL2, corresponding to the complete release of content and complete collapse of the vessels. Foundation, anchorage bolts and piping were assumed as critical elements for the definition of the possible failure mechanisms. More specifically, the failure mechanisms corresponds to the exceedance of the bolts resistance, as well as to the attainment of both foundation and piping rotation capacities. With reference to the selected failure mechanisms, specific limits and checking criteria were defined for each PL. For the connection capacity, the resistance of the anchor bolts (in terms of shear and tensile capacity) was estimated by dividing the characteristic properties of bolts by a safety factor equal to 1.5 for PL1 and to 1.0 for PL2. Regarding the piping rotation capacity, the expected rotation of the vessel was assumed equal to the expected rotation of the connected piping by referring to experimental data provided by Tial et al. for different pipe diameters [18]. Finally, the foundation capacity was expressed in terms of rotational stiffness degradation [19] by fixing limits which able to avoid large non-linear soil deformations during and after the earthquake shaking, which may lead to collapse of the foundation system.
FIGURE 1
Damages suffered by a) horizontal and b) vertical vessels during Northridge Earthquake, 1994 [7].

Once given the EDPs, the definition of the seismic risk index ($\rho$) was derived, for each vessel and for the single performance level, as ratio between the rotation or force demand ($D_{P1,PL}$) and the system capacity ($C_{PL}$) for each direction of analysis. Then, the risk indicator $Y$ corresponding to each PL was defined from the envelope of the seismic risk index obtained for each damage state, for all the seismic intensities and directions and for all the case studies. The definition of the risk indicator allowed the estimation of the number of failures, corresponding to the condition $Y>1$, which represents the final result to fit for obtaining the fragility curves [20].

Fragility Curves for Vertical Vessels. A procedure similar to that used for horizontal vessels, was also used for studying vertical vessels. Once fixed the deterministic (mechanical properties), epistemic (vessels height and radius) and aleatory (seismic hazard) parameters, two classes of vessels were defined by uniformly vary the slenderness ratio $H/R$ into two different ranges. The first class (CL1) corresponds to the range 4 to 7 while the second one (CL2) to the range 7 to 11. The $H/R=4$ was used as lower bound for which a beam model was still applicable, $H/R=7$ was the upper limit for which higher mode effects were negligible and $H/R=11$ was the upper bound of the database considered. For each class, a set of 10 statistically independent vessels were defined and consequently 20 statistically independent case studies were studied.

Starting from these assumptions, a simulated design was initially performed with the aim to define all the relevant geometrical properties. The Italian seismic code [15] was followed for the characterization of the seismic hazard, while the prescriptions provided by FEMA P751 [14] were assumed for the estimation of the fundamental period of vibration and the shear distribution along with the vessel height. A fixed height of 10 m was assumed for the vessels with an height of 2 m for the skirt. The skirt thickness was defined by assuring a higher strength with respect to the one of the base connection and by following the Eurocode prescriptions [10,11].

Concerning the base connection, the component was conceived as a base plate welded to the vessel and anchored to the r.c. foundation by means of steel anchor bolts. This connection was preliminary designed by following the approach provided by Cook et al. [21].

Given the assumption of higher strength for the base plate, the anchor bolts represented the weakest component of the connection [21]. Both flexural and shear failure mechanisms were accounted in the simulated design of the base connections, however the recurrence of flexural collapse as dominant failure mechanism leads to the assumption to model the base connection by means of a multi-linear plastic link associated with a cyclic non-linear moment-rotation law [21].

The bending moment is taken as the minimum between the resisting moment of the bolts and the base plate. The rotation capacity of the connection accounts for both the elastic deformation of the anchor bolts and the rotation of the base plate.

Once defined the geometry of the vessels and the corresponding supports, non-linear numerical models were implemented for carrying out the vulnerability analyses by using the software SAP2000. Each model was conceived as a system in series whose main source of non-linearity was assumed concentrated in the base connection. The foundation structure was assumed with infinit stiffness and strength for all the vessels because of the relative flexible behaviour of the vertical vessels compared to the foundation flexibility.

In the case of vertical vessels, the fragility curves are derived by performing non-linear incremental dynamic analyses (IDA) with ground motion records scaled to increasing seismic intensities [22]. A set of 8 natural acceleration time-histories were selected to be compatible with the reference spectra for a return period of 475 years. Then the corresponding response spectra were scaled with respect to 6 return periods varying from $T_1 = 30$ years to $T_6 = 2475$ years.

The rotation capacity at the base, mid-height and top of the vessel were assumed as EDPs in compliance with the recurrent failure mechanisms observed in existing vessels under seismic actions.
With reference to the same PLs introduced for horizontal vessels, the limit states were expressed in terms of rotational capacity. In the case of the base connection, the limit for the rotational capacity was set to the value of the yielding rotation [21] for the PL1 and twice the same value for PL2, in accordance with the acceptance criteria of plastic rotation for structural steel components provided by ASCE 41-16 [23]. In the case of the piping connections, an equivalence was assumed between the vessel rotation and the one of the connected piping and consequently the limits provided by specific experimental tests on piping safety were assumed as reference. Finally the fragility curves were derived with a procedure similar to that described for horizontal vessels.

Estimation of Seismic Risk. The final objective of the present study was the estimation of the seismic risk expressed in terms of frequency of a specific event per year and the corresponding consequences in terms of hazardous fluid release. The seismic risk is generally defined as a function of the following factors: hazard, exposure and vulnerability.

With reference to a structural system having a specific resistance R and submitted to a seismic input S, the seismic risk can be derived by the combination of the fragility curves and the hazard curve [24]. In mathematical terms, the seismic risk can be expressed as the unconditional probability of failure:

\[ P_f = \int_0^\infty f_s(S)F_R(S)dS \]  

(1)

where: \( f_s \) expresses the probability density function of the ground motion parameter (which can be derived by deriving the seismic hazard curve), while \( F_R(S) \) represents the probability that seismic intensity \( S \) overcomes the system resistance \( R \) (expressed by the fragility curves).

Trying to mathematically express the terms of Eq. (1), the fragility curves can be expressed as follows (assuming a log-normal distribution):

\[ P(D \geq \text{PGA}_{\text{PL}}) = \Phi \left( \frac{1}{\beta} \ln \left( \frac{\text{PGA}_{\text{PL}}}{\text{PGA}_{\text{PL}}} \right) \right) \]  

(2)

where: \( \Phi \) is the standard distribution, \( \beta \) is the log-normal standard deviation and \( \text{PGA}_{\text{PL}} \) is the median value of the seismic intensity. An example of fragility curve is reported in Figure 2b.

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Concerning the seismic hazard, this parameter is dependent exclusively on the seismicity of the reference area. These curves put in correlation the specific level of seismic intensity of the ground motion, expressed in the present study in terms of PGA, with the annual frequency of exceedance (AFE) associated with the specific level of seismic intensity (corresponds to the inverse of the return period \( T_r \) for the selected seismic intensity).

To simplify the derivation of the seismic risk, a linear correlation can be assumed, at least for return periods of engineering interest, between the logarithm of a ground-motion parameter and the logarithm of the corresponding annual frequency of exceedance, as shown in Figure 2a. With this approximation, the hazard curve can be simply defined by the following relation:

\[ \text{AFE} = \text{AFE}_{475} \left( \frac{\text{PGA}_{475}}{\text{PGA}_{g}} \right)^k \]  

(3)

where: \( \text{AFE}_{475} \) and \( a_{475} \) are the annual frequency of exceedance and the PGA corresponding to a return period \( T_r \) of 475 years, respectively, while \( S \) represents the soil factor.

With reference to the horizontal and vertical vessels defined in the previous sections, the final objective of the present study was the estimation of the probability of reaching a performance level in a time window of 1 year and the corresponding mean annual frequency of occurrence of a specific performance level \( (\lambda_{DS}) \). The first output represents the seismic risk in 1 year and it can be calculated by directly integrating the Eq. (1).

Under the assumption of fragility curves defined with log-normal distribution and linearized hazard curve, the mean annual frequency of occurrence can be defined in a closed form as proposed by Jalayer and Cornell [25]:

\[ \lambda_{DS} = \lambda(PGAPL) \exp \left( \frac{1}{2} (k \beta_{tot})^2 \right) \]  

(4)

where: \( \lambda(PGAPL) \) is the mean annual frequency of occurrence of the median value of PGA of the fragility curve, \( k \) is the exponential of the linear fitting of the hazard curve in log scale, while \( \beta_{tot} \) is the total dispersion of the fragility curve.

Under the assumption of Poisson process (considering that hazard and fragility do not vary with time), the two parameters defined above can be directly correlated to each other. More specifically, the probability of exceeding a specific damage state \( P_{DS} \) in a period of time \( T \), can be derived from the mean annual frequency of exceedance \( (\lambda_{DS}) \) as follows:

\[ P_{DS} = 1 - \exp(-\lambda_{DS}T) \]  

(5)

RESULTS AND DISCUSSION

Basing on the procedure described in the previous sections, the fragility curves reported in Figure 3 were derived.

In the case of horizontal vessels, the fragility curves demonstrate the greater weakness of the models in the transverse direction. The fragility curves show a relatively low seismic vulnerability of the horizontal vessels. Concerning the vertical vessels, the slight difference measured between the two fragility classes are a combination of two effects: the differences in the fundamental period of vibration of the vessels and the bigger rotation capacity of the vessels in CL2.

The estimation of the probability of reaching a performance level and the corresponding mean
Estimation of the seismic risk by combining the hazard (a) and the fragility (b) curves [26].

Fragility curves for horizontal (a) and vertical (b) vessels.

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<tr>
<td>Longitudinal Dir.</td>
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<th>Prob. PL1 (%)</th>
<th>λ, PL1 (-)</th>
<th>λ, PL1 (-)</th>
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<td>0.0033</td>
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</tr>
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<td>0.0006</td>
<td>0.0029</td>
<td>0.0007</td>
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</table>

annual frequency of occurrence are reported in Table 1.

CONCLUSIONS

A computationally-efficient framework for the estimation of seismic risk is presented for the assessment of existing equipment usually included in petro-chemical plants. In particular, the study has focused on horizontal and vertical pressure vessels that were considered for both (i) their recurrence in industrial plants and (ii) the hazard associated with their fluid content. Simplified numerical models were thus derived by selecting a set of random variables so as to generate a population of statistically independent vessels.

For all these statistically independent structures mentioned above, a simulated design was performed. Then, simplified numerical models were simulated and submitted to different structural analyses (i.e. equivalent linear static incremental analysis and non-linear dynamic incremental analysis for the horizontal and vertical vessels respectively) in order to evaluate their seismic capacity.

Fragility curves, expressing the probability of damage occurrence as a function of the seismic intensity, were derived by following simplified and easy reproducible procedures derived by literature references, international standards and experimental tests.

The combination of the fragility curves with a reference hazard curve, defined as a function of the selected site, allowed the estimation of the seismic risk. The final output data were expressed in terms of mean annual frequency of exceeding a damage state (frequencies) and consequent probability of spilling of the fluids contained in the structures under consideration (consequences). The final output, frequencies and consequencies, are useful for the
implementation of further multi-hazard risk analyses.

The procedures presented here are simple but at the same time based on a careful calibration of geometrical and mechanical properties that stems from scientific results. In this way it was preserved the general reliability of the proposed approach. The simplicity of the proposed approach allows its applicability to the seismic assessment of further structural components in petrochemical plants and its reproducibility for large portfolio of vessels.

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