

**T.R.**  
**GEBZE TECHNICAL UNIVERSITY**  
**GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

**ASSESSMENT OF WATER AND SEDIMENT QUALITY IN  
MUSTAFAKEMALPAŞA STREAM, USING STATISTICAL  
TECHNIQUES AND GEOGRAPHICAL INFORMATION  
SYSTEM ANALYSIS**

**PHILIP ISAAC OMWENE**  
**A THESIS SUBMITTED FOR THE DEGREE OF**  
**MASTER OF SCIENCE**  
**DEPARTMENT OF ENVIRONMENTAL ENGINEERING**

**GEBZE**  
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**THESIS SUPERVISOR  
PROF. DR. MEHMET KOBYA**

**GEBZE  
2018**

**T.C.  
GEBZE TEKNİK ÜNİVERSİTESİ  
FEN BİLİMLERİ ENSTİTÜSÜ**

**MUSTAFAKEMALPAŞA ÇAYI SU VE  
SEDİMENT KALİTESİNİN İSTATİSTİK  
TEKNİKLERİ VE COĞRAFİK BİLGİ  
SİSTEMİ ANALİZLERİ KULLANILARAK  
DEĞERLENDİRİLMESİ**

**PHILIP ISAAC OMWENE  
YÜKSEK LİSANS TEZİ  
ÇEVRE MÜHENDİSLİĞİ ANABİLİM DALI**

**DANIŞMANI  
PROF. DR. MEHMET KOBYA**

**GEBZE  
2018**



GTÜ Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 27/06/.2018 tarih ve 2018/33 sayılı kararıyla oluşturulan jüri tarafından 12/07/2018.tarihinde tez savunma sınavı yapılan Philip Isaac OMWENE'in tez çalışması Çevre Mühendisliği Anabilim Dalında YÜKSEK LİSANS tezi olarak kabul edilmiştir.

JÜRİ

ÜYE

(TEZ DANIŞMANI) : Prof. Dr. Mehmet KOBYA

ÜYE

: Prof. Dr. Taşkın KAVZOĞLU

ÜYE

: Doç. Dr. Orhan Taner CAN

ONAY

Gebze Teknik Üniversitesi Fen Bilimleri Enstitüsü Yönetim Kurulu'nun  
...../...../..... tarih ve ...../..... sayılı kararı.

# SUMMARY

Mustafakemalpaşa stream emerges from confluence of Emet and Orhaneli streams in Gediz district of Kütahya at Çamandar Village and discharges into Lake Uluabat. Emet stream is about 180 km long and originates from the Şahhane mountain whereas Orhaneli stream is about 115km long and originates from Murat mountain. Mining of boron, chromium, coal, silver, iron, copper, manganese and marble cutting operations, in addition to the regions's geology have for long been linked to deteriorating quality of water and sediment in the region. During this study, water and sediment samples were collected in March, July and October 2017 and analysed in situ and in the lab. More hydrological and water quality data was acquired from General Directorate of State Hydraulic Works (DSI). Water quality index model (WQI) was applied to rate the geneneral water quality status and geographical information systems (GIS) was used to aid the visualization of results. Sediments pollution level were assessed using contamination factor (CF), enrichment factor (EF), geo-accumulation index ( $I_{geo}$ ), Probable Effect Concentrations (PEC) and the Threshold Effects Level (TEL) were used as the Sediment quality guidelines to examine the ecological risk. Also, Pearson Correlation Matrix (PCM), Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) were used to identify the main sources of pollutants for the study area. The results showed no significant differences in the WQIs for the three-monitoring periods ( $p < 0.05$ ). Arsenic and boron were the main contaminants in region, while DO (dissolved oxygen) levels were generally lower than the world health organization (WHO) guideline in urban settlement areas. Extreme sediment contamination was revealed by B, Cr, Ni, Zn and As. The As, Cd and Ni levels exceeded their respective PECs of 17 mg/kg, 3.53 mg/kg and 36 mg/kg, respectively. The sources of heavy metals in the sediments were attributed to fly ashes of coal-powered plants, urban waste leachate and weathering of sulfide ore minerals for Pb, Zn and Cu; urban-industrial wastes and mining wastes for Ni. Although Cr, As, Cd and B were ascribed to natural occurrence, their presences in river sediment is accelerated by mining. The deteriorating water quality in the two streams, if not addressed may adversely affect both human health and aquatic life.

**Key words: River pollution, sediment quality, Mustafakemalpaşa catchment.**

# ÖZET

Mustafakemalpaşa çayı, Emet ve Orhaneli derelerinin Kütahya'nın Gediz ilçesinde bulunan Çamandar Köyü'nde birleşmesinden oluşur ve Uluabat Gölü'ne dökülür. Emet deresi yaklaşık 180 km uzunluğundadır ve Şahhane dağından doğmaktadır. Orhaneli deresi ise yaklaşık 115 km uzunluğundadır ve Murat dağından doğmaktadır. Bölgenin jeolojisine ek olarak, bor, krom, kömür, gümüş, demir, bakır, manganez ve mermer madenciliğinin, bölgedeki su ve sediment kalitesinin bozulmasına neden olduğu düşünülmektedir. Bu çalışma kapsamında; Mart, Temmuz ve Ekim 2017'de bölgeden su ve sediment örnekleri toplanmıştır. Ayrıca Devlet Su İşleri Genel Müdürlüğü'nden (DSİ) hidrolojik ve su kalitesi verileri alınmıştır. Çalışmada, genel su kalitesi durumunu değerlendirmek için su kalitesi indeksi modeli (WQI) uygulanmış ve sonuçların görselleştirilmesine yardımcı olmak için coğrafi bilgi sistemleri (GIS) kullanılmıştır. Sediment kirliliği, kirlilik faktörü (KF), zenginleştirme faktörü (EF), jeo-birikim indeksi (Igeo), Muhtemel Etki Konsantrasyonları (PEC) metotları ile değerlendirilmiştir. Eşik Etkileri Seviyesi (TEL) metodu ise ekolojik risklerin incelenmesi amacıyla sediment kalitesi kılavuzu olarak kullanılmıştır. Ayrıca, çalışma alanı için temel kirletici kaynaklarını tespit etmek amacıyla Pearson Korelasyon Matrisi (PCM), Temel Bileşen Analizi (PCA) ve Hiyerarşik Küme Analizi (HCA) teknikleri de kullanılmıştır. Sonuçlar değerlendirildiğinde, üç izleme periyodu için WQI'lerde anlamlı bir farklılık görülmemiştir ( $p < 0.05$ ). Bölgedeki başlıca kirleticiler arsenik ve bor iken, DO (çözünmüş oksijen) seviyeleri genellikle kentsel yerleşim alanlarında Dünya Sağlık Örgütü'nün (WHO) sınır değerlerinden daha düşüktür. Sediment örneklerinde en fazla kirliliğe B, Cr, Ni, Zn ve As elementlerinin sebep olduğu görülmüştür. As, Cd ve Ni konsantrasyon değerleri sırasıyla 17 mg / kg, 3,53 mg/kg ve 36 mg/kg olarak ölçülmüş ve PEC değerlerini aşmıştır. Sedimentlerdeki ağır metal kaynaklarını termik santraller ve katı atık sahaları oluşturmaktadır. Ayrıca Pb, Zn ve Cu için sülfid cevheri minerallerinin ayrışması, Ni için kentsel sanayi atıkları ve madencilik atıkları kaynak olarak gösterilebilir. Cr, As, Cd ve B kirliliği doğal oluşumlara atfedilse de, nehir sedimentindeki varlıkları madencilikle hızlandırılmıştır. İki dereye kötüleşen su kalitesi iyileştirilmediği takdirde hem insan sağlığını hem de su yaşamını olumsuz yönde etkileyebilir.

**Anahtar Kelimeler: Nehir kirliliği, sediment kalitesi, Mustakemalpaşa havzası.**

# ACKNOWLEDGEMENT

I thank the almighty God for guiding me through my education and providing me protection and strength. I would like to thank my academic supervisors Prof. Dr. Mehmet KOBYA, Prof. Dr. Mehmet Salim ÖNCEL, Dr. Meltem ÇELEN and the entire staff of the department of Environmental Engineering, Gebze Technical University who endeavoured their best to guide me where necessary throughout my master's studies, may the Almighty Lord bless them. In addition, I thank Turkiye Scholarships for giving me the opportunity to study in Turkey. I also appreciate the General Directorate of State Hydraulic Works (DSI), for providing me with data about the Mustafakemalpaşa Stream and its tributaries.

With great concern I send my sincere appreciation to my friends İbrahim ILKKAYA, Yasin Abdullah USLU, Mihrican YURTARSLAN, Sanaz MUHAMADZADE, Zubede UKUNDIMANA for all the encouragement, social and moral support they offered to me, while I was far away from my family. I must say I never felt lonely, they made my life so easy while I was in Turkey.

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## **LIST of ABBREVIATIONS and ACRONYMS**

<b><u>Abbreviations</u></b> <b><u>and Acronyms</u></b>	<b><u>Explanations</u></b>
APHA	: American Public Health Association
BOD	: Biochemical Oxygen Demand
BOD <sub>5</sub>	: Five-day biochemical oxygen demand
DSI	: State Directorate of Hydrualic Works
TDS	: Total Dissolved Solids
TDS	: Total Dissolved Solids
PEC	: Probable Effect Concentration
SQI	: Sediment Quality guideline
TEC	: Threshold Effect Concentration
WHO	: World Health Organization
WQI	: Water quality Index

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# **1. INTRODUCTION**

## **1.1. Meaning and Significance of the Research**

Water is a natural resource that is essential for socio-economic activities and ecosystems. Today, over 748 million people still lack access to improved drinking water sources, a global increase in industrial water demand of about 400% is expected by 2050. Unsustainable use of water resources has affected both its quality and availability, hence elevating the demand for freshwater. Global demand for water is majorly influenced by rapid population increase, urbanization and industrialisation. An increase of 55% in global water demand is estimated by 2050, this anticipated increase is mainly ascribed to growing consumptions in sectors of manufacturing, thermal generation of electricity and domestic water. These activities have not only polluted the water resources but also reduced accessibility to safe water, thus compromising the ability of natural ecosystems and to meet the global water demand [MEA, 2005]. Furthermore, the global agricultural food production is anticipated to raise by 60% by the year 2050, and subsequently, water pollution from agricultural sources may worsen with the intensive agriculture.

## **1.2. Purpose and Scope of the Research**

This study was aimed at obtaining a deeper understanding of water and sediment quality in Mustafakemalpaşa catchment through analysis of the surface water and sediment samples collected from the stream and its tributaries (Emet and Orhaneli). Spatial variations in the water quality was analyzed through the WQI model and geographical information systems (GIS) was used to aid results visualization. Possible sources of heavy metal (Pb, As, B, Cd, Mn, Zn, Cr, Mn, Mo, Co, Ni, Cu) in surface sediments were identified using, sediment quality indicators, such as contamination factor (CF), enrichment factor (EF) and geo-accumulation index ( $I_{geo}$ ). Also, Pearson correlation matrix (PCM), principal component analysis (PCA) and hierarchical cluster analysis (HCA) were used to identify the main sources of metals in the sediment samples.

### **1.3. Project Justification**

The study will provide significant and credible scientific basis for stakeholders both in government and private sector to make informed decisions while dealing with issues related to water resources management and water quality in Mustafakemalpaşa catchment in terms of natural and human influence on water quality. In addition, the findings may also assist government in making key policies regarding regulation and monitoring of surface waters in the watershed. I hope that the relevant stakeholders will take this as a warning on the adverse influence of anthropogenic activities in the basin.



## 2. BACKGROUND AND LITERATURE REVIEW

This section introduces to the global occurrence and use of water resources, with emphasis on climatic and geographical features of Turkey and the study area.

### 2.1. Occurrence and Distribution of Water

Water is an important part of the ecological environment, and is an indispensable substance to life. The availability of water determines human settlement and quality of life. The hydrosphere has waters in constant motion, under the influence of gravitational force and solar radiation. The total quantity of water in the hydrosphere is made up of water in liquid form, solidified water, or in gaseous forms in the earth's surface and atmosphere. Water distribution and occurrence between the atmosphere, oceans and land follows the global water cycle (Figure 2.1). Water vapour from surface water sources, vegetation and soil is transported by air currents from one place to another and condenses with decrease in temperature. The condensed vapour returns into the earth's surface in form of precipitation. The hydrosphere consists of approximately 1,386 million cubic kilometres of water (km<sup>3</sup>). But, only 2.5% of this is fresh water, saline water makes up the balance (97.5%) [Shiklomanov, 2000]. The largest portion of the fresh water (68.7%) exists as ice and snow cover in Antarctic, the Arctic, and mountainous regions (Figure 2.2) [Shiklomanov and Rodda, 2003].

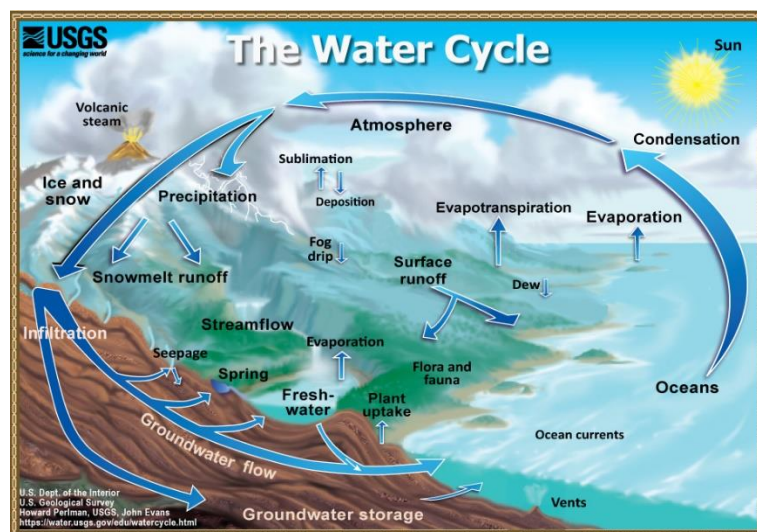


Figure 2.1: The Global Water Cycle.

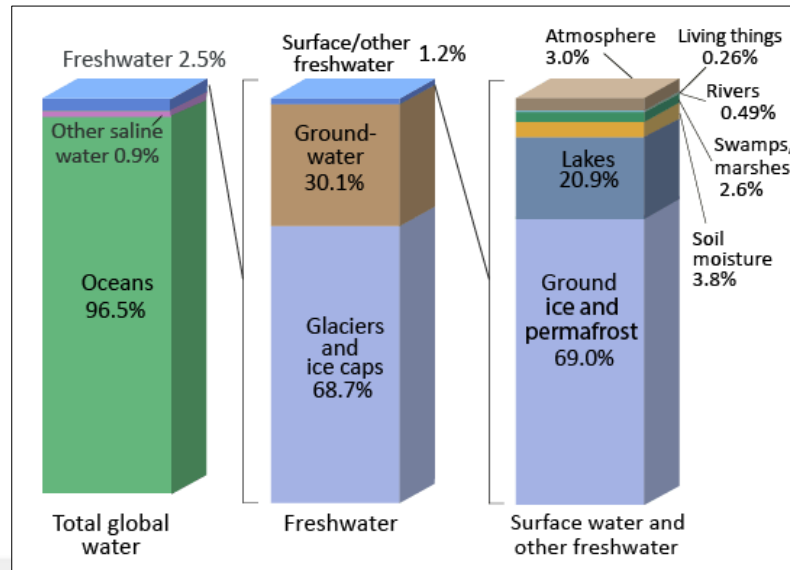


Figure 2.2: Distribution of Earth's Water.

Lakes and rivers account for only a small amount of freshwater resources. This therefore calls for sustainable use of our water resources to encounter the ever growing water demands. As per the United Nations Environment Program report [WWAP, 2015], over half of the world's population shall live in water shortage in the next half-century if nothing is done to reverse the deteriorating quality of water resources, this calls for intervention of stakeholders at both national and international platforms. Classification of countries in terms of their water wealth is as follows: poor (< 1,000 m<sup>3</sup> annual water volume per capita), insufficient or water stress (< 2,000 m<sup>3</sup> annual water volume per capita), and rich (> 8,000- 10,000 m<sup>3</sup> annual water volume per capita). Currently, the exploitable quantity of water in Turkey is approximately 1,500 m<sup>3</sup> per capita/per year, a decrease from around 4000 m<sup>3</sup> in the 1960's. This is attributed to rapid population growth, making it a water stressed country [Dogdu and Sagnak, 2008]. According to the State Institute of Statistics, Turkey's population is estimated to be 100 million by 2030. This will subsequently reduce the annual available water per capita to 1,000 m<sup>3</sup> by 2030 [Arslan-Alaton et al., 2011].

## 2.2. Global Water Use

Global use of freshwater according to sectors (industrial, domestic, and agricultural) is given in Figure 2.3. Rapid population growth, industrialization and urbanization have resulted into excessive consumption of the water resources. The wastes generated from human activities are always discharged into the water resources causing major pollution. Currently, the largest freshwater consumer is the agricultural sector: In the United States, about 49% of the total freshwater use is for agriculture, of which 80% of this volume is used for irrigation. Whereas, in Africa and Asia, agriculture accounts for about 85-90% of all the freshwater used [Shiklomanov, 2000].

Integrated water resources management is therefore required to ensure equitable water use amongst all sectors. According to 2015 data by the General Directorate of State Hydraulic Works, agricultural irrigation accounts for about 73.2% (32.21 billion m<sup>3</sup>) of Turkey's total water supply, making it the largest consumer. The remaining 15.5% (6.82 billion m<sup>3</sup>) and 11.3% (4.84 billion m<sup>3</sup>) are for domestic and industrial uses, respectively. Irrigatable agricultural land in Turkey is about 25.8 million hectare, but currently only 6.09 million hectares are being irrigated.

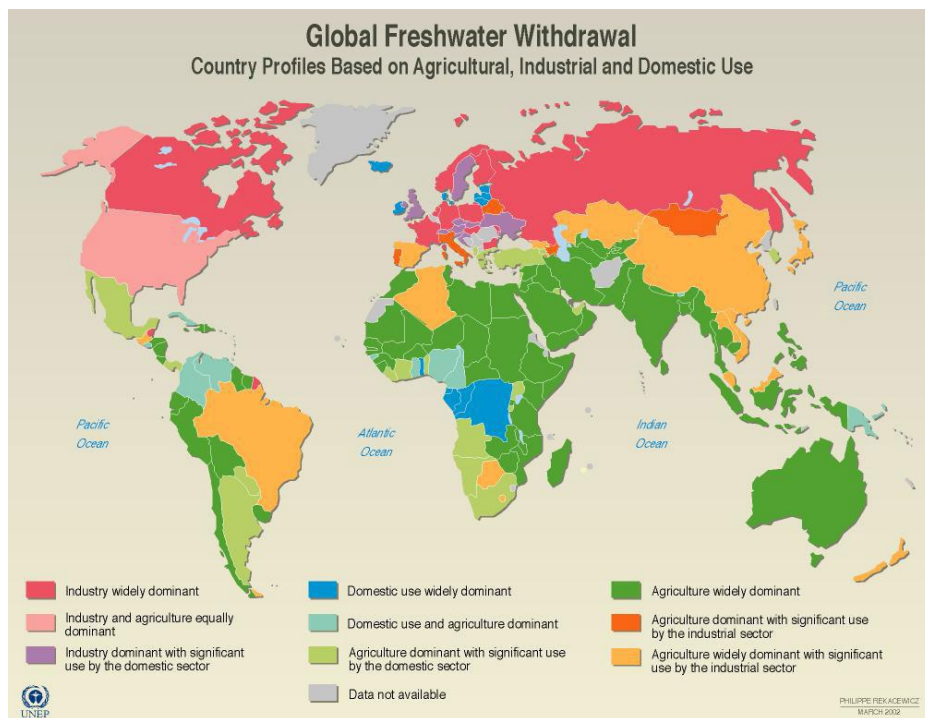


Figure 2.3: Global freshwater use by sectors.

According to the water usage statistics of 2014, the manufacturing and industrial sector in Turkey abstracted about 2.4 billion m<sup>3</sup> of water, and 77.4% of this was used for cooling purposes. The sources of abstracted water was as follows: sea accounted for 70.7%, well accounted 14.5%, organized industrial zone water supply network accounted for 3.8%, dams accounted for 3.5%, river accounted for 2.7%, municipal water supply network accounted 1.5%, spring accounted 1.3%, and other water resources accounted 2%. The established wastewater discharge from Manufacturing industry was 1.9 billion m<sup>3</sup>. 80.7% of the generated wastewater was discharged to sea, river discharge accounted for 7.3% of the generated wastewater, organized industrial zone sewerage accounted for 6.3%, municipal sewerage accounted for 3.1% and the remaining 2.6% was discharged to other receiving bodies. [Web 1, 2017].

### **2.3. The Water Resources of Turkey**

Turkey occupies 26°- 45° E longitudes and 36°-42° N latitudes, with a unique geographic position, lying both in Asia and Europe. There are about 120 natural lakes in Turkey. Lake Van (3,712 km<sup>2</sup>) with an altitude of 1,646 m above sea level and depth of over 100 m is the Turkey's largest and deepest Lake. Lake Tuz (1,500 km<sup>2</sup>) is considered the second largest lake, with altitude of 925 m above sea level. Other major lakes in Turkey include; Egirdir, Beysehir, Burdur, Sapanca, Acigol, Ulubat, İznik and Kus. Turkey has 555 large dam reservoirs, the major ones include; Ataturk (817 km<sup>2</sup>), Keban (675 km<sup>2</sup>), Karakaya (268 km<sup>2</sup>), Hirfanli (263 km<sup>2</sup>), Altinkaya (118 km<sup>2</sup>) and Kurtbogazi (6 km<sup>2</sup>).

The population of Turkey is about 80 million with density of population 92 persons/km, and growth rate of 1.3 percent per annum. Being largely situated in the Mediterranean, Turkey experiences significant differences in climatic conditions. The coastal regions are milder, whereas inland Anatolian plateau is characterised by very hot summers and cold winters [Web 3, 2017]. Most of the precipitation in Turkey is received during winter with mean temperature below 5°C. However, rainy and cold winters, hot and dry summers are experienced around the Mediterranean and Aegean seas. Geographical distribution of mean annual temperature of Turkey is shown in Figure 2.4 [Şensoy et al., 2017].

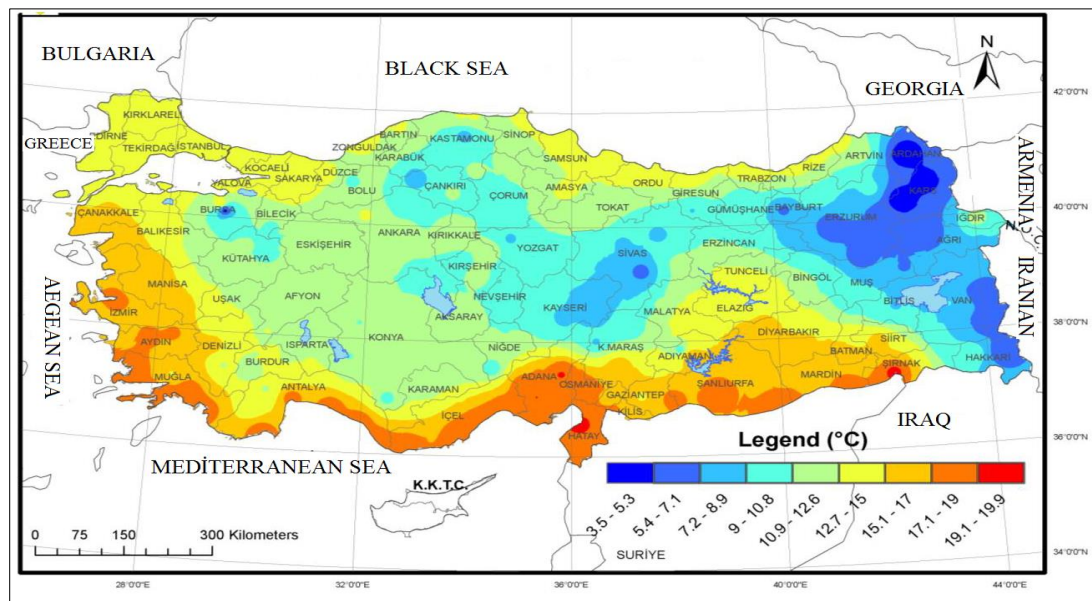


Figure 2.4: Geographical Distribution of Mean Annual Temperature in Turkey.

The coastal areas of Turkey receive about 800–1,000 mm of rainfall [DSI, 2009], with variation in annual precipitation of about 580–1,300 mm. Precipitation in the eastern Black Sea region is about 2,200 mm, and occurs throughout the year. Figure 2.5 illustrates the general distribution of annual precipitation in Turkey. The Aegean, Marmara and East Anatolia plateau receive precipitation of about 500–1,000 mm/year. Annual precipitation of about 350–500 mm is received in most parts of South-Eastern and Central Anatolia. The variation in annual precipitation is mainly influenced by differences in elevation and topography. Due to its location in Northwestern Turkey, the Mustafakemalpaşa catchment has a typical transitional climate of that between the Mediterranean and the Black Sea climates. With the highest precipitation received in winter and the least precipitation received in summer [Web 3, 2017].

According to DSI (2009), evaporation from soils and surface water bodies in Turkey is 274 billion m<sup>3</sup>/year, groundwater leakage is about 69 billion m<sup>3</sup>/year, whereas groundwater contribution to surface water is about 28 billion m<sup>3</sup>/year, and inflows from neighboring countries is about 7 billion m<sup>3</sup>/year. It can be assumed that the annual ground and surface water potentials for Turkey are 44 billion m<sup>3</sup> and 112 billion m<sup>3</sup>, respectively [DSI, 2009], corresponding to a mean annual amount of 501 billion m<sup>3</sup> (Figure 2.5). About 70% of the precipitation is received from October to April, and summers have very little effective rainfall. The Black Sea region receives the highest

mean annual precipitation (1,120 mm). However, the other coastal areas also exceed 800 mm/year. Mean annual precipitation of < 500 mm/year is received in the Thrace, eastern Anatolia and the remaining 70% of the country [Cakmak et al., 2004].



Figure 2.5: Geographical Distribution of areal Annual Precipitation in Turkey.

The focus area of this study, Mustafakemalpaşa catchment has annual precipitation in the range of 40 mm to 65 mm with the maximum precipitation recorded in winters and the lowest precipitation is recorded in summers. The summers are hot and dry while winter are cold and rainy. Average annual temperatures in the basin is 13.2°C (Turkish metrological institute, 2017). Turkey’s water security is high compared to countries in European, and may increase as a result of rapid population increase and the drying due to rising temperatures [Vörösmarty et al. 2010; MET Office 2011]. Projections have estimated changes in runoff between -52% to -61% [Fujihara et al., 2008], and a fall in surface waters in the Turkish watersheds of 20%, 35% and 50% for years 2030, 2050 and 2100, respectively have been reported [Özkul, 2009]. Turkey’s annual surface runoff is projected to decrease by 26 - 57% by the end of the current century. Consequently, other countries in the same basin will feel the stress, since most of the headwaters are in Turkey [Web 2, 2017]. Turkey’s annual water supply from groundwater reserve is 41 billion m<sup>3</sup>, with exploitable groundwater capacity of 12 billion m<sup>3</sup>. At present, 8 billion m<sup>3</sup> is exploited on annual basis, of which

irrigation consumes 55% while industrial and domestic activities take 45%. Hydrological data from 1935 to 2008 according to the State Hydraulic Works of Turkey, indicated average surface run-off as 186 billion m<sup>3</sup>/year with 7 billion m<sup>3</sup>/year as inflow from neighboring countries. Furthermore, groundwater leakage is estimated as 41 billion m<sup>3</sup>/year. The exploitable amount of surface run-off and groundwater, due to technical and economic reasons are respectively, 98 and 14 billion m<sup>3</sup>/year [Duzen and Ozler, 2013],[Ünal et al., 2009].

## 2.4. General Characterization of Turkish Rivers

The 25 hydrological basins of Turkey according to State Hydraulic Works are shown in Figure 2.6 [DSI, 2009]. The rivers, dams and lakes in these basins are given in Figure 2.7. The major rivers in Turkey include; Kizilirmak, Yesilirmak and Sakarya, which all discharge into the Black Sea [Duzen and Ozler, 2013], [Unal et al., 2009].



Figure 2.6: Hydrological Basins in Turkey.

Kizilirmak, Yesilirmak, Sakarya, Coruh and Filyos discharge into the Black Sea. Kizilirmak is Turkey's longest river with a length of 1,355 km and discharges into the Black Sea with annual average discharge rate of 184 m<sup>3</sup>/s [Öztürk and Sesli, 2015]. Yesilirmak river with mean annual flow rate of 121 m<sup>3</sup>/s is approximately 519 km long, and basin area of 38,730 km<sup>2</sup> (5% of Turkey's surface area), with Kelkit (320 km) and Cekerek ( 256 km) as its main tributaries.



Figure 2.7: Major Rivers, Lakes and Dams in Turkey.

Sakarya river with length of 824 km, has mean annual flow of 193 m<sup>3</sup>/s. The River basin area is 58,160 km<sup>2</sup>, with annual average water potential of 6,827.9 hm<sup>3</sup>, respectively [Öztürk, 1996]. Sakarya river originates from plateau located northeast of Afyon province, passes through Polatli town and Adapazarı (Sakarya) province, as it confluences with tributaries (Goksu, Porsuk, Kirmir, Goynuk, Aladag, Cark streams and Mudurnu) before finally discharging into the Black Sea.

Coruh River with length of 431 km (of which 21 km area in Georgia), has a catchment area and annual average flow rate of 19,872 km<sup>2</sup> and 278 m<sup>3</sup>/s, respectively. The major dams built on Coruh river are; Borcka, Deriner and Muratli. Filyos river with a length of 228 km and basin area of 13,156 km<sup>2</sup>, is located in the Koroglu mountains of Cankiri, west of the Black sea. The main tributaries of Filyos River are Devrek and Yenice streams. The total discharge of the river is 3213,910 hm<sup>3</sup> per year [Demirci, 2008].

On the otherhand, rivers discharging into Aegean Sea are Buyuk Menderes, Kucuk Menderes, Gediz and Meric. Buyuk Menderes River is about 548 km long, and is the largest river in the Aegean region with a catchment area of 24,976 km<sup>2</sup> [Akbulut et al., 2009]. Gediz river is 401 km long, with basin area and annual average flow rate of 3502 km<sup>2</sup> and 11.45 m<sup>3</sup>/s, respectively. It's headwaters originate from Murat and Saphane mountains in western Anatolia, then moves westwards merging with tributaries; Kunduzlu, Deliinis, Selendi, Nilüfer and Demrek, finally discharging into

the Aegean Sea. Kura and Aras rivers discharge into Caspian Sea, whereas the Tigris and Euphrates rivers discharge into Gulf of Basra.

The rivers discharging into Mediterranean Sea are Seyhan, Ceyhan, Tarsus, Dalaman and Asi. Seyhan with 850 km length originates from central Taurus mountain range south of Sivas and passes through the province of Adana [Akbulut et al., 2009]. The rivers discharging into the Marmara sea are the Mustafakemalpaşa stream (including Emet and Orhaneli streams as its major tributaries), Gonen, Susurluk/Simav stream, Biga stream, and Susurluk stream. The location of Mustafakemalpaşa catchment is shown in Figure 2.8.

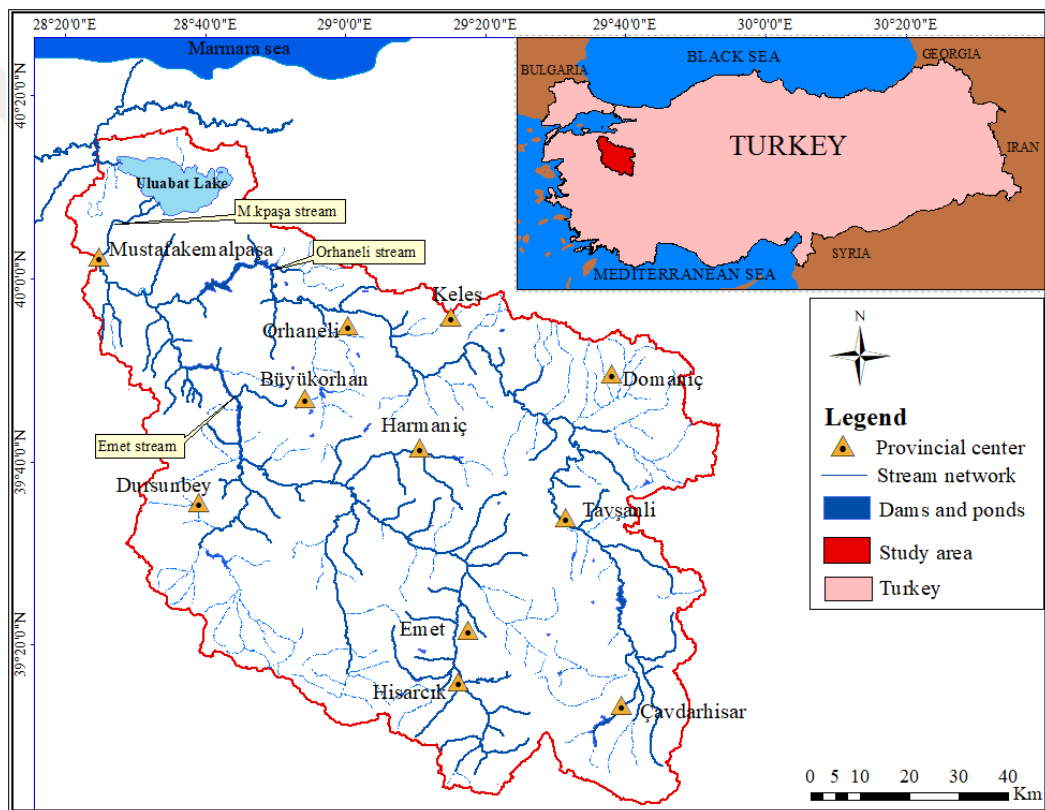


Figure 2.8: Position of Mustafakemalpaşa watershed in Turkey.

## 2.5. Streams in Mustafakemalpaşa Catchment

Water pollutants sources are classified as non-point and point sources. Point pollution sources are discrete sources such as drainage pipe, stack among others, while the non-point pollution sources are diffuse sources such as atmospheric deposition and runoff [EPA 2009]. Water of clean quality is of paramount importance

for human wellbeing and aquatic ecosystems. Mustafakemalpaşa catchment encompasses many large and small streams which finally discharge into Uluabat lake. The catchment is within the borders of Bursa, Kütahya and Balıkesir provinces. Orhaneli and Emet streams are the major tributaries of Mustafakemalpaşa stream.

Orhaneli stream with a total length of 276 km, originates from Murat Mountain near Kütahya-Gediz district, and then flows northwards, merging with Emet stream near Camandar village, at the edge of Kestelek open pit boron mine. Orhaneli stream passes through Tavşanlı and Tunçbilek districts where thermal power plants, lignite mining and chrome mines exist, and takes up a good deal of pollutants. In 2008, Cınarcık Dam, with an annual capacity of 145 million m<sup>3</sup> was constructed in this stream to provide Energy, Irrigation and Drinking Water supply.

Emet stream with a total length of 180 km and average flow rate of 130 m<sup>3</sup>/s, originates from Saphane Mountain near Saruhanlar and Asik Pasa villages, it flows northern wards through Hamamkoy-Emet plain, into Mustafakemalpaşa valley and then merges with Orhaneli stream near Camandar village. Major pollutants in Emet stream originate from domestic wastewater discharges, mining operations, industrial and agricultural wastewater. Mineral deposits such as boron (ETI Mining Hisarcik-Emet colemanite operations), coal operations, marble operations, chromium operations, and sand and gravel operations in Emet stream basin are other pollution sources.

Mustafakemalpaşa stream with annual average flow of 64 m<sup>3</sup>/s is one of the most prominent streams of Susurluk River Basin. The stream is formed after confluence of Emet and Orhaneli streams and discharges into Uluabat Lake, 45 km downstream of confluence point. Water from Uluabat lake discharges into Marmara sea through Uluabat stream, whose flow is regulated by DSI. The stream is mainly used for irrigation, industrial water supply, receiving domestic wastes and fishing. In addition to the geologic structure of Mustafakemalpaşa basin, mining facilities, intensive agricultural activities and solid waste dumping sites located upstream of the basin are the main contamination sources in the region [Bebek, 2001]. The suspended sediment load of the Mustafakemalpaşa stream is about 1258143 ton/year for the past 30 years and the mean linear sediment accumulation rate is ~1.6 cm/year [Kazancı et al., 2004],[Kazancı et al., 2010]. The drainage basin of Uluabat Lake is about 10,555km<sup>2</sup>, and 9856 km<sup>2</sup> of this is from Mustafakemalpaşa stream and its tributaries. The average annual flow of Mustafakemalpaşa stream is 2 billion m<sup>3</sup>/year. Domestic wastewaters

and landfill leachate from Çavdarhisar, Orencik, Tavşanlı, Tunçbilek, Orhaneli and Keles settlement areas are transported into the streams of the basin.

Uluabat Lake, formed as a result of tectonic forces has a surface area of ~138 km<sup>2</sup> and an average depth of 6m with eutrophic freshwaters. The lake is located 20 km south of Marmara sea in the province of Bursa, at the eastern end of the Manyas-Karacabey depression [Kazanci et al., 2004] between 42° 12' North latitude and 28° 40' East longitude. The Lake is rich in aquatic plants, in addition to fish and birds [İleri et al., 2014]. At the exit of Uluabat Lake, Simav, Kocacay and Nilufer streams merge near the town of Karacabey and form Kocasu stream just before discharging into the Sea of Marmara. Nutrient enrichment in the lake has caused intensive growth of algal blooms. Lake Uluabat falls into water class III (polluted water) and water class IV (very polluted water) according to Turkish Water Pollution Control Act (1988) [Ince and Yenigun, 1995].

The arsenic contamination in surface waters is also increased by geothermal water (thermal springs). The thermal springs in Emet stream basin are shown in Table 2.1. The release of arsenic (As) from geothermal systems into surface waters and groundwaters and the use of these waters as drinking and irrigation water resources and may also affect aquatic ecosystems. Furthermore, spring and groundwaters of the villages (Camandar, Yenibalçık, Çaltılıbük, Kestelek and Devecikonağı i.e.) in the vicinity of mine deposits contain high arsenic (>10 µg/L) and boron (>1 mg/L) concentrations. According to our field results of 2016, average arsenic and boron concentrations in spring waters of Kestelek, Camandar, Yenibalçık and Devecikonağı villages were 3.63, 0.16, 33.60 and 0.62 mg B/L and 66.3, 12.2, 14.1 and 10.3µgAs/L, respectively.

Table 2.1: Important Geothermal Springs in Emet Basin.

Location	Name of thermal spring	Flow (L/s)	T (°C)
Kutahya-Simav	Eynal thermal spring	2.1-510	25-96
Kutahya-Simav	Citgol thermal spring	32	77-83
Kutahya-Simav	Nasa thermal spring	2	43-64
Kutahya-Tavşanlı	Yoncali thermal spring	6-118	32-43
Kutahya-Tavsanlı	Gobel thermal spring	60	34.3
Kutahya-Gediz	Gediz spring	23	78
Kutahya-Gediz	Murat mountain springs	7.5	38
Kutahya-Gediz	Abide thermal spring	11-152	65-74
Kutahya-Emet	Emet thermal spring	24	41-47
Kutahya-Emet	Dereli thermal spring	75	40-42
Kutahya-Emet	Hamamkoy thermal spring	-	51
Kutahya-Emet	Ilica village-Harle thermal spring	-	43
Kutahya-Emet	Yenicekoy thermal spring	1	41
Kutahya-Hisarcik	Esire thermal spring	-	51
Kutahya-Hisarcik	Yukariyoncağac thermal spring	-	29
Kutahya-Hisarcik	Samrik thermal spring		43
Kutahya-Saphane	Saphane thermal spring	88	25-90
Bursa- Mustafakemalpaşa	Tumbuldek thermal spring	50	49

## 2.6. Effects of Borate Mines and Deposits in the Area.

Over 70% of the world borate reserves are in the Neogene basins in western Turkey, and the main borate districts are Bigadic, Sultancayiri, Kestelek, Kirka and Emet [Helvacı, 2005]. The boron is mostly open pit mined and the mine areas drain into Mustafakemalpaşa Stream, Simav Stream, Porsuk Stream and other smaller tributaries. Boron and arsenic concentrations in surface and ground waters downstream of Mustafakemalpaşa plain are due to anthropogenic effects. Leachates from borate mine enrichment operations are collected tailing ponds built near streams, this is also a risk to groundwater pollution in the region. Since boron, arsenic, and other minerals

in the borate mining wastes may desolve in surface waters and drain into the streams. The confluence point of Emet and Orhaneli streams is shown in Figure 2.9, and Figure 2.10 shows the proximity of Emet stream to Hisarcik boron mine operations.



Figure 2.9: Confluence Point of Orhaneli and Emet Stream in the Camandar Village.

The previous studies have also revealed arsenic and boron concentrations in water resources around boron deposit areas such as Kütahya-Emet, Hisarcık, Eskişehir-Kırka and Balıkesir-Bigadiç as generally higher [Yüce and Yasin, 2012], [Gemici et al., 2008; Dogan and Dogan, 2007; Çolak et al., 2003].

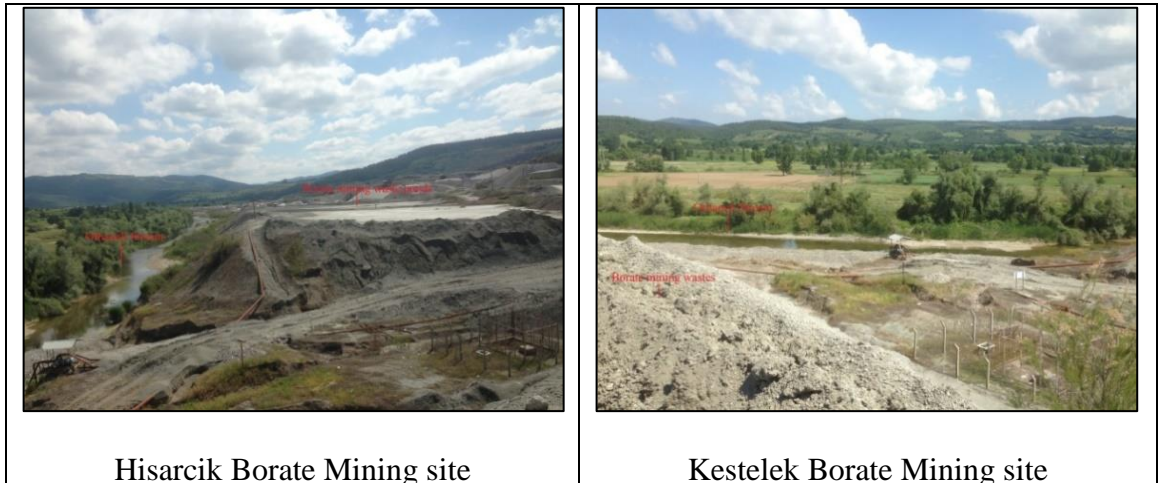


Figure 2. 10: Photographs of some of Hisarcik and Kestelek Borate Mining sites.

Devecikonağı dam with a volume of 6.2 hm<sup>3</sup>, reservoir area of 660,000 km<sup>2</sup> and water level of 95 m is located on Emet stream about 5 km south of the Devecikonağı district. The dam has an installed hydroelectric power plant (established power of

28.03 MW and production capacity of about 60.28 GWh-year). Some of the waste ponds from mining areas are built very close to the streams as seen in Figure 2.11. The wastes from this coal mine drain to the dam, posing a potential pollution. ETI Mines at Emet and Hisarcik Boron Works produce concentrate colemanite and boric acid. Colemanite contains arsenic minerals (realgar and orpiment), which are responsible for arsenic contamination in surface and groundwaters in the region [Dogan and Dogan, 2007], [Çolak et al., 2003]. Groundwaters near arsenical boron deposits were reported to contain up to 600 mg/L As and 1500 mg/L B [Helvacı, 1984]. Studies on water samples near borax open pit operations in Kutahya-Emet-Hisarcik revealed average arsenic and boron levels in water samples from Emet Stream as  $86.5 \pm 125.6$  mg/L and  $0.726 \pm 0.97$  mg/L, respectively [Ünlü et al., 2011]. In comparison with the global average boron (10 µg/L) and arsenic (2 µg/L) values, the As and B concentrations in Emet Stream are 8000 times and 350 times, respectively more polluted [Rose et al., 1979].



Figure 2.11: Some of Photographs of pollution Sources along Emet Stream.

## 2.7. Geological Setting and Effects of Geothermal Resources

The Hisarcik-Emet Neogene basin is elongated towards north-south direction. Neogene rocks composed of terrestrial sediments and volcanic rock outcrops are widespread in the area. The Neogene lacustrine sediments overlay the Paleozoic metamorphic rocks that are composed of various schists and marble intercalations. Neogene lacustrine sediments begin with a basal conglomerate overlaid by alternating laminated limestone, marl, lignite, tuff and red unit (sandstone, claystone, marl, limestone and conglomerate). The upper limestone rocks outcrop around Hisarcik borate and overlay the borate bearing unit of clay forming unconfined aquifers [Çolak et al., 2003], [Helvacı, 1984]. Groundwaters in the lower aquifer are in contact with the borate bearing clay zone and also form contact with arsenic bearing springs. The lower limestone consists of thin layers of marl and tuff lenses overlaid by borate-bearing unit of clay with alternating tuffites and abundant realgar, and orpiment in some horizons [Helvacı, 1984]. Thick-bedded limestone shows increased alternations with calcareous clays towards the borate zone. The major borate mineral in Hisarcik open pit mine is colemanite, the other minor borate minerals are hydroboracite, ulexite, meyerhofferite, teruggite, veatchite-A, cannite and tunelite [Helvacı and Firman, 1976]. Dogan and Dogan [2007] indicated that As-minerals such as realgar and orpiment may be entrapped in evaporate minerals in the Emet-Hisarcik borate basin. Realgar crystals are associated with colemanite nodule, in the Hisarcik open pit mine Realgar preserves its original red color in the clay layers. Orpiment has a yellowish color (Figure 2.12). Orpiment and realgar are rarely observed in cavities of the colemanite nodules. Arsenic content of the second quality colemanite upper zone is between 0.03 and 4%. Whereas the As content ranges from 500-600 mg/kg in the upper limestone [Çolak et al., 2003].



Figure 2.12: Photographs of some arsenic minerals (Realgar, Orpiment and Colemanite) in Emet-Hisarcik Open Pit Boron Mines.

## 2.8. Effect of Other Mining Operations in the Catchment

The catchments of Emet and Orhaneli streams are famous for intensive mining of boron, chromium, lignite, iron, copper and silver among others. The various mines are discussed below.

- Coal and lignite deposits and operations

Some of the existing Coal and lignite deposits in Mustafakemalpaşa catchment operate very close to the Emet, Orhaneli and Mustafakemalpaşa streams. Pollution from thermal power plants wastes (slags, fly ash, particles and fired gases) in the region also deteriorates the surface waters of the regions. Tunçbilek thermal power plant (365 MW, no desulphurization units, production capacity of 2373 GWh/year, used lignite calorific value of 2600 kcal/kg; moisture, ash and sulphur contents of lignite of 23%, 42% and 2%, respectively) is also another pollution source for Orhaneli stream. The composition in the fly ash samples was 56.323% SiO<sub>2</sub>, 22.251% Al<sub>2</sub>O<sub>3</sub>, 9.251% Fe<sub>2</sub>O<sub>3</sub>, 5.382% MgO, 2.047% CaO, 1.738% K<sub>2</sub>O, 0.871% SO<sub>3</sub>, 0.857% TiO<sub>2</sub>, 0.132% Na<sub>2</sub>O, 0.19% NiO, 0.136% BaO, 0.365% P<sub>2</sub>O<sub>5</sub>, 0.135% Cr<sub>2</sub>O<sub>3</sub>, 0.191% MnO<sub>2</sub>, 0.013% CoO, 0.015% CuO, 0.023 % ZnO, 0.023 As<sub>2</sub>O<sub>3</sub>, 0.043% SrO, and 0.008% PbO [Turkmenoğlu, 2010]. The amount of Pb, Cd, Cr, Cu, Ni, Zn, Co, and Mn in fly ash samples was obtained as 16.4, 1.95, 296.7, 34.8, 515, 262.2, 46.8, and 690.6 mg/kg, respectively [Turkmenoğlu, 2010]. The Semitone Coal-Fired Power Plant in Kutahya Province (capacity of 600 MW, date of first operation of 1973, no desulphurization units, production capacity of 3900 GWh/year, electrical production capacity of 3.38 GWh/year, calorific value of used lignite of 1500 kcal/kg; moisture, ash and sulphur contents of lignite are 34%, 40% and 2%). Studies by Turkmenoğlu [2010] on this Power Plant indicated that the amount of Pb, Cd, Cr, Cu, Ni, Zn, Co, and Mn in fly ash samples as 49.8, 2.01, 417.5, 99.5, 1292.3, 524.9, 89.5, and 546.7 mg/kg, respectively. The levels of Minor elements in fly ash of Semitone Coal-Fired Power Plant were 29200, 41.4, 0.18, 195.1, 71.29, 52290, 0.141, 1173.1, 17.41 and 62.5 µg/g for Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, and Zn, respectively [Gur, 2006].

Orhaneli Coal-Fired Power Plant in Bursa Province (installation capacity: 210 MW, production capacity of 1365 GWh/year, date of first operation of 1992, electrical production capacity of ~1.003 GWh/year, calorific value of used lignite of 2560 kcal/kg; moisture, ash and sulphur contents of lignite are 34%, 23% and 1.9%). Minor

elements as Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, and Zn in fly ash of the Orhaneli Coal-Fired Power Plant were 48400, 52.3, 0.27, 70.4, 35.1, 36980, 0.417, 181.6, 19.14, and 61.6  $\mu\text{g/g}$  [Gur, 2006].

- Chromite deposits and operations

Turkey's chromite deposits exist as remnants of the Neo-tethyan oceanic crust, with various mineralization sizes in tons. Most of mineralizations show alpine-type structures and textures. Ferrichromite and aluminum chromite ( $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ ) are the major chromite categories of Turkey. Figure 2.13 shows Chromium Mining Operating Near Emet Stream. About 40 million tons of chromite ore have been produced from Harmancik-chromines since its discovery in 1848. The current chromite reserves in Turkey are estimated to be around 30 million tons [Ucurum et al., 2006]. The 2016 reports from the department of environmental affair in the three provinces (Bursa, Kutahya and Balikesir) are summarized in Table 2.2.

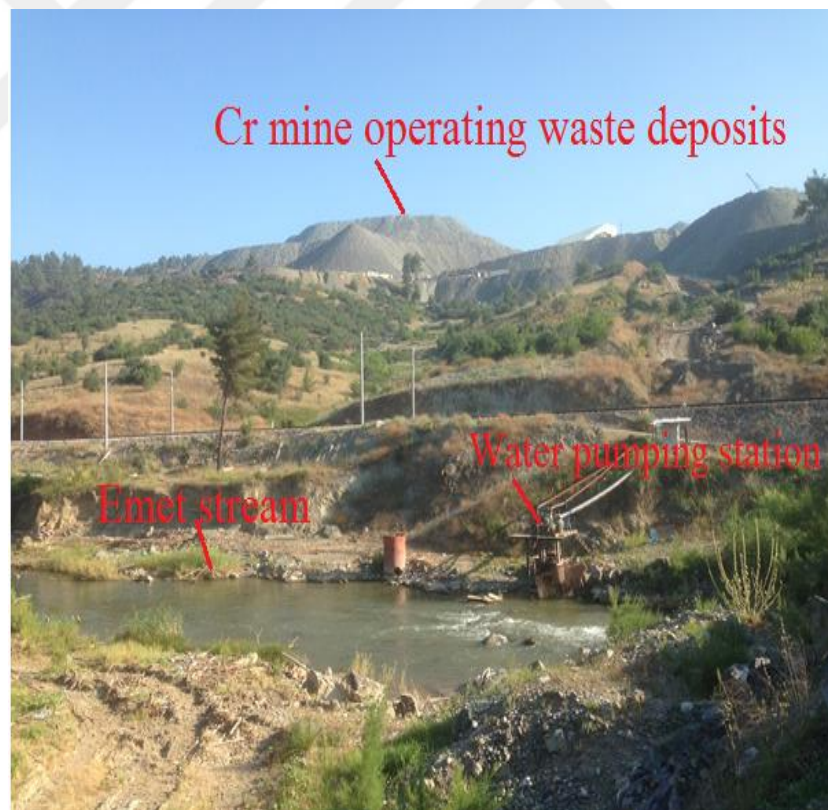


Figure 2. 13: Photograph from Chromium Mining Operating Near Emet Stream.

Table 2.2: Industrial discharge points in Mustafakemalpaşa Catchment.

Industry Name	Q (m <sup>3</sup> /day)	Discharge point		Discharge stream
		X (E)	Y (N)	
Seref Beyhan ve Ort.Der.	61	28°10'13"E	39°54'14"N	Simav
Bigadic Belediye Mezhabasi	65	28°06'04"E	39°24'56"N	Simav
Bigadic Kose Et Gida Besicilik	75	28°08'37"E	39°41'31"N	-
Akyuz Sut Urunleri Gida San	50	39,19043	29,29123	Emet
İc İctas Zafer Uluslararası Havalimani Yatırım A.S.	10	4333972	252041	Koca Cay
Emet Bor (Hisarcık)	50	694953,159	4344919	Koca Cay
Derekoy Sut Urn. Petrol Gida Hayv. San. Tic. Ltd. Sti	50	39,19266	29,29072	Emet
Tuncbilek Coal power Plant	7740	29.27 E	39.37 N	Adranos
Emet Boron Opertaions Borik (Acid production)	60	39°20'56" 35	29°17'13"	Kinak
Emet Boron Opertaions	50	695916	4360134	Gelenbek
<sup>1</sup> Source: Reports from provincial environmental departments, 2016				

## 2.9. Population of Mustafakemalpaşa Catchment Area

Mustafakemalpaşa catchment area occupies 15 districts in the three provinces of Balıkesir, Kutahya and Bursa, the total population in the catchment area is about 288,852 according to data from Turkish Statistic Institute [July, 2017]. The population in Mustafakemalpaşa catchment area is summarized in Table 2.3.

Table 2.3: Population in Mustafakemalpaşa area according to provincial location.

Province	District	Population
Balıkesir	Disobey	37435
Bursa	Büyükorhan	10421
	Keles	12452
	Mustafakemalpaşa	99753
	Orhaneli	19656
Kotahi	Çavdarhisar	2325
	Domaniç/Cukurca	2115
	Domaniç	4619
	Emet	11290
	Hisarcik/Hisarcik	5223
	Tavşanlı/Balikoy	2112
	Tavşanlı/Kuru cay	1998
	Tavşanlı/Tavşanlı	71054
	Tavşanlı/Telerik	2772
	Tavşanlı/Tunçbilek	5627
	Total	

## 2.10. Land Cover in Mustafakemalpaşa Catchment

Land use maps based on the CORINE Land Classification System for this study area area shown in Figure 2.14, the land use maps were obtained from the Ministry of Environment and Forestry-Turkey. The Land use in Mustafakemalpaşa catchment can be grouped into six major categories; Artificial surfaces (including urban,

transportation and commercial facilities), water bodies, wetlands, mining sites, forests (natural vegetation), agricultural lands.

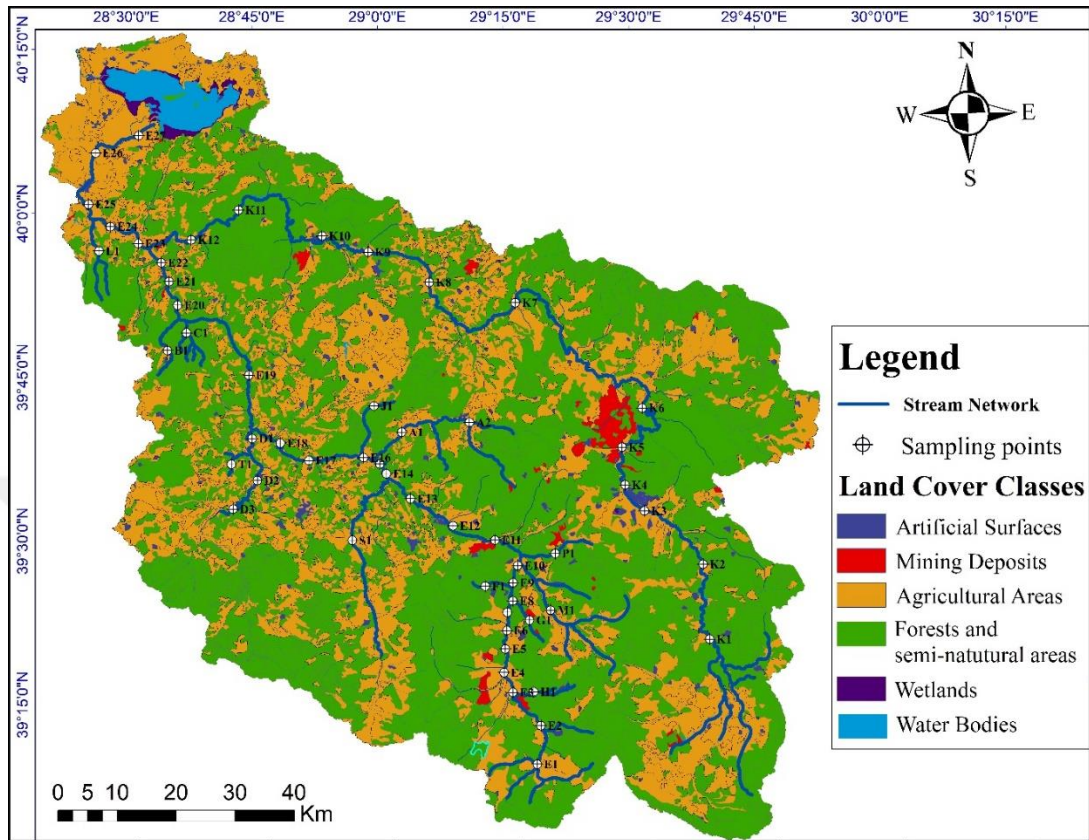


Figure 2.14: Land Cover map of Mustafakemalpaşa catchment.

Forests and semi-natural areas cover the largest part of the basin. Despite the fact that a large part of the catchment area is hilly and mountainous, climate in the basin still favours agricultural productivity. Consequently, agricultural areas account for the second largest land use in the catchment, followed by mining deposits.

## 2.11. Classification of Inland Water Quality in Turkey

The Turkish Water Pollution Control Act (1988) classifies inland waters into four categories, according to the level of pollution (Table 2.4). The act entails all aspects of pollution prevention in water resources including surface and groundwater quality, industrial and domestic wastewater and discharges regulations, among others. Inland waters are classified as:

- Class i): high quality waters

- Class ii): slightly contaminated waters
- Class iii): contaminated waters
- Class iv): severely polluted waters.

The Class i) waters can be disinfected and used for drinking, recreational, and for farm animals. Class ii) waters can be used for: drinking purposes (after advanced treatment), recreational purposes, fish farming and irrigation. Class iii) waters can be used for industrial purposes (except food and textile industries). Class v) waters cannot be used for any purpose without prior treatment [Ince and Yenigun, 1995].

Table 2.4: Inland Water quality classification for Turkey.

Water quality variables	Water quality classes			
	i) High quality	ii) Moderate quality	iii) Polluted	iv) Highly polluted
<i>Physical and inorganic-chemical parameters:</i>				
Temperature (°C)	25	25	30	>30
pH	6.5-8.5	6.5-8.5	6.0-9.0	6.0-9.0
Dissolved oxygen (mg O <sub>2</sub> /L) <sup>1</sup>	8	6	3	>3
Oxygen saturation (%) <sup>1</sup>	90	70	40	>40
Chloride ion (mg/L)	25	200	400 <sup>2</sup>	>400
Sulfate ion (mg/L)	200	200	400	>400
Ammonia-nitrogen (mg NH <sub>4</sub> -N/L)	0.1 <sup>3</sup>	1 <sup>3</sup>	2 <sup>3</sup>	>2 <sup>3</sup>
Nitrite-nitrogen (mg NO <sub>2</sub> -N/L)	0.002	0.01	0.05	>0.05
Nitrate-nitrogen (mg NO <sub>3</sub> -N/L)	5	10	20	>20
Total phosphate (mg PO <sub>4</sub> -P/L)	0.02	0.16	0.65	>0.65
Total dissolved solids (mg/L)	500	1500	5000	>5000
Color (Pt-Co Unit)	5	50	300	>300
Sodium (mg/L)	125	125	250	>250
<i>Organic parameters:</i>				
Chemical oxygen demand (COD, mg/L)	25	50	70	>70
Biological oxygen demand (BOD, mg/L)	4	8	20	>20
Total organic carbon (TOC, mg/L)	5	8	12	>12
Total Kjeldahl-Nitrogen (mg/L)	0.5	1.5	5	>5
Emulsified oil and grace (mg/L)	0.02	0.3	0.5	>0.5

Table 2.4: Continued.

Water quality variables	Water quality classes			
	i) High quality	ii) Moderate quality	iii) Polluted	iv) Highly polluted
Methylene-blue-active-substances (mg/L)	0.05	0.2	1	>1.5
Phenolic substances (mg/L)	0.002	0.01	0.1	>0.1
Mineral oil and derivates (mg/L)	0.02	0.1	0.5	>0.5
Total pesticides (mg/L)	0.001	0.01	0.1	>0.1
<i>Inorganic parameters<sup>4</sup>:</i>				
Mercury ( $\mu\text{g Hg/L}$ )	0.1	0.5	2	> 2
Cadmium ( $\mu\text{g Cd/L}$ )	3	5	10	> 10
Lead ( $\mu\text{g Pb/L}$ )	10	20	50	> 50
Arsenic ( $\mu\text{g As/L}$ )	20	50	100	> 100
Copper ( $\mu\text{g Cu/L}$ )	20	50	200	> 200
Chromium (as total, $\mu\text{g Cr/L}$ )	20	50	200	> 200
Chromium ( $\mu\text{g Cr}^{+6}/\text{L}$ )	-	20	50	> 50
Cobalt ( $\mu\text{g Co/L}$ )	10	20	200	> 200
Nickel ( $\mu\text{g Ni/L}$ )	20	50	200	> 200
Zinc ( $\mu\text{g Zn/L}$ )	200	500	2,000	> 2,000
Cyanide (as total, $\mu\text{g CN/L}$ )	10	50	100	> 100
Fluorine ( $\mu\text{g F/L}$ )	1,000	1,500	2,000	> 2000
Free chlorine ( $\mu\text{g Cl}_2/\text{L}$ )	10	10	50	> 50
Sulfur ( $\mu\text{g S}^{2-}/\text{L}$ )	2	2	10	> 10
Iron ( $\mu\text{g Fe/L}$ )	300	1,000	5,000	> 5000
Manganese ( $\mu\text{g Mn/L}$ )	100	500	3,000	3000
Boron ( $\mu\text{g B/L}$ )	10,005	10,005	10,005	> 1000
Selenium ( $\mu\text{g Se/L}$ )	10	10	20	> 20
Barium ( $\mu\text{g Ba/L}$ )	1,000	2,000	2,000	> 2000
Aluminium (mg Al/L)	0.3	0.3	1	> 1
Radioactivity (pCi/L as $\alpha$ activity)	1	10	10	>10
Radioactivity (pCi/L as $\beta$ -activity)	10	100	100	>100
<i>Bacteriologic parameters:</i>				
Fecal coliform (MPN/100 mL)	10	200	2,000	>2000
Total coliform (MPN/100 mL)	-	20,000	100,000	>100000

<sup>1</sup>Either concentration or saturation ratios must be satisfied. <sup>2</sup>This concentration limit should be decreased when Cl susceptible plants are irrigated. <sup>3</sup>The value of free ammonia-nitrogen should not exceed 0.02 mg NH<sub>3</sub>-N/L due to pH value. <sup>4</sup>The criteria under this group indicate the total concentrations of chemicals. <sup>5</sup>The criteria may have to be decreased down to  $\mu\text{g/L}$  when boron-susceptible plants are irrigated.

## 2.12. Water Quality Classification by Water Quality Index

The Water quality index (WQI) is a technique used to rate the combined effect of different water quality parameters, according to their impact on health and the overall drinking water quality [Şener et al. 2017]. The concept of WQI was first presented by Horton [1965] and has gone through several modifications. The WQI integrates complex water quality datasets and enhances understanding of the general trend in water quality by assessing its appropriateness for intended usage through comparison with regulatory standards [Cude, 2001]. In addition, WQI presents an overall picture of the water quality in the basins being studied, in a concise manner for the different stakeholders, especially policy makers to understand [Bordalo et al. 2006]. The traditional approaches used in water quality analysis to check compliance with environmental regulations, do not reveal an overall perspective of the spatial and temporal variations in water quality of a basin [Debels et al., 2005]. WQI development generally involves four steps i.e. (i) parameter selection (ii) development of sub index for each parameter (iii) determining the weight of each parameter (iv) combining of the indices to determine WQI [Boyacioglu, 2007]. Many WQI forms have been developed by different global organisations for specific uses, some of these are given below; [Tyagi. *et al.*2013].

- National Sanitation Foundation Water Quality Index

The National Sanitation Foundation Water Quality Index compares water quality based on selected water quality parameters. The formula for NSFQI is given by equation (2.1):

$$WQI = \sum_{i=1}^n Q_i W_i \quad (2.1)$$

Where,  $Q_i$  is sub-index for water quality parameter  $i$ ;  $W_i$  is the weight of the  $i$ th parameter;  $n$  is the number of parameters considered. The value of  $Q_i$  obtained from a weighting curve according to the water quality parameters. The WQI rating is then determined by table below. The water quality ratings according to National Sanitation Foundation Water Quality Index is presented in Table 2.5.

- Canadian Council of Ministers of the Environment Water Quality Index

The Canadian Council of Ministers of the Environment Water Quality Index was developed by Canadian authorities to provide information related to water quality and protect aquatic life, The model has been adopted and modified by many countries and agencies [Tyagi. et al.2013]. The CCME-WQI is computed according to following expression:

$$WQI = 100 \sqrt{\frac{F_1^2 + F_2^2 + F_3^2}{1.732}} \quad (2.2)$$

Where;  $F_1$  is the percentage number of parameters whose pollution levels exceed the permissible values.

$$F_1 = \frac{\text{Number of failed parameters}}{\text{Total number of parameters}} \times 100 \quad (2.3)$$

$$F_2 = \frac{\text{Number of failed tests}}{\text{Number of tests}} \times 100 \quad (2.4)$$

$F_3$  is the extent to which objectives are not achieved. Where,  $n$  is the number of sub-indices,  $SI$  is the sub-indices for  $i^{\text{th}}$  parameter. The water quality ratings according to Canadian Council of Ministers of the Environment Water Quality Index is presented in Table 2.5.

- Oregon Water Quality Index

The Oregon Water Quality Index was established to assess the water quality of Oregon's streams, the index combines eight water quality parameters into a single variable. The WQI according to this method is computed from [Tyagi et al., 2013]:

$$WQI = \sqrt{\frac{n}{\sum_{i=1}^n \frac{1}{SI_i^2}}} \quad (2.5)$$

Where, n is the number of sub-indices, SI is the sub-indices for i<sup>th</sup> parameter. The water quality ratings according to Oregon Water Quality Index is presented in Table 2.5.

Table 2.5: Quality rating for different WQIs.

National Foundation Water quality index	
WQI Value	Rating
91-100	Excellent water quality
71-90	Good water quality
51-70	Medium water quality
26-50	Bad water quality
0-25	Very bad water quality
Canadian Council of Ministers of the Environment Water Quality Index	
95-100	Excellent water quality
80-94	Good water quality
60-79	Fair water quality
45-59	Marginal water quality
0-44	Poor water quality
Oregon Water Quality Index	
90-100	Excellent water quality
85-89	Good water quality
80-84	Fair water quality
60-79	Poor water quality
0-59	Very poor water quality

- Arithmetic Weight Water Quality Index

The Arithmetic Weight Water Quality Index classifies water quality depending on the purity level obtained from the measured parameters [Chowdhury et al. 2012; Rao et al. 2010] and the calculation of WQI is made from equation (2.6) and (2.7):

$$WQI = \frac{\sum Q_i W_i}{\sum W_i} \quad (2.6)$$

Where;  $Q_i$  is computed from the equation below,

$$Q_i = \left( \frac{C_i - C_a}{S_i - C_a} \right) \times 100 \quad (2.7)$$

Where;  $C_i$  is the measured concentration of the parameter mg/L or  $\mu\text{g/L}$ ,  $C_a$  is the ideal value, which is taken as 14.6 mg/L for dissolved oxygen and 7.0 for pH. The value of  $C_a$  is taken as 0 for all the other parameters.  $S_i$  is the permissible drinking water standard.  $W_i$  is the unit weight determined from:  $W_i = \frac{K}{S_i}$ ,  $K$  is a constant of proportionality. The water quality ratings according to Arithmetic Weight Water Quality Index is presented in Table 2.6.

Table 2.6: WQI rating according to Arithmetic Weight Water Quality Index.

WQI Value <sup>1</sup>	Rating of Water Quality	Grading
0-25	Excellent water quality	A
26-50	Good water quality	B
51-75	Poor water quality	C
76-100	Very Poor water quality	D
Above 100	Unsuitable for drinking purpose	E
<sup>1</sup> Adopted from Tyagi. <i>et al.</i> 201		

## **3. METHODOLOGY**

### **3.1. Study Area**

Mustafakemalpaşa catchment is located within the boundaries of Bursa, Balıkesir and Kütahya provinces in the 39° 00' to 40° 20' N and 28° 20' to 30 °00' E geographic coordinates with a total catchment area of 10,622 km<sup>2</sup>, Northwestern Turkey, an area characterized by intensive mining of boron, chromium, lignite, coal, iron and marble among others. The drainage network in the region discharges into Lake Uluabat and finally into the Marmara Sea. The climate in the region is a typical transitional climate of that between the Mediterranean and the Black Sea climates, with the highest precipitation received in winter and the least precipitation received in summer, the summers are generally hot and dry while winter are cold and rainy. The hottest months are July and August while the coldest months are January and February. Annual precipitation in the basin ranges between 40 - 65 mm with the maximum precipitation recorded in winters.

### **3.2. Data Collection**

A four years' dataset (2012-2016) was obtained from the Turkish State Hydraulic Works (DSI), more data was obtained from three field campaigns in 55 designated GPS coordinate sampling points as presneted in Figure 3.1, in Mustafakemalpaşa stream and its tributaries in March 2017, July 2017 and September 2017. The field data collection was done in consideration of the different meteorological and hydrologic conditions of these periods. In October, the weather is characterised by rainy but warm conditions with an average flow rate of 17.356 m<sup>3</sup>/s, in the main Mustafakemalpaşa stream. In March, the weather is characterised by rainy and foggy conditions with an average stream flow rate of 115.089 m<sup>3</sup>/s, in July the weather is characterised by hot and dry conditions with a flow rate of 19.053 m<sup>3</sup>/s. Water samples were collected using sterilized polyethylene bottles and analyzed within 5days of sampling. For sediment samples, approximately 500g of sediment was collected from top 0-4 cm using a plastic spoon. After the sampling, the sediment samples were sealed in polyethylene bags and transported to Gebze Technical

University environmental engineering laboratory, where they were dried at  $105^{\circ}\text{C} \pm 2^{\circ}\text{C}$  for 48 hours and ground to powder using a mortar and pestle ( $< 100\mu\text{m}$ ). All the sampling and analysis procedures were performed in accordance with the Standard Method for the Examination of Water and Wastewater [AWWA].



Figure 3.1: Mustafakemalpaşa catchment and the monitoring stations.

### 3.3. Analysis of Collected Samples

#### 3.3.1. Elemental Analysis in Water

Water samples were analyzed for pH, water temperature, biochemical oxygen demand (BOD), dissolved oxygen (DO), nitrates, total phosphorus (TP), total organic carbon (TOC), arsenic, boron, calcium, magnesium, potassium, sodium, conductivity, sulphates, silicate, and total dissolved solids (TDS). The analyses on pH, temperature, conductivity and dissolved oxygen were performed on site by a “Mettler Toledo Seven Go” device. BOD<sub>5</sub> was determined in bottles the by Winkler method at  $20^{\circ}\text{C}$  incubation. Inorganic anions such as nitrate ( $\text{NO}_3$ ),  $\text{SO}_4$  and chloride (Cl) were

determined by ion chromatograph (HIC-20A Super, Shimadzu). TOC were determined by TOC-L-CPH/CPN, Shimadzu analyzer. The total arsenic, boron, TP and Si concentrations were determined by Inductively Coupled Plasma – Optical Emission Spectrophotometer (ICP-OES, Optima 7000 DV, PerkinElmer, USA). Prior to analysis, all the water samples were filtered through 0.45µm filter. All the analyses were recorded as a mean of triplicate measurements. Total Alkalinity was determined by titrating with 0.02N sulfuric acid to the methyl orange end point and the amount of standard sulfuric acid consumed was recorded. Total Alkalinity was calculated form Equation 3.1 below.

$$\text{Total Alkalinity (mg CaCO}_3\text{)} = \frac{(\text{Volume\_of\_acid\_used}) \times 0.02N \times 50000}{\text{Sample\_volume}} \quad (3.1)$$

### **3.3.2. Analysis of Elements in Sediment**

In order to determine the elemental concentrations in sediment, 0.25 g of each sediment sample was microwave digested (Model Milestone Ethos 1600 advanced microwave digestion apparatus) in Teflon vessels with an acid mixture of nitric acid (2 ml, HNO<sub>3</sub>), hydrofluoric acid (2 ml, HF), hydrochloric acid (1 ml, HCl) and hydrogen peroxide (1 ml, H<sub>2</sub>O<sub>2</sub>). The volume of digestate was raised to 50 ml by ultra-pure water and subsequently filtered through Whatman filter paper No. 1. All the metal analyses were determined by Inductively Coupled Plasma – Optical Emission Spectrophotometer (ICP-OES, Optima 7000 DV, PerkinElmer, USA). Samples analyses was done in duplicates, the analytical precision was generally better than 1 % for major elements and 2 % for trace elements. All reagents used were of analytical grade.

### **3.3.3. Assessment of Sediment Pollution Levels**

In this study, the degree of sediment contamination has been analyzed through the calculations and interpretation of contamination factor (CF) and Pollution Load Index (PLI), geo-accumulation index ( $I_{geo}$ ), Enrichment factor (EF), and Sediment Quality Guidelines (SQGs).

### **3.4. Statistical Analyses**

This study used statistical techniques to evaluate the variation of water quality with sampling points. For this purpose, statistical software SPSS Version 21.0 was used. Principal Component analysis (PCA) and Pearson correlation analyses (PCM) were performed to show the interrelationship among the different elements. The WQI results for the three field campaigns were also subjected to one-way analysis on variance (ANOVA) to determine the extent of seasonal variation.

### **3.5. Water and Sediment Quality Mapping by GIS Maps**

Geographical Information Systems GIS consists of both spatial and non-spatial data, computer software, hardware and users, designed to capture, process, store, update, analyze and display geographically referenced information [Shaban et al., 2010]. GIS has become a wide spread software in water resources management, it provides a faster and accurate mechanism for spatial data analysis. In this study, GIS was applied through ArcGIS 10.5.1 desktop software. Relevant maps, data and text material of the studied area were collected and digitized. The GIS system was used to establish a spatial database of the study area with pertinent attribute data such as rivers, villages, sampling point and water quality among others. The geodetic coordinates of each sampling was taken using the Global Positioning System (GPS). These data was subsequently used to generate sampling point layers in ArcGIS. The generated WQIs and sediment PLIs were visualized by thematic maps based on obtained field data imported in a GIS database. The maps drawn are useful as a decision support tool in water resources management of Mustafakemalpaşa catchment. The points in Mustafakemalpaşa that require agent pollution control strategies are also indicated in the maps. Consequently, the maps shall help the stakeholders at different levels to understand the state of water resources in the basin. The procedure for generating the water quality maps was as below;

- i) The streams in catchment were delineated from digital elevation model (DEM)
- ii) The sampling points were geographically located by a hand held GPS, a point shapefile layer of sampling point was created and overlain on the generated stream network layer.

iii) The stream network was divided into multiple reaches each represented by the sampling point.

The WGS\_1984\_UTM\_Zone\_35N was the reference coordinate system used in this study. The GIS data layers used in this study include:

- Landuse data
- Dams and ponds for the basins
- Lakes in the basins.
- Watershed boundary
- Hydroelectric power generation sites along the rivers
- Urban centers and settlement areas
- Rivers and streams

## 4. DATA PRESENTATION AND ANALYSIS

### 4.1 Analysis of Stream Water and Sediment Quality

The water quality results for the field campaigns in March, July and October are discussed in this chapter. Computation of Water quality index, correlation coefficients, Principal component analysis and Hierarchical cluster analysis are discussed.

### 4.2. Physicochemical Parameters of the Stream Water

The water quality at any given point of a watershed is affected by stream flow, chemical reactions within river course, inflow from tributaries and their respective pollutant concentrations, existing human activity and the geological setting [Altansukh and Davaa, 2011]. Table 4.1 and Table 4.2 provide basic statistical summary for the water quality parameters measured in Emet and Orhaneli streams.

Table 4.1: Basic statistical analysis of parameters for Emet stream.

	March			July			October			WHO
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
As <sup>1</sup>	3	16210	582.6	1.88	11480	538.2	2.19	19070	989.9	10
B	0.1	1900	70.01	0.01	884.1	34.1	0.07	1760	62.6	2.4
Ca	20.9	416.4	79.7	23.7	182.6	82.7	29.7	490.8	104.2	250 <sup>2</sup>
DO	6.0	9.2	7.5	4.53	22.6	7.71	3.17	11.3	7.2	5
BOD	0	12	3.36	0	13	4.71	0	21	4.62	5
K	1.15	6.84	2.88	0.63	13.44	4	1.37	13.88	4.54	12 <sup>a</sup>
Mg	3.05	305.3	43.11	4.6	187	48.64	5.57	349.9	66.18	30
Na	4.05	142.1	15.88	5.08	93.97	20.07	7.15	197.4	27.92	200
pH	7.09	8.85	7.99	6.79	9.47	8.31	7.31	8.71	8.23	7.5
Temp	6.3	21.9	12.75	18	31.4	24.81	18.4	26.9	21.79	-
TDS	90.8	1990	441.05	140.7	1707	393.88	156.8	1856	469.78	100
TP	0.1	0.29	0.19	0.04	0.24	0.14	0.06	0.32	0.19	1.63
TOC	1.45	5.45	3.09	2.32	4.26	3.82	0.77	11.17	2.17	-
Cl	1.99	281.68	23.31	1.81	357	28.43	2.1	420	33.71	250
Fe	113.1	2543.4	1077.1	89.3	2009.1	839.32	54	1602	629.3	200
Si	3.95	20.79	8.02	4.89	31.73	10.16	5.55	32.23	9.6	-
NO <sub>3</sub> -N	0.52	4.07	1.99	0.41	3.68	1.74	0.1	3.1	1.27	11
SO <sub>4</sub>	7.18	1210.3	127.41	8.27	1491.7	171.9	9.8	1790	199.76	250

<sup>1</sup>Concentration is ppb and other parameters is mg/L.  
<sup>2</sup>UK drinking water standards.

Table 4.2: Basic statistical analysis of parameters for Orhaneli stream.

Element	March			July			October			WHO Value
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
As <sup>1</sup>	5.17	116	29.79	9.49	89.83	39.96	6.54	56.88	27.48	10
B	1.34	5.45	3.14	0.01	0.3	0.2	0.1	0.3	0.24	2.4
Ca	28.7	66.73	52.11	58.95	100.5	77.88	46.95	100.3	72.72	250 <sup>2</sup>
DO	2.38	12.88	6.94	0.68	11.83	6.3	0.99	10.42	5.4	5
BOD	2	24	7	1	40	9.5	1	31	7.33	5
K	1.36	4.74	2.47	2.01	5.65	3.4	1.5	4.3	2.95	12 <sup>2</sup>
Mg	20.4	88.59	46.63	22.94	112.7	58.69	24.21	85.95	55.33	30
Na	4.4	20.44	9.39	5.46	29.82	13.98	5	19.4	12.64	200
pH	7.01	8.59	7.7	7.44	8.64	8.24	7.68	8.57	8.16	7.5
Temp	10.7	21.7	14.81	12.8	25	20.52	14.7	22	18.4	-
TDS	447	1078	651.25	203	512	339.42	191.7	429	336.31	100
TP	0.05	0.53	0.25	0.08	0.28	0.16	0.08	0.47	0.24	1.63
TOC	1.35	4.51	3.06	2.43	5.1	3.98	1.15	3.15	2.12	-
Cl	3.59	13.94	9.17	4.98	18.09	11.49	5.6	20.1	11.3	250
Fe	93.2	1465	811.11	76.08	1061	628	63.3	808	445	200
Si	4.04	9.81	6.85	5.65	10.06	8.9	5.04	10.11	8.22	-
NO <sub>3</sub> -N	0.75	3.8	2.16	0.6	3.68	1.99	0.4	3.3	1.58	11
SO <sub>4</sub>	32.0	167.9	97.88	40.31	239.27	131.05	47.8	305.2	152.17	250

<sup>1</sup>Concentration is ppb and other parameters is mg/L.  
<sup>2</sup>UK drinking water standards.

One of the most important parameter in water quality assessment is DO as it affects biota [Naubi et al., 2016]. The measured DO levels in Emet stream ranged from 6 - 9.2 mg/L in March 4.53 - 11.6 mg/L in July and 3.17 - 11.3 mg/L in October. In Orhaneli stream, DO levels ranged from 2.38 - 12.88 mg/L in March, 0.68 - 11.83 mg/L in July and 0.99 - 10.42mg/L in October. Generally, DO levels at sampling points near settlement areas were less than 5 mg/L, below WHO standard. Very low DO levels were recorded at sampling points near Tavşanlı, Tunçbilek and Muhacilar settlements (points K3-K6). However, after these areas the stream runs through a deep valley passing the mountainous regions with great velocity and turbulence, favouring re-aeration and DO gain. Low DO levels were also observed at sampling points E3, E4, E5 and E6 around Emet and Hisarcik towns, where domestic wastewater is discharged into the stream causing great reductions in DO and turbidity problems in

the water. The variations of DO levels along Orhaneli stream is presented in Figure 4.1.

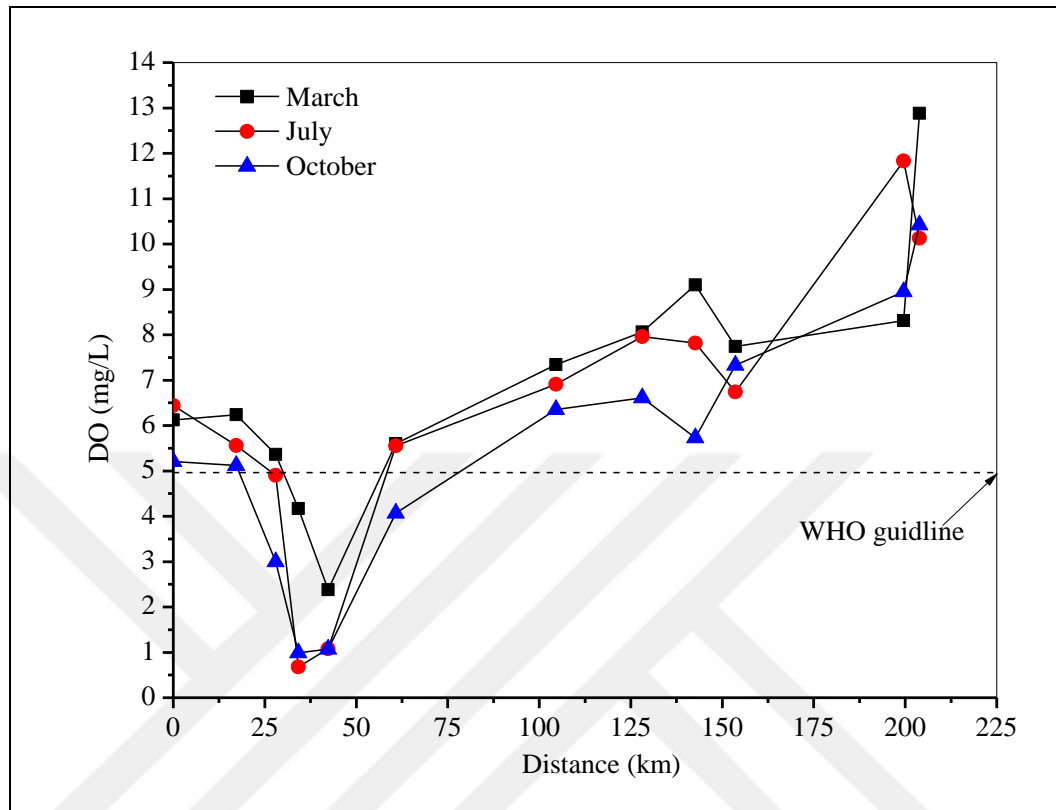


Figure 4.1: DO Variation in Orhaneli Stream.

The mean TDS in Emet stream ranged from 394 to 470 mg/L. However, tributary G1 showed the highest mean annual TDS of 1851 mg/L during the study period. In the case of Orhaneli stream, the mean annual TDS levels varied from 336 to 669 mg/L (Table 4.2). The TDS levels were generally below the guideline value of 1000 mg/L. Water pH is an indicator of the degree of acidity or basicity of the water and affects metal solubility, the water hardness and alkalinity [Osibanjo et al., 2011]. The mean annual pH for both the streams showed slight alkaline properties. The samples from Emet stream and its tributaries fluctuated in the pH range of 6.79 - 9.47. Whereas in Orhaneli stream, the pH fluctuated from 7.01 - 8.59 (Table 4.1 and 4.2). Studies by other researchers revealed water samples from Emet stream to have relatively high electrical conductivity (865-924  $\mu\text{S}/\text{cm}$ ) and pH values of 8.2 - 8.36 [Gemici et al., 2004], [Çolak et al., 2003].

Excessive nitrate concentration in water can cause adverse effects to human health. The measured  $\text{NO}_3\text{-N}$  levels in Emet stream and its tributaries varied from 0.52

- 4.07 mg/L in March, 0.41 - 3.68 mg/L in July and 0.1 - 3.1 mg/L in October, whereas for Orhaneli stream  $\text{NO}_3\text{-N}$  levels changed from 0.75 - 3.8 mg/L in March, 0.6 - 3.68 mg/L in July and 0.4 - 3.3 mg/L in October. All the measured  $\text{NO}_3\text{-N}$  values were below the WHO guideline of 11 mg/L (Table 4.1). The measured  $\text{SO}_4^{2-}$  levels fluctuated from 7.18 - 1210.3 mg/L in March, 8.27 - 1491.72 mg/L in July and 9.8 - 1790 mg/L in October for Emet stream. Whereas for Orhaneli stream, the fluctuations in  $\text{SO}_4^{2-}$  levels were 32.02 to 167.93 mg/L in March, 40.31 - 239.27 mg/L in July and 47.8 - 305.2 mg/L in October (Table 4.2). Sulphate pollution mainly originates from drainage from agricultural fields where sulphate fertilizers are applied, depositions from the atmosphere and oxidation of sulphur compounds. In addition, sulphates may originate from domestic wastewater containing sulfuric salts and weathering of soils [Varol and Davraz, 2015], [Şener et al., 2017].

The measured chloride ion levels varied from 1.99 - 281.68 mg/L, 1.81 - 357 mg/L and 2.1 - 420 mg/L for March, July and October, respectively for Emet stream and its branches whereas for Orhaneli stream, chloride ion levels changed from 3.59 - 13.94 mg/L, 4.98 to 18.09 mg/L and 5.6 - 20.1 mg/L for March, July and October, respectively (Table 4.1 and Table 4.2). The availability of chloride ions in stream water may be attributed to anthropogenic sources such as pollution by sewage discharges and/or geogenic sources such as saline leachate from soil [Chatterjee et al., 2010]. The highest levels of chloride and sulphate ions were revealed at points G1.

The concentrations of total organic carbon (TOC) and total phosphorous (TP) in Emet stream varied from 1.45 - 5.45 mg/L and 0.1 - 0.24 mg/L, respectively in March, 2.32 - 4.26 mg/L and 0.04 - 0.24 mg/L, respectively in July, 0.77 - 11.17 mg/L and 0.06 - 0.32, respectively in October. In Orhaneli stream, TOC and TP varied as follows; 1.35 - 4.51 mg/L and 0.05 - 0.53 mg/L respectively in March, 2.43 - 5.1 mg/L and 0.08 - 0.28 mg/L, respectively in July, 1.15 - 3.15 mg/L and 0.08 to 0.47 mg/L, respectively in October. Excessive phosphorus in water bodies causes eutrophication resulting in the fast growth of algae and other planktons [Ansari and Gill, 2014].

Natural surface waters may also contain trace metals and their presences are attributed to natural and/or human activities. In this study, the collected water samples were analyzed for Ag, Cd, Co, Cr, Cu, Mo, Ni and Zn. However only concentrations of Cd, Cr, Cu and Zn were above detection limit and ranged from 0.005 - 0.195 mg/L, 0.011 to 0.025 mg/L, 0.007 to 0.012 mg/L and 0.037 to 0.071 mg/L, respectively. All the analyzed trace elements in water were within the WHO permissible limits.

The major pollutants in the water of Emet stream were As and B. The concentrations of As and B in Emet stream varied from 3 - 16210  $\mu\text{g/L}$  and 0.1 - 1900mg/L respectively in March, 1.88 - 11480  $\mu\text{g/L}$  and 0.01 - 884.1mg/L, respectively in July, 2.19 - 19070  $\mu\text{g/L}$  and 0.07 - 1760 mg/L, respectively in October (Table 4.1). In Orhaneli stream, As and B varied as follows; 5.17 - 116 $\mu\text{g/L}$  and 1.34 - 5.45 mg/L, respectively in March, 9.49 - 89.83  $\mu\text{g/L}$  and 0.01 - 0.3 mg/L, respectively in July, 6.54 - 56.88  $\mu\text{g/L}$  and 0.1 - 0.3mg/L, respectively in October (Table 4.2). Previous studies on Emet stream revealed arsenic levels of 137.1-1002  $\mu\text{g/L}$  and boron levels of 2421-14490  $\mu\text{g L}^{-1}$  [Benzer et al., 2017]. The highest levels of As and B were revealed at branches G1 and H1 along Emet stream (Figure. 4.2 and Figure. 4.3).

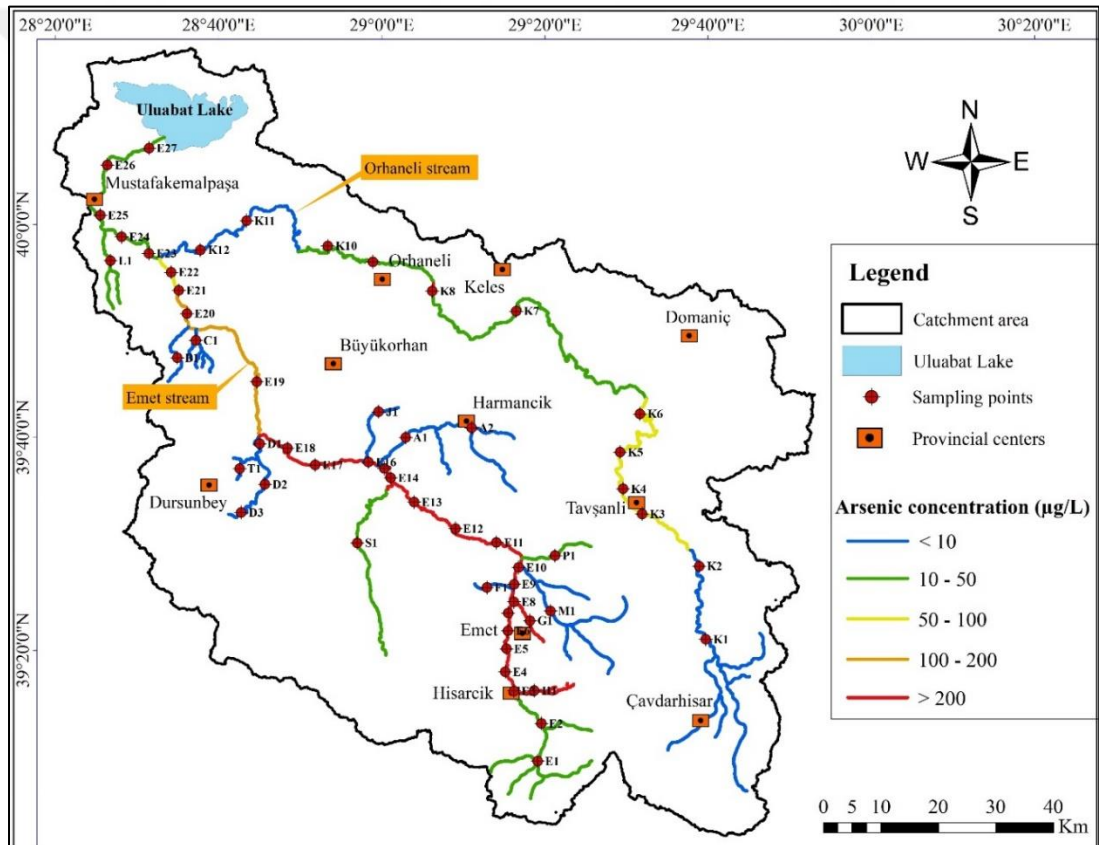


Figure. 4.2: Spatial distribution of arsenic in the study area.

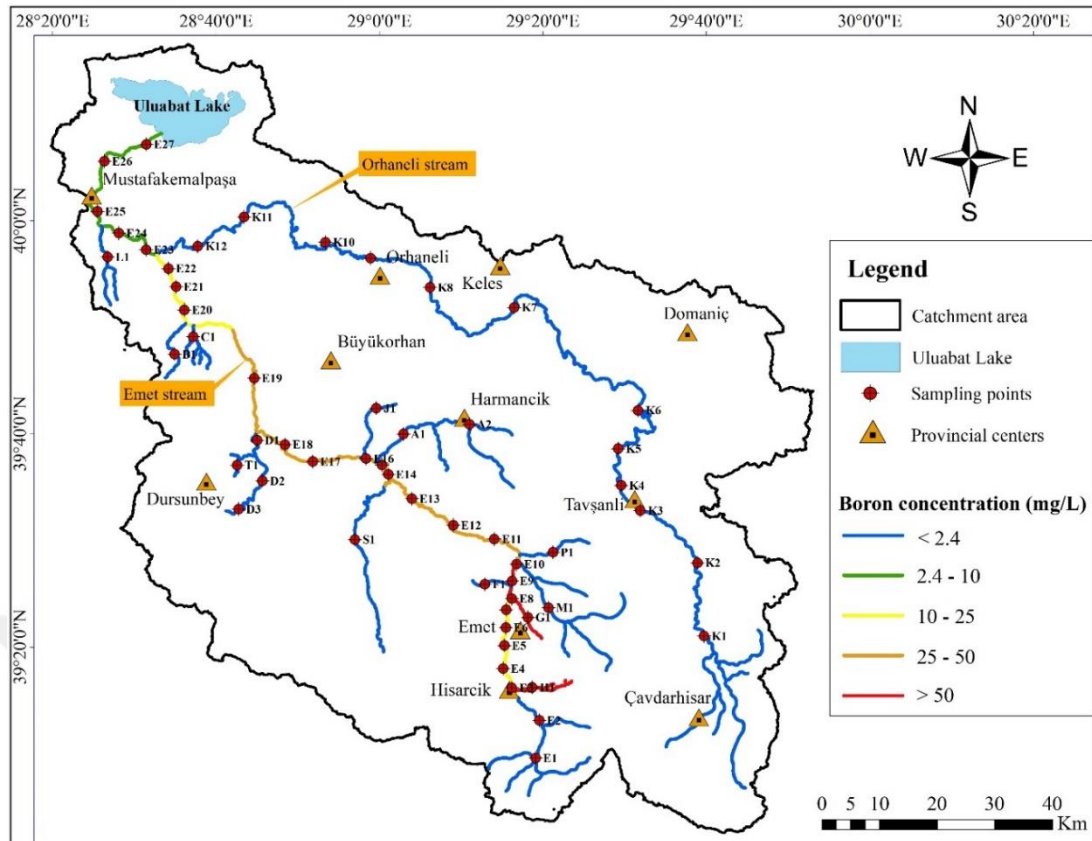


Figure.4.3: Spatial distribution of boron in the study area.

The most upstream points E1(0 km) and E2 (11km) showed B and arsenic pollution below the WHO guideline (Figure.4.4 and Figure.4.5). As the stream passes through Hisarcik boron mines, and Hisarcik and Emet settlement areas, at sampling points E3 (14.3 km), E4 (17.7 km), and E5(20.9 km), an increase in both arsenic and boron pollution starts to occur. Another extremely high concentration for both arsenic and boron is seen by the peak at point E7 (33.1 km), the arsenic pollution thereafter rapidly drops possibly due to dilution and absorption and then maintains constant concentration downstream until confluence with Orhaneli where the arsenic pollutions are diluted and drop to variation of about 30-50  $\mu\text{g/L}$  in Mustafakemalpaşa stream. Similarly, after point E7 (33.1 km), the boron pollution sinuates along Emet stream until confluence with Orhaneli stream where it shows a constant trend.

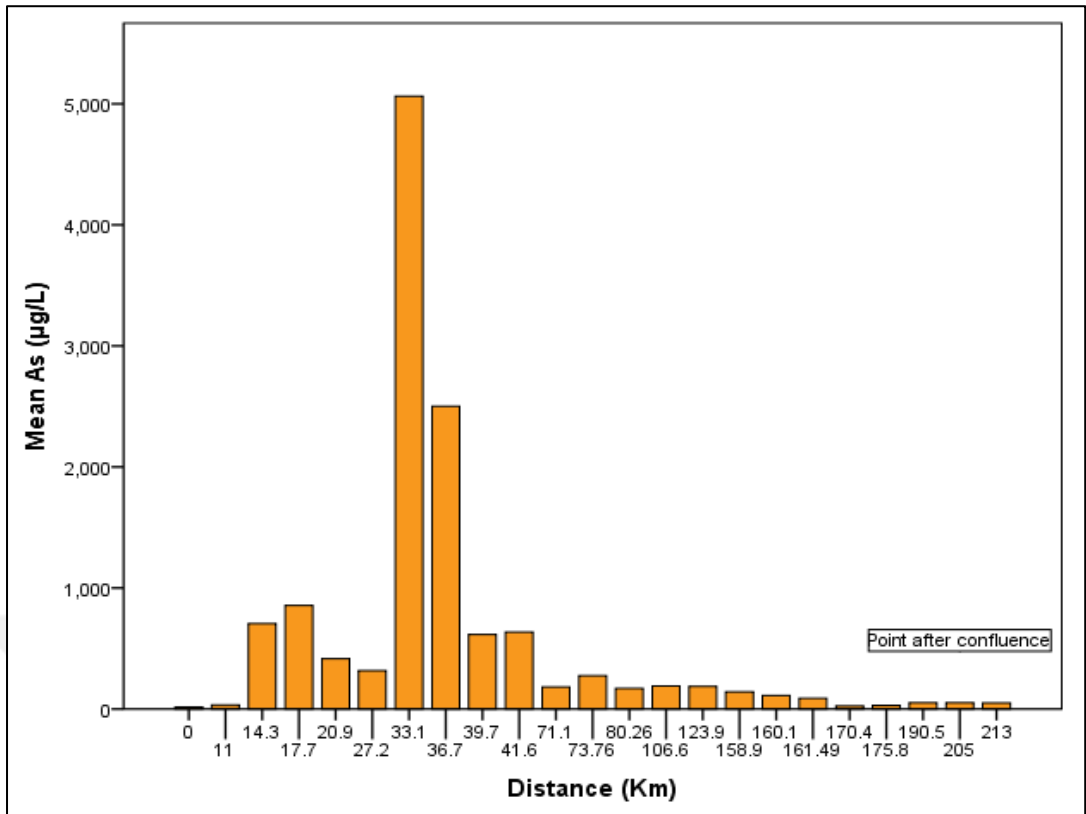


Figure 4.4: Variation of Arsenic Along Emet Stream.

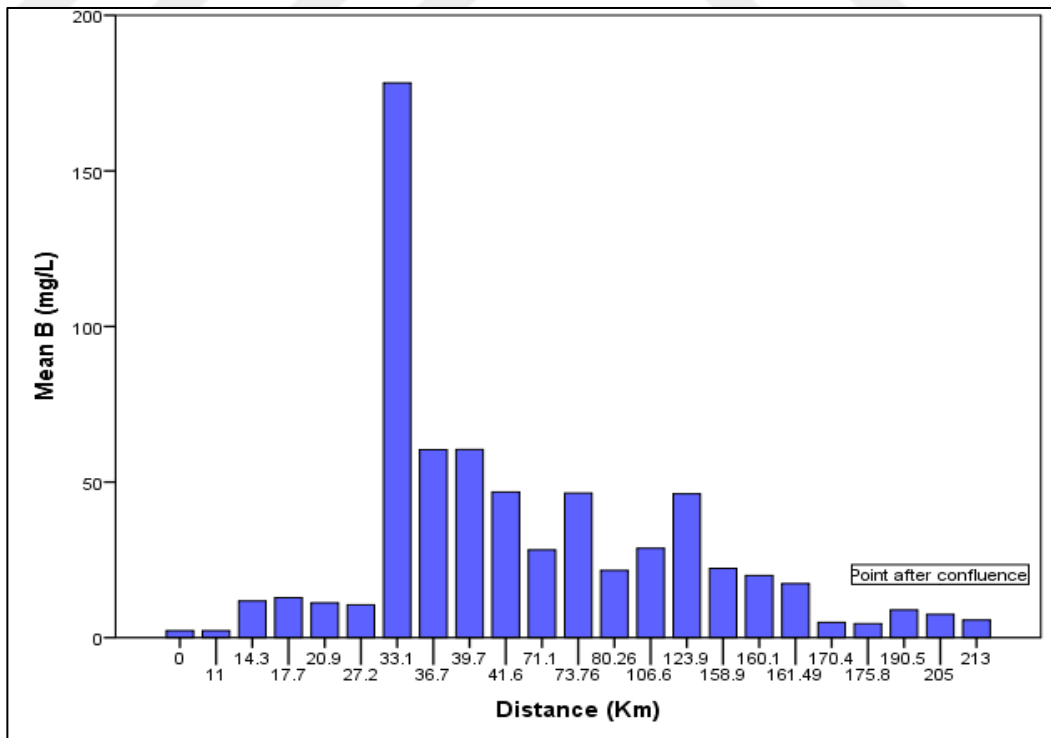


Figure 4.5: Variation of Boron Along Emet Stream.

The maps presented in Figure 4.6 and Figure 4.7 compare the concentration of arsenic and boron with the distribution of the minefields based on subcatchments. Thus, it is aimed to better analyze the effect of mine-fields in the basin on pollution distribution. As it is clearly seen from Figure 4.6 the subcatchment numbered 6 has the highest mean As concentration (905 $\mu\text{g/L}$ ). This subcatchment has the most intense mining activities. Boron mines are located in the southern and central parts of the basin, and lignite mines are intensively located on the northern boundary of the basin. Subcatchments numbered 4 and 2 have the second and third highest mean arsenic concentration values respectively. These high values are ascribed to the presence of lignite mining areas and influence of inflows from subcatchment numbered 6. Subcatchments numbered 3 and 5 have the lowest As concentration, respectively as 8.01  $\mu\text{g/L}$  and 13.5. These two subcatchments have no boron or lignite mining areas. Finally, subcatchment numbered 7 is for Orhaneli stream, with mean arsenic concentration of 34.65  $\mu\text{g/L}$ . There are numerous mining areas in the subcatchment numbered 7 but the effect of these activities on As pollution is limited. This could be explained by geochemical characteristics of rocks minerals. Additionally, the technological level of mining activities in this region may be attributed to the relatively low pollution concentration. The subcatchment numbered 1 represents Mustafakemalpaşa stream and has a mean value of 42.09  $\mu\text{g/L}$ .

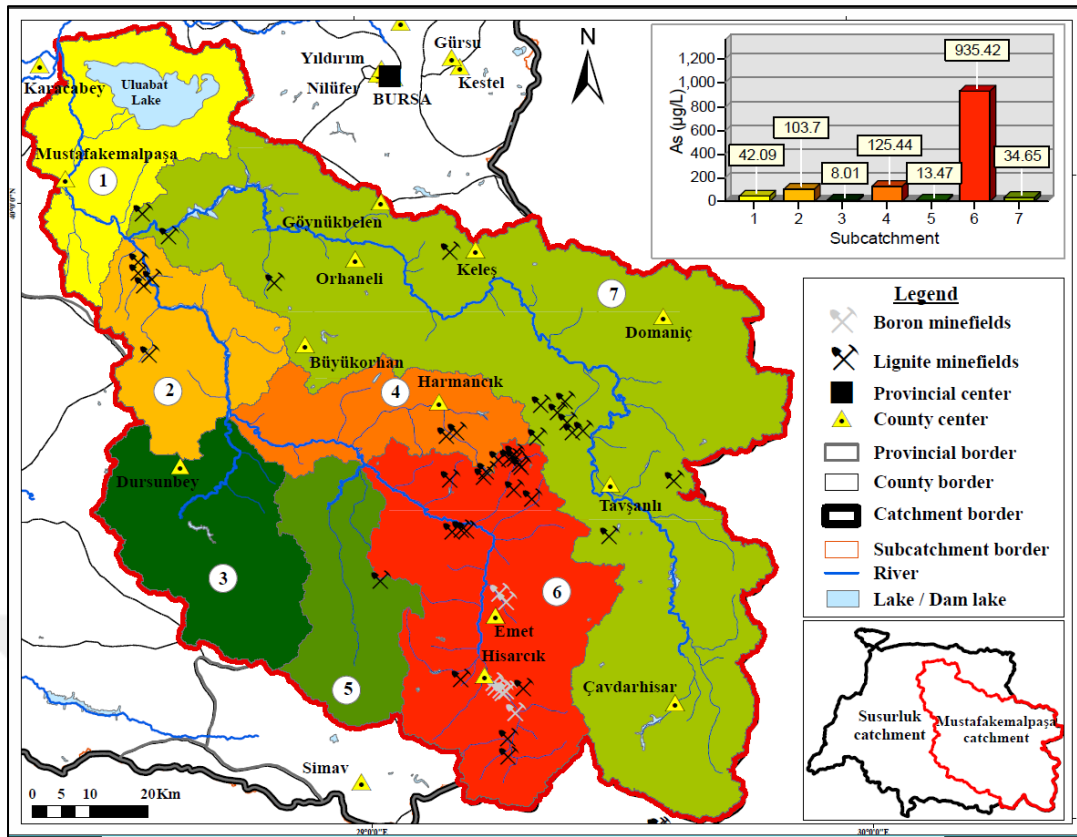


Figure 4.6: Annual average As distribution in the subcatchments.

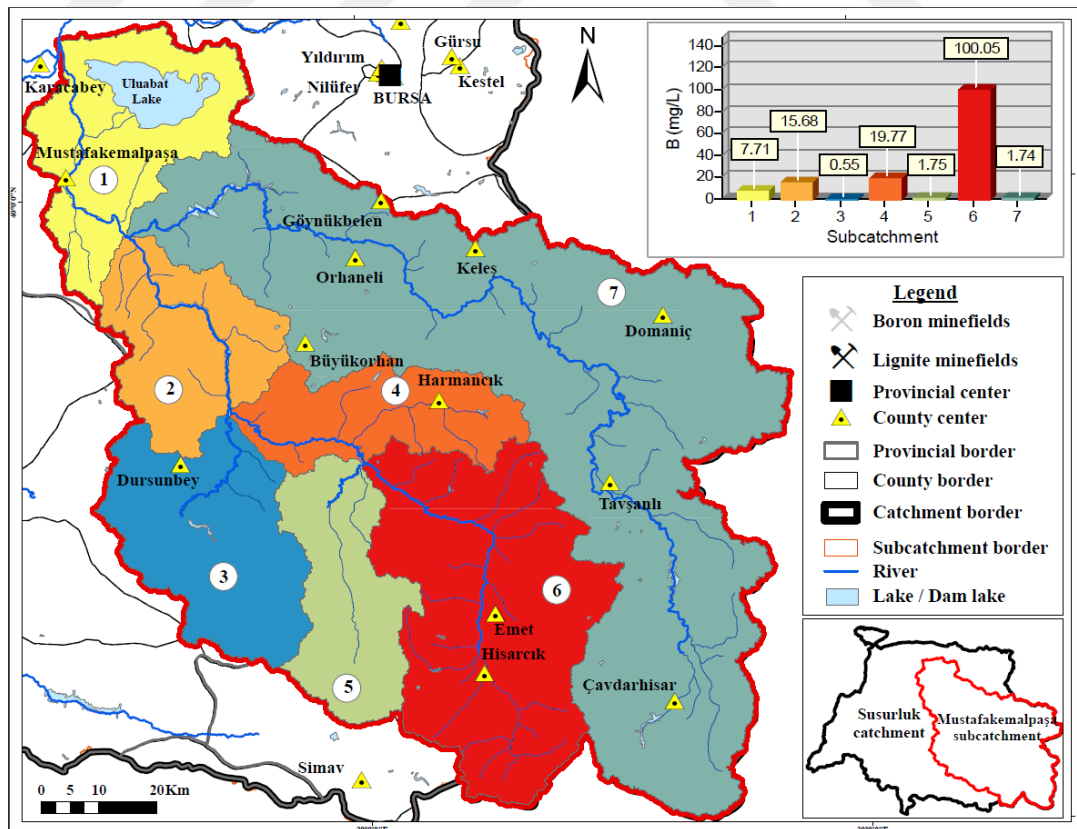


Figure 4.7: Annual average B distribution in the subcatchments.

The distribution of boron pollution in the subcatchments is very similar to that of arsenic pollution.

### 4.3. Assessment of Water Quality by Water Quality Index

Computations of WQI through weighted arithmetic water quality index method was first suggested by Horton [1965] and later modified by Cude [2001]. The WQI integrates complex water quality datasets and enhances understanding of the general trend in water quality by assessing its appropriateness for intended usage through comparison with regulatory standards [Cude, 2001]. In addition, WQI presents an overall picture of the water quality in the basins being studied, in a concise manner for the different stakeholders, especially policy makers to understand. The traditional approaches used in water quality analyses to check compliance with environmental regulations, do not reveal an overall perspective of the spatial and temporal variations in water quality of a basin [Debels et al., 2005]. WQI development generally involves four steps i.e. (i) parameter selection (ii) development of sub index for each parameter (iii) determining the weight of each parameter (iv) combining of the indices to determine WQI [Boyacioglu, 2007]. In this study, WQI was calculated for each sampling point for the three field campaigns of March, July and October. Principal Component analysis (PCA) was used as a parameter reduction method and subsequently, the parameters that were used in the computation of WQI are As, B, pH,  $Cl^-$ , TP,  $SO_4^{2-}$ , Ca, Mg, Mg, BOD, DO,  $NO_3^-$  and Fe. The WQI was obtained from the following set of equations.

$$WQI = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n W_i} \quad (4.1)$$

Where;  $Q_i$  is the quality rating of  $i^{th}$  parameter based on its concentration [Ramakrishnaiah et al., 2009].  $W_i$  is the weight of the  $i^{th}$  parameter and was calculated from equation (4.2) [Şener et al., 2017].

$$W_i = \frac{w_i}{\sum w_i} \quad (4.2)$$

Where;  $w_i$  is the relative weight assigned to each parameter.  $Q_i$  was computed from equation (4.3).

$$Q_i = \left( \frac{C_i - C_a}{S_i - C_a} \right) \times 100 \quad (4.3)$$

$C_i$  is the measured concentration of the parameter mg/L or  $\mu\text{g/L}$ ,  $C_a$  is the ideal value, which is taken as 14.6 mg/L for dissolved oxygen and 7.0 for pH. The value of  $C_a$  is taken as 0 for all the other parameters.  $S_i$  is the permissible drinking water standard for the parameter according to WHO, 2011. The classification for WQI used in this study is shown in Table 4.3. [Sahu and Sikdar, 2008], [Yidana and Yidana, 2010], [Şener et al., 2017].

Table 4.3: Classification of Water Quality Index.

WQI	Water classification	Characteristics
< 50	Very clean water	Oxygen saturated tributaries, low nutrients in water; low bacteria contamination and can directly be used for drinking purpose without treatment.
50 - 100	Clean Water	Presences of organic pollutants with slight oxygen depletion, low bacterial contamination, can be used for human consumption after filtration and disinfection.
100 - 200	Slightly polluted water	Low DO, nutrients inputs, bacteria contamination not suitable for human consumption unless treated. However, be used for recreation and livestock purposes.
200 - 300	Moderately polluted	This includes water bodies that incur frequent oxygen depleted due to organic contamination; hence cannot sustain aquatic life during oxygen depletion periods. However, this water can be used for industrial purposes and irrigation after pretreatment.
> 300	Heavily polluted	This water is very unsuitable for drinking and has encountered critical oxygen depletion, due to high organic pollution. This water can cause fish kills in the streams.

A further analysis was done to establish the water quality parameters that highly influenced WQI, through computation of effective quality rating ( $Q_{\text{eff}}$ ) of each parameter in percentage. The  $Q_{\text{eff}}$  results for all the three seasons are presented in Table 4.4.

$$Q_{eff} = \frac{W_i Q_i}{WQI} \times 100 \quad (4.4)$$

The most influential variables in WQI were As, B, pH, DO and BOD. The mean  $Q_{eff}$  for arsenic, boron, pH, DO and BOD varied from 30 - 40, 9 - 23, 10 -12, 2.97 - 4.37, 3.77 - 5.96, respectively.

Table 4.4: Statistical Evaluation of Effective Quality for Parameters ( $Q_{eff}$ ).

	March				July				October			
	Mean (%)	Min (%)	Max (%)	SD (%)	Mean (%)	Min (%)	Max (%)	SD (%)	Mean (%)	Min (%)	Max (%)	SD (%)
As	30.3	5.37	76.8	16.93	42.8	11.29	84.4	22.45	43.47	13.0	93.6	24.7
B	22.3	4.3	55.2	13.6	9.0	0.03	24.6	9.07	11.95	0.23	38.3	13.8
Ca	0.42	0.03	1.3	0.28	0.66	0.05	2.5	0.56	0.68	0.03	2.4	0.6
DO	2.97	0.12	10.0	2.24	3.47	-3.81	15.6	3.52	4.37	0.07	15.6	3.9
Mg	3.41	0.02	11.6	2.65	4.13	0.02	11.6	3.21	4.60	0.05	12.7	3.7
pH	10.1	0.25	31.7	7.59	12.7	0.25	32.0	9.50	12.08	0.22	32.7	10.4
TDS	2.07	0.06	6.0	1.82	1.63	0.10	4.6	1.16	1.83	0.06	4.3	1.4
TP	0.61	0.02	1.6	0.48	0.53	0.02	1.48	0.39	0.77	0.01	2.1	0.6
Cl	0.14	0.02	0.4	0.08	0.19	0.02	0.4	0.10	0.22	0.01	0.63	0.2
Fe	0.14	0.02	0.4	0.08	16.3	0.68	36.1	9.42	12.04	0.40	29.0	8.8
NO <sub>3</sub>	0.91	0.07	3.0	0.63	0.96	0.06	2.9	0.70	0.76	0.04	2.4	0.7
BOD	3.77	0.21	19.6	4.11	5.73	0.09	27.9	5.96	5.04	0.09	29.2	6.7
SO <sub>4</sub>	1.18	0.12	3.4	0.76	1.88	0.18	4.9	1.31	2.16	0.14	7.7	1.9

### 4.3.1. Spatial and Temporal Variation in Water Quality Index

Most of the tributaries monitored in this study showed average WQI <100, which is water of good quality (Table 4.5). The most polluted tributaries were H1 and G1, with WQI > 21906. Spatially, these polluted tributaries are in the upstream of the sub basin, which in turn contaminates the entire stream.

Table 4.5: WQI Index for Mustafakemalpaşa Catchment Area.

Km <sup>1</sup>	SPN	Mar	July	Oct	Mean	Km	SPN	Mar	July	Oct	Mean
Emet Stream											
213	E26	186	158	146	163	42	E10	764	795	1363	974
205	E25	240	167	132	180	Br	M1	60	789	64	304
190	E24	209	204	124	179	40	E9	782	980	1250	1004
Br	A1	124	120	92	112	37	E8	710	984	6988	2894
176	E23	193	119	82	131	Br	F1	65	55	61	60
170	E22	163	101	97	120	Br	G1	23828	15313	26578	21906
161	E21	194	187	334	238		E8	495	404	503	467
160	E20	253	208	366	276	33	E7	5249	5268	7079	5865
159	E19	279	246	422	316	27	E6	404	441	551	465
Br	B1	62	52	49	54	21	E5	391	510	794	565
Br	C1	38	37	37	37	18	E4	425	796	1817	1013
Br	T1	62	64	54	60	14	E3	489	757	1411	886
Br	D2	59	59	51	56		H1				
	E18	353	396	484	411	11	E2	185	165	110	153
124	E17	577	374	504	485	0	E1	109	77	67	84
Br	D1	92	79	77	83	Orhaneli Stream					
Br	D3	61	63	92	72	0	K1	69	44	46	53
106.6	E16	491	335	529	452	17	K2	86	67	61	71
Br	A1	104	93	97	98	28	K3	218	162	114	165
	E15	504	466	555	508	34	K4	192	229	123	181
80.26	E14	478	274	447	400	42	K5	172	197	110	160
Br	J1	79	75	84	79	61	K6	195	198	134	176
Br	A2	91	80	90	87	105	K7	124	118	97	113
	E13	573	546	771	630	128	K8	154	128	106	129
Br	S1	162	124	152	146	143	K9	149	124	113	129
73.76	E12	559	537	805	634	154	K10	81	83	77	80
71.1	E11	472	405	558	478	200	K11	94	72	61	76
Br	P1	87	74	71	77	204	K12	122	84	73	93
Br	D3	61	63	92	72	0	K1	69	44	46	53

<sup>1</sup>Br stands for the branches or Tributaries feeding the main stream.

The water quality was monitored for spring (March), summer (July) and autumn (October). In October, the weather is characterized by rainy but warm conditions with an average flow rate of 17.4 m<sup>3</sup>/s, in the main Mustafakemalpaşa stream. In March, the weather is rainy and foggy with an average stream flow rate of 115 m<sup>3</sup>/s, in July the weather is hot and dry with a flow rate of 19.1 m<sup>3</sup>/s.

In general, the data obtained showed a spatial decrease in water quality downstream of both Mustafakemalpaşa and Orhaneli streams. This is attributed to the several point and non-point pollution sources in the catchment area.

In Emet stream, the main point sources of pollution in were identified as follows.

- Point G1 at about 33 km downstream, this is a tributary from a mine tailings dam with an estimated average flow rate of 0.37 m<sup>3</sup>/s. At this point, the average arsenic and boron pollutions were measured as 15586µg/L and 1514 mg/L respectively.
- Point H1 about 14 km downstream of Emet stream originating from the Hisarcik boron mine operation.
- Direct discharge of domestic wastewater near settlements of Emet and Hisarcik.

In Orhaneli stream, the main point sources of pollution in were identified as follows.

- Points E47 and E48 at Kütahya-Tavşanlı and Tunçbilek, respectively.

The Line plot of WQI along Emet and Orhaneli streams is presented in Figure 4.8. The Figure shows only sample points along the main stream course (excluding tributaries).

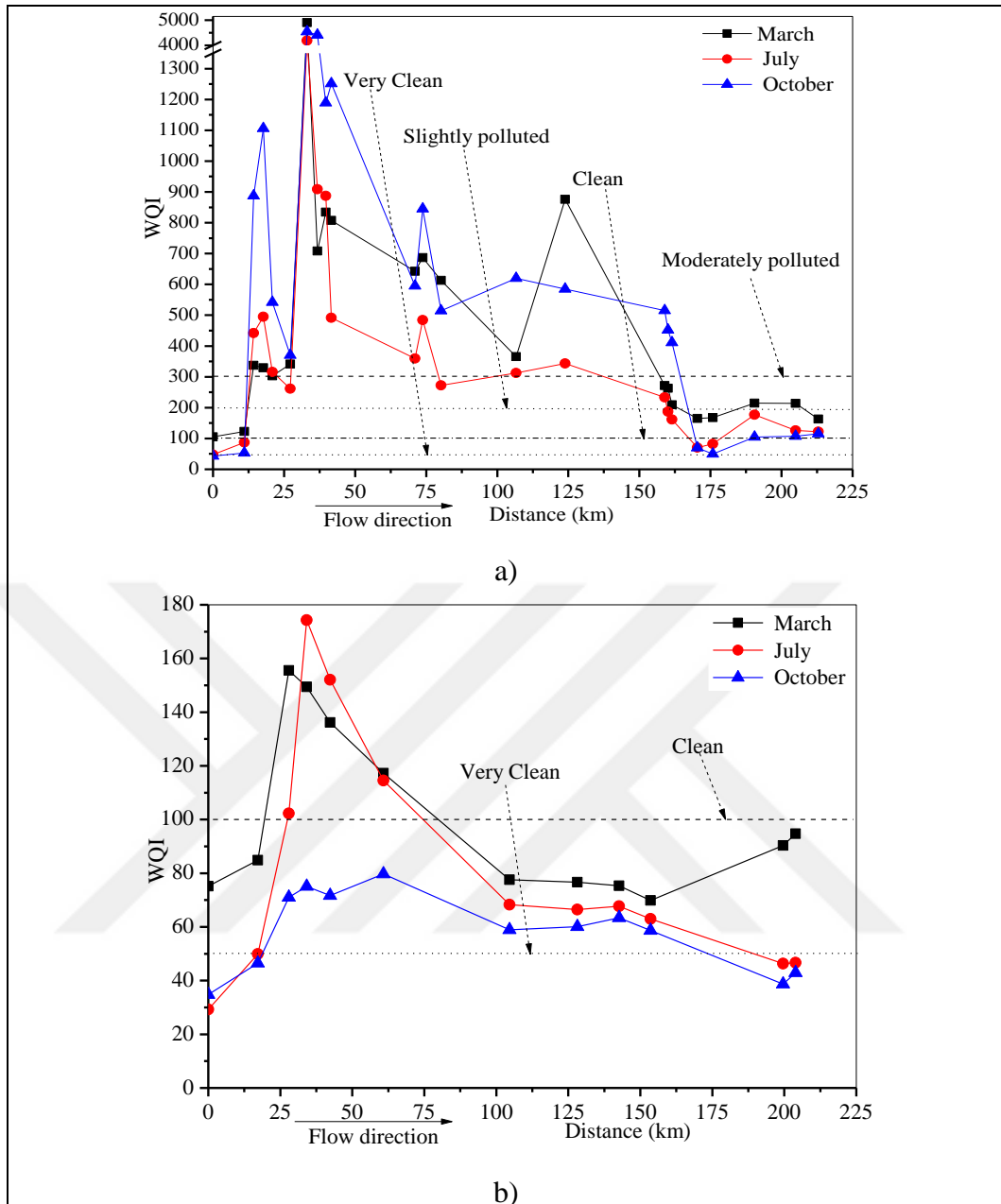


Figure 4.8: a) Line plot of WQI along Emet stream, b) Line plot of WQI along Orhaneli Stream.

The WQI trend for March was as follows; the WQI revealed heavily polluted water quality ( $WQI > 300$ ) from 14.3 km to 123.9 km along Emet stream, accounting for about 37.14% of the data. The moderately polluted water quality ( $200 < WQI < 300$ ) was revealed from 158.9-161.49 km (E19- E20) in Emet stream and 190.5 - 205 km (E24-E25) in Mustafakemalpaşa stream. The slightly polluted water quality represented 37.14% of the data points and was dominant in Orhaneli stream from K4 to K12 (34-142 km) and the points E22 and E23 (Mustafakemalpaşa stream). Water of

clean category ( $50 < WQI < 50$ ) was revealed only at upstream points of Orhaneli stream i.e. from 0 km to 17 km (K1 -K2) and points K10 and K11. The analysis did not reveal water of clean category ( $WQI < 50$ ) in March.

For the case of July, The WQI trend was as follows; the heavily polluted water quality ( $WQI > 300$ ) was dominant over the sampling points in stream reach from 14 to 124 km (E3 to E17) along Emet, except for point E14, accounting for about 34.3% of the data. The moderately polluted water quality represented 14% of the data points and was noted at points, E19, E20, E24 and K4. Slightly polluted water quality ( $200 < WQI < 300$ ) accounted for 37% of the data and was predominant at Mustafakemalpaşa stream (E22-E26) and in Orhaneli stream (K5- K9). Water of clean category ( $50 < WQI < 100$ ) was revealed at the most upstream points of the watershed (E1, K2 and K3) and the most downstream points of Orhaneli stream (K10-K12). The only point that showed water of clean category was point K1 in Orhaneli stream.

In October, the WQI trend was as follows; Heavily polluted water quality ( $WQI > 300$ ) was revealed from 14.3 - 161.5 km (E3-E21) along Emet stream, accounting for about 45.71% of the data. The moderately polluted water ( $200 < WQI < 300$ ) was not revealed. The slightly polluted water quality represented 28.57% of the data points and occurred in Mustafakemalpaşa stream (E24-E26) and predominated parts of Orhaneli stream from K4 - K9. Water of clean category ( $50 < WQI < 100$ ) represented 22.85% of the data points, and was revealed at the most upstream points of the catchment and most downstream points of Orhaneli stream.

In general; the highest WQI along Emet main stream showed extremely high peaks of 5249, 5268 and 7079 for the months of March, July and October respectively. All these peaks occurred at sampling point E7, at 33 km along Emet stream. The water quality rating at this point was highly influenced by arsenic and boron concentration. According to field observations and collected results, point E7 is in the immediate downstream of point G1 which is a highly polluted tributary with WQI of 23828, 15313 and 26578 for the sample campaigns of March, July and October, respectively and originating from a mine tailings dam site.

The WQI for Orhaneli tributary were high at sampling points K3 (28 km), K4 (34 km), K5 (42 km) and K6 (61 km) particularly for the samples taken in March and October. Unlike the case of Emet stream, the WQI rating in Orhaneli stream was dominated by DO and BOD. Sample points K3 to K6 are found in urban settlements without adequate wastewater treatment facilities hence domestic effluent is discharged

directly to the stream endangering water quality. The general trend in Water quality index is illustrated in Figure 4.9.

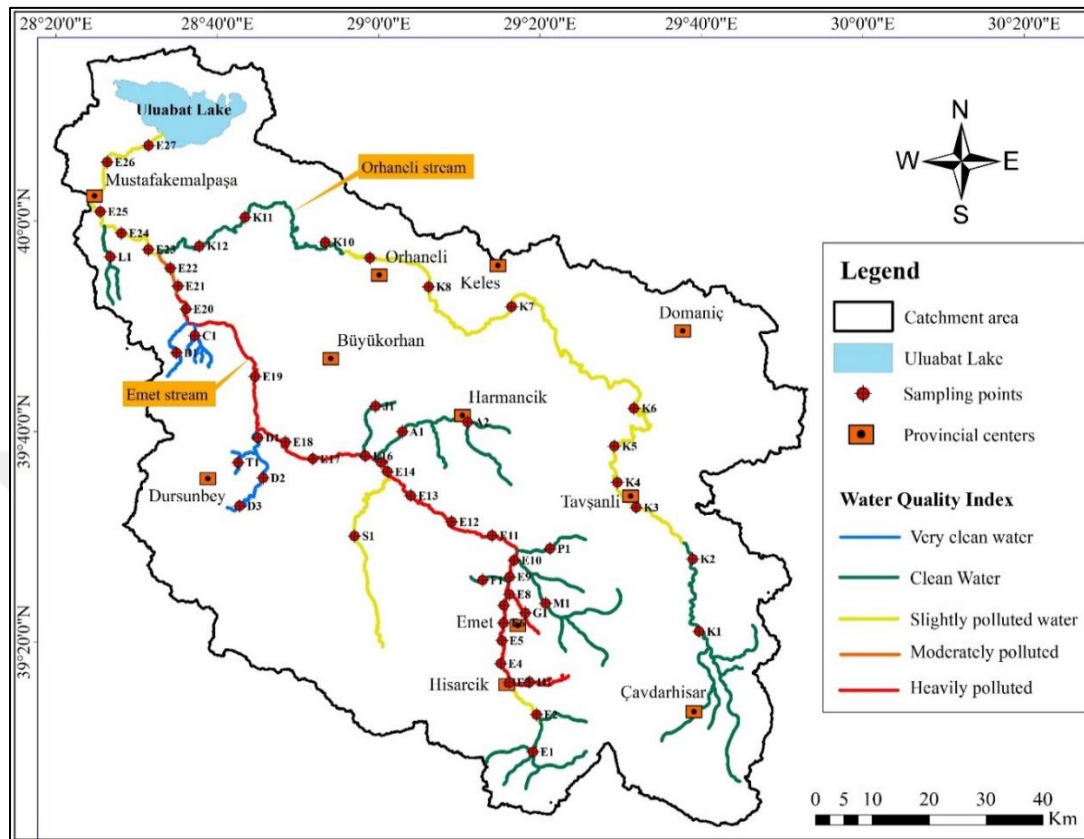


Figure 4.9: Spatial variation of Water Quality Index in the study area.

#### 4.3.2. Analysis of WQI with the Exclusion of Boron and Arsenic

The high levels of boron and arsenic measured in Emet stream prompted for analyses of WQI with their exclusion. Figure 4.10, Table 4.6 and Table 4.7 provide a comparative illustration of WQI with and without boron and arsenic. In the case of WQI without B and As, most of the sample points showed  $WQI < 200$ , suggesting that the stream water could be classified as slightly polluted. Consequently, the most upstream point E1 revealed a very clean characteristic ( $WQI < 50$ ). It should be emphasized that Orhaneli stream showed an overall better WQI, however, if boron and arsenic are eliminated, the WQI of the two streams are very similar, with both streams being stressed by low DO and high BOD at points near urban settlements due to discharge of untreated wastewater into the streams.

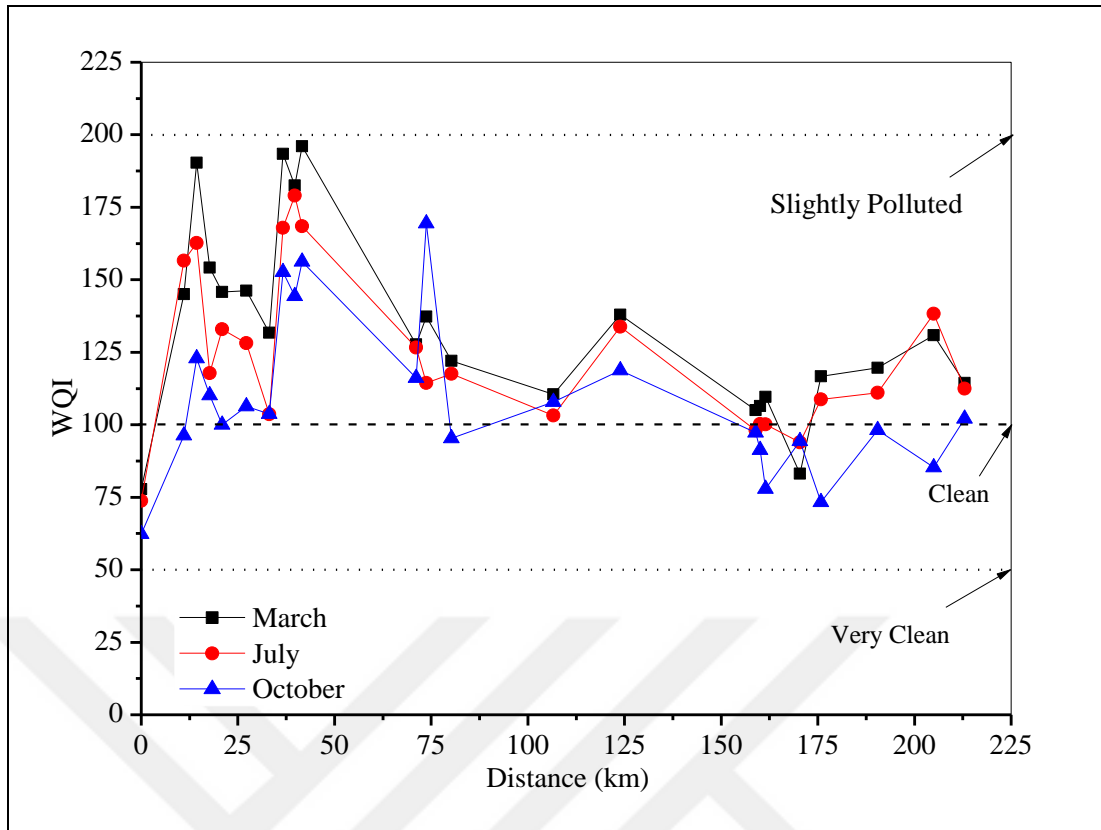


Figure 4.10: Evaluation of WQI without As and B.

Table 4.6: Comparison of WQI with and without arsenic and boron for Emet stream.

Length km	WQI Including B and As						WQI Excluding B and As				
	No.	Mar	July	Oct	Mean	Remark <sup>1</sup>	Mar	July	Oct	Mean	Remark
0	E1	109	77	68	85	clean	78	74	62	71	Clean
11	E2	185	165	126	159	SP	145	157	96	133	SP
14	E3	489	757	1424	890	HP	190	163	123	159	SP
18	E4	425	796	1849	1023	HP	154	118	110	127	SP
21	E5	391	510	819	574	HP	146	133	100	126	SP
27	E6	404	441	560	469	HP	146	128	106	127	SP
33	E8	5249	5268	7080	5866	HP	132	104	104	113	SP
37	E9	710	984	6995	2896	HP	193	168	153	171	SP
40	E10	782	980	1255	1006	HP	183	179	144	169	SP
42	E11	764	795	1363	974	HP	196	168	156	174	SP
71	E12	472	405	564	480	HP	128	127	116	123	SP
74	E14	559	537	773	623	HP	137	114	169	140	SP
80	E16	478	274	454	402	HP	122	118	95	112	SP
106	E17	491	335	516	447	HP	110	103	108	107	SP
124	E19	577	374	494	482	HP	138	134	119	130	SP

<sup>1</sup>SP for slightly polluted, MP for moderately polluted and HP for heavily polluted.

Table 4.6: Continued.

Length km	WQI Including B and As						WQI Excluding B and As				
	No.	Mar	July	Oct	Mean	Remark	Mar	July	Oct	Mean	Remark
159	E20	279	246	415	314	HP	105	98	97	100	clean
160	E21	253	202	360	271	MP	106	100	91	99	clean
161	E22	194	175	338	236	MP	110	100	78	96	clean
170	E23	163	101	92	119	SP	83	94	94	90	clean
175	E24	193	119	84	132	SP	117	109	73	100	clean
190	E25	209	204	121	178	SP	120	111	98	110	SP
205	E26	240	167	147	185	SP	131	138	85	118	SP
213	E27	186	158	144	163	SP	114	112	102	110	SP

<sup>1</sup>SP for slightly polluted, MP for moderately polluted and HP for heavily polluted.

Table 4.7: Comparison of WQI with and without As and B for Orhaneli stream.

Length km	WQI Including B and As						WQI Excluding B and As				
	No.	Mar	July	Oct	Mean	Remark <sup>1</sup>	Mar	July	Oct	Mean	Remark
0	K1	69	44	50	54	clean	51	41	48	47	Very clean
17	K2	86	67	65	73	clean	76	71	57	68	clean
28	K3	218	162	114	165	SP	105	89	70	88	clean
34	K4	192	229	170	197	SP	153	173	82	136	SP
42	K5	172	197	151	173	SP	132	140	74	115	SP
61	K6	195	198	132	175	SP	159	142	110	137	SP
105	K7	124	118	95	112	SP	113	114	94	107	SP
128	K8	154	128	111	131	SP	147	130	109	129	SP
142	K9	149	124	115	130	SP	144	127	115	129	SP
153	K10	81	83	79	81	clean	78	77	73	76	clean
199	K11	94	72	63	77	clean	83	76	57	72	clean
204	K12	122	84	75	94	clean	105	93	73	90	clean

<sup>1</sup>SP for slightly polluted, MP for moderately polluted and HP for heavily polluted.

The WQI results for the three field campaigns were subjected to one-way analysis on variance (ANOVA) and no significant difference in WQI data collected in summer, Autumn and Spring was revealed. The Means Comparisons (Tukey Test) showed that the seasonal variations in WQI were not significantly different at 0.05 levels (95% confidence). The mean WQI for the field campaigns of March, July and October were 441.73, 445.07 and 774.03, respectively. The lowest mean WQI difference of 70.29 was noticed between July and March whereas the highest mean

difference of recorded between October and July as 229.74. This follows the same trend as the stream flow characteristics.

### 4.3.3. Relation Between Stream Flow and WQI

The correlation between WQI and stream flow for October, July and March are shown in Figure 4.11, Figure 4.12 and Figure 4.13, respectively. The Pearson correlation coefficient was computed for the samples along Emet stream starting from point E11 (70.1 km) after input from the points pollution sources H1 and G1. The Pearson correlation coefficient between WQI and stream discharge for October was -0.95 ( $p < 0.001$ ). The Pearson correlation coefficient between WQI and stream discharge for July was -0.86125 ( $p < 0.001$ ). For samples collected in March, the Pearson correlation coefficient between WQI and stream discharge was -0.93151 ( $p < 0.001$ ). Overall, there is a very strong negative correlation between the WQI and stream flow. The strong negative correlation suggests that the relatively low pollutant concentrations measured downstream are because of dilution due to inflows from less polluted tributaries. Stream discharge greatly influenced the concentration of monitored parameters. During March, the highest discharge is experienced and accordingly the worst WQI was recorded, this could be due to increased pollutant leaching from geologic sources.

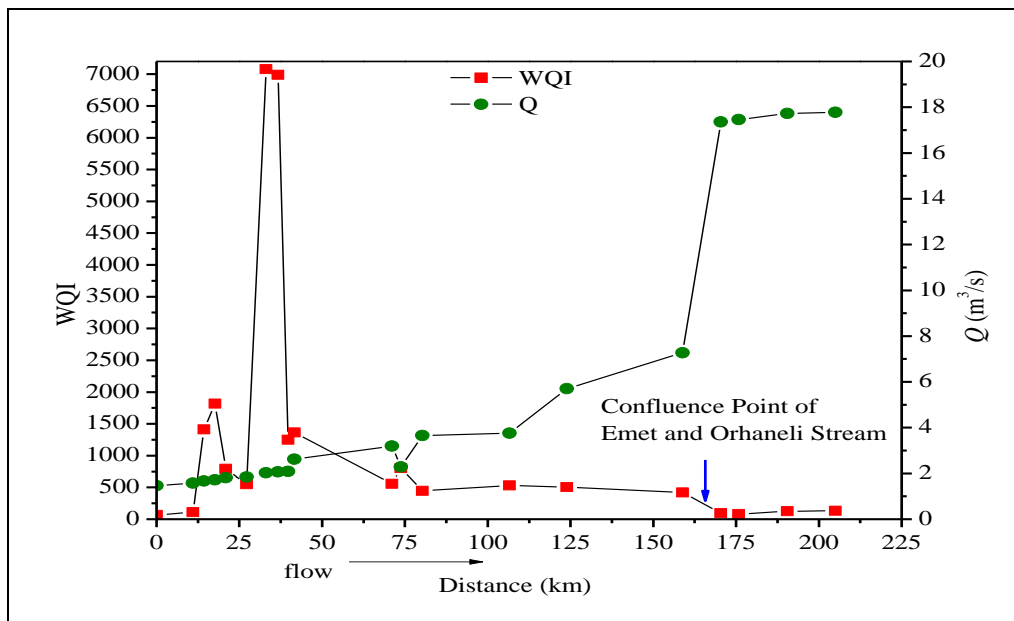


Figure 4.11: Correlations between WQI and Stream Discharge for October.

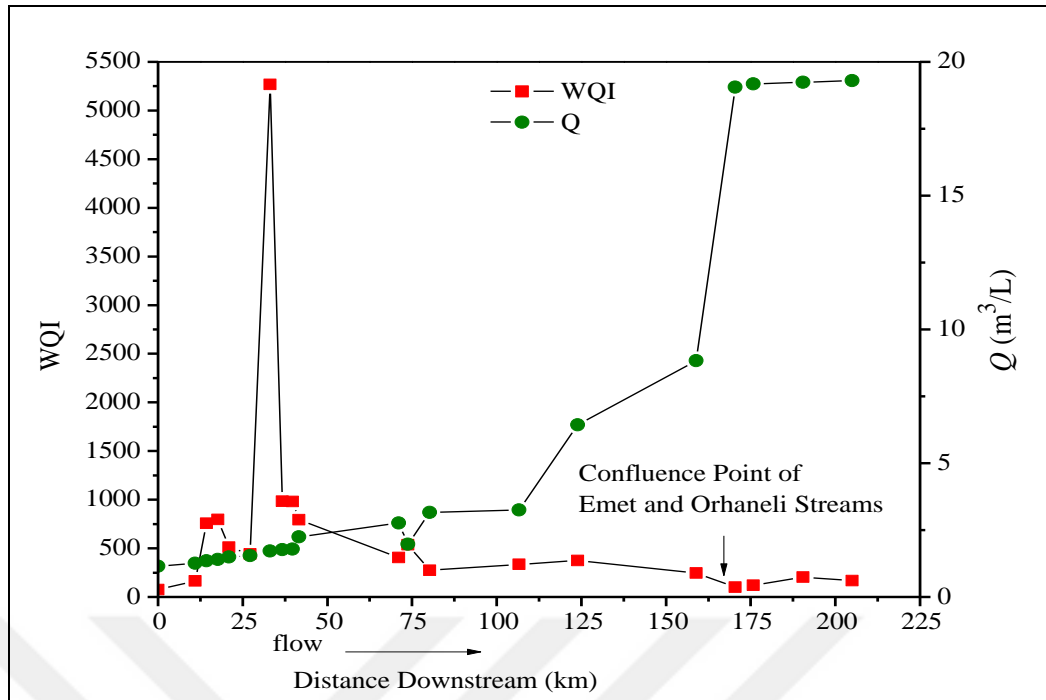


Figure 4.12: Correlations between WQI and Stream Discharge for July.

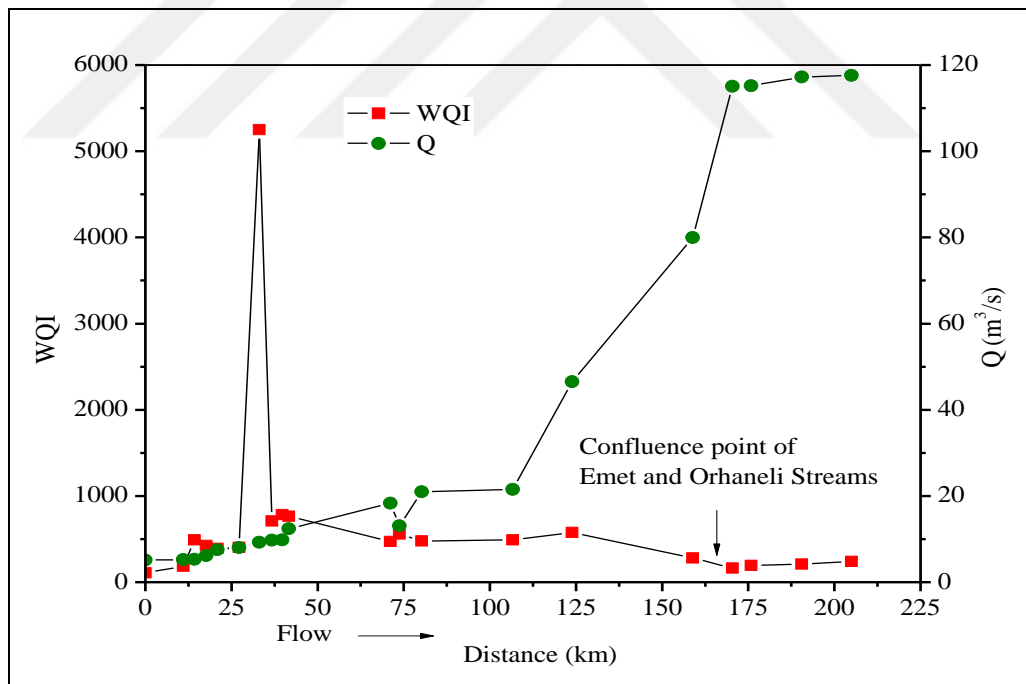


Figure 4.13: Correlations between WQI and Stream Discharge for March.

The WQI in July and October were related due to the similar stream flow characteristics between these two months.

## 4.4. Multivariate Statistical Analysis

### 4.4.1 Principal Component Analysis (PCA)

Principal Component Analysis was used as a parameter reduction technique after normalising the data. PCA aids in establishing the most important parameters that explain the variation in water quality dataset and in identifying the possible sources of pollution. In PCA technique, the environmental factors are chosen based on absolute factor loadings and variance among principal components [Naiman et al., 2009], [Primpas et al., 2010]. The PCA results are shown in Table 4.8 (Varimax rotation), five components were extracted based on eigen value > 1, the five extracted components accounted for 81.23% of total variance in the original data.

Table 4.8: Rotated component matrix loading and their respective possible sources.

Parameters	PC1	PC2	PC3	PC4	PC5
B	0.944				
As	0.943				
SO <sub>4</sub>	0.943				
Cl	0.915	0.311			
TDS	0.895				
Ca	0.842				
Na	0.725	0.410			
Mg	0.635	0.420			
Si		0.764			
TOC		0.708			
Fe			0.795		
NO <sub>3</sub>			0.712		
K		0.440	0.555		0.480
DO	-	-	-	0.896	-
pH	-0.305	-	-	0.828	-
TP	-	-	-	-	0.793
Total	6.289	1.893	1.840	1.746	1.229
% of Variance	39.308	11.831	11.498	10.910	7.680
Cumulative %	39.308	51.138	62.637	73.547	81.227

The rotated component matrix (Varimax with Kaiser Normalization) from PCA analysis for the annual mean of the data sets is presented in Table 4.8. The variables that correlated positively with Principal Component one (PC1) were B, As, SO<sub>4</sub>, Cl, TDS, Ca, Na and Mg, and accounted for 39.3% of the total variance in the dataset. This suggests that these elements are of the same anthropogenic origin associated with the catchment like mining of boron, Chromium, magnesite lignite and pollution from agricultural pesticides and fertilisers. Geological factors such as abundant hot springs, coal rocks and Igneous rocks may also account for the arsenic pollution. The variables that highly loaded in Principal Component two (PC2) were Si and TOC and accounted for 11.83% of variance in the data. The variables that highly loaded in Principal Component three (PC3) were Fe and NO<sub>3</sub> and accounted for 11.5 % of variance in the data. The variables that highly loaded in Principal Component four (PC4) were DO and pH, and accounted for 10.9 % of variance in the data. PC5 had high loading coefficient for only TP and accounted for 7.6% of the variance in the data set. This therefore suggests that the source of TP in water was different from the other elements and this cluster can be classified as eutrophic cluster. Moreover, TP did not show any significant Pearson correlation coefficient with other elements analyzed. The sources of phosphorous in Mustafakemalpaşa catchment area are both diffuse and point discharges. The main diffuse sources of phosphorus pollution may be from application of phosphorous fertilizers in the agricultural fields that drain to the streams and its tributaries.

#### **4.4.2. Pearson Correlation Analyses**

The interrelationship between the parameters in this study was done through Pearson correlation analyses (Table 4.9). The matrix was generated for 12 parameters (As, B, Ca, DO, Mg, Na, TDS, TP, TOC, Cl, Fe, Si, NO<sub>3</sub>, SO<sub>4</sub>) using mean annual concentrations. The results indicate strong positive correlations (at  $p < 0.05$ ) between As and B ( $r^2 = 0.939$ ), As and SO<sub>4</sub> ( $r^2 = 0.906$ ), B and Cl ( $r^2 = 0.975$ ), As and Cl ( $r^2 = 0.906$ ), Ca and SO<sub>4</sub> ( $r^2 = 0.89$ ), NO<sub>3</sub> and SO<sub>4</sub> ( $r^2 = 0.781$ ). The strong positive correlations among the elements suggests a similar anthropogenic origin.

Table 4.9: Correlation matrix for the physiochemical parameters in water samples.

	As	B	Ca	DO	Mg	TDS	TP	TOC	Fe	Si	NO <sub>3</sub>	SO <sub>4</sub>
As	1											
B	.939 <sup>1</sup>	1										
Ca	.816 <sup>1</sup>	.745 <sup>2</sup>	1									
DO	-0.095	-0.070	-0.161	1								
Mg	.543 <sup>2</sup>	.623 <sup>2</sup>	.344 <sup>1</sup>	0.054	1							
TDS	.841 <sup>2</sup>	.845 <sup>2</sup>	.838 <sup>2</sup>	-0.155	.714 <sup>2</sup>	1						
TP	-0.038	-0.028	-0.036	0.107	-0.110	-0.102	1					
TOC	.355 <sup>2</sup>	.409 <sup>2</sup>	0.039	-0.062	.418 <sup>2</sup>	.270 <sup>1</sup>	0.014	1				
Fe	0.247	0.196	.516 <sup>2</sup>	-0.124	0.087	.364 <sup>2</sup>	-0.163	-0.002	1			
Si	0.257	.350 <sup>2</sup>	0.170	-0.007	.383 <sup>2</sup>	.343 <sup>1</sup>	0.056	.313 <sup>1</sup>	-0.071	1		
NO <sub>3</sub>	-0.067	-0.117	0.192	-0.046	-0.016	0.168	-0.175	-0.087	.377 <sup>2</sup>	-0.117	1	
SO <sub>4</sub>	.906 <sup>2</sup>	.912 <sup>2</sup>	.890 <sup>2</sup>	-0.085	.590 <sup>2</sup>	.912 <sup>2</sup>	-0.086	.282 <sup>1</sup>	.447 <sup>2</sup>	0.239	0.179	1

<sup>1</sup>P < 0.05 (2-tailed), <sup>2</sup>P < 0.01 (2-tailed).

#### 4.4.3. Cluster Analysis for Water Dataset

The dendrogram for hierarchical Cluster analysis of WQI is shown in Figure 4.14. Five clusters were extracted. Cluster I is the largest cluster with 19 sample points (54 %). The locations in this cluster included all the points in Mustafakemalpaşa stream and Orhaneli stream, and the two most upstream points E1 and E2 (at 0 and 11 km) in Emet stream. This cluster contained mostly points with WQI < 150 which is water considered to be relatively clean. The relatively low value of WQI in Mustafakemalpaşa stream is attributed to dilution of pollutants from Emet stream by the high discharge of low polluted Orhaneli stream at confluence points. Moreover, analysis between WQIs and stream flow for all the three sampling periods indicated a very strong negative Pearson correlation coefficient ( $R^2 = -0.85 - 0.92$ ). Cluster II is the second largest cluster with 8 sample points (23 % of data). The points in this cluster were E5 (20.9 km), E6 (27.2 km), E11(71.1 km), E19 (158.9), E20 (160.1), E21 (161.49). The WQI for this cluster was in the range of 260 - 420. This cluster is in a stream course dominated by mining of lignite, chromium, manganese, iron and marble, the anthropogenic influence on this part of the watershed is partly responsible for the high WQI, the water at these points were highly turbid with mean arsenic pollution ranging from 100 - 400 µg/L. Cluster III has 5 sample points (E4, E9, E10, E13 and E17) representing 14% of data. All the points in cluster III are in areas dominated by pollutant inputs from point sources including discharges from mine tailing dams and discharge of domestic waste water from urban settlements of Emet and Hisarcik. In

addition to the intense mining activities and domestic wastewater discharges, the stream reach here has numerous inflows from hot springs with high arsenic content of geological origin [Dogan and Dogan, 2007], [Çolak et al., 2003] the points E3 and E4 in cluster III are located near Hisarcik town and downstream of a polluted tributary (H1) with high average arsenic and boron concentrations of about 4557  $\mu\text{g/L}$  and 98 mg/L, respectively. Furthermore, domestic waste water from the town of Hisarcik is discharged to the stream near this point, which reduces DO and increases BOD, the DO and BOD at these points ranged from 4.5 - 6.5 and 9 -13, respectively. Cluster IV and V have one sample point each, point E8 in cluster 4 and point E7 in cluster 5 are just 3.6 km apart, with point E7 being upstream. Field observations identified a major polluted tributary (G1) from a mine tailings dam, with extremely high mean annual arsenic and boron concentration of 15586.67  $\mu\text{g/L}$  and 1514.7 mg/L, respectively discharging upstream of point E7.

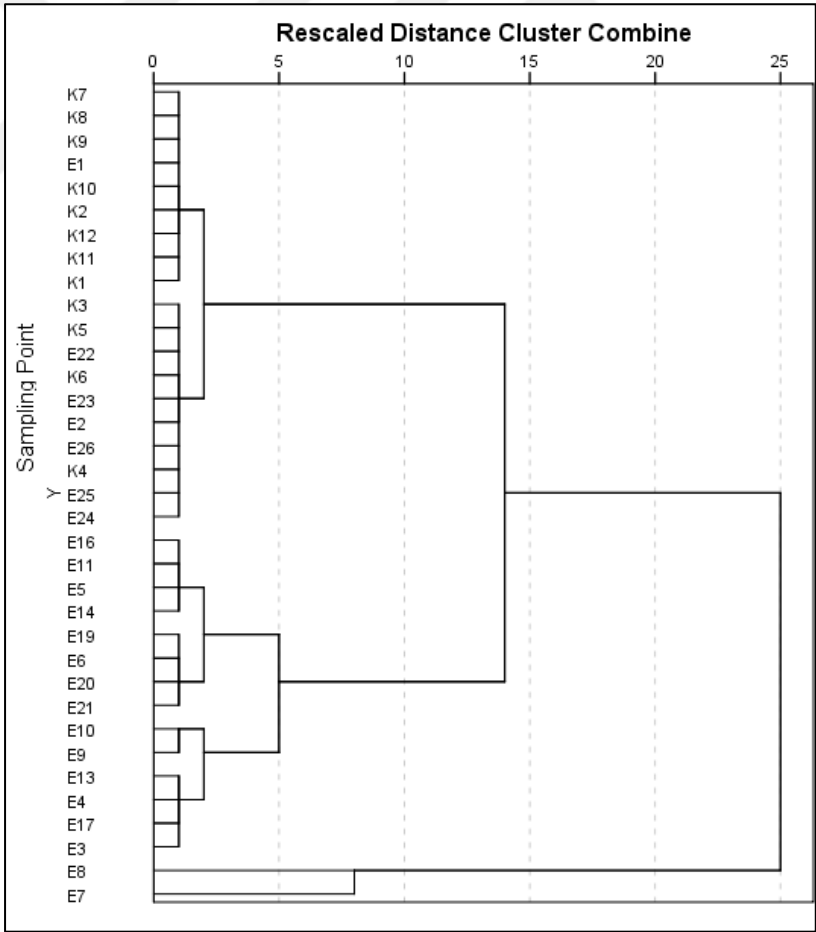


Figure 4.14: Dendrogram of WQI Cluster Analysis.

## 4.5. ANALYSIS OF SEDIMENT QUALITY

In this study, the degree of sediment contamination has been analyzed through the calculations and interpretation of contamination factor (CF), geoaccumulation index ( $I_{geo}$ ), Enrichment factor (EF), pollution load index (PLI) and Sediment Quality Guidelines (SQGs).

### 4.5.1. Metal Contamination in Sediment

Basic statistical analyses and pollution levels for heavy metals and other parameters analyzed in this study are presented in Table 4.10 and Figure 4.15. A research by Tokatlı et al [2014] on surface sediment of Emet basin revealed seasonal average concentrations in the range of 22.3- 332.1 mg/kg for Cr, 217.9-437.9 mg/kg for Mn and 15.2 – 187.63 mg/kg for Ni. In comparison with results obtained in this study (Table 4.10), these heavy metal concentrations have rapidly increased. This could be explained by the expansion of mining activities.

Table 4.10: Basic statistics for heavy metals and other parameters in sediment.

	Min	Max	Mean	Median	Range	Std. dev.
Ag	0.53	9.67	2.45	1.63	9.13	2.08
Cd	4.33	46.36	8.78	6.83	42.03	7.06
Co	6.88	64.88	18.56	15.37	58	11.24
Cr	104	3714	516	353	3611	569
Cu	11.6	49	26.19	24.2	37.4	9.21
Mo	4.5	33.87	12.65	11.31	29.37	6.39
Ni	31.23	1,243	274	176	1,212	259
Pb	16.07	275.8	65.59	53.13	259.73	52.33
Zn	45.2	870.07	110.06	82.07	824.87	120.85
B	7,086	124,871	23,535	16,782	117,785	22,072
Ba	74.93	450.67	213.54	222.73	375.73	75.25
Ca	2,445	39,094	13,757	12,639	36,649	7,428
Fe	7288	40843	18815	17185	33555	6899
K	7,439	43,048	16,246	16,715	35,609	5,706
Mg	299	10234	1828	1252	9935	1751
Mn	264	972	550	567	708	145
Na	10,849	137,069	28,059	21,007	126,220	22,765
As	15	1542	154	75	1528	239
Al	3,825	60,381	10,608	9,102	56,555	10,253

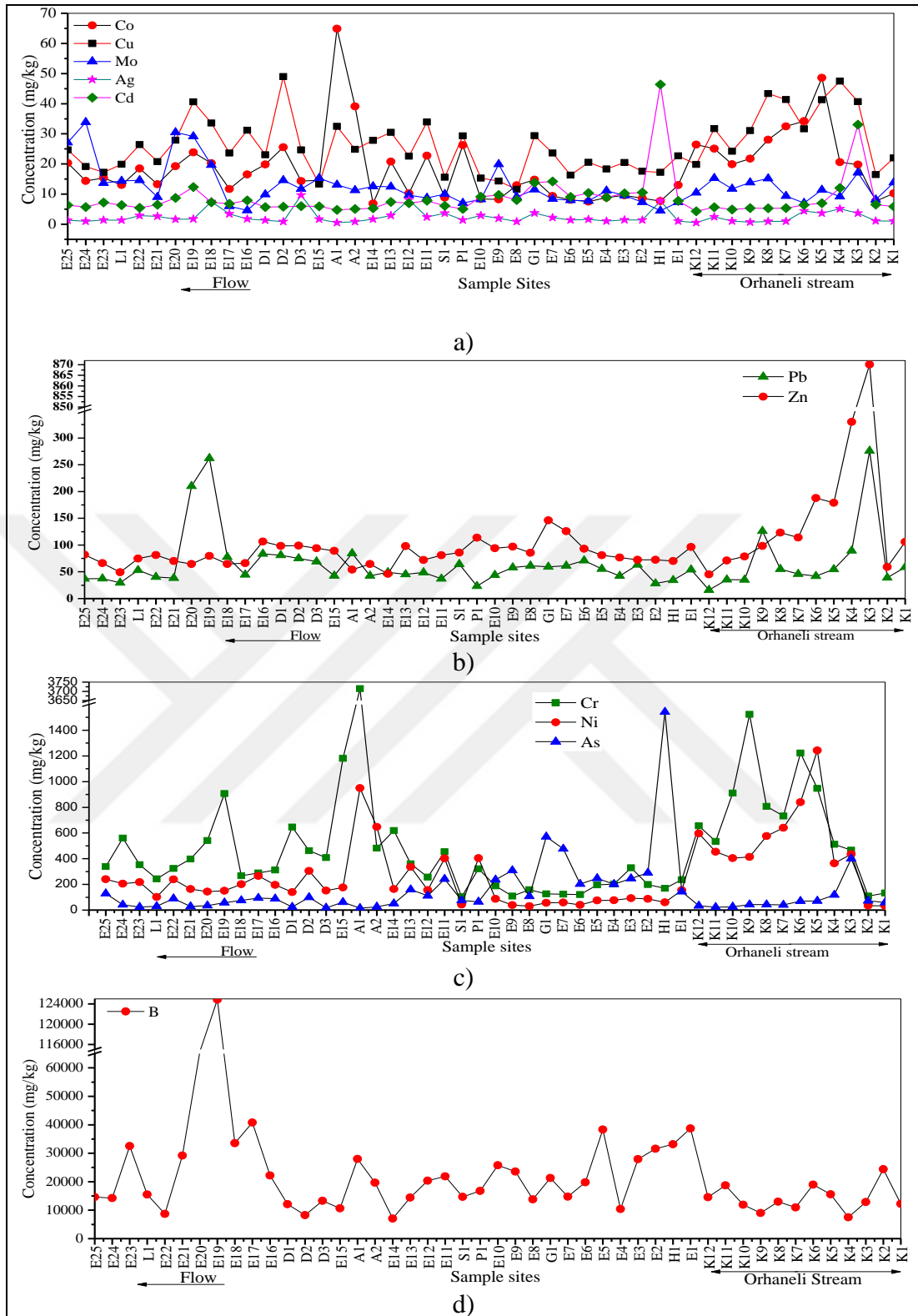


Figure 4.15: a) Co, Cu, Mo, Ag and Cd distribution, b) Pb and Zn distribution, c) Cr Ni, As distribution, d) B distribution in surface sediment.

The extremely high As and B is linked to the geology of the region. Previous studies in this region revealed high arsenic and boron concentrations in water resources around boron deposit areas of Kutahya-Emet, Hisarcik, Eskisehir-Kirka and Balikesir-

Bigadic [Yüce and Yasin, 2012], [Gemici et al., 2008], [Dogan and Dogan, 2007], [Colak et al., 2003]. However, anthropogenic activities that involve excavations and disturbance of the earth crust may have intensified their dissolution into surface waters and streams.

#### 4.5.2 Contamination Factor (CF) and Pollution Load index (PLI)

The contamination factor is an index that assesses the level of sediment pollution by metals. It's a ratio between the element concentration at the sampling site and the background value or reference value [Qingjie et al., 2008]. The contamination factor was calculated from equation (4.4).

$$CF = \frac{C_{heavy\ metal}}{C_{background}} \quad (4.4)$$

Where;  $C_{heavy\ metal}$  = metal concentration at sampling site,  $C_{background}$  = background concentration of the metal at the site. The choice of background values is very important in the interpretation of geochemical data. Currently, the background values of the metal concentrations in the study area are not available. Most studies have used the average crustal abundance data or the lowest mean annual concentrations of the elements as reference values [Zhao et al., 2017], [Erol et al., 2016], [Varol and Sen, 2012]. For the present study, the background values were computed from raw trace element data of surface sediments after eliminating the anomalously high concentrations of elements corresponding to contamination and calculating the statistical mean and standard deviation. The CF results were interpreted as follows [Hakanson, 1980], [Islam et al., 2015]: low contamination for  $CF < 1$ , moderate contamination for  $1 < CF < 3$ , considerable contamination for  $3 < CF < 6$  and very high contamination for  $CF > 6$ . Subsequently, the Pollution Load Indices (PLI) were calculated from CFs. PLI is a simple way of assessing heavy metal pollution levels, it shows general toxicity state of the site for the elements considered. The pollution index for the entire sample site was calculated from the equation (4.5) below [Maanan et al., 2015].

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \quad (4.5)$$

Where; n is the number of heavy metal parameters taken in the computation for the site of interest. The interpretation of PLI is as follows;  $PLI > 1$  indicates polluted and  $PLI < 1$  means no pollution.

The results of CF and PLIs for the analyzed heavy metals and other elements in surface sediment sample are presented in Table 4.11 and Table E1.1. The mean CFs values for Ag, Cd, Co, Cr, Cu, Mo, Ni, Pb, Zn, B and As were determined as 1.50, 1.28, 1.21, 1.46, 1.08, 1.12, 1.55, 1.23, 1.34, 1.40 and 2.05, respectively. The general CF trend for elements of focus in this study was  $As > Ni > Ag > Cr > B > Zn > Cd > Pb > Co > Mo > Cu$ . High contamination ( $CF > 6$ ) was revealed by Cd (at site H1), Zn (at sites K3) Cr (at site A1) and Ni (at site K5). Overall, sites near urban settlements were more polluted than those in rural settings or far away from settlements areas. This strongly indicates the influence of anthropogenic activities on soils and streams. Arsenic showed high CF in all samples collected from tributaries of mining sites. Literature studies in the region indicate that the Neogene borate-bearing clay unit, which contains some arsenic minerals such as realgar ( $AsS$ ) and orpiment ( $As_2S_3$ ) found in colemanite ( $Ca_2B_6O_{11} \cdot 5H_2O$ ) nodules, are responsible for the arsenic contamination [Dogan and Dogan, 2007], [Colak et al., 2003].

The pollution load indices varied from 0.64 - 2.52 (Figure. 4.16). Moreover, 57% the sites revealed high polluted status ( $PLI > 1$ ). Sediments samples from sites E22, E21, A1, E12, K3, K5 and K6 revealed high PLI ( $> 1.4$ ). All these sites are very close to coal mines (Figure. 4.17), Cr mines, and sites receiving large amounts of untreated domestic wastewaters.

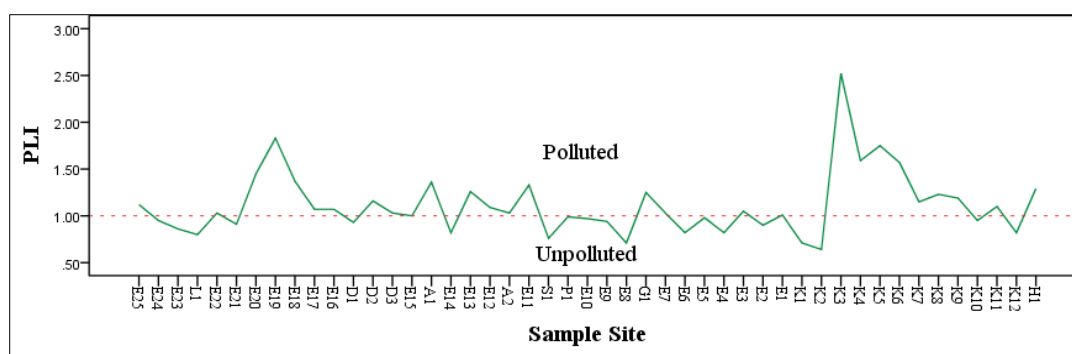


Figure 4.16: PLIs for surface sediment in Mustafakemalpaşa catchment, the dotted line separates the polluted and non-polluted region.

Sites E21 and E22 are in the immediate downstream of Devecikonağı dam close to Devecikonağı Coal Mining, and many marble cutting-machining operating exist near this point, on the edge of Emet Stream. Coal mining removes coal seams which may cause surface subsidence. Subsequently, as water flows through the subsidence, it dissolves contaminants, transports and deposits them in sediments downstream (Wright and Ryan, 2016).

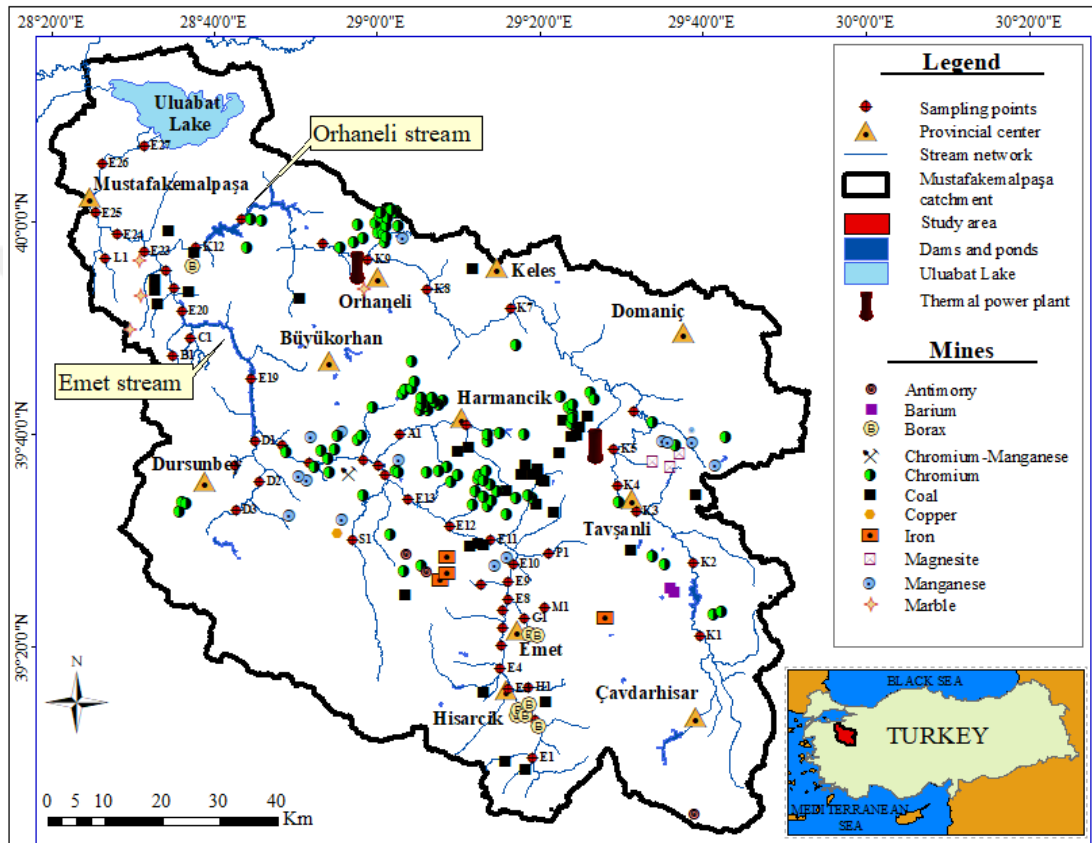


Figure 4.17: Mining sites in Mustafakemalpaşa catchment area.

Point A1 is a tributary from part of the catchment where most intense mining of coal and chromium is exhibited. Moreover, previous studies identified Harmancık chromium mines as the main inorganic pollution source for the ecosystem [Tokatlı et al., 2014]. Point E12 is in Emet main stream reach and similarly receives water from tributaries of sub catchments with mining of chromium, coal, iron and antimony. The elements that greatly influenced the PLI at this point were Ag, Ni and As with CFs of 1.47, 2.28 and 3.23, respectively. Depending on the mineralogical composition of the ores and the mining technology employed, these elements are usually washed away from the mining sites by runoff into streams and subsequently accumulate in the

sediments. Generally, the PLIs exhibited lower patterns in areas of high stream velocity compared to areas of low stream velocity, even if major pollutant input routes existed. This could be because spatial distribution of metals is largely influenced by their sources and hydrodynamic conditions of the stream reach [Wang et al., 2015; Han et al., 2016]. Another factor to consider in sediment pollution is the land cover and land use dynamics. The land cover map of the study areas is presented in Figure 2.14 of Chapter 2.

Table 4.11: Contamination factors (CFs) and Geo-accumulation Index ( $I_{geo}$ ).

	Contamination Factor				Geo-accumulation Index					
	Min	Max	Mean	Range	Element	Min	Max	Mean	SD	Median
Ag	0.33	5.92	1.5	5.59	Ag	-0.78	3.4	1.03	1.01	0.83
Cd	0.63	6.78	1.28	6.15	Cd	4.3	7.72	5.12	0.65	4.96
Co	0.45	4.22	1.21	3.77	Co	6.14	9.38	7.36	0.76	7.3
Cr	0.29	10.52	1.46	10.23	Cr	14.57	19.74	16.4	1.12	16.34
Cu	0.48	2.02	1.08	1.55	Cu	7.55	9.63	8.64	0.5	8.61
Mo	0.4	3	1.12	2.6	Mo	5.08	8	6.43	0.63	6.41
Ni	0.18	7.04	1.55	6.87	Ni	11.84	17.16	14.36	1.39	14.34
Pb	0.3	5.19	1.23	4.89	Pb	9.15	13.25	10.92	0.78	10.88
Zn	0.55	10.6	1.34	10.05	Zn	11.27	15.54	12.28	0.7	12.13
B	0.42	7.44	1.4	7.02	B	26.24	30.38	27.65	0.86	27.48
As	0.2	20.56	2.05	20.36	As	9.52	16.24	12.06	1.46	11.87

### 4.5.3. Geoaccumulation Index ( $I_{geo}$ )

The geoaccumulation index ( $I_{geo}$ ) was first proposed by Muller [1969], and is widely used by many researchers in sediment quality analysis to assess the levels of heavy metal pollution [Saleem et al., 2015]. The geoaccumulation index in this study was calculated from the following equation [Yu et al., 2011].

$$I_{geo} = \text{Log}_2 \left( \frac{C_n}{1.5B_n} \right) \quad (4.6)$$

Where;  $C_n$  = concentration of metal n in the sediment and  $B_n$ =background value of element in the background sample. The factor 1.5 is to cater for variations in the background values. The interpretation of  $I_{geo}$  was as follows [Malvandi, 2017].

Table 4.12: Interpretation of geoaccumulation index.

<i>Value</i>	<i>Interpretation</i>
$I_{geo} < 0$	Uncontaminated
$0 \leq I_{geo} \leq 1$	Uncontaminated to Moderately contaminated
$1 \leq I_{geo} \leq 2$	Moderately contaminated
$2 \leq I_{geo} \leq 3$	Moderately to heavily contaminated
$3 \leq I_{geo} \leq 4$	Heavily contaminated to extremely contaminated
$5 < I_{geo}$	Extremely contaminated

The results of geo-accumulation indices are presented in Table 4.11 and Table D1.1. Most  $I_{geo}$  values for Ag were less than 1, indicating uncontaminated to moderately contaminated status. The highest  $I_{geo}$  values (mean  $I_{geo} > 10$ ) were exhibited by Cr, Ni, Pb, Zn, B and As, and this occurred in urban settlements and near coal and chromium mining sites, which agrees with EF and CF results. In mining dominated watersheds, minerals associated with mine wastes dissolve in the waters and accumulate in the sediments downstream overtime [Ali et al., 2018], [Wright et al., 2016]. Arsenic and boron  $I_{geo}$  values ranged from 9.52 – 16.24 and 26.24 – 30.38, respectively.

Arslan [2013] determined boron levels in the sediments of the two streams (Emet and Orhaneli) to vary between 18.05 and 36.7 mg/kg. Borate mine operations have increased in the past years, especially in Emet stream. The leachates from borate mine (colemanite) operations is collected in big tailings ponds built near streams, this is also a potential risk for both water and sediment pollution. Since boron, arsenic, and other minerals in the borate mining wastes are easily soluble in water, they dissolve after contact with runoff in the tailing area and drain into the streams, and are later absorbed into the sediments.

#### **4.5.4. Enrichment Factor (EF)**

The metal enrichment factor is usually applied for assessment of anthropogenic and geogenic activities on sediment quality. The EF is expressed as follows [Sinex and Wright, 1988], [Alkan et al. 2015].

$$EF = \frac{\left(\frac{M_e}{Al}\right)_{Sample}}{\left(\frac{M_e}{Al}\right)_{Background}} \quad (4.7)$$

Where;  $M_e$  represents the concentrations of metals in the sample, Al is concentration of background or reference material. Many studies suggest the use of either Fe or Al as a conservative material in the determination of EF [Erol *et al.*2016]. In this study, Al was taken as the reference material. The “

The Enrichment factor for heavy metals and other parameters analyzed in this study are shown in Appendix F. Extremely severe enrichment factor ( $EF > 50$ ) and very severe enrichment factor ( $25 < EF > 50$ ) were not revealed in all the sampling sites. Most of the sampling sites exhibited moderate to severe enrichment ( $3 < EF > 25$ ). Extreme EF values for Ag, Cd, Cu, Ni, Pb and Zn were predominant over sample sites K3, K5 and K6 in urban settlements of Tavşanlı, Tunçbilek and Muhaciler, respectively, which discharge untreated effluent into the stream. Arsenic showed moderate to severe enrichment factor ( $3 < EF > 25$ ) mostly in the sediments of Emet stream at sites H1, G1, E8 and E2 (Table F1.1). The high arsenic concentration at these sites is attributed to polluted tributaries G1 and H1 both originating from boron mine tailing dams. Moderately severe Ni enrichment in Orhaneli stream was predominant from sample sites A1 and K4 - K11. Studies on the fly ash samples of Tunçbilek coal-fired power plant (Figure. 4.17) located near these sampling points obtained concentrations of Pb, Cd, Cr, Cu, Ni, Zn, Co, and Mn in fly ash samples as 16.4, 1.95, 296.7, 34.8, 515, 262.2, 46.8, and 690.6 mg/kg, respectively [Turkmenoglu, 2010]. Ni levels were also high at tributaries from Cr mines. Therefore, fly ash pollution and Cr mines may be partly responsible for the severe Ni enrichment at these points. All the points showed minor or no enrichment for Mo, B, and Co suggesting their presence in sediment was majorly from the general geology of the catchment.

#### **4.5.5. Sediment Quality Guidelines (SQG) and Ecological Risk**

Several sediment quality guidelines have been proposed in literature. Probable effect concentrations PEC and the threshold effects level (TEL) presented in Table 4.13 [MacDonald and Ingersoll, 2002] were used due to unavailability of sediment quality regulations for the study area. TEL indicates the concentration below which

adverse effects can rarely occur whereas PEL shows the concentration above which adverse effects are expected to frequently occur [Smith *et al.*, 1996].

All As values were above TEL, the minimum value of As was 14.73, which is about 2.5 times the TEL. Moreover over 97% of the sampling points exceeded arsenic PEL of 17 mg/kg, this can pose potential negative impact to the biota within the catchment. Similarly, all the sampling points revealed Cr concentrations above PEL. The Cr concentration in the collected samples ranged from 103.53 to 3714.20 mg/kg (mean of 515.95 mg/kg) with the highest Cr concentration revealed by sampling points E19, A1 and K6. Pollution of Cr in the catchment is attributed to the presences of chrome mines and deposits. The results for Cd also revealed sediment contamination above the PEL, and ranged from 4.33 to 46.36 mg Cd/kg (mean of 8.78 mg/kg). Particularly, highest Cd levels were seen at points H1, K3, E8, E23, G1 and K4. Most of the Cu values were below TEL and PEL, meaning less risk to biota. About 93% of the sampling points exceeded TEL for Pb and only 8.5% exceeded its PEL. All the Ni levels were above PEC except at upstream point K1. Zn levels were below TEL at most of the points except at points G1, E9, K3, K4 and K5.

Table 4.13: Sedimnet Qulaity Guidelines.

SQGs	Elements (mg/kg)						
	As	Cd	Cr	Cu	Pb	Ni	Zn
TEL <sup>1</sup>	5.9	0.596	37.3	35.7	35	18	123
PEC <sup>2</sup>	17	3.53	90	197	91.3	36	315

<sup>1</sup>Threshold effect level; dry weight.  
<sup>2</sup>Probable effect level; dry weight [Smith et al. 1996].

#### 4.5.6. Pollution Source Identification of Elements in Sediment

The Pearson correlation matrix (Table 4.14), principal components analyses, and hierarchical cluster analyses were used to show the interrelation between the elements and aid in identifying the possible origin of sediment pollution.

Table 4.14: Pearson correlation matrix (PCM) for elements in sediment.

	Ag	Cd	Co	Cr	Cu	Mo	Ni	Pb	Zn	B	Fe	As	Al
Ag	1												
Cd	0.38	1											
Co	-0.14	-0.23	1										
Cr	-0.19	-0.19	0.770	1									
Cu	0.08	0.002	0.577	0.313	1								
Mo	-0.14	-0.10	0.104	0.128	0.15	1							
Ni	-0.07	-0.18	0.91	0.64	0.57	-0.03	1						
Pb	0.03	0.33	0.098	0.164	0.402	0.457	-0.02	1					
Zn	0.16	0.49	0.08	-0.01	0.40	0.03	0.19	0.57	1				
B	-0.01	0.13	-0.005	0.034	0.055	0.421	-0.16	0.58	-0.144	1			
Fe	-0.16	-0.13	0.48	0.57	0.40	0.54	0.29	0.58	0.16	0.37	1		
As	0.36	0.89	-0.3	-0.25	-0.16	-0.24	-0.26	-0.02	0.15	0.03	-0.31	1	
Al	-0.01	0.1	-0.02	0.024	0.06	0.55	-0.21	0.66	-0.08	0.95	0.46	-0.04	1

The correlation among the element was as follows; Co showed a significant positive correlation with Cr, Cu and Ni (at  $r^2 = 0.770$ ,  $0.577$  and  $0.906$ , respectively,  $p < 0.01$ ). The relatively high Cu levels at urban sites could be ascribed to copper usage in production of alloys and pigments, electrical wiring, cooking utensils and piping. Ni is commonly used in household products like stainless steel, nonferrous alloys, electroplating, Ni–Cd batteries, and coins [Pandey et al., 2017]. Therefore, the high Ni levels at urban sites (K3-K8) is expected. As and Cd showed a significant correlation ( $r^2 = 0.891$ ,  $P > 0.01$ ), and did not show significant correlation with any other elements, suggesting similar anthropogenic origin. Cadmium is mostly used in nickel-cadmium batteries, electroplating, heating systems, plastic stabilizers and is also released into the environment by power stations, metal working industries or urban traffic [Jumbe and Nandini, 2009]. High Cd levels were recorded near settlement areas (K3 and H1), we can infer that the anthropogenic sources of cadmium were urban–industrial wastes. Pb showed a significant positive correlation of  $0.570$ ,  $0.584$  and  $0.581$  with zinc, boron and Fe, respectively at  $p < 0.01$ . Major anthropogenic sources of Pb include vehicle emissions, weathering, incineration, leather and tannery effluents, Pb containing paints and pesticides [Hanif et al., 2016]. The strong positive correlation ( $r^2 = 0.948$ ) between B and Al, which is a typical lithogenic element usually found in aluminosilicate minerals, suggests that both elements are of terrigenous origin.

The HCA and PCA results perfectly matched with each other. HCA dendrogram is shown in Figure 4.18, and the PCA results are presented in Table 4.15 (Rotation Method: Varimax with Kaiser Normalization). The HCA grouped the elements into four

statistically significant clusters, corresponding to four PCs of Eigen values greater than one. The four PCs accounted for 79.68% of the total variance in the data set, these show the different factors (sources) influencing sediment pollution in the study area.

Table 4.15: Rotated component matrix loading for elements in sediment samples.

Element	Component			
	PC1	PC2	PC3	PC4
Ag	-0.062	-0.035	0.604	0.073
Cd	0.103	-0.137	0.898	0.287
Co	0.026	0.959	-0.133	0.053
Cr	0.136	0.846	-0.127	-0.069
Cu	0.1	0.585	-0.012	0.543
Mo	0.676	0.014	-0.307	0.186
Ni	-0.186	0.905	-0.085	0.13
Pb	0.723	0.072	0.107	0.61
Zn	-0.047	0.056	0.247	0.922
B	0.915	-0.013	0.131	-0.172
Fe	0.605	0.481	-0.253	0.265
As	-0.055	-0.184	0.911	-0.053
Al	0.966	-0.058	0.048	-0.069
Eigen value	3.201	3.094	2.292	1.772
% of variance	24.621	23.800	17.631	13.627
Cumulative %	24.621	48.421	66.053	79.680

The first HCA consisted of Al, Fe, B, Pb and Mo, which correlated to PC1. PC1 explained 24.62% of total variance in the data and 3.201 of the Eigen value. Fe and Al are lithogenic elements. B levels in the sediments are mostly attributed to natural occurrence, since the study area has major colemanite and ulexite borate deposits [Helvacı and Alonso, 2000]. Pb levels may partly be due to geogenic weathering of sulfide ore minerals. Therefore, elements in PC1 were mostly from natural sources and geologic weathering. The second HCA cluster (Figure 4.18) consisted of Co, Cr and Ni, which highly loaded in PC2. PC2 explained 23.80 % of total variance in the data and 3.094 of the Eigen value. The anthropogenic source of the elements in PC2 is attributed to mining of coal and chromium, and leaching from urban waste. Coal mining removes coal seams which may cause surface subsidence. Subsequently, as water flows through the subsidence, it dissolves contaminants, transports and deposits them in sediments downstream [Wright and Ryan, 2016].

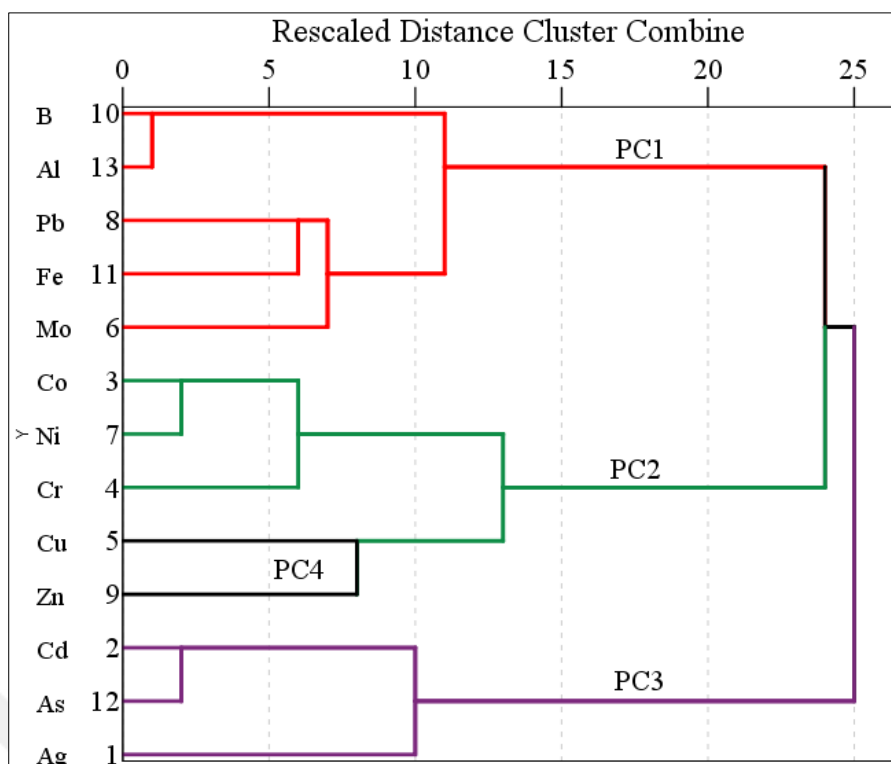


Figure 4.18: Dendrogram of hierarchical cluster analysis among the heavy metals and other elements.

The third HCA consisted of Cu and Zn. Zn highly loaded in PC4, whereas Cu showed moderate loading in both PC2 and PC4 (Table 4.15). PC4 explained 13.63% of total variance in the data and 1.772 of the Eigen value. The high levels exhibited by these elements at urban sites is attributed to leachates from urban wastes. Another possible source of heavy metal enrichment may be influenced by atmospheric dispositions from fly ashes of coal-fired power plant. Studies by Turkmenoğlu, 2010 obtained concentrations of Pb, Cd, Cr, Cu, Ni, Zn, Co, and Mn in fly ash samples of Tunçbilek coal-fired power plant as 16.4, 1.95, 296.7, 34.8, 515, 262.2, 46.8, and 690.6 mg/kg, respectively. The fourth cluster in HCA comprised of Ag, Cd and As, which correlated with PC3, in which they revealed higher loadings of 0.604, 0.898 and 0.911, respectively. PC3 explained 17.63% of total variance in the data and 2.292 of the Eigen value. The components in this cluster were generally attributed to natural occurrence, but the deposition of Cd could have been enhanced by human activities involving use of Cd products, especially in settlement areas.

## 5. CONCLUSION AND RECOMMENDATIONS

### 5.1. Conclusion

This study successfully assessed the present situation regarding water and sediment quality in Emet and Orhaneli streams. The study did not present a new theory but rather achieved its objectives of assessing the water and sediment quality in Mustafakemalpaşa stream and its tributaries of Orhaneli and Emet streams whose catchments are characterized by various mining activities.

The WQI results showed no significant difference in water quality data for March, July and October. Overall, WQI in the middle and downstream reaches of the streams varied from slightly to heavily polluted status. However, water of clean category ( $50 < \text{WQI} < 100$ ) was revealed at upstream points of both Emet and Orhaneli streams and most of the tributaries. The main point sources of pollution in Emet stream were identified as (1) tributary G1 about 33 km downstream and originating from a Emet boron mining tailings dam, with average arsenic and boron pollutions of 15586  $\mu\text{g/L}$  and 1514  $\text{mg/L}$  respectively, (2) point H1 about 14 km downstream of Emet stream originating from Hisarcik boron mine operation and (3) direct discharge of domestic wastewater at Emet and Harmancik settlements. These greatly compromises the quality of water for human consumption and agricultural use, as a matter of fact, interactions with the locals revealed that they can no longer use the water in most parts of Emet stream even for irrigation as some crop varieties wither due to the poor water quality.

For the case of Orhaneli stream, the most polluted points were identified as Points K4 and K5 at Tavşanlı and Tunçbilek settlement areas, respectively. These polluted points are in the upstream of the catchment, which exposes the entire streams to contamination. The parameters that greatly influenced the WQI were As, B, DO and BOD. This study presents a warning to the stakeholders on the deteriorating water quality of Emet and Orhanli streams due to anthropogenic influence.

The analyses tools used to investigate heavy metal pollution levels included: geo-accumulation index ( $I_{\text{geo}}$ ), contamination factor (CF) and pollution load index (PLI), enrichment factor (EF) and sediment quality guidelines (SQGs). PCA and HCA were employed to identify the potential pollution sources. The elements that showed

highest contamination in surface sediments (annual average >110.06 mg/kg) were B, Cr, Ni, Zn and As. The obtained minimum As, Cd and Ni levels exceeded PEC of 17 mg/kg, 3.53 mg/kg and 36 mg/kg, respectively, which poses potential negative impact to the biota. Most of the Cu and Pb values were between their respective TEL and PEC values. The sediment pollution levels in the main stream reach was affected by the stream hydraulic conditions, areas of high stream velocity exhibited lower pollution patterns compared to areas of low stream velocity.

The elements that showed highest  $I_{geo}$  values were Cr, Ni, Pb, Zn, B and As, this occurred near coal and chromium mining sites. Most of the sampling sites exhibited moderate to severe enrichment ( $3 < EF < 25$ ). Extreme EF values for Ag, Cd, Cu, Ni, Pb and Zn were predominant over sample sites K3, K5 and K6 in urban settlements of Tavşanlı, Tunçbilek and Muhaciler, respectively, which discharge untreated effluent into the stream. The sources of heavy metal pollution in the catchments was attributed to fly ashes of coal powered plants, leachate from urban waste and natural weathering of sulphide ore minerals for Pb and Zn, urban-industrial wastes and mining wastes for Ni. The sources of Cr, Cd, As and B seemed to originate from the geology of the catchment however, their distribution depended on mining activities. Although previous studies mainly seem to support the argument that pollution in this region is linked to the geology. This study emphasizes that the anthropogenic activities involving excavations and disturbance of the earth crust have escalated the dissolution of heavy metals and other related pollutants into surface water and streams. This argument is supported by the high pollution levels in samples taken from sample points receiving drainage from mining sites. Moreover, sediment pollution levels were high in the towns of Tavşanlı and Tunçbilek, where discharge of untreated domestic effluent into the stream occurs.

## **5.2. Recommendations**

As a result of this research, the critical issues affecting water quality in Mustafakemalpaşa catchment have been identified, suggestions and recommendations are presented below to the relevant stakeholders.

- The outcomes from this research work and other relevant research in the study area should be shared with all stakeholders including government, private miners and the local community in order to create awareness and promote environmental sustainability.
- The discharge of domestic wastewater without sufficient treatment into the streams should be prohibited. Furthermore, settlements with population greater than 20,000 should have modern urban wastewater treatment facilities and the existing wastewater treatment facilities should be monitored to ensure compliance with the discharge standards.
- To address issues related to pollution originating from mine wastes, all industrial and mining activities should be monitored to ensure compliance with discharge standards specified in the Turkish legislation.
- Agricultural pollution control studies should be carried out in the basin, to control nutrient input from agricultural fields especially those related to use of fertilisers and management of animal waste.

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## **BIOGRAPHY**

Philip Isaac OMWENE was born in 1990 in Tororo - Uganda. In 2015, he successfully completed the Bachelors of Science Degree in Water Resources Engineering in the Faculty of Engineering at Busitema University (Uganda) and started his graduate education at Gebze Technical University, Institute of Science and Department of Environmental Engineering in the same year.



## APPENDICES

### Appendix A: Publications from this Thesis Study

Omwene P.I., Öncel M.S., Çelen M., Kobya M., (2018), “Heavy metal pollution and spatial distribution in surface sediments of Mustafakemalpaşa stream located in the world’s largest borate basin (Turkey)”, *Chemosphere* 208, 782–792.

Omwene P.I., Oncel M.S., Çelen M., Kobya M., (2017), “Mapping of Arsenic and Boron Pollution in Orhaneli and Emet Streams Using GIS Technique”, *International Symposium on GIS applications in Geography and Geosciences*, 64-73, Turkey, 18-21 October.

### Appendix B: Geographical Information of Sampling Stations

The geographical coordinates of sampling points used in this study are given in Table B1.1.

Table B1.1: Coordinates of sampling points.

Point	Coordinates		Point	Coordinates	
	Northing	Easting		Northing	Easting
E27	40 07,653	28 32,368	E14	39 35,232	28 59,939
E26	40 6,050	28 28,732	P1	39 27,895	29 19,603
E25	40 5,024	28 29,142	E11	39 27,401	29 15,371
L1	39 58,643	28 25,692	M1	39 27,063	29 15,365
E24	39 58,024	28 29,144	E10	39 26,654	29 14,857
E23	39 57,087	28 30,990	E9	39 25,120	29 14,378
E22	39 53,667	28 34,302	F1	39 24,878	29 14,355
E21	39 52,826	28 34 225	G1	39 23,688	29 14,300
E20	39 52,261	28 34,481	E7	39 23,543	29 14,566
B1	39 49 8531	28 34, 964	E8	39 23,544	29 14,423
C1	39 49,648	28 36,506	E6	39 23,574	29 14,440
T1	39 37,042	28 41,627	E5	39 20,954	29 13,680
D2	39 37,640	28 43,675	E4	39 17,875	29 13,446
E18	39 39,842	28 44,175	E3	39 16,449	29 13,642
E19	39 39,877	28 43,806	E14	39 14,795	29 14,193
D1	39 39,728	28 43,926	E2	39 13,478	29 15,514
D3	39 33,984	28 43,328	E1	39 09,196	29 17,139
E17	39 36,963	28 52,472	K1	39 19,660	29 37,550

Table B1.1: Continued.

Point	Coordinates		Point	Coordinates	
	Northing	Easting		Northing	Easting
A1	39 36,882	28 58,484	K2	39 26,541	29 37,033
E15	39 36,845	28 58,506	K3	39 31,582	29 30,281
E16	39 36,823	28 58,460	K4	39 33,995	29 28,080
J1	39 38,861	28 57,679	K5	39 37,447	29 27,831
A2	39 40,054	29 4,073	K6	39 40,990	29 30,352
E13	39 34,345	29 1,411	K7	39 50,942	29 15,629
S1	39 35,081	28 59,903	K8	39 53,001	29 05,472
E13	39 55,213	29 0,017	K9	39 55,891	28 58,307
H1			K10	39 57,464	28 52,862

### Appendix C: Pearson Correlation matrix (PCM) for Sediments

The pearson correlation matrix for the different elements measured in sediment samples is shown in Table C1.1.

Table C1.1: Pearson correlation matrix for elements in sediments.

	Ag	Cd	Co	Cr	Cu	Mo	Ni	Pb	Zn	B	Fe	As	Al
Ag	1												
Cd	0.383	1											
Co	-0.14	-0.225	1										
Cr	-0.188	-0.188	<b>0.770</b>	1									
Cu	0.084	0.002	<b>0.577</b>	0.313	1								
Mo	-0.14	-0.104	0.104	0.128	0.15	1							
Ni	-0.067	-0.185	<b>0.906</b>	<b>0.641</b>	<b>0.571</b>	-0.034	1						
Pb	0.028	0.33	0.098	0.164	0.402	0.457	-0.021	1					
Zn	0.162	0.491	0.083	-0.01	0.398	0.027	0.187	<b>0.57</b>	1				
B	-0.014	0.134	-0.005	0.034	0.055	0.421	-0.159	<b>0.584</b>	-0.144	1			
Fe	-0.165	-0.133	0.483	<b>0.567</b>	0.405	<b>0.535</b>	0.289	<b>0.581</b>	0.163	0.367	1		
As	0.357	<b>0.891</b>	-0.297	-0.252	-0.159	-0.241	-0.265	-0.015	0.15	0.025	-0.313	1	
Al	-0.006	0.098	-0.025	0.024	0.059	0.555	-0.207	0.663	-0.085	<b>0.948</b>	0.464	-0.039	1

## Appendix D: Index of Geoaccumulation ( $I_{geo}$ ) for Sediments

The calculated index of geoaccumulation for the different sample sites is shown in Table D1.1.

Table D1.1: Geo-accumulation Index for sediment samples.

Sample	Geo-accumulation Index										
	Ag	Cd	Co	Cr	Cu	Mo	Ni	Pb	Zn	B	As
E25	0.49	4.88	7.68	16.1	8.66	7.64	14.7	10.3	12.1	27.3	12.6
E24	0.08	4.73	7.18	16.9	8.30	7.96	14.5	10.3	11.8	27.3	10.9
E23	0.56	5.06	7.28	16.2	8.14	6.65	14.6	10.0	11.4	28.5	10.2
L1	0.49	4.88	7.04	15.7	8.36	6.73	13.5	10.8	12.0	27.4	10.5
E22	1.60	4.67	7.55	16.1	8.76	6.75	14.7	10.4	12.1	26.6	12.1
E21	1.46	4.91	7.07	16.4	8.42	6.05	14.1	10.4	11.9	28.3	10.4
E20	0.77	5.34	7.61	16.8	8.84	7.81	14.0	12.8	11.8	30.3	10.7
E19	0.88	5.84	7.91	17.6	9.38	7.74	14.0	13.1	12.1	30.4	11.4
E18	2.99	5.08	7.67	15.8	9.11	7.17	14.4	11.4	11.8	28.5	11.8
D2	-0.13	4.75	8.01	16.6	9.65	6.75	15.0	11.3	12.4	26.5	12.2
E16	0.87	5.20	7.38	16.0	9.00	5.08	14.4	11.5	12.5	27.9	12.0
E17	1.86	4.99	6.89	15.9	8.60	5.45	14.8	10.6	11.8	28.8	12.1
D1	0.49	4.73	7.65	17.1	8.57	6.18	13.9	11.4	12.4	27.1	10.2
D3	3.35	4.80	7.18	16.4	8.66	6.42	14.0	11.2	12.3	27.2	9.6
E15	0.82	4.78	7.20	17.9	7.78	6.82	14.2	10.5	12.3	26.9	11.5
A1	-0.77	4.47	9.36	19.6	9.06	6.59	16.7	11.5	11.5	28.3	9.4
E13	1.63	5.10	7.71	16.2	8.97	6.52	15.2	10.6	12.4	27.3	12.9
E14	0.86	4.62	6.12	17.0	8.84	6.53	14.1	10.7	11.3	26.3	11.2
A2	-0.11	4.56	8.62	16.6	8.67	6.38	16.1	10.5	11.8	27.8	10.3
E11	1.34	5.18	7.84	16.6	9.12	6	15.4	10.3	12.1	27.9	13.5
S1	1.95	4.83	6.48	14.4	8	6.2	12.2	11.1	12.2	27.3	11.8
E12	3.09	5.02	6.7	15.7	8.54	6.15	14.1	10.7	11.9	27.8	12.4
P1	0.56	4.56	8.05	16.1	8.91	5.7	15.4	9.6	12.6	27.5	11.6
E10	1.63	5.41	6.41	15.3	7.98	5.92	13.2	10.6	12.3	28.2	13.4
E9	1.08	5.5	6.38	14.5	7.88	7.19	12.1	11	12.4	28	13.8
E8	-0.15	5.22	7.03	15	7.57	6.06	11.7	11	12.2	27.2	12.3
G1	1.98	6	7.22	14.7	8.92	6.4	12.6	11	13	27.9	14.7
E6	0.56	5.4	6.35	14.7	8.06	5.88	12.1	11.3	12.3	27.8	13.2
E7	1.22	6.04	6.57	14.7	8.6	5.95	12.7	11	12.8	27.3	14.5
E5	0.79	5.59	6.24	15.4	8.4	5.83	13	10.9	12.1	28.7	13.5
E4	0.17	5.37	6.48	15.4	8.24	6.35	13	10.5	12	26.8	13.2
E3	0.63	5.57	6.6	16.1	8.39	6.13	13.3	11.1	12	28.3	13.5
E2	0.56	5.61	6.44	15.4	8.18	5.75	13.2	9.9	12	28.4	13.7
E1	0.17	5.17	7.03	15.6	8.54	5.75	14.1	10.9	12.4	28.7	12.7
H1	3.03	7.75	6.28	15.1	8.14	5.05	12.7	10.2	11.9	28.5	16.2

Table D1.1: Continued.

Sample	Geo-accumulation Index										
	Ag	Cd	Co	Cr	Cu	Mo	Ni	Pb	Zn	B	As
K1	0.17	4.77	6.69	14.8	8.5	6.67	11.8	11	12.5	27.1	11.4
K2	0.26	4.92	6.28	14.5	8.08	5.9	11.9	10.4	11.7	28.1	11.7
K3	1.95	7.26	7.64	16.6	9.38	6.98	15.5	13.2	15.5	27.2	14.2
K4	2.44	5.8	7.7	16.7	9.61	6.08	15.3	11.6	14.1	26.4	12.4
K5	1.95	5.02	8.94	17.6	9.41	6.39	17.1	10.9	13.3	27.4	11.7
K6	2.22	4.89	8.43	18	9.02	5.7	16.5	10.5	13.3	27.7	11.7
K7	0.08	4.63	8.36	17.3	9.41	6.11	16.1	10.6	12.6	26.9	10.9
K8	-0.02	4.61	8.15	17.4	9.48	6.8	16	10.9	12.7	27.2	11
K9	-0.37	4.63	7.78	18.3	9	6.67	15.5	12.1	12.4	26.6	11
K10	0.17	4.5	7.65	17.6	8.64	6.43	15.4	10.2	12.1	27	10.2
K11	1.38	4.72	7.98	16.8	9.03	6.82	15.6	10.2	11.9	27.7	10.1
K12	-0.83	4.33	8.06	17.1	8.35	6.26	16	9.1	11.3	27.3	10.7

## Appendix E: Contaminant Factor for Surface Sediments

The calculated contaminant factor (CF) for the different sample sites is shown in Table E1.1.

Table E1.1: Contaminant factor (CF) for sediment samples.

Sample	Contaminant Factor											
	Ag	Cd	Co	Cr	Cu	Mo	Ni	Pb	Zn	B	As	PLI
E25	0.82	0.93	1.32	0.96	1.02	2.40	1.36	0.70	1.00	0.87	1.72	1.12
E24	0.61	0.84	0.94	1.59	0.79	3.00	1.16	0.70	0.81	0.85	0.55	0.95
E23	0.86	1.05	1.00	1.00	0.71	1.21	1.24	0.56	0.60	1.94	0.32	0.86
L1	0.82	0.93	0.85	0.69	0.82	1.27	0.58	1.00	0.91	0.92	0.40	0.80
E22	1.76	0.80	1.20	0.92	1.09	1.29	1.36	0.76	0.99	0.52	1.21	1.03
E21	1.59	0.95	0.86	1.13	0.86	0.80	0.93	0.72	0.85	1.74	0.37	0.91
E20	0.99	1.28	1.25	1.53	1.15	2.69	0.81	3.96	0.78	6.80	0.46	1.45
E19	1.06	1.80	1.55	2.57	1.68	2.58	0.85	4.94	0.97	7.44	0.77	1.83
E18	4.61	1.06	1.32	0.76	1.39	1.74	1.14	1.46	0.78	2.00	1.00	1.37
D2	0.53	0.85	1.66	1.31	2.02	1.29	1.73	1.41	1.21	0.49	1.33	1.16
E16	1.06	1.16	1.08	0.88	1.29	0.41	1.11	1.57	1.30	1.32	1.18	1.07
E17	2.11	1.00	0.76	0.82	0.98	0.53	1.51	0.84	0.81	2.43	1.25	1.07
D1	0.82	0.84	1.29	1.83	0.95	0.87	0.79	1.52	1.20	0.72	0.32	0.93
D3	5.92	0.88	0.93	1.16	1.02	1.03	0.86	1.30	1.14	0.79	0.23	1.03
E15	1.02	0.87	0.95	3.35	0.55	1.36	1.00	0.80	1.08	0.63	0.83	1.00
A1	0.34	0.70	4.22	10.52	1.34	1.16	5.38	1.59	0.66	1.67	0.20	1.36
E13	1.80	1.08	1.35	1.02	1.26	1.10	1.91	0.85	1.19	0.86	2.13	1.26
E14	1.05	0.77	0.45	1.76	1.15	1.11	0.93	0.93	0.56	0.42	0.68	0.82
A2	0.54	0.74	2.54	1.37	1.03	1.00	3.67	0.80	0.78	1.17	0.35	1.03
E11	1.47	1.14	1.48	1.29	1.40	0.77	2.28	0.69	0.98	1.30	3.23	1.33
S1	2.24	0.90	0.58	0.29	0.64	0.88	0.24	1.21	1.04	0.87	1.00	0.76
E12	4.94	1.02	0.67	0.73	0.93	0.85	0.88	0.92	0.88	1.21	1.48	1.09
P1	0.86	0.74	1.71	0.91	1.21	0.63	2.29	0.44	1.39	1.00	0.86	0.99
E10	1.80	1.34	0.55	0.53	0.63	0.73	0.50	0.82	1.15	1.54	3.15	0.97
E9	1.22	1.42	0.54	0.31	0.59	1.76	0.22	1.09	1.18	1.40	4.12	0.94
E8	0.52	1.18	0.84	0.45	0.48	0.80	0.18	1.15	1.04	0.82	1.44	0.71
G1	2.29	2.02	0.96	0.36	1.21	1.02	0.32	1.12	1.78	1.27	7.61	1.25
E6	0.86	1.33	0.53	0.34	0.67	0.71	0.23	1.34	1.13	1.18	2.71	0.82
E7	1.35	2.08	0.61	0.35	0.98	0.74	0.33	1.15	1.53	0.88	6.36	1.03
E5	1.00	1.52	0.49	0.56	0.85	0.68	0.43	1.05	0.99	2.28	3.29	0.98
E4	0.65	1.31	0.58	0.57	0.76	0.98	0.43	0.80	0.94	0.62	2.69	0.82
E3	0.90	1.50	0.62	0.93	0.85	0.84	0.52	1.19	0.88	1.66	3.27	1.05
E2	0.86	1.54	0.56	0.56	0.73	0.65	0.49	0.53	0.88	1.88	3.86	0.90
E1	0.65	1.13	0.84	0.67	0.94	0.65	0.87	1.02	1.18	2.31	1.92	1.01

Table E1.1: Continued.

Sample	Contaminant Factor											
	Ag	Cd	Co	Cr	Cu	Mo	Ni	Pb	Zn	B	As	PLI
K1	0.65	0.86	0.67	0.38	0.91	1.23	0.18	1.11	1.29	0.73	0.78	0.71
K2	0.69	0.96	0.50	0.31	0.68	0.72	0.20	0.74	0.72	1.45	0.96	0.64
K3	2.24	4.84	1.29	1.32	1.68	1.52	2.47	5.19	10.60	0.77	5.34	2.52
K4	3.14	1.76	1.34	1.45	1.96	0.81	2.06	1.68	4.02	0.45	1.57	1.59
K5	2.24	1.02	3.16	2.68	1.71	1.01	7.04	1.03	2.18	0.93	0.95	1.75
K6	2.69	0.94	2.22	3.46	1.31	0.63	4.76	0.79	2.29	1.13	0.93	1.57
K7	0.61	0.78	2.11	2.07	1.71	0.83	3.63	0.86	1.39	0.65	0.54	1.15
K8	0.57	0.77	1.83	2.29	1.79	1.34	3.26	1.04	1.5	0.77	0.58	1.23
K9	0.45	0.78	1.42	4.31	1.28	1.23	2.34	2.37	1.2	0.54	0.57	1.19
K10	0.65	0.71	1.3	2.58	1	1.04	2.29	0.66	0.96	0.71	0.34	0.95
K11	1.51	0.83	1.63	1.51	1.31	1.36	2.57	0.67	0.87	1.12	0.31	1.1
K12	0.33	0.63	1.72	1.86	0.82	0.93	3.38	0.3	0.55	0.87	0.45	0.82
H1	4.73	6.78	0.5	0.48	0.71	0.4	0.34	0.64	0.86	1.97	20.56	1.29

## Appendix F: Enrichment Factor for Surface Sediments

The calculated Contaminant factor (CF) for the different sample sites is shown in Table F1.1.

Table F1.1: Contaminant Factor (CF) for Sediment Samples.

Sample	Enrichment Factor										
	Ag	Cd	Co	Cr	Cu	Mo	Ni	Pb	Zn	B	As
E25	0.50	0.57	0.81	0.58	0.62	1.47	0.83	0.43	0.61	0.53	1.05
E24	0.63	0.86	0.96	1.63	0.81	3.08	1.19	0.72	0.83	0.87	0.57
E23	0.68	0.84	0.80	0.80	0.57	0.96	0.99	0.44	0.48	1.55	0.26
L1	0.73	0.82	0.75	0.61	0.73	1.13	0.51	0.89	0.81	0.82	0.35
E22	3.48	1.59	2.39	1.82	2.16	2.56	2.69	1.50	1.96	1.03	2.39
E21	1.20	0.72	0.65	0.85	0.65	0.60	0.70	0.55	0.65	1.32	0.28
E20	0.15	0.19	0.19	0.23	0.17	0.41	0.12	0.60	0.12	1.03	0.07
E19	0.18	0.30	0.26	0.43	0.28	0.44	0.14	0.83	0.16	1.25	0.13
E18	3.04	0.70	0.87	0.50	0.92	1.15	0.75	0.97	0.52	1.32	0.66
D2	0.96	1.54	3.02	2.37	3.67	2.34	3.13	2.57	2.19	0.89	2.41
E16	1.06	1.16	1.08	0.88	1.29	0.41	1.11	1.57	1.30	1.32	1.18
E17	1.89	0.90	0.69	0.74	0.88	0.47	1.35	0.76	0.72	2.18	1.12
D1	0.78	0.80	1.23	1.75	0.91	0.83	0.76	1.46	1.15	0.69	0.31
D3	5.15	0.76	0.81	1.01	0.89	0.90	0.75	1.13	1.00	0.69	0.20
E15	1.68	1.43	1.56	5.49	0.90	2.23	1.64	1.32	1.78	1.04	1.36
A1	0.26	0.54	3.27	8.14	1.04	0.90	4.17	1.23	0.51	1.29	0.15
E13	2.35	1.42	1.77	1.33	1.65	1.44	2.49	1.11	1.56	1.13	2.79
E14	1.52	1.12	0.65	2.54	1.67	1.61	1.34	1.34	0.81	0.61	0.98
A2	0.70	0.96	3.28	1.76	1.32	1.29	4.74	1.03	1.01	1.51	0.45
E11	1.60	1.24	1.61	1.40	1.52	0.84	2.48	0.75	1.07	1.42	3.51
S1	1.76	0.70	0.45	0.23	0.50	0.69	0.19	0.94	0.82	0.68	0.78
E12	3.85	0.80	0.52	0.57	0.73	0.67	0.69	0.72	0.68	0.95	1.15
P1	1.17	1.02	2.34	1.25	1.66	0.86	3.14	0.60	1.90	1.37	1.17
E10	1.67	1.24	0.51	0.49	0.59	0.68	0.46	0.76	1.06	1.42	2.93
E9	1.22	1.42	0.53	0.31	0.59	1.75	0.22	1.09	1.17	1.4	4.1
E8	0.56	1.25	0.89	0.48	0.51	0.85	0.19	1.23	1.11	0.87	1.53
G1	2.57	2.27	1.08	0.4	1.36	1.15	0.36	1.26	2	1.43	8.55
E6	0.72	1.11	0.44	0.29	0.56	0.59	0.19	1.12	0.95	0.99	2.27
E7	1.15	1.78	0.52	0.3	0.84	0.64	0.29	0.99	1.31	0.75	5.45
E5	0.61	0.93	0.3	0.34	0.52	0.42	0.26	0.64	0.61	1.4	2.02
E4	1.23	2.47	1.09	1.08	1.43	1.86	0.82	1.5	1.77	1.17	5.08
E3	0.83	1.39	0.58	0.86	0.78	0.78	0.48	1.1	0.82	1.54	3.02

Table F1.1: Continued.

Sample	Enrichment Factor										
	Ag	Cd	Co	Cr	Cu	Mo	Ni	Pb	Zn	B	As
E2	0.73	1.3	0.47	0.48	0.62	0.55	0.42	0.45	0.75	1.59	3.27
E1	0.51	0.89	0.66	0.53	0.74	0.51	0.69	0.8	0.93	1.82	1.51
K1	0.88	1.16	0.9	0.51	1.23	1.66	0.25	1.5	1.74	0.99	1.06
K2	0.8	1.1	0.58	0.35	0.78	0.83	0.23	0.85	0.83	1.67	1.11
K3	2.1	4.53	1.2	1.23	1.57	1.42	2.31	4.85	9.92	0.72	4.99
K4	7.48	4.19	3.19	3.45	4.67	1.94	4.91	4.01	9.57	1.06	3.74
K5	3.8	1.74	5.35	4.54	2.89	1.71	11.93	1.75	3.7	1.57	1.6
K6	3.7	1.29	3.06	4.76	1.8	0.86	6.53	1.08	3.14	1.55	1.28
K7	1.32	1.68	4.55	4.47	3.69	1.79	7.82	1.86	2.99	1.41	1.17
K8	1	1.34	3.18	3.98	3.12	2.34	5.69	1.81	2.62	1.35	1.01
K9	1	1.73	3.14	9.57	2.85	2.72	5.2	5.27	2.66	1.19	1.27
K10	1.26	1.38	2.51	4.99	1.94	2.01	4.44	1.28	1.86	1.38	0.66
K11	2.27	1.25	2.45	2.28	1.97	2.04	3.87	1	1.3	1.68	0.46
K12	0.65	1.27	3.43	3.7	1.64	1.85	6.75	0.6	1.1	1.73	0.9
H1	4.2	6.02	0.44	0.43	0.63	0.35	0.3	0.57	0.76	1.75	18.25

## Appendix G: Average Annual Water Quality Results for Mustafakemalpaşa Catchment

The concentration of elements and other parameters observed in surface sediments of both Emet and Orhaneli streams are summarized in Table G1.1.

Table G1.1: Average Annual Water quality results for Mustafakemalpaşa catchment.

ID	As (µg/L)	Fe	B	Ca	DO	K	Mg	Na	TDS	TP	TOC	Cl	Si	N03-N	SO4	Alk <sup>1</sup>	Cond µs/cm	pH	Temp °C
E27	49.71	822	5.68	63.57	6.58	3.05	47.53	16.21	335.67	0.21	3.75	33.44	7.00	2.01	99.44	363	668.67	8.41	19.63
E26	51.27	1030	7.48	63.69	5.88	3.56	48.84	18.33	338.00	0.17	6.16	28.58	6.97	1.98	116.48	363	679.33	8.36	19.00
E25	52.41	787	8.87	64.05	7.45	3.10	46.68	14.47	431.00	0.18	2.87	23.97	8.43	1.99	96.08	298	860.67	8.62	22.17
L1	12.72	1326	0.78	51.43	5.75	10.06	14.51	76.73	326.27	0.14	3.62	44.22	8.52	0.59	10.63	204	647.87	7.63	22.63
E24	30.50	907	4.46	64.60	9.97	2.51	49.58	12.07	304.00	0.19	3.19	9.88	7.10	0.70	13.44	258	623.33	8.49	17.07
E23	25.56	714	4.88	61.75	8.63	2.84	50.25	13.49	312.00	0.18	3.14	14.07	7.74	1.87	118.84	254	618.33	7.32	16.83
E22	88.56	477	17.36	55.33	13.15	2.60	41.77	19.21	294.67	0.17	3.14	12.41	6.48	1.94	124.10	175	585.67	8.65	23.03
E21	112.24	610	19.99	63.75	10.72	3.20	46.59	21.64	323.00	0.17	3.04	12.60	7.10	1.64	122.93	245	643.33	8.54	22.87
E20	141.83	669	22.26	64.61	7.93	3.39	45.61	19.27	327.00	0.15	2.97	16.33	8.19	1.92	129.32	249	633.33	8.53	22.30
B1	2.97	301	0.64	53.60	7.26	1.40	24.58	7.43	210.92	0.14	1.84	6.79	6.45	0.89	18.81	231	425.67	8.35	17.27
C1	2.35	85	0.14	49.56	7.10	1.37	4.41	5.70	131.03	0.07	2.00	4.12	5.03	0.35	10.10	153	259.93	8.29	17.83
T1	12.38	95	0.10	60.41	6.77	6.78	16.45	23.15	231.67	0.19	3.65	1.97	28.25	0.44	8.42	213	462.67	8.57	22.43

<sup>1</sup> Alkalinity was measured as mg/l CaCO<sub>3</sub>

Table G1.1: Continued.

	As	Fe	B	Ca	DO	K	Mg	Na	TDS	TP	TOC	Cl	Si	NO <sub>3</sub> -N	SO <sub>4</sub>	Alk <sup>1</sup>	Cond	pH	Temp
ID	(µg/L)	mg/kg															µs/cm		°C
D2	6.55	147	0.17	49.96	7.71	2.82	21.01	11.44	196.30	0.15	3.40	11.48	8.31	1.75	15.44	212	392.00	8.21	22.00
E18	181.80	1086	30.01	77.49	7.72	3.90	62.43	24.35	401.67	0.17	2.51	24.00	7.88	1.89	203.10	280	808.67	8.42	22.67
E19	187.90	1079	46.19	73.51	7.39	4.40	60.17	26.12	400.00	0.20	2.59	21.85	7.98	1.92	188.75	290	802.67	8.40	22.40
D1	6.48	595	0.81	49.72	6.86	2.58	18.96	9.95	187.73	0.13	3.25	16.01	8.88	1.68	20.00	227	376.67	8.16	20.56
D3	6.92	294	0.57	52.43	6.85	2.87	19.47	11.6	201	0.14	3.58	9.92	7.14	1.36	11.71	231	403.67	7.99	16.5
E17	191.1	671	28.73	84.5	7.43	3.87	62.08	24.69	416	0.19	2.84	18.55	8.21	2.14	170.7	260	831.67	8.3	17.73
A1	7.57	420	0.81	32.43	6.98	1.8	130.73	8.51	453.33	0.24	3.06	10.62	12.31	1.27	25.64	515	905.67	8.62	18.23
E15	237.23	1089	41.1	82	6.64	4.54	52.1	27.08	415	0.18	2.45	23.64	7.72	2.01	227.65	357	828	8.19	17.5
E16	169.87	790	33.72	81	7.04	3.63	69.11	21.19	412	0.21	3	16.36	9.1	1.55	162.88	363	827.67	8.2	17.6
J1	3.21	131	2.08	30	7.92	1.77	176.43	11.26	513	0.24	4.16	45.86	13.05	1.25	15.49	53	899.67	8.22	16.47
A2	8.79	503	0.5	38	8.99	2.03	126.67	8.66	455.67	0.27	3.95	7.2	14.63	0.46	25.13	513	900.33	8.39	17
E13	331.07	1038	46.96	106	7.64	4.81	68.77	31.49	491.67	0.19	2.87	32.96	7.86	2.67	281.68	261	1007.67	8.27	19.4
S1	15.35	1556	1.86	56	7.97	3.13	27.49	18.26	268	0.12	2.49	9.21	8.03	0.38	18.41	263	536.67	8.06	18.9
E13	276	1096	46.47	99	7.72	4.62	66.35	31.41	510.33	0.18	3.04	36.32	7.77	2.65	289	264	1041.33	8.11	19.83
E14	182.74	1139	28.2	87	8.06	3.79	52.52	24.62	416.33	0.17	3.02	26.36	7.85	2.34	211	289	832	8.19	20.33
P1	17.15	248	1.82	87	7.35	4.78	27.64	10.48	310.67	0.15	2.24	39.22	9.22	1	15.87	312	622	8.28	19.77
E11	636.47	2024	46.8	125	8.15	4.79	44.99	23.36	438.33	0.19	2.87	35.86	9.26	2.99	274.33	283	887.67	8.21	20
M1	9.06	219	0.92	72	8.69	4.81	19.85	12.82	244	40.02	3.16	13.58	10.14	0.53	26	246	489.33	8.27	18.9
E10	615.1	1883	60.46	136	7.58	4.43	46.97	22.99	456.33	0.18	3.44	43.93	9.33	2.12	308.98	333	917.33	8.13	20.23
E9	2501.67	1967	60.41	132	7.8	4.58	45.93	24.1	462	0.17	3.04	48.46	9.43	3.34	325.22	234	930	8.04	20.53

<sup>1</sup> Alkalinity was measured as mg/l CaCO<sub>3</sub>

Table G1.1: Continued.

	As	Fe	B	Ca	DO	K	Mg	Na	TDS	TP	TOC	Cl	Si	N03-N	SO4	Alk <sup>1</sup>	Cond	pH	Temp
ID	(µg/L)	mg/kg															µs/cm		°C
F1	8.44	156	1.75	88	7.5	3.18	40.42	12.52	427	0.16	2.9	5.01	7.94	0.68	20.97	137	809.33	8.04	17.17
G1	15586	1311	1514	314	6	7.56	227	118	1851	0.21	5.56	352.89	18.25	0.54	1497.34	439	3706.67	7.46	23.4
E7	323.23	465	16.78	120.44	6.78	4.28	37.01	19.63	534	0.19	2.48	8.75	9.24	3.28	211.02	250	1069.33	8.14	19.43
E8	5062	946	178.27	159.11	7.91	3.32	33.75	19.03	876.67	0.19	3.15	55.44	10.7	3.62	373.43	256	1755.33	7.78	20.23
E6	317.77	1155	10.54	129.26	6.5	4.5	37.6	21.22	559.67	0.17	2.38	17.07	9.59	3.16	220.37	260	605.98	8.11	19.87
E5	415.48	1126	11.17	134.95	5.86	4.26	39.86	16.79	548	0.15	2.64	12.41	9.4	1.8	249.76	267	1126.33	7.79	18.1
E4	855.23	1213	12.83	144.73	6.09	4.23	43.58	15.52	609	0.17	2.37	7.28	9.44	1.69	182.12	293	1205.67	7.84	19.5
E3	705.43	1702	11.81	135.07	5.51	3.99	41.44	16.32	607	0.17	2.27	16.66	8.49	1.48	268.67	241	1218.33	7.98	20.1
E2	33.46	1359	2.25	116.29	5.21	3.87	36.26	12.19	529.33	0.14	2.64	15.18	7.26	1.2	195.04	222	1057.33	7.87	22.1
E1	17.05	411	2.23	118.57	6.66	2.51	37.1	9.79	509	0.13	2.11	7.46	7.14	0.98	81.8	201	1020	7.96	21.37
K1	8.31	232	1.68	75.74	5.92	1.63	22.78	4.95	340.33	0.12	1.64	5.67	7.11	1.02	48.38	241	683.33	7.56	14.73
K2	10.59	310	1.44	51.43	5.64	2.16	22.57	5.88	197.35	0.11	3.25	4.72	4.92	0.79	40.04	204	561	8.04	17.1
K3	87.48	559	1.33	57.4	4.42	2.31	36.24	7.29	343.33	0.15	2.87	7.06	6.61	1.98	64.18	243	691.33	7.94	15.23
K4	65.49	883	1.18	56.8	1.95	4.09	42.55	12.64	407.33	0.33	3.57	17.26	8.86	2.29	90.6	281	817.33	7.47	17.2
K5	61.3	665	1.08	59.24	1.51	3.99	46.94	14.96	435.67	0.39	3.97	14.85	8.72	0.98	58.15	280	871.67	7.6	18.43
K6	58.84	992	1	68.12	5.07	4.9	95.07	23.22	668.67	0.42	3.78	17.31	9.17	3.59	217.33	278	629.05	8.09	19
K7	21.37	726	0.9	77.91	6.87	3.01	57.53	13.64	459.67	0.27	2.63	13.27	7.72	2.35	235.28	283	915.33	8.07	18.97
K8	20.23	1077	0.63	86.23	7.54	2.94	59.42	13.65	485.67	0.24	2.83	11.14	8.44	3.17	221.36	300	978	8.17	20.13
K9	19.24	1067	0.72	84.38	7.55	2.89	59.7	13.6	487.67	0.2	2.38	9.98	8.4	2.84	191.13	293	830	8.22	19.83

<sup>1</sup> Alkalinity was measured as mg/l CaCO<sub>3</sub>



Table G1.1: Continued.

	As	Fe	B	Ca	DO	K	Mg	Na	TDS	TP	TOC	Cl	Si	N03-N	SO4	Alk <sup>1</sup>	Cond	pH	Temp
ID	(µg/L)	mg/kg														µs/cm	°C		
K10	17.21	78	0.61	82.91	7.27	2.87	58.97	13.55	464	0.21	3.13	7.9	8.48	2.48	144.17	309	936	8.37	20.17
K11	9.69	329	1.87	54.27	9.7	2.28	70.58	9.91	468.33	0.07	3.11	8.1	8.84	0.77	105.58	263	941.33	8.27	17.03
K12	9.18	622	1.88	56.42	11.14	2.22	70.22	10.73	466.67	0.08	3.47	10.58	8.62	0.65	108.19	282	943.67	8.58	17.07

<sup>1</sup> Alkalinity was measured as mg/l CaCO<sub>3</sub>