DOKUZ EYLÜL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

THE INVESTIGATION OF THE INFLUENCE OF MINING ACTIVITIES ON SURFACE AND SUBSURFACE WATER QUALITY

by

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April, 2009

İZMİR

THE INVESTIGATION OF THE INFLUENCE OF MINING ACTIVITIES ON SURFACE AND SUBSURFACE WATER QUALITY

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THE INVESTIGATION OF THE INFLUENCE OF MINING ACTIVITIES ON SURFACE AND SUBSURFACE WATER QUALITY

ABSTRACT

It is well known that mining activities have negative impacts on surface and subsurface water quality. These impacts could cause an environmental disaster, especially when necessary mitigation and rehabilitation activities are not implemented. Interaction of pyritic ores with oxygen and water in abandoned non-rehabilitated open pit mines of coal and iron is responsible for the formation of Acidic Mining Lakes. In addition to high acidity associated with average pH levels of around 2, these lakes also have high heavy metal and trace element concentrations and are considered to influence surface and subsurface water quality. Within the scope of this research, an acidic mining lake that formed as a result of the inundation of an abandoned open pit lignite mine located in Çan district of Çanakkale province was investigated limnologically in order to assess water quality. In this study, lake water has been sampled from a total number of 56 points (23 surface samples and 33 depth samples) in order to determine the vertical and areal distribution patterns of numerous water quality parameters including primary physical parameters, major anions and cations and heavy metal and some trace elements. Furthermore, morphological characteristics of the lake (i.e., bathymetry, area and volume) were also computed to predict the possible risks if lake waters seep into groundwater and in case the lake is intentionally emptied. Finally, possible rehabilitation techniques for acidic mining lakes were explained. Upon the analysis of these techniques, neutralization and metal adsorption with fly ash option was recommended for the lake under consideration.

Keywords: Acidic Mining Lake, limnological study, abandoned open pit mines, low pH, high trace element levels

MADENCİLİK FAALİYETLERİNİN YÜZEYSEL SU VE YERALTISUYU KALİTESİNE ETKİLERİNİN İNCELENMESİ

ÖZ

Madencilik faaliyetlerinin yüzeysel sulara ve yeraltı sularına etkisi olduğu bilinmektedir. Bu etki, özellikle önlem alınmadığı ve gerekli rehabilitasyon işlemleri yapılmadığı durumlarda ciddi bir çevre felaketine sebep olmaktadır. Söz konusu etkiye neden olan en önemli etmenlerden biri olan Asidik Maden Gölleri, işletme sonrası rehabilitasyonu yapılmadan terk edilmiş kömür ve demir açık ocaklarında, piritli bileşenlerin oksijen ve su ile etkileşimi sonucunda oluşmaktadır. Ortalama pH seviyeleri 2 civarında olan bu göllerde yüksek asiditeye ek olarak çok yüksek ağır metal ve iz element derişimleri de bulunabilmekte ve bu nedenle yüzey ve yeraltı sularının kalitesini önemli ölçüde tehdit etmektedir. Bu araştırma kapsamında Çanakkale ili Çan ilçesi sınırları içerisinde bulunan terk edilmiş bir açık linyit madeni işletmesinde oluşan bir asidik maden gölünde su kalitesini belirlemek amacıyla limnolojik çalışmalar yapılmıştır. Çalışmada göl su karakterizasyonun düşey ve alansal değişimini tespit etmek için 23 adet yüzey ve 33 adet de farklı derinliklerden olmak üzere toplam 56 adet su örneği toplanmış ve toplanan bu numunelerde; başlıca fiziksel parametreler, temel anyon ve katyonlar, ağır metaller ve bazı iz elementlerin konsantrasyonları ölçülerek değerlendirilmiştir. Ayrıca yeraltı suyuna oluşacak bir sızma veya gölün olası bir boşaltılma durumu ihtimali göz önünde bulundurularak, gölün morfolojik özellikleri de (batimetrisi, alanı ve hacmi) belirlenmiştir. Son olarak, asidik maden gölleri için muhtemel rehabilitasyon teknikleri açıklanmış ve bu çalışmaya konu olan göl için uçucu küllerle nötralizasyon ve metal adsorpsiyonu alternatifi önerilmiştir.

Anahtar Kelimeler: Asidik Maden Gölleri, limnolojik çalışmalar, terkedilmiş açık maden ocakları, düşük pH, yüksek iz element derişimleri

CONTENTS

CHAPTER ONE
INTRODUCTION

1.1 Problem Statement

Mining activities are essential for economic development and progress throughout the world. Typically, mining is implemented for the production of industrial minerals, coal, oil and gas. Mining activities, by definition, are not sustainable as the mineral or the energy resource is limited by nature and is not renewed when consumed. Furthermore, regardless of the entity mined, there is some extent of environmental pollution, which pose serious risks unless proper mitigation measures are implemented. Thus, mining is considered to be one of the sectors with significant pollution potential on the environment.

The environmental impacts of mining activities occur not only throughout the actual operational phase of the mine but also during pre- and post-operational stages. In each one of these stages, environment is damaged in various ways as a result of the activities including but not limited to mine preparation, ore extraction, enrichment, purification and regain. In addition to these, the extent of the mining area, physicochemical composition and service life of the mine also have a negative effect on the environment.

Air, water and soil pollution (physical, chemical and biological), degradation of the visual environment (destruction of the topography and morphology), vibration from blasting and noise pollution and corruption of the ecology could be considered as major environmental impacts of mining activities. Storage of large volumes of the non-mineralogical altered material (residue) and tailings that are extracted in order to reach the ore as well as fine particle wastes originating from ore enrichment cause land destruction and water/soil pollution with the requirement of continuous monitoring and mitigation.

Among the environmental impacts of mining that are summarized above, acid mine drainage (AMD) and acidic mining lakes (AMLs) are probably the most

important consequence which significantly alter the quality of surface and subsurface water and soil resources as a result of high acidity and elevated levels of toxic element and heavy metal concentrations.

AMD and AMLs have almost similar chemical and physical properties and influence the environment negatively with the characteristic of low pH and high sulfate and heavy metal concentrations. AMD refers to outflow of acidic water from (usually) abandoned metal mines or lignite/coal mines with significant sulfur contents. Acid mine drainage may also be observed in other areas where the earth has been disturbed (i.e. construction of subdivisions and transportation corridors). In many localities, the liquid that drains (i.e. AMD) from the mine or waste disposal site are highly acidic due to the oxidation of sulfur containing minerals.

The oxidation of pyrite (FeS_2), a common form of sulfur bearing iron mineral associated with coal or metal ores, often results in the formation of AMD, which typically forms extremely acidic lakes in the depression areas of abandoned open-pit mines (Gündüz, Okumuşoğlu & Baba, 2007). Iron species such as pyrite can be washed out by leaching rainwater and/or by the fast-rising groundwater table of abandoned lignite pits. Thus, many mining lakes are expected to become strongly acidic reaching pH levels as low as 2.0 with high contents of iron upon inundation of the open-cast basin (Geller, Klapper & Schultze, 1998). Thus, AMLs typically have more importance than AMD as a result of the huge volume that is problematic for the receiving environment. In essence, AMLs, with a characteristic of high acidity, high electrical conductivity, reddish-yellow color, high metal (i.e. Al, Cd, Cr, Cu, Fe, Mn, Pb, Zn) and sulfate concentrations, limited aquatic life and low slope stability, are considered to create a major environmental problem.

The extremely acidic conditions in these lakes results in the deterioration of the bicarbonate alkalinity in water. Under such conditions; acid- alkali equilibrium of the organisms are negatively affected, metabolic defections emerge, enzyme systems are pacifizied, respiration of the vegetations and roots cannot utilize water. Briefly, sensitive species disappear and limited numbers of acidity tolerant species survive in

such waters. Thus, aquatic life in these lakes is significantly altered. On the other hand, direct and indirect impacts of high heavy metal concentrations are also observed on all living organisms that have some sort of contact with these waters. Vegetation and animals are destroyed or mutations in behaviour and reproduction are observed due to exposure to high metal concentrations. Bioaccumulation in vital organs is also considered to be an indirect impact. If the living beings are exposed to products, which are grown in a field receiving the AML or AMD water in its irrigation source, the negative effects of high metal concentrations and acidity would also affect the humans indirectly (Dilek, 2008; Klukanova & Rapant, 1999; Lottermosser 2003)

Acidic mining lakes are commonly observed in the Lusatian Region of Germany in Central Europe and around Iron Mountain, California in the USA. In the Lusatian district, more than 100 lakes of various sizes are acidified to pH values below 4 (Pietsch, 1979). Especially in the 1990s, chemical characteristic and microbial activities of sediment and water are studied in limnological researches. In 1995, the Environmental Protection Agency estimated that about 5,000 km of streams were impacted by AMD in the northern Appalachian area of the United States (Pennsylvania, Maryland, Ohio, and West Virginia). In the abandoned pit areas the formation of the AMLs occurred especially in these parts of the USA (US EPA, 1995).

1.2 Objectives of the Study

Based on the fundamentals discussed above, acidification has serious impacts on the environment and human health. In particular, the interaction of these lakes with surface and subsurface waters significantly alters water quality. Low pH values cause dissolution of numerous heavy metals and trace elements, which already exist in the geological formations. Such acidic waters are inundated to form acidic lakes that have specific characteristics. A number of such lakes were found in the Çan Coal Basin of the province of Çanakkale in Biga Peninsula where lignite mining is done. This region is rich in lignite, which is also known as brown coal characterized by low

calorific value and high sulfur content. With these properties, Çan coal district demonstrate favorable conditions for the formation of acidic lakes. Due to their low calorific value, Çan coals are particularly suitable for mass energy generation and thus are utilized in Çan Thermal Power Plant and partially used for domestic heating purposes. In addition to the open-pit coal mine of the General Directorate of Turkish Coals, there exist several small-to-moderate scale open-pits operated by private companies. These small scale pits are abandoned without any post closure mitigation measure and typically form ideal conditions for AML formation.

In a recent study conducted by Baba et al., (2009), the impacts of mining activities in Çan coal district were assessed from a medical geology point of view. The acidic lakes in Çan basin were initially identified and partly characterized as a part of this study. According to the results of Baba et al., (2009), these lakes were highly acidified and contained elevated concentrations of aluminum, arsenic, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel and zinc. As a result of this chemical composition, these lakes did not have suitable conditions for a rich aquatic life. It was further found that these lakes were also quite unstable as a result of the depleted carbonate minerals in soil within the immediate vicinity of the lake, thus creating potential conditions for landslides. With all these characteristics, the AMLs in Çan coal district were considered to be environmental disasters and were to be rehabilitated to prevent further damage to the environment and human health.

This study takes a step further to characterizing these lakes and focuses on one particular lake to conduct detailed analysis and assessments. Of the several acidic mining lakes found in Çan district, the lake situated within the vicinity of Keçiağılı village is selected to be the primary scope of this study. This lake was named as Hayırtepe AML representing the name of the hill on which it is situated. Hayırtepe AML is one of largest acidified lakes in the region with a surface area of 23,810 m^2 and an average depth of 7.1 m during the time of the field survey. The lake was abandoned about 15 years ago and no mitigation measures have been implemented ever since.

With this lake being the particular focus of this thesis, detailed physical and morphological properties of the lake are studied and a complete water quality monitoring survey was undertaken to characterize the areal and vertical distributions of numerous parameters. A large database is formed as a result of this study. This database is stored in a GIS-platform for spatial interpretation of quality patterns within the lake. Considering the significant impact potential of the acidic mining lake on the environment and human health, possible mitigation measures are also assessed as a part of this research to propose probable and economically viable alternatives to mitigate the impacts associated with high acidity and high heavy metal and trace element content of lakes' waters. Considering the context and the procedures implemented, this study is believed to be one of the earliest examples of a comprehensive acidic mining lake study conducted in Turkey.

1.3 Scope of the Study

With the above mentioned objectives, this thesis is organized in seven chapters. In Chapter 1, a problem statement and an objective of the study is presented. The following section, Chapter 2, continue with literature review, where the main impacts of mining activities on surface and subsurface waters and regional ecology are discussed and the limnological characteristics of acidic mining lakes are presented from some case studies throughout the world. In Chapter 3, the details pertaining to the project area (i.e., Çan district and Çan Coal Basin of the province of Çanakkale) are described with particular emphasis on morphological, geological and hydrogeological features as well as the properties of Çan coals and Çan Thermal Power Plant. In Chapter 4, the materials and methods implemented for field studies, laboratory analysis and data interpretations are discussed. The outcomes of the study are presented in Chapter 5, within the which morphology of the studied AML, its light penetration characteristics and results of the water quality monitoring survey are detailed. Furthermore, the comparison of the results with national and international standards is also given in this chapter. In Chapter 6, general remediation methods for mitigating acidic mining lakes are discussed together with the proposed mitigation

scheme for the studied AML. Finally, Chapter 7 concludes the thesis with major conclusions of the study and recommendations for further investigations.

CHAPTER TWO
LITERATURE REVIEW

Mining is indispensable for economic development as it supplies raw materials for energy generation and industrial production; and thus, is a vital component of human well-being. Nevertheless, it is also one of the most problematic sectors when ecological and environmental issues are concerned. It disturbs the natural balance and could result in environmental disasters, if not implemented in an environmentally sound way.

It is well known that mining has environmental impacts that are observed pre-, during- and post- operation phases. Removal of soil and natural vegetation, formation of acidic mining drainage, contamination of surface and surface water resources with elevated concentrations of heavy metals and trace elements, formation of leachate from mine tailings are among the major impacts of mining activities. The associated duration, type and extent of the impact depend on the particular ore mined and the technical procedures implemented.

Based on these fundamentals, this chapter focuses on the direct and indirect effects of mining activities on surface and subsurface waters as well as on the natural ecology of the mine site. In this regard, sources and characterization of these impacts, their monitoring practices and associated control methods are also explained briefly.

2.1 Acid Mine Drainage and Acidic Mining Lakes

Mine wastes have negative impacts on surface and subsurface water quality, which are mostly associated with leached soluble acids and alkalis, leached metals and soluble metallic salts. The effect of these pollutants including the ones that have toxic consequences on aquatic organisms is dependent on a wide range of physical factors including but not limited to pH, redox potential (Eh) or ORP and temperature. For instance, pyrite oxidation causes low pH values, which in turn result in high heavy metal concentrations such as iron, aluminum or manganese.

The most common type of mine impact for surface and subsurface waters is Acid Mine Drainage (AMD). Although it does also occur naturally in undisturbed environments, acid production from sulphidic minerals is greatly accelerated when the rock is crushed and grounded and is exposed to atmospheric oxygen. AMD is the result of the chemical reaction that takes place when a metal sulphide combines with oxygen and water, yielding a metal hydroxide precipitate and sulfuric acid. The results are leaching of metals and reduced pH of water that comes into contact with oxidized surfaces (Ripley, Redmann & Crowder, 1996, p: 78). When AMD is inundated in the depression areas of open-pit mines, the so-called acidic mining lakes (AML) are formed. Such lakes demonstrate similar characteristics to AMD but might demonstrate different properties as a result of the extented residence times and high water depths.

AMD and AMLs are the most difficult environmental aspects of the hydrospheric residuals to manage, as in most cases these are extremely acidic and contain elevated concentrations of dissolved metals. Ideally, these should be prevented prior to their occurrence but in many cases they need to be rehabilitated by some suitable treatment technique after they are formed. Treatment should be considered as a "must" to prevent surface and subsurface contamination of water resources.

There are also problems with regards to disposal of mine wastes. In addition to the direct physical effects of mine waste disposal, there are a number of other hydrospheric effects that may have an even greater impact on the biosphere. Therefore, surface and subsurface contamination should be considered in every single step of mining activities. The two most important of these are the toxicity and closely related acid-generation capability of many mining wastes. Toxicity is primarily due to the presence of residual metals and process chemicals in the tailings slurry. After deposition in water bodies, waste may continue to oxidize, increasing acidity and metal dissolution. It has been found that one of the most effective ways of controlling the chemical reactivity of sulfide wastes may be to deposit them under deep water, an environment which lacks the oxygen that is an essential element in the process. One of the close relations between acidity and metal release is that, for most

sulfides, solubility (and thus metal release) increases dramatically as pH decreases. Some mine wastes may include essential nutrients (N, P) which could thus result in eutrophication. Nevertheless, this is not a really important and major part of mining pollution (Ripley et al., 1996, p: 79).

2.1.1 Formation Mechanisms and General Characterization

The acidification of pits and water due to acidic mine drainage is a very common problem in many mining regions (Fischer, Reißig, Peukert & Hummel, 1987). Considerable quantities of the deposit soils in the dumps contain iron sulfides minerals such as pyrite, and marcasite, which are oxidized when the layers are removed and mixed, and, thereby, aerated. Therefore, pyrite oxidation takes place when the mineral is exposed to air and water (Evangelou & Zhang, 1995).

Generation of acidic mining drainage is expressed with the following reactions (with pyrite ore) (Gündüz, Okumuşoğlu & Baba, 2007). First reaction of pyrite under atmospheric conditions consists of pyrite oxidation with oxygen (Reaction 1). Sulfur is oxidizing to sulfate (SO_4^{-2}) and ferrous iron is released. Two moles of acids are generated with this reaction for each mole of oxidated pyrite.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{+2} + 4H^+ + 4SO_4^{-2} \qquad (1)$$

In the second reaction, ferrous iron is oxidized to ferric iron (Fe^{3+}) and one mole acid is depleted. Bacteria increases the rate of oxidation. The limiting stage of this reaction is known as oxidation of ferrous iron. This reaction is referred as "governing phase of oxidation rate".

$$4Fe^{+2} + O_2 + 4H^+ \rightarrow 4Fe^{+3} + 2H_2O \qquad (2)$$

Hydrolysis of iron is shown in reaction 3. Hydrolysis is the reaction that disrupts the water molecule. Many metals could be hydrolyzed. As a result of this reaction, the generation of ferric hydroxide precipitate (solid) depends on pH.

$$4Fe^{+3} + 12H_2O \rightarrow 4Fe(OH)_3 \downarrow + 12H^+ \tag{3}$$

The sum of these equations is given below:

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4 \tag{4}$$
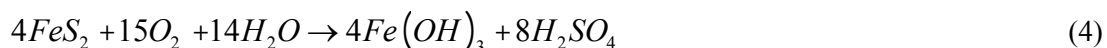
According to these equations, the main reason for AMD generation is dissolved oxygen, water and sulfur-containing compounds such as pyrite.

Geller, Klapper & Schultze (1998) described acidic component H_2SO_4 of AMD and AMLs as the result of oxidation of FeS_2 by leaching rainwater and/or by the fast-rising groundwater table of closed-down lignite pits. Therefore, many mining lakes are expected to have strongly acidic character with their high contents of iron after inundation of the open-cast basin. Based on the fundamental reactions given above, Lottermosser (2003) describes the general characteristics of AMLs are follows:

- *Low pH values*:
  Many natural surface waters could be acidic due to dissolution of atmospheric carbon dioxide in the water and production of carbonic acid. Waters with a pH value of less than 5.5 are most probably associated with the oxidation of sulfide minerals such as pyrite.

- *High electrical conductivity*
  Due to the fact that AMLs have elevated concentrations of numerous anions and cations, their electrical conductivity values are typically much higher than natural waters.

- *High metal concentrations*:
  With increased solubility under acidic conditions, many toxic heavy metals and trace elements (i.e. Al, Cd, Cr, Cu, Fe, Mn, Pb, Zn) dissolve in the water easily

and thus have concentrations reaching 3-4 order of magnitudes higher than their values found naturally in neutral waters.

- ***Disturbed or absent aquatic and riparian fauna and flora***:
  AMLs have low pH and high levels of heavy metals, metalloids, sulfate, and TDS. This chemical composition does not favor an aquatic ecosystem and thus AMLs have limited or no aquatic life in them. Furthermore, the terrestrial ecosystem is also degraded within the immediate vicinity of these lakes.

- ***Reddish-yellow and yellowish-brown colors***:
  The observations of colorful yellow-red-brown precipitates are signal for AMD- AML generation that includes iron-rich precipitates.

- ***Low slope stability***:
  Reduced slope stability is associated with low pH values that remove carbonates found in soil material, which normally provide stability to the soil. Therefore, landslides are mostly observed around these lakes and the water line is extremely loose and muddy and does not even support moderate loads.

2.1.2 Limnological Case Studies on AMLs

Numerous studies have been done in order to determine water and sediment quality of the AMLs. These lakes are commonly observed particularly in areas of surface lignite mining with high sulfur contents. Surface mining of lignite (brown coal) causes numerous environmental problems including a disturbed ecology, billions of tons of soil hauled and an acidified drainage originating from the mine. Among these, water acidification is the most significant and well-known effect where sulphide minerals, i.e, pyrite and marcasite that are commonly associated with coal and most metal ores are oxidized to yield low pH values and elevated heavy metal concentrations (Friese, Hupfer & Schultze, 1998). These lakes are especially formed in the abandoned surface coal mines where the depression cones are filled with the surface drainage from the watershed or the rising groundwater table. In districts with bedrock rich in pyrite/marcasite and poor in carbonate, many mining

lakes are strongly acidified (Schultze & Geller, 1996). In the Lusatian region of Germany, more than 100 such lakes of various sizes are acidified to pH values below 4 (Pietsch, 1979).

Friese et al. (1998) surveyed several mining lakes in Lusatian region, Germany for their general sediment characterization and their metal contents and distribution. 13 selected mining lakes were examined and influence of FeS_2 oxidation and acid mine drainage on the chemical composition of lake water and sediments are expressed. Especially in the acidic lakes, high concentrations of metals were observed, showing different behaviors as a function of water depth. The dissolved metal concentrations were then compared with neutral lakes. The depth profiles of measured parameters were drawn and analyzed. The neutral lakes usually showed quite lower values of dissolved solids and lower concentrations of dissolved metals. It has been found out that the concentration of iron increased by depth as dissolved oxygen decreased.

Karakaş G., Brookland I. & Boehrer (2003) also studied in the Lusatian Region, Germany, and specifically focused on acidic mining lake 111 (ML111). The aim of this study was to determine the physical characteristics of the lake. A relationship between conductivity, temperature and density was developed for ML111 to illustrate the physical characteristics of the lake under seasonal variations.

Nordstrom, Alpers, Ptacek & Blowes (2000) surveyed extremely acidic mine waters which have negative pH such as -3.6 in Iron Mountain, California. Twelve acid mine waters were sampled, in the range of pH between -3.6 and 1.5. Maximum concentrations of SO_4, total iron, Zn and Cu were measured to be 760 g/L, 141 g/L, 23.5 g/L and 4.76 g/L, respectively. Such high concentrations of elements and acidity levels were described in detail as the subsequent steps of pyrite oxidation.

Pedersen, McNee, Flather, Mueller & Pelletier (1998) revised their studies which were conducted on Anderson, Manitoba and Buttle Lakes, Canada. Datasets were collected in winter and summer so that seasonal variations could be detected. This

study included the determination of many physical and chemical characteristics of water, natural sediment quality and pure tailings in the lakes.

Steinberg, Schäfer, Tittel & Beisker (1998) investigated phytoplankton and zooplankton presence in acidic mining lakes. Their study showed a clear difference between in community structure and amount between the acidified and the circumneutral mining lakes. While the diversity of both phyto- and zooplankton communities was quite high in non-acidified lakes; only a few insensitive species were found in lakes with very low pH values.

Kwong & Lawrence (1998) studied in an acidic lake in central Yukon Territory, Canada. Field observations were coupled with analysis on water chemistry, sediment geochemistry and microbiology of a suite of water and sediment samples in order to explain the acid generation and metal immobilization processes occurring at the site. They also discussed alternatives for rehabilitating acidic mining lakes in general. In their measurements, they have found dissolved iron levels of 49,720 µg/L (at a pH level of 2.8) and 367,200 µg/L (at a pH level of 4.6) at depths of 0.2m and 8.5 m, respectively. Moreover, iron, sulfate and chromium concentrations showed an increasing pattern as a function of depth in contrast to zinc, aluminium and cobalt, which showed a decreasing pattern with water depth. It has been concluded that lake acidification is the result of natural subsurface oxidation of reactive pyrite in an adjacent sulphide lens and the entrainment of the acidity thus produced in subsequent groundwater discharge. Dissolved metals, particularly zinc, are immobilized in the lake bottom and along the downstream drainage mainly through adsorption onto iron and manganese oxides and/or through sulphide precipitation. It was suggested that rehabilitations of these kind lakes should be considered with regards to technological feasibility as well as environmental and economic costs.

2.1.3 Mitigations and Remedial Actions

Acid mine drainage and acidic mining lakes could have severe impacts to aquatic resources, plant growth and wetlands, contaminate surface and subsurface water resources, raise water treatment costs and damage concrete and metal structures.

Consequently, implementing suitable treatment techniques for rehabilitating these acidic waters is extremely crucial for environmental sustainability. The economical losses that occur as a result of these acidic waters make such rehabilitation works a priority. For example, in the Appalachian Mountains of the eastern United States alone, more than 7,500 miles of streams are impacted by acidic waters and the Pennsylvania Fish and Boat Commission estimated that the economic losses on fisheries and recreational uses were approximately $67 million annually (Fripp, Ziemkiewicz & Charkavorki, 2000). Following this necessity, Fripp et.al. (2000) have discussed AMD treatment methods in to 13 groups:

(1)   Grout injection

This treatment involves the injection of a grout (typically a mixture involving fly ash) into a mine to control acid mine drainage and mine subsidence.

(2)   Sealing of mine portals

Portals are typically sealed with a plug of expansive grout with steel reinforcement to prevent leakage of acidic waters.

(3)   Mine capping

Capping is usually used for surface mining in order to prevent or reduce the amount of rainfall from reaching acid-forming units in a backfilled mine.

(4)   Limestone damping

Limestone zones can be placed in an acidic stream for direct water treatment.

(5)   Limestone dosing

Limestone could also be introduced into an acidic stream to buffer acidity in regular increments from a large hopper or a plant-type operation.

(6)   Anoxic limestone drains

An anoxic limestone drain (ALD) is an adequately sized buried channel containing limestone that is designed to limit diffusion of atmospheric oxygen with the mine discharge. It requires relatively low metal concentrations (less than 10 to 25 ppm iron and aluminum) and low dissolved oxygen (less than 1 to 2 ppm).

(7)   Anaerobic wetlands

An anaerobic wetland generates alkalinity through bacterial activity and the use of Fe^{+3} as a terminal electron acceptor. Limestone can be added to the organic substrate for additional treatment through limestone dissolution. This type of treatment is limited to cases where the discharge has a pH greater than 4.

(8)   Aerobic wetlands

An aerobic wetland is typically designed to promote precipitation of iron hydroxide. Limestone can be added to the organic substrate for additional treatment through limestone dissolution. This treatment is also limited to cases where the discharge has a pH greater than 4.

(9)   Successive alkalinity producing systems

A successive alkalinity producing system (SAPS) is a combination of an ALD with an anaerobic wetland/pond.

(10)   Open limestone channel

An open limestone channel (OLC) is an adequately sized open channel containing large amounts of limestone to treat AMD.

(11)   Modified open limestone channel

A modified open limestone channel (MOLC) resembles a limestone French drain. It is basically an OLC with a perforated pipe to carry large flows.

(12)   Leach bed

This treatment mechanism involves passing surface water through a bed lined with alkaline material into acidic mine spoil.

(13)   Oxic limestone drain

An oxic limestone drain (OLD) resembles an ALD that has provisions for periodic flushing of sludge. It can operate with relatively high dissolved oxygen but has only been tested for low metal concentration.

Polat, Güler, Akar, Mordoğan, İpekoğlu & Cohen (2002) analyzed the possibility of using Turkish lignitic fly ashes from power plants (Soma and Yatagan) for neutralizing AMD. The possibility of fixing toxic heavy metals in the structure of the aggregate produced was also examined. In some cases, used engine oil was added to

increase the degree of fixation and eliminate another waste material. They have concluded that Turkish lignitic fly ashes can neutralize large amounts up to 150 times their weight.

Surender & Etchebers (2006) used ESKOM (South Africa) power plant's fly ashes as AMD neutralizing agent. They have concluded successfully at both laboratory and pilot plant scales that under suitable agitation and effective aeration ESKOM was effective in neutralizing AMD. Alkaline fly ash effectively increased pH and allowed for the removal of heavy metals (Al, Fe) and sulphate by precipitation.

Wendt-Potthoff & Neu (1998) discussed various reduction processes since bacteria use them as favourable electron acceptors. Microbial processes as a potential approach to in-situ acidic lake remediation include not only sulfate reduction but also other reduction processes such as iron and manganese.

George & Davison (1998) described the results of a large-scale field experiment designed to test the feasibility of increasing the pH of an acid lake by adding fertilizer. A major advantage of the treatment is the very small quantity of fertilizer required. For the treatment mentioned in this study, a total of 5.9 m^3 phosphate solution was applied. If calcium carbonate has been used in this study, a total of 34 tons of calcium carbonate would have been needed.

2.2 Radioactive Wastes

Apart from the acidic wastes, mines also have radioactive wastes that need to be considered carefully. It is known that mining and milling uranium results in solid and liquid wastes or tailings that are radioactive. After the milling process, as much as 98% of the mined uranium ore could remain as solid waste. Because radioactivity remains in the tailings, these wastes could contaminate the environment for centuries if allowed to seep into natural water systems or if exposed to air (Radioactive Waste Management, (n.d)).

Uranium ore minerals can be classified in two groups as reduced and oxidized species. Reduced uranium minerals incorporate uranium as U^{4+} whereas oxidized species have uranium as U^{6+}. Uraninite (UO^{2+}_x) is the most common reduced U^{4+} mineral species, and it is the main ore mineral in many uranium deposits (Burns, 1999). Other important uranium ore minerals are: brannerite (($U,Ca,Y,Ce)(Ti,Fe)_2O_6$); coffinite ($USiO_4.nH_2O$); and pitchblende (i.e. amporphus or poorly crystalline uranium oxide) (Finch & Murakami, 1999).

The hydrometallurgical processing of powered uranium ore is very selective for uranium and removes most of the uranium from the ore. The extracted uranium is only weakly radioactive because of the long half-life of U-238 and the uranium oxide concentrate contains approximately 15% of the initial radioactivity of the uranium ore (OECD, 1999)

Uranium ores have the specific issue of radioactivity, and uranium mine wastes are invariably radioactive. This property differentiates uranium mine wastes from other mine waste types. For example, gold mine tailings contain cyanide, and cyanide can be destroyed using natural, naturally enhanced or engineering techniques. Sulfidic wastes have the potential to oxidize, and oxidation of sulfuric wastes can be curtailed using covers. In contrast, the decay of radioactive isotopes and the associated release of radioactivity cannot be destroyed by chemical reactions, physical barriers or sophisticated engineering methods. Therefore, appropriate disposal and rehabilitation strategies of radioactive uranium wastes have to ensure that these wastes do not release radioactive substances into environment and cause significant environmental harm (Lottermoser, 2003, p: 189)

Groundwater that percolates through rock which contains radium becomes rich in radon which is the daughter product of raidum. An increase in water interchange within the ore mass leads to a higher concentration of radon in groundwater. The enrichment of water by radon takes place because of the following factors (Sengupta, 1990, p:136):

- Rocks contain radium and release radon into percolating waters.

- Water, which carries a normal amount of clay, deposits iron hydroxide in fine rock fissures. In time, iron hydroxide is enriched with radium by circulating waters, and the hydroxides become strong radon emanators. The emanation coefficient of hydroxides approaches 100%.

- Uranium ore, which is widely dispersed in rocks, is dissolved by groundwater.

Previously, uranium mill tailings were often abandoned and left unrehabilitated, or they were discharged into local creek and lake systems. Today, finite disposal options for uranium tailings include: (a) placing them under water in a lake, ocean or wetland environment (MEND, 1993); (b) backfilling them into a mined-out open pit; and (c) dumping them into a tailing dam. Disposal of uranium mill tailings into open pits (for solid radioactive wastes) and tailings dams (for liquids) are the main waste management strategies by doing required isolations from soil and water bodies.

2.3 Tailings

The tailings mass produced worldwide is usually pumped into large surface impoundments so called "tailing dams". The impoundments are best thought of as purpose-built sedimentation lagoons where fine-grained waste residues and spent process water are captured. There are at least 3500 tailings dams worldwide (Davies & Martin, 2000). The slurry pumped into tailings dams commonly contains 20 to 40 wt. % solids (Robertson, 1994). This means that there is a strong possibility for groundwater or surface water pollution. Seepage from a tailings dam through the embankment and base into ground and surface waters is a common environmental concern. The amount of seepage is governed by the permeability of tailings and permeability of the liner or ground beneath the impoundment. There are various clay and synthetic liner systems applied to tailings to reduce leakage into groundwater.

If the tailings have been placed on a permeable base, regional groundwater may migrate into tailings, or tailings seepage may enter the aquifer underlying the tailings dam. Hence, tailings impoundments may represent groundwater discharge/recharge

areas, depending on whether the water table elevation in the tailings is lower or higher than in the surrounding terrain. Active tailings impoundments have higher water table elevations than inactive ones. Inactive tailings impoundments have unsaturated and saturated zones separated by a ground water table. The impoundment should be designed to achieve negligible seepage of tailing liquids into ground and surface waters and to prevent failures of tailings dam structures (Lottermoser, 2003, p: 150). These dams should be engineered for: (a) long-term stability in order to prevent mass movement and erosion; (b) prevention of environmental contamination of groundwater and surface water; and (c) return of the area for future land use. The design objective should be achieving a safe impoundment (Davies & Martin, 2000) as the failure of a tailing dam could result in vital disasters (Table 2.1).

As it could be seen from Table 2.1, the failure of dams resulted in human deaths and damage to ecology, especially in the water bodies. Thus, the control and monitoring of tailing dams are very important in order to prevent contamination to surface and subsurface waters. A tailings dam monitoring program should include the following aspects (Lotermosser, 2003):

- *Dam performance monitoring*:
  Monitoring of water balance, backfilling rate, grain size distribution and process chemical levels such as cyanide must be implemented in the dam.

- *Impoundment stability*:
  Since the collapses of the dams caused many disasters in the past, the slope stability and the pore pressure within the tailings should be monitored.

- *Other environmental aspects*:
  Other parameters including evaporation rates, and radioactivity levels must be monitored. In addition, chemical analysis of ground, surface and seepage waters and downstream stream sediments for numerous contaminants, should be conducted on a periodical basis.

Table 2.1 Some examples of tailings dam failures which resulted with fatalities (after Genevois & Tecca 1993; Morin & Hutt, 1997; Lindahl, 1998)

Date	Location	Release	Impact
22.06.2001	Sebastiao das Aguas Claras, Brazil	?	At least 2 mine workers killed
18.10.2000	Nandan, China	?	At least 15 people killed, 100 missing; more than 100 houses destroyed
11.10.2000	Inez, USA	950 000 m^3 of coal waste slurry released into local streams	Contamination of 120 km of rivers and streams; fish kills
30.01.2000	Baia Mare, Romania	100 000 m^3 of cyanide-bearing contaminated liquid and tailings	Contamination of streams; massive fish kills and contamination of water supplies of> 2million people
19.08.1995	Omai, Guyana	4.2 million m^3 of cyanide bearing tailings	80 km of local river declared environmental disaster zone
1986	Huangmeishan, China	?	19 people killed (dam failure from seepage/instability)
16.07.1979	Church Rock, USA	360 000 m^3 of radioactive tailings water; 1000 t of tailings by dam wall breach	Contamination of river sediments up to 110 km downstream
01.03.1976	Zlevoto, Yugoslavia	300 000 m^3	Tailings flow into river (Dam failure due to excessive water levels and seepage)
11.11.1974	Bafokeng, Impala, South Africa	3 million m^3	15 people killed; tailings flow 45 km downstream (Embankment failure of platinum tailings dam due to excessive seepage)
26.02.1972	Buffalo Creek, USA	500 000 m^3	150 people killed, 1500 homes destroyed because of the failure of coal refuse dam after heavy rain

2.4 Cyanidation Wastes

Cyanide leaching is currently the dominant process used by the minerals industry to extract gold (and silver) from geological ores. Gold extraction is carried out through the selective dissolution of the gold by cyanide solutions through the "process of cyanidation". The wastes of cyanidation are called cyanidation wastes. Unfortunately, large quantities of cyanide-bearing wastes are generated in order to extract very small quantities of gold.

Gold extraction and recovery is a two-stage process. In the extraction stage, gold is dissolved using cyanide. In the recovery stage, dissolved gold is recovered from cyanide solution generally using cementation with zinc or adsorption onto carbon. The extraction stage starts with the preparation of the cyanide solution at the mine site. Solid sodium cyanide (NaCN) and quicklime (CaO) are dissolved in water producing a "barren" cyanide solution. The solution is alkaline and typically contains 100 to 500 ppm sodium cyanide (Logsdon, Hagelstein & Mudder, 1999). If such high concentrations of cyanide are released into the environment, it can pollute surface and ground waters. It is a potentially toxic substance and can be lethal if sufficient amounts are taken up by fish, animals and humans.

Low levels of cyanide could be converted into less toxic compounds in water bodies. The degradation of cyanide takes time and the rates of destruction of the different cyanide species are affected by numerous factors including the intensity of light, water temperature, pH, salinity, oxidant concentration, and complex concentration (Smith & Mudder 1999). Treatment of cyanide occurs naturally in contaminated soils, process waters, tailings and heap leach piles. The natural reduction of dissolved cyanide in mine wastes can be accelerated by applying enhanced natural or engineered treatment process.

2.5 Waste Originated from Phosphate and Potash Ores

In many cases, waste rocks or overburden must be removed to extract phosphate deposits. When mine rocks are processed with water to remove undesired minerals and to concentrate the phosphate for phosphoric acid production, a phosphate mineral concentrate and unwanted rock and mineral particles are generated. These tailings are stocked in tailings ponds or are discharged into water bodies such as rivers and oceans. Thus, waste rocks and tailing from phosphate production are the most important environmental impacts. Mine waste rocks are usually disposed of in piles near the mine. The long term stability of waste rock pits is of prime concern, especially for those piles constructed in areas with high erosion rates. If wastes contain significant quantities of metals and metalloids (e.g. Ag, As, Cd, Cu, Mo, Ni,

Sb, Se, V, Zn), leachates with significant metal and metalloid concentrations may be formed (Vance, 2000). On the other hand, highly sulfidic waste rocks may cause AMD, and such waste materials require appropriate characterization, treatment, monitoring and control.

The production of potash and other salts is based on the mining of evaporatic salt deposits. Mineral processing of potash ores includes flotation of the crushed salt, which results in the concentration of the salt minerals and rejection of the gangue phases. Otherwise, dissolution of the entire crude salts occurs by hot aqueous solutions, and various salts are precipitated. Mined potassium ores have 8 to 30 wt. % K_2O and consequently, potash mineral processing leads to the rejection of the majority of the mined ore as liquid and solid wastes. The major waste products of potash processing contain brines and tailings. Brines may be disposed of by: (a) reinjection into deep aquifers below the orebodies; (b) discharge into ocean; (c) collection in large ponds and release into local rivers or suitable water bodies; and (d) pumping with or without the solid residues. The tailings may be backfilled into underground workings or are stocked near the mine site into large piles or dumps (Lottermosser, 2003).

2.6 Other Environmental Impacts of Mining

Mining activities have also negative effects to the ecology and landscape of the areas surrounding the mine site. Mitigation of disturbed landscape is typically possible when the site is closed and no longer used. Routine monitoring is required until vegetation dominates the mine site.

Another environmental concern of mining activities is dust emissions. Dust could be classified according to their harmful physiological effects. Fibrogenic dust (harmful to the respiratory systems) could originate from iron and tin ores, coal, silica-silicates (talc, asbestos, mica), beryllium ore, metals fumes. Dust could result in carcinogenic effects, if it contains radon daughters, asbestos and arsenic minerals. Toxic dusts (poisonous to human organs) originate from elements such as arsenic,

lead, uranium, nickel and silver. Radioactive dust comes from uranium and thorium ores. Limestone, gypsum and kaolin quarries could also create impact as nuisance dusts. Exposure time, dust composition, particle size are other factors to be considered during mitigation of dust impacts, which typically involves humidifying the dust by water spraying as a source minimization technique.

Noxious gases are also considered to be other environmental concerns of mining activities. Majority of these gases are highly explosive. Most important products of detonation responsible for the creation of fumes are the oxides of nitrogen and carbon monoxide. NO_x are more toxic than CO at a given concentration, while CO is more toxic than other products of detonation. Some of the gases could be absorbed by the blasted rock and carried out of the mine (Sengupta, 1990). In addition to toxicity problems of detonation, noise control is also important for mining. In areas of high noise levels, earplugs and noise helmets are often used if it is impossible to control it. With regards to the inflammable materials, safety precautions are needed to prevent mine fires, the greatest hazards of which are the noxious gases produced by combustion.

CHAPTER THREE
DESCRIPTION OF THE STUDY AREA

The study area for this research is geographically located in Çan district of Çanakkale province in western Turkey. Of the several acidic mining lakes found in Çan district, the lake situated within the vicinity of Keçiağılı village is the primary focus of this study. This lake was named as Hayırtepe AML representing the name of the hill on which it is situated. The Hayırtepe AML is located in the 1/25000 scale topographical map I7b1.

Preliminary investigations regarding the acidic mining lakes in Çan district were first conducted as a part of a research project funded by the Scientific and Technological Research Council of Turkey (TÜBİTAK) through project no. 106Y041. This study focuses specifically on the Hayırtepe AML and provides detailed assessments of this particular lake. In this chapter, a general description of the Çan Mining District and the neighboring Bayramiç Region is discussed to provide a basis for further assessment of the research area. In this regard, general morphological and geological characteristics, hydrologic and hydrogeological features and climate and vegetation patterns are discussed in this chapter. In addition, the characteristics of major mining activities within Çan region are also given with special emphasis on the properties of Çan lignites and the Çan Thermal Power Plant that generates electricity by utilizing these coals.

3.1 General Morphology of the Çan District

The general morphology of Çan district and its surroundings are given in Figure 3.1. As seen from the figure, the district of Çan has a mountainous topography where the mythological Mount İda (1774 m above MSL) and Mount Ağı (934 m above MSL) are the major peaks of the region. Relatively flat topography is typically observed along Kocaçay and Karamenderes Creeks. Ignoring the anthropogenic impacts due to the Çan Coal Works of the General Directorate of Turkish Coals (TKİ), the lowest elevation of the Çan basin depicted in Figure 3.1. is the alluvium plain of Kocaçay Creek and has an altitude of 70 m. The open-pit coal mine has significantly altered

the natural topography of the region and has reached to an elevation of -30 m below mean sea level.

Kocaçay and Karamenderes creeks are the major components of the drainage networks where Kocaçay flows into the Sea of Marmara and Karamenderes flows to the Aegean Sea. These two creeks are seasonal rivers, which generally run dry during summer months. The drainage network of the Çan and Bayramiç Basins as well as the major residential areas is given in Figure 3.1. The study area, where this research was conducted, is located near the village of Keçiağılı and has an approximate elevation of 200 m as shown Figure 3.1.
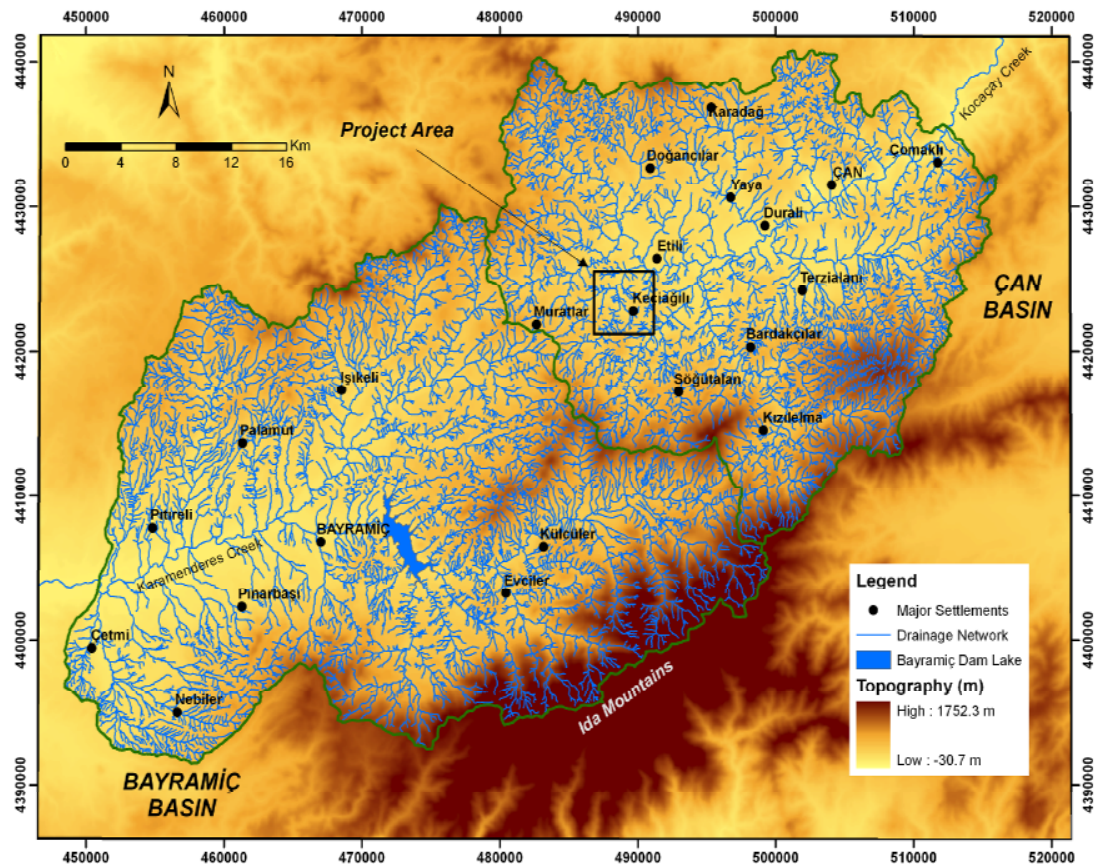
Figure 3.1 Morphology of Çan-Bayramiç Basins (modified from Baba et al., 2009)

3.2 Climate and Vegetation

Climatologically, Çan district is situated within a transitional climate region between Black Sea climate zone and Mediterranean climate zone. North winds are predominant in the area and the mean annual precipitation rates range between 600-850 mm. Precipitation is typically in the form of rain and is mostly observed in autumn, winter and spring months. The maximum and minimum temperatures are observed to be 38.7°C and 11.5°C, respectively (Baba et al., 2009).

The climatic conditions of the region provide suitable background for rich vegetation. About 60% of the total area of the province of Çanakkale is covered by forests within which white pine, black pine, fir, oak, beech, hornbeam and chestnut are the most common tree types.

3.3 Geology

The general geological map of the region is shown in Figure 3.2. Based on this map, four major units are dominant in Çan basin including: (i) lower volcanic units such as andezites, basalts, basaltic andezites, anglomerates and tuffs, (ii) lignite containing sedimentary rocks such as conglomerates, sandstones, claystones, lignitic clays and silicified marns, (iii) upper volcanic units such as anglomerates, weathered anglomeratic tuffs, rhyolitic tuffs and conglometate-sandstones, and (iv) alluviums. The Çan-Etili and Bayramiç basins shown in Figure 3.2 are two neighboring watersheds that are morphologically separated by a volcanic ridge. These two basins run along the east-northeast and west-southwest directions with a total length of 30-35 km and a width of 8-15 km. They are formed as a result of magmatic activity that was periodically dominant following the Eocene period as well as simultaneous tectonic events.
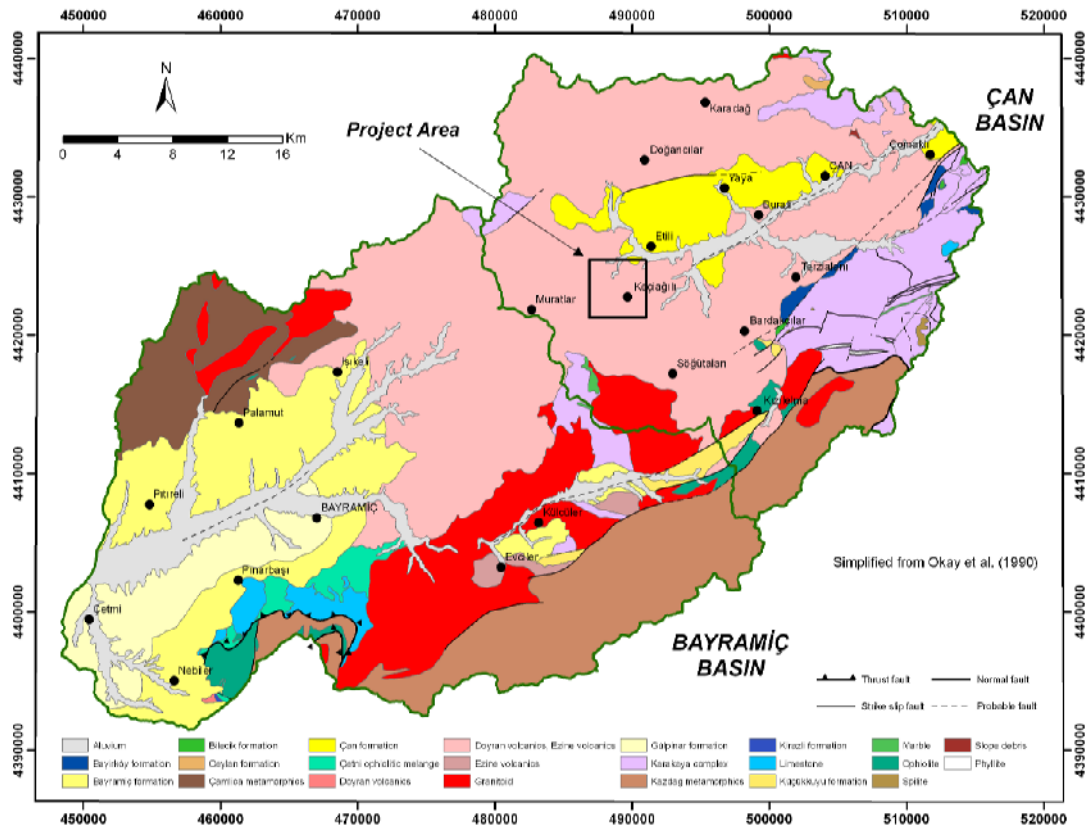
Figure 3.2 Geology of Çan and Bayramiç Basins (modified from Baba et al., 2009)

3.4 Mining Activities

General geology of Çan region has created a suitable environment for numerous mineral deposits that are operated since early ages. Currently, lignite and kaolin are economically extracted from the project area. Among the numerous mine sites, the open-pit lignite mines operated by TKİ and several private companies (i.e., Yiğitler, Er and Söğüt Mining Companies) as well as kaolin quarries are the most important mining activities conducted within the study area.

3.4.1 Properties of Çan Coals

First investigations of Çan coals were carried out during 1956-1957 by the General Directorate of Mineral Research and Exploration (MTA) in order to define the reserve and coal characteristics. Following exploration studies, Çan lignites have

started to be operated since 1979 by TKİ. A snapshot of the open-pit Çan coal mine of TKİ is shown in Figure 3.3.

Figure 3.3 Open pit of Çan Lignite Works operated by TKİ

According to these investigations, the total viable reserve of the open pit of Çan Lignites was defined to be 99,371,000 tons where as the total reserve of the area excluding the open pit reserve was calculated to be 43,288,000 tons based on the polygon method that uses the boring evaluations conducted by MTA during 2001 and 2002 (Baba et al., 2009).

Çan lignites contain approximately 6% (3–8%) sulfur, 23% (14.67– 28.42%) humidity and 24% (3.48–29.83%) ash. The major oxides in Çan coals are dominated by SiO_2 (0.65–20.64%), Al_2O_3 (0.4–6.09%), Fe_2O_3 (0.29– 4.09%) and others including MgO, CaO, NaO_2, TiO_2, K_2O, P_2O_5, MnO, Cr_2O_3, that are found less than 1.0% (Baba, Gürdal, Şengünalp & Özay, 2007).

3.4.2 Çan Thermal Power Plant

Çan Thermal Power Plant (ÇTPP) located in Çan district is constructed between the years 2000 and 2004 by Turkey's Electricity Generation Co. (TEAŞ) in order to supply the increasing energy requirement of Turkey by utilizing the low calorific value, high sulfur content lignites of the area (Figure 3.4). The 2x160 MW installed capacity power plant has a total annual production of 2.25 billion KWh and an estimated operational life of 30 years.

Figure 3.4 Çan Thermal Power Plant

ÇTPP is located about 3.5 km away from Çan Lignite Works and is situated to the northwest of the village of Durali. The coal requirement of the plant is provided from the Çan open-pit coal mine operated by TKİ. The operational reserve of the Çan-Durali coal zone is calculated to be 74 million tons. The ÇTPP utilizes 1.82 million tons of lignite per year with an average calorific value of 2400 Kcal/kg.

The ÇTPP is the first thermal power plant constructed in Turkey with a fluidized-bed combustion technology. In the fluidized bed system of ÇTPP, the high sulfur containing coals are co-burned with calcium carbonate to absorb the sulfuric gases

that originate from combustion processes. The collected ash and other solid by-products are humidified to prevent dust emissions and disposed in the ash disposal area within the power plant territory located along the Dombul Creek valley near the village of Yayaköy (Baba et. al, 2009).

The objective of utilizing fluidized-bed technology is to minimize SO_2 and NO_x emissions that occur during combustion. This is an environmentally friendly technology for energy generation that specifically utilizes low quality, high sulfur content coals with high ash that could not be utilized for any other purposes. During the selection phase of this technology for Çan lignites, burning and sulfur emission tests were implemented and successful results were obtained.

3.5 Hydrology and Hydrogeology

The creeks and rivers in Biga Peninsula have a variable flow regime that mainly depends on the seasonal precipitation pattern. The majority of these creeks practically dry up during the summer season (July, August and September) and start to flow again following autumn rains. The highest flows are observed during spring months where snowmelt is augmented by spring rains. The main elements of the drainage network shown in Figure 3.1 are Karamenderes, Sarıçay and Kocabaş (Kocaçay) creeks that primarily are fed from Ida Mountain.

Karamenderes Creek has a total length of 110 km and is the longest river in the region. It originates from the Ida Mountain and flows towards southwest and drains into the Aegean Sea. Kocaçay creek, on the other hand, is the most important drainage unit that pass through the Çan Basin flowing in east-northeast direction and drain into the Sea of Marmara. According to the data collected by the General Directorate of State Hydraulic Works (DSİ) during 1984-2006, the long term monthly averages of Kocaçay creek are given Figure 3.5. As seen from the figure, the average high (3.27 m^3/s) and average low (0.06 m^3/s) flow values are observed in March and August, respectively. The mean annual flow rate of Kocaçay creek is computed to be 1.29 m^3/s.
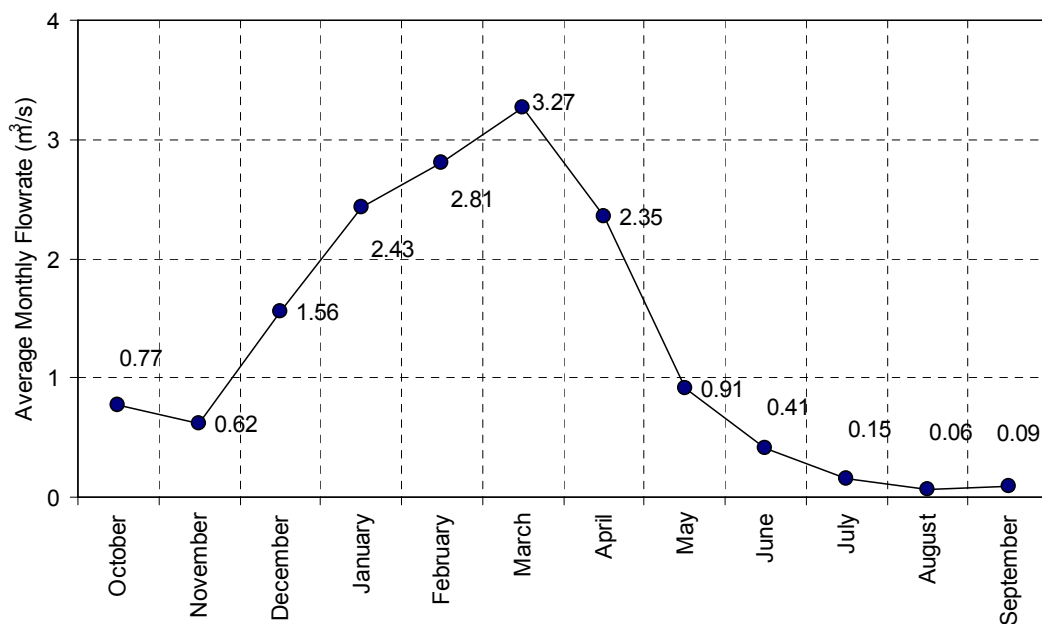
Figure 3.5 Long term monthly averages of flowrate of Kocaçay creek (DSİ, 2006)

As seen from Figure 3.1, Kocaçay Creek flows from west to east. The sediments originating from the western highlands of its watershed are deposited along the flow path in flat regions to the east of the project area. In such flat zones, small to moderate sized alluvial plains are formed with these deposits. These flat areas have significant ground water potential that is primarily used for domestic, irrigational and industrial water supply. In essence, the cooling water requirements of ÇTPP and the process water demand of Çanakkale Ceramic Factory are supplied from the well fields drilled in the highly permeable alluvial aquifer of Kocaçay creek near Çan district center.

The general hydrogeology of the area is given in Figure 3.6. As it is shown in the figure, four main units represent aquifer characteristics with variable productivity values. Accordingly, the permeable aquifer that is observed along the Kocaçay river bed is the most productive unit which is mainly formed from alluvial material deposited by Kocaçay creek. The water levels in this aquifer are very close to the surface characterizing a strong surface-subsurface interaction. The semi-permeable aquifer is another water bearing strata that is found in the vicinity of the river network. Karstic aquifers are also seen in the study area primarily to the south of Çan

Basin where Ida Mountain range is situated. The fractured aquifer is also observed widely in Çan Basin and the project area. Finally, impervious zones are observed in the south-southeast parts of the basin and are not a significant source for groundwater.
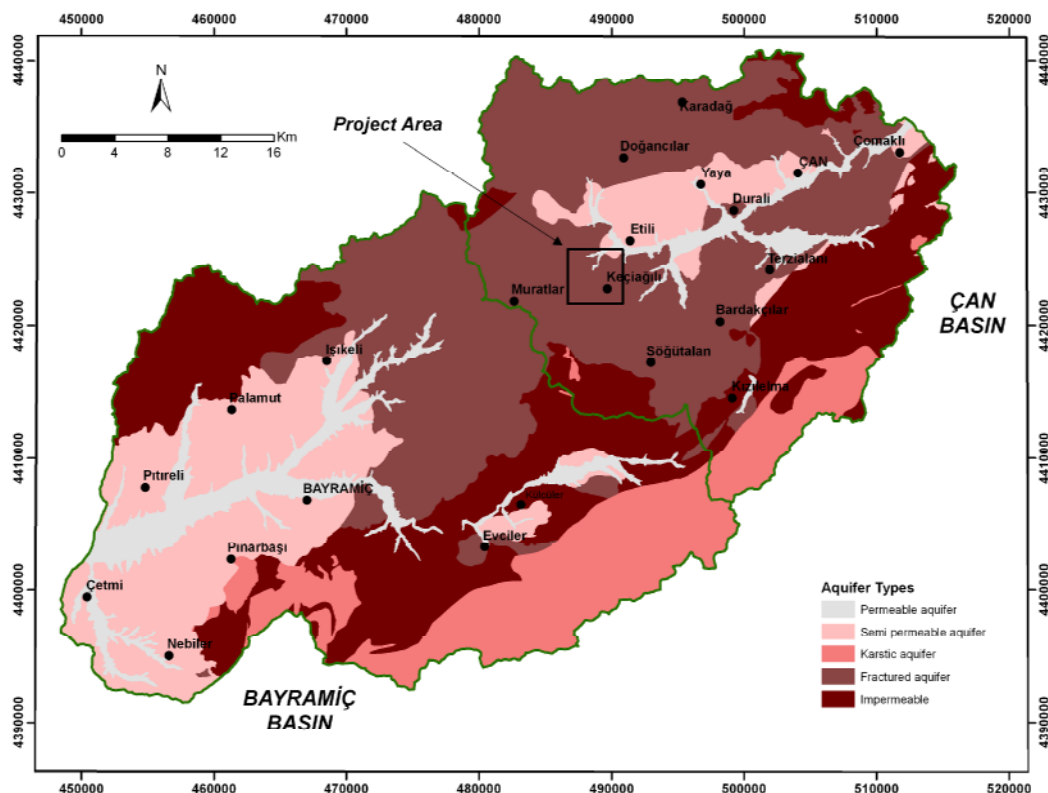
Figure 3.6 Hydrogeology of Çan and Bayramiç Basins (modified from Baba et al., 2009)

In a study conducted by Baba et al. (2009), water quality of both Çan and Bayramiç Basins are studied via samples collected from about 60 sampling locations in three different time frames (i.e., April 2007, July 2007 and January 2008) The primary statistics of the results of this study are given in Table 3.1. The most outstanding finding of this study was the presence of a number of acidic mining lakes in Çan Basin and the associated degraded water quality in these lakes. Thus, this research follows the study of Baba et al. (2009) and provides detailed assessment of one of these lakes.

Table 3.1 Water quality in Çan and Bayramiç Basin (from Baba et. al, 2009)

	April' 2007			July' 2007			January' 2008		
	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean
Physical Parameters									
T (°C)	22.2	9.6	15.17	34.5	12.6	24.37	18.7	6.03	11.84
pH	8.7	2.81	6.72	8.96	2.59	6.42	8.4	2.43	6.54
EC (μs/cm)	6730	116.5	1162.51	9310	105	1727.62	5080.00	67.80	862.26
Eh (mV)	239.8	-92.1	11.10	-	-	-	213.90	-106.70	-6.05
Static water level(m)	7.45	0	2.99	7.8	1.63	4.43	6.10	0.7	2.22
Chemical Parameters									
Cl (ppm)	49.3808	2.2165	15.21	-	-	-	250.82	3.65	41.56
F (ppm)	1.0422	0.2006	0.52	-	-	-	4.3968	0.0157	0.5426
SO_4 (ppm)	468.2	2.334	128.54	-	-	-	10891.77	2.9736	629.4742
HCO_3 (ppm)	2850	10	485.00	-	-	-	544.054	21.1027	255.396
Al (ppb)	771504	2	23413.54	1135151	1	37229.12	1039514	1	30367.74
As (ppb)	45.2	0.5	4.79	71.9	0.5	5.87	90.20	0.60	7.28
B (ppb)	3236	5	266.29	6335	5	737.81	4908	5	480.73
Ba (ppb)	331.68	0.86	63.57	409.94	0.5	64.58	462.21	1.17	74.82
Be (ppb)	263.76	0.05	6.87	384.61	0.05	13.12	207.20	0.06	24.35
Br (ppb)	812	18	124.72	1076	15	183.92	1009.00	16.00	169.10
Ca (ppb)	444714	4111	120759.03	617464	3439	151842.61	556441	4101	128585.2
Cd (ppb)	53.7	0.05	1.45	66.41	0.05	2.37	72.73	0.06	5.37
Ce (ppb)	3267.1	0.01	83.12	4692.6	0.01	162.56	4397.71	0.01	141.95
Co (ppb)	4698.4	0.02	136.58	6555.2	0.03	230.95	6402.34	0.02	195.36
Cs (ppb)	69.56	0.01	3.39	81.31	0.01	4.83	80.75	0.01	4.01
Cu (ppb)	413	0.1	20.01	467.2	0.2	36.62	331.20	0.30	23.99
Fe (ppb)	436000	10	13457.38	609371	10	25621.98	527599	12.00	26686.5
K (ppb)	36391	167	4751.78	34392	173	5925.90	36133	230	5240.81
La (ppb)	714.19	0.01	19.02	975.46	0.01	41.16	931.02	0.01	33.74
Li (ppb)	1246.9	0.4	67.38	1516.2	0.4	133.52	1218.30	0.40	89.76
Mg (ppb)	464046	2125	45756.23	808329	1139	66533.45	748778	1650	54244.7
Mn (ppb)	142989.6	0.06	5511.18	209658.3	0.05	8988.79	177640	0.09	7039.39
Mo (ppb)	15	0.1	1.08	20.1	0.1	1.69	14.80	0.10	1.33
Na (ppb)	433798	5528	65220.67	1479890	3027	134734.32	1186596	3198	76376.76
P (ppb)	878	20	104.56	2418	20	99.16	785	21	98.79
Pb (ppb)	30.6	0.1	0.96	37.6	0.1	1.89	42.70	0.10	2.69
Rb (ppb)	86.45	0.11	10.08	93.51	0.19	18.30	75.22	0.11	11.24
S (ppm)	2496	1	161.05	4198	1	338.90	3466.00	1.00	250.57
Sb (ppb)	0.99	0.05	0.15	1.41	0.05	0.24	1.17	0.06	0.21
Sc (ppb)	91	1	7.29	141	3	18.29	111	1.00	9.98
Se (ppb)	5	0.5	1.34	5	0.5	1.80	10.40	0.50	1.66
Si (ppb)	66308	3984	15285.45	75535	3399	20776.16	57104.0	3313.00	16913.95
Sr (ppb)	3758.16	32.06	861.73	4460.64	25.66	1097.78	5388.75	32.87	905.21
U (ppb)	182.94	0.02	11.16	250.78	0.02	15.50	271.30	0.04	14.18
V (ppb)	74.7	0.2	3.60	18.1	0.2	3.14	107.00	0.20	5.60
Y (ppb)	2662.85	0.01	70.23	3672.36	0.01	117.29	3617.36	0.02	99.38
Zn (ppb)	18034.5	0.5	485.44	24128.2	0.5	851.86	20328.8	1.60	614.53

CHAPTER FOUR
MATERIALS AND METHODS

The materials used and methods conducted for field studies, laboratory analysis and data interpretations are discussed in this chapter. The field studies include a general characterization of the study area, a morphological description of the acidic mining lake in particular and a water quality monitoring campaign. The water samples collected from different locations and different depths of the lake are then analyzed for primary physical parameters, major anions and cations and some trace elements and heavy metals in the laboratories of Dokuz Eylül University Environmental Engineering Department. Finally, all morphological and water quality data are then gathered in a Geographical Information System (GIS) platform for data visualization and interpretation.

4.1 Field Study

As a part of preliminary planning for field studies, numerous equipments and devices were prepared and made ready for the excursion. These included a boat for bathymetry measurements and water quality monitoring activities in the lake; a global positioning system (GPS) device for spatial positioning of sampling/bathymetry points and water surface boundary; a multi-parameter probe for in-situ measurements of a number of water quality parameters; a Nansen-type water sampling bottle for collecting samples from different depths; a Secchi Disk for measuring the extent of light penetration; an equipment for bathymetry measurement; and, auxiliary equipments such as marine ropes, luminous markers, stakes, sledgehammer, spray dye, acidifier, sampling bottles, and portable coolers. The field studies were then conducted in Hayırtepe AML located in Keçiağılı Village of Çan District, Çanakkale during 8-14 September 2008.

4.1.1 Preliminary Works

Determination of the Water Surface Boundary of Hayırtepe AML

Prior to field studies, a satellite image of the Hayırtepe AML was acquired from Google Earth v. 4.3, a high resolution aerial and satellite imagery software (Figure 4.1). The approximate coordinates of the water surface are obtained from this image, which was taken on April 30, 2003 and zoomed to an eye altitude of 570m. All preliminary works are planned with this draft water surface boundary, which has shown variations since 2003 due the yearly precipitation, evaporation and drainage patterns. The actual water surface boundary at the time of the field study is determined by GPS measurements. When Google Earth frame and the actual boundary obtained from GPS are compared, one could clearly observe the change in the AML's water surface that is also observed visuallyon the field (Figure 4.2).

Figure 4.1 Satellite image of Hayırtepe AML

During the course of the field works, the coordinates of Hayırtepe AML was determined with a handheld GPS device (Magellan Explorist 600) in September 2008. The device generates spatial coordinates (X, Y and Z) from satellite signals.

The number of satellites that the device could connect to is influenced by atmospheric effects, multipath effects, selective availability, relativity and Sagnac distortion. During the course of the field work, an average ±10 m error was detected on the device's display for the data points collected.

Figure 4.2 Water level decrease in Hayırtepe AML

An important characteristic of acidic mining lakes is low slope stability and carrying capacity of the surrounding soils. This phenomenon is particularly associated with the reduced carbonate levels in the soil structure due to the extremely acidic nature of water in the lake. Thus, soil's carrying capacity is reduced and one could not stand along the banks of the lake as seen from Figure 4.3. Therefore, the collection for water surface coordinates could only be performed with 1-2 m accuracy as it was dangerous to get coordinates directly from the water boundary. Nevertheless, this error was still within the internal error of the GPS device.

Figure 4.3 Low slope stability and carrying capacity of soils surrounding the lake

A total of 52 points were recorded with an average distance of 17m intervals between two consecutive data points. The 17m interval value was considered to be sufficient based on the local topographical conditions of the area as well as the accuracy of the device used to collect the coordinates. This data set is then transferred to GIS database and a point-to-polygon analysis is conducted to give a perimeter value of 892m for Hayırtepe AML during September 2008 as shown in Figure 4.4.

Formation of the Transects

When the data points for water surface boundary are processed, the lake surface area was computed to be 23810 m^2. From a morphological point of view, the maximum distance along the two diagonals of the lake was measured to be 349.50 m and 182.38 m (Figure 4.4). Considering the moderately small dimensions of the lake and the significant wind pattern on the lake surface, transects need to be formed that connects the two shore of the lake. To form these transects, stakes were piled and marine ropes were stretched in between. Along these transects, bathymetry measurements were made at every 10 m intervals and water quality sampling were

conducted at every 20-40 m distances. Without the support provided by the rope, significant amount of lateral displacement (i.e., 10-15 m) would have been experienced due to wind effects, creating inaccurate sampling locations for bathymetry measurements and water quality sampling. Such wind-induced displacement would have altered the overall accuracy of the field work on the lake.
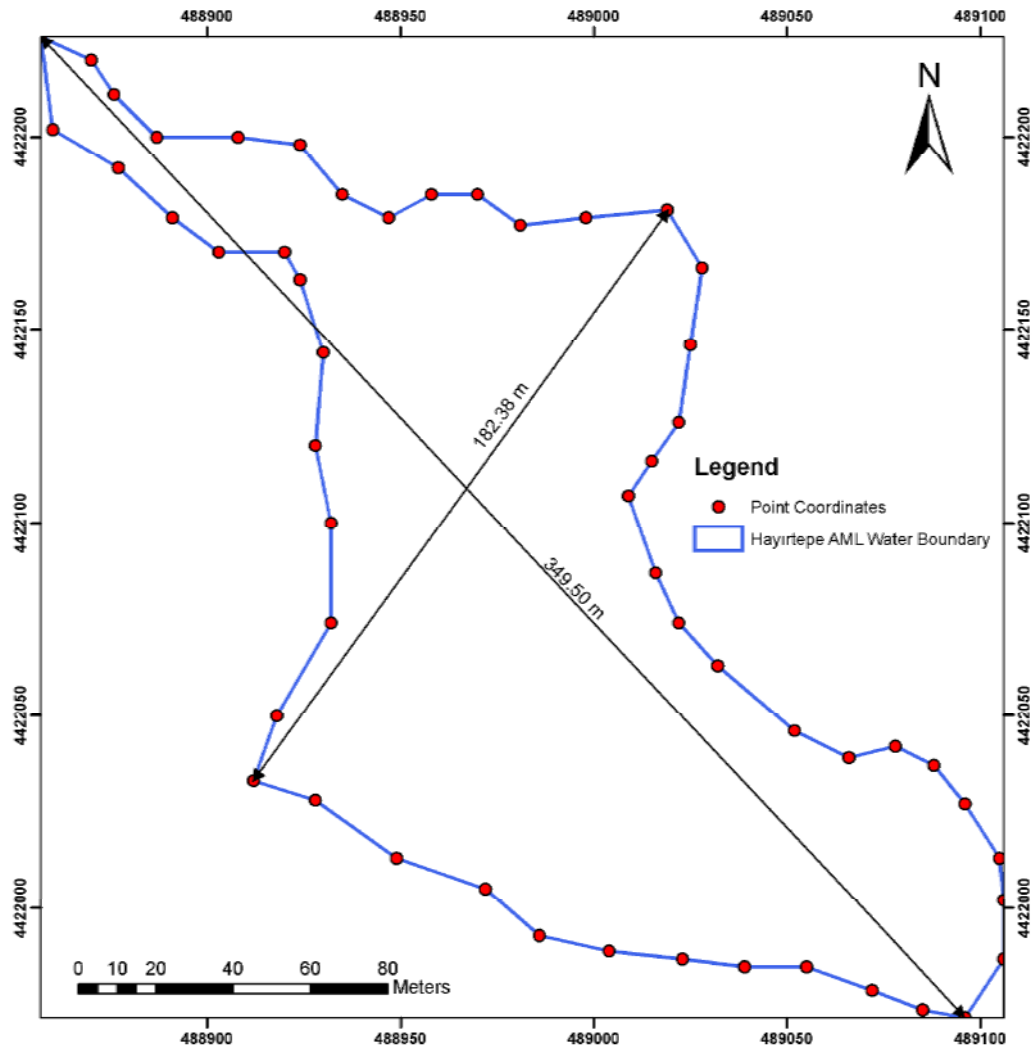
Figure 4.4 Water surface boundary of Hayırtepe AML during September 2008

In order to create transects, two stakes were piled at opposite shores of the lake and white marine ropes were tightly stretched in between. The stretching of the marine ropes is shown in Figure 4.5. In total, nine transects were formed on the lake at moderately uniform intervals based on lake morphology. The overall transect

pattern on the lake is shown in Figure 4.6. Despite the relative stability provided by transects, it should be noted that there were still certain amount of lateral displacement (i.e., 3-4 m) of the boat due to wind effect. The final locations of transects are shown in Figure 4.7.

Figure 4.5 Stretching of the marine ropes

4.1.2 Measurement of Lake Bathymetry

In order to measure the bathymetry of the lake, a 50 m marine rope is attached to a weight of 1 kg and is marked in every 1 m intervals by marking cords. This equipment is released from predefined bathymetry points that were marked on each transect at every 10 m (Figure 4.7). When the weight touched the bottom of the lake, the released rope length is measured and recorded (Figure 4.8). In total, bathymetry measurements were conducted in 62 different points, which were then used to compute the total lake volume (representing conditions in September 2008) by Surfer Software.

Figure 4.6 Transects on AML surface (indicated by white lines)

As it could be seen from Figure 4.7, the bathymetry points and transects' lines do not overlap due to wind effect. Despite the fact that bathymetry measurements were performed while the transect ropes were grabbed by a crew, small lateral displacements of the marine ropes were inevitable. Following bathymetry studies, the sampling locations were selected based on depth variations along transect lines.
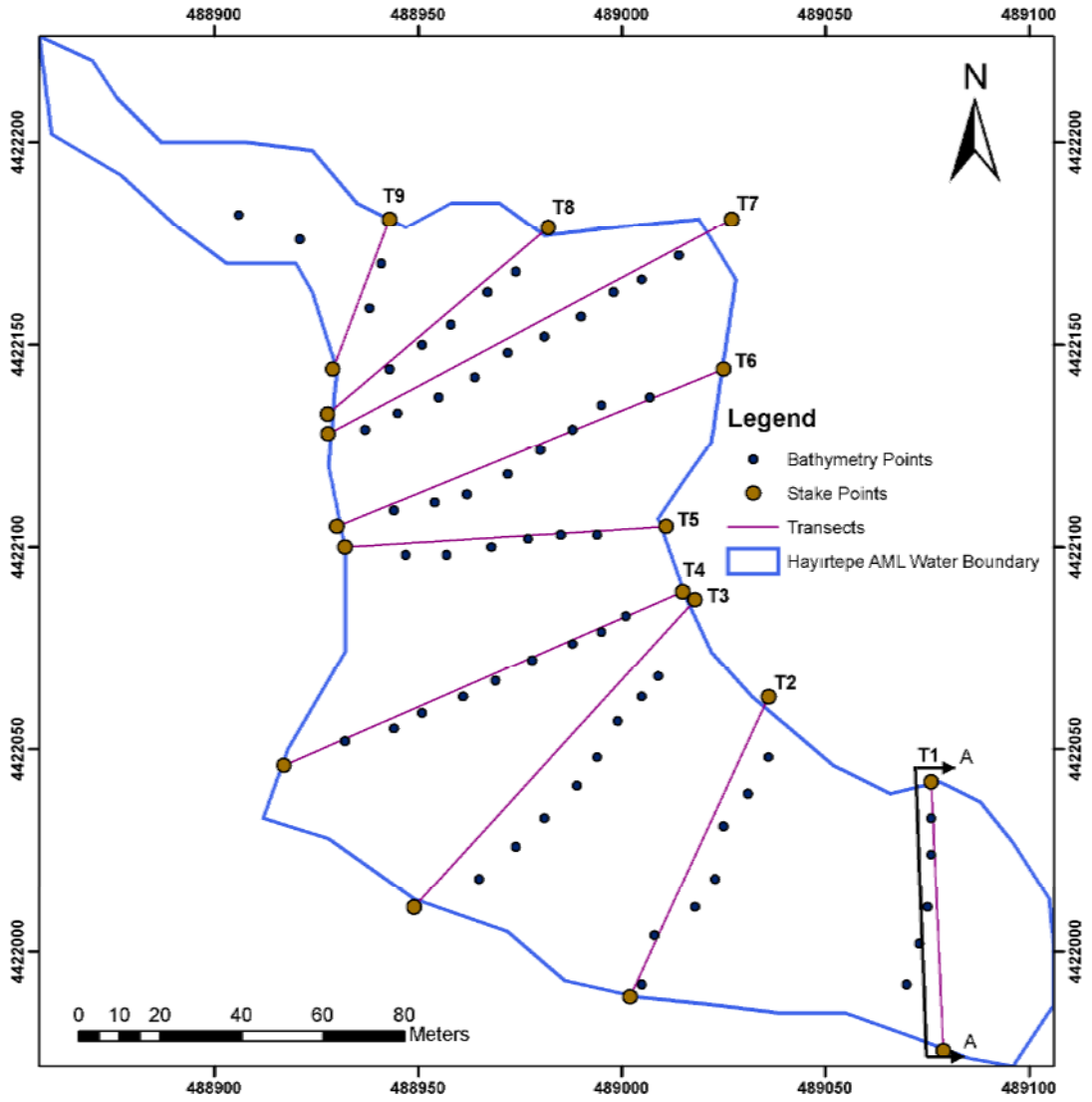
Figure 4.7 Bathymetry points and transects

Figure 4.8 Bathymetry measurements

4.1.3 Measurement of Field Parameters and Water Quality Sampling

Based on the results of the bathymetry study and the characteristics of general lake morphology, a total of 23 sampling locations were identified on lake surface (Figure 4.9). The locations of these sampling points always coincided with some of the bathymetry points. In general, it was aimed to achieve a relatively homogenous distribution of sampling points within the lake's surface area. At all 23 sampling locations, surface water samples were collected, which essentially represented the water quality of the top 50 cm of the water column. In addition, samples were also taken from different depths which were determined according to the bathymetry of the particular point. These samples collected from different depths represented a water column of ±50 cm of the corresponding depth. Totally, 56 water quality samples were collected from the lake. In general, the deepest point of each transect was used as a sampling point. This depth-integrated sampling allowed profile characterizations for all quality parameters.
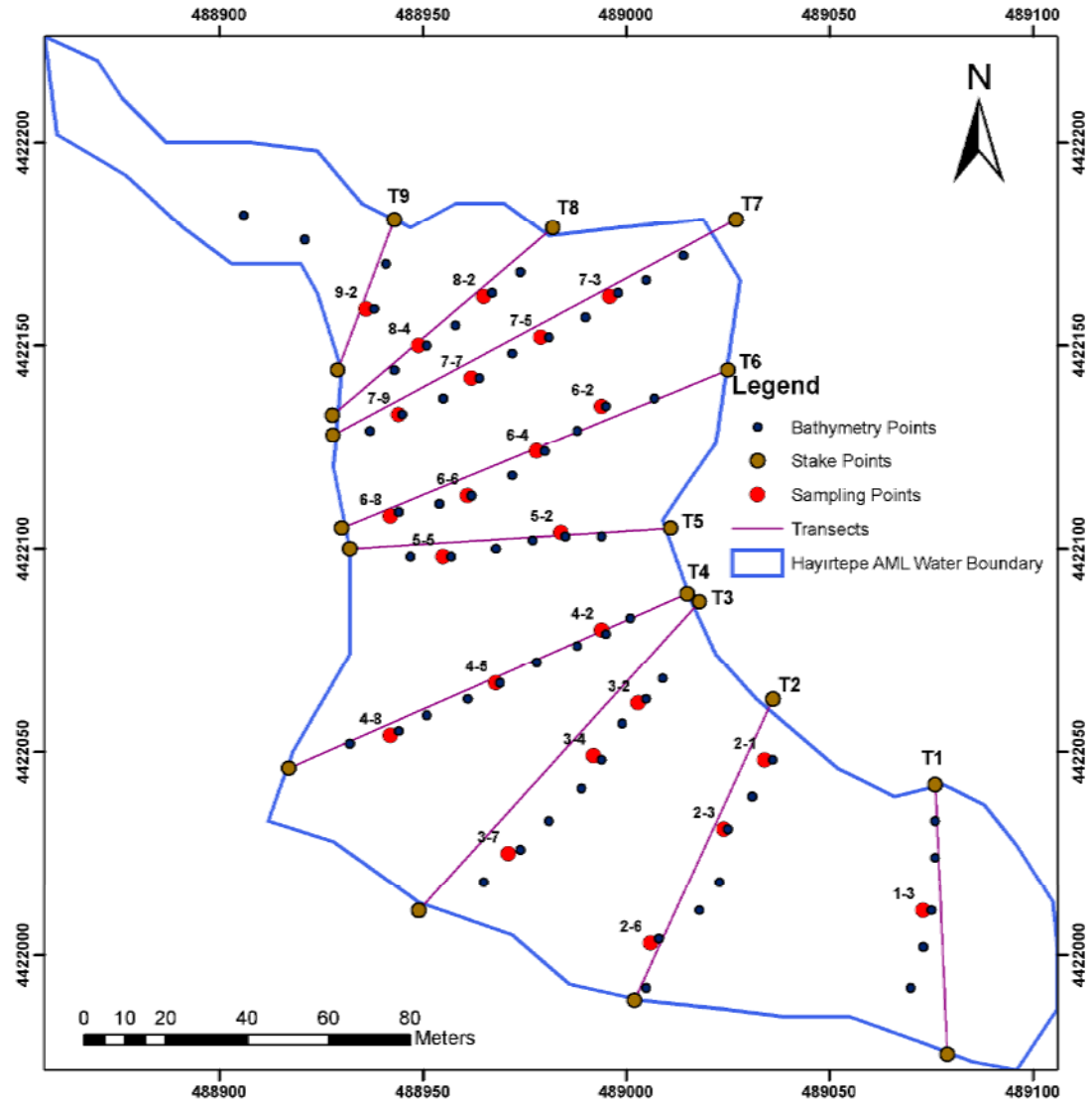
Figure 4.9 Sampling points of the lake

Sampling points were then numbered based on a two-numbered scheme, which identified not only the transect to which the sampling point belonged to, but also the relative sampling ID within the particular transect. For instance the sampling point "1-3" represents a sample along transect 1 located at the 30 m from the northern shoreline. Similarly, the sampling point "4-5" stands for a sample along transect 4 located at 50 m from the northern shoreline as shown in Figure 4.10. Then, three samples were collected from point "1-3" at d=0m, d=5m and d=9m as seen from the figure.
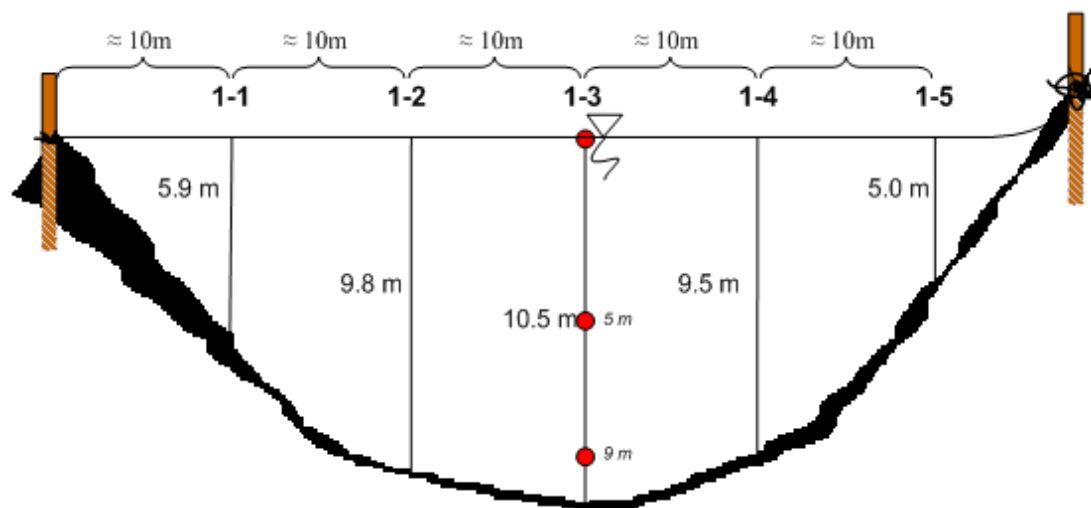
Figure 4.10 Cross-section of the 1st transect (A – A' section shown in Figure 4.7)

Measurement of Field Parameters

Physical parameters (pH, Oxidation Reduction Potential, Temperature, Electrical Conductivity, Dissolved Oxygen, Salinity and Total Dissolved Solids) were measured in-situ with a multi-parameter probe (Hanna Instruments HI 9828). Measured field parameters and their explanations are given in Table 4.1.

Table 4.1 Measured field parameters

Parameter	Explanation
pH	Negative logarithm of hydrogen activity; -log [H+].
Oxidation Reduction Potential (ORP)	Oxidation-reduction potential. Expressed as millivolt (mV).
Temperature	Expressed as ºC.
Electrical Conductivity	Ability to conduct electrical current. Expressed as µS/cm.
Dissolved Oxygen	Amount of dissolved oxygen. Expressed as mg/L and % saturation.
Salinity	Related to the amount of total dissolved solids. Expressed as PSU (Practical Salinity Scale)
Total Dissolved Solids	Amount of dissolved solids. Expressed as mg/L.

Water Quality Sampling

A water quality sampling bottle according to Nansen-type (Nansen-bottle) is used in water quality monitoring performed below surface. The transparent sampling bottle (HydroBios) had a capacity of 1.7 L and was made from hard plastic materials to avoid cross-contamination from metal ions. The bottle is equipped with a steel wire that is used to release the bottle to the desired sampling depth and a messenger to close the ball valves upon sampling. The steel wire was marked with a waterproof marker at every 1 m intervals. The Nansen-bottle is released from the boat to the desired sampling depth with ball valves open. When the desired depth is reached, the messenger is dispatched along the steel wire. The messenger hits the bottle and closes the ball valves while it rotates. The working principle of the Nansen bottle used in this study is given in Figure 4.11.

Preservation and Preconditioning

The water samples collected from the bottle where then transferred to polyethylene bottles of 500 mL and 50 mL capacity and kept in portable coolers. The 500 mL samples were used in anion and cation analysis and the 50 mL samples were used in trace element and heavy metal analysis. The samples for the trace elements and heavy metal analysis were acidified with nitric acid to achieve a pH value of below 2. The samples were then refrigerated and kept at 4ºC until analysis.

4.1.4 Measurement of Light Penetration

A Hydro-Bios, Kiel type secchi disc was used to measure the maximum depth of light penetration in the lake. The disc is made of white lacquered brass and has a diameter of 200 mm. The weight is 1.7 kg and is equipped with a rope of 3 meters length. There are 10 marks in distances of 200 mm on the first 2 meters above the disc. The disc is lowered into the water and reading of the depth is made by means of the marks at the rope when the disc is no longer visible in the water. It is lowered another 0.5 m and then released slowly again. The second reading is made when the disc becomes invisible. Now the arithmetic mean from both readings was taken to determine the visibility depth.
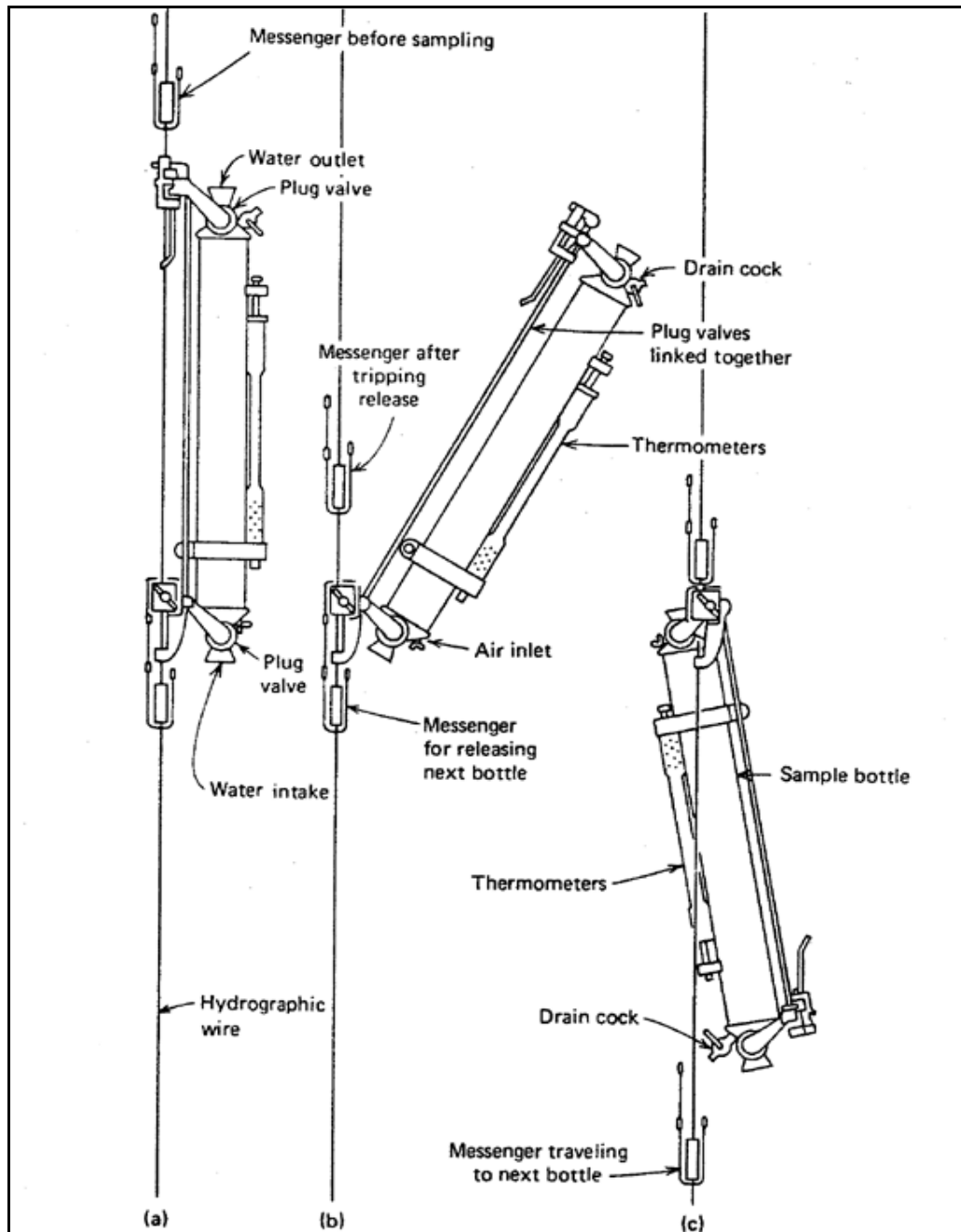
Figure 4.11 Working principles of Nansen-Bottle

4.2 Laboratory Analysis

4.2.1 Measurement of Major Anion and Cation Ions

Major anions (fluoride, chloride, nitrate, nitrite, bromide, phosphate and sulfate) and major cations (sodium, calcium, magnesium, potassium, ammonium, and

lithium) were analyzed with ion chromatography (Dionex ICS-3000) in Dokuz Eylül University laboratories. Because of the high sulfate concentrations in the samples, the analysis procedure required high dilution ratios for most of the samples.These dilution ratios for anions and cations were calculated according to the expected concentrations which are estimated with consideration of pre-sampling results of the AMLs' water quality in the vicinity. Finally the dilution ratios were conducted with regard to standard solution (mixed calibration solution) concentrations. For anions analysis dilution factor was calculated to be 50. Six-point calibration was selected as 0.2 ppm, 20 ppm, 40 ppm, 60 ppm, 80 ppm and 100 ppm for the anions and reporting limits in that for floride 2 ppm, for nitrate, nitrit, chloride and sulfate 10 ppm, and for phosphate 20 ppm.For cations analysis dilution factor was calculated to be 2. Five-point calibration was selected as 4 ppm, 60 ppm, 150 ppm, 225 ppm, and 300 ppm for the cations and reporting limits in that for potasium and calcium 8 ppm, for ammonium and magnesium 4 ppm, for sodium 3.2 ppm and for lithium 0.8 ppm.

The ion chromatography method used in this study incorporates a mobile phase and stationary phase. The mobile phase is usually a mixture of water and some buffer solution. Buffers are mixtures of acids and their salts or bases and their salts, and are used to maintain the pH of solutions. The stationary phase is the anion or cation column, which contain an active resin. The water samples are typically injected into the column thru an auto sampler mechanism. The sample is pushed through the column by the force of the constant flow of the mobile phase. As the sample contacts the column, the dissolved ions in the sample will have an affinity for the column and replace less retained ions like those which make up the buffer. This exchange process is continuous, however, and the length of time that the various ions retain themselves on the column is what delays their travel through the column. Since each ion has a different affinity for the column, some will spend less time while others will spend more time in the mobile phase. The fact that each ion has a different residence time in the mobile phase allows for its separation. Eventually, each ion will come out of the column and be detected by the conductivity detector. The result is a peak and the area under each peak represents the relative amount of each ion. When compared

against known standards, the amount of each ion is determined. (Ion Chromotography, n.d.).

4.2.2 Measurement of Trace Elements and Heavy metals

Trace elements and heavy metals in water samples were analyzed with inductively coupled plasma- optical emission spectrometry (Perkin Elmer OES 2100 DV, ICP-OES) in Dokuz Eylül University laboratories. ICP-OES is a fast multi-element technique with a dynamic linear range and moderate to low detection limits (~ 0.2-100 ppb). The instrument uses an ICP source to dissociate the sample into its constituent atoms or ions, exciting them to a level where they emit light of a characteristic wavelength.

When plasma energy is given to an analysis sample from outside, the component elements (atoms) are excited. When the excited atoms return to low energy position, emission rays (spectrum rays) are released and the emission rays that correspond to the photon wavelength are measured. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the rays' intensity. To generate plasma, first, argon gas is supplied to torch coil, and high frequency electric current is applied to the work coil at the tip of the torch tube. Using the electromagnetic field created in the torch tube by the high frequency current, argon gas is ionized and plasma is generated. This plasma has high electron density and temperature and this energy is used in the excitation-emission of the sample. Solution samples are introduced into the plasma in an atomized state through the narrow tube in the center of the torch tube. (ICP analysis, n.d.).

4.3 Data Interpretation

When the analysis of all samples was completed, the results were gathered in a database for further analysis and interpretation. This database was transferred to a GIS platform for spatial analysis. The platform used in this study was ArcGIS v9.1 by ESRI Inc. and Surfer v8 of Golden Software.

Prior to transferring the data to GIS platform, the database was organized to include all spatial coordinates of bathymetry and sampling points, results of physical and chemical parameters and bathymetry measurements. In addition, other necessary map layers such as DEM, drainage network and residential areas were created. Subsequently, the spatial distribution maps for selected parameters were drawn by using suitable interpolation algorithms thru Spatial Analyst tool. These parameters include all physical parameters measured in the field, major anion and cations as well as trace elements and heavy metals. Inverse Distance Weighted (IDW) interpolation algorithm was the implemented method for obtaining these maps. At the same time, Kriging and Spline methods were also attempted as alternative interpolation methods. However, the outcomes of the interpolation from these algorithms were not satisfactory and IDW were the best technique to represent the data. In this study, IDW technique was used with a fourth degree polynomial with 12 nearest neighbor.

In order to calculate the volume and area of the lake, Surfer software was used. The spatial locations and the corresponding water depths of bathymetry points were input to the program and a depth contour map was drawn. This map was later used to calculate the lake volume by numerical integration.

CHAPTER FIVE
RESULTS AND DISCUSSION

As it was mentioned in the previous chapter, water quality monitoring of an AML is generally classified in three major groups: (i) field parameters, (ii) major anions and cations and (iii) heavy metals and trace elements. This monitoring program was carried out to determine the areal distribution and the vertical profiles of these water quality parameters within the lake. Based on this fundamental perspective, this chapter is organized to present the results of both the physical morphological highlights of the Hayırtepe AML and the results of water quality monitoring program conducted in this lake. Consequently, the morphology of the lake is first presented with data from the bathymetry studies undertaken within the lake. Later, the results from light penetration data of the lake are given. Then, the results of the water quality monitoring program are presented with regards to field parameters, major anion and cations and heavy metals and trace elements. The areal distributions and vertical profiles of these parameters are drawn and evaluated in the following sections.

All data collected within the scope of this study are presented in details together with their statistical summaries and comparisons with pertinent water quality standards including the Turkish Regulation on Waters for Human Consumption (ITASHY, 2005), Water Quality Criteria of U.S. Environmental Protection Agency (EPA, 2003) and Drinking Water Quality Criteria of World Health Organization (WHO, 2004). These comparisons provided valuable information regarding human health implications since this lake influences the downstream local and regional water resources that are used for drinking and irrigational water supply. Finally, the water quality in Hayırtepe AML is classified according to water quality criteria classification for inland water resources of the Water Pollution Control Regulation (SKKY, 2004).

5.1 Morphology of the AML

The project area is located in Çan district of the province of Çanakkale. It is situated near the village of Keçiağılı within the close proximity of Etili sub-district. The Hayırtepe AML site is 1 km to the southwest of Keçiağılı village as shown in Figure 5.1. This site was operated as an open-pit coal mine by a private company during 1990s and was abandoned about 15 years ago. The large pit of the mine was then transformed into a lake due to surface drainage and subsurface infiltration. Currently, there is no outflow from the lake except a few small seepage points to the east of the lake. As seen fro Figure 5.1, there are other mining lakes that were formed in the vicinity of Hayırtepe AML where this study was conducted.

From a topographical point of view, the Hayırtepe AML is situated at the most upstream areas of the Kocaçay Creek, which passes through Çan District Center and eventually confluences the Sea of Marmara. Along the flow path of this creek, there are several residential areas that supply their drinking water requirements from wells drilled within the flood plain of Kocaçay creek including Etili sub-district and Çan district centers. Consequently, the water quality in Kocaçay Creek is of utmost importance for providing safe drinking water to the local residents. In this regard, both Hayırtepe and the other AMLs shown in Figure 5.1 have a strong potential to influence the human health creating significant environmental risks.

The bathymetry of Hayırtepe AML has been measured during field studies and the results are presented in Table 5.1. A total of 62 measurements were taken to derive the bathymetry of the lake. The measured depths represent the distance between the lake surface elevation (i.e., 220 m above MSL at the date of the field study) and the corresponding bottom elevation. The locations of bathymetry points are presented in Table 5.1 and are shown in Section 4.1.2. The measured depth values at these measurement points were then gridded using the Surfer Software to obtain the bathymetric contours and a corresponding contour map as given in Figure 5.2.
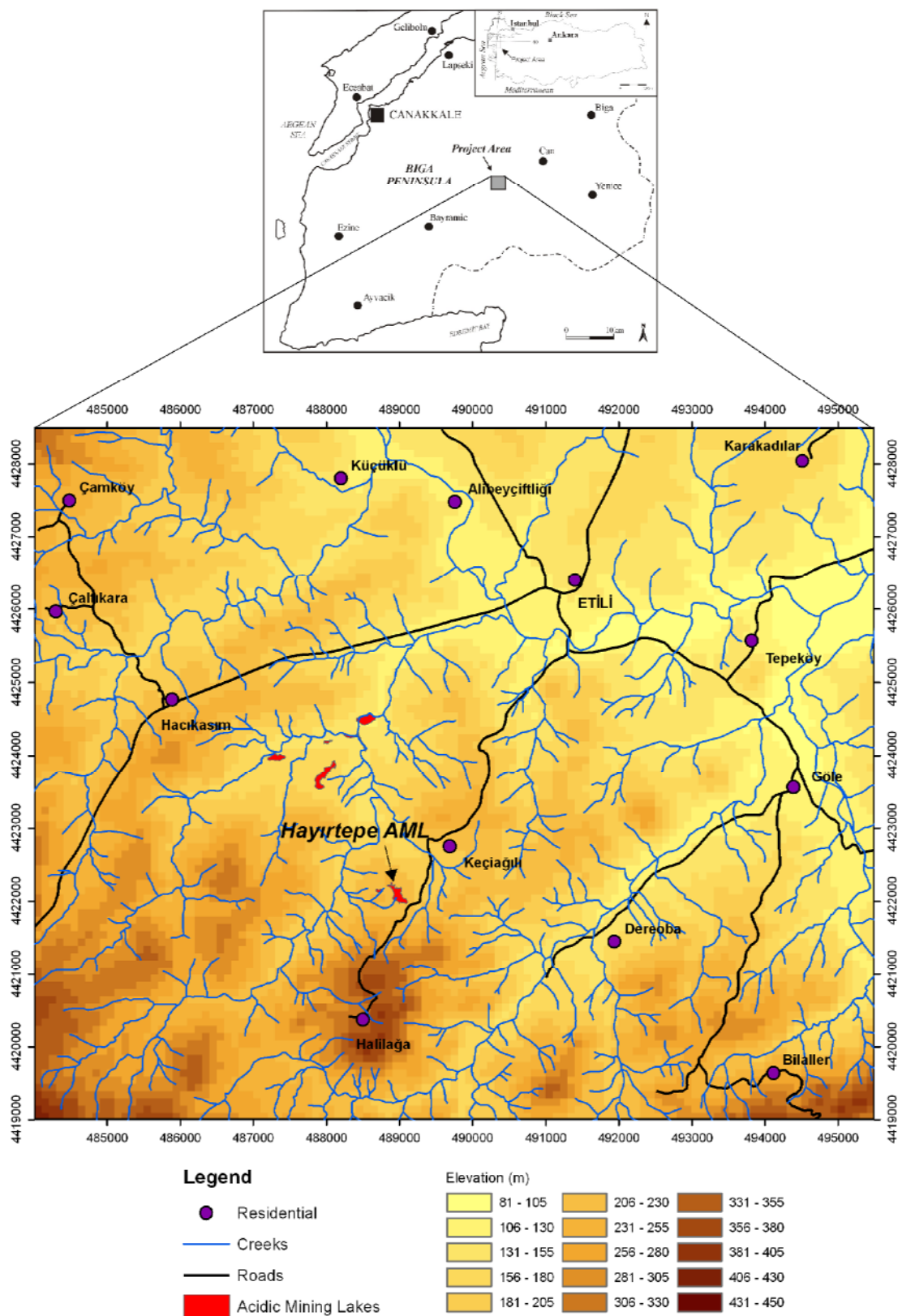
Figure 5.1 General morphology of the study area

Table 5.1 Bathymetry measurements

No.	X	Y	Point-ID	Depth (m)	No.	X	Y	Point-ID	Depth (m)
1	489076	4422033	1-1	-5.90	32	488977	4422102	5-3	-8.50
2	489076	4422024	1-2	-9.80	33	488968	4422100	5-4	-10.00
3	489075	4422011	1-3	-10.50	34	488957	4422098	5-5	-13.60
4	489073	4422002	1-4	-9.50	35	488947	4422098	5-6	-12.00
5	489070	4421992	1-5	-5.00	36	489007	4422137	6-1	-4.10
6	489036	4422048	2-1	-3.75	37	488995	4422135	6-2	-6.10
7	489031	4422039	2-2	-9.25	38	488988	4422129	6-3	-9.05
8	489025	4422031	2-3	-11.60	39	488980	4422124	6-4	-12.80
9	489023	4422018	2-4	-12.00	40	488972	4422118	6-5	-13.90
10	489018	4422011	2-5	-11.80	41	488962	4422113	6-6	-14.15
11	489008	4422004	2-6	-8.20	42	488954	4422111	6-7	-14.05
12	489005	4421992	2-7	-2.00	43	488944	4422109	6-8	-9.80
13	489009	4422068	3-1	-0.65	44	489014	4422172	7-1	-2.20
14	489005	4422063	3-2	-3.80	45	489005	4422166	7-2	-1.50
15	488999	4422057	3-3	-10.00	46	488998	4422163	7-3	-3.60
16	488994	4422048	3-4	-11.00	47	488990	4422157	7-4	-9.65
17	488989	4422041	3-5	-10.00	48	488981	4422152	7-5	-10.10
18	488981	4422033	3-6	-6.55	49	488972	4422148	7-6	-11.95
19	488974	4422026	3-7	-5.95	50	488964	4422142	7-7	-13.50
20	488965	4422018	3-8	-5.65	51	488955	4422137	7-8	-13.20
21	489001	4422083	4-1	-1.10	52	488945	4422133	7-9	-10.50
22	488995	4422079	4-2	-3.85	53	488937	4422129	7-10	-1.75
23	488988	4422076	4-3	-8.50	54	488974	4422168	8-1	-4.95
24	488978	4422072	4-4	-8.60	55	488967	4422163	8-2	-8.50
25	488969	4422067	4-5	-10.25	56	488958	4422155	8-3	-10.15
26	488961	4422063	4-6	-10.20	57	488951	4422150	8-4	-11.35
27	488951	4422059	4-7	-9.00	58	488943	4422144	8-5	-9.10
28	488944	4422055	4-8	-4.05	59	488941	4422170	9-1	-7.15
29	488932	4422052	4-9	-2.05	60	488938	4422159	9-2	-8.50
30	488994	4422103	5-1	-6.50	61	488921	4422176	10-1	-4.85
31	488985	4422103	5-2	-9.30	62	488906	4422182	11-1	-1.70
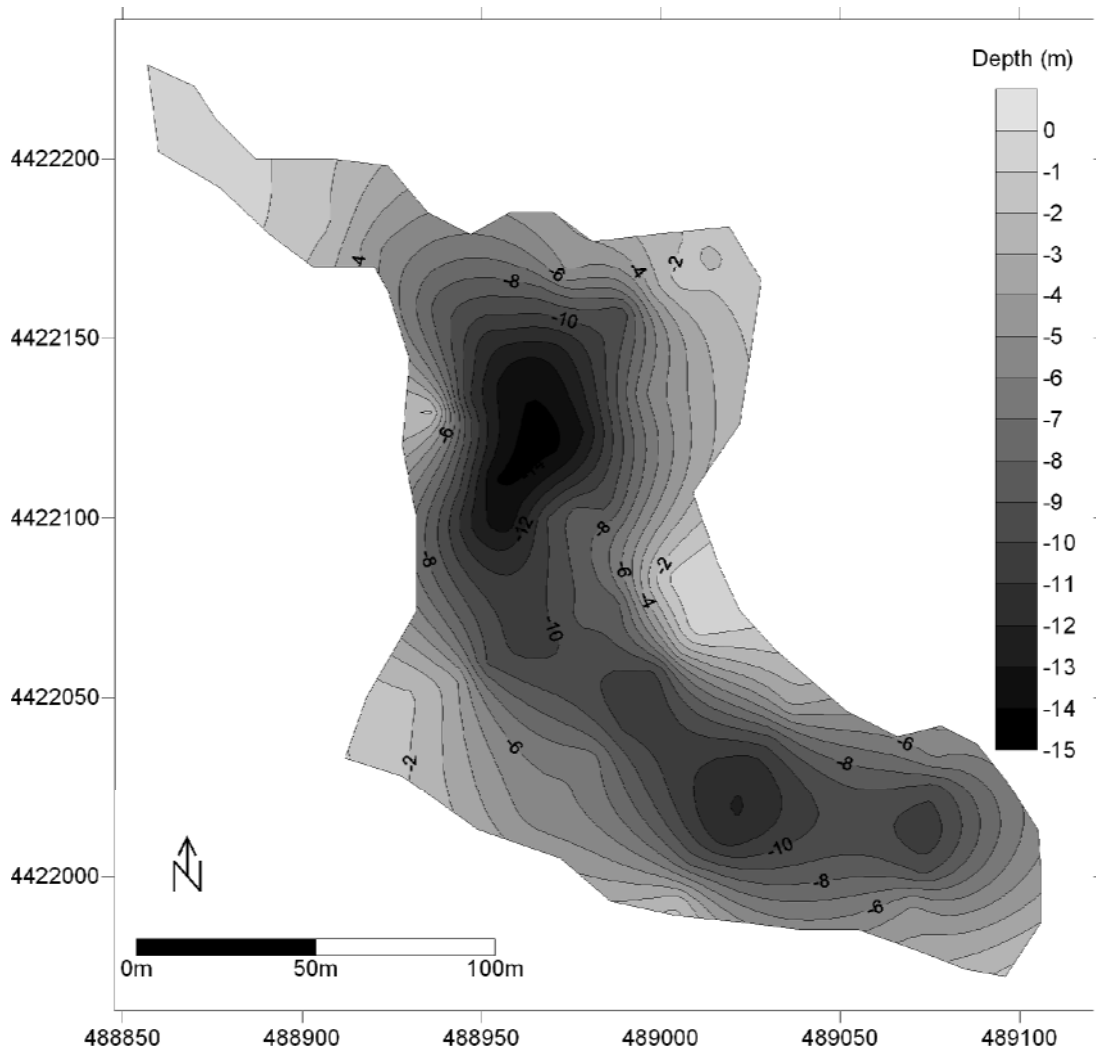
Figure 5.2 Contour map of Hayırtepe AML

According to the bathymetry map given in Figure 5.2, the deepest point in the lake corresponded to measurement point 6-6 that is situated roughly on the lake centerline and had a value of 14.15 m depth. In general, the bathymetry of the lake revealed the fact that the side slopes in the open pit were quite steep and had an inclination that reached values as high as 80°. The comparably shallow parts of the lake were found in the small bays to the northeast and southwest of the lake. The deepest area is believed to represent an area where the coal vein was located and major extraction activities were conducted during the operation phases. Based on the computations performed with Surfer Software, the volume and the surface area of the lake were found to be 169224 m³ and 23810 m², respectively. Thus, the average depth of the lake was found to be 7.11 m.

5.2 Light Penetration in the AML

The determination of the extent of light penetration is crucial with regards to primary productivity and ecological assessments. Despite the fact that no biological monitoring activity was conducted in Hayırtepe AML, the light penetration was measured at two different locations within the lake and the average of Secchi disc depth were recorded as 1.4m. As this lake was not exposed to any organic contamination, the limiting nutrient (i.e., phosphorus and nitrogen) concentrations were not high and the algae growth was not significant. In this regard, there were no signs of eutrophication in Hayırtepe AML. Thus, there were no mechanisms to prevent light penetration to deeper levels. The dark color of the lake, on the other hand, was not related to reduced light penetration but has originated from high concentration of both dissolved and precipitated iron species and other colorful metal precipitates.

5.3 Field Parameters

In this section, the results of field parameter measurements are presented. These parameters included temperature, pH, electrical conductivity (EC), dissolved oxygen (DO), oxidation reduction potential (ORP), salinity and total dissolved solids (TDS). These measurements were measured instantaneously on the field inside the boat and thus, represent the results of spatial and vertical variations at the particular date of the field survey. All results of field parameters are given in Table 5.2 and are discussed in the following subsections.

Table 5.2 Results of field parameters

Point	d (m)	T (ºC)	pH	D.O. (mg/L)	D.O (%)	EC (μs/cm)	ORP (mV)	Salinity (%)	TDS (mg/L)
1-3	0	26.1	2.05	5.25	66	5925	594	3.21	2964
1-3	-5	14.2	2.27	5.25	54	5782	613	3.16	2891
1-3	-9	10.6	2.53	0.91	9	5768	424	3.15	2885
2-1	0	25.1	2.07	5.92	74	6034	588	3.28	3020
2-3	0	25.4	2.02	5.65	71	6080	593	3.30	3042
2-3	-5	15.1	2.08	5.70	60	5812	612	3.17	2906
2-3	-10	10.7	2.52	0.90	8	5976	404	3.27	2987
2-6	0	25.1	2.05	5.90	74	6060	588	3.29	3031
2-6	-6	13.4	2.15	5.70	58	5766	597	3.15	2882
3-2	0	24.9	2.02	5.90	74	6095	593	3.31	3050
3-4	0	25.3	2.00	5.34	67	6112	595	3.32	3057
3-4	-5	15.5	2.10	5.50	59	5905	609	3.23	2953
3-4	-9	10.5	2.42	1.10	11	5968	414	3.26	2985
3-7	0	25.0	2.05	5.80	73	6080	588	3.31	3045
3-7	-4	18.6	2.05	5.62	63	5980	608	3.27	2990
4-2	0	25.3	2.30	6.00	76	6020	513	3.27	3013
4-5	0	24.8	2.22	5.20	64	6080	545	3.31	3045
4-5	-5	17.8	2.25	6.30	70	5853	573	3.19	2920
4-5	-9	11.0	2.68	1.55	15	5581	432	3.04	2790
4-8	0	24.5	2.20	6.10	76	6033	570	3.27	3015
5-2	0	25.1	2.10	6.40	78	6040	578	3.28	3023
5-2	-6	15.3	2.21	6.05	63	5820	591	3.18	2911
5-5	0	24.5	2.10	5.80	73	6055	586	3.29	3030
5-5	-5	17.8	2.17	6.00	65	5860	597	3.19	2930
5-5	-9	11.5	2.41	1.50	16	5895	439	3.17	2900
5-5	-12	11.2	2.82	1.05	10	5925	402	3.24	2965
6-2	0	24.3	2.13	6.20	75	6080	583	3.31	3040
6-2	-4	20.1	2.15	5.80	66	5960	596	3.25	2980
6-4	0	24.6	2.10	6.08	76	6090	591	3.31	3045
6-4	-5	19.5	2.14	6.17	70	5902	596	3.27	2952
6-4	-10	11.2	2.63	1.25	12	5873	419	3.21	2937
6-6	0	24.7	2.09	6.01	75	6020	584	3.27	3012
6-6	-5	17.9	2.13	6.18	68	5951	600	3.25	2976
6-6	-9	11.2	2.62	1.72	17	5567	433	3.03	2782
6-6	-13	10.5	2.81	1.13	10	5720	373	3.12	2860
6-8	0	24.1	2.13	5.80	72	6010	579	3.27	3007
6-8	-4	21.8	2.09	5.87	68	5713	573	3.10	2857
6-8	-8	12.9	2.43	3.10	31	5820	472	3.18	2906
7-3	0	25.0	2.40	6.03	76	6040	577	3.28	3020
7-5	0	24.7	2.13	6.10	76	6060	588	3.30	3032
7-5	-4	17.3	2.26	6.45	70	5840	603	3.19	2920
7-5	-8	11.1	2.62	2.00	18	5832	441	3.19	2917

Point	d (m)	T (ºC)	pH	D.O. (mg/L)	D.O (%)	EC (µs/cm)	ORP (mV)	Salinity (%)	TDS (mg/L)
7-7	0	24.4	2.17	6.03	75	6020	587	3.27	3013
7-7	-4	18.8	2.17	5.78	65	5923	598	3.22	2961
7-7	-8	10.8	2.56	1.67	16	5770	437	3.15	2885
7-7	-12	11.4	2.95	0.95	9	5970	375	3.25	2965
7-9	0	24.8	2.11	5.60	71	6033	590	3.28	3018
7-9	-5	14.1	2.27	6.20	63	5730	600	3.13	2867
7-9	-8	10.8	2.62	0.92	9	5885	426	3.22	2943
8-2	0	24.3	2.12	5.97	74	6040	585	3.28	3020
8-2	-5	15.4	2.32	5.75	60	5830	599	3.18	2916
8-4	0	24.6	2.09	6.00	75	6030	591	3.28	3017
8-4	-5	15.2	2.28	5.90	61	5820	602	3.18	2911
8-4	-9	10.6	2.67	0.83	8	5895	418	3.22	2948
9-2	0	24.3	2.10	5.82	72	6095	588	3.32	3049
9-2	-6	13.8	2.30	5.60	57	5791	585	3.16	2895
Mean		18.54	2.28	4.67	53.96	5925.27	543.48	3.23	2962.16
St. Dev.		5.90	0.24	2.05	25.61	132.95	77.51	0.07	67.74
90%Percent.		25.10	2.63	6.18	75.50	6080.00	601.00	3.31	3043.50
50%Percent.		18.25	2.17	5.79	65.50	5938.00	586.50	3.25	2965.00
10%Percent.		10.80	2.05	1.08	10.00	5767.00	418.50	3.15	2883.50
Max		26.10	2.95	6.45	78.00	6112.00	613.00	3.32	3057.00
Min		10.50	2.00	0.83	8.00	5567.00	373.00	3.03	2782.00
ITASHY (2005)		25	6.5-9.5	-	-	2500	-	-	-
EPA (2003)		-	6.5-8.5	-	-	-	-	-	-
WHO (2004)		-	6.5-8.5	-	-	-	-	-	-

5.3.1 pH

The results of the water quality monitoring program show typical characteristics of acidic mining lakes. The generation of low pH (or high acidity) is attributed to sulfide oxidation found primarily in pyrite and to a certain extent in other sulfide minerals. It is known that this low pH level increases the dissolution of many elements, which in turn results in high concentration of total dissolved solids. The acidity significantly enhances the mobility and bioavailability of otherwise immobile elements in soil structure. Therefore, the amount of metal dissolution decreases in with increasing pH levels waters influenced from mining activities. Based on this outcome, it is possible to conclude that pH control in acidic mining lakes is the primary mechanism for mitigating these systems for dissolved metals. In this regard, pH control coupled with precipitation is a viable approach for controlling the

concentrations of heavy metals and trace elements. Consequently, pH is a corner stone parameter to achieve treatment and rehabilitation of such highly metal concentrated mine waters.

It is well known that the primary mechanism for low pH in acidic mining lakes is pyrite oxidation. The pyrite oxidation equations are given below:

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-}$$

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+$$
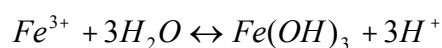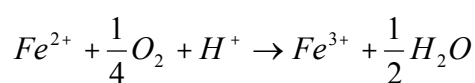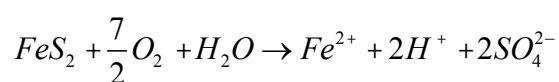
If the pyrite oxidation and subsequent equations are examined, it is important to note that the oxidation occurs in the presence of oxygen and water. As a result of these equations, hydrogen ion is released to the water, decreasing the pH and causing extremely acidic conditions. In the case of Hayırtepe AML, pyrite oxidation resulted in a pH range of 2.00 and 2.95. In general, pH was found to be lower on surface and increased with increasing depth. The depth profiles of pH are shown in Figure 5.3.
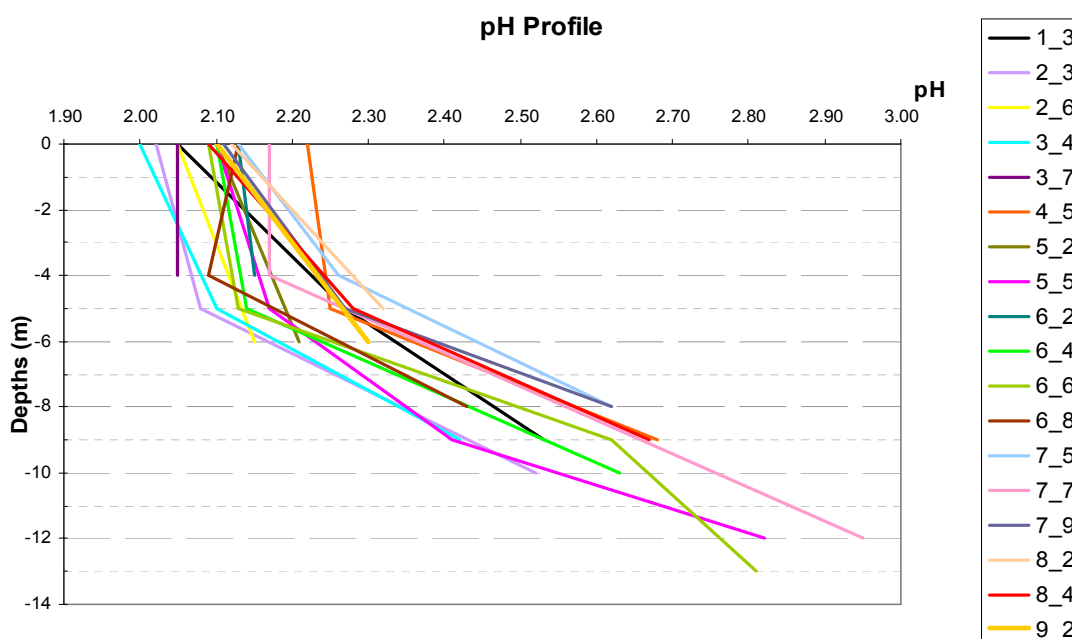

Figure 5.3 Depth profiles for pH

The highest pH value (i.e., 2.95) was recorded at the second deepest point of the lake (i.e., 13.5 m at point 7-7). On the contrary, the lowest pH value was measured at the surface sampling station on point 3-4. The pH distribution at the water surface is given in Figure 5.4. As seen from the figure, there is no significant behavior of pH distribution within the lake surface. When the pH database was compared with the standard values, it is clearly seen that the lake pH pattern is outside of the allowable range of 6.5-9.5.
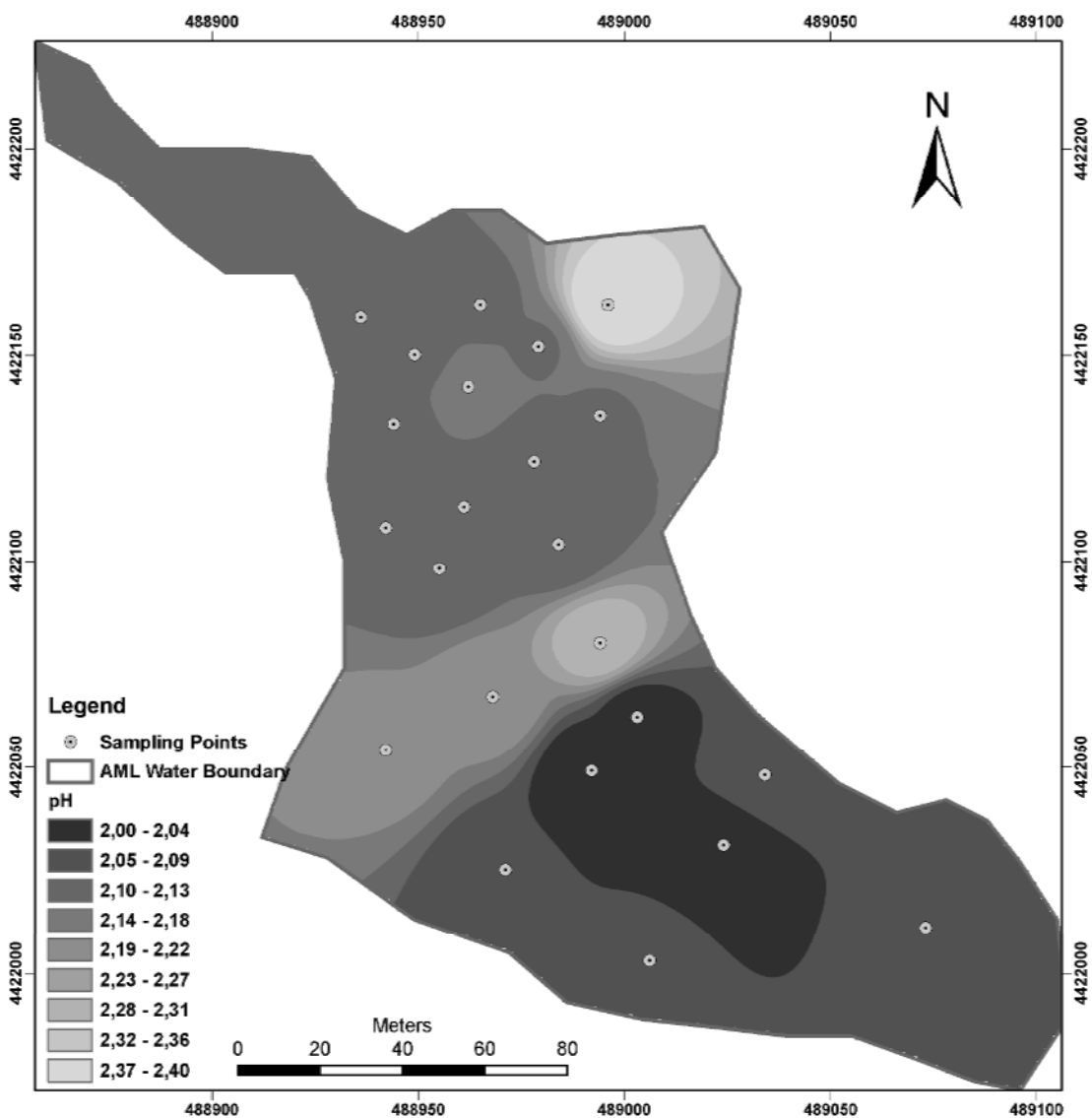

Figure 5.4 Distribution of pH at water surface

5.3.2 Dissolved Oxygen

Dissolved oxygen is one of the most significant parameters with regards to pyrite oxidation and aquatic life. In general, dissolved oxygen amount in natural waters depends on various conditions such as temperature, salinity, stratification patterns (extent of turbulence) and atmospheric pressure. Typically, the dissolved oxygen levels in natural systems that are not under anthropogenic influences range between 8 mg/L to 14 mg/L under normal conditions of 1 atm pressure and a temperature range of 0-30ºC. Dissolved oxygen in water is supplied from atmospheric oxygen and photosynthesis processes in water. Thus, oxygen levels are higher in surface layers of all natural waters when compared to lower strata except in turnover periods of spring and autumn. It must also be noted that when DO levels are lower than 0.5-1.0 mg/L, anoxic conditions take place and H_2S and CH_4 gases occur.

In this study, the amount of DO values were measured to range between 0.83 mg/L and 6.45 mg/L, with an average of 4.67 mg/L and the DO saturation levels were found to range between 8% and 78%, with an average of 53.96%. It has been found out that DO levels and their saturations decreased as a function of depth as shown in Figure 5.5 and Figure 5.6. This depth profile is typical for most lakes and particularly normal in acidic mining lakes where oxidation of sulfide minerals take place. While this oxidation process reduces the DO levels within the entire depth profile, the DO levels at the surface are renewed by gas transfer from the atmosphere whereas this mechanism is impossible in lower layers. Consequently, oxygen is required for all layers but only surface layers could renew their oxygen depletions.

5.3.3 Oxidation Reduction Potential

Oxidation reduction potential (ORP) is the tendency of a chemical specie to gain or to lose electrons. As it is expressed in the interpretation of pH, acidity increases the mobility and bioavailability of elements but the capability of water to transport metals is not only controlled by pH, it is also associated with ORP. The oxidation-reduction potential influences the mobility of most metals which can exist in several oxidation states.
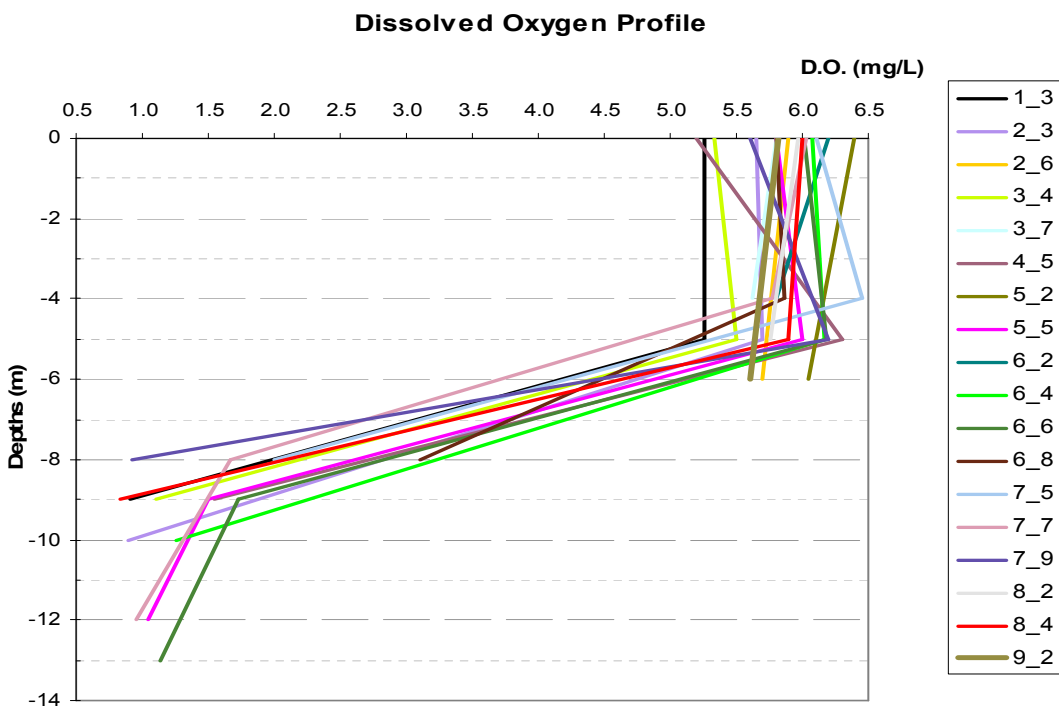
Dissolved Oxygen Profile

Figure 5.5 Depth profile for DO
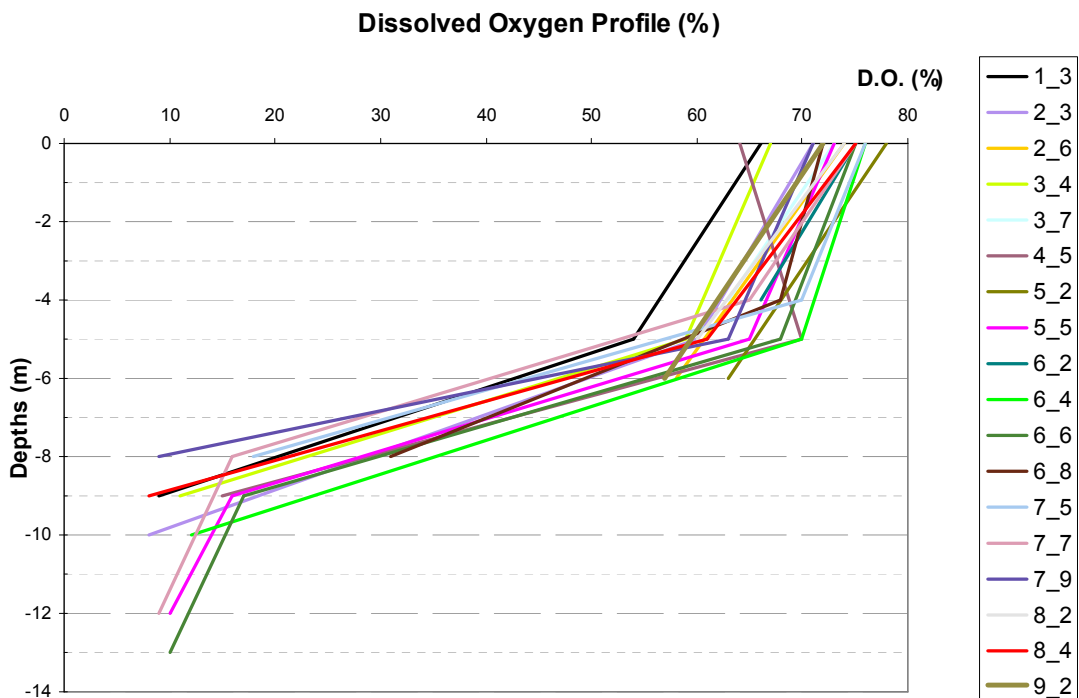
Dissolved Oxygen Profile (%)

Figure 5.6 Depth profile for oxygen saturation

On the oxidation reduction potential scale, the presence of oxidizing agent increases the ORP value. In the case of an AML, this oxidizing agent is mostly oxygen. Thus, ORP values are typically found to be high in measurement points with high DO levels.

In this study, the ORP values ranged between 373 and 613 mV, representing oxidizing conditions in all sampling points. Similar to the depth profile of DO given in Figure 5.5, the depth variation of ORP also show a similar pattern where high ORP values were observed at the surface with high DO concentrations and low ORP values were measured at deeper sampling locations with lower DO levels (Figure 5.7).
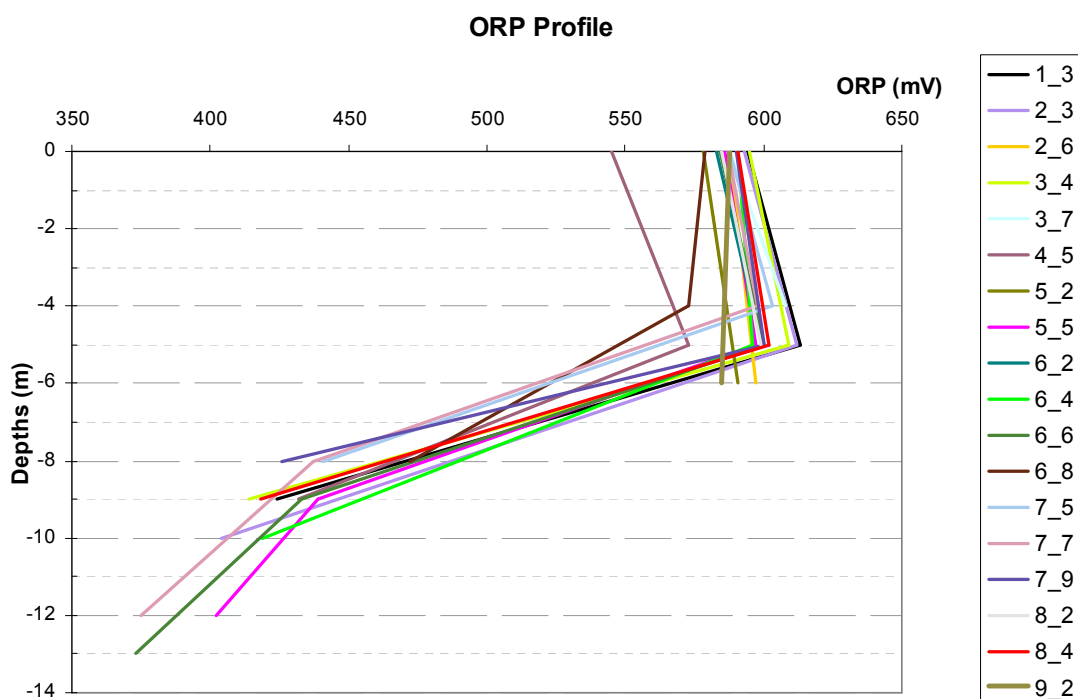

Figure 5.7 Depth profile for ORP

5.3.4 Temperature

Physical, biological and chemical processes are all influenced from water temperature. In general, temperature of surface waters change with geographical location, altitude, season, different time periods of day and depth of water body. In addition to these, temperature could also change according to the endothermic and

exothermic reactions which occur in the water column. In this particular study, temperature values ranged 10.50ºC and 26.10ºC with values decreasing as a function of increasing depth (Figure 5.8).
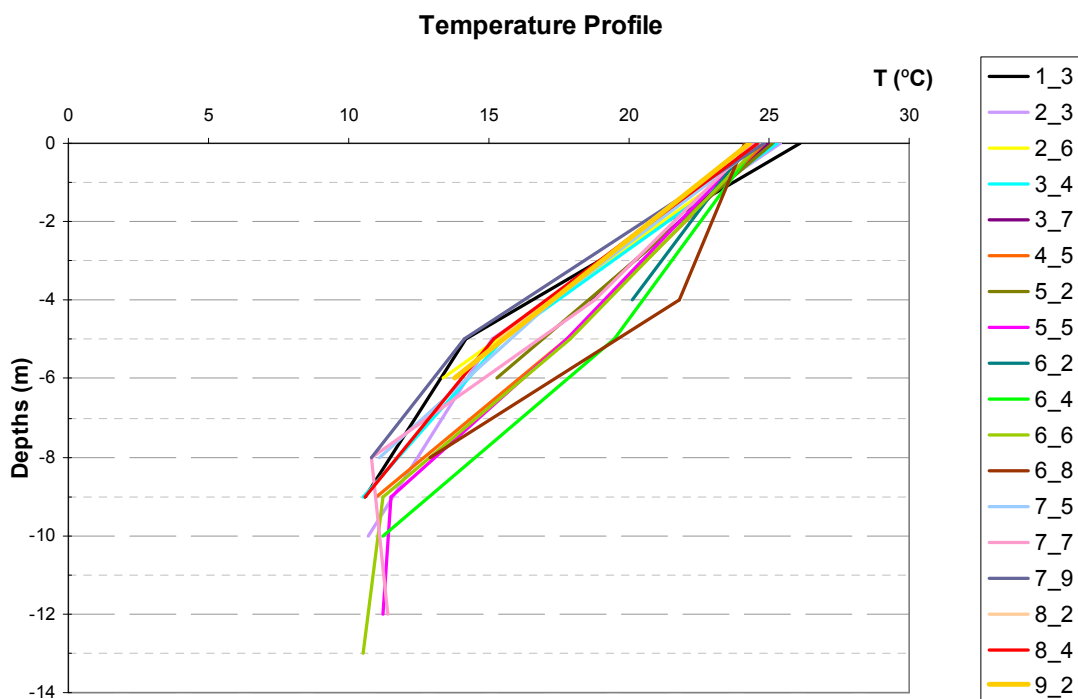

Figure 5.8 Depth profile for temperature

5.3.5 Electrical Conductivity

Electrical conductivity of water depends on total dissolved concentrations of anions and cations and water temperature. The EC values increase with increasing temperature values. Typical EC values in natural waters range between 50-1500 µS/cm. In this particular study, the EC values of the water samples ranged between 5567 µS/cm and 6112 µS/cm, with an average value of 5925 µS/cm. The vertical profiles of EC values are given in Figure 5.9. As seen from the figure, EC values decrease by depth and experience a slight increase within the close vicinity of the bottom layer. This phenomenon could be related to sediment resuspension from the bottom and the associated high ion concentrations. When the measured values are compared with the pertinent standards, one could observe that all EC values

exceeded the ITASHY standard value of 2500 µS/cm as shown in Figure 5.10. On the other hand, spatial distribution of EC along the surface is shown in Figure 5.11.
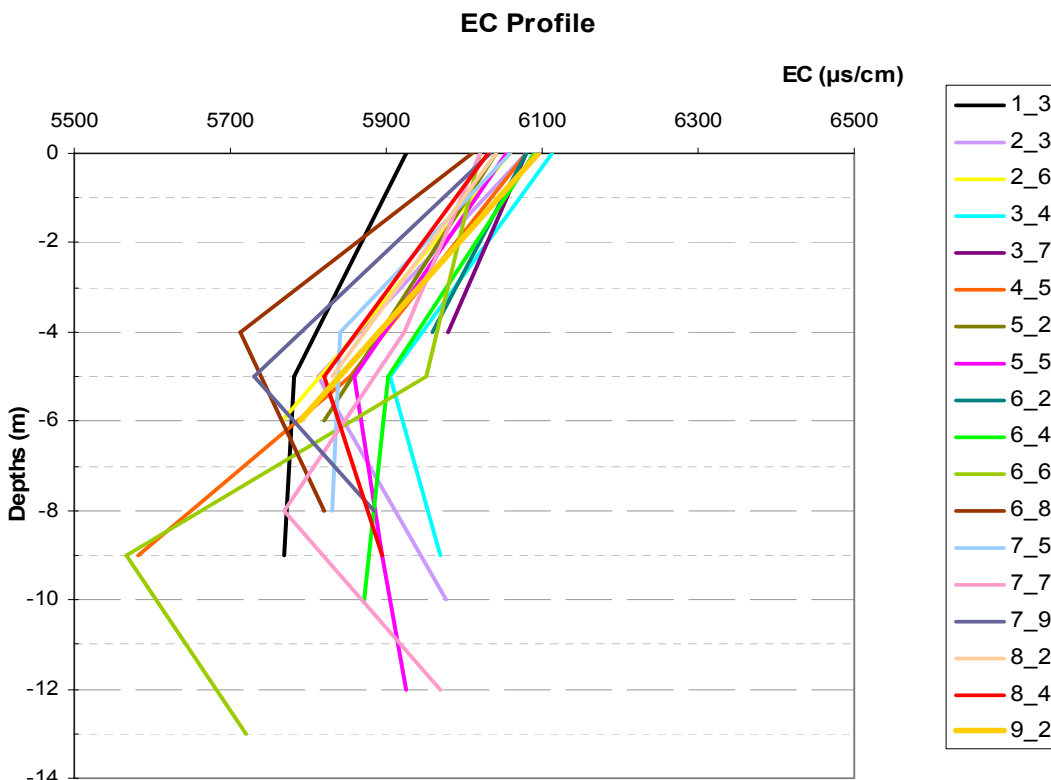
Figure 5.9 Depth profile for EC
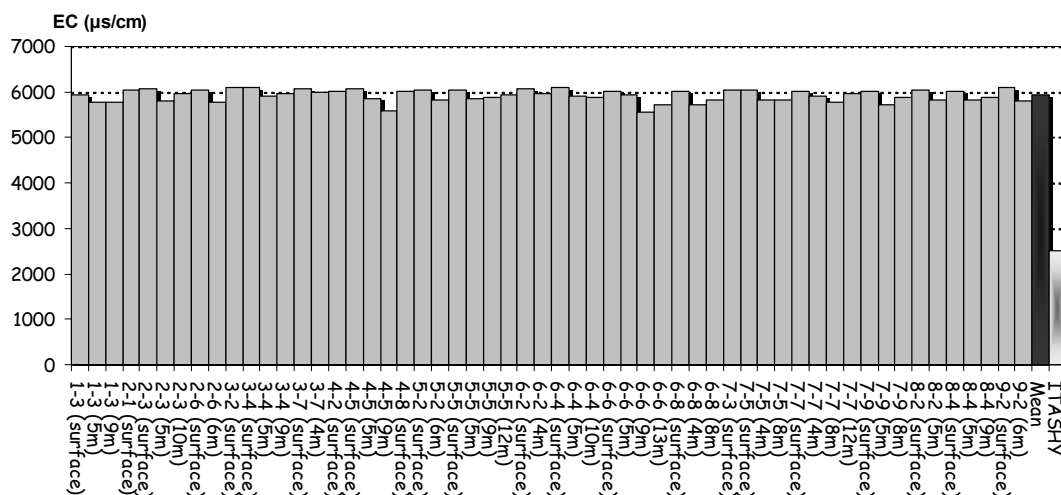
Figure 5.10 EC comparison in accordance to ITASHY (2005)
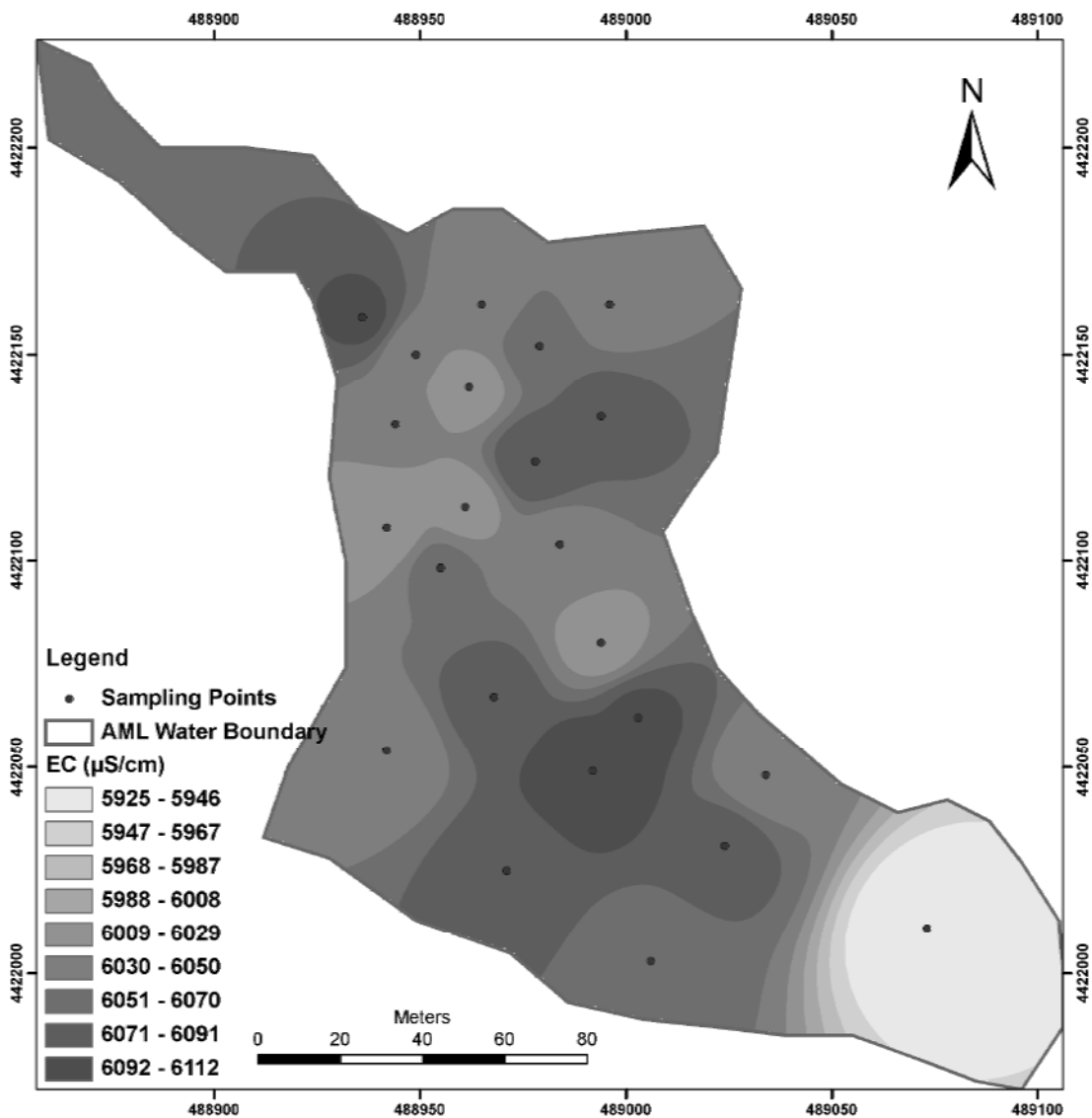
Figure 5.11 Distribution of EC at water surface

5.3.6 Total Dissolved Solids

As it is mentioned in the section 5.3.1 , total dissolved solids (TDS) decrease as a function of increasing pH values due to the reduced dissolution potential. In the case of an AML, relatively higher pH values are observed in deeper layers, thus having lower TDS concentrations in bottom elevations. In essence, TDS is calculated from the measured EC values using a pre-defined functional relationship, thus showing similar trends to EC. In this study, the TDS values ranged between 2782 mg/L and 3057 mg/L, with an average of 2962 mg/L. Due to the strong relation between EC

and TDS, TDS also showed similar variations along the vertical profile as shown in Figure 5.12).
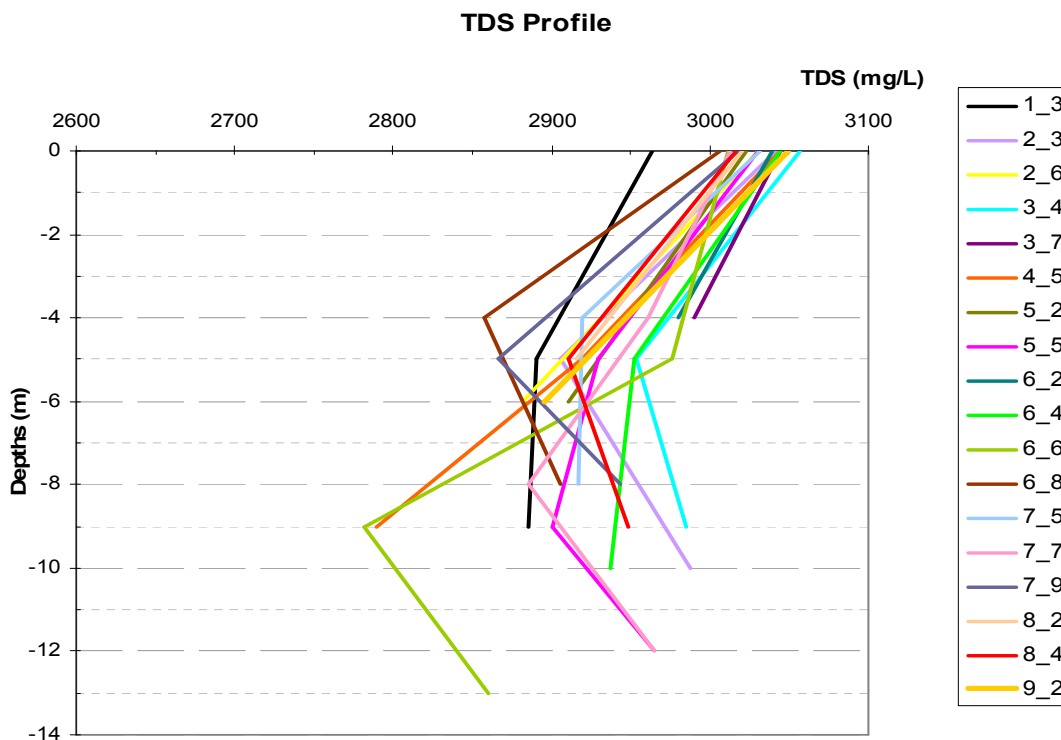
Figure 5.12 Depth profile for TDS

5.4 Major Anions and Cations

The Hayırtepe AML could not be considered as a typical surface water resource with a characteristic quality pattern. Based on the consequences of pyrite oxidation, it is possible to consider this lake an "environmental disaster" area with unusual ionic composition. In particular, sulfate levels are extremely high when compared to general inland water quality criteria. Such a distorted ionic composition makes analysis complicated as discussed in Chapter 4.

Within the scope of water quality monitoring program, fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate anions as well as lithium, sodium, ammonium, potassium, magnesium and calcium cations were measured and the results are given in Table 5.3.

Table 5.3 Results of major anions and cations

Point	d (m)	Cl⁻ (mg/L)	F⁻ (mg/L)	SO₄⁻ (mg/L)	Ca⁺⁺ (mg/L)	K⁺ (mg/L)	Li⁺ (mg/L)	Mg⁺⁺ (mg/L)	Na⁺ (mg/L)	NH₄⁺ (mg/L)
1-3	0	50.83	5.16	4296.68	473.79	0.91	0.24	235.65	122.10	0.99
1-3	-5	61.60	5.96	5104.05	451.51	0.91	0.21	234.15	115.74	0.91
1-3	-9	58.71	5.57	5283.07	435.89	3.49	0.20	235.73	118.84	6.97
2-1	0	72.84	9.05	7275.15	479.23	0.79	0.22	240.19	121.93	n.a.
2-3	0	64.19	6.43	5753.54	483.07	0.82	0.22	238.79	122.56	n.a.
2-3	-5	60.44	6.24	5494.32	460.70	0.80	0.21	227.99	116.13	n.a.
2-3	-10	54.02	6.11	5299.03	443.00	5.36	0.19	232.25	122.65	8.07
2-6	0	61.53	6.04	5649.10	490.93	0.76	0.22	234.55	123.50	n.a.
2-6	-6	57.68	5.91	5291.52	462.55	0.78	0.20	222.45	115.94	n.a.
3-2	0	64.10	6.57	5835.55	494.00	0.74	0.22	231.42	123.90	n.a.
3-4	0	63.05	6.31	6016.88	494.55	0.85	0.21	228.39	123.86	0.72
3-4	-5	62.99	7.04	5669.08	476.94	0.83	0.19	221.36	119.16	0.63
3-4	-9	59.52	6.01	5765.62	440.89	3.97	0.16	218.23	119.67	7.24
3-7	0	65.57	6.33	5735.95	576.71	0.88	0.22	256.72	141.04	0.67
3-7	-4	65.88	6.36	5761.28	476.44	0.67	0.18	214.16	118.76	0.48
4-2	0	63.87	6.22	5977.31	509.60	0.68	0.19	230.46	124.69	0.53
4-5	0	64.99	6.50	6050.05	511.30	0.67	0.19	229.27	125.13	0.51
4-5	-5	61.82	6.57	5745.47	478.58	0.68	0.18	217.48	116.91	0.55
4-5	-9	56.83	5.77	5460.62	458.61	3.56	0.16	219.82	121.38	7.40
4-8	0	63.62	6.35	5935.67	510.76	0.67	0.19	221.19	124.86	0.50
5-2	0	61.82	5.99	5705.01	513.15	0.70	0.20	218.99	125.53	0.64
5-2	-6	58.91	5.83	5525.27	477.44	0.70	0.17	207.09	116.48	0.67
5-5	0	65.42	6.48	6124.56	513.13	0.68	0.19	213.59	125.57	0.76
5-5	-5	60.91	6.12	5735.85	475.90	0.69	0.17	202.41	116.21	0.68
5-5	-9	62.10	6.35	5701.65	453.73	3.20	0.16	203.61	119.36	6.68
5-5	-12	61.58	5.76	6172.87	459.12	9.98	0.16	208.99	130.47	10.72
6-2	0	63.77	6.34	5972.39	508.63	0.68	0.20	209.47	124.73	0.74
6-2	-4	58.52	6.40	5747.15	487.96	0.68	0.18	201.75	119.69	0.83
6-4	0	65.38	6.50	6045.06	507.26	0.67	0.19	205.77	124.47	0.79
6-4	-5	62.83	6.11	5820.38	491.16	0.69	0.18	200.94	120.45	0.83
6-4	-10	64.77	6.75	6238.02	461.31	5.19	0.18	204.97	125.02	9.21
6-6	0	65.92	6.73	6423.53	511.68	0.68	0.19	205.75	125.50	0.86
6-6	-5	61.90	6.15	5838.78	480.84	0.71	0.18	197.27	117.77	0.78
6-6	-9	59.55	5.75	5786.76	457.00	3.56	0.16	199.23	121.38	7.39
6-6	-13	61.39	5.71	6183.21	455.82	13.85	0.15	202.33	132.69	12.36
6-8	0	66.39	6.36	6111.36	508.93	0.68	0.19	205.06	124.96	0.83
6-8	-4	65.96	6.64	6190.23	493.20	0.69	0.18	198.58	121.15	0.87
6-8	-8	63.87	6.65	5977.85	468.32	1.52	0.17	195.30	118.08	3.06
7-3	0	67.39	6.53	6291.30	497.17	0.67	0.19	198.55	122.01	0.91
7-5	0	67.73	6.69	6236.43	508.83	0.67	0.19	200.60	125.01	0.92
7-5	-4	60.08	6.25	5580.00	487.54	0.73	0.20	197.32	119.66	0.94
7-5	-8	65.14	7.20	6028.98	466.19	1.99	0.17	194.84	118.75	3.22

Point	d (m)	Cl⁻ (mg/L)	F⁻ (mg/L)	SO₄⁻ (mg/L)	Ca⁺⁺ (mg/L)	K⁺ (mg/L)	Li⁺ (mg/L)	Mg⁺⁺ (mg/L)	Na⁺ (mg/L)	NH₄⁺ (mg/L)
7-7	0	71.06	7.72	6449.90	504.02	0.70	0.19	198.88	123.88	0.87
7-7	-4	61.70	6.79	6213.35	500.41	0.74	0.19	197.23	122.01	n.a.
7-7	-8	63.70	6.56	5984.39	460.45	1.99	0.17	191.12	117.34	4.21
7-7	-12	57.92	6.30	6180.95	453.45	1.39	0.16	195.33	128.24	10.76
7-9	0	70.10	6.47	6266.74	506.61	0.70	0.19	200.31	124.42	0.91
7-9	-5	62.77	7.17	5970.02	477.89	0.73	0.18	191.55	117.44	0.86
7-9	-8	64.54	6.57	6156.19	460.33	2.83	0.17	193.41	120.23	6.08
8-2	0	69.69	6.72	6483.14	507.18	0.69	0.19	197.64	124.65	0.94
8-2	-5	66.75	6.54	6034.39	238.71	0.36	0.10	96.38	58.61	0.48
8-4	0	66.93	6.52	6157.75	245.79	0.33	0.09	97.26	60.38	n.a.
8-4	-5	64.08	6.26	5981.79	235.62	0.35	0.09	94.72	57.80	0.44
8-4	-9	65.42	5.50	6151.86	222.82	1.59	0.08	94.93	58.70	3.21
9-2	0	70.26	7.31	6511.58	247.84	0.34	0.09	97.20	61.01	0.45
9-2	-6	61.86	6.33	5721.98	231.91	0.35	0.09	93.31	57.01	0.40
Mean		63.75	6.40	5912.51	456.90	1.63	0.18	200.03	115.45	2.72
St. Dev.		4.03	0.58	423.25	80.68	2.35	0.04	39.51	20.25	3.38
90%Percent.		67.56	6.91	6279.02	510.18	3.56	0.22	234.35	125.52	7.60
50%Percent.		63.66	6.35	5974.85	477.67	0.73	0.19	205.01	121.38	0.87
10%Percent.		58.61	5.77	5477.47	341.87	0.67	0.12	144.19	88.38	0.50
Max		72.84	9.05	7275.15	576.71	13.85	0.24	256.72	141.04	12.36
Min		50.83	5.16	4296.68	222.82	0.33	0.08	93.31	57.01	0.40
ITASHY'05		250	1.5	250	200	-	-	50	200	0.5
EPA'03		250	2.0	250	-	-	-	-	-	-
WHO'04		250	1.5	250	-	-	-	-	200	-

As seen from Table 5.3, sulfate is the predominant anion in all water samples. The sulfate concentrations were measured to be extremely high when compared to typical natural waters as given in the national and international standards. These high sulfate concentrations required high dilution ratios for ion chromatographic analysis. Since all parameters are measured from the same vials that had been diluted according to sulfate, some of the anions could be under the reporting limit including nitrite, bromide and nitrate. The results for these anions were below the detection limits of the equipment and hence are not included in the above table. On the other hand, no such problems were experienced in cation analysis as none of the measured cations showed significant deviations from typical values as did the sulfate. In general, magnesium and calcium concentrations are relatively higher than other cations.

It is also important to note that all water samples were analyzed in the laboratory 2 weeks after the field study. Despite the fact that the samples are properly stored in refrigerated environment at 4ºC, this time period was higher than what is given in standard analysis procedures. These analyses should have ideally been conducted within 48 hours after sampling. Extented amount of time passed prior to analysis resulted in chemical reactions to continue within sampling bottles and thus created higher sulfate concentrations according to the reactions given in Section 5.3.1.

In all cations analyzed, chloride, lithium, sodium and potassium values were well below the standard values and thus are not discussed in details in the following sections. On the other hand, fluoride, sulfate, ammonium, magnesium and calcium exceed the standards and thus are discussed in the following sections.

5.4.1 Fluoride

Fluoride concentrations did not demonstrate a typical pattern along the vertical profile as shown in Figure 5.13. It showed a variation between 5.16 mg/L and 9.05 mg/L. The mean value was computed to be 6.40 mg/L and was found to be above the ITASHY standard value. Since fluoride is an electronegative ion, it is harmful for human and animal health when found in concentrations exceeding 4 mg/L. Such high levels create dental and skeleton system defects and provoke fluorosis. The maximum fluoride value of 9.05 mg/L measured in Hayırtepe AML is very close to the 10 mg/L threshold above which creates fractures in bones (Şahmurova, Hepsağ & Özkan, 2005)

5.4.2 Sulfate

Sulfate concentrations in Hayırtepe AML are extremely high when compared to other ions with a mean value of 5912.51 mg/L that is 24 times above the standard value of 250 mg/L (Figure 5.14). Sulfides are usually stable under reducing conditions. Exposure of sulfides to oxidizing conditions will quickly destabilize them, and sulfides will be destroyed via various oxidation mechanisms. Pyrite is the

most common sulfide mineral that occurs in nearly all types of geological environments and is usually associated with coal and metal ores deposits.
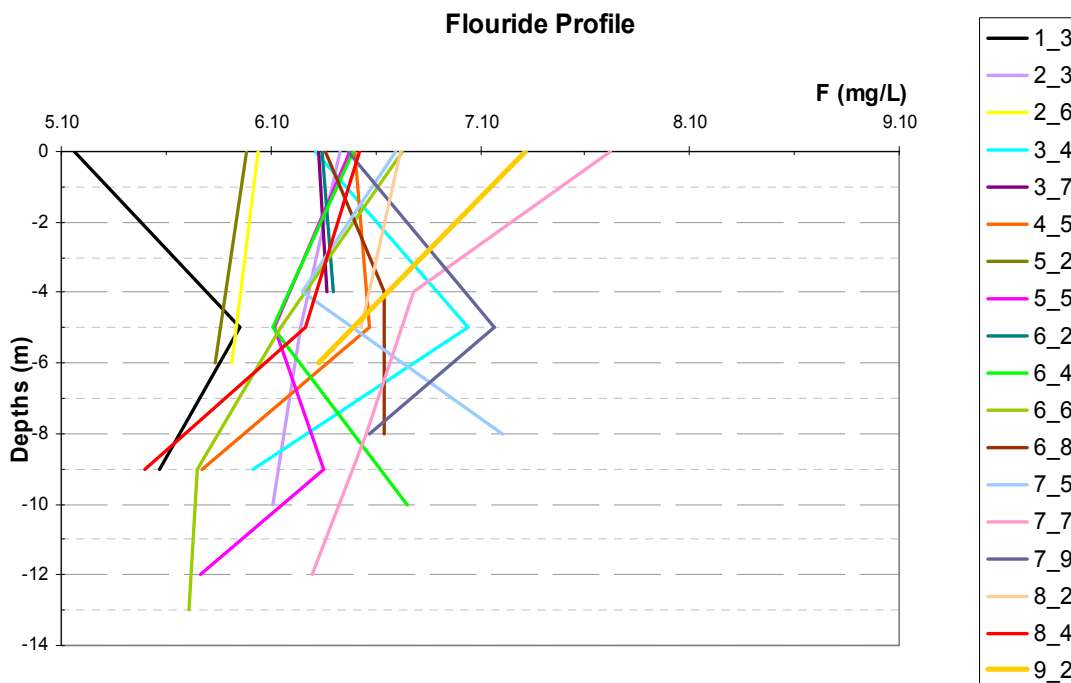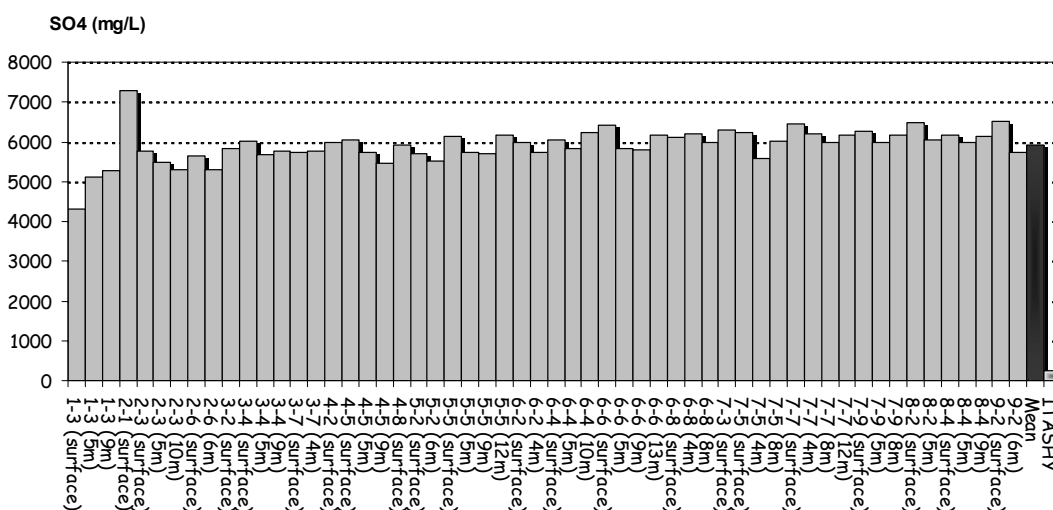

Figure 5.13 Depth profile for fluoride

Figure 5.14 Sulfate comparison in accordance to ITASHY (2005)

In this study, sulfate is generated by pyrite oxidation in first step of the equations given in Section 5.3.1 . Sulfate levels were observed to be between 4296.68 mg/L

and 7275.15 mg/L. The vertical profile and the distribution of sulfate at water surface are given in Figure 5.15 and Figure 5.16, respectively. From a structural point of view, high sulfate concentrations damage concrete structures and are harmful for pipes especially in infrastructure systems due to its corrosive effect thru H_2SO_4. High concentration of sulfate may also cause dehydration of the human body.
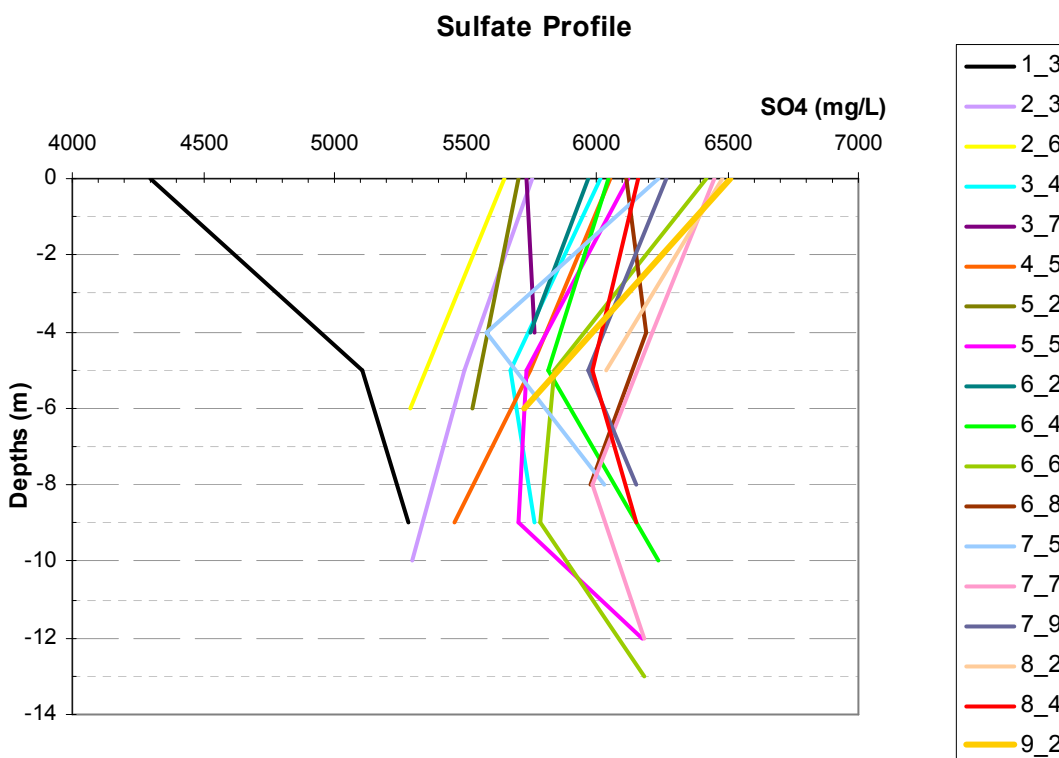

Figure 5.15 Depth profile for sulfate

5.4.3 Ammonium

Ammonium concentrations increase by depth as shown in Figure 5.17, which is closely related to dissolved oxygen concentrations. As dissolved oxygen concentration in surface layers is relatively higher, there are suitable conditions for ammonium oxidation to nitrite and nitrate. Thus, in the deeper layers, due to low dissolved oxygen levels, ammonium could not react with sufficient oxygen to oxidize to nitrite and nitrate. Consequently, ammonium concentrations inversely follow the trend of dissolved oxygen profiles in water column.
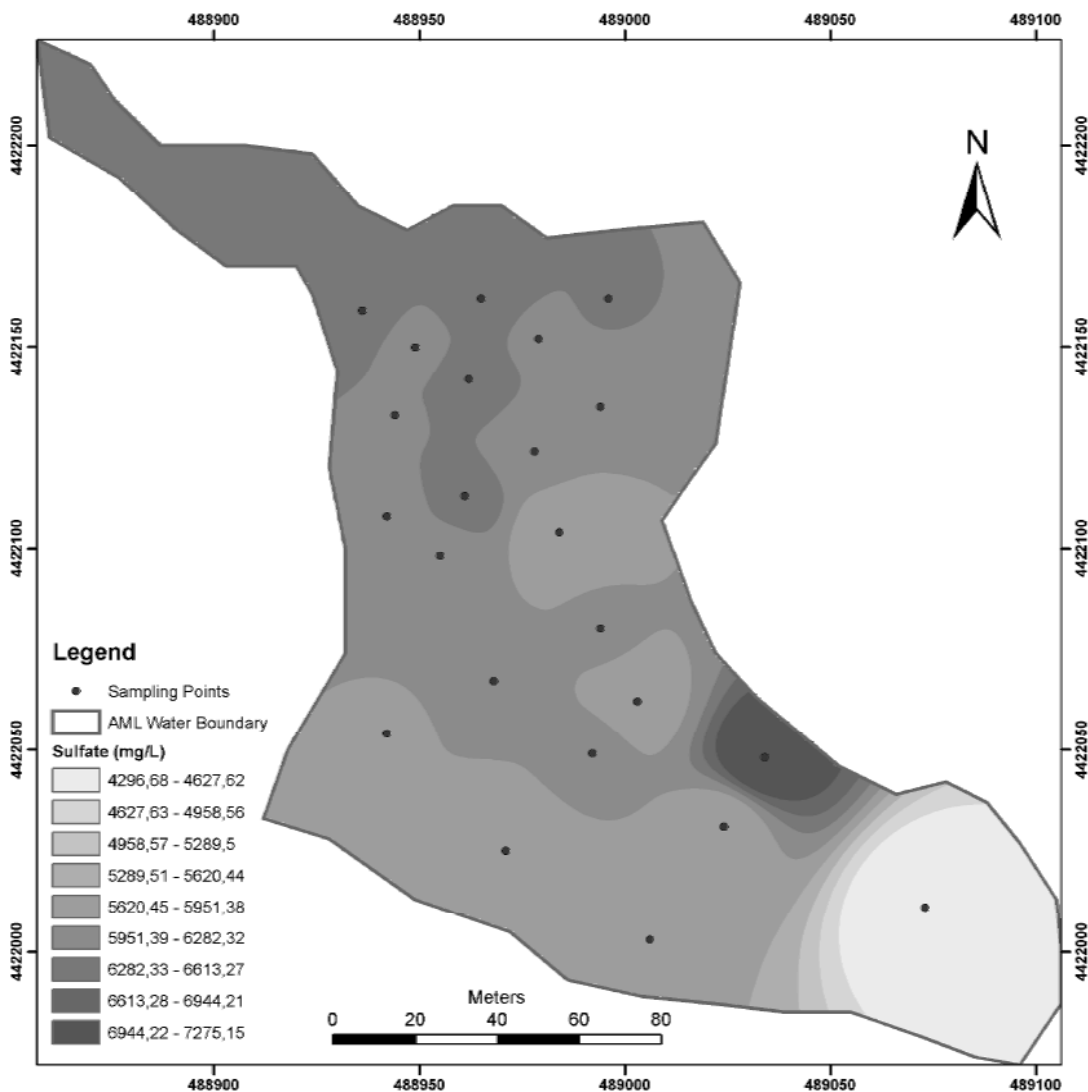
Figure 5.16 Distribution of sulfate at water surface

Within the scope of this study, ammonium concentrations were observed to be between 0.4 mg/L and 12.36 mg/L with an average value of 2.72 mg/L. This mean concentration exceeds the standard (ITASHY, 2005). High ammonium concentrations are very toxic to living beings and thus should be closely monitored. Ammonium is converted to nitrite and then nitrate under the suitable conditions for oxidation. High concentration of nitrate is lethal for especially babies creating the blue baby syndrome and is carcinogenic for adults when combined with amine and amide groups. On the other hand, ammonium could react with available chloride in water and generate chloramines, which are very toxic to living beings even at low concentrations such as 0.06 - 0.1 mg/L (Kurama & Poetzschke, 2002).
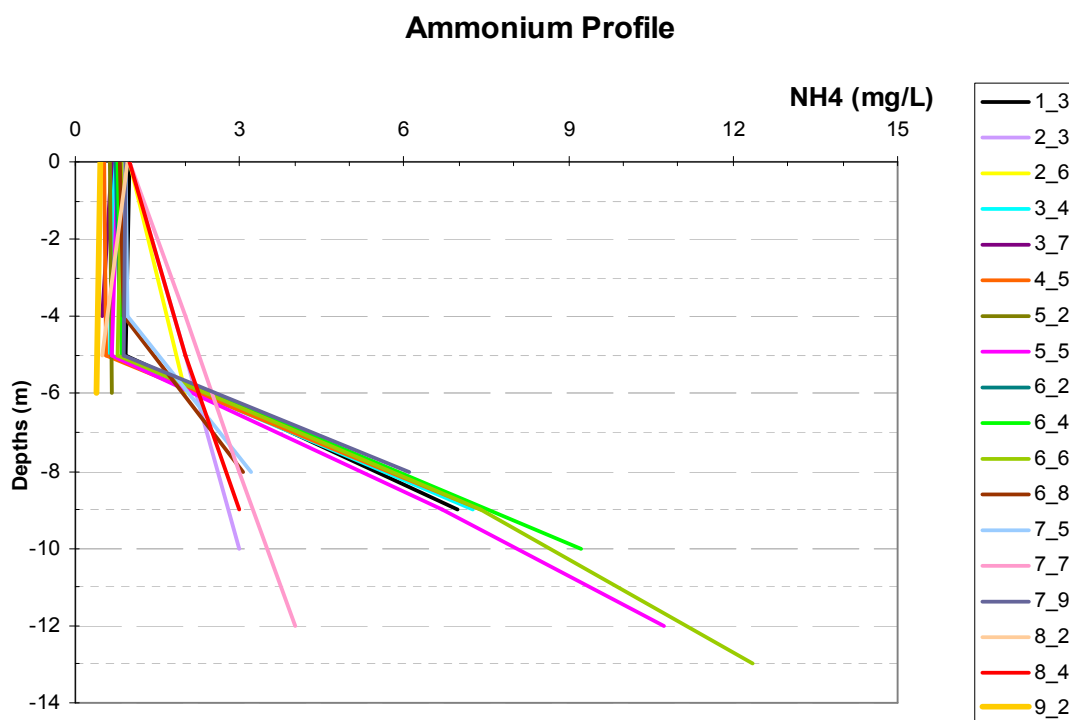
Ammonium Profile

Figure 5.17 Depth profile for ammonium

5.4.4 Magnesium

Magnesium and calcium cause hardness in water bodies. These elements were detected in high levels in Hayırtepe AML. The magnesium values ranged between 93.31 mg/L and 256.72 mg/L and had an average value of 200.03 mg/L. It did not show significant differences along the vertical profile as shown in Figure 5.18. The deviations observed in samples 8-2, 8-4 and 9-2 were probably related to error made during sample preparation and dilution.

The average magnesium value of 200.03 mg/L exceeds the standard value of 50 mg/L. Comparison of measured magnesium values with ITASHY standard is shown in Figure 5.19. Accordingly, all samples had concentrations exceeding the limit value. It has been found out that high concentrations of magnesium directly affect the nervous system and could reduce the number of heartbeat thus resulting in sudden heart attack and death when consumed in elevated concentrations.
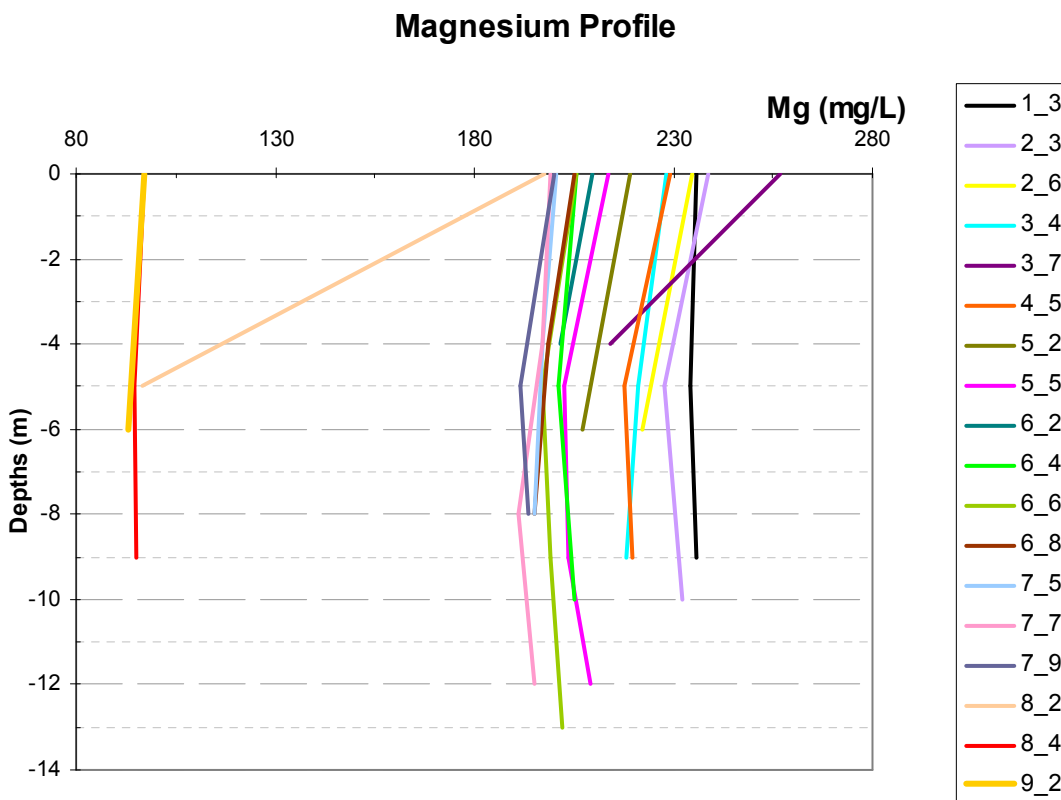
Magnesium Profile

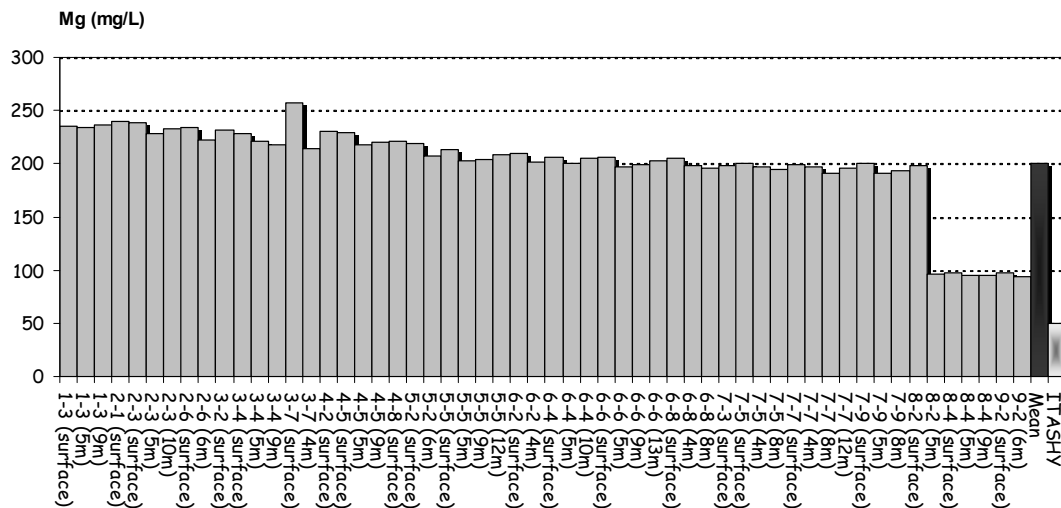Figure 5.18 Depth profile for magnesium

Figure 5.19 Magnesium comparison in accordance to ITASHY (2005)

5.4.5 Calcium

The calcium values measured in this study ranged between 222.82 mg/L and 576.71 mg/L. It did not show significant differences between the surface and the deeper layers similar to magnesium. Only the samples 8-2, 8-4 and 9-2 behave similarly as magnesium; supporting the fact that some dilution error were made in these three samples. When the errors in these points are neglected, there is not much of a variation between surface and deeper layers. The vertical profile for calcium is given in Figure 5.20.

The mean value was computed to be 456.90 mg/L that exceeds the ITASHY standard of 200 mg/L. The comparison with standard value is shown in Figure 5.21. High calcium concentrations are also harmful to the human body affecting the blood vessels and resulting with high blood pressure (Göğüş, 2007).
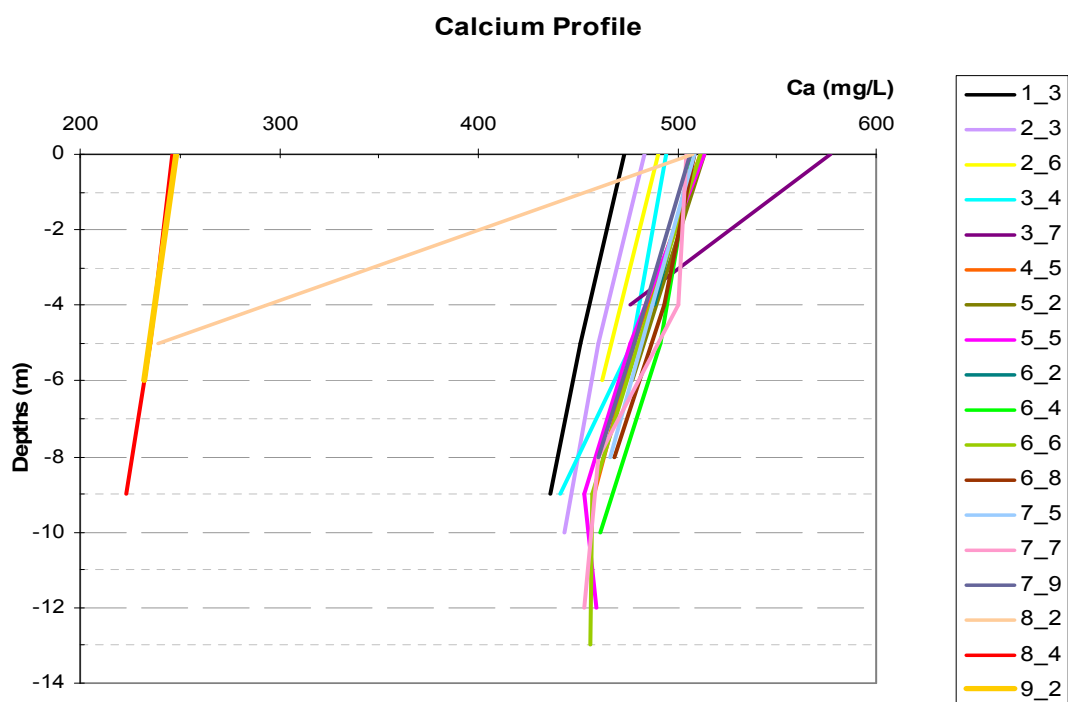

Figure 5.20 Depth profile for calcium
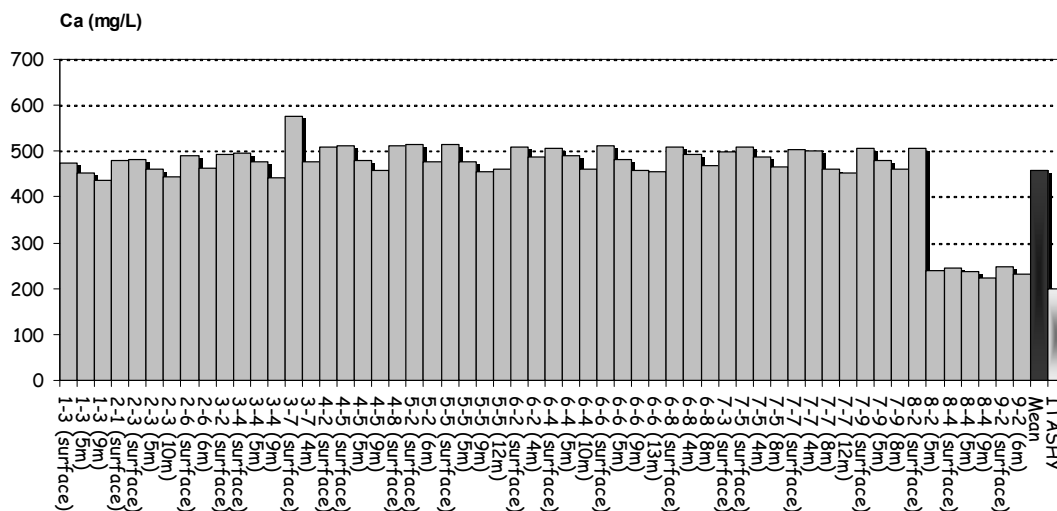
Figure 5.21 Calcium comparison in accordance to ITASHY (2005)

5.5 Heavy Metals and Trace Elements

Most metals have increasing ionic solubility under acidic and oxidizing conditions. Thus, metals are typically not absorbed onto solids in acidic mining lakes and therefore metal concentrations are significantly high. Based on these fundamentals, the results for heavy metals and trace elements are given in Table 5.4. Arsenic, chromium and copper concentrations are below the standard values and thus not discussed in following sections.

5.5.1 Iron

High iron levels are amongst the typical characteristics of pyrite oxidation. Iron could exist in mine waters in several forms (i.e. Fe^{2+}, Fe^{3+}, $Fe(OH)_2^+$, $Fe(OH)_3$, $Fe(SO4)^+$, $Fe(SO_4)_2^-$). In dissolved form, iron is found in two oxidation states: ferrous (Fe^{2+}) and ferric (Fe^{3+}). The rate of iron oxidation from Fe^{2+} to Fe^{3+} depends on pH and dissolved oxygen levels.

Table 5.4 Results of heavy metals and trace elements

| Point	d (m)	Al (μg/L)	As (μg/L)	Cd (μg/L)	Co (μg/L)	Cr (μg/L)	Cu (μg/L)	Fe (μg/L)	Mn (μg/L)	Ni (μg/L)	Pb (μg/L)	Zn (μg/L)
1-3	0	279200	0.84	16.80	2028	29.51	489.10	106600	81840	1022	9.12	4611
1-3	-5	269500	1.19	15.15	1860	28.05	466.40	88170	78250	976	7.35	4425
1-3	-9	244400	0.82	12.37	1966	35.09	375.70	322000	78070	1009	26.17	4322
2-1	0	294500	0.82	15.37	2083	28.94	484.10	94020	86140	1049	4.74	4920
2-3	0	290700	0.91	15.92	2085	29.06	483.10	107200	84320	1060	5.85	4805
2-3	-5	272900	0.87	14.68	1990	27.70	459.30	104100	78310	1018	5.33	4477
2-3	-10	246000	1.11	11.33	2059	37.41	345.70	424100	83250	1068	32.72	4408
2-6	0	295100	1.00	15.77	2100	29.54	481.30	105600	87410	1073	2.08	5021
2-6	-6	275500	0.51	14.69	1952	27.75	451.30	105500	81610	994	13.30	4672
3-2	0	292100	0.72	15.36	2145	27.89	483.70	112500	88040	1104	7.64	5236
3-4	0	297800	0.89	15.99	2188	29.32	494.90	101400	86610	1136	8.46	4962
3-4	-5	284000	0.52	16.64	2128	31.17	512.10	97680	85890	1120	6.60	4896
3-4	-9	256400	0.56	13.56	2090	39.57	399.50	249400	84360	1084	34.37	5594
3-7	0	307400	0.65	18.02	2199	32.47	556.70	119700	89160	1118	6.63	5204
3-7	-4	284200	0.58	16.06	2041	30.33	497.90	91840	85910	1063	7.75	4871
4-2	0	302000	0.65	17.01	2121	31.36	529.10	88730	90630	1109	10.20	5218
4-5	0	305200	0.63	17.93	2102	31.86	547.60	113600	92220	1088	6.24	5320
4-5	-5	285900	0.38	15.65	1930	22.35	380.50	139400	86960	1046	3.43	4912
4-5	-9	271600	2.59	9.93	2024	25.94	315.70	294500	89280	1080	21.20	5932
4-8	0	311700	2.10	12.87	2087	22.53	401.60	121700	95420	1110	4.91	5518
5-2	0	317800	5.39	12.54	2103	22.80	400.10	119400	97370	1107	8.05	5488
5-2	-6	288300	4.50	11.51	1953	21.55	378.00	103300	89470	1048	7.73	5220
5-5	0	315700	4.50	12.44	2100	23.09	400.70	116200	95690	1095	5.08	5575
5-5	-5	278900	2.37	12.09	1934	22.18	378.90	89570	85330	1048	4.74	4934
5-5	-9	265500	2.99	9.86	1974	25.24	310.10	270600	89270	1044	18.63	5017
5-5	-12	247700	7.64	8.27	1988	30.01	238.70	493300	89890	1077	33.23	4954
6-2	0	310500	4.16	12.86	2051	22.86	398.30	96040	96080	1078	6.63	5543
6-2	-4	308500	2.84	12.30	2010	21.84	393.60	89540	95110	1107	3.25	5564
6-4	0	312200	2.48	14.23	2063	24.44	422.40	112200	95660	1119	5.54	5978
6-4	-5	294400	2.01	12.17	2004	21.55	403.40	97890	90340	1097	5.29	5217
6-4	-10	263500	1.83	9.26	2063	27.09	304.70	343500	91280	1117	24.56	5108
6-6	0	316500	1.93	12.76	2309	23.12	413.00	120300	98260	1221	4.46	5612
6-6	-5	294800	1.56	12.40	2127	21.52	380.10	96960	91930	1149	8.81	5245
6-6	-9	265300	1.47	9.98	2057	24.99	317.70	266100	91370	1121	22.14	5350
6-6	-13	236700	3.10	7.81	2113	32.00	168.60	571000	90120	1150	38.42	4953
6-8	0	311900	1.31	12.58	2169	23.29	394.80	94230	98530	1174	-0.72	5652
6-8	-4	316000	1.15	12.68	2139	22.53	402.60	97790	95980	1168	7.75	5684
6-8	-8	291400	1.70	12.35	2052	23.67	363.80	134200	94220	1123	14.04	8472
7-3	0	325200	1.33	13.34	2218	22.93	407.30	118000	101600	1213	1.99	6012
7-5	0	298800	1.26	13.35	2030	22.95	413.60	123400	92910	1124	9.17	5585
7-5	-4	308200	1.10	11.80	2101	21.66	390.70	127600	97120	1167	4.55	5978
7-5	-8	295800	1.03	10.39	2105	24.92	327.80	267400	99210	1154	9.26	5665

Point	d (m)	Al (µg/L)	As (µg/L)	Cd (µg/L)	Co (µg/L)	Cr (µg/L)	Cu (µg/L)	Fe (µg/L)	Mn (µg/L)	Ni (µg/L)	Pb (µg/L)	Zn (µg/L)
7-7	0	323200	1.14	13.29	2204	23.69	403.80	143000	101000	1203	5.44	6012
7-7	-4	312600	1.04	12.99	2117	21.91	296.90	111700	96750	1180	2.43	5767
7-7	-8	279700	1.34	10.54	2050	25.34	330.80	299400	97040	1157	24.87	5468
7-7	-12	247500	3.90	8.33	2109	31.82	250.20	553500	92800	1173	41.57	4936
7-9	0	286200	1.37	13.22	2177	22.34	410.60	108200	88930	1194	5.34	5196
7-9	-5	265700	1.20	12.00	2064	21.56	371.20	94190	82970	1144	0.87	4746
7-9	-8	271800	1.11	10.70	2006	25.62	339.40	295100	94210	1099	16.72	5155
8-2	0	311700	1.22	13.18	2046	23.44	414.20	148000	96430	1125	6.83	5662
8-2	-5	297000	1.16	12.58	2006	21.70	392.50	121500	93930	1120	5.10	5430
8-4	0	326300	1.19	13.32	2167	23.46	406.90	132600	103500	1196	4.16	6187
8-4	-5	306000	1.08	12.17	2012	21.22	383.50	104600	96220	1106	7.61	5580
8-4	-9	273200	1.39	9.59	2041	26.45	294.10	358700	95580	1139	27.32	5453
9-2	0	321600	1.11	12.46	2129	21.92	392.50	134600	101700	1176	0.54	6026
9-2	-6	296500	1.11	12.25	1972	21.94	377.40	109900	93660	1122	5.02	5508
Mean		290155	1.70	12.94	2070	26.01	396.93	172344	91342	1110	11.09	5344
St. Dev.		22838	1.38	2.39	83	4.40	76.04	121144	6201	56	10.29	621
90%Percent.		316250	3.50	16.03	2173	31.84	492.00	332750	98395	1178	26.75	5978
50%Percent.		294450	1.19	12.63	2064	24.68	398.90	117100	91650	1114	7.09	5283
10%Percent.		259950	0.64	9.90	1969	21.68	307.40	94105	83110	1045	2.84	4709
Max		326300	7.64	18.02	2309	39.57	556.70	571000	103500	1221	41.57	8472
Min		236700	0.38	7.81	1860	21.22	168.60	88170	78070	976	0.00	4322
ITASHY'05		200	10	5	-	50	2000	200	50	20	10	5000
EPA'03		200	10	5	-	100	1000	300	50	-	15	5000
WHO'04		200	10	5	-	50	2000	200	400	20	10	5000

The dissolved iron concentrations are strongly related to ORP and pH. The oxidation reaction for Fe^{2+} is given below:

$$4Fe^{2+}{}_{(aq)} + O_{2(g)} + 4H^{+}{}_{(aq)} \rightarrow 4Fe^{3+}{}_{(aq)} + 2H_2O_{(l)}$$
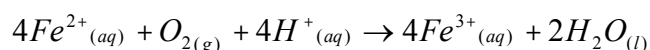
Fe^{3+} will become insoluble and precipitate as ferric hydroxide according to the following reaction:

$$Fe^{3+}{}_{(aq)} + 3H_2O_{(l)} \leftrightarrow Fe(OH)_{3(s)} + 3H^{+}{}_{(aq)}$$
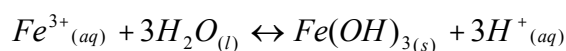
Pourbaix diagram is given in Figure 5.22 to determine the dominant form of iron in Hayırtepe-AML. Average ORP (Eh) and pH value in the lake are calculated to be 0.543 volt and 2.28, respectively. According to the figure, iron is found to be in Fe^{2+} form.
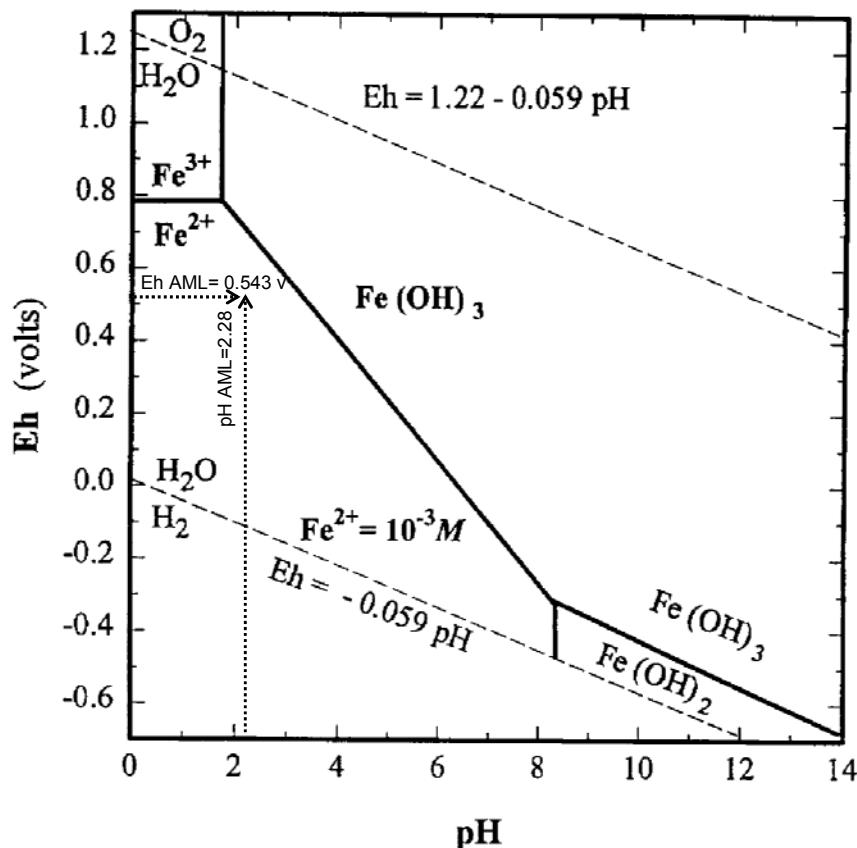
Figure 5.22 Pourbaix diagram for iron in relation to Eh and pH

As with most other AMLs, Hayırtepe AML also have a typical reddish-yellow or yellowish-brown color (Figure 5.23), which is caused by iron precipitates such as iron hydroxides.

In this study, iron concentrations ranged between 88170 µg/L and 571000 µg/L and concentrations increased with depth (Figure 5.24). Similar elevated levels were reported in other studies such as the one conducted by Kwong & Lawrance (1998) where they found dissolved iron levels of 49720 µg/L (at a pH level of 2.8) and 367200 µg/L (at a pH level of 4.6) at depths of 0.2m and 8.5 m, respectively. This depth variation is strongly related to ORP and dissolved oxygen levels, in which high DO concentrations at the surface creates iron precipitates and lower aqueous iron concentrations. On the other hand, bottom layers that are low in DO levels have higher aqueous iron concentrations as depicted by Friese, Hupfer & Schultze (1998). Therefore, it could be concluded that dissolved iron concentrations depend on not only low pH levels but also on dissolved oxygen levels.

Figure 5.23 Reddish- yellow color of the Hayırtepe AML

Iron Profile

Figure 5.24 Depth profile for iron

With a mean concentration of 172344 µg/L, the dissolved iron levels of Hayırtepe AML has been found to be three orders of magnitude above the ITASHY limit of 200 µg/L as shown in Figure 5.25. This is an expected situation in acidic mining lakes where iron is the key parameter. The distribution of iron at water surface is given in Figure 5.26.
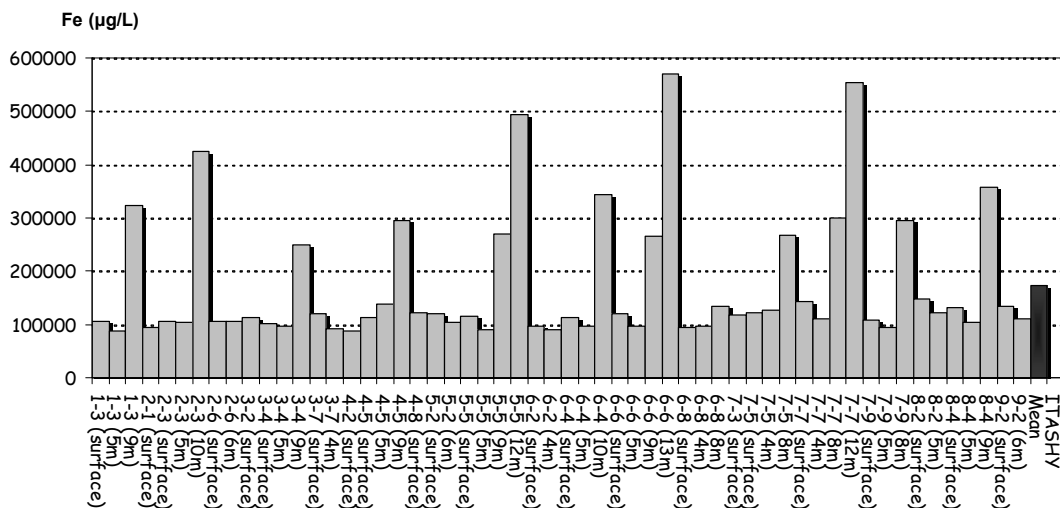
Figure 5.25 Iron comparison in accordance to ITASHY (standard value is 200 µg/L)
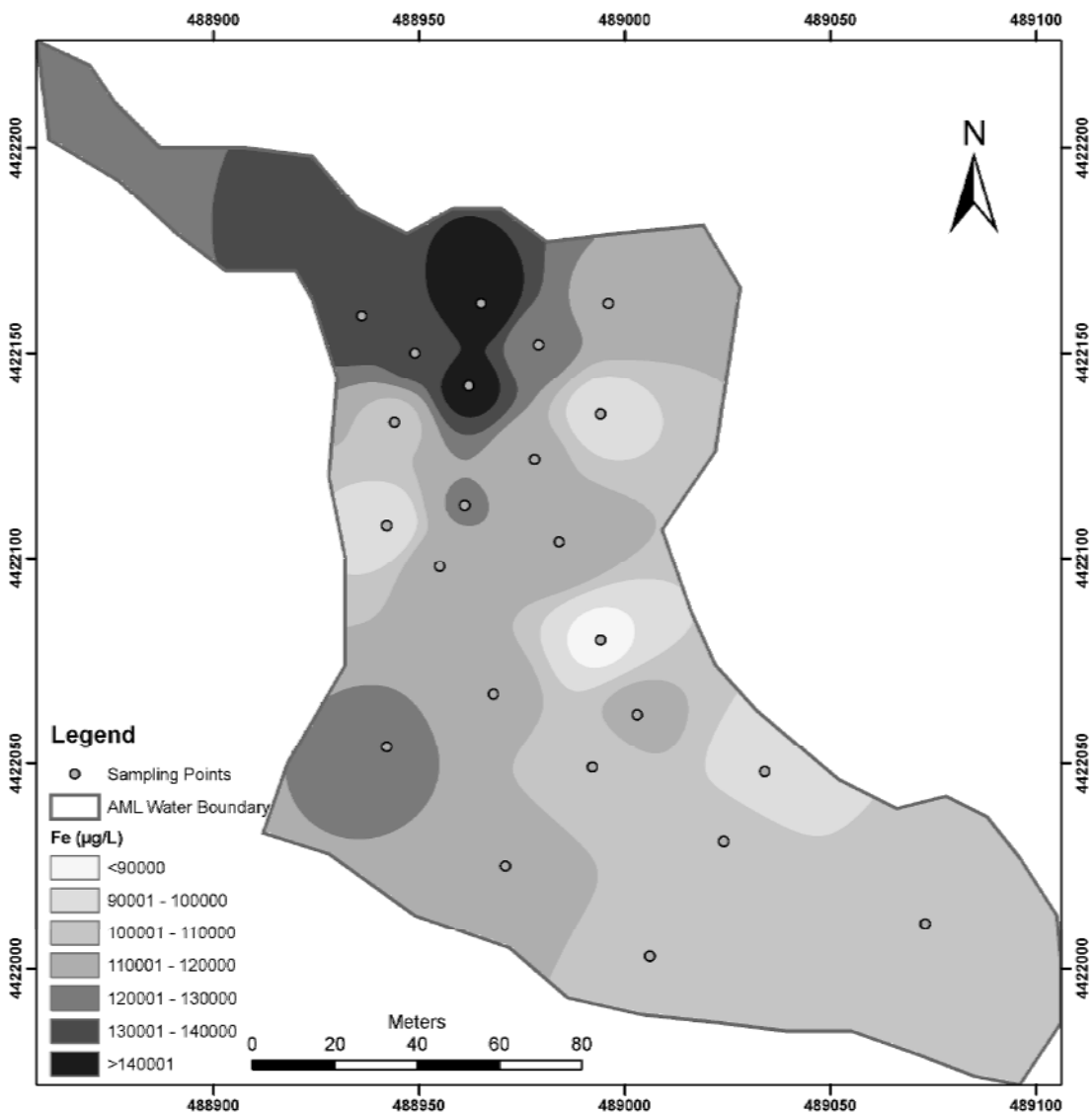

Figure 5.26 Distribution of iron at water surface

5.5.2 Aluminum

High aluminum concentrations in acidic waters result from the weathering of aluminosilicate minerals such as clays. Dissolved aluminum is found as Al^{3+}. And its chemistry resembles that of iron chemistry. Aluminum also precipitates as hydroxides and oxyhydroxides. During alkaline conditions, aluminum is found as aluminum hydroxides. The formation of aluminum hydroxides generates acidic conditions, which are expressed with the following equation:

$$Al^{3+}{}_{(aq)} + 3H_2O_{(l)} \leftrightarrow Al(OH)_{3(s)} + 3H^+{}_{(aq)}$$
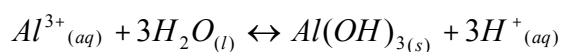
When the results are examined, it is seen that aluminum concentrations decrease by increasing depth (Figure 5.27). Similar results were observed in the study of Kwong & Lawrance (1998) where low pH values were coupled with high aluminum concentrations.
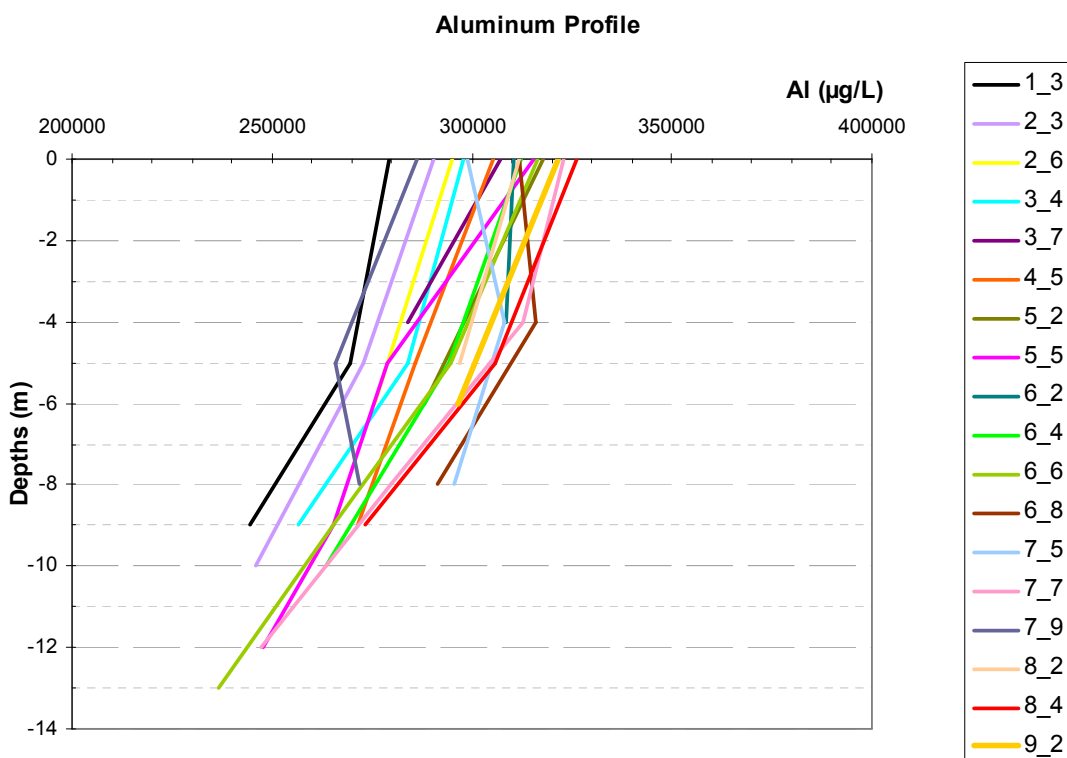

Figure 5.27 Depth profile for aluminum

The maximum aluminum concentration in Hayırtepe AML was found to be 326300 µg/L at the point 8-4, which was a surface sample. The minimum concentration, on the other hand, was 236700 µg/L observed at the point 6-6 taken from 13 m deep. As depth increases, pH increases and hence aluminum dissolution decreases giving lower aluminum concentrations.

Aluminum concentrations in Hayırtepe AML were found to exceed the currently effective standard value by 3-4 orders of magnitude representing extremely problematic conditions for human health (Figure 5.28).
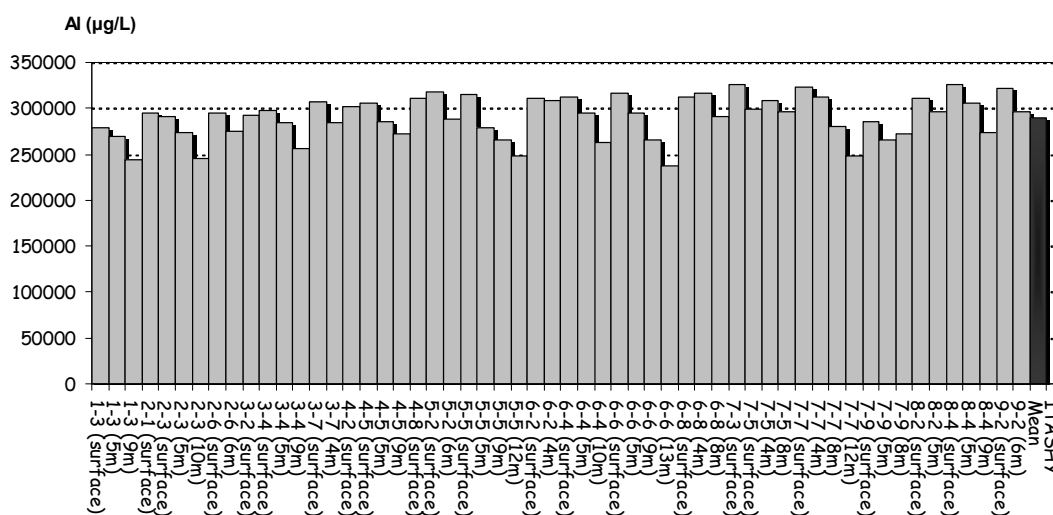

Figure 5.28 Aluminum comparison in accordance to ITASHY (standard value: 200 µg/L)

5.5.3 Manganese

Samples collected from Hayırtepe AML had extremely high manganese concentrations that range between 78070 µg/L and 103500 µg/L with a mean value of 91342 µg/L. Thus, Mn concentrations are 3-4 orders of magnitude higher than the standard value of 50 µg/L as shown in Figure 5.29. On the other hand, it did not show significant differences within the water column as given in Figure 5.30. Finally, the manganese distribution at the water surface is presented in Figure 5.31.
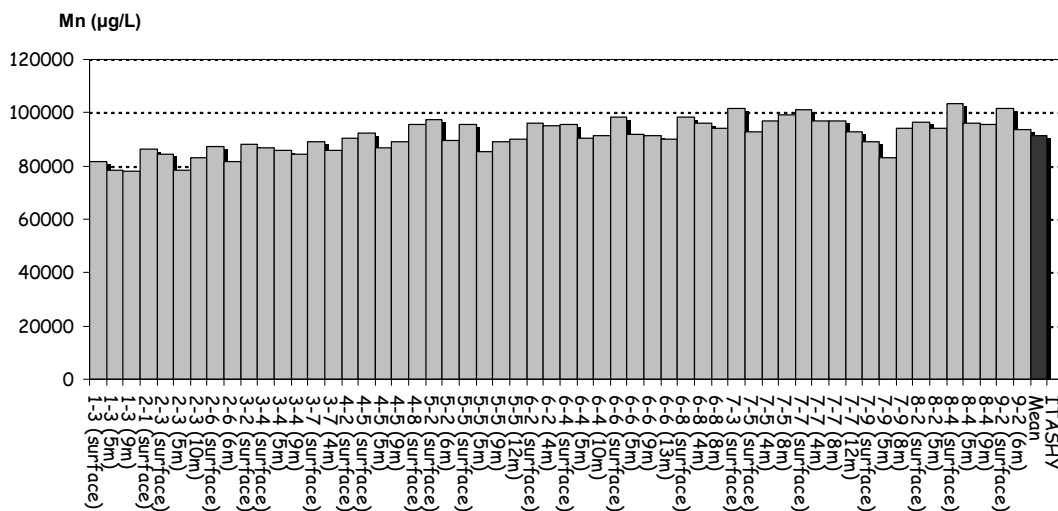
Mn (µg/L)

Figure 5.29 Manganese comparison in accordance to ITASHY (standard value: 50µg/L)

Manganese Profile
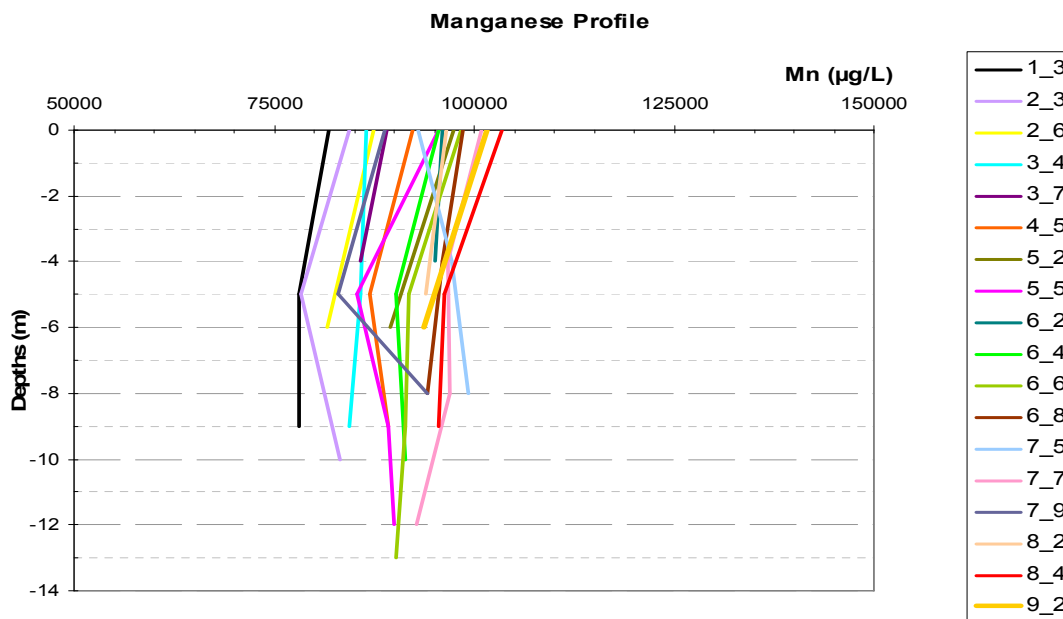
Mn (µg/L)

Depths (m)

Figure 5.30 Depth profile for manganese
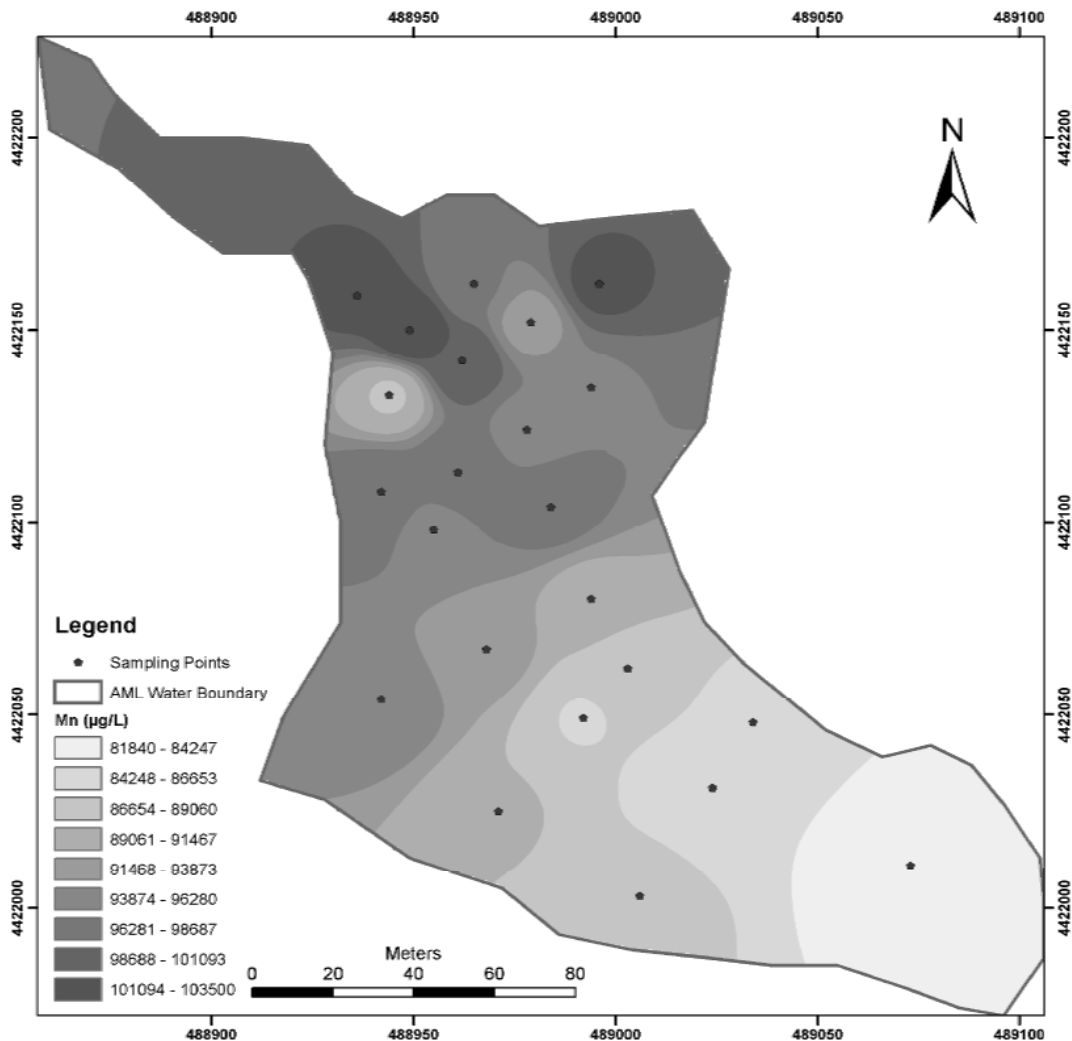
Figure 5.31 Distribution of manganese at water surface

5.5.4 Nickel

Nickel is a very toxic element and a potential carcinogen when found in high concentrations. It has been proved that nickel compounds in water could cause liver cancer (Boğa, 2007). Maximum and minimum nickel concentration in Hayırtepe AML was measured to be 1221 μg/L and 976 μg/L, respectively. The mean value was computed to be 1110 μg/L, which is about 50 times higher than the ITASHY standard value (Figure 5.32). Furthermore, nickel concentrations did not show a clear trend with depth (Figure 5.33).
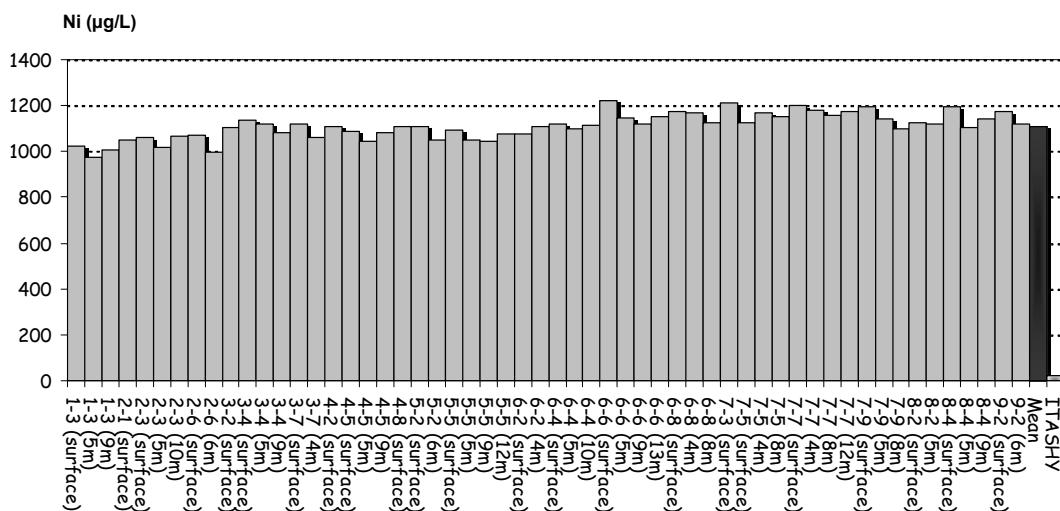
Figure 5.32 Nickel comparison in accordance to ITASHY (2005)

Figure 5.33 Depth profile for nickel

5.5.5 Cobalt

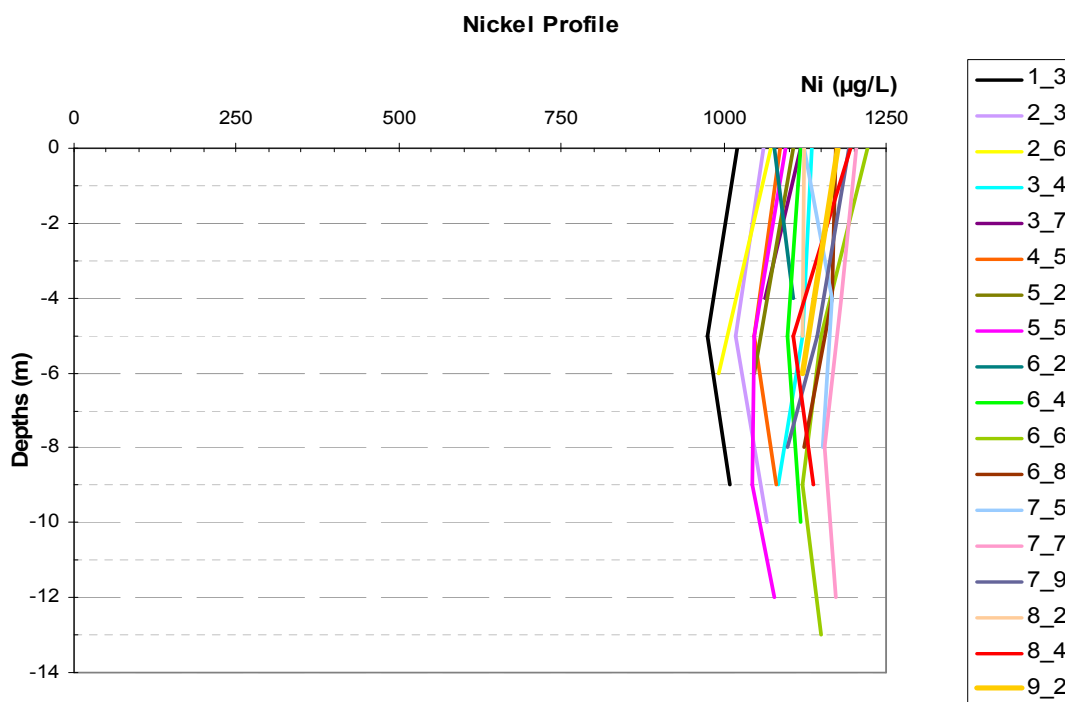Cobalt is a rare element in earth's crust and thus not typically found in high concentrations in surface waters. Thus, no standard value has been set for this chemical and for its compounds despite the fact that they are extremely toxic for humans. In addition, cobalt and its compounds are classified as carcinogenic and

tests conducted on animals have proven this carcinogenic effect (Boğa, 2007). In this study, cobalt concentrations were measured to be between 1860 µg/L and 2309 µg/L with a mean value of 2070 µg/L. The vertical profile for cobalt is given in Figure 5.34.
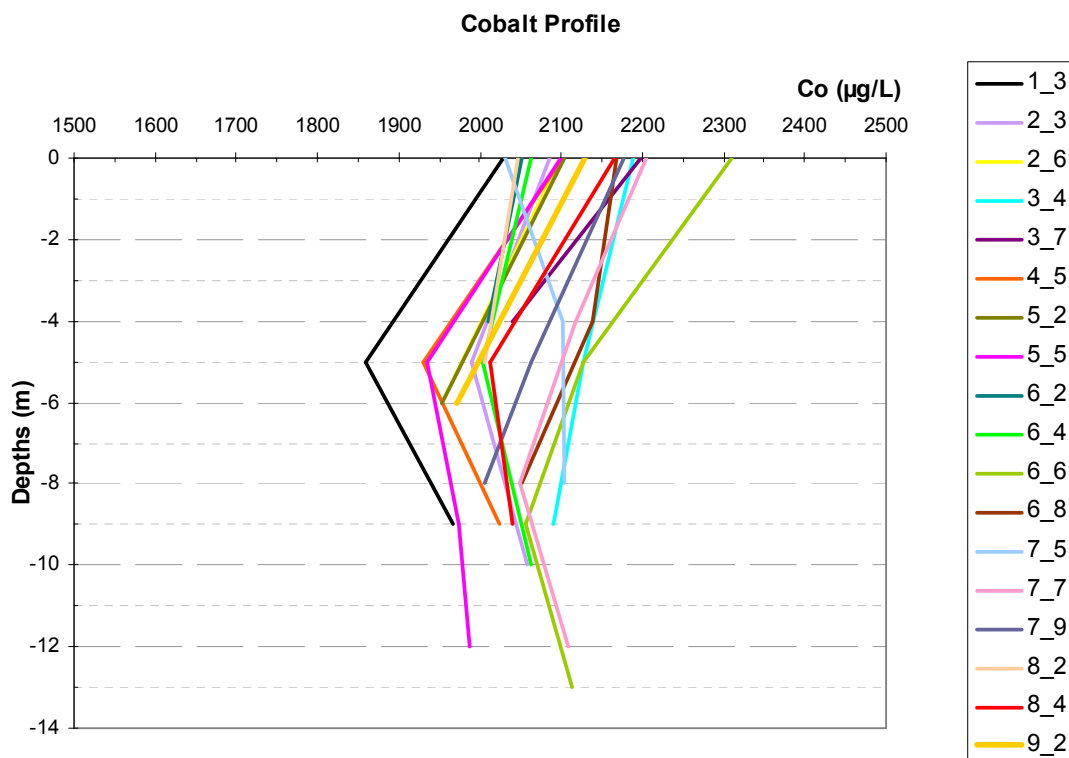
Figure 5.34 Depth profile for cobalt

5.5.6 Zinc

Zinc and many zinc compounds are moderately toxic when compared to other heavy metals. In this study, zinc values were measured to range between 4322 µg/L and 8472 µg/L, with a mean value of 5344 µg/L that is slightly over the ITASHY standard level of 5000 µg/L. The comparison with ITASHY standard is shown in the Figure 5.35. The depth profile for zinc, on the other hand, is presented in Figure 5.36 and the spatial distributions at water surface are given in Figure 5.37.
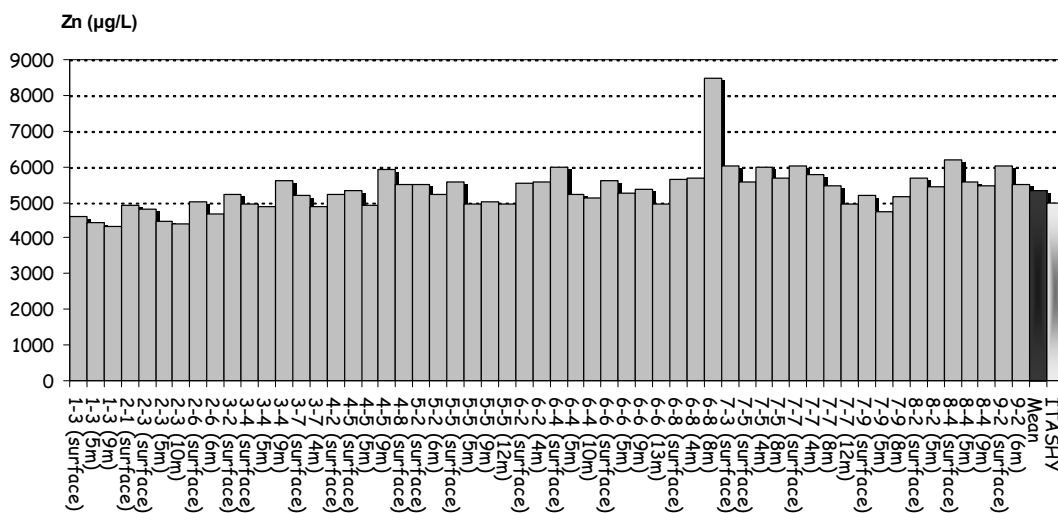
Figure 5.35 Zinc comparison in accordance to ITASHY (2005)
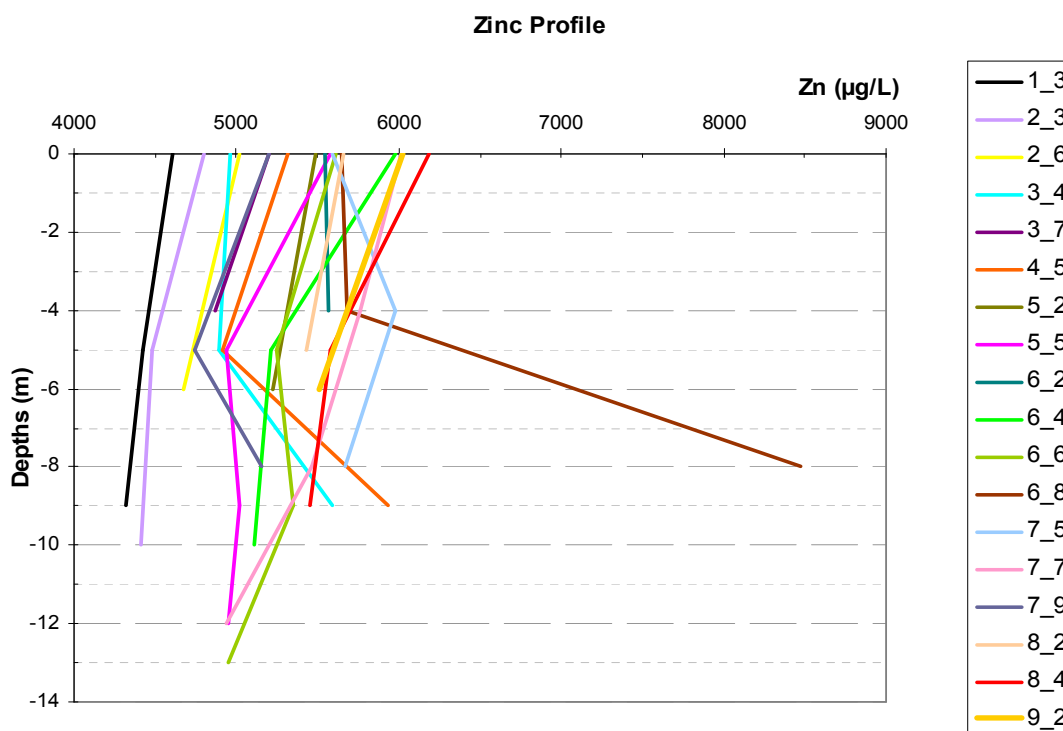
Figure 5.36 Depth profile for zinc
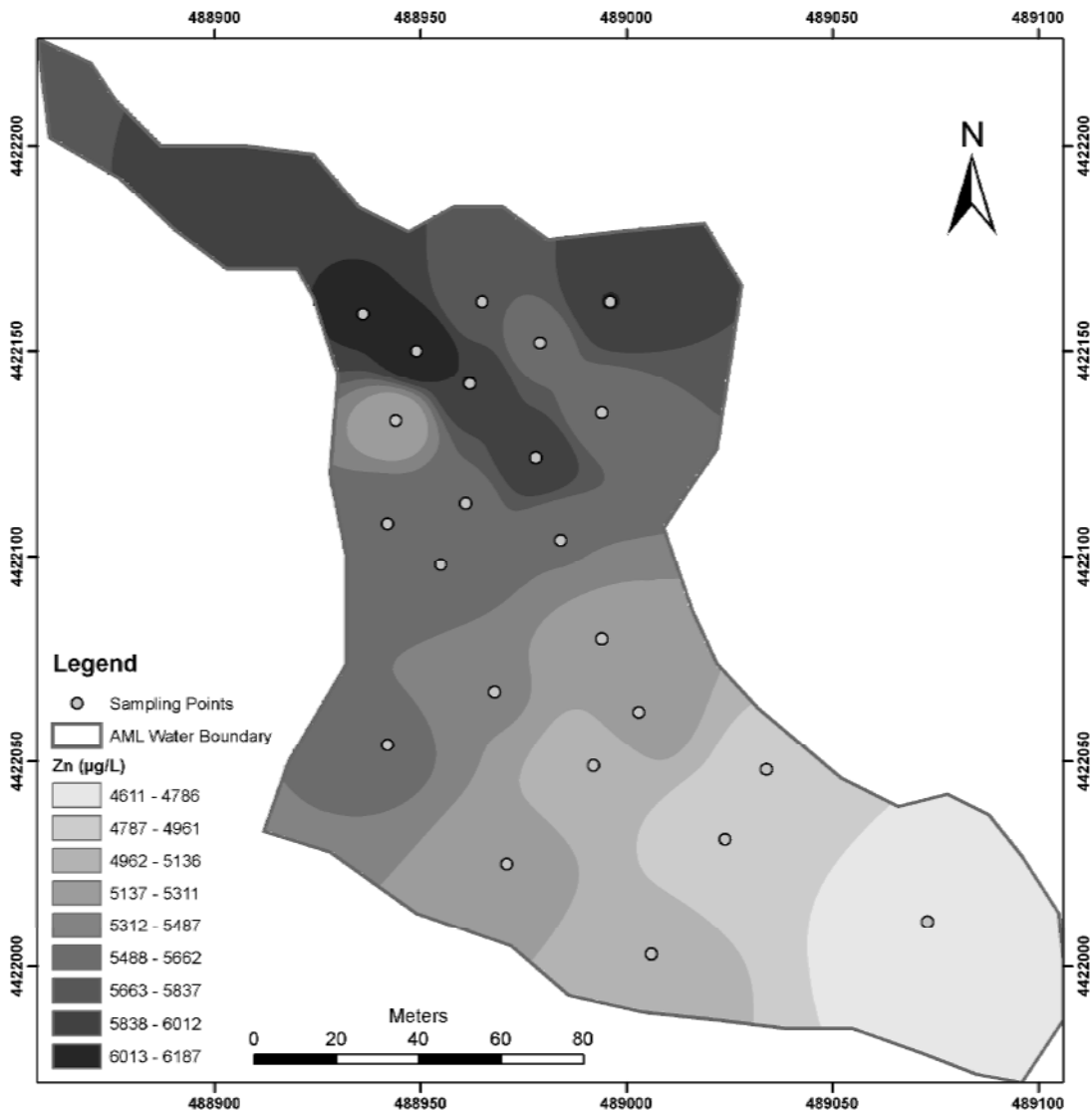
Figure 5.37 Distribution of zinc at water surface

5.5.7 Cadmium

Cadmium and its compounds are also proven carcinogens (Boğa, 2007). In this study, total cadmium levels were measured to range between 7.81 µg/L and 18.02 µg/L with a mean value of 12.94 µg/L that exceed the ITASHY standard value of 5 µg/L. The cadmium concentrations decrease by depth as a strong function of pH. The vertical profiles are given in Figure 5.38. Comparisons with the standard are shown in Figure 5.39.
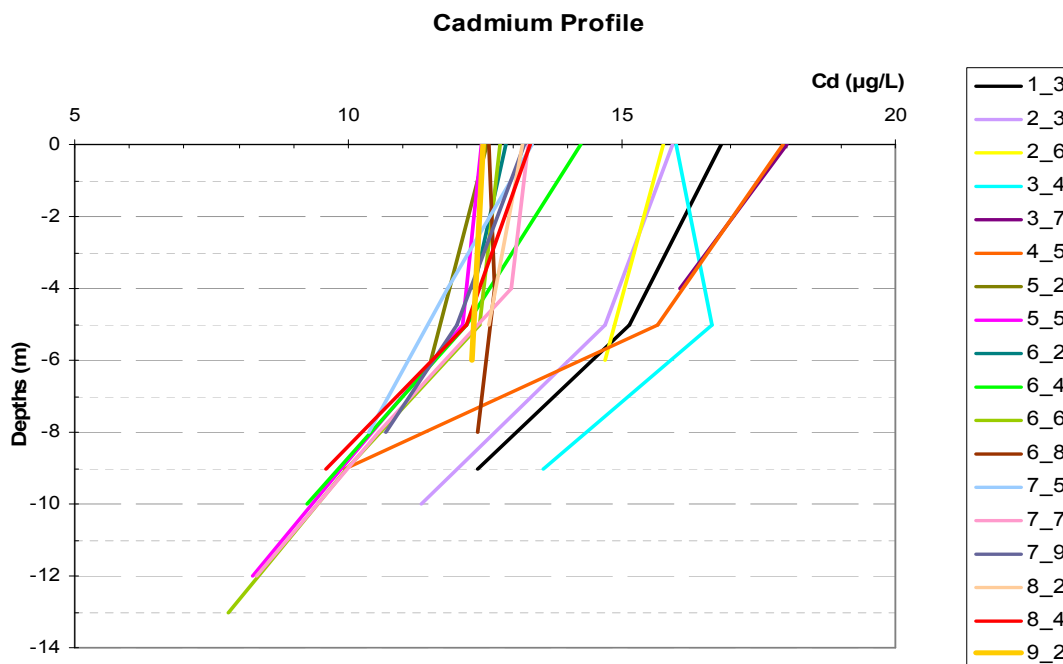
Cadmium Profile

Figure 5.38 Depth profile for cadmium
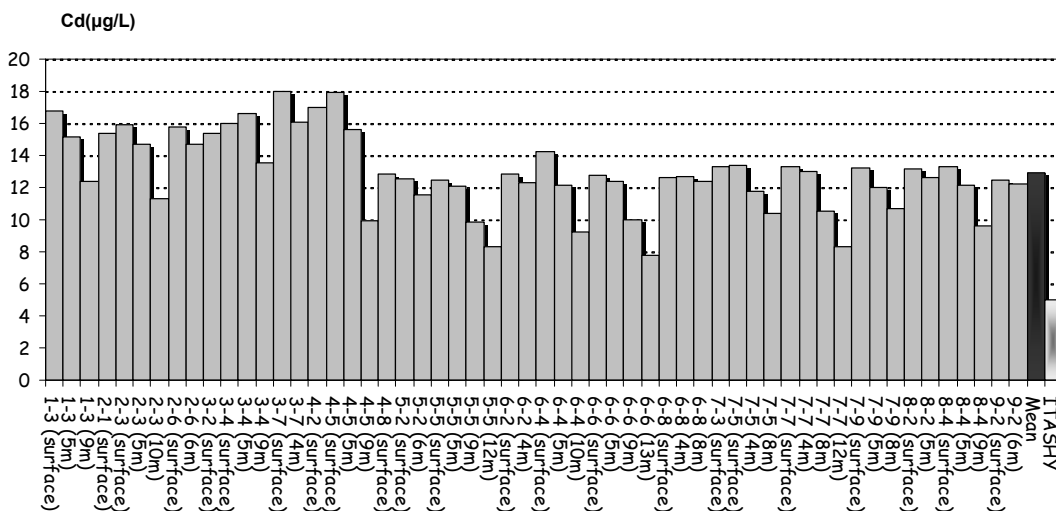
Figure 5.39 Cadmium comparison in accordance to ITASHY (2005)

5.5.8 Lead

Lead is also a very toxic element for humans when exposed to high levels. The lead levels in Hayırtepe AML were measured to range between 7.81 µg/L and 18.02 µg/L with a mean concentration of 11.09 µg/L. As seen from these values, the lead levels in Hayırtepe AML are within the range of EPA standard but slightly exceed

the WHO and ITASHY standards. The depth profile of lead levels in the lake show similar patterns to iron profile and increase as a function of depth (Figure 5.40).
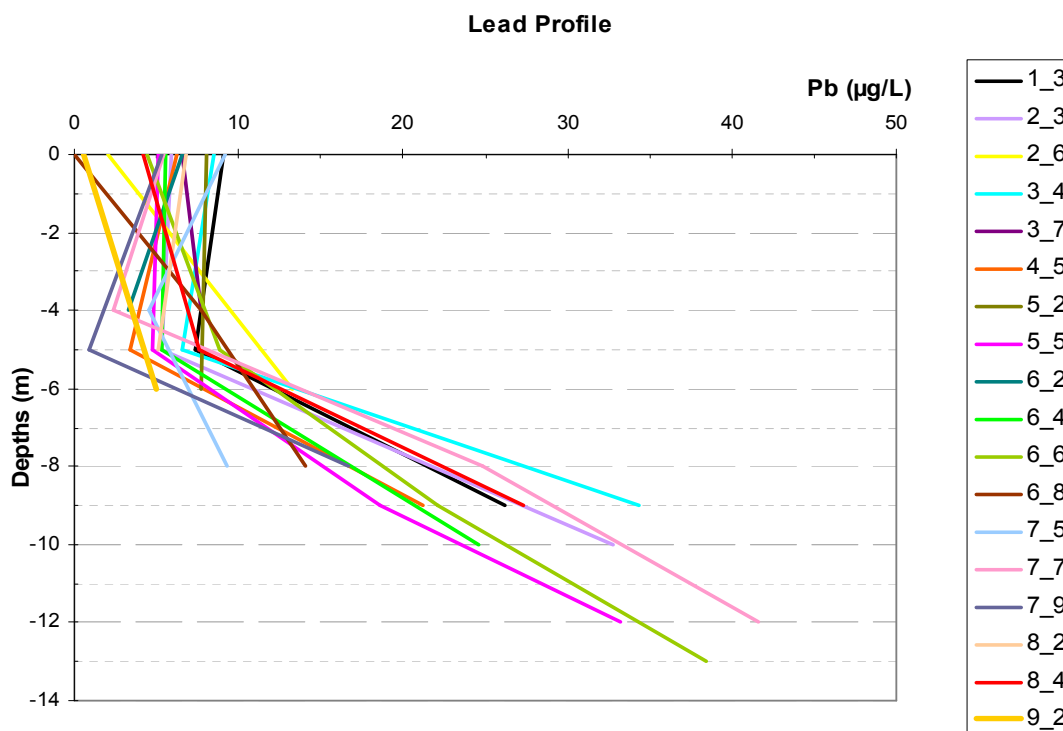
Lead Profile

Figure 5.40 Depth profile for lead

5.6 Classification of Hayırtepe AML According to Water Quality Criteria

As it was mentioned in the beginning of this chapter, the comparison of the mean value of each parameter with the pertinent drinking water standard was done to show the potential risk of AML to drinking water quality in downstream residential areas that use surface and subsurface waters without any treatment apart from simple chlorination for human consumption, animal breeding and agricultural irrigation. Thus, any water discharge from such lakes with impaired water quality has a strong likelihood to contaminate the drinking water resources of these residential areas situated downstream the lakes. These comparisons are summarized in Table 5.6. Accordingly, the parameters with values exceeding the standards are highlighted.

Table 5.5 Comparison of Hayırtepe AML water quality with national and international drinking water standards

Water Quality Parameter	Hayırtepe AML September'08 Results (Mean Values)	ITASHY (2005)	EPA (2003)	WHO (2004)
A) Physical Parameters				
Temperature (^{o}C)	18.54	25	-	-
pH	2.28	6.5-9.5	6.5-8.5	6.5-8.5
Dissolved oxygen (mg/L)	4.67	-	-	-
Oxygen saturation (%)	53.96	-	-	-
ORP (mV)	543.48	-	-	-
EC (μS/cm)	5925	2500	-	-
TDS (mg/L)	2962.16	-	-	-
Salinity (‰)	3.23	-	-	-
B)Anions and Cations				
F^- (mg/L)	6.40	1.5	2.0	1.5
Cl^- (mg/L)	63.25	250	250	250
$SO_4^=$ (mg/L)	5912.51	250	250	250
Li^+ (mg/L)	0.18	-	-	-
Na^+ (mg/L)	115.45	200	-	200
NH_4^+-N (mg/L)	2.72	0.5	-	-
K^+ (mg/L)	1.63	-	-	-
Mg^{++} (mg/L)	200.03	50	-	-
Ca^{++} (mg/L)	456.90	200	-	-
C) Heavy metals and trace elements				
Al (μg /L)	290155	200	200	200
As (μg /L)	1.70	10	10	10
Cd (μg /L)	12.94	5	5	3
Co (μg /L)	2070	-	-	-
Cr (μg /L)	26.01	50	100	50
Cu (μg /L)	396.93	2000	1000	2000
Fe (μg /L)	172344	200	300	200
Mn (μg /L)	91342	50	50	400
Ni (μg /L)	1110	20	-	20
Pb (μg /L)	11.09	10	15	10
Zn (μg /L)	5344	5000	5000	5000

In addition to the comparisons with drinking water quality criteria, the water quality in Hayırtepe AML was also compared with the water quality criteria classes for inland water resources of the Water Pollution Control Regulation and the class limits in this table are compared with the mean values of the measured parameters and the corresponding classes are given in Table 5.6. Consequently, of the 21 parameters assessed, 57% were in Class IV category, which corresponds to poor quality waters that should not be used for human and animal consumption, agricultural irrigation and recreational purposes without implementing advanced treatment techniques. Based on the regulation, a water body is finally classified

according to the lowest class level of each quality parameter. In this regard, Hayırtepe AML waters are classified as Class IV waters that have no practical use and have potential risks for the environment.

Table 5.6 Water quality classes according to Water Pollution Control Regulation

	Water Quality Classes According to SKKY (2004)				Hayırtepe AML September' 08 Results (Mean Values)	Water Quality Class
	I	II	III	IV		
A) Physical and Inorganic Chemical Parameters						
Temperature ($^{\circ}$C)	25	25	30	> 30	18.54	I
pH	6.5-8.5	6.5-8.5	6.0-9.0	<6.0 or >9.0	2.28	IV
DO (mg/L)	8	6	3	< 3	4.67	III
Oxygen saturation (%)	90	70	40	< 40	53.96	III
Cl^- (mg/L)	25	200	400	> 400	63.25	II
F^- (mg/L)	1	1.5	2	> 2	6.40	IV
Na^+ (mg/L)	125	125	250	> 250	115.45	I
NH_4^+-N (mg/L)	0.2	1	2	> 2	2.12	IV
$SO_4^=$ (mg/L)	200	200	400	> 400	5912.51	IV
TDS (mg/L)	500	1500	5000	> 5000	2962.16	III
B) Inorganic Parameters						
Al (μg/L)	300	300	1000	> 1000	290155	IV
As (μg/L)	20	50	100	> 100	1.70	I
Cd (μg/L)	3	5	10	> 10	12.94	IV
Co (μg/L)	10	20	200	> 200	2070	IV
Cr (μg/L)	20	50	200	> 200	26.01	II
Cu (μg/L)	20	50	200	> 200	396.93	IV
Fe (μg/L)	300	1000	5000	> 5000	172344	IV
Mn (μg/L)	100	500	3000	> 3000	91342	IV
Ni (μg/L)	20	50	200	> 200	1110	IV
Pb (μg/L)	10	20	50	> 50	11.09	II
Zn (μg/L)	200	500	2000	> 2000	5344	IV

CHAPTER SIX
MITIGATION MEASURES

This chapter discusses possible mitigation alternatives that are implemented throughout the world to alleviate the negative impacts of AMLs on surface and subsurface water quality. These alternative procedures are discussed within the general classification of active and passive systems. Following these fundamental techniques, a mitigation alternative is proposed for Hayırtepe AML studied in this study based on the water quality in the lake and other technical criteria. However it should be noted that the mitigation measure discussed herein is only an initial proposal to the problem and is not based on any laboratory or field scale tests. In this regard, a detailed feasibility is to be conducted prior to the selection of an actual mitigation technique.

6.1 Possible Mitigation Alternatives

The most suitable method for mitigating the impacts associated with an AML is to prevent its formation by implementing necessary post-closure procedures after the operational period of the mine ends. These procedures include leveling the open pit and the mine hole and minimizing the contact of mine waste that contains sulfidic minerals with air and water through the implementation of low permeability materials such as geomembranes. Otherwise, there is no practical way to avoid the formation of acidic mine drainage and acidic mining lakes. If the formation of AMLs is not prevented or the lake has already inundated and could economically and practically not be emptied, chemical or biological remediation measures should be applied in order to decrease the damage to the environment or at least to minimize the harmful effects. Through the application of suitable remedial actions, water quality in AMLs could be improved to the permissible levels enforced by water quality standards.

As represented in Figure 6.1 major environmental impacts of AMLs are degraded water quality (high trace element and heavy metal content and sulfate concentrations)

and extreme acidity. These conditions have impacts on aquatic and terrestrial life around the lake and surface and subsurface water quality in the vicinity. Thus, any mitigation measure should be designed with the intention of achieving the following objectives:

- ✓ to raise the pH of the lake water
- ✓ to lower the dissolved trace element and metal content
- ✓ to decrease sulfate concentrations
- ✓ to isolate the AML from any potential environmental risks
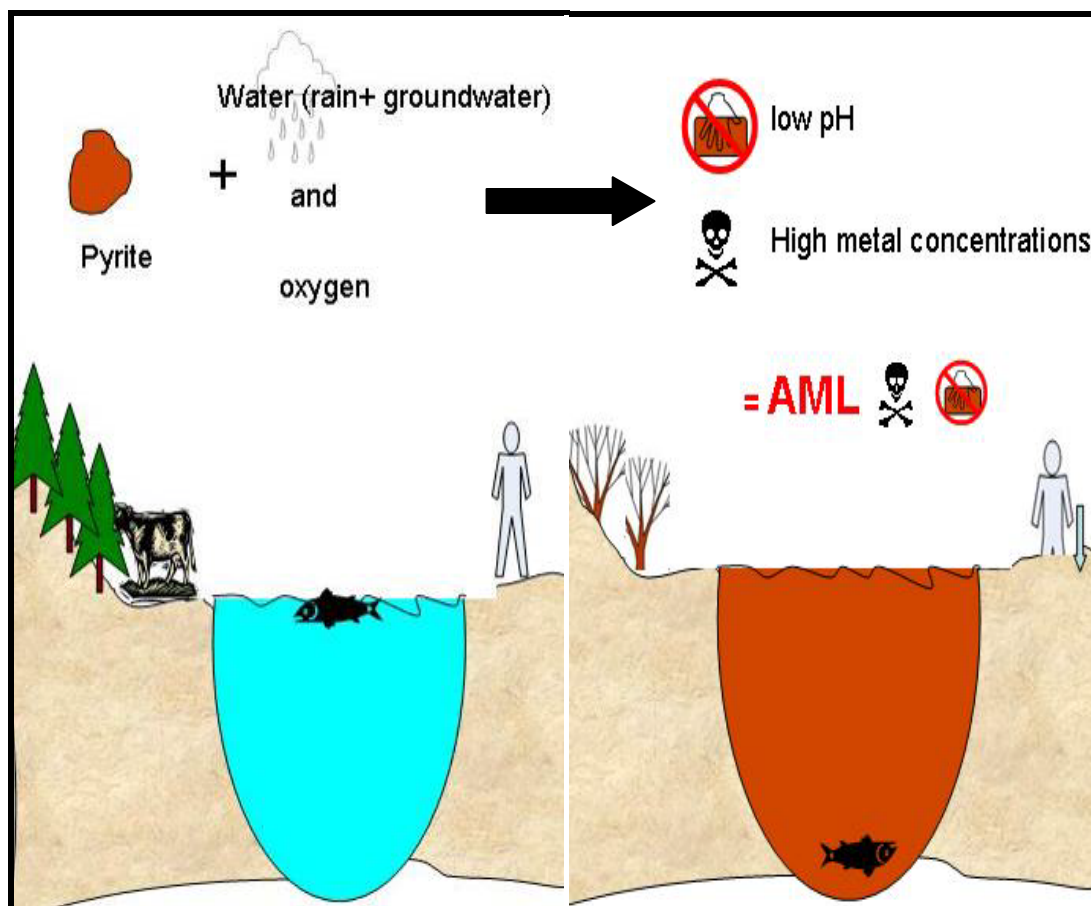

Figure 6.1 Illustration of the major effects to the environment which are needed reclamation and basic formation conditions in acidic mining lakes

With these objectives, it is possible to classify AMD and AML treatment techniques as active or passive methods as discussed by Lottermosser (2003). In active systems, such as neutralization, chemical reagents are continuously added to

control the pH levels and element concentrations in lake waters. This system requires active maintenance and monitoring as well as mechanical equipment to mix the reagent with the water. In active systems, mining lakes are considered as chemical reactor. On the other hand, in passive systems, such as wetlands, chemical and biological processes are used to reduce dissolved metal concentration and to neutralize the acidity. Such methods require little or no reagents, and thus do not need active maintenance and monitoring or any mechanical equipment.

6.1.1 Active Treatment Systems

All active treatment systems are based on the principle of "neutralizing" the acidic mine waters. The addition of neutralizing agents reduces the acidity and dissolved heavy metal concentrations of mine waters. Neutralization of mine waters should raise the pH to values necessary to precipitate and adsorb heavy metals. If the neutralizing agents have to be added to the acidic mine lake, the following ways of complete dissolution and mixing of the chemicals with the water of the mining lake should be considered. The objective is to design the neutralization, ferrous ion oxidation, hydrolysis and precipitation so that: (1) the neutralization capacity of the alkalization agents is completely used; and (2) the precipitation products are deposited in the deepest parts of the mining lake (Fisher, Guderitz & Reißig, 1998). Chemicals which are commonly used in neutralization and heavy metal removal in AML/AMD treatment are given in Table 6.1. The chemicals are applied to mine waters usually as slurry by a range of neutralization plants or dosing systems. Each chemical reacts differently with the specific mine water characteristics. Therefore, it is important that each AML treatment is evaluated with each chemical to determine which is most environmentally sound, efficient and cost effective.

All chemicals given in Table 6.1 have advantages and disadvantages related with the chemical characterization of mining lakes, costs, sludge generation, etc. For instance, the advantages of using *limestone* include low cost, ease of use, and formation of a dense, easily handled sludge. Disadvantages include slow reaction times and coating of limestone particles with iron precipitates (Lottermosser, 2003).

Table 6.1 Commonly used chemical agents in treatment of AMD-AML (after Skousen & Ziemkiewicz 1996; Environment Australia 1997)

Common name	Chemical name	Chemical Formula
Limestone	Mainly calcium carbonate	$CaCO_3$
Quicklime or caustic lime	Calcium oxide	CaO
Hydrated lime	Calcium hydroxide	$Ca(OH)_2$
Dolomite	Calcium-magnesium carbonate	$CaMg(CO_3)_2$
Caustic magnesia or brucite	Magnesium hydroxide	$Mg(OH)_2$
Magnesite	Magnesium carbonate	$MgCO_3$
Soda ash	Sodium carbonate	Na_2CO_3
Caustic soda	Sodium hydroxide	$NaOH$
Ammonia	Anhydrous ammonia	NH_3
Coal fly ash or kiln dust	-	Largely $CaCO_3$ and CaO

Hydrated lime is also easy and safe to use, effective, and moderately inexpensive. The main disadvantages are the voluminous sludge produced and high initial cost for the establishment of the active treatment plant (Zinck & Griffith 2000).

Caustic lime neutralization is efficient for removing metals such as cadmium, copper, iron, nickel, and zinc from solution. Nevertheless, the solubility of metals varies with pH, and the lowest metal concentration is not accomplished at the same pH (Kuyucak, 2000). Not all metals could be precipitated at the same pH, and a combination of neutralizing agents and other chemical additives may be required in order to achieve acceptable water quality.

Caustic soda is particularly successful for the treatment of acid mine waters having a high concentration level of manganese. Manganese is difficult to remove from mine waters because pH must be raised to above 10 before manganese precipitation to occur. Caustic soda could increase pH to above 10. Important disadvantages of caustic soda are its high costs, dangers in handling the chemical and poor sludge properties.

Unconventional industrial waste or byproducts such as *fly ash* from coal power stations or *kiln dust* from cement factories have been suggested as substitutes for lime. However, fly ash commonly contains elevated metal and metalloid concentrations, and its reaction rate is slow compared to lime (Kuyucak, 2000).

Enough alkalinity must be added to raise water pH and supply hydroxides (OH⁻) so dissolved metals in the water will form insoluble metal hydroxides and settle out of the water. The pH required to precipitate most metals from water ranges from pH 6 to 9 (except ferric iron which precipitates at about pH 3.5) (Skousen, Hilton & Faulkner, 1997). In many cases, the simple addition of any neutralizing agents could not be sufficient to reduce high heavy metal and metalloid concentrations in mine waters to acceptable water quality standards levels. These mine waters need other chemical or biological treatments to lower dissolved metal and metalloid loads. Ponds or wetlands may be required to further improve water quality prior to the discharge to a receiving stream after addition of neutralizing agents.

Watten, Sibrell & Schwartz (2005) (cited in Marchand & Dinkelman, 2006) studied the pulsed application of carbon dioxide (CO_2) to accelerate limestone dissolution and provide intermittent fluidization within limestone sand reactors treating coal mine drainage. The authors reported that field trials with three AMD sources confirmed that the process could increase the pH of drainage water above the level required to precipitate Fe^{3+} and Al^{3+} cations; however, both Fe^{2+} and Mn^{2+} solids were not observed in the process.

Fischer et al. (1998) studied the model calculations for active treatment of acidic, iron-containing lake water assuming mining lakes as chemical reactors. As possible restoration methods for an acidic mining lake, they have tested and discussed direct neutralization with alkalizing agents and soil treatment. In a compared assessment of the restoration of a fictitious mining lake with a volume of 10×10^6 m^3, it is sensible to apply the direct neutralization with lime hydrate method without risk, with acceptable costs and restoration time.

6.1.2 Passive Treatment Systems

Wetlands, known as passive treatment systems, are organic-rich, water-saturated shallow ponds. They are well recognized treatment options for sewage effluents and other wastewater treatments, especially including landfill leachates as well as agricultural and stormwater run-offs. For the treatment of acidic mine waters wetlands could also be used.

The wetland treatment is based on a number of physical, chemical and biochemical processes that improve the quality of acidic mining waters (Younger, Bantwart & Hedin, 2002). These processes consist oxidation and reduction reactions, cation exchange and adsorption of metals onto the organic substrate, neutralization of proton acidity, adsorption of metals by precipitating Fe^{3+} hydroxides, and metal uptake by plants (Walton- Day, 1999). Aerobic and anaerobic wetlands could be used for the treatment of acidic mining lakes.

Plants and microorganisms can control the behaviour of metals and metalloids in surface environments. The metals and metalloids, accumulated by these living plants and microorganisms or their dead biomass, may amount up to several weight percent of the cell dry weight. *Microbial processes* are studied and achieved in many mine water treatment. The basis of bioremediation of mine waters lies in the capabilities of some microorganisms to generate alkalinity and immobilise metals. The ability of particular plants and microorganisms to influence the cycling of metals can be used in the clean-up of metal contaminated soils, sediments, waters and wastes. Plants have also been used for some time to remove or immobilize environmental contaminants, a process which is generally referred as *phytoremediation* (Brooks 1998). Therefore, phytoremediation can be referred as an application of wetlands.

In aerobic wetlands constructed for the reclamation of mine waters, macrophytes such as Typha and Phragmites spp. are the most obvious forms of life present and their direct roles in improving water quality have been studied (Johnson & Hallberg, 2002). Johnson (1998) also studied the biological abatement of AMD and the role of iron and sulfate- reducing acidophilic bacteria. The author discussed the complexity

of the microbial ecology of highly acidic, metal-rich environments. The study has resulted in the indication that certain acidophilic microflora may be of considerable use in mitigating AMD.

A case study of metal accumulation in four wetland plant species was studied by Collins, Sharitz & Coughlin (2005), who concluded that the metal accumulation was a function of the individual plant species whether the plants were in shallow or deep wetlands. Overall, the collective contribution of both deep and shallow wetland plant species on metal removal was achieved in the remediation of acidic, metal-contaminated mine waters.

Anoxic limestone drains (ALD) are buried cells or trenches of limestone into which anoxic water is introduced (Skousen, 1998). The limestone dissolves in the acid water, raises pH, and adds alkalinity. Under anoxic conditions, the limestone does not coat or armor with Fe hydroxides because Fe^{+2} does not precipitate as $Fe(OH)_2$ at pH <6.0. ALDs were first described by the Tennessee Division of Water Pollution Control (TDWPC) (Turner & McCoy, 1990). Tennessee Valley Authority (TVA) subsequently observed that AMD seeping through a coal refuse dam was being treated passively by limestone contained in an old haul road buried under the dam. Once the water containing excess alkalinity reached aerobic conditions at the ground surface, the metals oxidized and precipitated while the water remained near pH 6 (Brodie, Britt, Taylor, Tomaszewski & Turner, 1990). TVA and TDWPC began building ALDs in 1989. Originally, ALDs were used for pre-treatment of water flowing into constructed wetlands. Brodie (1993) reported that ALDs improved the capability of wetlands to meet effluent limitations without chemical treatment. Since 1990, ALDs have also been constructed as stand-alone systems, particularly where AMD discharges from deep mine portals.

Longevity of treatment is a concern for ALDs, especially in terms of water flow through the limestone. If appreciable dissolved Fe^{3+} and Al^{3+} are present, clogging of limestone pores with precipitated Al and Fe hydroxides has been observed (Faulkner & Skousen, 1994). For waters with high sulfate (>1,500 mg/L), gypsum ($CaSO_4$)

may also precipitate (Nairn, Hedin & Watzlaf, 1991). For an accepted design, no Fe^{3+}, dissolved oxygen (DO), or Al^{3+} should be present in the AMD. Selection of the appropriate water and environmental conditions is critical for long term alkalinity generation in an ALD. The maximum alkalinity that ALDs may generate is about 300 mg/L as $CaCO_3$, although the specific level varies with water chemistry and contact time (Watzlaf & Hedin, 1993).

6.2 Possible Mitigation Techniques for Hayırtepe-AML in Çan

The possibility of neutralizing acid mine waters by mixing it with fly ash (FA) or aqueous extracts of FA, which originated from the combustion of coal in thermal power plants, has already been demonstrated (Preda, Scott, McCombe &Gimber, 2008; Loop, Scheetz & White, 2003). With the addition of FA as neutralizing agent into acidic mine waters, heavy metal concentrations were subsequently reduced by precipitation. Therefore, FA may be implemented to treat the AML and improve mine water quality. For Hayırtepe-AML, the mitigation technique by using FA is seen as the most viable option due to its close proximity to the Çan Thermal Power Plant.

6.2.1 General Properties of Fly Ashes

Fly ash contains inorganic particles, which have 0.01-0.02 micron diameter, is one of the residues of coal combustion. Fly ash composed of inorganic matter present in the coal that has been fused during coal combustion. Fly ash is solidified while suspended in the exhaust gases and is collected from the exhaust gases via electrostatic and mechanic precipitators. Since the particles solidify while being suspended in the exhaust gases, fly ash particles are usually spherical in shape. Depending upon the source and makeup of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO_2) and calcium oxide (CaO). Toxic constituents include arsenic, beryllium, boron, cadmium, chromium, cobalt, lead, manganese, mercury, molybdenum, selenium, strontium, thallium, and vanadium.

Fly ash has its own environmental impacts, particularly on the atmospheric environment. Thus, fly ash emissions from power plants should be controlled and the collected fly ash should properly be disposed in the vicinity of plant or any other suitable area. This storage of fly ash also creates significant dust emissions and leachate and could lead to important environmental problems. Consequently, a secondary use such as a concrete aggregate or AML treatment chemical is deemed to be a convenient solution to the fly ash problem of power plant managers.

Fly ash originates from mass-scale energy production and is emitted from the stacks of coal-fired power plants in the form of very fine particles. Bottom ash, on the other hand, originates from the bottom of coal furnaces and is larger in size which allows it to settle by gravitational forces. Thus, bottom ash containing relatively coarse particles is not emitted with stack gases and precipitate by gravity to bottom of furnaces. When combined with the unburned waste residue (slag), it forms the solid wastes originating from coal-fired power plants (Çancı, Güleç & Erler, 1997; Baba, 2000). The amount of such residue show differences depending on the ash ratio of the coal, power plant characteristics and the implemented ash removal techniques. Nevertheless, fly ash typically forms the majority of the waste produced in a power plant, whose typical composition are shown in Figure 6.2 (Finkelman, 1996).
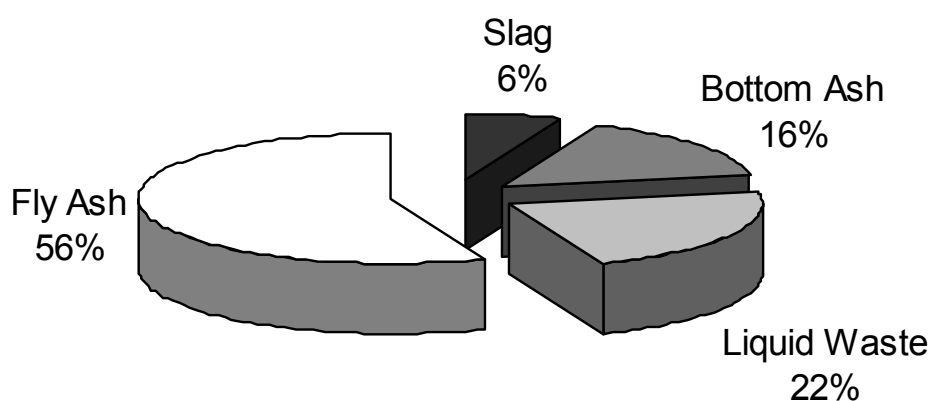

Figure 6.2 Waste composition of coal combustion (Finkelman, 1996)

Physical, chemical, mineralogical and pozzolanic properties of fly ashes show differences due to the conditions given below (Kefelioğlu, l998; Hycnar, 1983):

- Combusted coal type and variations
- Pulverizing level of coal before combustion
- Type of furnace
- Combustion temperature and other operational parameters
- Types of ash fusing and removal systems
- Additive agent factors that could be added with the intention of preventing the environment and differences of these factors by time.

Due to their pozzolanic properties, fly ash is commonly used in many industries as additive agent in cement and concrete. Because of fine and spherical particles, the tractability of the young concrete is increased, the dehydration temperature is decreased and the durability of the concrete is increased by filling the pores in cement. The lime content of fly ash originating from lignite coal is expected to be high, and these ashes also have high aggregating characteristics.

Annual amount of fly ash production is determined to be around 600 million tons throughout the world. In Turkey, this amount is calculated to be 13 million tons per annum from 12 thermal power plants (Türker, Erdoğan, Katraş & Yeğinobalı, 2007). Although, waste originated from thermal power plants (especially fly ash) has various utilizations all around the world, the utilization in our country is quite limited. Prior to its reuse, primary chemical characteristics as well as leaching, permeability and toxicity properties of the fly ash should be determined. Otherwise, these wastes could produce major problems for both environment and human health.

In general, fly ash is considered to be a pozzolanic material and is classified into two main classes, F and C, based on the silicium dioxide, aluminum oxide and sulfur trioxide contents and on other properties such as moisture content and loss on ignition values. According to ASTM C 618 (1998) standard, the classification of fly ash is done as shown in Table 6.2.

Table 6.2 Chemical Requirements for Fly Ash Classification

Properties	Fly Ash Class	
	Class F	Class C
Silicon dioxide (SiO_2) + aluminum oxide (Al_2O_3) + iron oxide (Fe_2O_3), min, %	70.0	50.0
Sulfur trioxide (SO_3), max, %	5.0	5.0
Moisture Content, max, %	3.0	3.0
Loss on ignition, max, %	6.0*	6.0

*The use of class F fly ash containing up to 12% loss of ignition may be approved by the user if acceptable performance results are available

6.2.2 Characteristics of ÇTPP Fly Ash

In order to determine the amount of the elements in ÇTPP fly ash, chemical analysis was done (TÜBİTAK, Project No: 106Y041) and SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, MnO, Cr_2O_3 contents were determined. The mineral composition of ÇTPP fly ash is given in Table 6.3 (Baba et al, 2009).

Table 6.3 Mineral composition (%) of ÇTTP fly ash (from Baba et al., 2009)

Sample No	Year	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	TiO_2	K_2O	P_2O_5	MnO	Cr_2O_3	SO_3
1		48.64	25.32	9.13	7.14	0.9	1.31	1.15	0.32	0.2	0.05	0.05	-
2		48.43	25.66	9.07	7.15	0.9	1.34	1.17	0.32	0.19	0.05	0.04	-
3	2006	48.51	25.43	9.18	7.04	0.89	1.31	1.17	0.32	0.19	0.05	0.04	-
4		48.56	25.31	9.15	7.1	0.9	1.32	1.16	0.32	0.2	0.05	0.05	-
5		48.29	25.48	9.1	7.03	0.91	1.32	1.18	0.32	0.2	0.05	0.04	-
Mean		48.486	25.44	9.126	7.092	0.9	1.32	1.166	0.32	0.196	0.05	0.044	-
2		29.29	15.82	7.91	25.75	0.44	0.57	0.61	0.32	0.201	0.15	0.005	-
3		29.31	15.16	5.97	18.96	0.43	0.57	0.57	0.39	0.322	0.11	0.003	-
4	2008	29.9	16.07	7.82	24.89	0.44	0.58	0.63	0.33	0.21	0.09	0.003	-
5		32.37	17.89	5.55	22.2	0.45	0.45	0.67	0.41	0.195	0.11	0.005	-
Mean		30.218	16.235	6.8125	22.95	0.44	0.543	0.62	0.3625	0.232	0.115	0.004	-

In the year 2006, before the addition of limestone for desulfurization of stack gases originating from combustion processes, the mean value of SiO_2 (%) + Al_2O_3 (%) + Fe_2O_3 (%) from 5 samples in ÇTPP fly ash was calculated to be 83% that is

larger than 70%. Moreover, CaO (%) mean value was smaller than 10 %. According to ASTM C 618 standards ÇTPP fly ash in 2006 was classified as Class F ash. In the year 2008, on the other hand, the chemical composition of the ÇTPP fly ash has changed significantly after the addition of limestone. As a result, the mean value of SiO_2 (%) + Al_2O_3 (%) + Fe_2O_3 (%) from 5 samples in ÇTPP fly ash was calculated to be 53%. Moreover, CaO (%) mean value was larger than 10 %. Thus, ÇTPP fly ash is now classified as Class C type fly ash according to ASTM C 618 standards given in Table 6.2.

In addition to the major constituents given in Table 6.3, trace and heavy metal analysis were conducted to understand the exact geochemical composition of ÇTPP fly ashes. The results of minor constituents of ÇTPP fly ash are presented in Table 6.4. Accordingly, copper, zinc and arsenic are the most common heavy elements found in ÇTPP fly ash.

Table 6.4 Heavy metal analysis results of ÇTPP fly ash, all units are ppm (from Baba et al., 2009)

Sample No	Year	Zn	As	Cu	Pb	Ni	Mo	Se	Tl	Au	Bi	Cd	Hg	Ag
1		118	74.3	69.4	38.8	25.5	11.7	3.7	1.2	0.5	0.5	0.3	0.24	0.1
2		114	72.4	68.8	36.3	25.9	10.6	3.6	1.1	0.5	0.5	0.3	0.24	0.1
3	2006	121	70.8	74.6	40	27.5	11	3.7	1.2	0.5	0.5	0.3	0.25	0.1
4		118	70.6	71	39	25.7	10.5	4	1.2	0.5	0.5	0.3	0.2	0.1
5		117	70.1	72	39.7	26.7	11.1	3.9	1.2	0.6	0.5	0.3	0.21	0.1
2		65	827.3	40.8	28.9	<20	8.5	2	1.3	0.7	0.3	0.3	0.18	<0.1
3	2008	67	445.6	32.8	23.9	31	6	1.4	0.8	<0.5	0.3	0.3	0.09	<0.1
4		69	806.8	40.1	27.5	<20	8.9	1.6	1.2	1.4	0.3	0.2	0.23	<0.1
5		69	249.2	30.3	22.8	<20	2.9	<0.5	0.9	1.9	0.3	0.2	<0.01	<0.1

6.2.3 Model Case Studies

The use of ÇTPP fly ash in mitigating the Hayırtepe AML was investigated in parallel to a number of case studies from the world with similar water and ash characteristics. As no laboratory or pilot scale tests were conducted on Hayırtepe AML waters, these studies could only be used as a preliminary tool until detailed analysis and feasibility studies are conducted. This assessment is realized in two

different sections. In the first assessment, ÇTPP fly ash from the year 2006 is used. This ash was low in calcium oxide levels as flue gas desulfurization unit was not operative during the year 2006. In the second assessment, ÇTPP fly ash from the year 2008 is used. This ash has higher calcium oxide levels as flue gas desulfurization unit was operative during the year 2008. A comparison of the results is then provided for evaluating the performance of mitigation action with regards to different ash composition. In both assessments, mitigation performances were calculated based on the results from case studies with similar water and ash characteristics to ÇTPP and Hayırtepe.

Assessment 1: ÇTPP fly ash from 2006

In the first assessment, the fly ash composition of ÇTPP is compared with a study conducted by Surender and Etchebers (2006) who studied on the neutralization principles of AMD with FA. They have focused on the neutralization and heavy metal removal capacities of FA. The parameters selected for removal were aluminum, iron and sulfate in their study. They have carried out this research in four phases:

Phase 1: This phase includes the selection of a suitable FA for AMD treatment. Surender & Etchebers have selected Arnot Power Station's fly ashes due to their chemistry, mineralogy and combustion conditions in the plant. This FA was then used to treat the AMD from the Landau colliery, which is in close proximity of Arnot Power Station. The comparison of ÇTPP fly ash with that of Arnot Power Station fly ash is given in Table 6.5. As seen from the table, the qualifications of Arnot and ÇTPP FA (2006) are almost the same. Furthermore, the chemical analysis of Landau AMD is also compared with Hayırtepe-AML water quality and is given in in Table 6.6.

Table 6.5 Arnot fly ash compositions comparison with ÇTPP fly ash (2006)

	Arnot FA	**ÇTPP FA**
SiO_2 (%)	50.9	48.49
Al_2O_3 (%)	26.5	25.44
Fe_2O_3 (%)	5.2	9.126
CaO (%)	6.9	7.09
MgO (%)	2.7	0.9
Na_2O (%)	0.01	1.32
TiO_2 (%)	1.4	1.17
K_2O (%)	0.4	0.32
P_2O_5 (%)	0.33	0.196
MnO (%)	0.05	0.05

Table 6.6 Comparison of the chemical characteristic of Landau AMD and Hayırtepe AML

	Landau AMD	**Hayırtepe AML**
pH	2.60	2.28
Conductivity	7.52 mS/cm	5.925 mS/cm
Sulphate concentration	1380 mg/L	5912.5 mg/L
Total iron concentration	5000 mg/L	172.34 mg/L
Aluminum concentration	200 mg/L	290.15 mg/L

The comparisons given in tables 6.5 and 6.6 clearly reflect a similarity between the two cases. pH and aluminum values are similar and EC values are close to each other. Only iron and sulfate concentrations deviate in Landau AMD. Thus, iron and sulfate removal percentages would probably not represent the conditions in Hayırtepe AML. Nevertheless, it is still possible to conclude that the conditions of treatment of Landau AMD with Arnot's FA would be very similar to the treatment of Hayırtepe AML waters with ÇTPP FA.

Phase 2: This phase includes the laboratory tests and optimization of the neutralization process by identifying the required amount of FA in order to improve Landau AMD. Tested FA:AMD ratios were: 1:1, 1:2, 1:3, 1:5, 1:10 and 1:20. The pH and EC changes are shown in Figure 6.3.
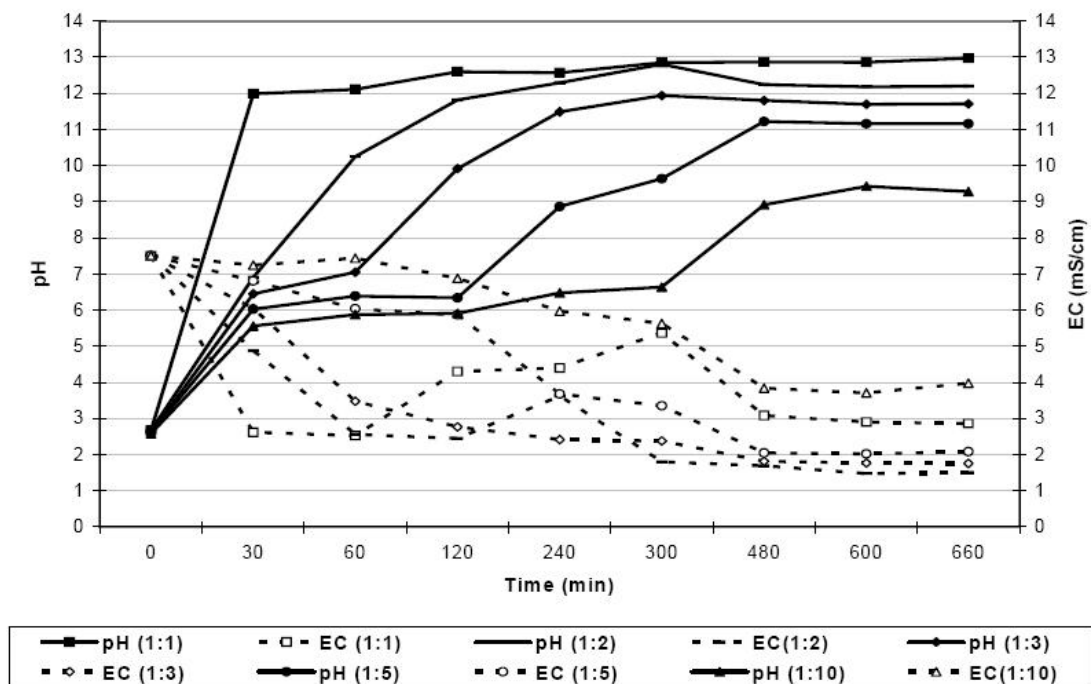
Figure 6.3 pH and EC during the neutralization of Landau AMD with Arnot FA under different FA:AMD ratios in laboratory tests (from Surender & Etchebers ,2006)

The test conducted by using a 1:20 (FA:AMD) ratio failed to achieve any considerable improvement in pH and conductivity. In addition to this, due to the large mass of ash added, consistency of the mixture was difficult to handle (i.e., thick slurry, difficult to stir and filter). As pH very rapidly increased from 2.6 to 13, the 1:1 ratio was also not regarded to be a viable treatment option either. The removal of the iron, aluminum and sulfate concentrations are given in Figure 6.4, Figure 6.5, Figure 6.6, respectively.

At the end of the laboratory study, it was concluded that power plant FA could be a successful neutralizing agent for AMD under proper agitation and aeration conditions. According to the early results, FA:AMD to be used should be in the range of 1:2 to 1:10. The 1:3 ratio seemed to be the best compromise to achieve the treatment with neutralization in a short period of time, and to achieve sufficient heavy metal and sulfate removal.
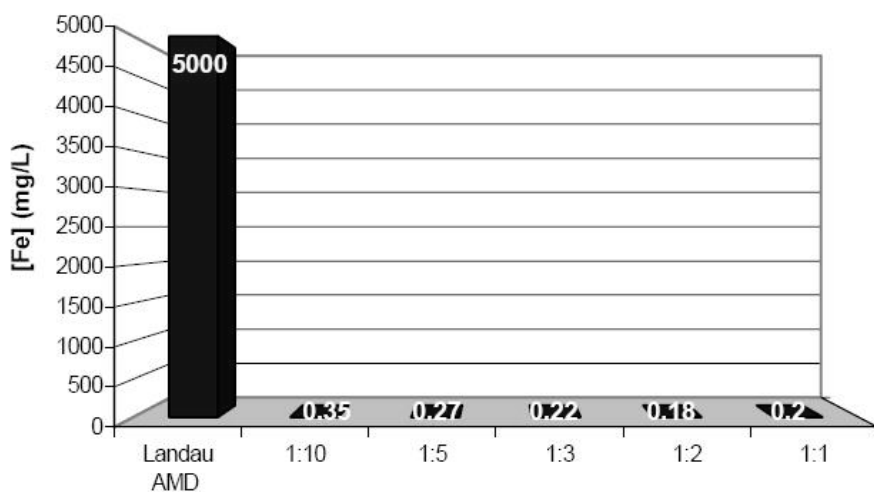
Figure 6.4 Iron concentrations during laboratory test with different FA:AMD ratio
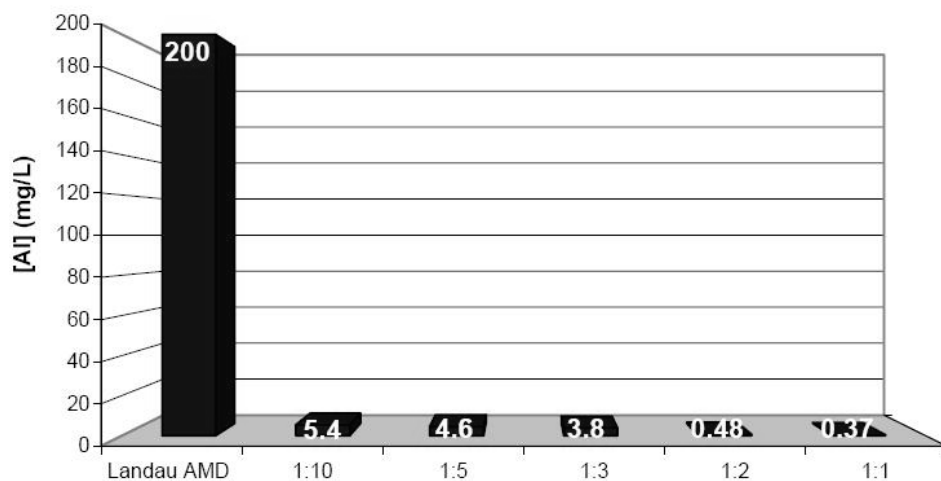

Figure 6.5 Aluminum concentrations during laboratory test with different FA:AMD ratio
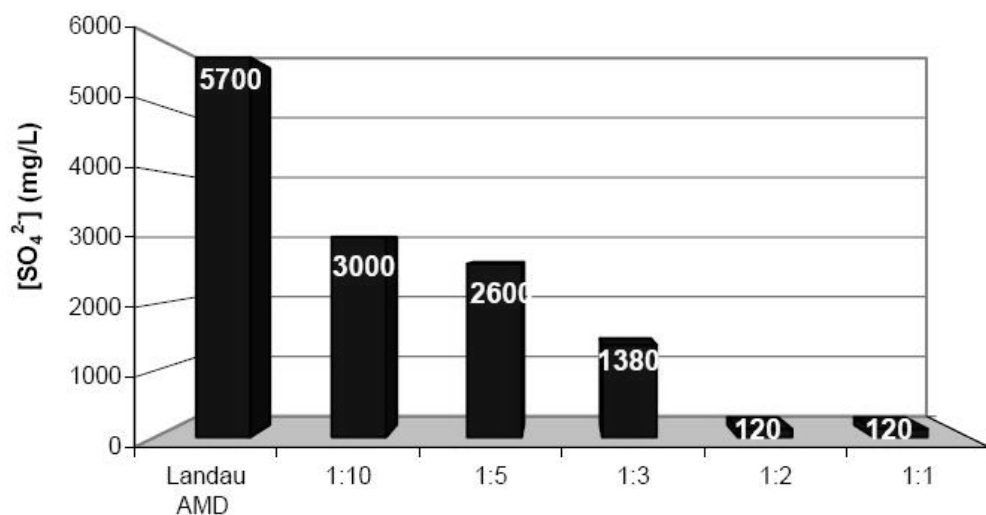

Figure 6.6 Sulfate concentrations during laboratory test with different FA:AMD ratio

Phase 3: In this part of study, a pilot scale neutralization test has been constructed. Various mixer design configurations have been considered. Slurry density and flocculation, bulk solids separation and handling and water recovery were considered as crucial parameters. A pilot scale mixer with 250 L tank capacity and turbulator/aeration unit has been constructed.

Phase 4: Pilot scale testing and optimization with different FA: AMD ratios are conducted in this phase of the research. The pH: EC change with respect to time has been observed differently as it expected (Figure 6.7). As a result of the pilot study, the removal of heavy metals and sulfate are achieved as given in Table 6.7. The 1:4 ratio is the selected ratio for neutralizing and removal of the major contaminants of Landau AMD.

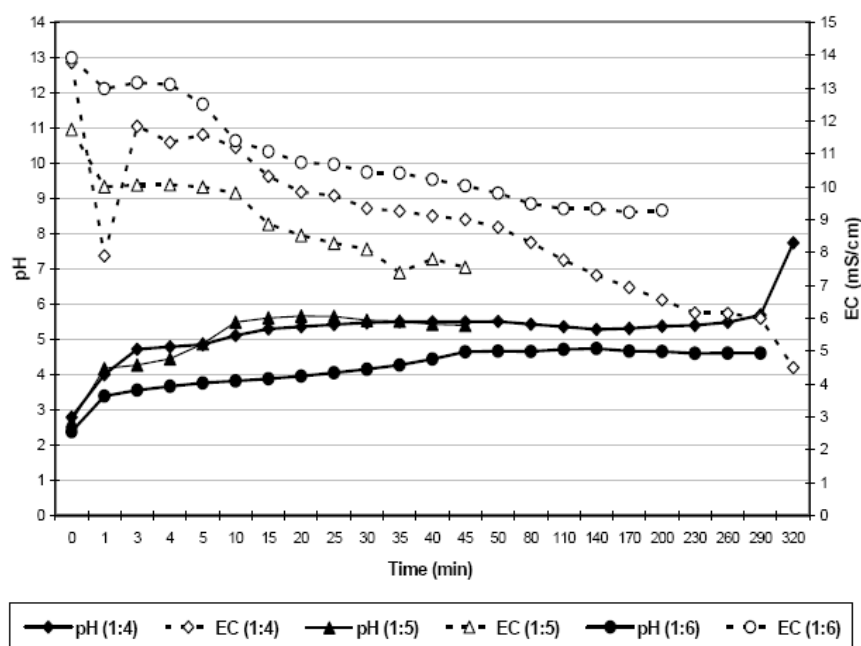Figure 6.7 pH and EC during the neutralization of Landau AMD with Arnot FA under different FA:AMD ratios in the pilot scale(from Surender & Etchebers, 2006)

Table 6.7 Removal of the Al, Fe and SO4 after 120 min, 1:4 FA: AMD ratio

	pH	Al (mg/L)	Fe (mg/L)	SO$_4$ (mg/L)
Landau AMD	2.55	267	4800	4812
Treated water	5.66	0.14	182	3264
Removal	-	99.9 %	96.2	32.2

Based on this study that demonstrates similar characteristics to ÇTPP fly ash and Hayırtepe AML water quality and considering the total volume of Hayırtepe AML as 169224 m^3, the required FA amount is calculated to be 42500 tons when 1:4 ratio is used as was done in Landau case. This amount is approximately equal to the amount of fly ash generated in one month from ÇTPP. Consequently, aluminum, iron and sulfate concentrations in the AML will be reduced to 0.14 mg/L, 6.55 mg/L and 4008.68 mg/L, respectively, with using the same removal efficiencies given in Surender and Etchebers (2006) achieved in the pilot plant for Landau AMD.

Assessment 2: ÇTPP fly ash from 2008

Polat et al. (2002) discussed the possibility of using Turkish lignitic fly ashes from Soma and Yatağan coal-fired power plants to achieve AMD neutralization. The possibility of fixing toxic heavy metals in the structure of the aggregate produced was also examined. In some of the experiments conducted, used engine oil was also added to increase the degree of fixation and eliminate another waste material. The Soma and Yatağan FA characterizations are given in Table 6.8 together with the ÇTPP fly ash produced in the year 2008. The comparisons of the quality characteristics of the AMD used by Polat et al. (2002) and the Hayırtepe AML waters are given in Table 6.9.

Table 6.8 Comparison the ÇTPP fly ash composition with the Soma and Yatağan fly ash for major elements

	Soma	**Yatağan**	**ÇTPP FA (2008)**
SiO_2 (%)	33.4	36.4	30.2
Al_2O_3 (%)	16.1	15.4	16.2
Fe_2O_3 (%)	6.0	7.8	6.8
CaO (%)	33.8	23.5	22.95
MgO (%)	6.07	8.8	0.44
Na_2O (%)	1.0	1.1	0.5
K_2O (%)	0.7	0.8	0.36
SO3 (%)	2.8	6.8	-

When ÇTPP fly ash values are compared with the FA used in this study, Yatağan fly ash is found to be more similar to ÇTPP fly ash than Soma FA due to its CaO content. Therefore, ÇTPP FA is expected to behave similar to Yatağan FA. The AMD used in the tests in Polat's study, was generated in laboratory conditions form pyritic ore samples from the Küre Mine in northern Turkey. This mine is one of the main sources of copper ore in Turkey and suffers from AMD problem as pyrite content of the ore is as high as 71%. Thus, it is not expected that the chemical composition of these two acidic mine waters would be the same. As Hayırtepe AML was formed 15 years ago, the chemical composition has changed as a result of chemical and biological reactions and represents different conditions from laboratory conditions of Polat et al. (2002).

Table 6.9 Comparison of chemical characteristic of AMD and Hayırtepe AML

	AMD	Hayırtepe AML
pH	2	2.28
Ca (mg/L)	415.6	456.9
Mg	88	200.03
Na (mg/L)	6.1	115.45
K (mg/L)	4.6	1,63
Al (µg/L)	54000	290155
Fe (µg/L)	519500	172344
Cd (µg/L)	10500	12.94
Cu (µg/L)	54600	396.93
Cr (µg/L)	80	26.01
Zn (µg/L)	17000	5344
Co (µg/L)	10900	2070
Ni (µg/L)	890	1110
Cl (µg/L)	3000	63750
SO_4 (mg/L)	2252	5912.51

The change in the pH in artificial AMD water with the addition of Soma and Yatağan fly ash is shown in Figure 6.8. Since it is well known that the required pH values for the precipitation of heavy metals take place around 9-10, corresponding AMD/ash ratios were used. It was reported by Polat et al. (2002), that fly ash was an efficient neutralizing agent, which can neutralize large amounts of AMD water.
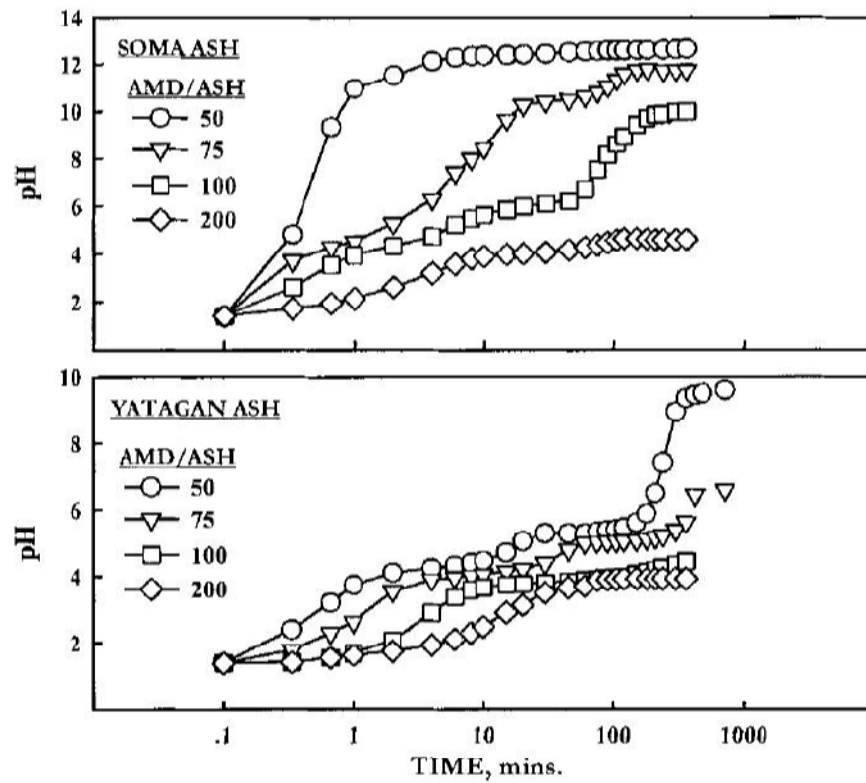
Figure 6.8 Titration behaviour of AMD with fly ash

As ÇTPP FA was more similar to Yatağan FA, a AMD/FA ratio of 1:50 seems suitable for Hayırtepe-AML conditions according to Figure 6.8. Nevertheless, this is only an initial estimate and detailed laboratory and pilot scale tests should be conducted. Thus, smaller ratios could be efficient and further research is needed. If it is assumed that a rough estimate of 1:50 is used, the amount of FA required to neutralize Hayırtepe AML is calculated to be 3400 tons, which corresponds to a FA amount that is generated from 3 days operation of ÇTPP.

CHAPTER SEVEN
CONCLUSIONS AND RECOMMENDATIONS

This study is conducted to assess the influence of acidic mining lakes on surface and subsurface water quality, which are formed as a result of mining activities. The acidic lake near Hayırtepe at Çan district of Çanakkale Province was selected as the study area. Limnological studies conducted within the lake were focused on determining the general morphology of the lake including lake's bathymetry and its water quality with regards to a number of parameters. To achieve this objective, bathymetric studies and depth-integrated sample collection activities were done in Hayırtepe Lake. Within the scope of this study a total of 56 samples were collected: 23 of which were collected from the water surface and 33 of which were collected from various depths. Samples were then analyzed for numerous water quality parameters including temperature, pH, ORP, EC, DO (mg/L and %), salinity, TDS, fluoride, chloride, nitrite, nitrate, bromide, phosphate, sulfate, lithium, sodium, magnesium, calcium, ammonium, potassium, iron, cadmium, chromium, copper, lead, cobalt, nickel, aluminum, manganese, zinc and arsenic. Based on the results of the water quality monitoring study, the following conclusions were reached:

- All characteristics of typical acidic mining lakes (i.e., reddish-brown color, low pH, and high heavy metal and trace element concentrations) were also observed in Hayırtepe AML.

- Morphology of the lake was analyzed in details and a general bathymetrical map of the lake was obtained. Based on the results of these studies, Hayırtepe AML had a surface area of 23810 m^2 and a volume of 169224 m^3 at the time the field studies were conducted. The deepest point of the lake was measured to be 14.15 m and the average depth of the lake was calculated to be 7.11 m according to the measurements at 62 bathymetry points.

- Hayırtepe AML, which was inundated about 15 years ago and is characterized by low pH values and elevated levels of a number of heavy

metals and trace elements has a significant water volume and hence is a potential treat to the environment in several ways.

- With an average pH value of 2.28, the concentrations of aluminum, manganese, iron, nickel, zinc, cobalt, cadmium and sulfate in Hayırtepe AML are above the standard values. In addition, the average EC value is also found to be high in lake waters.

- Surface distribution maps and vertical profiles were created for all quality parameters analyzed within the scope of this study. When these maps and graphics are analyzed, it was seen that the surface distribution of most of the quality parameters did not show any particular trend where as the vertical profiles of almost all parameters showed significant variations along the water column. In particular, iron, chromium and lead concentrations increased as depth increased. Slightly, aluminum, manganese and nickel concentrations also showed variations along the vertical profile at all sampling stations.

- Considering the potential risk of influencing the drinking water resources of the surrounding villages, the results of the water quality monitoring program were compared with the standards depicted in ITASHY (2005). As a result of these comparisons, it was found out that the concentrations of aluminum and manganese were 3-4 orders of magnitude greater than the standards. Furthermore, sulfate concentrations were 24 times higher than the standard value in ITASHY and nickel concentrations were 50 times greater than the standard value in ITASHY.

- Based on the comparisons with SKKY (2004), Hayırtepe AML was designated as a Class IV inland water resource. In this classification table, 57% of the 21 parameters considered were in Class IV, which showed that Hayırtepe AML waters demonstrates a significant risk for all forms of life

and is absolutely not suitable for human or animal consumption and agricultural irrigation unless advanced treatment techniques are implemented.

- In addition to Hayırtepe AML, there are other acidic lakes present in Çan district, which were all formed as a result of coal mining activities and a direct consequence of abandonment of these open pit mines without implementing any post closure rehabilitation or mitigation measures. All of these lakes demonstrate similar water quality characteristics to Hayırtepe AML that was studied in this particular research.

- The water quality monitoring program in Hayırtepe AML has revealed a very poor water quality in the lake. Consequently, limited, if any, aquatic life could survive in lake waters. In addition, the lake demonstrates significant risks with regards to influencing the water resources in its immediate vicinity. The flora around the lake is altered and the vegetation near the lake surface is weak and diverse. High acidity of lake waters has altered the carbonate structure of the soil and the stability of the soils in close proximity to the lake is extremely weak. This situation brings in the risk of landslides when the topography around the lake is steep.

- Mitigation measures should be implemented as soon as possible not only to the lake itself but also to the disturbed topography nearby. To achieve this objective, active treatment techniques such as chemical neutralization (by lime, kiln dust, fly ash, caustic soda) to increase the pH and precipitate the heavy metals or passive treatment methods such as wetlands should be implemented. Leveling the topography to its pre-mining stage is to be realized.

- The nearby Çan Thermal Power Plant produces an annual total of 500000 tons of fly ash. Rehabilitation with fly ash is thus deemed to be a viable option. This rehabilitation will include neutralization of lake waters with the fly ash that demonstrates basic characteristics and adsorption of dissolved

heavy metals on fly ash particles. The thermal plant ash might be a potential solution to the problem due to its close proximity to the lake site. There is quite a lot of successful research studies conducted on using power plant fly ash on treating acidic mining drainage and lakes. In addition, the fly ash disposal is another environmental problem that needs to be addressed. Such a beneficial use of fly ash will not only rehabilitate the acidic lakes but also ease the fly ash disposal problem of power plants nearby. About 45 million tons of coal is used in power plants in Turkey and about 13 million tons of fly ash is formed. Preliminary assessments on the rehabilitation of Hayırtepe AML would require approximately 170000 tons of fly ash considering a fly ash to mine water ratio of 1. This amount corresponds to four month ash production of Çan power plant. When other lakes in the area are also considered, a one year ash production of the power plant would be sufficient to rehabilitate these lakes.

- Despite the possibility of using fly ash in rehabilitating Hayırtepe AML and other lakes in the area, detailed laboratory and field scale test are necessary before a final decision is reached. Otherwise, excess sludge production and its disposal might pose a problem. Other issues such as operational and investment costs should also be analyzed within the scope of a feasibility study.

- Since post-closure rehabilitation activities of AMLs are typically considered as additional economical costs, some sort of government support or subsidy should be realized for such activities. A program related to technology transfer on prevention of acid mine drainage and formation of acidic mining lakes as well as rehabilitation of such problems could also be carried out to assist private mining companies. For instance, for the abandoned mine sites, operating and abatement techniques Mine Environmental Neutral Drainage (MEND) Programme (1983) have been developed by the Canadian Mining Industry, the Government of Canada (CANMET- the Canada Center for Mineral and Energy Technology) and the governments of several provinces.

Canadian Universities and international agencies also encouraged this Programme. It provides support to the projects about prevention and control of mine wastes, investigating methods of treatment, monitoring and technology transfer.

- While it is generally not possible and reasonable to limit or stop mining activities, it is, however, quite possible to minimize the impacts that mining would cause on the environment. Legal enforcements and controls should strictly be conducted to guarantee a sustainable environmental record for the mining industry.

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