

**EFFECT OF HIGH SALINE GEOTHERMAL  
FLUID ON SOIL AND SURFACE WATER:  
A CASE STUDY FROM  
TUZLA, ÇANAKKALE-TURKEY**

**A Thesis Submitted to  
the Graduate School of Engineering and Sciences of  
İzmir Institute of Technology  
in Partial Fulfillment of the Requirements for the Degree of**

**MASTER OF SCIENCE**

**in Environmental Engineering**

**by  
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**DECEMBER 2013  
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## **ACKNOWLEDGEMENTS**

I would like to express my gratitude to my supervisor, Prof. Dr. Alper BABA, for his support, encouragement and patience throughout my thesis study. I always felt lucky to have a supervisor who, besides teaching me valuable lessons regarding academic research, always found time for listening me. I would like to thank my other advisor Assist. Prof. Mustafa M. DEMİR for his recommendations, support, and thoughtful advises.

I would like to appreciate to Tuzla Jeothermal A.Ş. for provide the opportunity for our research and my special thanks to Tuncay Usta for his help with the field study. I would also like to thank Onur SOLAK and Gamze ÇETİNKAYA MUNGAN for helping me with the field study and ArcGIS. I would also thank to research specialists of IZTECH Environmental Research Center, JEOMER and MAM for their help during the laboratory works.

I would like to appreciate deeply to my friends, Durmuş SINMAZ, Çiğdem ÖZCAN, Melis TOPRAK, Derya BAYTAK, Yılmaz OCAK, and Pınar KAVCAR ARCAN for their patience, encouragement and friendship.

Finally; I would also like to express my heartfelt gratitude to my parents, Adnan and Nazife KATIRCIOĞLU and my brother, Gökhan KATIRCIOĞLU for their endless love, support, encouragement and understanding.

## ABSTRACT

### EFFECT OF HIGH SALINE GEOTHERMAL FLUID ON SOIL AND SURFACE WATER: A CASE STUDY FROM TUZLA, ÇANAKKALE-TURKEY

Geothermal energy can be defined as a heat from core of Earth and utilized for power generation, district heating and greenhouse. Use of geothermal energy has low environmental impact, particularly when compared with fossil fuels. However, geothermal fluid has some adverse effects for environment for instance contamination of surface water and soil. Examples of these effects occur in different parts of world. The objective of this study is to evaluate the effect of geothermal fluid particularly on surface water and soil in Tuzla Geothermal Field (TGF) where is located on Biga Peninsula, in the northwestern of Anatolia. TGF is 5 km far from Aegean Sea and 80 km south of Çanakkale. Geothermal fluid of TGF has high salinity ( $EC > 91$  mS/cm) and high temperature (reservoir temperature is  $173$  °C). Water samples were taken from February 2012 to April 2013 to determine the physical and chemical (major anions and heavy metals) properties of the surface water quality. Furthermore, the soil samples analyzed for physical and chemical properties. All data were evaluated with ArcGIS 10.1 and Aquachem 4.0 software. The results showed that the levels of some major element such as Lityum (4-7 ppm), Barium (1-4 ppm) and Manganese (1-5 ppm) and some heavy metals such as Boron ( $> 13$  ppm) and Strontium ( $> 14$  ppm) in surface water, exceeded national and international limits. Boron and Strontium values of creek ranged from 13 to 27 ppm and from 14 to 154 ppm, respectively. Soil samples contain high concentration of Silisium ( $> 23800$  mg/kg) and Aluminum ( $> 9000$  mg/kg). Particularly, the uncontrolled discharge of geothermal fluid that is rich in terms of toxic elements into soil and surface water resources of the area influences other potential uses of these resources.

## ÖZET

### YÜKSEK TUZLU JEOTERMAL AKIŞKANIN TOPRAK VE YÜZEY SUYUNA ETKİSİ: TUZLA ÖRNEĞİ, ÇANAKKALE-TÜRKİYE

Jeotermal enerji Dünya'nın merkezindeki enerji olarak tanımlanabilir ve elektrik üretimi, şehir ısıtması, seralar, termal turizm için kullanılır. Jeotermal kaynaklar açısından son derece zengin olan ülkemizde, jeotermal enerji kaynaklarının kullanımına yönelik araştırmalar ve sondajlar son yıllarda hızla artmıştır. Özellikle Batı Anadolu'da yüksek sıcaklıklı bazı sahalardan elde edilen jeotermal akışkan hem yüzey sularını hem de toprağı etkileyebilmektedir. Bu çalışma kapsamında; hidrojeokimyasal açıdan son derece kompleks olan, yüksek sıcaklık (173 °C) ve tuzluluğa (EC > 91 mS/cm) sahip Tuzla Jeotermal Sahası'ndaki akışkanın, yüzeysel su kaynakları ve toprak üzerine etkisi irdelenmiştir. Çalışma kapsamında jeotermal saha ve çevresinden Şubat 2012 ve Nisan 2013 dönemleri arasında su numuneleri alınmıştır. Alınan yüzeysuyu numunelerinde major anyon-kasyon ve ağır metal analizleri yapılmıştır. Bununla birlikte, toprak numunelerinin fiziksel özellikleri ve kimyasal içeriğı analiz edilmiştir. ArcGIS 10.1 ve Aquachem 4.0 ile su ve toprak numunelerine ait tüm datalar değerlendirilmiştir. Elde edilen verilere göre; inceleme alanındaki yüzeysel su kaynaklarında yüksek oranda, Lityum (4-7 ppm), Baryum (1-4 ppm), Mangan (1-5 ppm), Boron (> 13 ppm) ve and Strontium (> 14 ppm) gibi bazı ağır metallerin ulusal ve uluslararası yönetmeliklerde belirtilen limit değerlerin üzerinde olduğu belirlenmiştir. Yüzeysel sulardaki bor ve stronsiyum değerleri sırasıyla 13 - 27 ppm ile 14 - 154 ppm arasında değişmektedir. Toprak örnekleri ise yüksek miktarlarda Silisyum (> 23800 mg/kg) ve Alüminyum (> 9000 mg/kg) içerir. Toksik elementlerce zengin olan jeotermal akışkanın yüzey suları ve toprağı kontrolsüz deşarjı sonucu, diğere kaynakların potansiyel kullanımı etkilenmektedir.

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# CHAPTER 1

## INTRODUCTION

Geothermal energy is defined as heat from the Earth. A geothermal reservoir contain heat both in the solid rock and in the fluids that fill the fractures and pore spaces within the rock geothermal fluids acting as the carrier for the transfer of the heat from depth to sub-surface firstly by conduction and then by convection. Mostly the rainwater penetrated into the Earth's crust from the recharge areas, has been heated on contact with the hot rocks. It has accumulated in aquifers, and it can reach at high pressures and temperatures. At the plate boundaries and well within the plates, heat may be locally transferred within a few kilometers of the Earth's surface through the process of convection by magma or molten rocks (up to above 300°C) (Barbier, 1997; Gupta and Roy, 2007)

A geothermal system is comprised of a heat source, a reservoir and fluid (Figure 1.1.). The heat source can be at high temperature magmatic that reaches relatively shallow depths or as in certain low temperature systems in which the Earth's normal temperature increases with depth. The reservoir is a volume of hot permeable rocks which overlaid by a cover of impermeable rocks from which the circulating fluids extract heat (Dickson and Fanelli, 2004). The reservoir is connected to a surficial recharge area in which the fluid can replace or partly replace the fluids that escape from the reservoir through springs. Geothermal fluid is the carrier that transfers the heat. The geothermal fluid is meteoric water, in the liquid or/and vapour phase, depending on its temperature and pressure. This water often contains heavy metals and gases (Dickson and Fanelli, 2004; Kristmannsdottir and Armannsson 2003)

Geothermal is a renewable and sustainable source of energy. Use of geothermal energy has low environmental impact, particularly when compared with fossil fuels. Most environmental impacts are associated with the usage of high-temperature systems while low-temperature systems rarely have significant environmental effects.

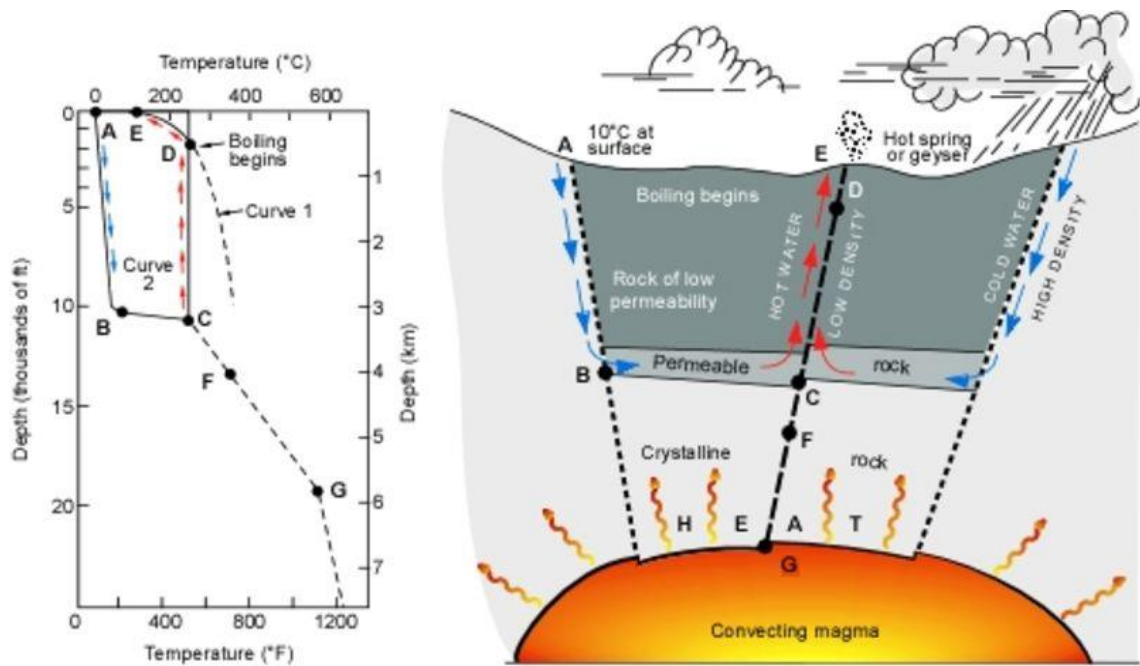


Figure 1.1. Model of a Geothermal System  
(Source: White, 1973)

Tuzla geothermal site is located in the western part of Turkey. This region is very important for geothermal application. Therefore, many private and government companies have been working on geothermal fluid in this region. Geothermal fluid of Tuzla geothermal field has high salinity, high temperature (174 °C) and high dissolved ion content. This fluid can affect the water and soil quality. In this respect, this study is intended to determine the effect of geothermal fluid composition on surface water and soil. The aim of this thesis is to define the hydrogeochemical properties of geothermal fluid of Tuzla Geothermal Field and to determine of its environmental effects on surface water and soil quality. To achieve this objective, representative samples from the geothermal wells, surface water, and soil have been collected as a part of a field survey and physical and chemical properties of samples have been analyzed.

## 1.1. Scope of the Thesis

This thesis is organized in 7 chapters. In Chapter 1 the definition of the geothermal energy is presented. The following section, Chapter 2, continues with the utilization of geothermal energy in the World and Turkey. In Chapter 3, the effects of geothermal systems on the environment are presented. In Chapter 4, the details of the study area are described with particular emphasis on geological and hydrogeological

features of the area. In Chapter 5 the materials and methods implemented for field studies, laboratory analysis and the data interpretations are discussed. The findings of the study are presented in Chapter 6, where the main results of the water and soil quality monitoring work conducted. Water and soil quality monitoring results are given together and comparisons with national and international standards. Finally, Chapter 7, the conclusion part includes the major findings of the study and recommendations for further investigations.

## CHAPTER 2

### UTILIZATION OF GEOTHERMAL ENERGY

Geothermal fluids have been used for bathing, balneotherapy, washing dishes and clothes since prehistoric times. Utilization of geothermal depends on thermodynamic characteristics and chemistry of fluid. These factors are determined by the geothermal system from which the fluid originates (Mburu, 2009).

Low-temperature fields are used for district heating, industrial processes agriculture (greenhouse) activities, domestic water and space heating, fish industry, balneotherapy, thermal tourism, swimming pool and snow-melting systems. High enthalphy geothermal areas are more convenient for power generation in terms of efficiency. Power generation is the most important form of utilization of high-temperature geothermal resources which are above 150°C. The Lindal diagram (Lindal, 1973) shows the possible uses of geothermal fluids at different temperatures, but the generation of electric energy in binary cycle plants can now be added to diagram above 85°C (Figure 2.1.).

Geothermal fluids were classified differently based on fluid temperature by Muffler and Cataldi (1978), Hochstein (1990), Benderitter and Cormy (1990), Nicholson (1993), Axelsson and Gunnlaugsson (2000). Table 2.1 shows the classification of geothermal resources that mentioned above.

Table 2.1. Classification of Geothermal Resources  
(Source: Dickson and Fanelli, 2004)

	Muffler and Cataldi (1978)	Benderitter and Cormy (1990)	Hochstein (1990),	Nicholson (1993)	Axelsson and Gunnlaugsson (2000)
Low enthalphy	< 90 °C	< 125 °C	< 100 °C	≤ 150 °C	≤ 190 °C
Intermediate enthalphy	90 – 150 °C	125 - 225 °C	100 - 200 °C	-	-
High enthalphy	> 150 °C	> 225 °C	>200 °C	>150 °C	>190 °C

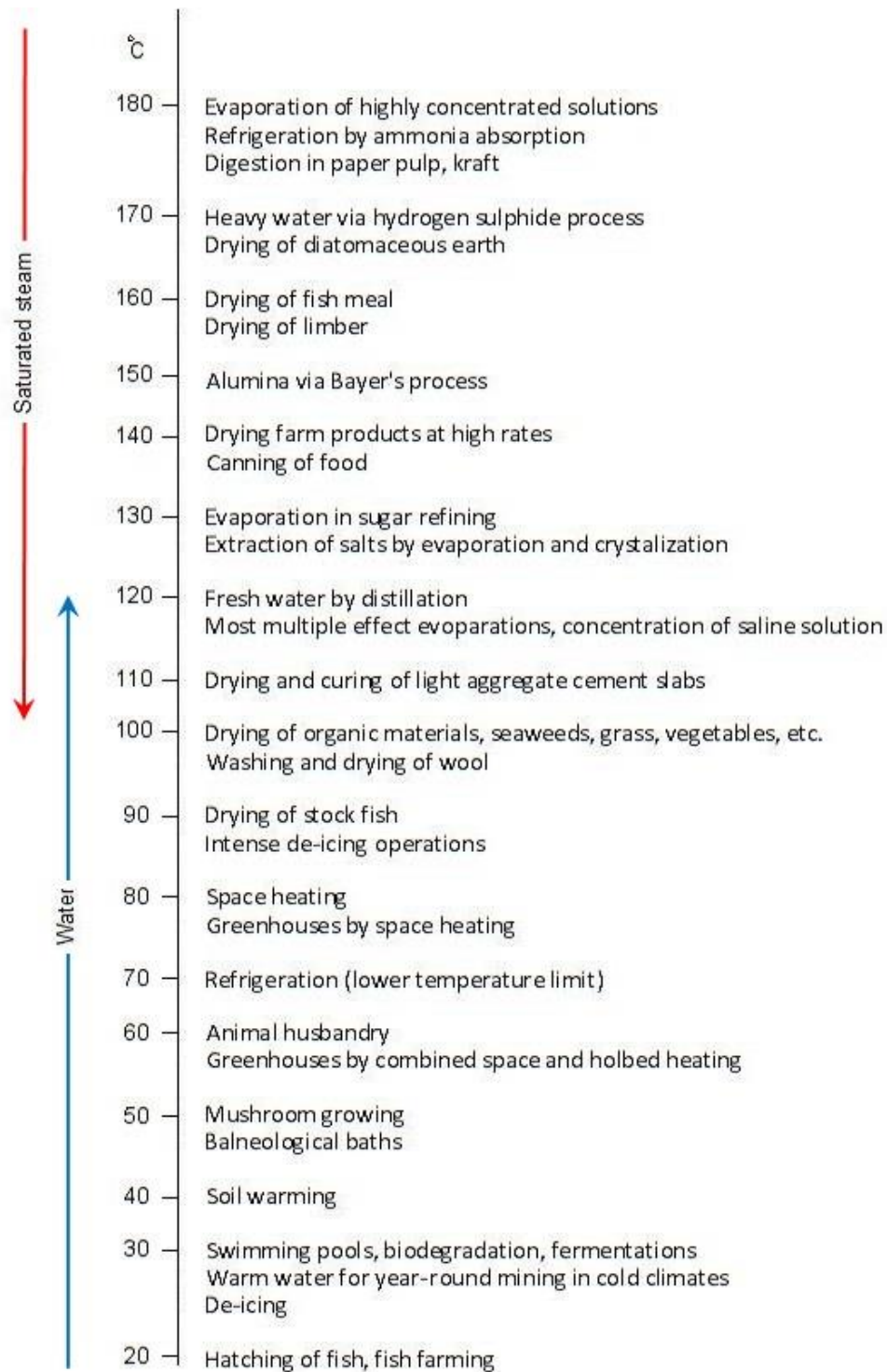


Figure 2.1. The Lindal Diagram  
(Source: Lindal, 1973)

Geothermal energy is used in 78 countries in power generation (67,246 GWh/year in 24 countries) and in direct heating (121,696 GWh/year in 78 countries) (see Table 2.2.; Bertani, 2010 and Lund et al., 2010)

Table 2.2. Worldwide Geothermal Status  
(Source: Bertani, 2010 and Lund et al., 2010)

Year	Power generation			Direct use		
	2000	2005	2010	2000	2005	2010
Installed capacity (GWe)	7.97	8.93	10.71	15.14	28.27	50.58
Power production (GWh/yr)	49.261	55.709	67.246	53.014	75.997	121.696
Countries	21	23	24	58	72	78

## 2.1. Geothermal Resources and It's Applications in Turkey

Turkey is located between the African and Eurasian plates, within the Mediterranean Earthquake Belt where marked by young volcanics and active faults. The border of these plates allow circulation of water, heat flow and geothermal energy (Bozkurt, 2001; Baba and Sözbilir, 2012; Satman, 2013). Hot springs in Turkey are located generally nearby the fault systems, young volcanism, and hydrothermally altered areas (Simsek et al., 2003). The most important geothermal fields situated on west part of Turkey are located in the major grabens of the region.

Turkey has approximately 1500 thermal and mineral springs. Two-hundred-twenty two geothermal field have been discovered in different parts of Turkey The temperature of geothermal systems of Turkey ranges from 20 to 287 °C (Baba, 2013; Satman, 2013). The first geothermal well was drilled in Balçova (İzmir) in 1963 with 40 m depth and 124 °C enthalphy. Some important geothermal fields are given in Table 2.3. Some power plants have been built in this region (Table 2.4. and Figure 2.2.). Currently, eleven geothermal power plants have been generating electricity actively in Turkey.



Table 2.3. Important Geothermal Fields in Turkey

<b>Geothermal Field</b>	<b>(°C)</b>	<b>Geothermal Field</b>	<b>(°C)</b>
Manisa-Alaşehir-Köseali	<b>287</b>	Kütahya-Simav	<b>162</b>
Manisa Alaşehir X	<b>265</b>	Aydın-Umurlu	<b>155</b>
Manisa-Salihli-Caferbey	<b>249</b>	İzmir-Seferihisar	<b>153</b>
Denizli-Kızıldere	<b>242</b>	Denizli-Bölmekaya	<b>147</b>
Aydın-Germencik-Ömerbeyli	<b>239</b>	Aydın-Hıdırbeyli	<b>146</b>
Manisa-Alaşehir-Kurudere	<b>214</b>	İzmir-Dikili-Hanımınçiftliği	<b>145</b>
Manisa-Alaşehir-Y	<b>194</b>	Aydın-Sultanhisar	<b>145</b>
Aydın-Yılmazköy	<b>192</b>	Aydın-Bozyurt	<b>140</b>
Aydın-Pamukören	<b>188</b>	Denizli-Karataş	<b>137</b>
Manisa-Alaşehir-Kavaklıdere	<b>188</b>	İzmir-Balçova	<b>136</b>
Manisa-Salihli-Göbekli	<b>182</b>	İzmir-Dikili-Kaynarca	<b>130</b>
Kütahya-Şaphane	<b>181</b>	Aydın-Nazilli-Güzelköy	<b>127</b>
Çanakkale-Tuzla	<b>174</b>	Aydın-Atça	<b>124</b>
Aydın-Salavatlı	<b>171</b>	Manisa-Salihli-Kurşunlu	<b>117</b>
Denizli-Tekkehamam	<b>168</b>	Denizli-Sarayköy-Gerali	<b>114</b>

Table 2.4. Geothermal Power Plants in Turkey  
(Source: Baba, 2013)

Location	Name	Type	Start-up Day	Reservoir Temperature (°C)	Average Temperature (°C)	Installed Power (MWe)
<b>Aydın</b>	Salavatlı Dora-1	Binary Cycle	2006	172	157.5	7.35
	Salavatlı Dora-2	Binary Cycle	2010	174	157.5	11.2
	Salavatlı Dora-3	Binary Cycle	2013	174	157.5	17
	Ömerli Gürmat	Double Flash	2009	232	220	47.4
	Hıdırbeyli İrem	Binary Cycle	2011	190	170	20
	Bozkoy Deniz	Binary Cycle	2010			24
	Bozkoy Sinem	Binary Cycle	2012			24
<b>Çanakkale</b>	Tuzla	Binary Cycle	2010	174	160	7.5
<b>Denizli</b>	Kızıldere I Zorlu	Single Flash	1984	242	217	17.4
	Kızıldere II Zorlu	Binary Cycle	2013	242	217	60
	Sarayköy Bereket	Binary Cycle	2007	145	145	7.5
	<b>Total</b>					<b>243.35</b>

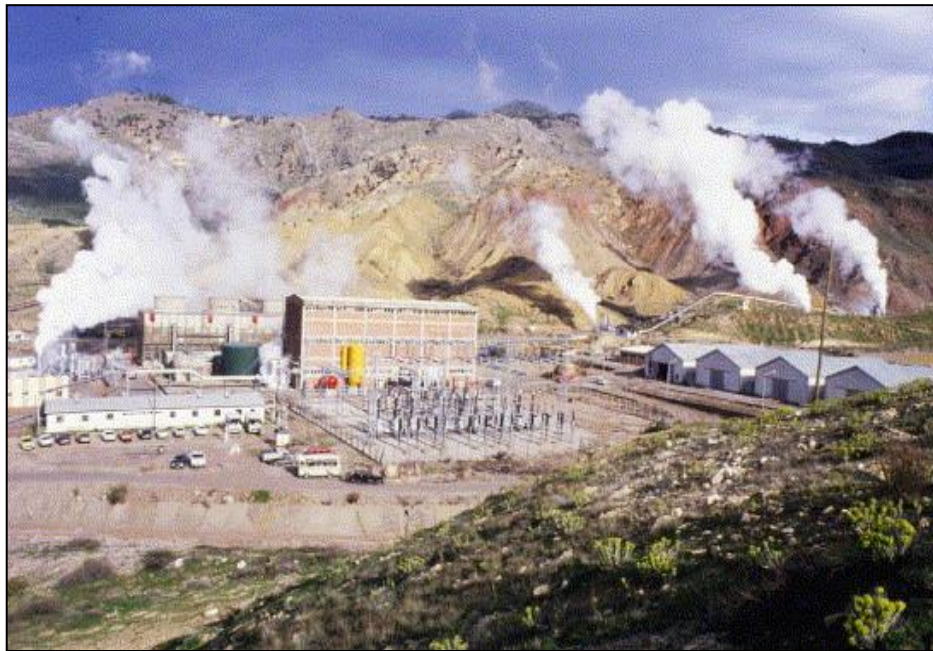


Figure 2.2. Geothermal Power Generation in Western Turkey

Tuzla Geothermal Power Plant has an installed power of 7.5 MWe and yearly energy production capacity of 51 GWh. (Figure 2.2) Tuzla power plant is a binary cycle type plant that acquired a 40-year license was in May 2004 and facility started on January 2010.

Most of geothermal reservoirs, especially the ones at high temperature ones, are located in geologically unstable zones that have volcanic activity, deep earthquakes and heat flow that is higher than the average. Reinjection of geothermal fluid into the reservoir may induce further seismic activity. Cooling of production wells (thermal breakthrough) is also a potential risk that can originate from reinjection process (Barbier, 1997).

Low-temperature fields have been mainly used for district heating and greenhouse in Turkey (Table 2.5. and Figure 2.3). District heating is proceed to use in Afyon, Diyarın-Ağrı, Kızılcahamam-Ankara, Gönen-Balıkesir, Balçova - İzmir, Kırşehir, Simav - Kütahya, Kozaklı - Nevşehir, Salihli - Manisa and Sarayköy – Denizli region. Most of greenhouses have been built around Dikili, Salihli and Simav Region

Table 2.5. Direct Use Applications in Turkey  
(Source: Mertoglu and Basarir, 2013)

<b>APPLICATIONS</b>	<b>CAPACITY</b>
Geothermal District Heating (City, Residences)	805 MWt
Greenhouse Heating	612 MWt
Thermal Facilities Heating	380 MWt
Balneological Use	870 MWt
Geothermal Heat Pump	38 MWt
Total Geothermal Heat Use	2705 MWt

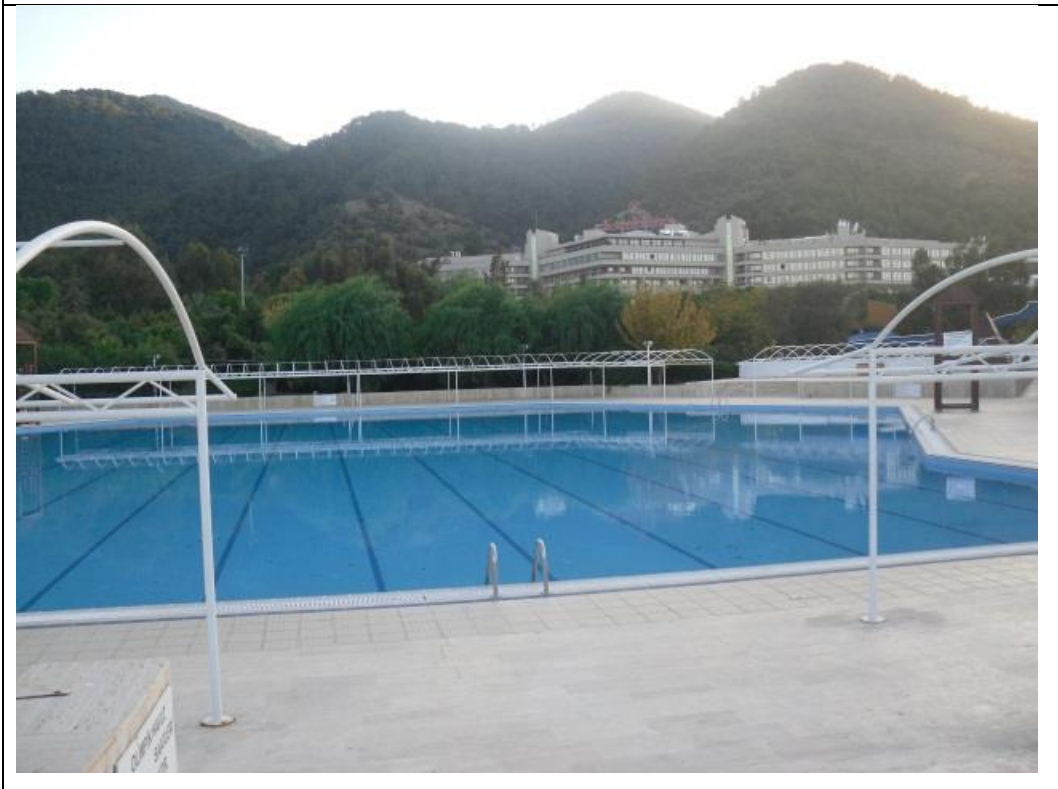


Figure 2.3. District Heating and Greenhouse Applications in Turkey

## CHAPTER 3

### LITERATURE REVIEW

The use of geothermal energy produces less waste when compared to unrenewable sources. But geothermal systems still affect the environment. Geothermal utilization can cause surface disturbances, chemical and physical effects due to fluid withdrawal, noise (Hunt, 2001), thermal effects (Ellis, 1978), and social effects. Geothermal fluid currently causes some environmental problems for air, soil, and water because of their high salinities and heavy metals (Bussotti et al., 1997; Barbier, 1997; Birkle and Merkel, 2000)

#### 3.1. Effect of Geothermal Systems on Environment

One of the main environmental problems in operating geothermal power plants is gas disposal. Waste gas disposal can cause microclimate which behaves as fog or rainfall. In addition to that, gas disposal in the form of steam may affect cloud formation and change the weather locally. Discharge of chemicals into the atmosphere via steam also affects air quality. Gases present in geothermal fluids include two of the greenhouse gases: major constituent carbon dioxide ( $\text{CO}_2$ ) and methane ( $\text{CH}_4$ ). When the greenhouse gas emissions of different type of electrical generations are compared, the concentration of  $\text{CO}_2$  is very low in geothermal generation (Figure 3.1.). Hydrogen sulfide ( $\text{H}_2\text{S}$ ) probably causes an unpleasant smell as well as it is toxic even in very low concentrations. As a result of geothermal field applications, the concentration of  $\text{H}_2\text{S}$  increases more than the concentration of  $\text{CO}_2$ , The  $\text{H}_2\text{S}$  gas might be oxidized to  $\text{SO}_2$  which causes acidification of rain and soil (Kristmannsdottir and Armannsson 2003; Kristmannsdottir et al., 2000; Axelsson, 2003)

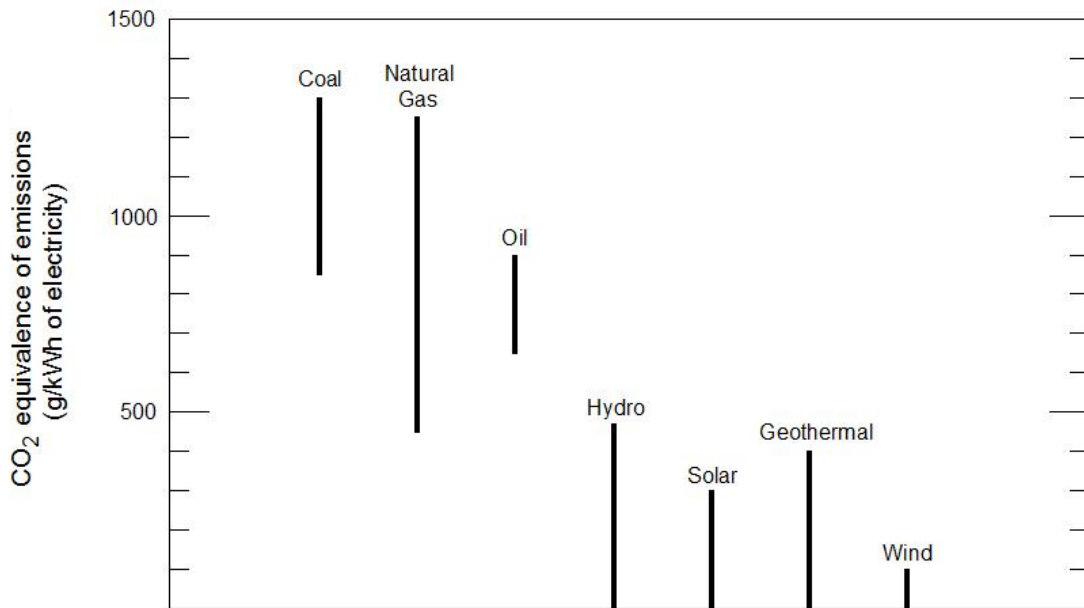


Figure 3.1. Greenhouse Gas Emissions (CO<sub>2</sub> equivalent) of Different Types of Electricity Generation Technologies (Source: Hunt, 2001)

Generally the main pollutant chemicals in the liquid fraction of geothermal are aluminium (Al), ammonia (NH<sub>3</sub>), arsenic (As), boron (B), cadmium (Cd), iron (Fe), lead (Pb), lithium (Li), manganese (Mn), mercury (Hg), and zinc (Zn) in harmful concentrations (Kristmannsdottir and Armannsson 2003; Baba and Armannsson 2006). The health effects of chemicals are associated with frequency, duration of exposure, and the nutrition status of the exposed population.

Discharge of waste geothermal liquid is a potential source of chemical and thermal pollution. Especially, waste liquid disposal affects on surface water and groundwater quality (Birkle and Merkel, 2000; Dođdu and Bayarı, 2004; Kristmannsdottir and Armannsson, 2003; Baba, 2003; Baba and Özcan, 2005; Baba et al. 2005; Baba and Armannsson, 2006; Baba et al. 2008; Aksoy et al. 2009; Çakın et al., 2012; Baba and Murathan, 2012). Wastewater may seriously affect the biological and ecological system with high heavy metal concentration and high temperature, when it pipes into streams, rivers, lakes or local groundwaters (Loppi, 1997; Dođdu and Bayarı, 2004; Baba and Özcan, 2005; Yağın et al. 2008). Disposal of water that is rich in heavy metals, especially in As and Hg, may accumulate in sediments and organisms. Boron has harmful effects on vegetation.

Effects of geothermal fluid on environmental problems have been investigated in different parts of the world. For example; Widagda et al. (2000) studied the physical and chemical properties of liquid waste of geothermal wells of Tulus River, Italy. Total dissolved solids, conductivity, sodium absorption ratio, chloride, sulphate, and boron were analyzed to determine the quality of water. Boron and chloride content of fluid were greater than the regulation limits and geothermal fluid was unsuitable for use as irrigation water. In Mexico, environmental impact by spill of geothermal fluids at Los Azufres geothermal field was studied by Birkle and Merkel (2000). High concentrations of heavy metals, especially Fe, Mn, F, B, and As were found in surface waters within the geothermal field up to 10 km outside. Boron values reached to 125 mg/L and arsenic to 8 mg/L in surface water. In addition to the effect of As, B and Hg in geothermal fluid on soil were studied in the Mt. Amiata Geothermal Field, Italy (Loppi, 1997). The results showed that the geothermal power plants did not represent a macroscopic source of arsenic and boron contamination in the field. On the contrary, at the Hg mining area of Mt. Amiata concentrations were extremely high both in soil and epiphytic lichens, and anomalous content in these organisms was due to the uptake of elemental mercury originating from soil. In May 2012 during drilling operations in Alasehir Geothermal Area, uncontrolled surface eruptions occurred in Turkey. The waste geothermal fluid originating from the field, where the geothermal drill collapsed, was found to cause significant thermal and chemical contamination such as arsenic and boron (Baba and Murathan, 2012).

Turkey has great potential of geothermal resources and has similar environmental problems. Especially the western part of Turkey has similar environmental problems with the other areas. To determine the scale of these problems, some studies were conducted. For instance, Baba et al. (2005) studied the environmental effects of geothermal brine spill at Tuzla geothermal site. The study indicates that especially western part of Tuzla stream has been affected by spill of hot water (Figure 3.2). Tuzla has NaCl type brine and geothermal fluid is enriched in B and Sr. B values reached up to 83 ppm and Sr values to 134 ppm, these values were above the international surface water standards. Cold and hot springs were contaminated by geothermal brines. EC values and concentration of some elements such as Na and Cl were very high in Tuzla River. Tuzla Stream feeds from the Tuzla geothermal brine during the dry season, infiltration caused an increase in sodium and chloride

concentrations in the shallow groundwaters. Baba et al. (2009) conducted a study to determine hydrogeochemical properties of the Tuzla geothermal fluid, groundwater and surface water. This study indicated that salts and trace elements from geothermal brine accumulated on the surface water. Geothermal brine directly mixed with shallow groundwater via vertical faults and cracks.



Figure 3.2. Discharge of Geothermal Fluid on Soil and Water in Northwest of Turkey

Spill of waste geothermal fluid affects the surface water, groundwater, sediment, and soil quality. Earlier studies were conducted in Tuzla geothermal field to investigate the effect of geothermal fluid on surface water and soil, and the relationship between them. Baba and Özcan (2005) monitored and evaluated the spill of geothermal fluid on soil and water in Tuzla Geothermal Field. This study indicated that EC values of soil reached up to 16 dS/m. In addition Baba et al. (2008) determined the geochemical profile of surface and subsurface waters and radionuclide concentrations in soils. This study mentioned that high concentrations of heavy metals (Cr, Fe, K, Sr and Zn) were found in soil. Heavy metal concentrations in soil samples were higher in the east part of Tuzla Geothermal Field in which hot geothermal springs are located. Also, Yağan et al, (2008) studied on soil quality and its effect on plants in Tuzla geothermal site. The result of this study showed that high amounts of Al, B, K, Sr and Pb were found in



plants which are grown around Tuzla geothermal field. Effect of geothermal fluid on environment have been seen different part of Turkey. For example; Dođdu and Bayarı (2004) studied environmental impact of geothermal fluids on surface water, groundwater and streambed sediments in the Akarcay Basin (Afyon), Turkey. The field had low enthalpy (95°C) and salty geothermal fluid (EC = 4,000 dS/cm). The result of this study showed that geothermal fluid affected soil and water. As, Al, Fe, and Mn concentrations were high in surface, groundwater and soil at some points.

Earlier studies were conducted in Tuzla geothermal field while geothermal wells had opened and abandoned by MTA (General Directorate of Mineral Research and Exploration). In 2010, Tuzla power plant was started to operate. It supplies geothermal fluid from wells for power generation. The present study was needed to investigate the effect of the fluid on the surface water and soil after the changes mentioned above.

## CHAPTER 4

### STUDY AREA

Tuzla geothermal field, which is located 5 km from Aegean Sea and 80 km from south of Çanakkale, is on Biga Peninsula, in the northwestern Anatolia (Figure 4.1. and 4.2.). Tuzla Village is the only settlement in study area, located near Ayvacık (Çanakkale). The village is located nearly 300 m east of the geothermal power plant.

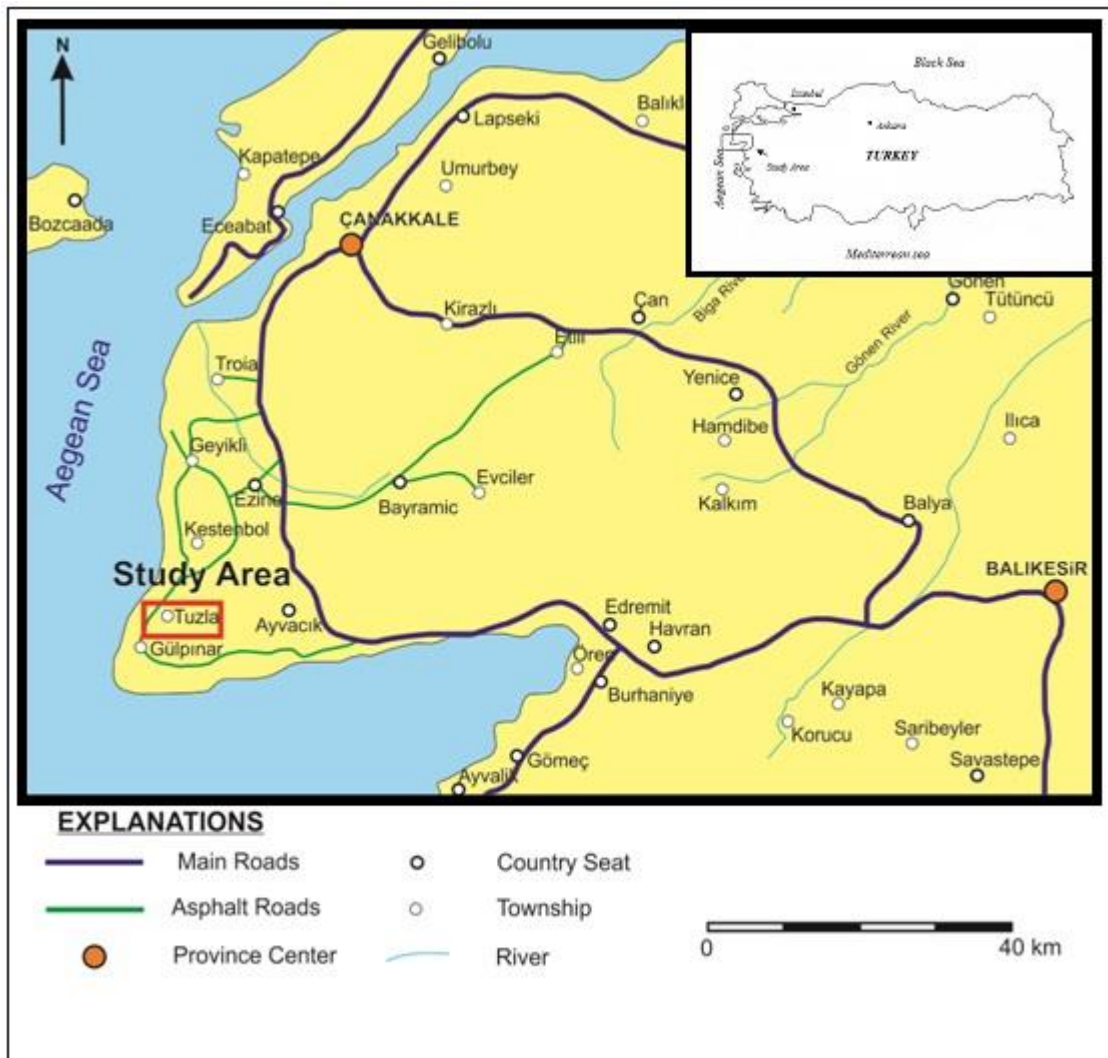


Figure 4.1. Location Map of Tuzla Geothermal Field



Figure 4.2. View of Tuzla Geothermal Field

#### **4.1. Geological and Hydrogeological Properties of Tuzla Geothermal Field**

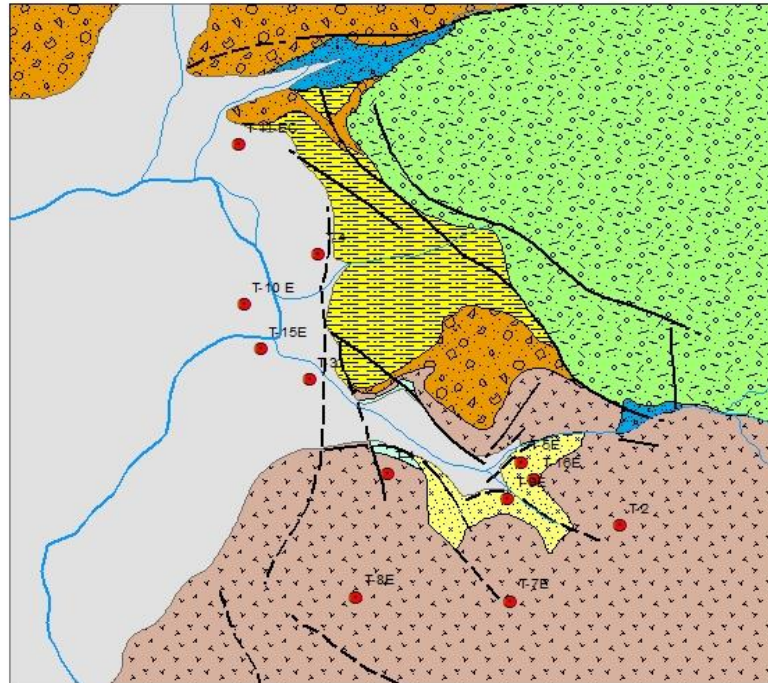
Tuzla Geothermal field is located on an active fault zone and this site is one of the most important geothermal fields. Plenty of studies have been conducted on this site by researchers. Geothermal studies of Tuzla field started in 1966. Samigil (1966), Erdogan (1966), Urgun (1971), Öngur (1973) and Alpan (1975) studied geological and volcanic features of Tuzla. Geophysical investigations were performed by Demirörer (1971) and Ekingen (1972). According to geological and geophysical surveys 10 thermal gradient wells were drilled from 50-100 m depth in 1974. Some of these wells' temperatures reached to 145 °C at 50 m depth because dynamic boiling within some was lost in blow-outs (Karamandersi and Öngur, 1974). Two deep exploration wells (between 814 -1020 m depth range) were drilled in 1982 and 1983 by MTA. The reservoir depth was estimated between 333 and 553 m in volcanic rock at 173 °C, a

production rate of 130 t/h and steam content of 13 %. The general characteristics of hydrothermal alteration were described by Gevrek and Sener (1985), and they stated that geothermal fluid can range from 150 to 225°C temperature (Sener and Gevrek 2000). Similarly, Mutlu and Gülec, (1998) calculated the reservoir temperature of Tuzla to be between 187°C - 212°C by using different geothermometers. Baba and Deniz (2005) calculated subsurface reservoir temperatures that ranged from 182°C to 232°C.

Tuzla is hosted by rhyolite lavas and pyro-clastic deposits. Base zone consists of calcschiste, quartzite and marble, which are metamorphic rocks that include quartz, orthoclase, albite and mica minerals. Granodiorite intrusion consisting of quartz, orthoclase, albite and biotite, intruded the metamorphic basement. The metamorphic rocks and granodiorite intrusion are covered by andesitic volcanic rocks; trachyandesite, trachyte and rhyodacitic ignimbrite. These rocks, especially trachyandesite, include quartz, calcite minerals that are highly altered and covered by sediments and alluvium (Baba et al. 2008; Baba et al. 2009, Demir et al. 2013)

The currently active thermal regime in Tuzla is associated with volcanism. Generally, the major geologic structures are recognized to be N–S and NW–SE trending fault systems (see Figure 4.3.). Along the N–S trending fault system, many geothermal springs are developed. The major faults trending NW–SE along the western and southern slope of the Tuzla Tepe are normal faults (Demir et al. 2013).

## Geological Map of Tuzla



### LEGEND

- Geothermal Well
- River
- Faults
- - - Probable Faults

### Geology

- Alluvium
- Claystone-Sandstone
- Conglomera
- Ignimbrite
- Fine Textured Ignimbrite
- Tuff
- Stream River
- Trachyandesite

Figure 4.3. Geology Map of Tuzla  
(Source: modified from Demir et. al, 2013)

The origin of the thermal springs in Tuzla geothermal field was investigated by Mutzenberg (1997), Balderer (1997) and Vergosh et al (2002). Na-Cl water composition indicates a marine origin and also water-rock interactions. According to Balderer (1997) and Mützenberg (1997), geothermal fluid of Tuzla is fossil saline water that stuck

between Miocene sediments. Besides, Vergosh et al (2002) have predicted that Tuzla geothermal water is formed by dissolution of marine evaporations. The water from the wells is acidic due to an excess of free CO<sub>2</sub> (freemineral acidity), which is the result of the high partial pressure of this gas in the well. The temperature of geothermal fluid in well T9E and T16E in Tuzla geothermal site are 149.1°C and 150.6, respectively. The wellhead pressure ranges from 3.61 to 3.74 bar in production wells (Demir et al. 2013).

## 4.2. Climate of the Study Area

Meteorological data from Çanakkale station was used to determine the meteorological conditions of Tuzla. The climate diagram of Çanakkale represents the amount of rainfall and temperature changes per month (Figure 4.4.). From 1960 to present, observations on many parameters have been made in this station including total daily precipitation and daily average temperatures (DMI, 2013). The mean daily temperature was 15.03 °C while the lowest temperature was -11.2 °C and the highest was 39 °C for the period 1960-2012. In the same period, the mean annual precipitation was 51.34 mm (DMI, 2013)

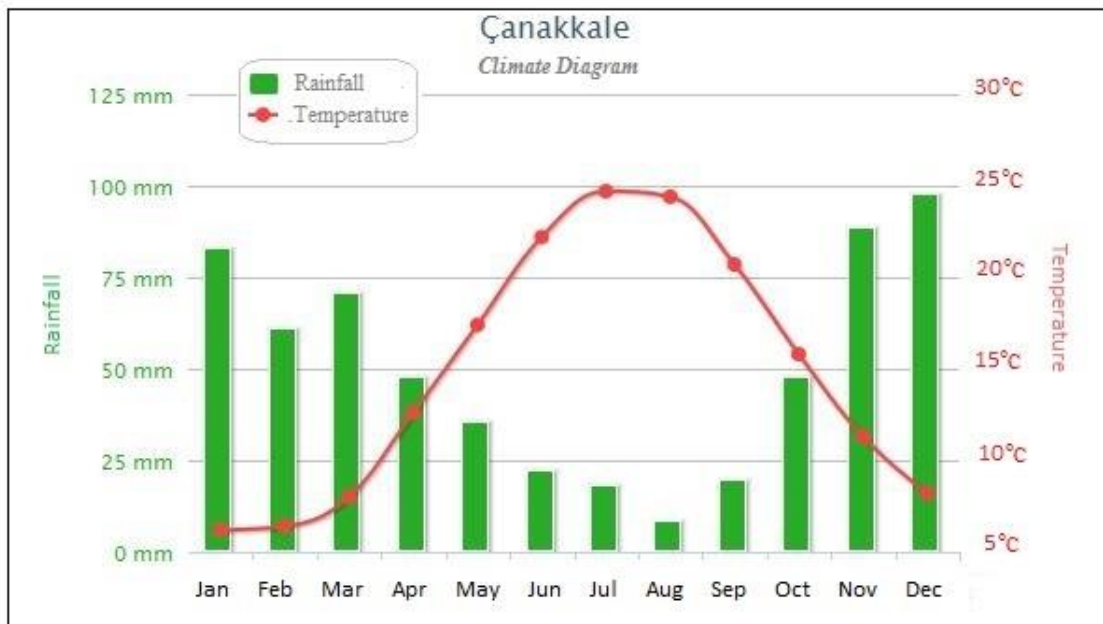


Figure 4.4. Climate Diagram of Çanakkale  
(Source: DMI, 2013)

### 4.3. Surface Water of Tuzla

Tuzla River is the main water source for usage and agricultural activities (Figure 4.5.). Tuzla River (15-14000 km/d flow rate) is 52 km length and the source of the river is Kaz Mountain. The creek has lower flow rate. Especially in dry periods the flow rate of the creek is approximately zero because of the evaporation.

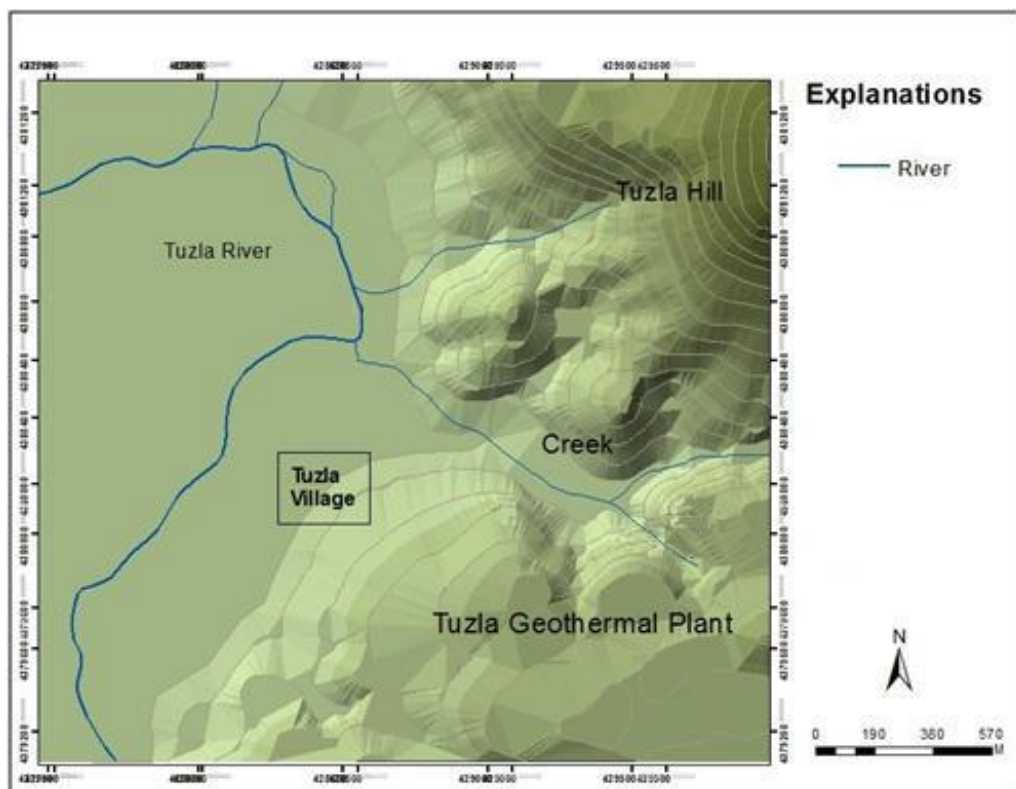


Figure 4.5. Drainage Map of Tuzla

## CHAPTER 5

### MATERIAL AND METHODS

This chapter contains material and methods for field studies, laboratory analysis and data interpretations. The field studies include the analysis of field parameters and the collection of samples from surface waters, soil and water samples from geothermal wells. To determine the effect of geothermal fluid on soil and surface water, representative samples from surface water and soil were collected as part of a field survey and these samples were analyzed using standard techniques. With the aim of understanding geothermal fluid composition before interfering to the environment, water samples from geothermal wells were taken in Tuzla Region.

The surface water samples were collected from different locations that completely represented the study area and then analyzed for primary physical parameters, major anions and cations and heavy metals and trace elements. The analysis of anions and cations were performed using ion chromatography (IC) in the laboratories of İzmir Institute of Technology Environmental and Research Center and the analyses of heavy metals and trace elements were performed with inductively coupled plasma – mass spectrometry (ICP-MS) in Acme Laboratories (Canada).

The soil samples were collected from the same locations as surface water sampling points and six extra points to comprehend the effect from the geothermal fluid. The physical parameters were analyzed in the field. The element analysis of soil samples were performed using Scanning Electron Microscope (SEM-EDX), X-Ray Diffraction (XRD) and X-Ray Fluorescence Spectroscopy (XRF) in IZTECH Center for Materials Research.

#### 5.1. Field Study

The field studies were conducted in four periods (February 2012, May 2012, February 2013, and April 2013). Hydrogeological, geological and morphological properties of study area were checked and evaluated. Locations of geothermal wells,



surface water samples points, soil sample points were determined by handheld GPS device before and during the field study. Physical parameters (temperature, pH and electrical conductivity) were measured on the field with a multi-parameter probes. The samples were collected from each sampling point: 500 mL for the analysis of standard anions and cations, and 50 mL for the analyses of heavy metals and trace elements. Polyethylene bottles were used for collection of the samples. These bottles reduce the photochemical reactions and they have strength to high temperatures. By the addition of 2.5 % nitric acid solution to water samples (1.25 mL nitric acid for 50 mL sample), metals in water with the pH less than 2 will be permanently dissolved in a form of highly soluble nitrates, to stop bacterial activity and preserve the chemical state of contaminant.

### 5.1.1. Geothermal Fluid

In February and May 2012 totally five samples were collected from geothermal production (T9 and T16) and T10 geothermal well to comprehend physical and chemical properties of the geothermal fluid (Figure 5.1.).

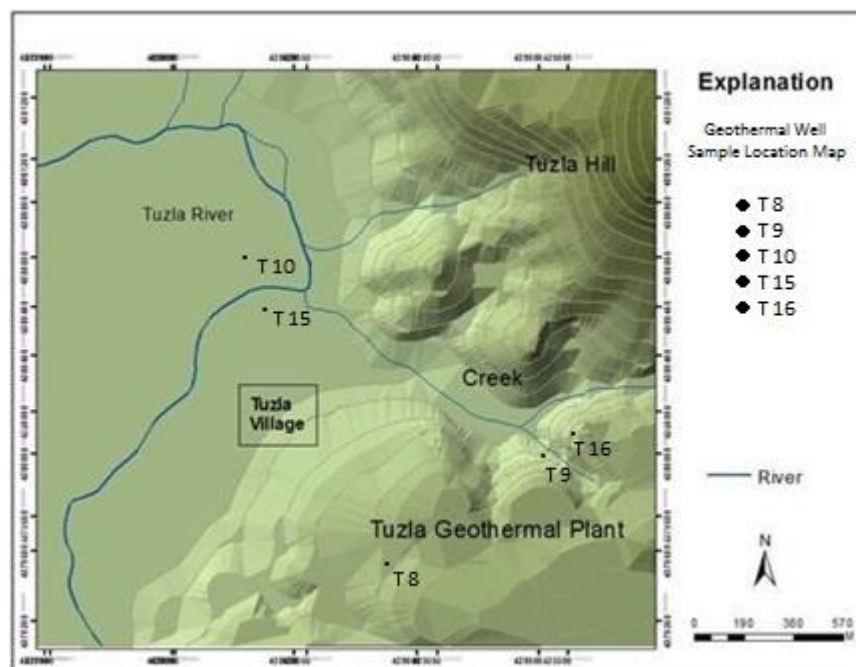


Figure 5.1. Geothermal Fluid Sample Location Map

### 5.1.2. Surface Water Sampling

Before field study, the locations of sampling points were selected to observe the effect of geothermal fluid clearly and better characterize the quality, general circulation and contamination mechanisms of surface waters with a high accuracy. For this reason, nine surface water sampling points were used in this study. Six of these locations are on the small creek below the Tuzla Geothermal Power Plant, three of the locations are on the Tuzla stream (Figure 5.2.). The selection criterias for these locations are to comprehend the effect of geothermal fluid to the creek and to apprehend the effect of difference concentrations that affected and non-affected sampling points on the Tuzla River from the geothermal fluid.

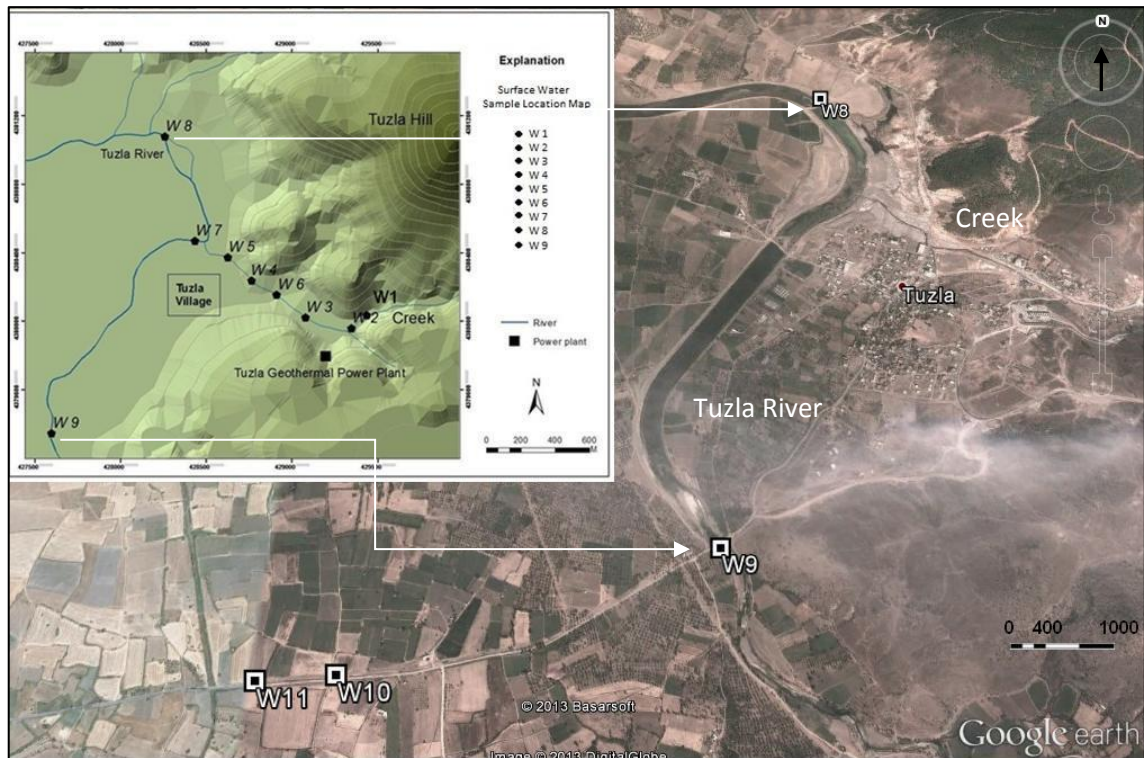


Figure 5.2. Location Map of Surface Water Sample

The analysis of anions and cations were performed using ion chromatography (IC) with IonPac AS9-HC 4x250 mm analytical column and IonPac AG9-HC 4x50 mm guard column with 10mM  $\text{Na}_2\text{CO}_3$  eluent for cations. IonPac CS12A 4x250 mm

analytical column and ionPac CG12A 4x50 mm Guard Column with 18mN MSA (Methanesulfonic acid) eluent were used for anions.

### 5.1.3. Soil Sampling

To investigate the effect of geothermal fluid in soil, totally fourteen locations were selected. Ten of them had same coordinates with the surface water samples, four of them were near locations to geothermal wells and hot water springs (Figure 5.3.).

Soil samples were collected from 0 to 30 cm range depth. pH and temperature were measured with digital soil pH meter during the field study. 0.5-1 kg soil samples were taken for elemental analysis.

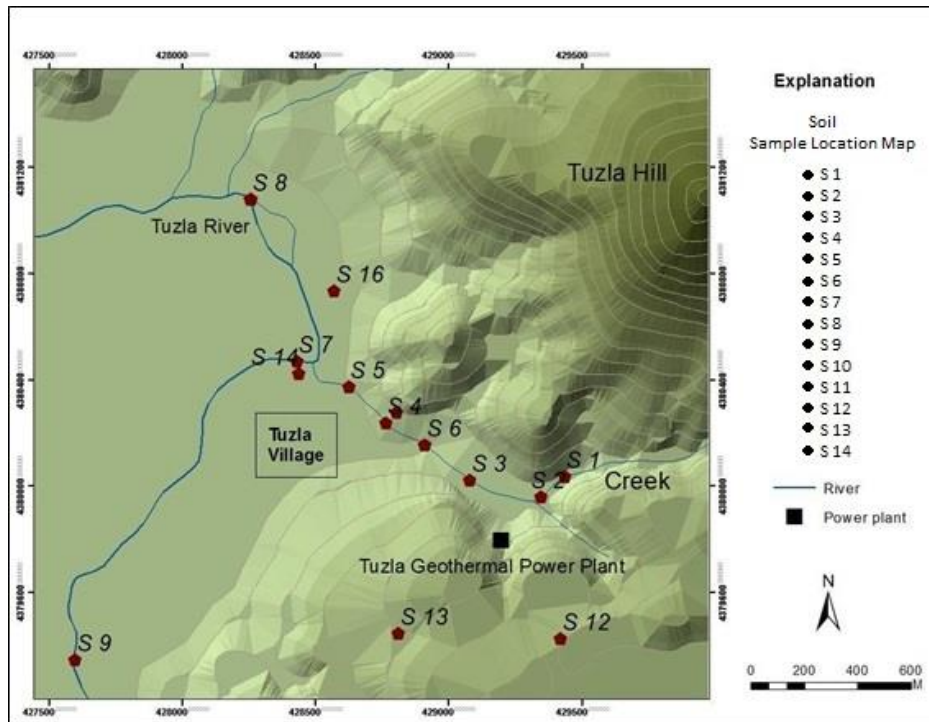


Figure 5.3. Soil Sample Location Map

Soil samples were dried at 40 °C to remove the moisture of samples, and grind to the powder size for SEM and XRD analysis. To prepare samples for XRF analysis, soil samples grinded less than 100 µm and ignition loss was performed. Ignition loss consists of strongly heating the sample of the soil at 1000 °C, and volatile substances allowed to escape for one hour and it is calculated as percentage.

Scanning Electron Microscope (SEM-Philips XL-305 FE6) EDX method of SEM was performed for determining element oxides and elements ratio to the total sample. Results are given as percentige. High-resolution images with different dimensions of the sample were produced with Scanning Electron Microscope. XRD (Philips X`Pert Pro) identifies chemical composition, and physical properties of soil. X-Ray Fluorescence Spectroscopy (XRF-SpectroIQ 2) defines elements with bombarding high-energy X-rays or gamma rays, and it gives properly results when compared with XRD.

The data obtained from field studies and from laboratory analysis were then processed by using ArcGIS 10.1 and Aquachem 4.0 software. Aquachem is a program that used for managing, analyzing and plotting water quality data (major anion and cations)

## CHAPTER 6

### RESULTS AND DISCUSSIONS

This chapter presents the results of geothermal fluid, surface water and soil quality monitoring program. Different methods were used to evaluate properties of soil and water. Surface water quality results are compared with the related water quality standards including the Turkish Regulations on Waters for Human Consumption (ITASHY, 2005) and Surface Water Quality Standards of U.S. Environmental Protection Agency (EPA, 2005).

#### 6.1. Physical and Chemical Properties of Geothermal Fluid in Tuzla

In this section, to describe the properties of Tuzla geothermal fluid and see the correlations between soil and surface water pollution five geothermal well samples were collected in May 2012 are discussed. Physical parameters and major anion - cation concentrations in Tuzla wells are given in Table 6.1. The results showed that pH and EC values of geothermal fluid ranged from 6.62 to 8.73 and from 57.5 to 83.6, respectively.

Table 6.1. Anion-Cation Concentrations, pH, and EC Values of Tuzla Geothermal Fluid

Well	pH	EC (mS/cm)	Concentration (ppm)						
			Na	K	Ca	Mg	Cl	SO <sub>4</sub>	HCO <sub>3</sub>
T8	8.73	83	174	29	26	3	284	146	115
T9	6.64	60	19765	2098	2501	74	39112	210	118
T10	7.39	57	17706	1965	2193	72	36878	205	172
T15	7.40	58	18934	2037	2471	108	38885	263	160
T16	6.42	60	18832	2031	1859	27370	37770	246	140

Major anion and cation results represent source of fluid and water-rock interactions. For this purpose, chemical results were evaluated with Piper ve Scholler diagrams (Figure 6.1. and 6.2.). According to these diagrams, Tuzla geothermal fluid have high Na and Cl content and paralel lines exhibit that all samples have the same

reservoir and Na-Cl water composition indicates a marine origin. T8 showed different but a parallel profile to the other wells (Figure 6.2.). Rain water interference into the T8 well was the main the reason of this situation. These type saline geothermal waters classify as “Brine”. According to the Piper and Scholler diagrams in Figure 6.1. and 6.2., the geothermal brine are in NaCl facies (in the same facies as seawater) in annual periods.

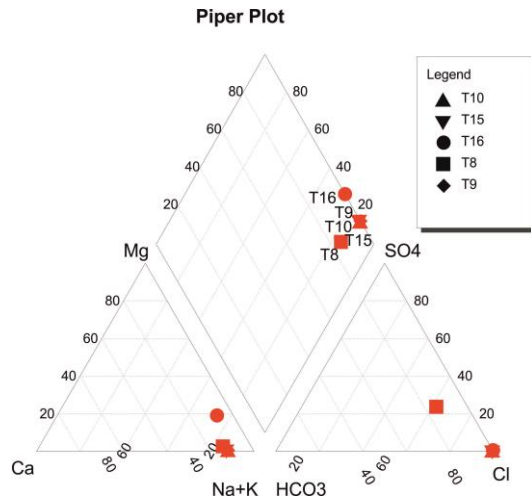


Figure 6.1. Piper Diagram of Geothermal Fluid

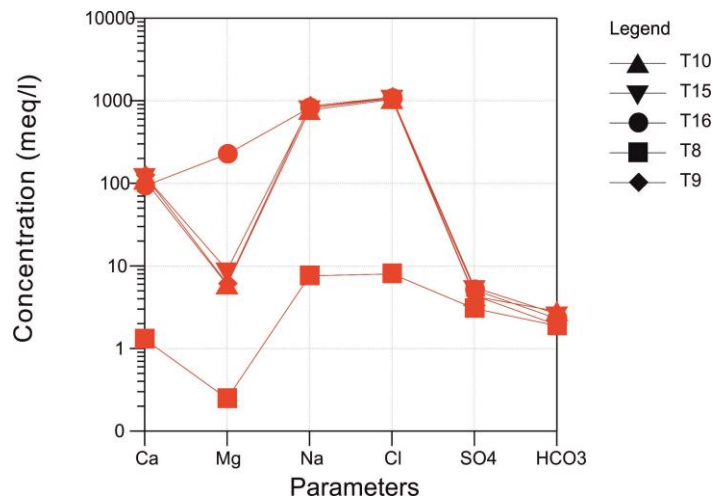


Figure 6.2. Schoeller Diagram of Geothermal Fluid

All heavy metals were such as B, Ba, Br, Li, Mn, S, and Sr measured in the fluid and (Table 6.2.). The results indicated that Tuzla geothermal fluid contained highly boron, lithium and strontium. Boron concentrations ranged from 1.7 ppm to 69 ppm in

geothermal fluids in Turkey (Baba and Armansson, 2008). This situation is related to volcanic and sedimentary rocks and also may be controlled by the degassing of magma intrusives (Baba and Ármannsson, 2006). Production wells (T9 and T16) contain nearly 30 ppm boron and nearly 170 ppm Sr concentrations in Tuzla.

Table 6.2. Heavy Metals of Tuzla Geothermal Fluid

Well	Concentration (ppb)						
	B	Ba	Br	Li	Mn	S	Sr
T9	29214	8659	68.84	29289	5117	79000	169968
T16	28544	8481	63.57	28706	5337	79000	165609
T10	27942	8339	52.47	27662	5394	75000	164572

## 6.2. Physical and Chemical Properties of Surface Water in Tuzla Geothermal Field

In this section, the results of the field parameter measurements (temperature, pH, electrical conductivity (EC), and major anions and cations as well as the results of trace elements and heavy metals are presented (Table 6.3.)

### 6.2.1. Physical Parameters

The field parameters were measured directly at field in four periods. The results of these measurements are given at Table 6.3. The Surface water temperatures ranged from 15.2 to 25.6 °C in February 2012 sampling period with an average value of 20.72 °C. The maximum surface water temperature of 25.6 °C was measured next to a fountain close to a geothermal spring (W2). The minimum surface water temperature of 15.2°C was measured at a point close to T11 geothermal well on the Tuzla River (W8). In May 2012 sampling period, the surface water temperatures ranged from 21.5 to 33 °C with an average value of 25.77 °C. The maximum surface water temperature value of 33 °C was measured next to a fountain close to a geothermal spring (W2). The minimum surface water temperature value of 21.5 °C was measured at W9 (under-the-bridge on Tuzla River). Surface water temperatures ranged from 16 to 40 °C in February 2013

sampling period with an average value of 21.08 ° C. The maximum surface water temperature of 40 ° C was measured at in front of Tuzla spa (W4). During the study there was leakage from the pipes to the creek for a few days at sampling point W4 (Figure 6.3.). The minimum surface water temperature of 16 ° C was measured at W9 (under-the-bridge on Tuzla River) (Figure 6.4.).



Figure 6.3. Leakage from Pipes and Discharge of Geothermal Fluid near The Creek

In April 2013 sampling period, surface water temperatures ranged from 17.1 to 38.2 ° C with an average value of 23.66 ° C. The maximum surface water temperature value (40 ° C) was measured near a new drill south west of study area (W10). The minimum surface water temperature with 17.1 ° C was measured at W9 (under-the-bridge on Tuzla River)



Table 6.3. Physical Properties of Tuzla Surface Waters

Sample	Date	pH	Temperature °C	Conductivity mS/cm
W1	25.02.2012	8.87	20.9	30.8
W2	25.02.2012	7.77	25.6	49.3
W3	25.02.2012	8.05	20.8	24,8
W8	25.02.2012	8.64	15.2	2.3
W9	25.02.2012	9.77	21.1	0.3
W1	29.05.2012	7.34	21.5	52.7
W2	29.05.2012	8.02	33.0	59.6
W3	29.05.2012	7.89	30.0	59.1
W5	29.05.2012	8.53	26.1	56.7
W7	29.05.2012	8.43	24.0	0.2
W8	29.05.2012	8.68	23.8	3.1
W9	29.05.2012	9.55	22.0	0.1
W1	05.02.2013	7.94	17.7	10.2
W2	05.02.2013	7.73	18.3	15.1
W3	05.02.2013	8.20	21.0	17.6
W6	05.02.2013	8.05	19.9	11.3
W4	05.02.2013	7.96	40	43.8
W5	05.02.2013	9.02	21.1	16.9
W7	05.02.2013	8.57	18.5	3.7
W8	05.02.2013	8.72	17.2	3.8
W9	05.02.2013	9.00	16	0.4
W1	15.04.2013	8.49	19.9	15.1
W2	15.04.2013	7.85	31.8	31.4
W3	15.04.2013	8.50	22.6	27.4
W4	15.04.2013	8.86	22.1	32.2
W5	15.04.2013	9.27	19.3	31.1
W7	15.04.2013	9.57	20.1	3.6
W8	15.04.2013	9.06	17.8	3.6
W9	15.04.2013	9.43	17.1	0.6
W10	15.04.2013	8.59	38.2	66
W11	15.04.2013	8.66	27.7	52.5

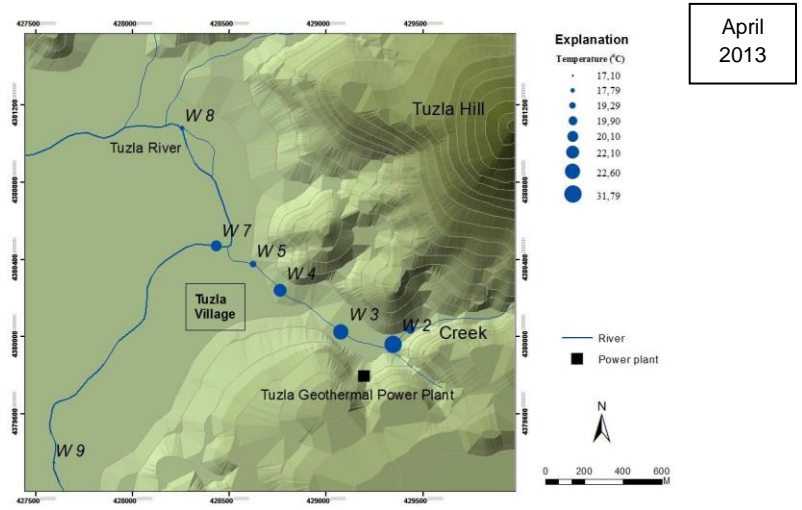
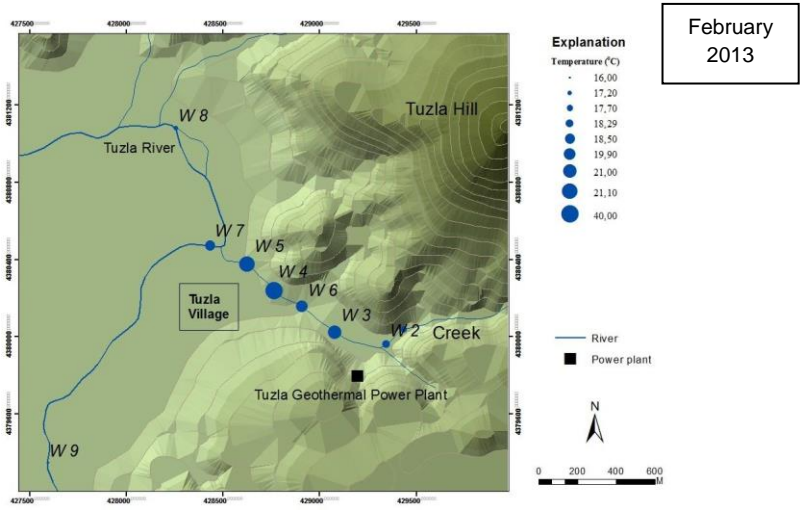
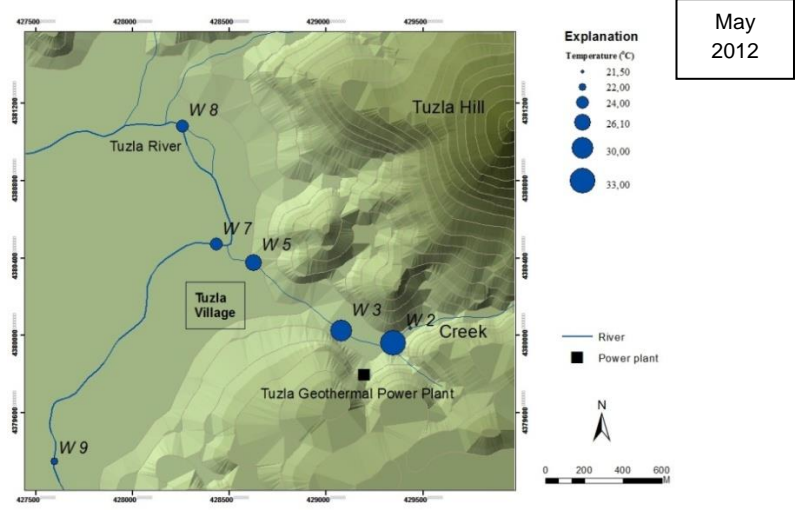
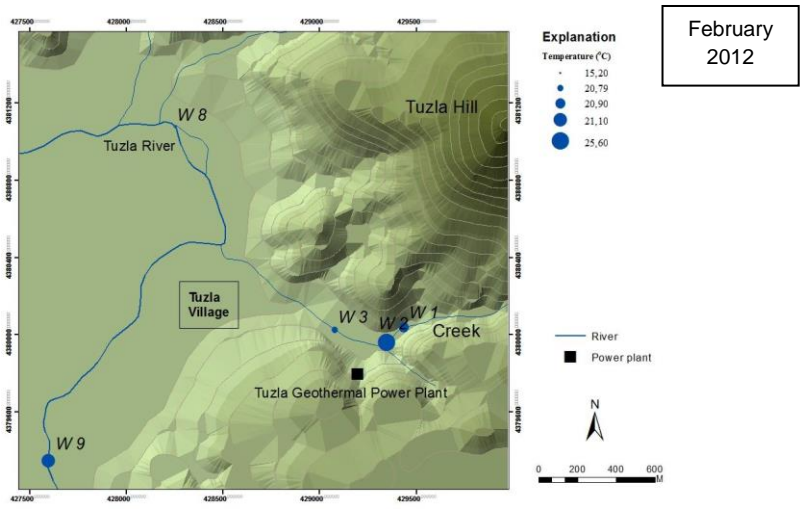


Figure 6.4. Temperature Distribution Map for Surface Water of Tuzla Geothermal Field

As seen in Figure 6.6. surface water pH values varied at natural pH and had an alkaline profile a range of 7.77 – 9.77 in February 2012 sampling period with an average value of 8.62. The maximum pH value of 9.77 was measured at under-the-bridge (W9). The minimum pH value of 7.77 was measured next to fountain (W2). Surface water pH values varied a range from 7.34 to 9.55 in May 2012 sampling period with an average value of 8.35. The maximum pH value of 9.55 was measured at under-the-bridge (W9). The minimum pH value of 7.34 was measured at beginning of creek (W1). In February 2013 sampling period surface water pH values range from 7.85 to 9.57 with an average value of 8.35. The maximum pH value of 9.57 was measured at close point to T7 geothermal well on the Tuzla River (W7). The minimum pH value of 7.85 was measured next to fountain (W2). Surface water sampling results for pH are all within the allowable range of 6.5-9.5 when compared to water quality standards.

Electrical Conductivity (EC) defines dissolved ions content as sodium, potassium, sulfate and chlorine in surface water and represents the salinity of water. High EC values indicate the conductive capacity of the electric current of water (Orebiyi et al., 2010). Measured EC values ranged from 0.34 to 49.3 mS/cm with an average value of 21.50 mS/cm in February 2012 sampling period (Figure 6.7.) The maximum EC value of 49.3 mS/cm was measured next to fountain (W2). The minimum EC value of 0.34 mS/cm was measured at under-the-bridge (W9). In May 2012 sampling period, EC values ranged between 0.032 and 33.07 mS/cm with an average value of 25.77 mS/cm. The maximum EC value of 33.07 mS/cm was measured next to fountain (W2). The minimum EC value of 0.032 mS/cm was measured at under-the-bridge (W9). EC values ranged between 0.39 – 43.8 with an average value of 13.631 mS/cm in February 2013 sampling period. The maximum EC value of 43.8 mS/cm was measured in front of Tuzla spa (W4). The minimum EC value of 0.39 mS/cm was measured at Under-the-bridge (W9). In April 2013 sampling period, EC values ranged from 0.55 to 66 mS/cm with an average value of 26.351 mS/cm. The maximum EC value of 66 mS/cm was measured at a new drill south west of study area (W10). The minimum EC value of 0.55 mS/cm was measured at Under-the-bridge (W9).

Both W8 and W9 sample locations were on the Tuzla River. However, W9 was not affected by geothermal fluid because of the flow direction of the River. The comparison of electrical conductivity values of these two locations were given in Figure 6.5. The result shows that W8 have been affected from geothermal fluid.

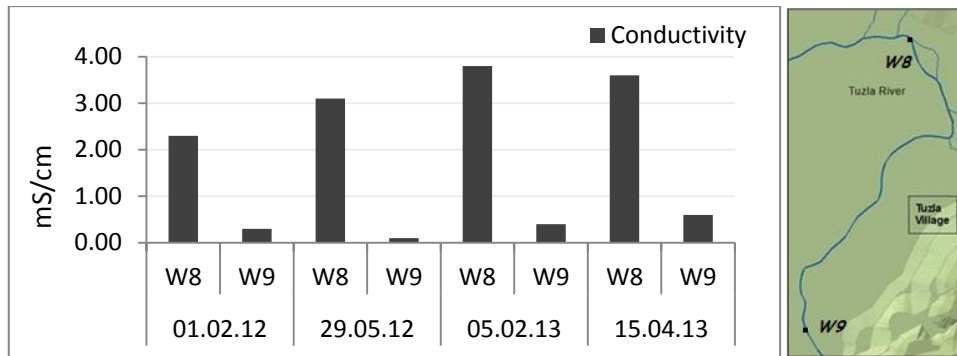


Figure 6.5 Comparison of the Conductivities of W8 and W9 in Four Sampling Period.

In previous studies measured EC values reached to 158 mS/cm and minimum measured EC value was 64 mS/cm in Tuzla geothermal field (Baba et al., 2005). After the study, geothermal wells were started to use for electricity generation and reinjection well of the plant was built. These arrangements led to a considerably reduction in geothermal fluid interaction to surface water and EC values.

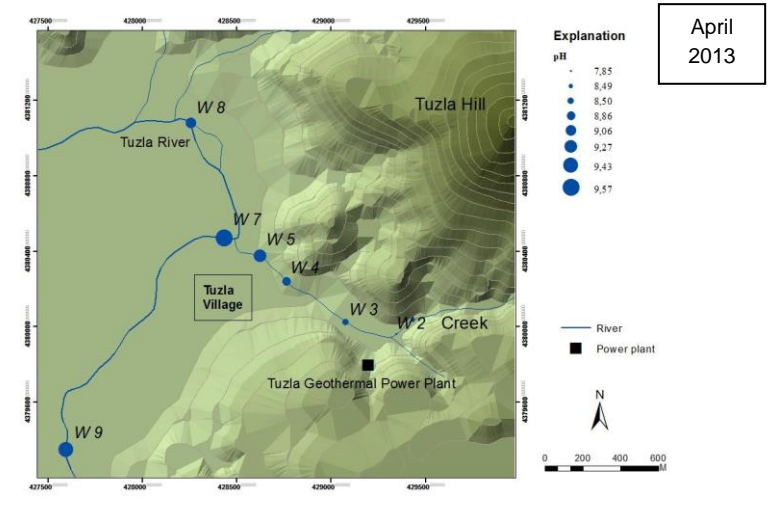
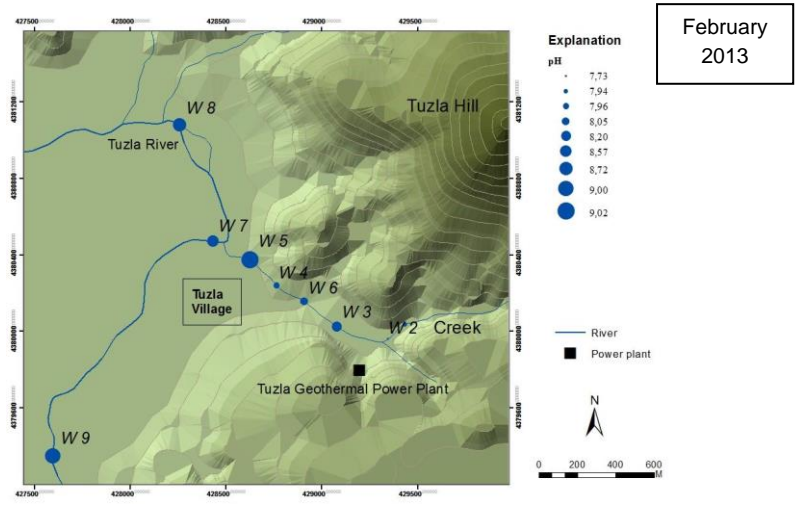
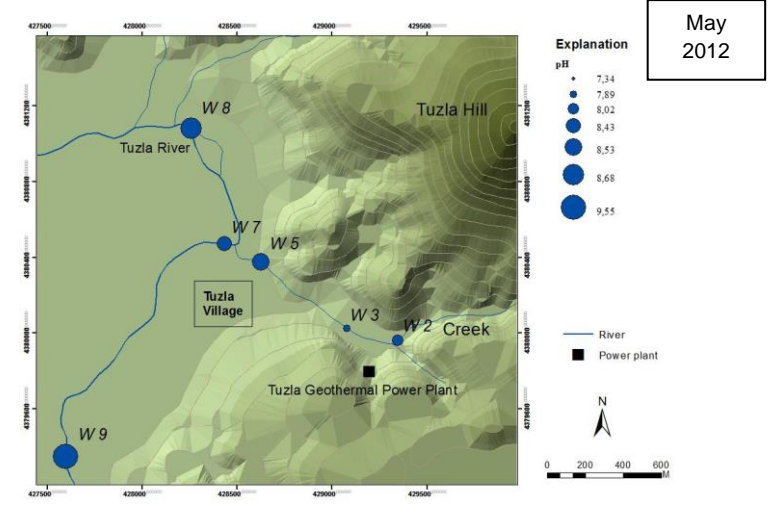
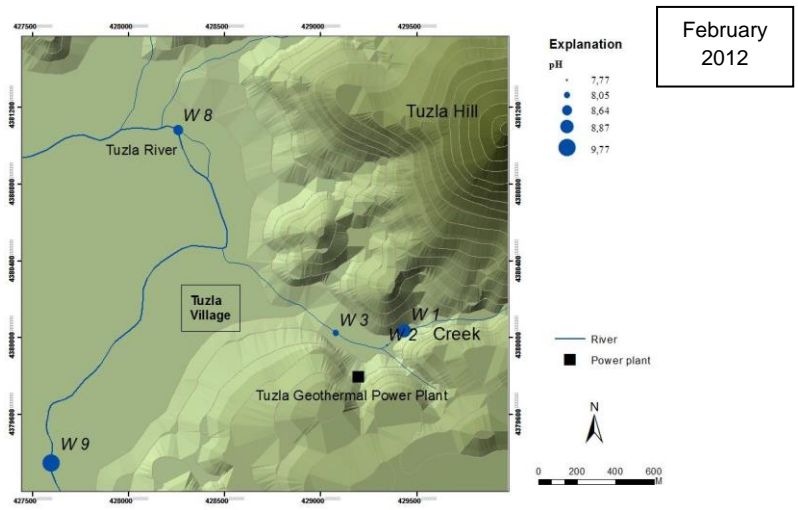


Figure 6.6. pH Distribution Map for Surface Water of Tuzla Geothermal Field

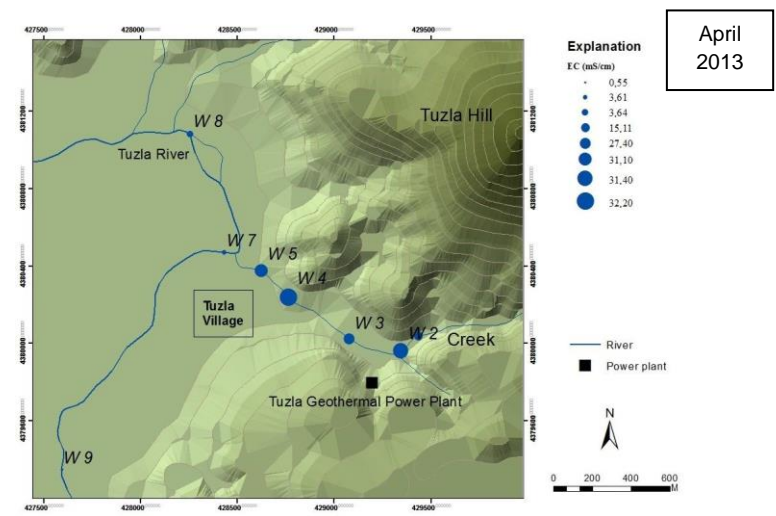
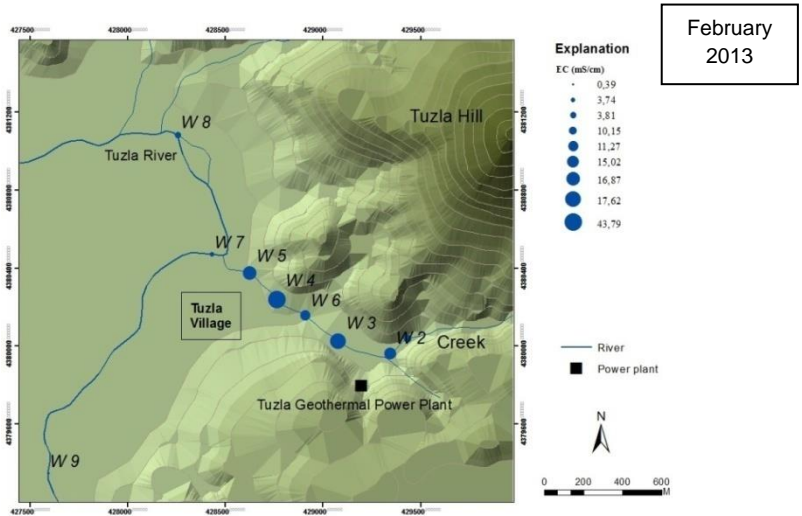
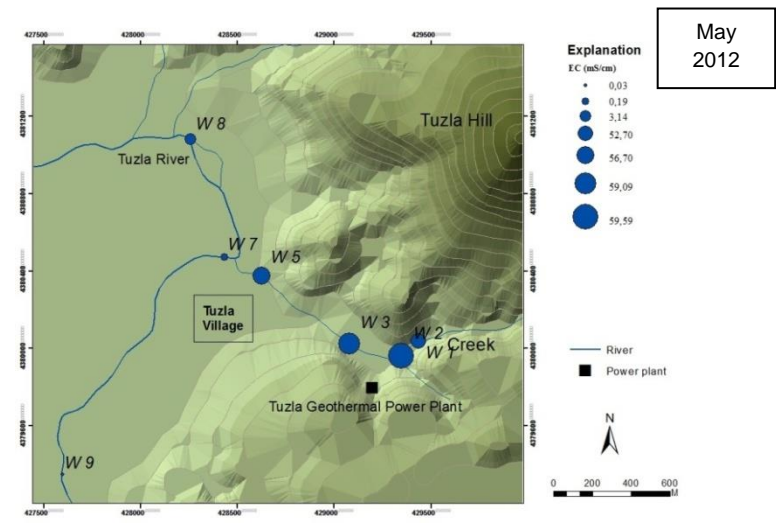
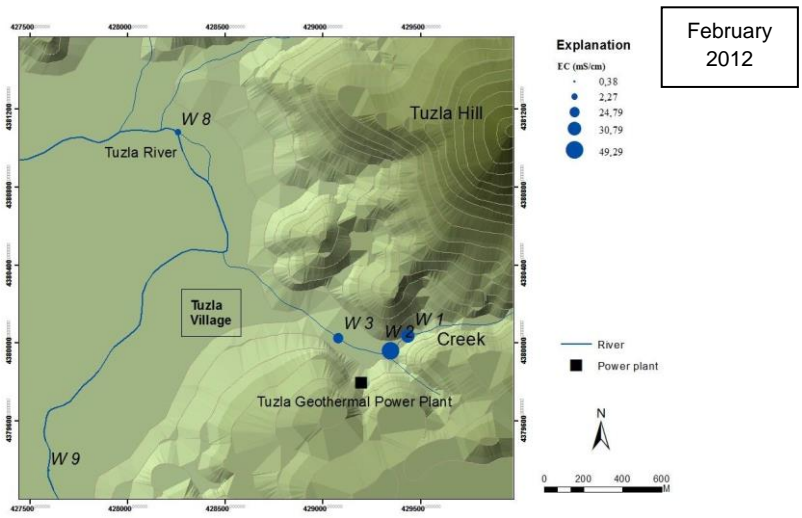


Figure 6.7. EC Distribution Map for Surface Water of Tuzla Geothermal Field

## 6.2.2. Alkalinity and Major Anion - Cations

Major anion - cation results represent properties of surface water. The results for alkalinity, major anion-cation are presented in Figures 6.12. - 6.19. Comparisons of the results with standards are presented below in Table 6.4.

Piper, Schoeller, Durov and Scatter plots are used for classification of water types. Especially with triangle diagrams (Piper and Durov) anion and cation classification can be done separately. Piper diagram of results indicates that most of surface water has Na-Cl water profile with all sampling periods. However, in February 2012 (Figure 6.8.) and May 2012 (Figure 6.9.) the same sampling point, W9, has Na-Ca-Mg-HCO<sub>3</sub>-Cl profile. Addition to that, surface water sample that has been taken from W9 sampling point has Ca-Mg-HCO<sub>3</sub> profile during the February 2013 (Figure 6.10) and April 2013 sampling periods (Figure 6.11.). W8 sampling point in February 2013 and W10 sampling point in April 2013 have Na-Ca-Cl profile.

Scatter plot shows only Na-Cl correlations at surface water sampling points. In February 2012 (Figure 6.8.) W2, where is on the small creek below the power plant, has max Na-Cl concentrations. In May 2012 (Figure 6.9.), sampling points W3 and W5, where were on the creek, had the maximum sodium-chlorine concentrations, too. The lowest concentration sampling point is W9 which is on the Tuzla River. In February 2013 (Figure 6.10.) sampling day, maximum concentration was measured at W4 which is much close to leakage point and a new drill at south west of study area has the maximum Na-Cl values in April 2013 (Figure 6.11.) sampling day.

Schoeller and Durov plots indicate the major anion and cation concentrations. With Schoeller diagram, the water profile of samples can easily be understood with peak points of lines. Durov plots include triangle and square diagrams which represented the same results.

Table 6.4. Major Anion and Cations of Surface Waters

Sample	Sampling Date	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Cl (mg/L)	SO <sub>4</sub> (mg/L)	NO <sub>4</sub> (mg/L)	NO <sub>3</sub> (mg/L)
W1	25.02.2012	9346.99	1156.98	49.14	1522.55	18037.40	138.45	-	-
W2	25.02.2012	14568.31	1181.23	37.20	2056.63	44327.03	218.27	53.16	-
W3	25.02.2012	6755.58	649.17	34.54	1154.03	20160.51	119.97	-	32.30
W8	25.02.2012	497.91	43.75	25.11	128.40	3305	37.36	-	1.92
W9	25.02.2012	27.59	3.14	19.33	19.33	41.42	35.60	-	1.42
W1	29.05.2012	18363.65	1930.76	61.36	2496.60	16401.20	116.28	-	-
W2	29.05.2012	18625.15	1956.65	61.70	2257.80	18442.20	92.21	-	-
W3	29.05.2012	18954.65	2206	67.85	2834.42	36172	146.36	-	-
W5	29.05.2012	19013.35	2159.70	75.08	2400.70	33350	155.18	-	-
W7	29.05.2012	427.50	47.52	14.77	60.48	393.05	35.12	-	-
W8	29.05.2012	743.97	83.68	19.89	101.76	1455.26	32.66	-	-
W9	29.05.2012	26.71	3.83	17.60	32.47	36.52	26.49	-	-
W1	05.02.2013	2781	277	47	551.40	7067.70	296.67	2.84	7.72
W2	05.02.2013	4693	506	57	876.60	7679.77	249.47	-	1.15
W3	05.02.2013	5137	560	53	972.40	9051	247.60	-	25.20
W6	05.02.2013	3915	406	44	709.00	6238.95	155.58	-	26.96
W4	05.02.2013	14155	1392	104	2256.50	25605.40	184.59	-	14.70
W5	05.02.2013	5203	551	57	943.20	8512.30	185.08	-	34.08
W7	05.02.2013	1007	108	29	208.90	1504.20	58.09	-	21.77
W8	05.02.2013	1027	104	33	241.60	1538.29	51.31	0.32	7.35
W9	05.02.2013	23.23	3	21.34	64.25	32.52	41.08	0.06	7.89
W1	15.04.2013	4138	415	67	831.70	8025.70	443.96	-	3.41
W2	15.04.2013	8643	903	65	1536.40	15956.40	314.76	-	11.59
W3	15.04.2013	8019	835	55	1372.10	14900.10	196.25	-	48.09
W4	15.04.2013	8575	896	62	1504.10	16759.20	227.26	-	54.31
W5	15.04.2013	9468	1000	65	1663.90	17392.90	219.84	-	18.17
W7	15.04.2013	952	93	31	201.00	1685.12	55.80	6.42	1.81
W8	15.04.2013	948	89	32	213.40	1540.35	54.61	-	2.89
W9	15.04.2013	27	3.92	26.95	73.31	37.76	49.42	-	2.28
W10	15.04.2013	1718	97	130	469.90	2385.94	177.37	-	15.77
W11	15.04.2013	16165	914	336	2117.80	28273.50	697.98	-	10.38
	EPA	-	-	-	-	250	250	44.30	-
	ITASHY	200	-	50	200	250	250	50	-



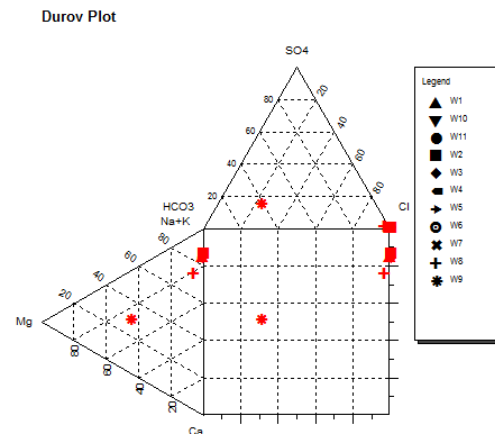
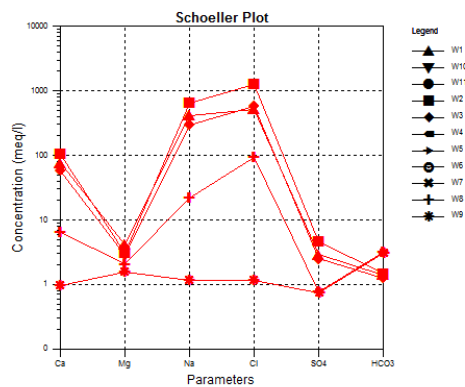
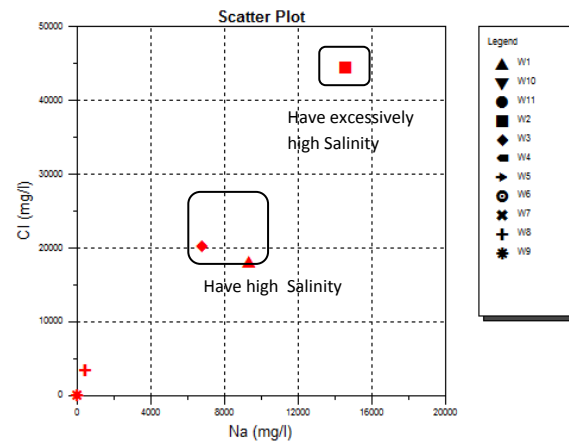
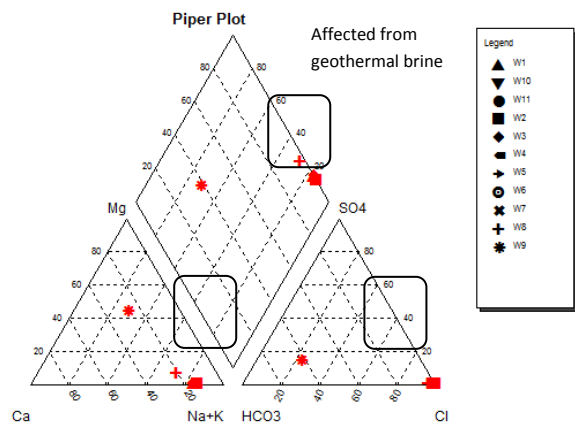


Figure 6.8. Piper, Durov, Schoeller and Scatter Diagrams of February 2012

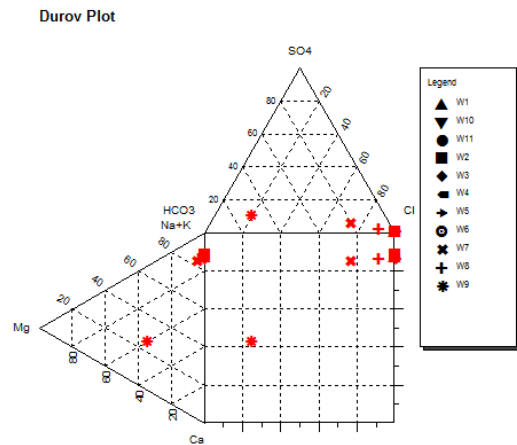
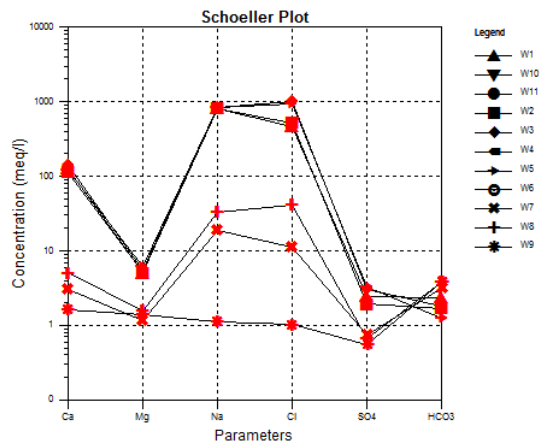
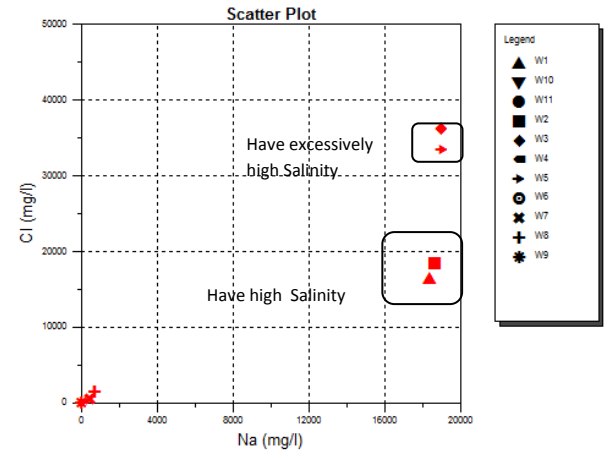
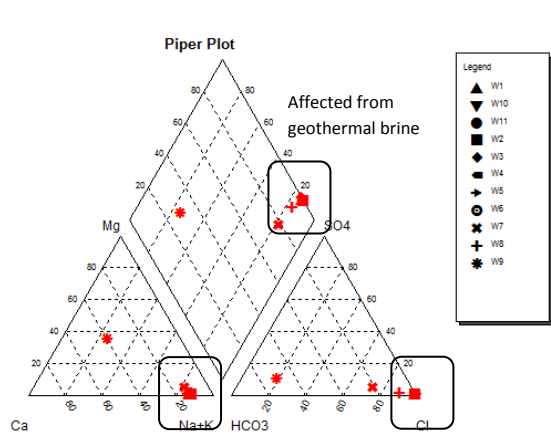


Figure 6.9. Piper, Durov, Schoeller and Scatter Diagrams of May 2012

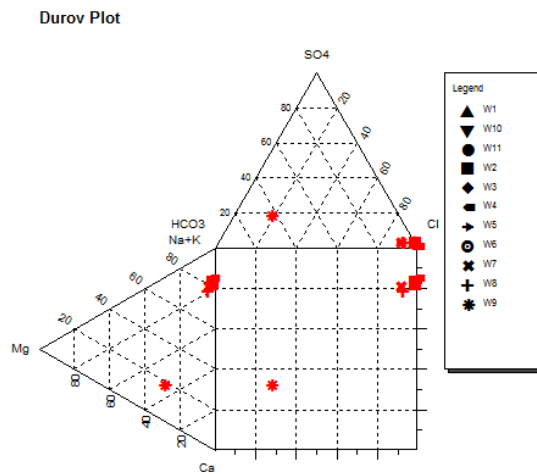
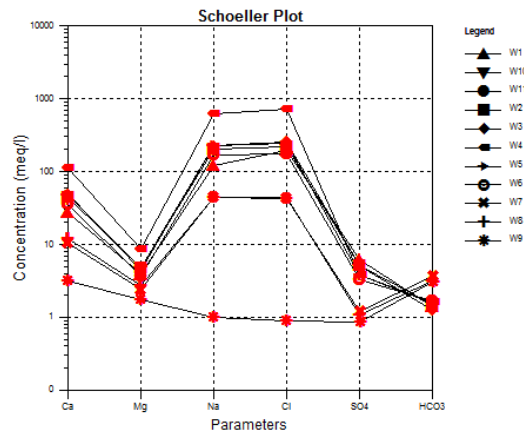
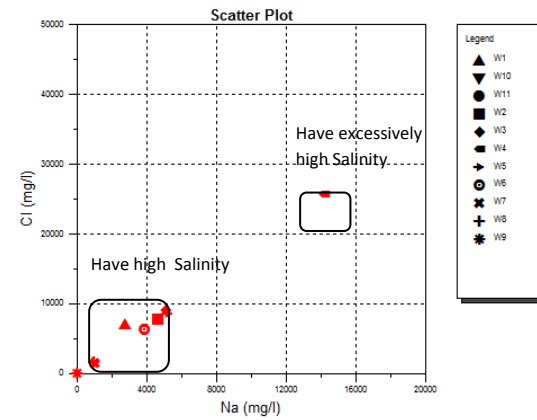
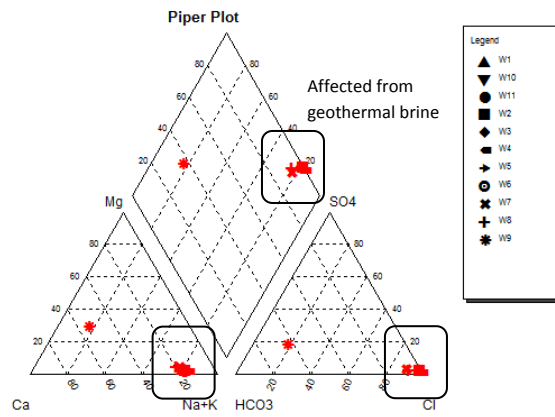


Figure 6.10. Piper, Durov, Schoeller and Scatter Diagrams of February 2013

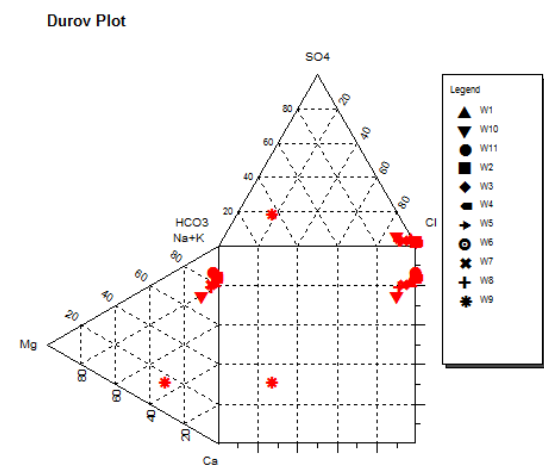
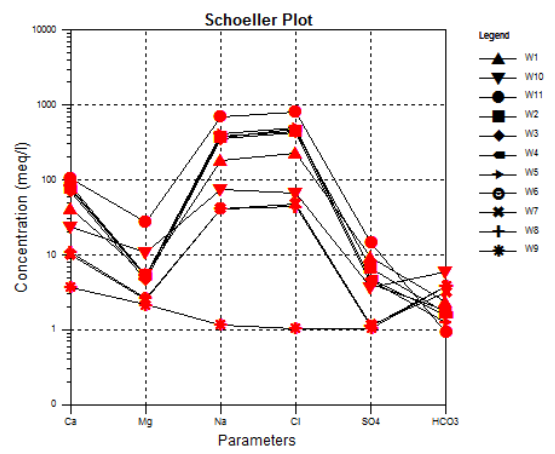
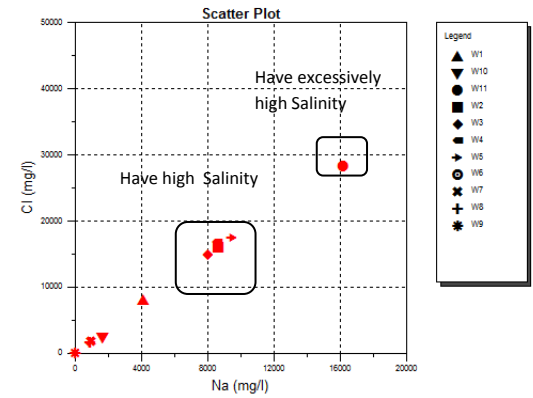
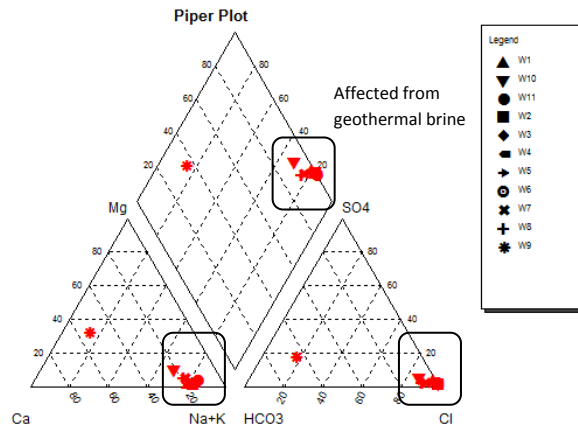


Figure 6.11. Piper, Durov, Schoeller and Scatter Diagrams of April 2013

In February 2013 sampling period,  $\text{HCO}_3^-$  values ranged from 75.64 mg/L to 224.48 mg/L with an average value of 128.1 mg/L. The minimum  $\text{HCO}_3^-$  value of 75.64 mg/L was measured at W3 (in front of the destroyed house). The maximum  $\text{HCO}_3^-$  value of 224.48 mg/L was measured at close point to T7 geothermal well on the Tuzla River (W7) (Figure 6.12.).  $\text{HCO}_3^-$  values ranged from 57.34 mg/L to 364.78 mg/L with an average value of 160.918 mg/L in April 2013 sampling period. The minimum  $\text{HCO}_3^-$  value of 57.34 mg/L was measured at W11 (under-the-bridge that is close to W10 sampling point). The maximum  $\text{HCO}_3^-$  value of 364.78 mg/L was measured at a new drill discharge at south west of the study area (W10).

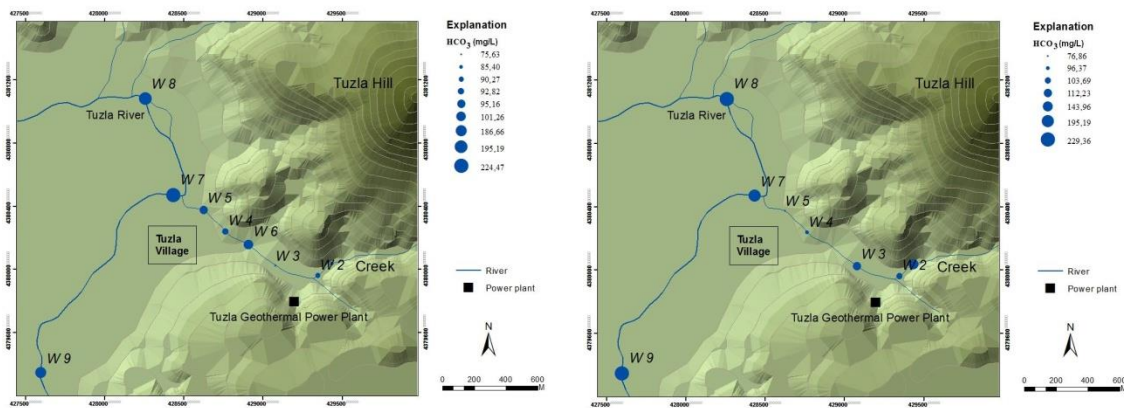


Figure 6.12.  $\text{HCO}_3^-$  Distribution Maps for Surface Water in February 2013 and April 2013

Due to the saline geothermal brine of Tuzla, surface water included high amounts of sodium and chlorine. The maximum sodium concentration of 14568.31 mg/L was measured at W2 in February 2012, and 19013.35 mg/L at W5 in May 2012. The maximum sodium value of 14155 mg/L was measured at W4 where is at the leakage point. In February 2013 sampling period, maximum sodium value (16165 mg/L) was measured at W11. In all sampling periods the minimum sodium values were measured at under-the-bridge that on the Tuzla River (W9) from 23.23 to 27.6 mg/L. (Figure 6.14.). Sodium values were measured between 5000 and 14000 ppm by Baba et al. (2005) in Tuzla geothermal field. The highest values of sodium did not change remarkably however at some sampling points sodium concentration decreased.

The maximum chlorine concentration of 44327.3 mg/L was measured at W2 as sodium concentrations in February 2012 and 36172 mg/L at W5 in May 2012 sampling period. The maximum chlorine value of 26605.4 mg/L, was measured at W4 in February 2013. In April 2013 sampling period, maximum chlorine value of 28273.5 mg/L was measured at W11. In all sampling periods the minimum values of chlorine were measured at W9 (under-the-bridge that on the Tuzla River) changed from 32.51 to 41.42 mg/L (Figure 6.15.). Both W8 and W9 sample locations are on the Tuzla River. However, W9 has not been affected by geothermal fluid because of the flow direction of the River. Comparasion of sodium and chlorine values of these two locations were given in Figure 6.13.

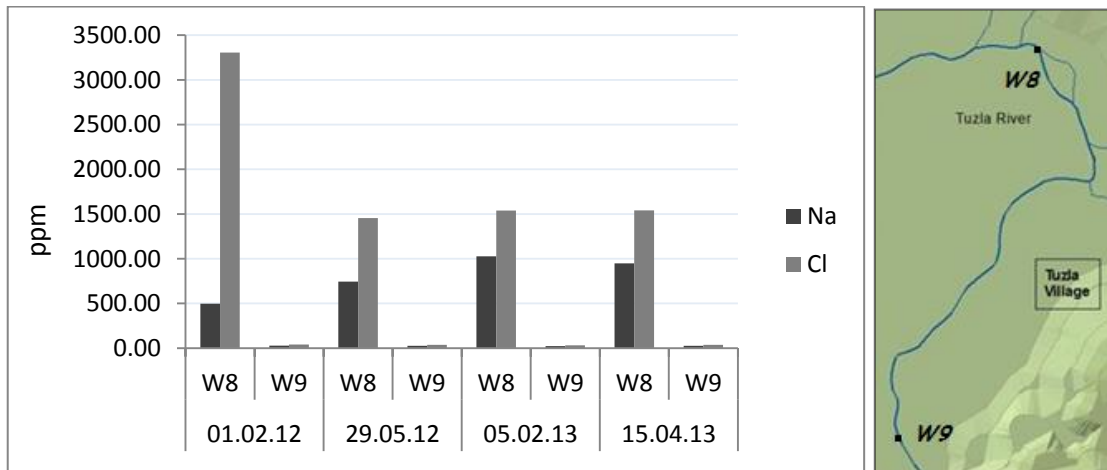


Figure 6.13. Comparasion of the Conductivities of W8 and W9 in Four Periods

Geothermal of Tuzla has a saline water character. Low chlorine and sodium results indicated that W9 was not affected from geothermal fluid due to its location (see Figure: 5.2.). From W1 to W6 surface water sample locations are all on the creek. Sodium and chlorine values of these points were excessively high. These results clearly indicated that the creek has been affected by geothermal brine. W7 and W8 sample locations are also on the Tuzla River. These locations were affected by geothermal because of direction of the river flow. Still W7 and W8 samples included low concentrations of sodium and chlorine due to the dilution of water that interfere from creek into the river.

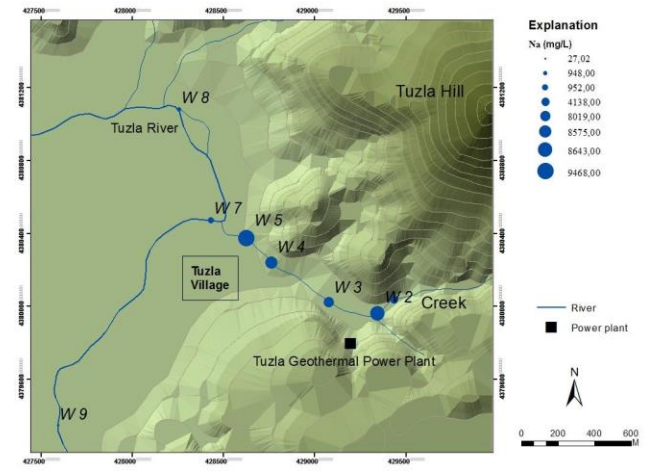
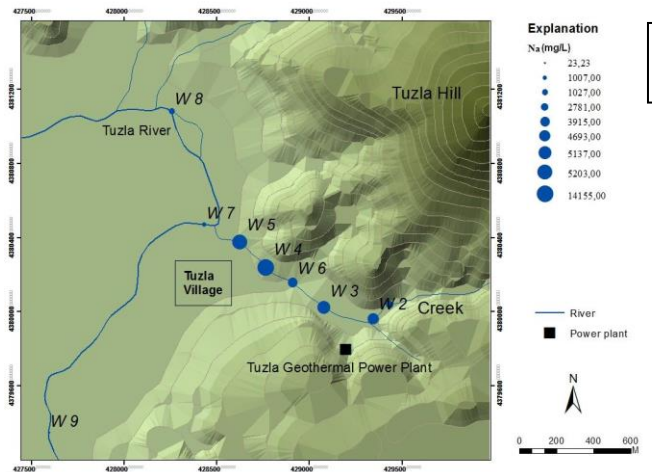
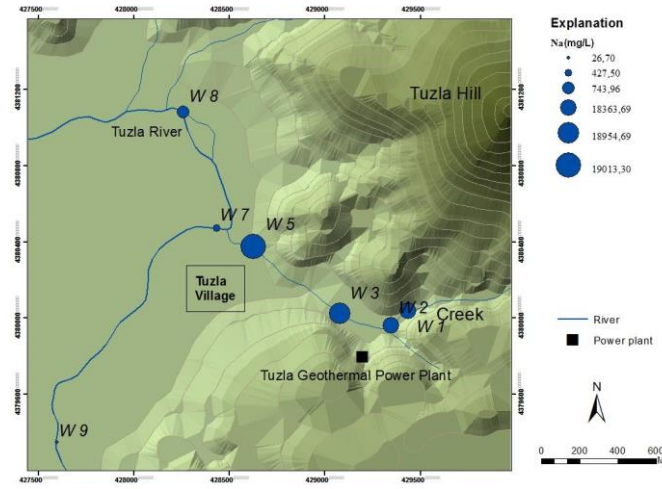
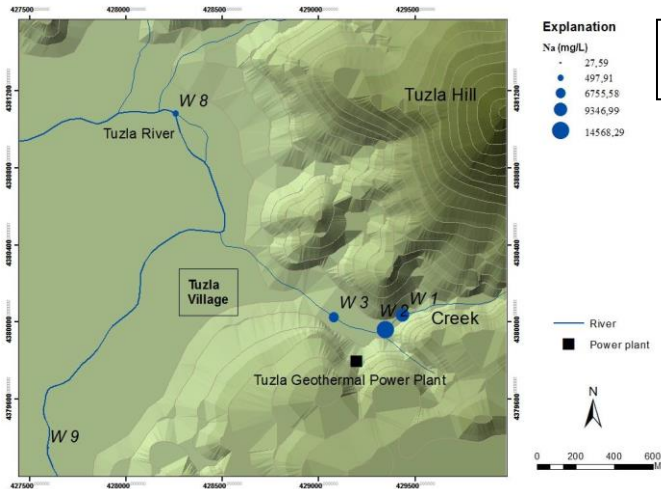


Figure 6.14. Na Distribution Map for Surface Water of Tuzla Geothermal Field

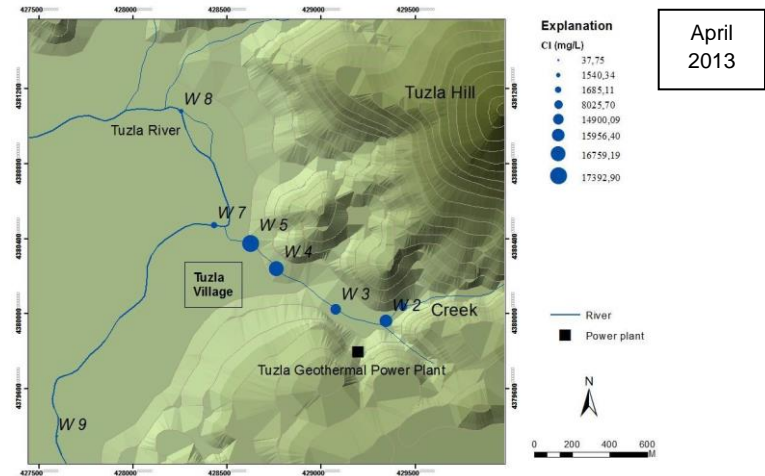
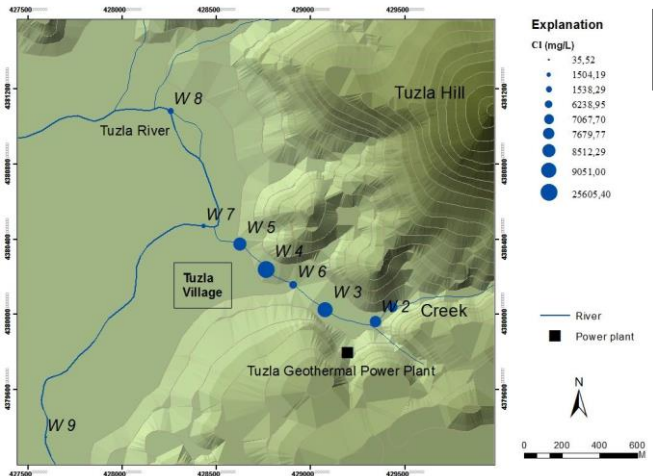
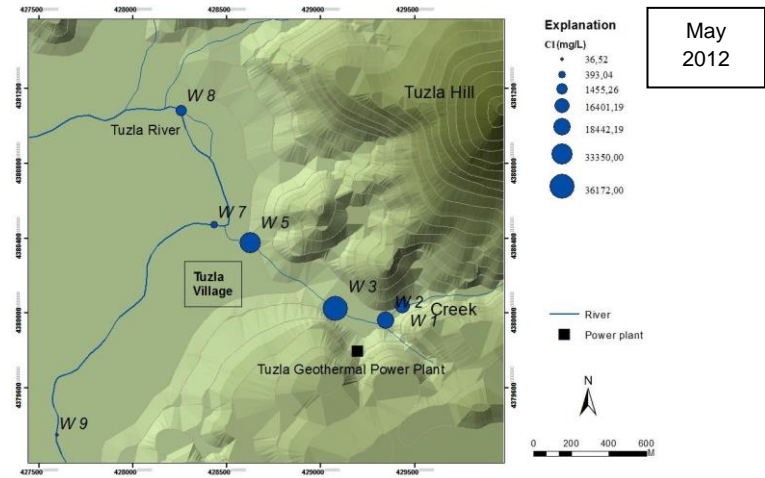
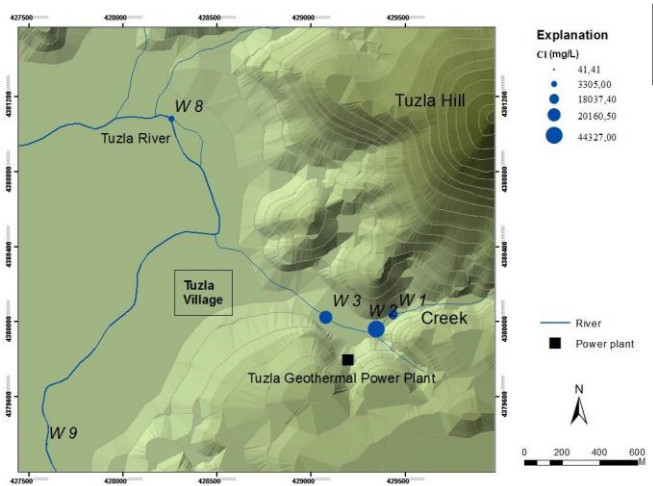


Figure 6.15. Cl Distribution Map for Surface Water of Tuzla Geothermal Field



Calcium concentrations of samples that are on the Tuzla River are (W7, W8 and W9) mostly below the ITASHY standard value of 200 mg/L. On the other hand, the other surface water calcium values were excessively upon the limit. The maximum calcium value of 2056.65 mg/L was measured at W2 in February 2012 sampling period. In May 2012 sampling period, maximum Calcium concentration was measured 2834 mg/L at W3. The maximum calcium concentration of 2256.5 mg/L was measured at W4 at 15.02.13 and 2117.8 mg/L at W11 in April 2013 sampling period. In all periods the minimum values of Calcium were measured 19.33, 32.47, 64.25 and 73.31 mg/L respectively at W9 (under-the-bridge that on the Tuzla River) (Figure 6.16.).

In February 2012, the maximum magnesium concentration of 49.14 mg/L was measured at W1. The maximum magnesium value of 75.08 mg/L was measured at W5 in May 2012 sampling period. As many other elements, maximum magnesium value of 104 mg/L at W4 in February 2013 and 336 mg/L were measured at W11 in April 2012 sampling period. Magnesium concentrations of samples that are on the Tuzla River are (W7, W8 and W9) mostly below ITASHY standard value of 50 mg/L. In all periods the minimum values of magnesium were measured at W9 (under-the-bridge that on the Tuzla River) respectively 19.33, 1.77, 21.34 and 26.95 mg/L (Figure 6.17.).

All measured SO<sub>4</sub> values in February 2012 and May 2012 were below ITASHY standard value of 250 mg/L. In all periods the minimum values of sulfate measured at W9 (under-the-bridge that on the Tuzla River). In February 2013 sampling period, only W1 was upon the standard with a concentration of 296.67 mg/L. SO<sub>4</sub> values ranged from 49.42 to 697.98 mg/L in April 2013 sampling period (Figure 6.18.).

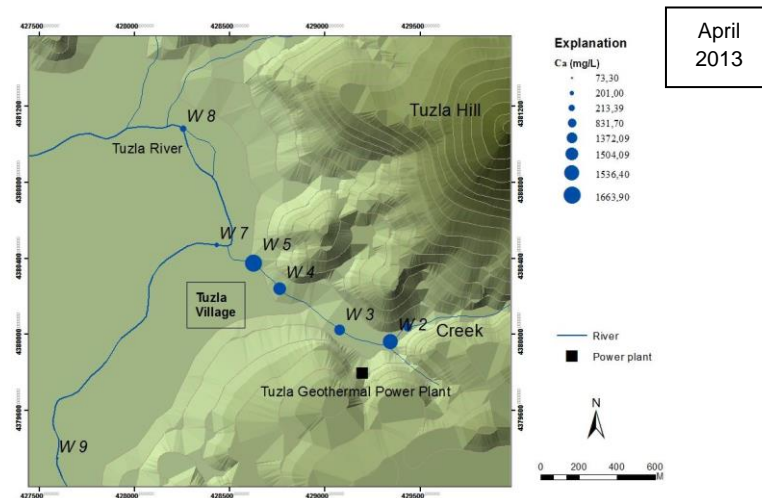
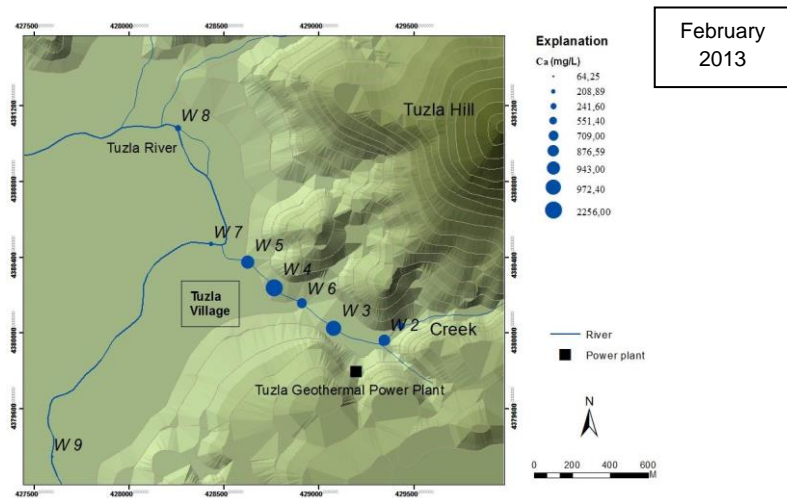
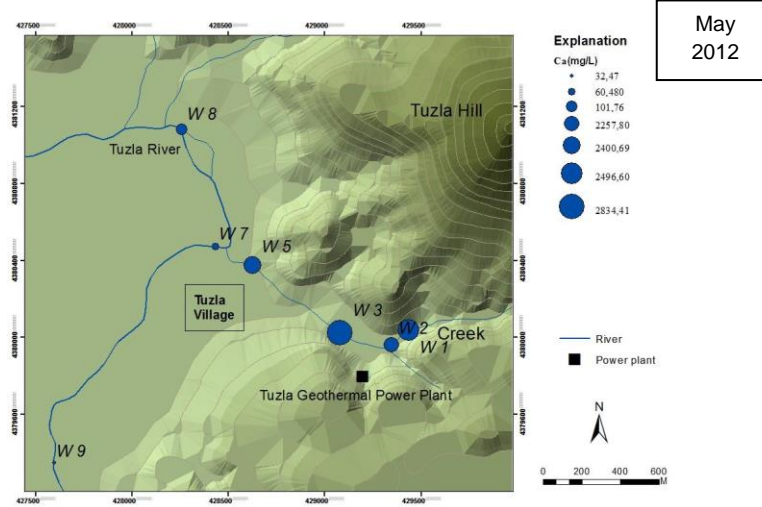
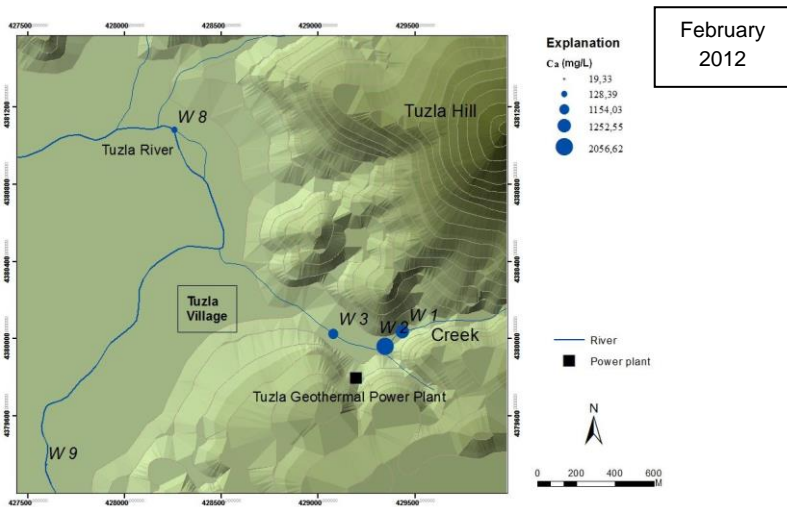


Figure 6.16. Ca Distribution Map for Surface Water of Tuzla Geothermal Field

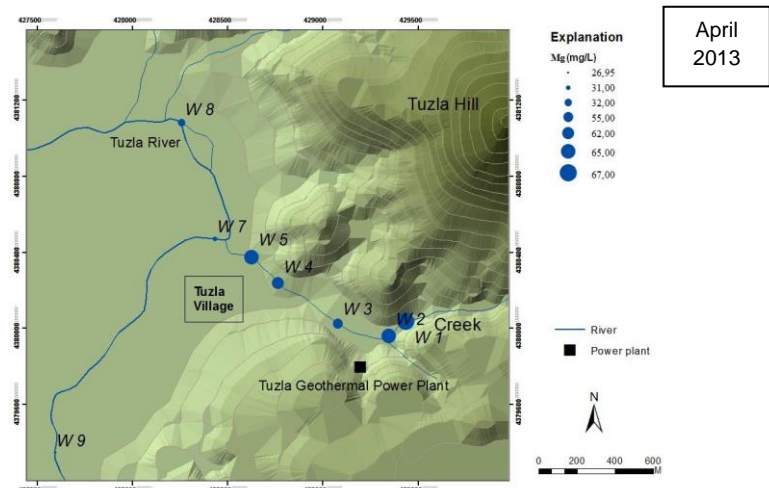
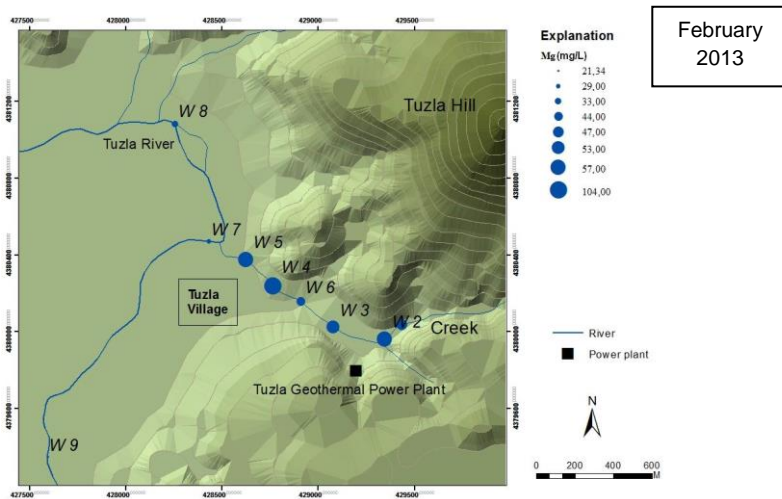
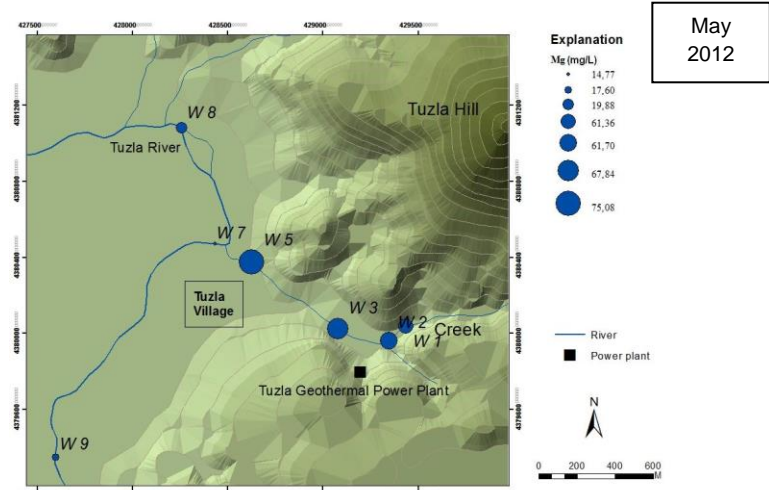
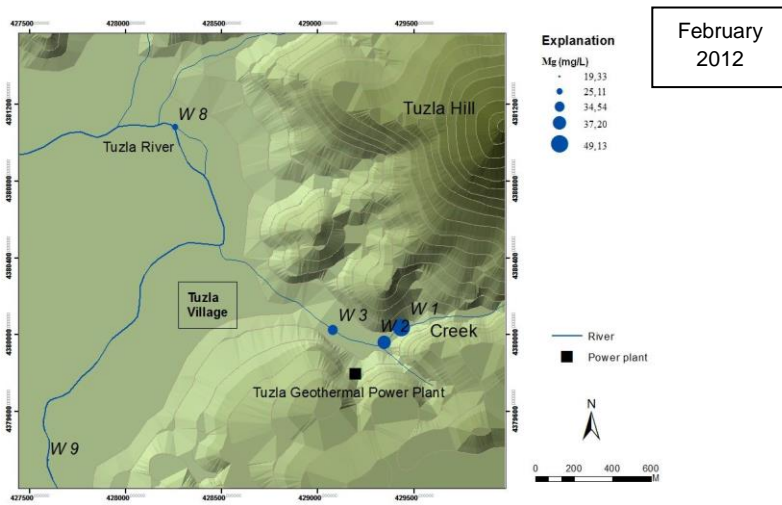


Figure 6.17. Mg Distribution Map for Surface Water of Tuzla Geothermal Field

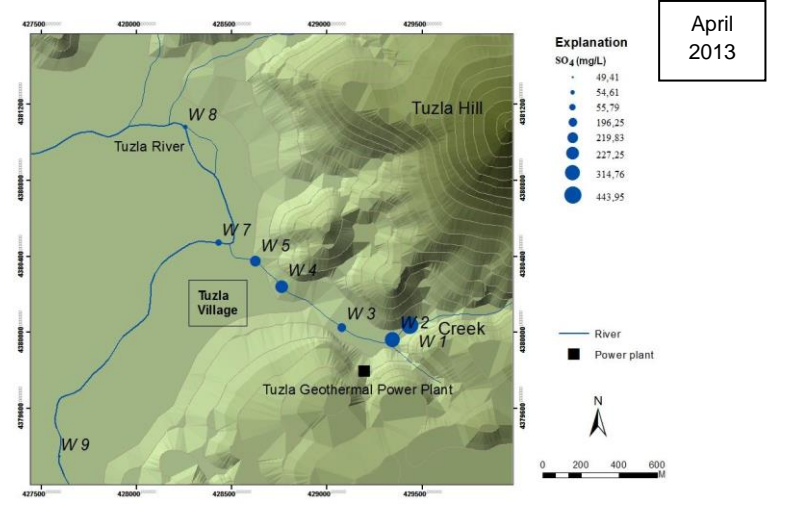
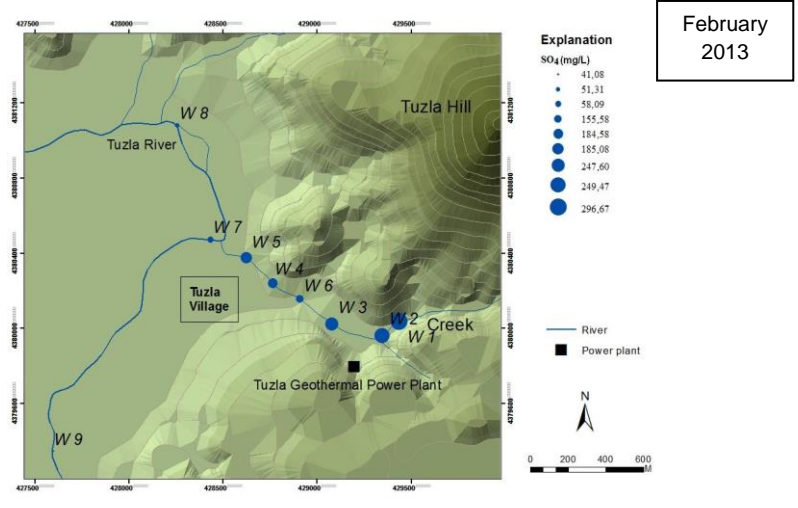
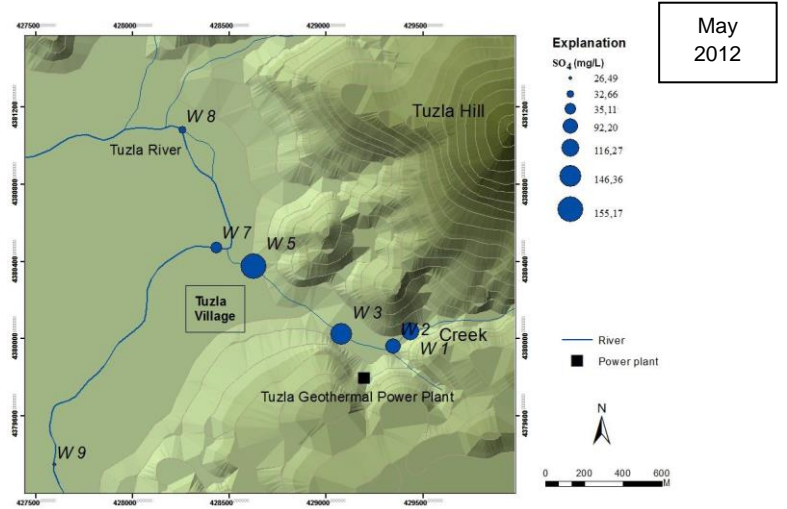
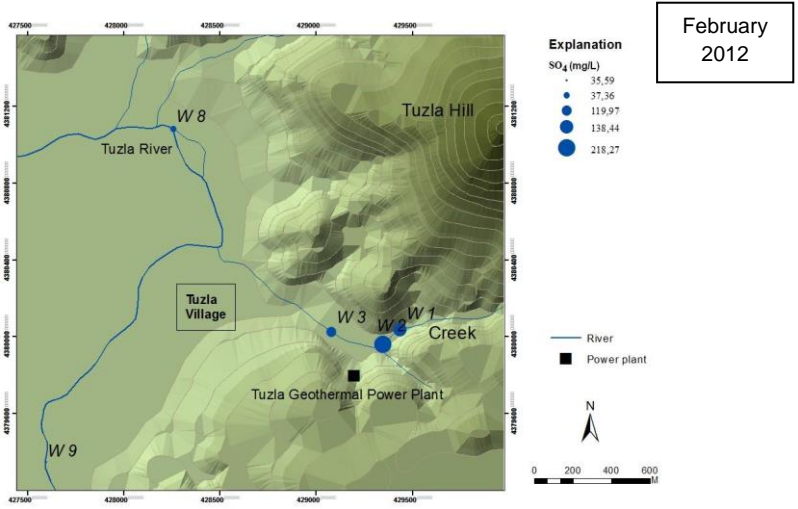


Figure 6.18.  $SO_4$  Distribution Map for Surface Water of Tuzla Geothermal Field

In February 2012 sampling period, the minimum potassium value of 3.14 mg/L was measured at under-the-bridge on the Tuzla River (W9). As well as the maximum value of potassium, 1181.23 mg/L, was measured at near the fountain (W2) (Figure 6.19). During all sampling periods minimum potassium values were measured at W9 sampling point. In May 2012, the maximum potassium value of 2206 was measured at point in front of the destroyed house (W3). In February 2013 and April 2013 the maximum potassium values were measured at W4 and W5.

Major anion and cation concentrations represent the type of surface water. One sampling point was (W9) chosen to understand the background data that was not affected directly. The analyses results showed that the points which were on the creek and near the geothermal springs (W1-W6) had the most concentration of major anion and cations, especially sodium and chlorine. The upstream (W8) of the Tuzla river had higher concentrations of anion and cations than the downstream (W9) of the river.

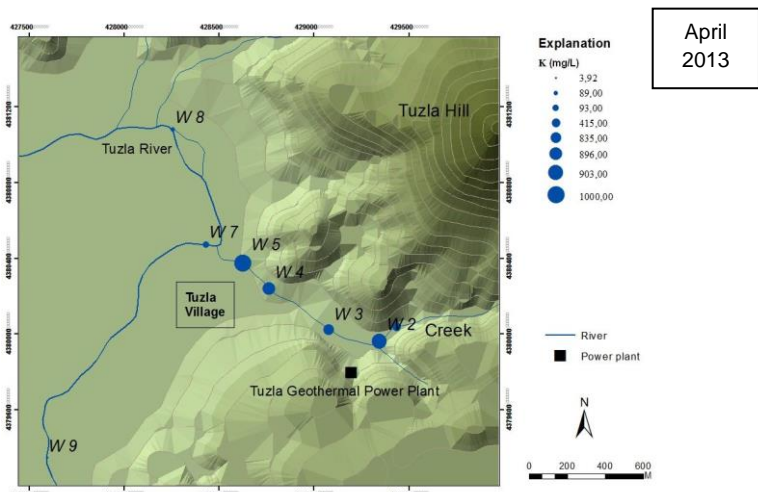
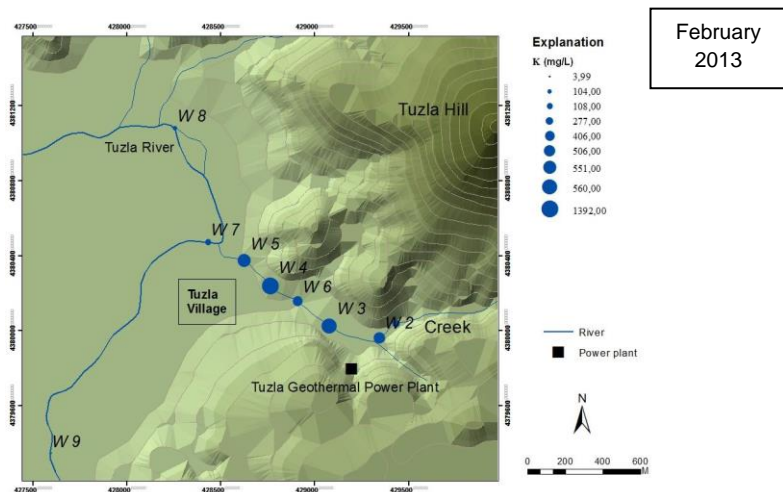
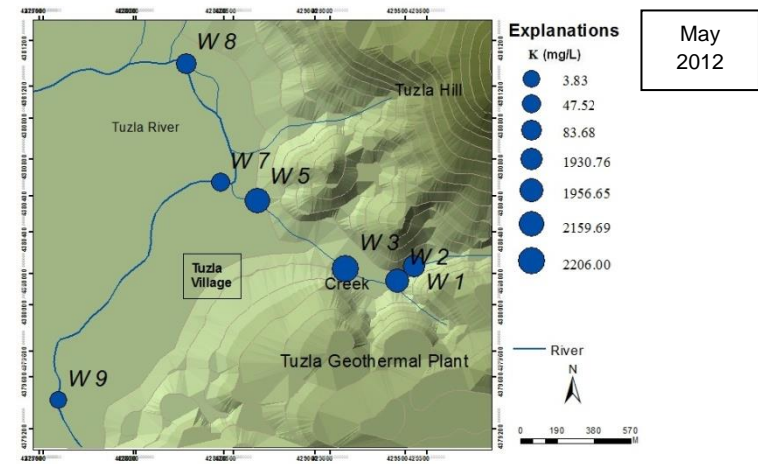
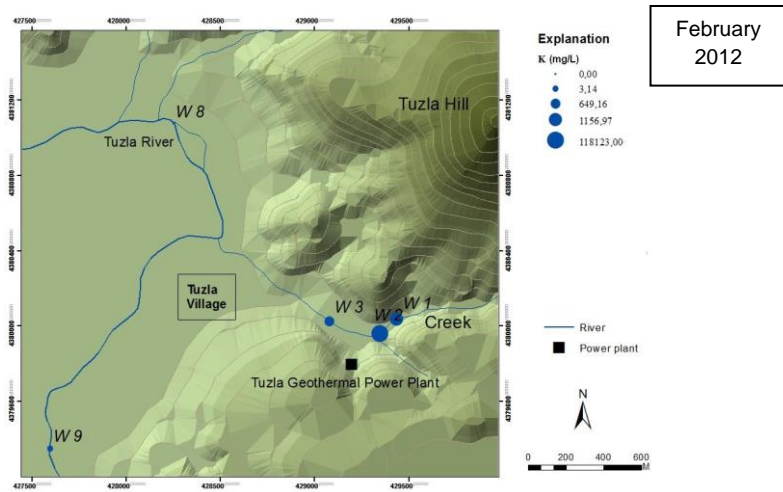


Figure 6.19. K Distribution Map for Surface Water of Tuzla Geothermal Field

### 6.2.3. Trace Elements and Heavy Metals

Presence of the most heavy metals and trace elements in water depend on parameters such as pH, temperature, pressure, rock type as well as their solubility, and presence of some oxyhydroxides. To comprehend the effect of geothermal fluid on surface water, element analyses were done. Some metals were analyzed in surface water in Tuzla region (see Table 6.5.). The concentrations of these minor components B, Ba, Br, F, Mn, Li and Sr of the surface waters ranged from 0.04 to 27.121; from 0.14 to 4.11; from 0.07 to 67.29; from 0.11 to 2.82; from 0.02 to 5.56; from 0.01 to 26.94 and from 0.38 to 162.29 mg/L, respectively. The results showed that, boron and strontium concentrations in surface waters were extremely high in the Tuzla geothermal field when compared with national and international surface water standards.

Li values ranged from 0.001 mg/L to 13.23 mg/L with an average value of 6.77 mg/L February 2013 sampling period. The minimum Li value of 0.001 mg/L was measured at W9 (under-the-bridge that on the Tuzla River). The maximum Li value of 13.23 mg/L was measured at near the fountain (W2). The minimum Li value of 0.01 mg/L was measured at W9 (under-the-bridge that on the Tuzla River). The maximum Li value of 26.935 mg/L was measured in front of the destroyed house (W3). In may 2013, Li values ranged from 0.012 mg/L to 20.616 mg/L with an average value of 6.09 mg/L. The minimum Li value of 0.012 mg/L was measured at W9 (under-the-bridge that on the Tuzla River). The maximum Li value of 20.616 mg/L was measured at in front of Tuzla spa (W4). Li values range from 0.016 mg/L to 14.589 mg/L with an average value of 7.63 mg/L In 15/04/13 sampling period. The minimum Li value of 0.016 mg/L was measured at W9 (under-the-bridge that on the Tuzla River). The maximum Li value of 14.589 mg/L was measured at under-the-bridge that close to W10 sampling point (W11) (Figure 6.21.). According to data from Tuzla results, especially in May 2012 surface water contained highly Li. The lithium values on the creek were greater than 23.90 mg/L. In the last period, due to the regeneration around the geothermal field, Li concentrations of surface water reduced. Lithium is taken up by plants when it is not necessary for plant growing. Environmental toxicity of lithium is low and does not tend to deposit in tissues. However, when lithium is at 10 ppm in blood, a person is mildly-poisoned and at 20 ppm lithium indicates a risk of death (Aral and Sadus, 2008).

Table 6.5. Heavy Metals of Tuzla Surface Water

Sample	Sampling Date	B (mg/L)	Ba (mg/L)	Br (mg/L)	F (mg/L)	Mn (mg/L)	Li (mg/L)	Sr (mg/L)
W1	25.02.2012	15.05	2.21	-	0.98	2.85	12.36	84.59
W2	25.02.2012	24.47	3.50	50.05	0.14	5.40	13.23	14.37
W3	25.02.2012	13.25	2.03	22.07	-	2.97	7.72	78.71
W8	25.02.2012	0.75	-	1.69	-	0.36	0.51	-
W9	25.02.2012	-	-	-	-	-	0.00	-
W1	29.05.2012	23.86	3.58	32.42	-	5.28	23.90	145.30
W2	29.05.2012	27.12	4.11	36.21	-	5.56	26.94	162.28
W3	29.05.2012	26.73	4.10	67.29	-	4.63	26.71	162.29
W5	29.05.2012	25.44	3.94	61.65	-	3.25	25.39	154.05
W7	29.05.2012	0.52	0.21	1.39	0.31	0.25	0.42	2.76
W8	29.05.2012	1.19	0.31	2.03		0.41	1.10	6.38
W9	29.05.2012	0.05	0.13	-	0.11	0.01	0.01	0.38
W1	05.02.2013	4.14	0.50	7.79	1.35	0.95	3.77	26.88
W2	05.02.2013	7.56	1.07	11.82	1.29	1.70	6.95	45.62
W3	05.02.2013	8.22	1.27	16.64	1.41	1.93	7.62	49.78
W6	05.02.2013	6.09	1.10	10.57	1.02	1.33	5.62	36.18
W4	05.02.2013	20.24	5.57	44.70	2.50	3.86	20.62	119.76
W5	05.02.2013	8.23	1.64	15.36	1.32	1.61	7.53	48.63
W7	05.02.2013	1.67	0.39	2.37	1.39	0.47	1.32	8.31
W8	05.02.2013	1.60	0.35	2.54	0.34	0.41	1.38	9.67
W9	05.02.2013	0.04	0.14	0.07	0.16	0.02	0.01	0.52
W1	15.04.2013	6.46	0.82	13.35	1.88	1.44	5.80	40.56
W2	15.04.2013	13.64	1.94	29.54	2.17	2.96	12.90	81.56
W3	15.04.2013	12.85	1.90	33.15	1.73	2.61	11.90	74.71
W4	15.04.2013	13.56	2.17	29.52	2.82	2.91	12.90	81.24
W5	15.04.2013	15.35	2.38	32.81	2.09	2.99	14.60	91.04
W9	15.04.2013	0.04	0.18	0.10	0.18	0.16	0.00	0.55
W7	15.04.2013	1.61	0.37	2.79	0.49	0.37	1.30	8.61
W8	15.04.2013	1.43	0.33	2.64	0.30	0.41	1.20	8.73
W10	15.04.2013	1.67	0.50	6.42	0.22	0.17	1.20	8.78
W11	15.04.2013	13.60	1.37	71.39	3.15	0.73	14.60	58.59
	EPA	5.00	2.00	-	4.00	0.50	2.50	17.00
	ITASHY	1.50	-	-	1.50	0.50	-	-



Strontium exists in nature in celestite (strontium sulfate) and strontianite (strontium carbonate) form. Naturally, in earth's crust the total amount of strontium is estimated to be 430 g/ton; in sea water 10 ppm (Browning, 1969). Strontium behaves like calcium in the human body and attempt to accumulate in bone and blood-forming tissue. Strontium can join the food chain. In acut exposure the cancer risks may be high above the exposure limit of 25 mg/L and lifetime (chronic) exposure limit is 17 mg/L for non-cancerogenic Sr (EPA, 2002; EPA, 2007). Strontium concentrations were extreemly high at almost every sampling location. Strontium values reached to 162 ppm. Maximum values of strontium were measured at W2 and W3 in all periods. These points were located close to geothermal springs. During all sampling periods minimum strontium values were measured at W9 sampling point (Figure 6.19.). In four periods, maximum strontium values were measured at (84.59 mg/L) W1, (162.291 mg/L) W3 (119.76 mg/L) W4 and (91.043 mg/L) W5, respectively (Figure 6.23.). Both W8 and W9 sample locations are on the Tuzla River. However, W9 has not been affected by geothermal fluid because of the flow direction of the River. Comparasion of strontium concentrations of these two locations are given in Figure 6.20.

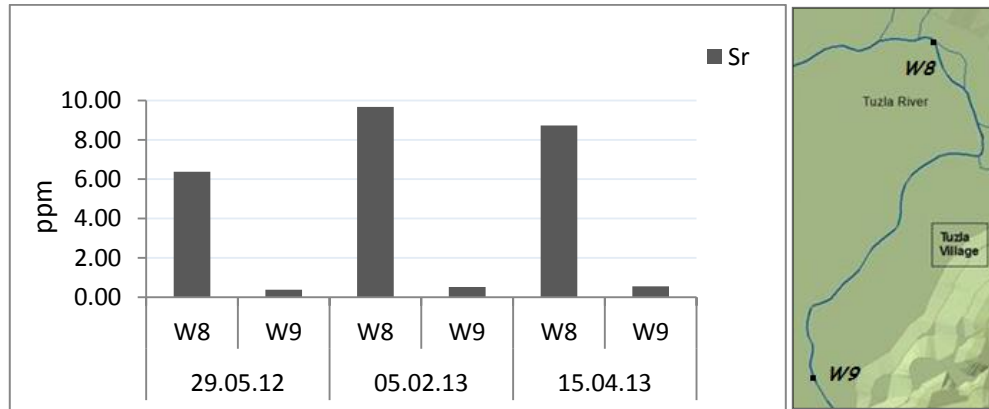


Figure 6.20. Comparasion of the Strontium Concentrations of W8 and W9 in Four Sampling Periods.

During all sampling periods minimum bromide values were measured at W9 sampling point (Figure 6.22.). In four periods maximum bromide values were measured at (50.05 mg/L) W2, (67.29 mg/L) W3, (44.7 mg/L) at W4 and (71.39 mg/L) at W11 respectively. The main natural source of bromide is sea and bromide concentration level in sea is approximately 67 ppm. In surface water bromide naturally exist with the range of 0,004 - 1 ppm.

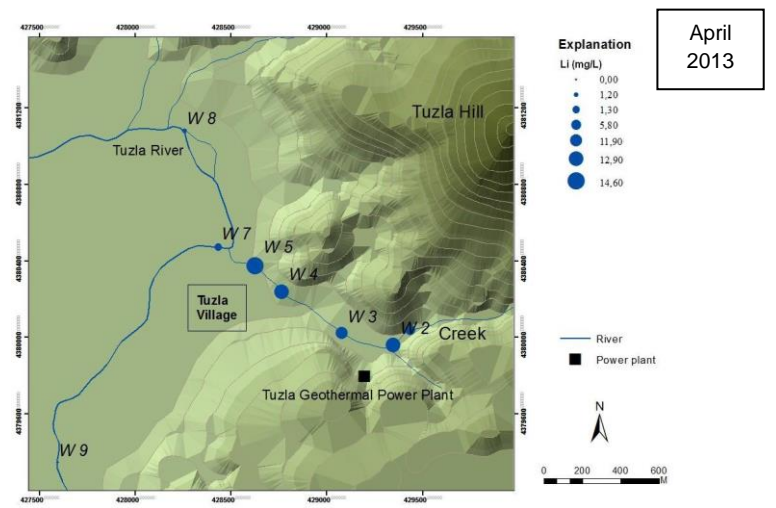
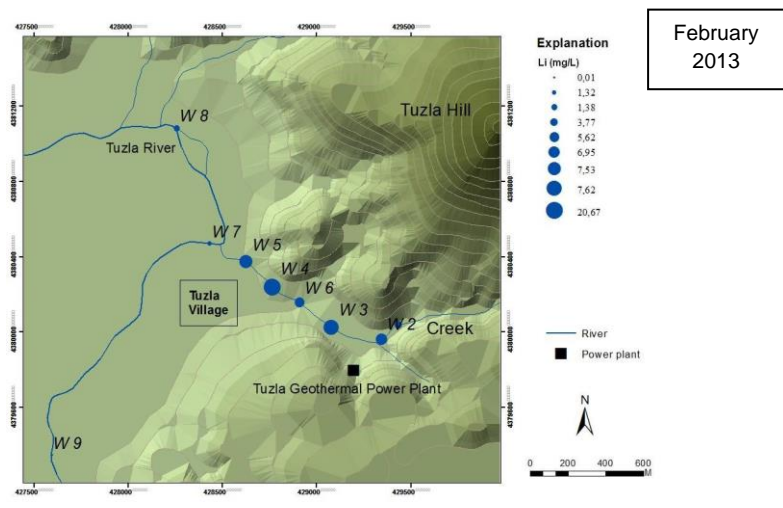
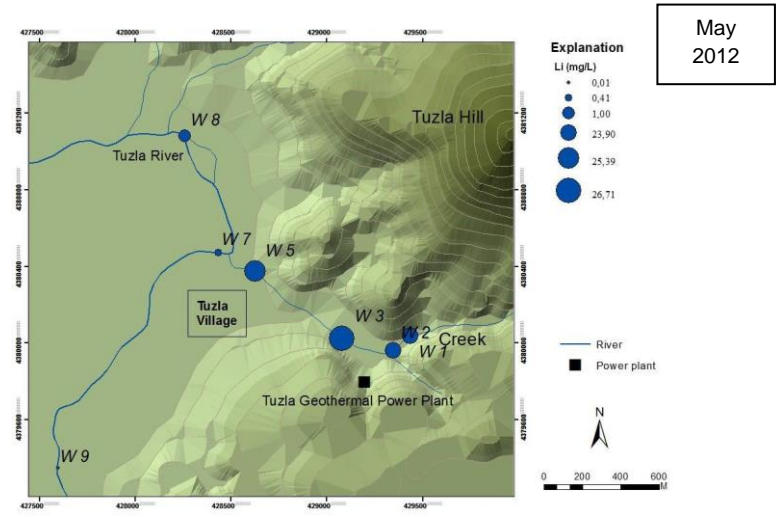
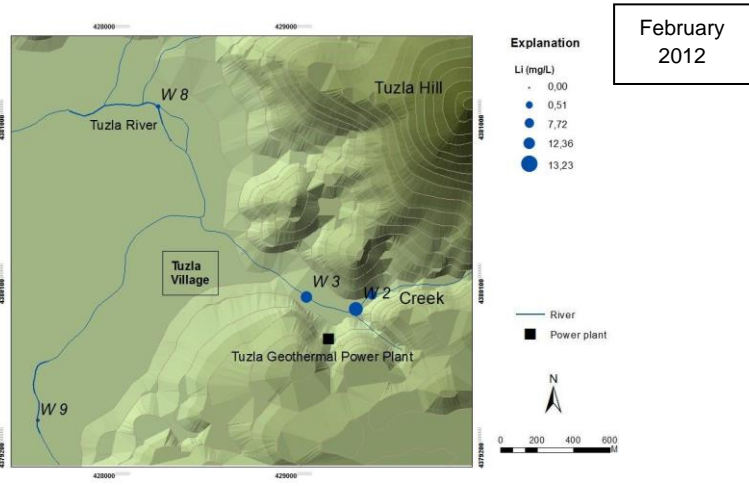


Figure 6.21. Li Distribution Map for Surface Water of Tuzla Geothermal Field

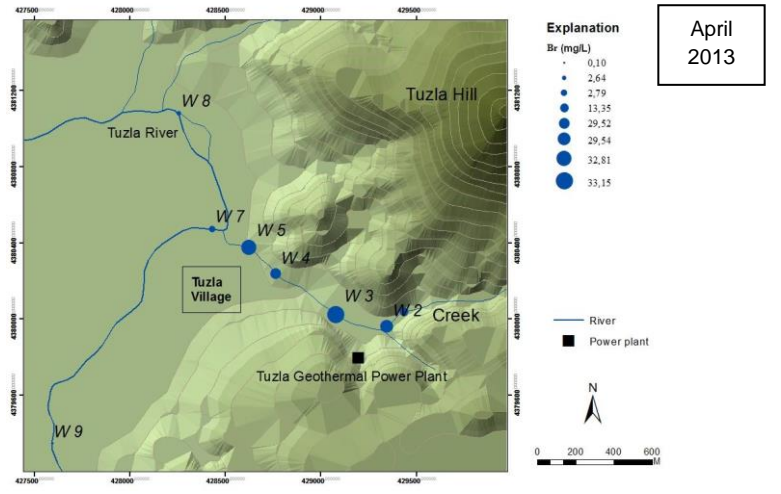
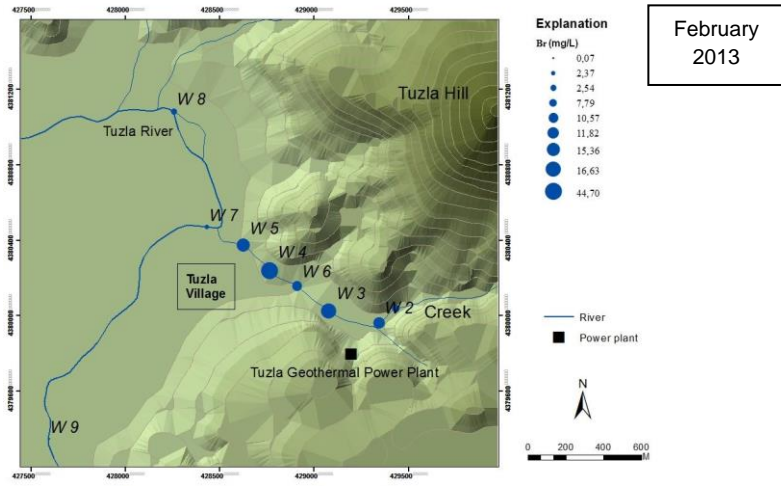
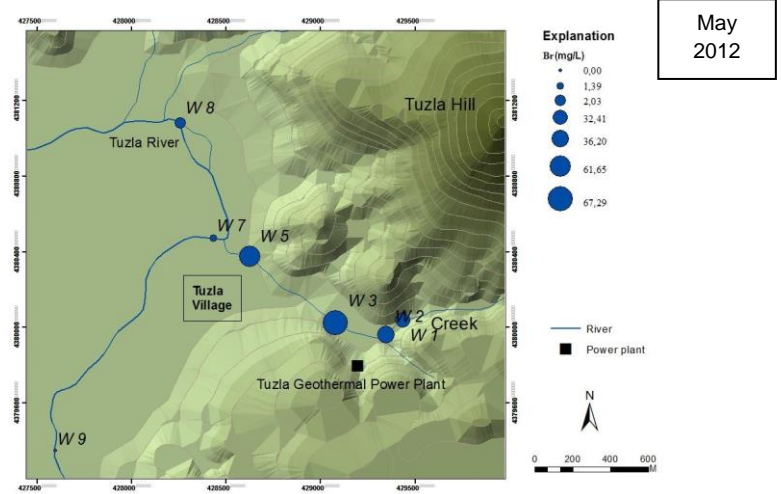
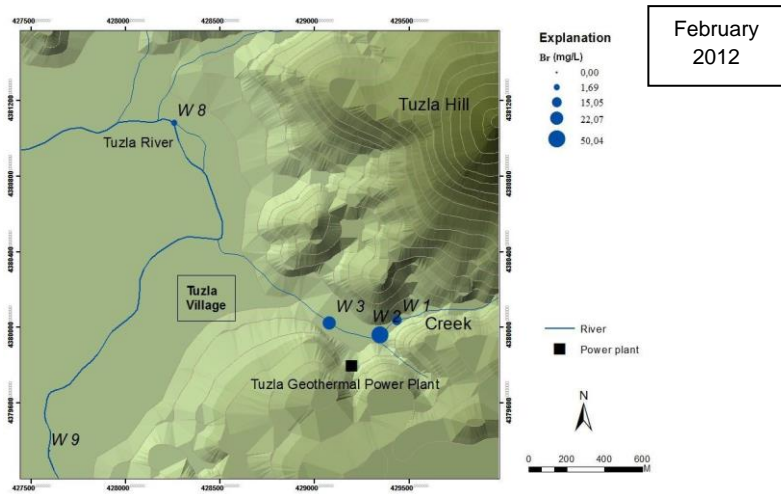


Figure 6.22. Br Distribution Map for Surface Water of Tuzla Geothermal Field

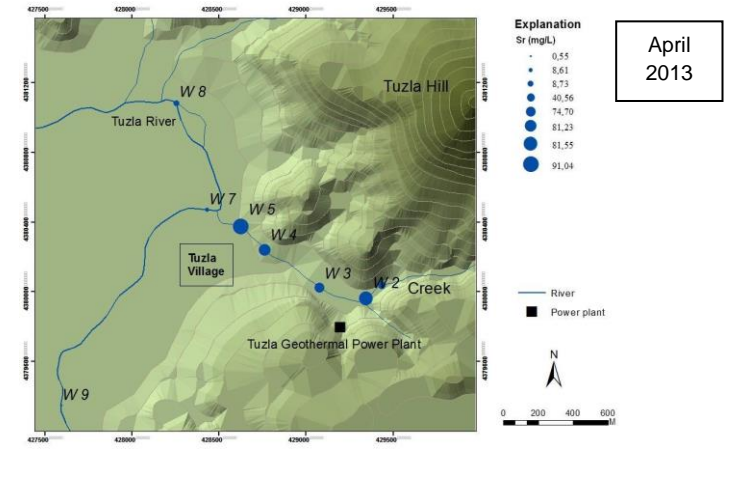
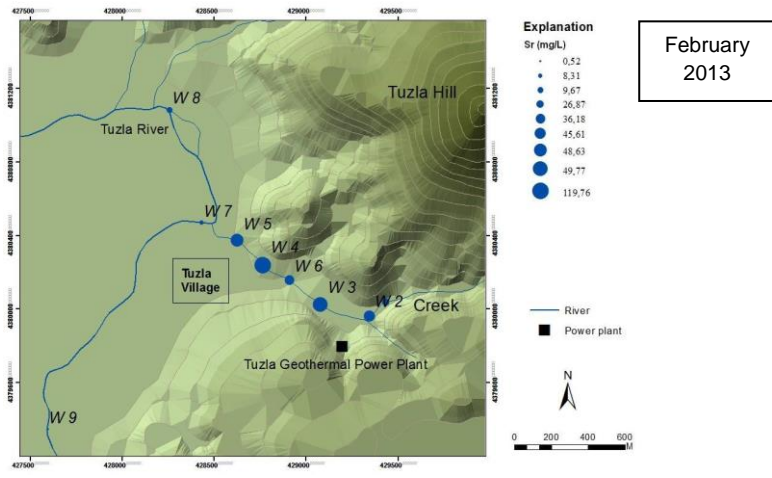
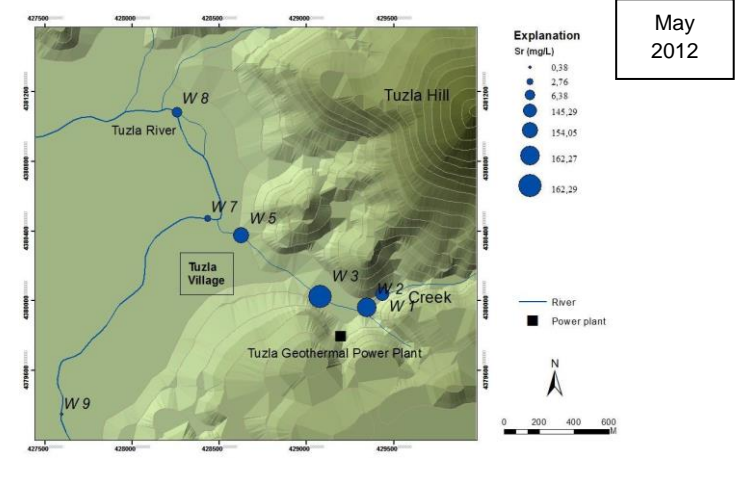
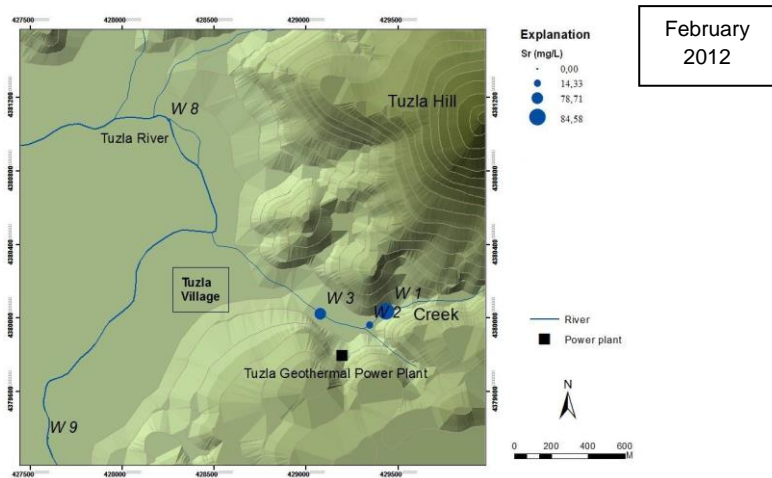


Figure 6.23. Sr Distribution Map for Surface Water of Tuzla Geothermal Field

During all sampling periods minimum boron values was measured at W9 sampling point. In four periods boron maximum values were measured at (24.47 mg/L) (27.121 mg/L) W2, (20.24 mg/L) W4 and (15.351 mg/L) W5 respectively (Figure 6.25.). In geothermal systems when steam and water parts of fluid separate, boron enters the water phase with the ratio of 99 %. Generally, boron concentrations are high in thermal waters in Turkey and this is related to volcanic and sedimentary rock origin (Baba and Armannsonn, 2006; Ellis, 1978). Up to 0.7 ppm boron is safe for sensitive crops (for example, grape, pear, orange, lemon) are in the soil saturation extract; 0.7-1.5 ppm can be acceptable as limit, and more than 1,5 ppm appears to be unsafe for all crops (Camp, 1963). Boron has an irritant effect to the mucus and skin, and is also phytotoxic even at low concentrations. Boron may be deposited on soils and, in case of leaching to underground, then it might interfere to groundwater. And also boron, in particular, can have a serious impact on vegetation. Concentrations of groundwater exceeding 1 mg/l are harmful to plants (Hunt, 2001; Richards 1954). According to these informations that were mentioned above, boron concentrations of surface water were extreamly high and these high concentration may had negative effects to plants and vegetation.

Both W8 and W9 sample locations are on the Tuzla River. However, W9 has not been affected by geothermal fluid because of the flow direction of the River. Comparasion of Boron concentrations of these two locations were given in Figure 6.24.

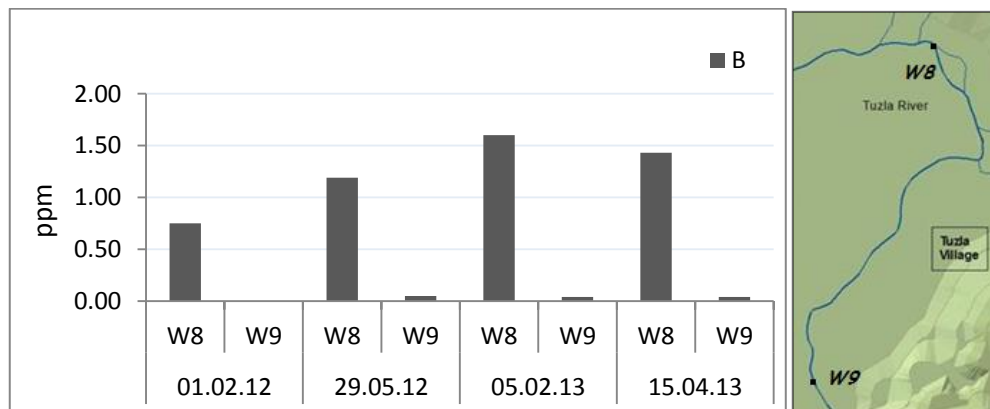


Figure 6.24. Comparasion of the Boron Concentrations of W8 and W9 in Four Sampling Period

In previous studies measured boron values were reached to 69 ppm and minimum measured boron value was 1.7 ppm in Tuzla geothermal field (Baba and

Armansson, 2008). After the study, the new arrangements had led to a considerably reduction in geothermal fluid interaction to surface water and boron values.

The results showed that Tuzla River has been affected from geothermal springs. The sampling points which were on the creek and near the geothermal springs (W2 and W3) had the highest concentrations of boron and strontium. Boron concentrations of W7 and W9, which were on the Tuzla River, were within the limits. However, these concentrations were quite close to the maximum allowed value (1.5 ppm) by national standard. The river is used for irrigation and agricultural activities by the people of Tuzla village. Nevertheless, the downstream of Tuzla River (W9) had metals and heavy metals which concentrations were not exceeded the national and international surface water quality limits. The results showed that only the part which were affected from geothermal fluid of the Tuzla river was not recommendable for consumption and agricultural activities.

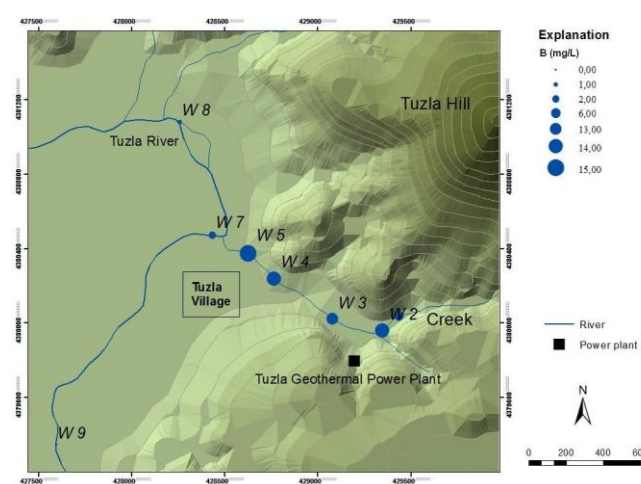
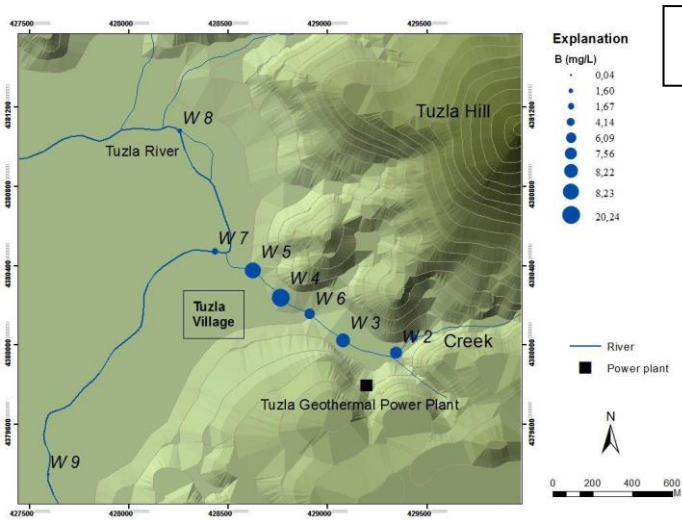
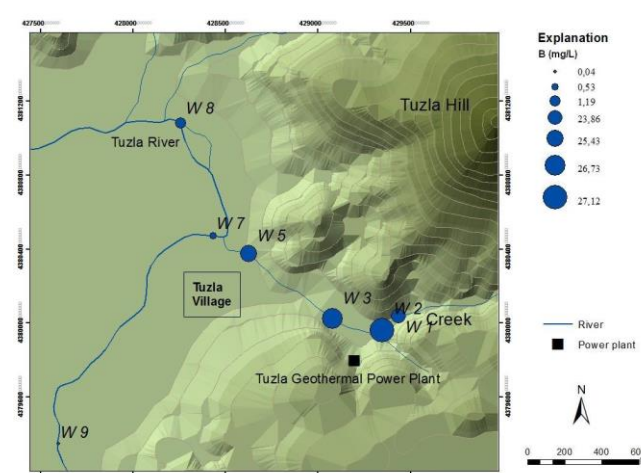
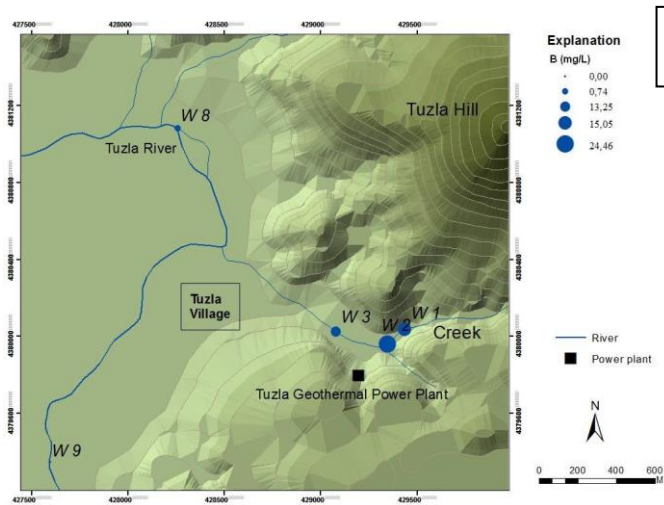


Figure 6.25. B Distribution Map for Surface Water of Tuzla Geothermal Field

### **6.3 Physical and Chemical Properties of Soil in Tuzla Geothermal Field**

In this section, to investigate the effect of the geothermal fluid on soil, some element analyses were conducted. Temperature and pH values and element content of soil is presented and discussed. According to the results, sodium and chlorine elements were found at very high amounts due to the high salinity. Silisium, aluminum, boron and barium values were also found above the national regulation.

Physical parameters (temperature and pH) of soil were measured during the field study instantly with a multi-parameter probe. The results of these measurements are given in Table 6.6. and represented in Figure 6.26. and Figure 6.27.

Measured pH values ranged between 6.18 and 8.70 with an average value of 7.20. The maximum pH value of 8.70 was measured at S1 location. The minimum pH value of 6.18 was measured at on the creek in front of entrance of Tuzla village label (S5). In May 2012, measured temperature of soil values ranged from 22 °C to 30.8 °C with an average value 26.1 °C. The maximum temperature value 30 °C was measured in S1 location (beginning spot of creek) which had the same coordinates with W1 sampling point. Minimum temperature value of 22.4 °C was measured at a close point to T15 geothermal well (S14).

In second sampling period (February 2013) measured temperature values ranged from 16.2 °C to 22.7 °C with an average value of 18.42 °C. The maximum temperature value of 22.7 °C was measured at S1 like previous period and minimum temperature value of 16.2 was measured at S3 (reinjection of geothermal fluid was interfered with creek). Measured pH values were around natural pH with an average of 6.88.

In April 2013, measured temperature values ranged from 18.1 °C to 25.4 °C with an average value of 20.66 °C. The maximum temperature value of 25.4 °C was measured at a point near to a fountain (S2) and the minimum temperature value of 18.1 was measured at close point to T11 near the Tuzla River (S8). Measured pH values ranged from 5.82 to 10.04 with an average of 7.07. Minimum pH value was measured of 5.82 at S8 and maximum pH value of 10.04 was measured at S1.



Table 6.6. Locations and Physical Properties of Soil Samples

Location	Coordinate		Definition	29.05.2012		05.02.2013		15.04.2013	
				Temperature	pH	Temperature	pH	Temperature	pH
S1	35S0429498	4380247	Next to T16	30.8	8.74	22.7	6.89	19.1	10.37
S2	35S0429292	4380124	Next to fountain	27.2	7.85	18.6	6.53	25.4	7.56
S3	35S0429176	4380176	Point of geothermal water was interfered with creek	27.3	7.30	16.2	6.73	-	-
S4	35S0428960	4380360	In front of Tuzla Spa	26.3	6.84	17.6	6.95	19.4	6.29
S5	35S0428677	4380541	In front of entrance of Tuzla village label	26.0	6.08	17.2	7.20	21.1	6.17
S6	35S0429141	4379979	Near the reinjection point	-	-	16.9	6.83	-	-
S7	35S0428402	4380623	T15 well	25.2	7.27	17.1	7.52	21.6	7.42
S8	35S0428370	4381238	Next to T11	23.9	6.86	17.5	7.33	18.1	5.82
S9	35S0427835	4379234	Under-the-bridge	24.0	6.92	17.8	6.73	18.7	6.71
S10	35S0426766	4378654	Near a new drill south west of study area	-	-	-	-	22.8	6.97
S11	35S0426127	4378617	Under-the-bridge that close to W10 sampling point	-	-	-	-	18.7	6.71
S12	35S 0429203	4379630	T7 well	-	-	18.5	6.53	21	7.16
S13	35S0428657	4379651	T8 well	-	-	20.6	6.36	19.6	7.01
S14	35S0428483	4380639	T15 well	22.4	7.78	18.3	7.04	20.7	7.12
S15	35S0429047	4380468	Near a spring opposite to the power plant	27.0	6.69	21.9	6.13	-	-
S16	35S0428789	4381261	Opposite of thermal spring	26.9	6.59	17.6	7.54	22.4	6.64

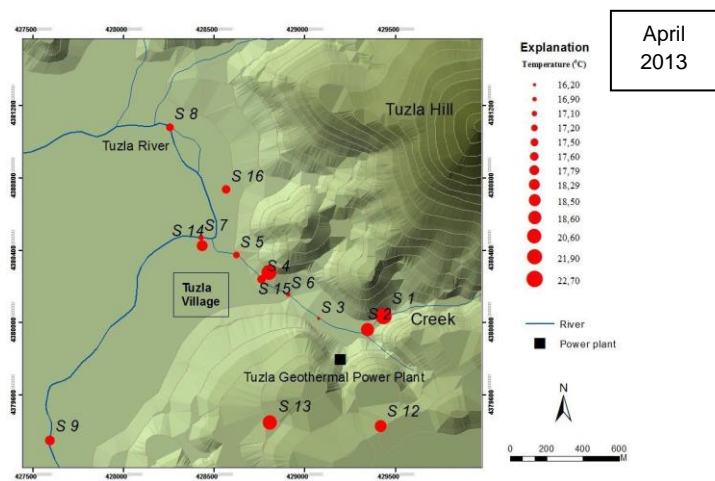
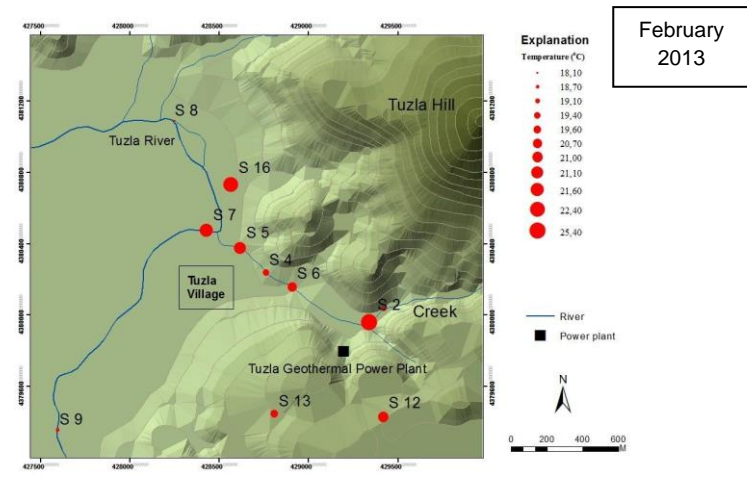
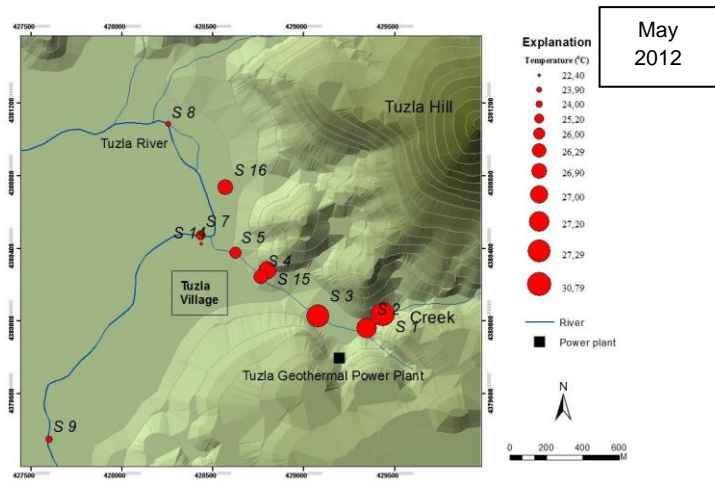
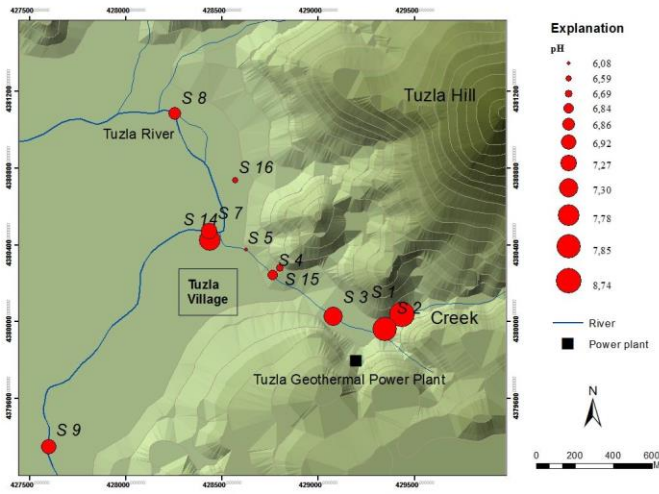
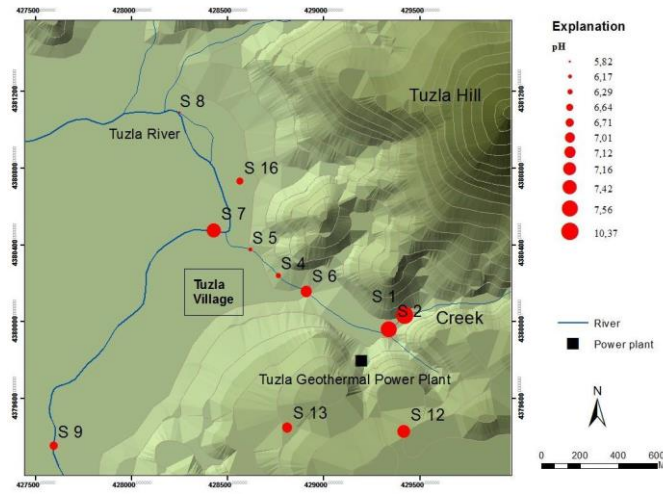


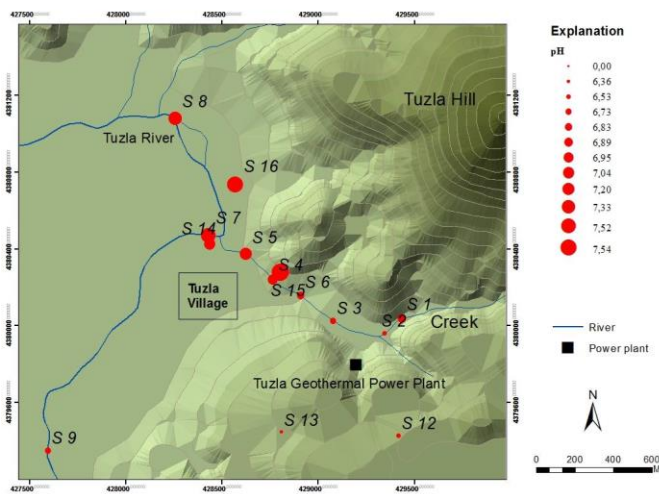
Figure 6.26. Temperature Distribution Map for Soil of Tuzla Geothermal Field



May  
2012



February  
2013



April  
2013

Figure 6.27. pH Distribution Map for Soil of Tuzla Geothermal Field

The main resource of soil minerals are rocks. However, the chemical and mineralogical properties of soil depend on weathering factors (Sayın, 1999). To investigate the element composition, some element analyses were conducted. Element analyses of soils in Tuzla were done with 3 methods which are XRD, XRF and SEM-EDX. The reason for using XRF data in distribution map, XRF results are the most dependable technique among the others (Table 6.7.). XRD and EDX results are also discussed with graphics.

### Sodium

Sodium exist in Earth's crust with the ratio of 2.4 % and in soil 0.8 % (Sayın, 1999). In soil samples Na values are given in map as mg/kg (Figure 6.28.). S3, S4 and S7 are above the natural sodium limits in soil and rocks. All sodium values are above the limit of Soil Pollution Prevention Regulation (TKKY) that is 125 mg/L for sodium. The measured Na values ranged from 410 to 4060 mg/kg. Maximum concentration of Na was measured in front of Tuzla spa (S4) and minimum concentration of Na was measured at a spring opposite to the power plant (S15)

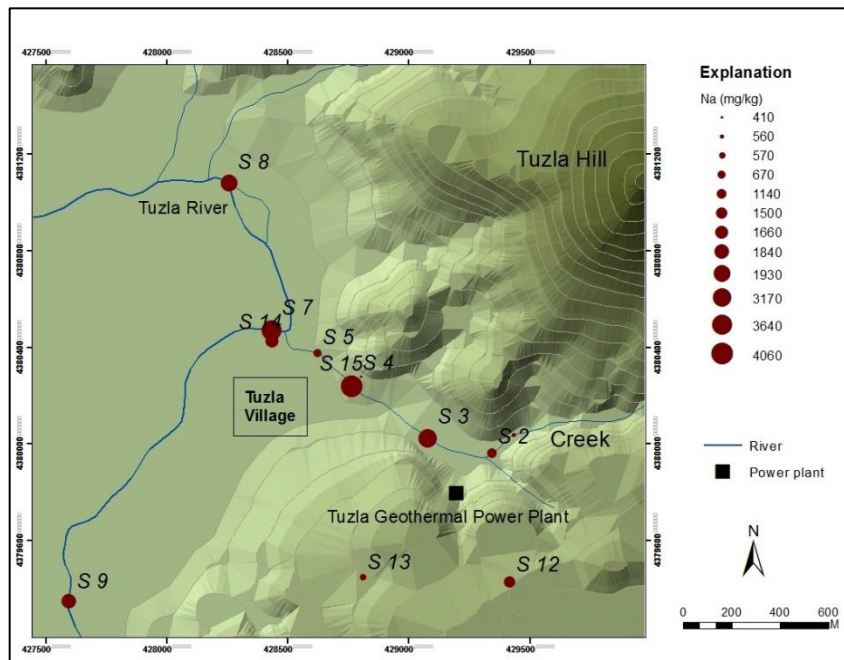


Figure 6.28. Sodium concentration distribution in Tuzla soil sampling points

Table 6.7. Soil Samples Element Composition (XRF)

Element (mg/kg)	S1	S2	S3	S4	S5	S7	S8	S9	S10	S11	S12	S13	S14	S15
Sodium (Na)	560	1140	3170	4060	670	3640	1930	1840	2090	2270	1500	570	1660	410
Magnesium (Mg)	1000	980	950	1040	940	1410	1740	1630	1050	1770	590	730	1750	790
Aluminum (Al)	12320	9360	11300	11320	11570	10240	10220	10810	10850	8950	11590	10470	11030	10990
Silicon (Si)	25570	26510	25540	23900	27220	23880	24250	23520	26600	18070	29300	30200	24750	28070
Phosphorus (P)	140	160	50	80	120	100	160	100	60	60	50	50	110	140
Sulfur (S)	20	50	50	40	160	230	90	40	10	60	10	10	80	30
Chlorine (Cl)	10	10	20	50	10	20	60	10	10	130	0	0	20	10
Potassium (K)	4320	3280	2720	3050	3150	3570	3140	3100	3020	2270	3410	3430	3050	2920
Calcium (Ca)	1170	2080	2690	3100	1840	3730	5330	5540	2730	19060	1010	860	4880	1240
Titanium (Ti)	660	380	490	540	460	580	740	780	580	460	440	600	620	440
Manganese (Mn)	110	60	70	60	80	80	100	110	120	90	80	60	110	340
Iron (Fe)	6560	5570	4630	5170	4430	6550	5930	6590	5490	4610	3350	4080	5370	4750
Zinc (Zn)	10	20	0	0	10	40	10	0	10	0	10	0	0	40
Strontium (Sr)	150	410	190	220	130	110	150	110	120	80	70	100	110	170
Yttrium (Y)	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Zirconium (Zr)	170	80	140	190	90	60	110	150	70	0	100	110	50	70
Niobium (Nb)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barium (Ba)	720	4760	2100	2320	2150	670	510	380	650	400	420	460	400	2520
Tantalum (Ta)	430	460	520	530	400	430	550	470	420	470	380	370	450	460

## Chlorine

Chlorine exists in earth's crust with a small ratio 0.0013 % and limit of Soil Pollution Prevention Regulation (TKKY) is 25 mg/L for sodium. In soil sample analysis results, Cl values ranged from 10 to 130 mg/kg. S4, S8 and S11 sampling points were above the regulation limit and chlorine contents of these soil samples were 50, 60 and 130 mg/kg respectively (Figure 6.29.).

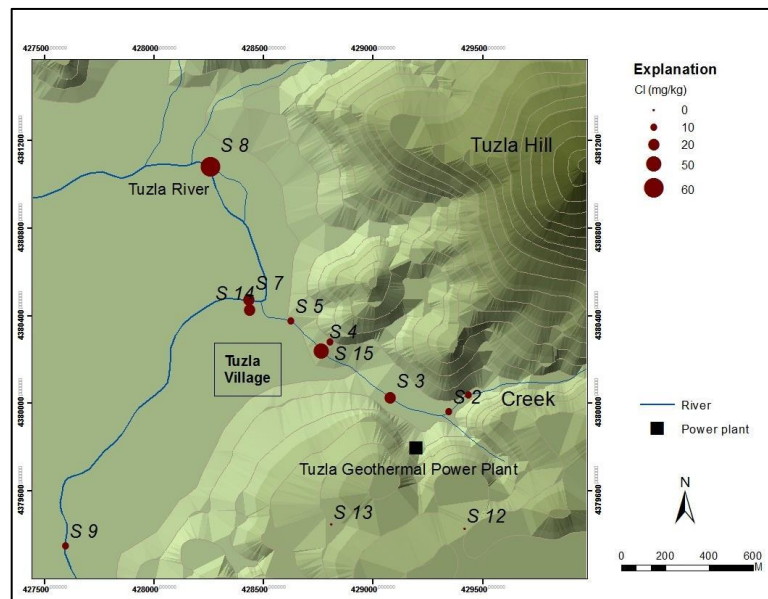


Figure 6.29. Chlorine Concentration Distribution in Tuzla Soil Sampling Points

Salinity, content of Na and Cl elements, of topsoil increased because of irrigation with high salinity water. This situation has caused degradations with soil structure and plant grown. Also soil salinity depends on precipitation amount of the area (Maas and Hoffman, 1977; Ben-Hur et al., 1998).

## Potassium

Potassium (K) exists in Earth's crust with the ratio of 2.1%, and in soil 1.5%. All of potassium values are present in soil more than natural and the limit for K in Soil Pollution Prevention Regulation is not specified. Potassium values range from 4.32

mg/kg to 2.27 mg/kg with an average value of 3.19 mg/kg. Minimum K value of 2.27 mg/kg was measured at S11 and the maximum value of 4.32 mg/kg was measured at S1 (Figure 6.30.)

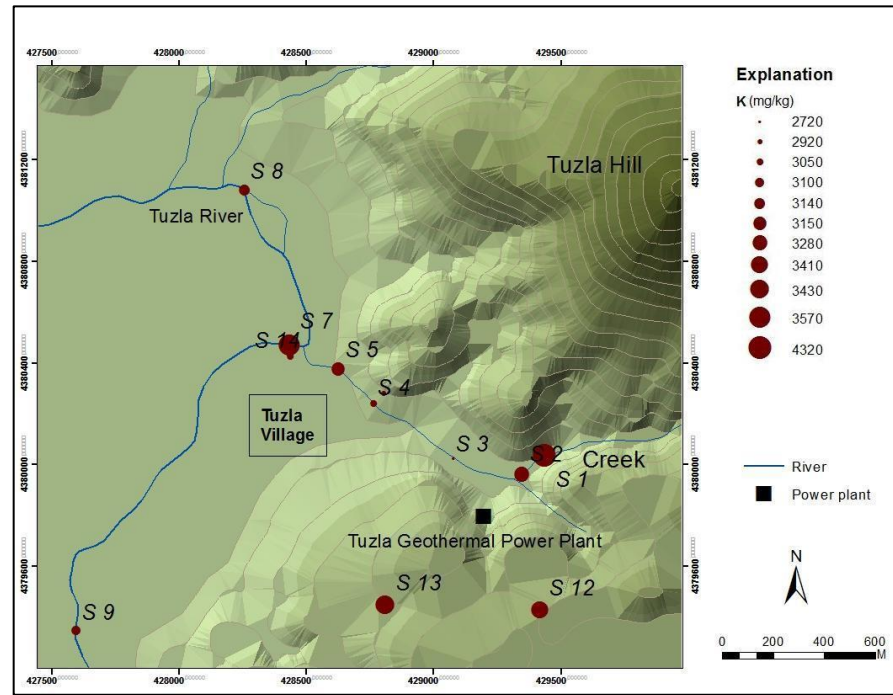


Figure 6.30. Potassium Concentration Distribution in Tuzla Soil Sampling Points

## Magnesium

Magnesium naturally exists in rock and soil structure between 2.3 and 0.59 % (Sayın, 1999). The limit for magnesium in Soil Pollution Prevention Regulation is not specified. All of the Mg concentrations are between the natural ratios (Figure 6.31.).

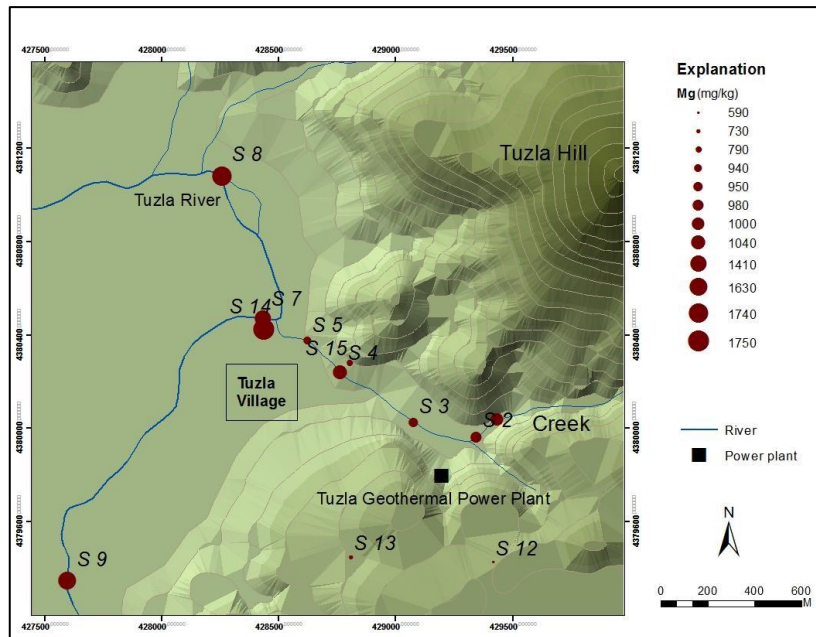


Figure 6.31 Magnesium Concentration Distributions in Tuzla Soil Sampling Points

### Calcium

Calcium exists in soil and rock structure with a range of 1.2 – 4.1 %. Maximum analysed Ca concentration of %19.6 was measured at S11, and minimum concentration of 0.06 was measured at a close point to T1 geothermal well (S13).

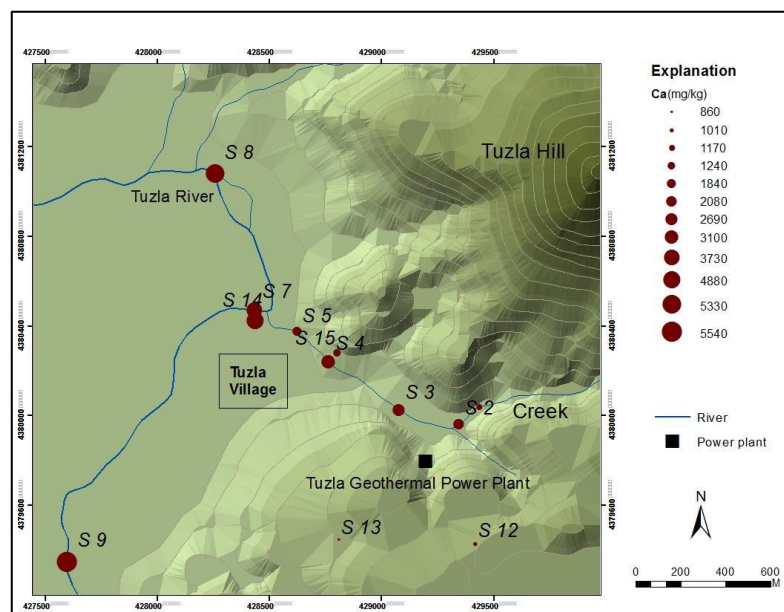


Figure 6.32 Calcium Concentration Distributions in Tuzla Soil Sampling point



## Barium

Analysed barium values ranged from 380 to 4760 mg/kg in Tuzla soil sampling points (Figure 6.33-6.34). Maximum Ba value of 4760 mg/kg was measured at S2, and minimum Ba value of 380 mg/kg was measured at under-the-bridge (S9). The limit for Barium in Soil Pollution Prevention Regulation is 200 mg/kg. Barium values were high especially at southeast of study area where the geothermal springs are located.

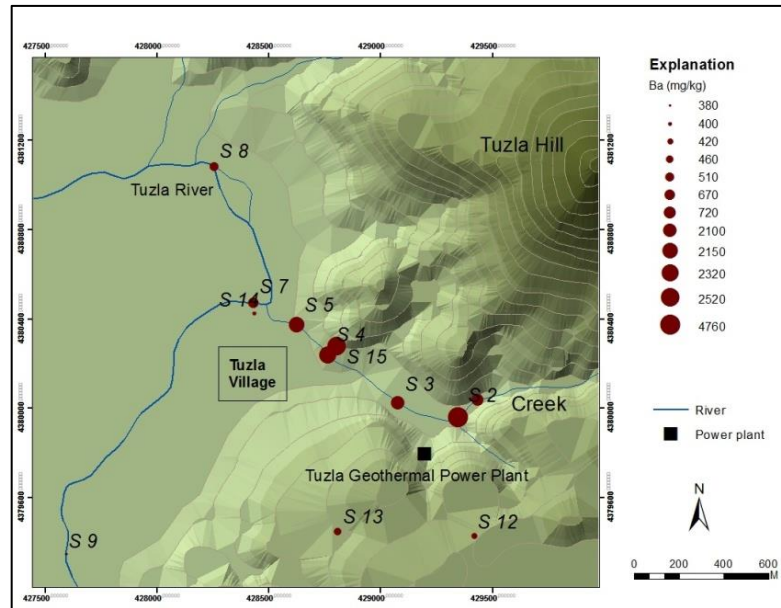


Figure 6.33. Barium Concentration Distribution in Tuzla Soil Sampling Points

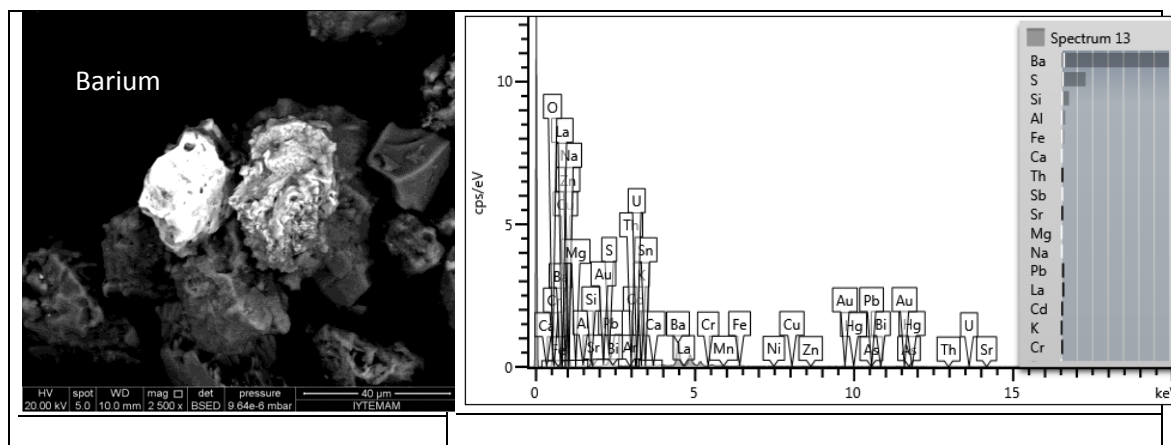


Figure 6.34. SEM Image and EDX Result of S8

## Boron

Boron analysis with XRF method was unavailable. However element analysis with SEM (EDX) showed that almost all soil samples included boron with high amounts (Figure 6.35.) and mostly at high concentrations after aluminum and silisium (Figure 6.36)

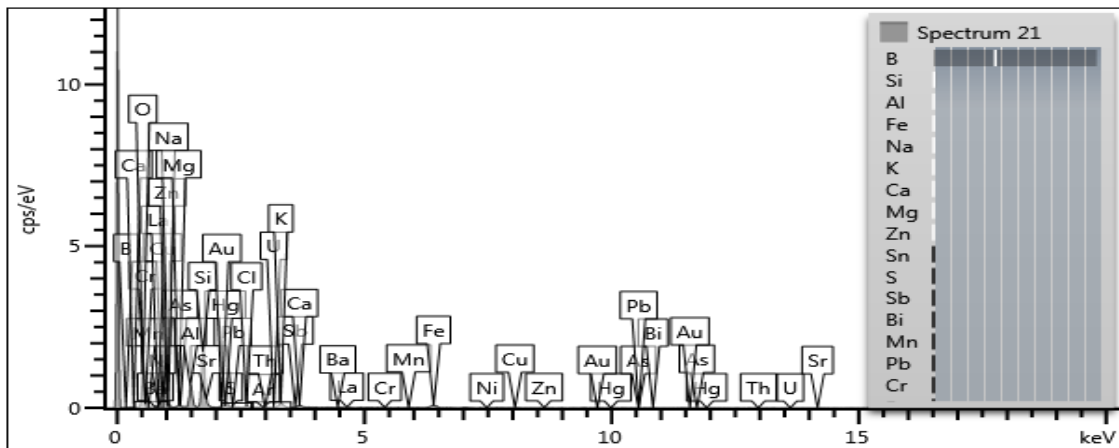


Figure 6.35. Element Composition of S11 (SEM-EDX)

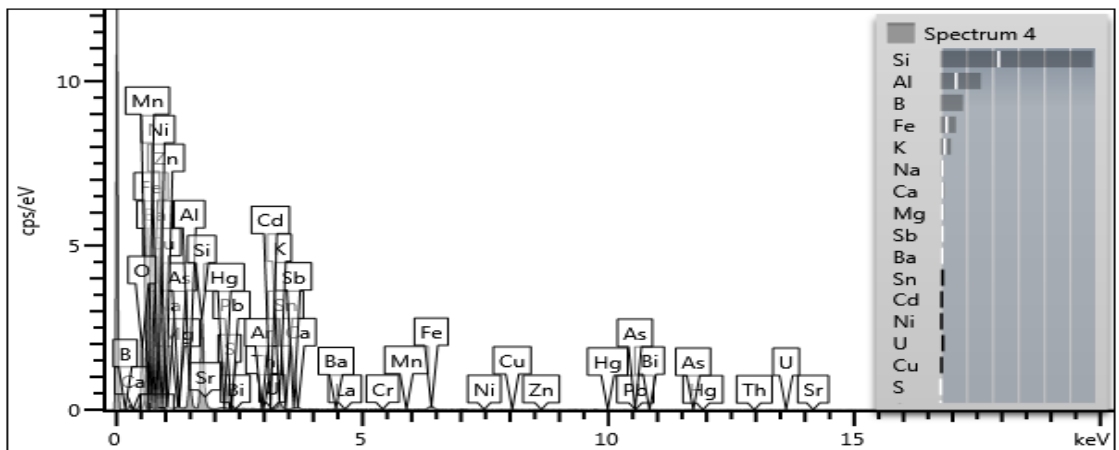


Figure 6.36 Element Composition of S2

## Manganese

Manganese exists in soil and rock structure naturally with a range of 0.0095 to 0.12 % (Sayın, 1999). Only at one location the natural present limitation exceeded. The maximum Mn value was measured at S15 (Figure 6.37.). The limit for manganese in Soil Pollution Prevention Regulation does not exist.

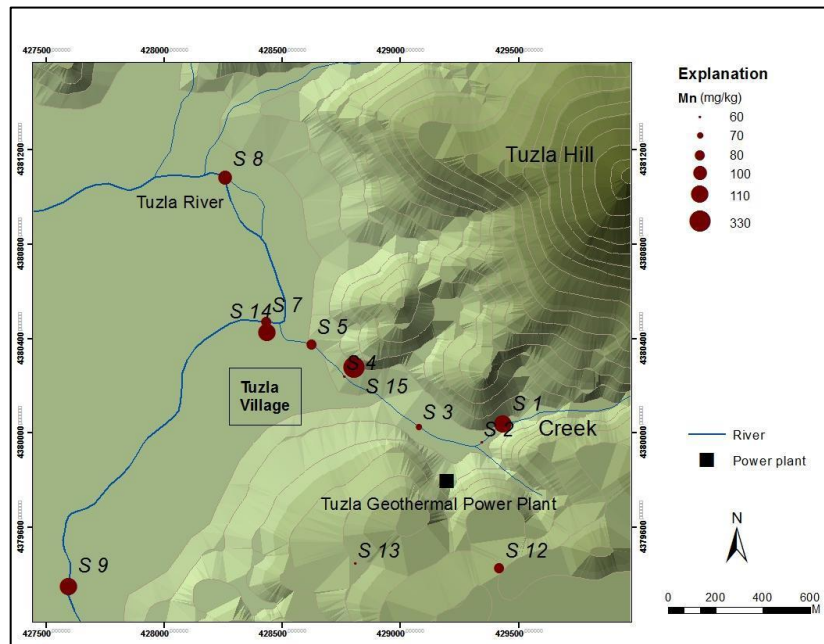


Figure 6.37. Manganese Concentration Distribution in Tuzla Soil Sampling Points

## Iron

The limit for iron in Soil Pollution Prevention Regulation does not exist, too. Iron naturally exists in Earth's crust and soil range from 2.7 to 5.6 % (Sayın, 1999). Most of sample's iron concentrations were measured within the limits. Maximum Fe values of 6.59 mg/kg were measured at S9 (Figure 6.38.).

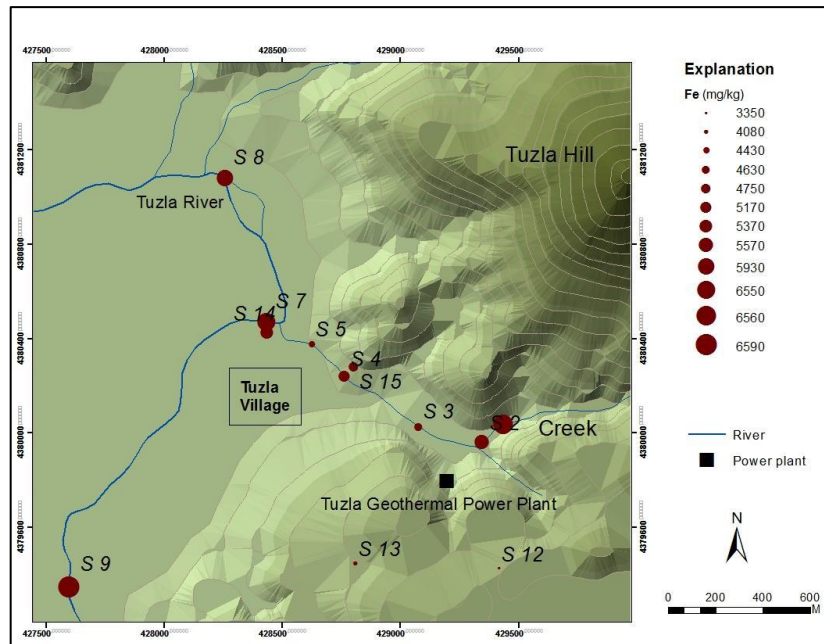


Figure 6.38. Iron Concentration Distribution in Tuzla Soil Sampling Points

### Aluminum

The limit for Aluminum in Soil Pollution Prevention Regulation does not exist, too. The natural limits for Al is between 6.0-8.2 % (Sayın, 1999) Maximum aluminum value of 12320 mg/kg was measured at S1 and minimum Al values value of 8950 was measured at S11 (Figure 6.39.).

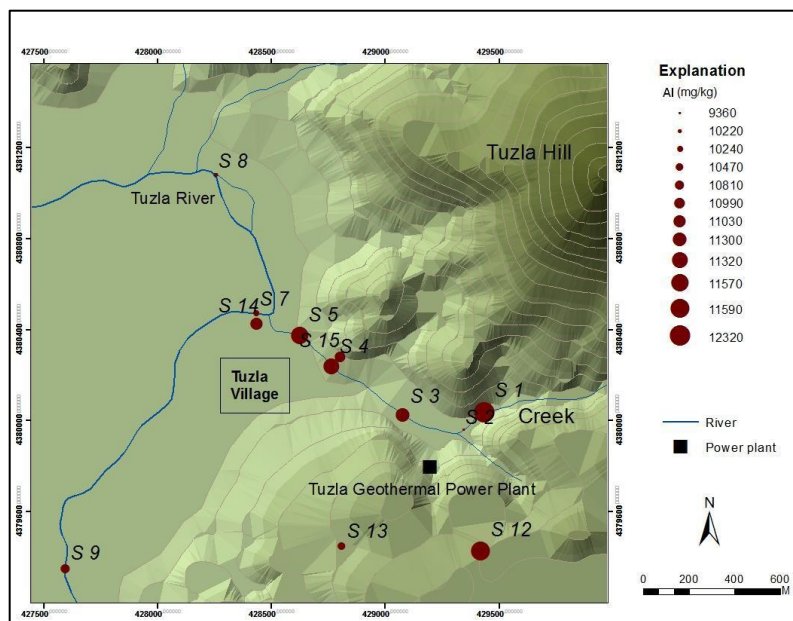


Figure 6.39. Aluminum Concentration Distribution in Tuzla Soil Sampling Points

## Silisium

Silisium values ranged from 18070 - 30200 mg/kg with an average of 25353 mg/kg. Maximum Si concentration value of 30200 mg/kg was measured at S13, minimum Si value of 18070 was measured at S11 (Figures 6.40.-6.43). The limit for silisium in Soil Pollution Prevention Regulation does not exist. The search match method was conducted to determine the elements of soil. The peak points of graphics matched with  $\text{SiO}_2$ .

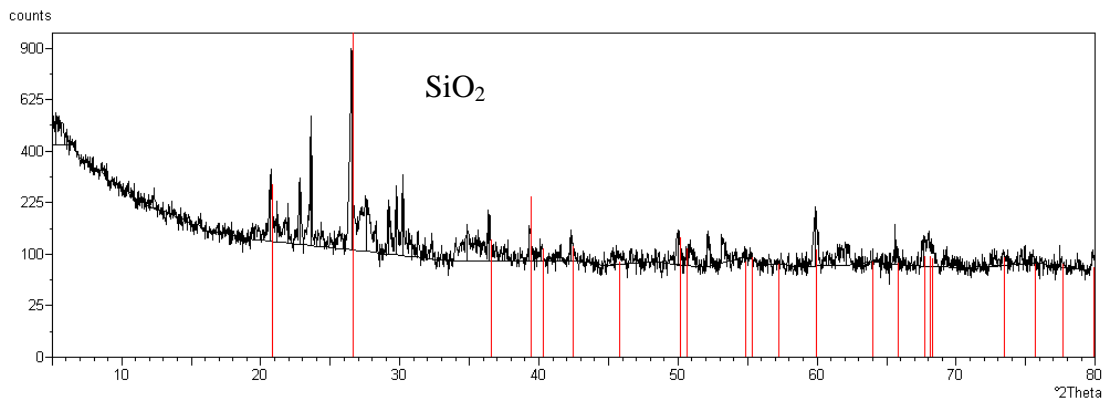


Figure 6.40. XRD Search Match Results of S14

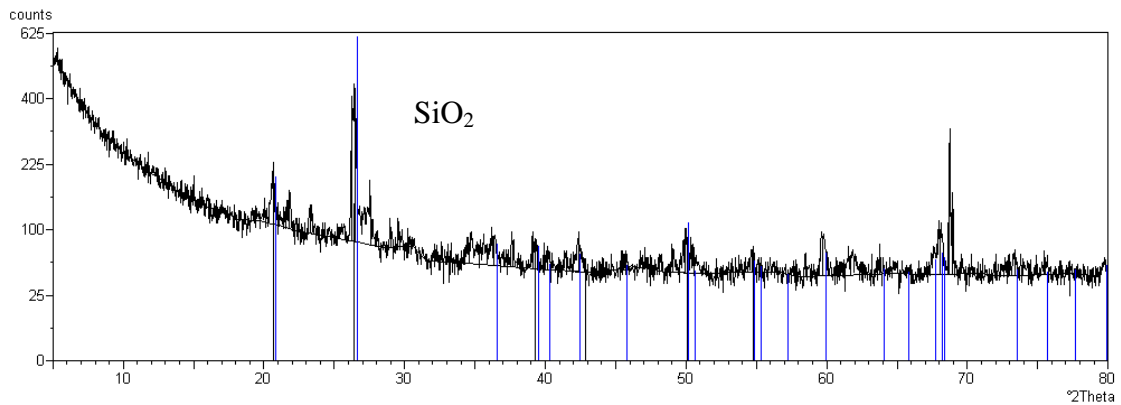


Figure 6.41. XRD Search Match Results of S13

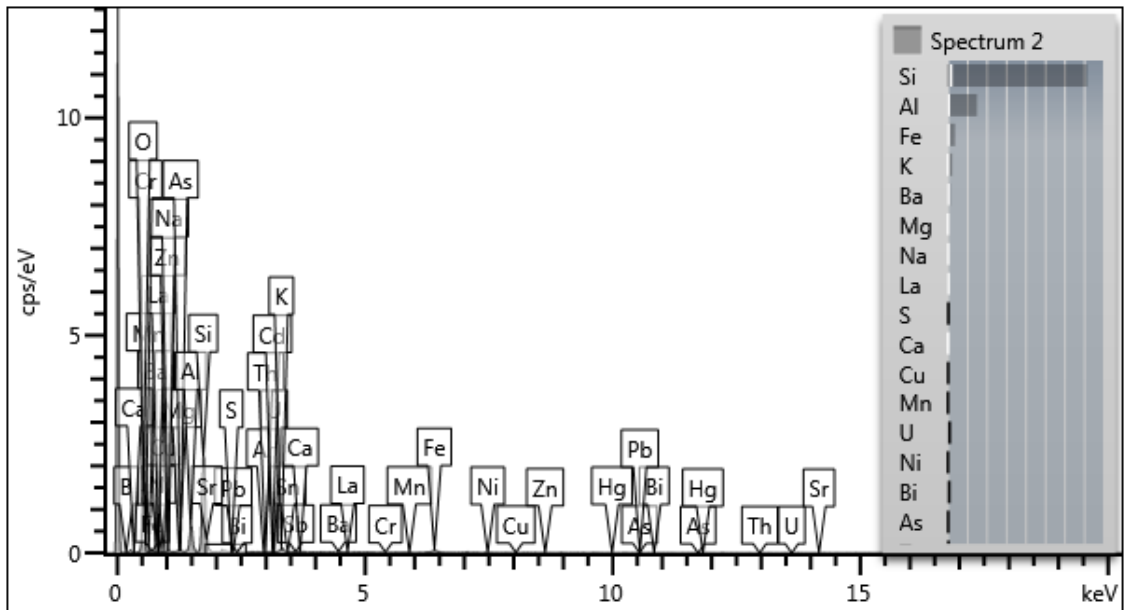


Figure 6.42. Element Composition of S12 (SEM-EDX)

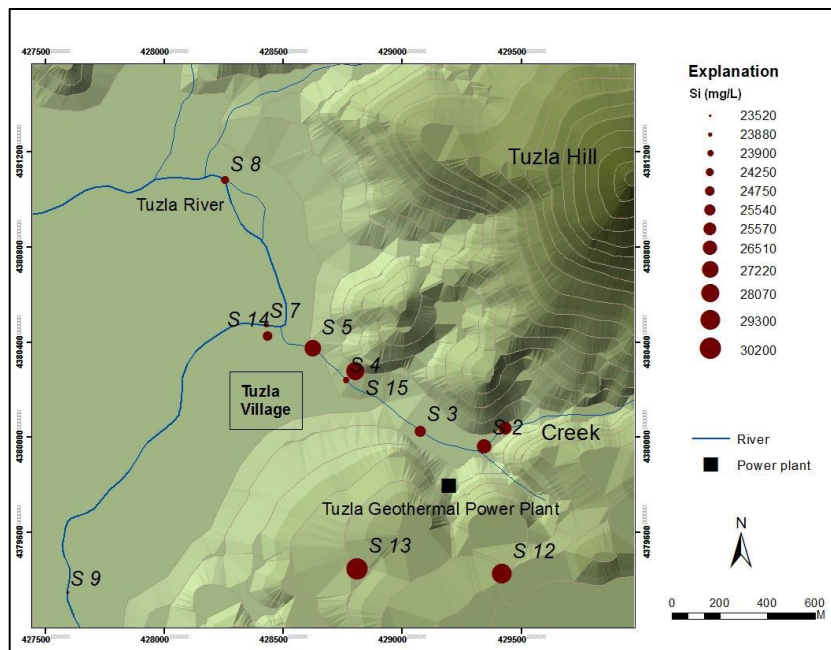


Figure 6.43. Silisium Concentration Distribution in Tuzla Soil Sampling Points

### Sulfur

Sulfur naturally exists between 0.026 and 0.06 % in soils. In Tuzla soil samples, the maximum value of 230 mg/kg was measured at S7, and minimum value of 10 was

measured at S10 and S13 (Figures 6.44. and Figure 6.45.). The limit for S in Soil Pollution Prevention Regulation is 2 mg/kg. This high sulfur concentration may originate from precipitation of the H<sub>2</sub>S emissions of plant and altered volcanics. Peak points of XRD are matched with SiO<sub>2</sub> (red) and silicon sulfide (blue) that includes Si and S.

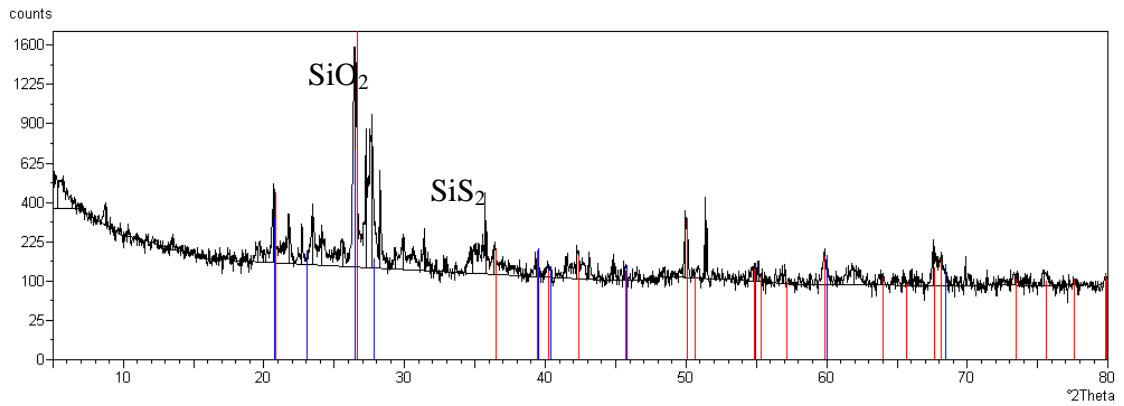


Figure 6.44. XRD Search Match Results of S8

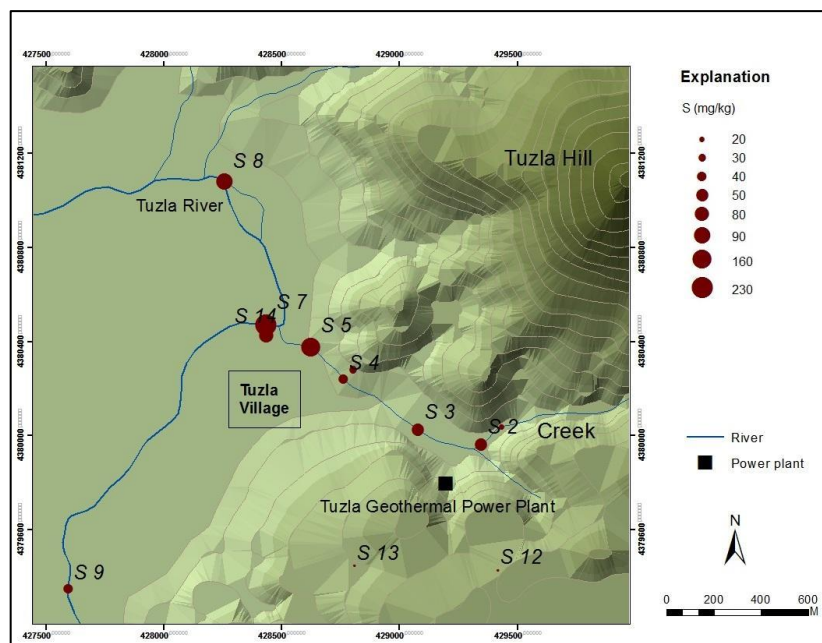


Figure 6.45. Sulfur Concentration Distribution in Tuzla Soil Sampling Points

Most of soil sampling points were close to Tuzla River or a small creek. Soil samples have a swamp profile. Therefore, photoplankthon species can be seen in soil samples (Figure 6.46.).

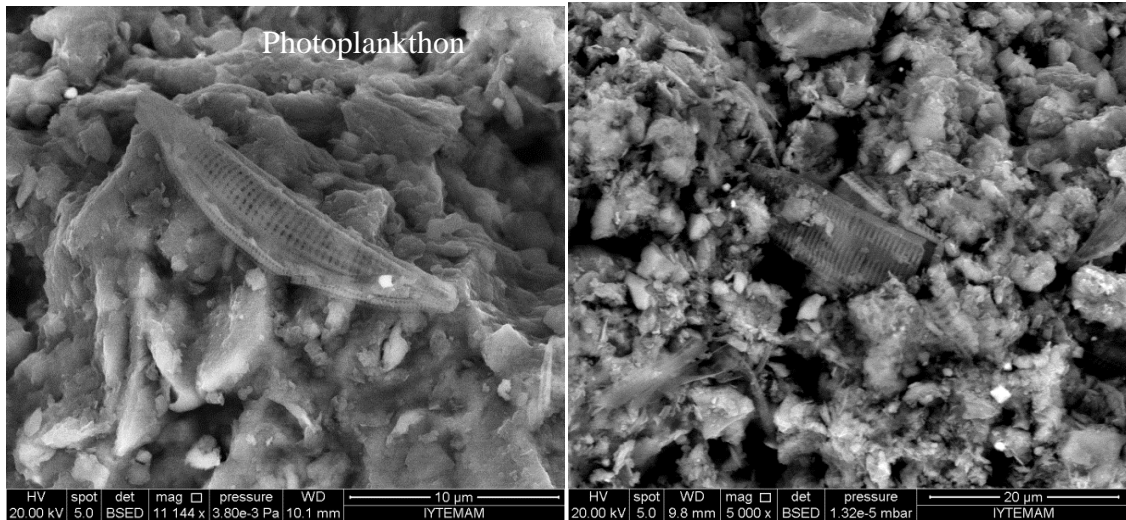


Figure 6.46. SEM Image of S5 and S7

Soil has high sodium and chlorine content that might be hazardous to the plant and vegetation. Although there are many species exist to survive in salty soils, most of them can not. Barium concentrations were above the standards. This situation originates from the rock type of soil. Despite surface water, soil contains highly silisium especially around the creek and hot springs where altered rocks are seen. Some elements measured within the limits such as manganese and iron. All element analyses, which are XRD, XRF and SEM, were indicated nearly the same element composition.



## CHAPTER 7

### CONCLUSION

Tuzla geothermal water is formed by dissolution of marine evaporations. The water from the wells is acidic due to an excess of free CO<sub>2</sub>, which is the result of the high partial pressure of this gas in the well. The temperature of geothermal fluid in well T9E and T16E are 149.1°C and 150.6, respectively. These geothermal fluids have been used for power generation since 2010.

Tuzla River is the main water source for usage and agricultural activities. To determine the effect of geothermal fluid on soil and surface water, representative samples from surface water and soil were collected and these samples were analyzed.

The results show that the geothermal brine is NaCl water type. During all sampling periods, minimum heavy metal values were measured at W9 sampling point which is the background point. Maximum boron and strontium values of surface water were ranged from 15 to 27 mg/L, from 85 to 162 mg/L in all periods, respectively. While temperature and pH values of surface water were ranged in the national and international limits, EC values of the creek reached up to 59.6 ms/cm. Boron and strontium values decrease remarkably compared with previous similar studies in Tuzla. Reason of this decrease can be explained with geothermal power plant started to operate. The concentration of contaminant has been decreased with reinjection of plant waste water and the decrease of spring flow rate. Nevertheless, some major and minor element concentrations exceed the national and international water quality standards. Increasing surface water quality affects both soil and groundwater quality. Soil samples have high sodium (410-4060 ppm) and chlorine (10-130 ppm) that indicate high salinity. On the other hand, heavy metal concentrations did not exist at high amounts.

Spent geothermal fluids with high concentrations of chemicals such as boron, fluoride or arsenic should be treated and/or re-injected into the reservoir. Although the low temperature geothermal fluids generally contain low levels of chemicals, the discharge of waste geothermal fluids is a major problem.

Many private companies have been working on geothermal resources in this region. However, local people have been using densely surface water for irrigation. It is

very important to sustainable water resources of this region. Therefore; all water sources should be monitored and protected from the discharge of geothermal fluid on water source.

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