## **DOKUZ EYLÜL UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

# **ARSENIC POLLUTION AND HEALTH RISK ASSESSMENT IN THE GROUNDWATER OF**  SİMAV PLAIN, KÜTAHYA

**by Merdiye MUTLU**

> **December, 2010 iZMİR**

## **ARSENIC POLLUTION AND HEALTH RISK ASSESSMENT IN THE GROUNDWATER OF**  SİMAV PLAIN, KÜTAHYA

**"A Thesis Submitted to the**

**Graduate School of Natural and Applied Sciences of Dokuz Eylül University In Partial Fulfillment of the Requirements for the Degree of Master of Science in Environmental Engineering, Environmental Technology Program"**

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### **M.Sc THESIS EXAMINATION RESULT FORM**

We have read the thesis entitled **"ARSENIC POLLUTION AND HEALTH**  RISK ASSESSMENT IN THE GROUNDWATER OF SİMAV PLAIN, KÜTAHYA" completed by MERDİYE MUTLU under supervision of ASSIST. PROF. DR. ORHAN GÜNDÜZ and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

Assist. Prof. Dr. Orhan GÜNDÜZ

Supervisor

(Jury Member) (Jury Member)

Prof.Dr. Mustafa SABUNCU **Director** Graduate School of Natural and Applied Sciences

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### **ARSENIC POLLUTION AND HEALTH RISK ASSESSMENT IN THE GROUNDWATER OF SİMAV PLAIN, KÜTAHYA**

### **ABSTRACT**

Simav Plain was chosen as the study area due to high arsenic levels detected in groundwater in a previous study. Thus, a multidisciplinary research was conducted to understand the origin of high arsenic levels within the water resources of Simav Plain, to identify relations between drinking water quality and observed diseases in the villages, and to make risk assessment for the public health. To achieve this objective, representative samples from geothermal fluids, surface waters, and groundwater were collected as part of a field survey and were analyzed using standard techniques. Besides, individual household surveys and oral autopsies were made by interviewing villagers. In water quality monitoring, a total of 45 points (33 which of are from groundwater, nine which of are from surface waters and three which of are from geothermal waters) were sampled to determine physical parameters, major anions and cations and heavy metals and trace elements. Mean arsenic levels were found to be 162.64 µg/L for groundwater and 76.56 µg/L for surface waters. Cardiovascular diseases (37.7%), gastrointestinal system diseases (16.7%), diabetes mellitus (12.7%) and cancers (%2.6) were detected during health surveys. Among cancer group, uterus malign neoplasm (41.2%), colon malign neoplasm (17.8%), breast malign neoplasm (11.8%) and amiloidosis (11.8%) were mostly observed. According to results, high arsenic levels were mostly related to iron oxyhydroxides/hydroxides sorption in the groundwater samples. In surface waters, high arsenic levels were mostly related to metal oxyhydroxides/hydroxides sorption and uncontrolled discharge of geothermal fluid into surface drainage network. The health risk assessment showed that there is a high possibility for internal organ cancers and adverse health problems in the study area.

**Keywords:** Arsenic, health risk assessment, groundwater quality, metal oxyhydroxides/hydroxides

### **KÜTAHYA SİMAV OVASI YERALTI SUYUNDA ARSENİK KİRLİLİĞİ VE** SAĞLIK RİSK DEĞERLENDİRMESİ

### **ÖZ**

Daha önce yapılan çalışmalarda yüksek arsenik değerlerine rastlanması nedeniyle çalışma sahası olarak Simav Ovası seçilmiştir. Sahada çok disiplinli bir çalışma yapılmak suretiyle, su kaynaklarında tespit edilen yüksek arsenik değerlerinin kaynağı belirlenmiş; köylerde gözlenen hastalıklar ve içme suyu arasındaki ilişki ortaya konmuş ve bir halk sağlığı risk değerlendirmesi yapılmıştır. Bu amaçla, saha çalıĢmasının bir parçası olarak, yüzey ve yeraltı sularından ve jeotermal sulardan su örnekleri toplanmıĢ, köylülerle görüĢülerek bireysel hane halkı ve sözel otopsi anketleri yapılmıştır. Çalışma kapsamında 33'ü yeraltı, dokuzu yüzeysel ve üçü jeotermal su olmak üzere toplam 45 adet noktadan numuneler alınmış ve fiziksel parametreler, toplam organik karbon, temel anyon ve katyonlar, ağır metal ve iz elementlerin analizleri yapılmıştır. Ortalama arsenik seviyeleri yeraltı suyu için 162,64 µg/L yüzeysel sular için 76,56 µg/L olarak bulunmuĢtur. Sahada gözlenen hastalıklar arasında en önemlileri kardiyovasküler hastalıklar (%37,7), mide-bağırsak sistemi hastalıkları (%16,7), Ģeker hastalığı (%12,7) ve kanser (%2,6) sayılabilir. Tüm kanser vakaları içinde rahim kanseri %41,20, kolon kanseri %17,8, göğüs kanseri %11,8 ve amiloidozis %11,8 ile en çok rastlanan kanser türleridir. Analiz sonuçlarına göre yeraltı suyundaki yüksek arsenik seviyelerinin kaynağı, daha çok demir oksihidrositler ya da hidroksitlerin üzerine tutunma ve daha sonra salıverilmedir. Yüzeysel sulardaki yüksek arsenik seviyelerinin kaynağı olarak ise, daha çok metal oksihidrositler ya da hidroksitlerin üzerine tutunma ve salıverilme ve doğal drenaj ağına yapılan kontrolsüz jeotermal akışkan boşaltımı sayılabilir. Sonuç olarak sağlık risk değerlendirmesi sonuçlarına göre bölgede iç organ kanserleri dâhil çeĢitli sağlık sorunlarına yakalanma riski oldukça yüksektir.

**Anahtar Kelimeler:** Arsenik, sağlık risk değerlendirmesi, yeraltı suyu kalitesi, metal oksihidrositler/hidroksitler

### **CONTENTS**





### **CHAPTER ONE INTRODUCTION**

### **1.1 Problem Definition**

Because of climate change and its effects on water supplies, water turned out to be a limited natural resource in recent years and many pollutants in natural waters have been identified as toxic and harmful to the environment and the human health. Arsenic is among these pollutants and ranks high in the priority list (Vaclavikova, Gallios, Hredzak, & Jakabsky, 2008).

Most environmental arsenic problems are the result of mobilization under natural conditions such as weathering reactions, biological activity and volcanic emissions as well as through a range of anthropogenic activities (Terlecka, 2005). Besides, man has had an important additional impact through mining activities, combustion of fossil fuels, use of arsenical pesticides, herbicides and crop desiccants and use of arsenic as an additive to livestock feed. Although the use of arsenical products such as pesticides and herbicides have decreased significantly in the last few decades, arsenical products used for wood preservation are still very common (Smedley & Kinniburgh, 2002).

Drinking water probably poses the greatest threat to human health because of various sources of arsenic in the environment. Lots of health problems related to arsenic have been reported from many parts of world such as USA, Chile, Mexico, China, Taiwan, Bangladesh, India, etc. The adverse health effects of arsenic depend strongly on dose, duration of exposure and the nutrition status of the exposed population. Chronic exposure to arsenic via drinking water can cause many adverse health effects on respiratory, gastrointestinal, cardiovascular, nervous, hematopoetic systems. The United States Environmental Protection Agency (USEPA) categorizes arsenic as a "Class A" carcinogen and International Agency for Research on Cancer (IARC) has classified arsenic as a "Group 1" human carcinogenic substance (IARC, 2004).

The ion arsenic has four valence states:  $-3$ ,  $0$ ,  $+3$ , and  $+5$ . In water, arsenic occurs in both inorganic and organic forms under dissolved and gaseous states. The form of arsenic in water depends on its pH, Eh, organic content, suspended solids level, dissolved oxygen concentration and on several other variables. The toxic effects of arsenic are related to its oxidation states and its chemical forms. The toxicity of arsenic compounds increases 100 times from organic complex compounds of arsenic to inorganic forms and six times from arsenate  $(As<sup>5+</sup>)$  to arsenite  $(As<sup>3+</sup>)$ . The toxicity of arsenicals conforms to the following order from greatest to least toxicity: arsines > inorganic arsenites > organic trivalent compounds (arsenoxides) > inorganic arsenates > organic pentavalent compounds > arsonium compounds > elemental arsenic (Jain & Ali, 2000).

As a result of its high toxicity level, many countries established stringent regulations of maximum allowable limits in drinking water. Due to its high toxicity and health related concerns, these limits were lowered from 50 to 10 µg/L total As in the last decade in many countries. For example, the United States has reduced the arsenic standard level from 50  $\mu$ g/L to 10  $\mu$ g/L. Similarly, Turkey has also reduced its arsenic limit from 50 µg/L to 10 µg/L level. Since the limits have been reduced, arsenic contamination in natural waters has become an even more important issue.

In general, it is necessary to determine arsenic concentration to recognize its accumulation, transformation and toxicity to organisms. Speciation of arsenic provides a new point of view between exposure, toxicity and metabolism. Arsenic speciation is expected to greatly influence potential health risks. Risk assessments are used to characterize carcinogenic and non-carcinogenic adverse effects of arsenic exposure by calculating the lifetime cancer risk and hazard quotient based on exposure concentration, duration and pathways. The lifetime cancer risk and hazard quotient associated with chronic arsenic exposure in drinking water can be divided into four categories based on the calculated risk and arsenic concentrations: minimal, low, high and extreme. Determining potential arsenic risk based on speciation data provides an accurate representation of potential lifetime cancer risk (Markley & Herbert, 2009).

### **1.2 Objectives of the Study**

Being typically considered a natural pollutant, arsenic has several proven negative effects on human health. It is a cancer-causing chemical that has a worldwide spread. Countries such as Bangladesh, India, United States, Argentina, Chile, Taiwan and China experience arsenic related health problems, which are primarily related to exposure to high arsenic containing groundwater. In particular, arsenic is now considered a triggering compound for diseases such as cancers of gastrointestinal tract as well as skin disorders. Today, numerous cases of arsenic-based cancers are reported in Bangladesh, Taiwan and Argentina (Suzuki & Mandal, 2002).

Recently, climate change and its effects on water resources have intensively taken its place on the public agenda. One of the most important issues is related to the effects of this change on the water quantity and quality. Particularly, the three big cities of Turkey experience water shortages and related problems every summer. Consequently, a growing public concern concerning water quantity and quality is now on the rise. In this regard, research related to changes in water quality and quantity patterns as a result of such changes is geared towards understanding their potential consequences and proposing potential mitigation measures. From local to regional and from regional to national scales, these issues occupy the agenda of the public, which also lead to some conflicts between local and national administrations. Recently, arsenic contamination in groundwater that is used to supply drinking water to communities has become an important issue. In particular, high arsenic levels have been detected in the drinking water supply systems of large metropolitan areas such as Izmir and Ankara. The "arsenic problem" that occurred in Izmir in 2008 is a good example to such conflicts and has served as a textbook example demonstrating the significance of the problem.

The tectonical characteristics and geological structure of Turkey provide a suitable environment for the occurrence of arsenic containing geological formations, which are likely to contain groundwater with high arsenic levels. In addition to Izmir and Ankara, other areas in the country also experience similar problems with

different extends. Increasing public awareness on the subject matter in such regions also helped to identify the problem. One such area is the Simav Plain located in the Simav District of Kütahya Province in the Aegean region where high arsenic levels are observed in groundwater. Local administrators have asked and motivated universities to conduct research on the possibility of the link between high cancer related deaths in their region with drinking water quality in general and arsenic in particular.

Simav Plain represents a complex geological structure in a tectonically active faulty graben zone where alteration zones and geothermal systems are observed. Research conducted in the area as a consequence of the requests made by local people and local administrators has led to the discovery of very high arsenic levels in Simav Plain (Gunduz, Simsek & Hasozbek, 2010). Total arsenic levels were about two-orders of magnitude above the limit value of 10 µg/L in 22 of 28 water samples, taken from groundwater resources of the area. The highest arsenic value observed in this study was 561 µg/L with an average of 99 µg/L. Similarly, three samples from three geothermal fields in the plain had an average arsenic level of  $502 \mu g/L$ . These levels are considered to be extremely high based on the currently effective national standard level of 10 µg/L. Such high levels in cold and hot waters of the area as well as complains from local inhabitants regarding high cancer rates in the area have clearly showed the fact that there is a very serious problem in the area.

Based on the fundamental concepts discussed above, this study is intended to determine the presence of arsenic contamination in groundwater of Simav Plain and to identify the associated health risks on the local people. With the carried out geological and hydrogeological studies, the geomorphological structure of Simav Plain was determined and factors influencing arsenic contamination in the plain were resolved. A comprehensive water quality monitoring program was then initiated to understand the arsenic presence in surface and subsurface waters and to depict the distribution of contamination in the plain. Accordingly, sources, pollution mechanisms and distribution state of arsenic in the groundwater and its relationship with the geothermal fields and mineral deposits were studied. Once the status of arsenic contamination was set, a human health survey was conducted within the plain to assess the current conditions of the health of inhabitants of the plain with the primary objective of statistically correlating cancer risk with arsenic in drinking waters. Finally, risk levels in the plain were calculated and risk maps were prepared to better understand the influence of arsenic exposure.

### **1.3 Scope of the Thesis**

With the above-mentioned objectives, this thesis is organized in six chapters. In Chapter 1, a problem statement and an objective of the study is presented. The following section, Chapter 2, continue with literature review, where the main aspects of arsenic in groundwater are discussed and human health implications are presented. In Chapter 3, the details pertaining to the project area (i.e., Simav Plain of the Province of Kütahya) are described with particular emphasis on morphological, geological and hydrogeological features of the area. In Chapter 4, the materials and methods implemented for field studies, laboratory analysis and data interpretations are discussed. The outcomes of the study are presented in Chapter 5, where main results of the water quality monitoring work conducted on surface and subsurface waters are discussed with particular emphasis on arsenic. The statistical summaries of water quality monitoring are given together with comparisons with national and international standards. This chapter also discusses the results of the health assessment study. Finally, Chapter 6 concludes the thesis with major conclusions of the study and recommendations for further investigations.

### **CHAPTER TWO LITERATURE REVIEW**

Arsenic is a ubiquitous element that is commonly found in natural waters, soils and rocks, atmosphere and in organisms. Arsenic ranks high in abundance of elements;  $20^{th}$  in the earth crust,  $14^{th}$  in seawater and  $12^{th}$  in the human body (Suzuki & Mandal, 2002). Arsenic compounds (such as realgar  $(As_4S_4)$ , orpiment  $(As_2S_3)$ , arsenolite  $(As_2O_3)$  etc.) are used in a wide variety of products such as pigments, medicines, alloys, herbicides, pesticides, embalming fluids, wood preservatives. They are also used in chemical warfare agents, and in depilatory chemicals in leather manufacturing. It is a common agent to commit murder or suicide since early ages. Despite the decreasing trend of arsenic compounds in these areas, it still continue to be a part of our daily lives and millions of people are being chronically exposed via food, water, air and soil to high doses of arsenic leading to detrimental long term consequences.

### **2.1 A Chemical of Concern: Arsenic**

Arsenic is categorized chemically as a metalloid, having both properties of a metal and a nonmetal, but it is frequently referred to as a metal. Elemental arsenic is a gray crystalline material characterized by atomic number 33, atomic weight of 74.92 gr, density of 5.727 gr/cm<sup>3</sup>, melting point of 817°C and a sublimation point of 613°C. It shows chemical properties similar phosphorus.

The arsenic ion is most commonly found in four valence states:  $-3$ ,  $0$ ,  $+3$ ,  $+5$ . Arsenic in nature is rarely found in its free state. Arsines and methylarsines are usually unstable in the air. Elemental arsenic  $(As^0)$  is formed by the reduction of arsenic oxides. Arsenic trioxide  $(As<sup>3+</sup>)$  is a product of smelting operations and is the material used to synthesize most of arsenicals. It is oxidized chemically or bacteriologically to arsenic pentaoxide  $(As<sup>5+</sup>)$  or orthoarsenic acid  $(H<sub>3</sub>AsO<sub>4</sub>)$  (Eisler, 2000).

Arsenic occurs rarely in water in its elemental state  $(As<sup>0</sup>)$  and is occasionally found in  $(-3)$  oxidation state  $(As<sup>3</sup>)$ , which requires extremely low Eh values. Arsenic in water exists primarily in the form of dissolved ionic species. Arsenic in particulate forms account for less than 1% of total measurable arsenic (Eisler, 2000). Common forms of arsenic in water are arsenate  $(As<sup>5+</sup>)$ , arsenite  $(As<sup>3+</sup>)$ , monomethanearsonic acid (MMA), and dimethylarsinic acid (DMA). The inorganic pentavalent arsenic is the most common species in water under the conditions of high dissolved oxygen, basic pH, high Eh and reduced content of organic materials. The arsenites and arsenic sulfide forms are usually found in opposite conditions. Some arsenite forms are associated to biological activities (Jean, Bundschuh, Chen, Guo, Liu, Lin & Chen, 2010).

Eh, pH and dissolved oxygen (DO) are all important factors controlling arsenic speciation and chemistry in groundwater (Figure 2.1). In general, pH has a great impact on solubility of toxic trace element cations such as  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$  and  $\text{Zn}^{2+}$ . Their solubility generally decreases with increasing pH. On the contrary, solubility of most oxyanions including arsenate, increase with high pH values. But these anions exist at high concentrations in the solution even at near-neutral pH under some special conditions. Similar to pH, Eh has also an important role on transport, mobility and bioavailability of metals in aquatic environments. With positive Eh values, natural waters show oxidizing conditions and most of the multivalent elements are expected to be in the oxidized state. Negative Eh values correspond to reducing conditions. As dissolved oxygen concentrations in water increase, Eh values become more positive. In natural waters, Eh ranges from -500 mV to +700 mV. Surface waters and groundwaters containing dissolved oxygen are usually characterized by an Eh range of  $+100 \text{ mV}$  and  $+500 \text{ mV}$  (Chapman, 1996).

Under oxidizing conditions, arsenic usually exists as pentavalent forms such as  $H_3AsO_4^0$ ,  $H_2AsO_4^0$ ,  $HAsO_4^2$  and  $AsO_4^3$  depending on the Eh and pH levels (Smedley and Kinniburgh, 2002).  $H_3AsO_4^0$  ion is only important in very acidic waters such as acid mine drainage. In the range of pH common to most natural waters (pH 6.5-8.5), both  $H_2AsO<sub>4</sub>$  and  $HAsO<sub>4</sub><sup>2</sup>$  are present. Arsenic is present in its

trivalent form, which undergoes a similar series of dissociation reactions from  $H_3AsO_3^0$  to  $H_2AsO_3^-$  and  $HAsO_3^2$ . The important difference between arsenite and arsenate is that the uncharged ion  $(H_3AsO_3^0)$  dominates when the pH is less than 9.2, and limits the extent to which arsenite is absorbed (Ravenscroft, Brammer & Richards, 2009).



Figure 2.1 Redox potential (Eh)–pH diagram for aqueous arsenic species in the system As-O<sub>2</sub>-H<sub>2</sub>O at  $25^{\circ}$ C and 1 bar total pressure (Smedley and Kinniburgh, 2002)

Arsenic normally occurs in groundwater with one of four chemical associations, each linked to a particular mobilization mechanism. The four water types are:

- Near neutral, strongly reducing (NNR) waters that are rich in bicarbonate, iron and/or manganese and poor in oxidized species such as nitrate and sulfate. Nearneutral reducing waters are dominated by  $As<sup>3+</sup>$ . These waters are associated with the reductive-dissolution (RD) mobilization mechanism.
- Alkali-oxic (AO) waters, with pH≥8.0 that contain dissolved oxygen and/or nitrate and sulfate and poor in iron and manganese. Alkali-oxic waters are dominated by  $As<sup>5+</sup>$ . These waters are associated with alkali-desorption (AD) mobilization mechanism.
- Acid-sulfate (AS) waters that are slightly to strongly acidic (pH<1-6) and have high sulfate concentrations, and often, high iron concentrations. Acid-sulfate waters are also dominated by  $As<sup>5+</sup>$ . These waters are associated with the sulfideoxidation (SO) mobilization mechanism.
- Geothermal (GT) waters that are distinguished primarily by a temperature well above the background, and that have a strong correlation between arsenic and chloride (Ravenscroft, Brammer & Richards, 2009).

### **2.2 Arsenic Contamination in Natural Waters**

As discussed by Henke (2009), arsenic may originate from anthropogenic or natural sources including but not limited to:

- Improper manufacturing, use, and disposal of arsenic-containing products
- Extensive application of arsenic-bearing pesticides and phosphate fertilizers
- Mine drainage and smelter emissions
- Percolation of evaporative brines into the subsurface or runoff from weathering outcrops and irrigation
- Oxidation of arsenic-containing sulfide minerals in unsaturated zones resulting from declining water tables
- Geothermal waters and discharges from power plants
- Reductive dissolution of arsenic-bearing iron and manganese (oxy)(hydr)oxides
- Bacterial degradation of natural or artificial organic materials, production of carbonate species, and subsequent desorption of arsenic from mineral surfaces.

Arsenic inputs to the environment can be through either natural (geogenic) or anthropogenic processes. Arsenic is mostly released from rocks with primary and secondary arsenic or arsenic-containing minerals. There are numerous geogenic arsenic sources with more than 200 arsenic bearing minerals. Physical, chemical or microbiological weathering can release huge amounts of arsenic into the environment that may be transported over long distances as suspended particulates

through both water and air. Most of the arsenic contamination problems all around the world result from its mobilization and retention, which occur in a wide variety of natural environmental systems under both oxidizing and reducing conditions. Typical concentrations of arsenic in the environment are given in Table 2.1.

<b>Medium</b>	Unit	<b>Arsenic concentration</b>			
Air	$\frac{mg}{m^{3}}$	$1.5 - 53$			
Rain from unpolluted ocean air	$\mu$ g L <sup>-1</sup>	0.019			
Rain from terrestrial air	$\mu$ g L <sup>-1</sup>	0.46			
Rivers	$\mu$ g L <sup>-1</sup>	$0.20 - 264$			
Lakes	$\mu$ g L <sup>-T</sup>	$0.38 - 1000$			
Groundwater	$\mu$ g L <sup>-1</sup>	$1.0 - 1000$			
Seawater	$\mu$ g L <sup>-1</sup>	$0.15 - 6.0$			
Soil	$mg \, kg^{-1}$	$0.1 - 1000$			
Stream/river sediment	$mg \, kg^{-1}$	$5.0 - 4000$			
Lake sediment	$mg \, kg^{-1}$	$2.0 - 300$			
Ingenous rocks	$mg \, kg^{-1}$	$0.3 - 113$			
Metamorphic rocks	$mg \, kg^{-1}$	$0.0 - 143$			
Sedimentary rocks	$mg \, kg^{-1}$	$0.1 - 490$			

Table 2.1 Typical arsenic concentrations in environment (USEPA, 2000).

#### *Natural Sources*

More than 99% of the total arsenic in the environment originates from rocks. Igneous rocks generally have uniform arsenic contents with an average value of about 1.5 mg  $kg^{-1}$ . In metamorphic rocks, arsenic concentration is controlled by that of the original host rock. Most metamorphic rocks contain arsenic with the highest values in schists and phllytes. The arsenic concentration in sediments is variable and depends on many factors such as original rock type, type of weathering, mechanism of transport from weathering to deposition area, including the prevailing geochemical, mechanical and sedimentological processes and formation of secondary minerals (Jean, Bundschuh, Chen, Guo, Liu, Lin & Chen, 2010).

Under typical soil-forming conditions, the nature of soil arsenic is controlled by the lithology of the parent rock material, volcanic activity, weathering history, transport, sorption, biological activity and precipitation (Escobar, Hue & Cutler, 2006). Over 200 minerals include arsenic in their crystalline structure and about 10%

of them are important. The most important of these are arsenopyrite (FeAsS), realgar  $(As<sub>2</sub>S<sub>2</sub>)$  and orpiment  $(As<sub>2</sub>S<sub>3</sub>)$ . The principal arsenic minerals are given in Table 2.2.

<b>Mineral</b>	Composition	<b>Occurrence</b>	
Native arsenic	As	Hydrothermal veins	
Orpiment	$As_2S_3$	Hydrothermal veins, hot springs, volcanic	
		sublimation products	
Realgar	$As_2S_2$	Vein deposits, often associated with	
		Orpiment, clays and limestones, also	
		deposits from hot springs	
Arsenopyrite	FeAsS	The most abundant As mineral, dominant in	
		mineral veins	
Niccolite	<b>NiAs</b>	Hydrothermal veins	
Cobaltite	CoAsS	High-temperature deposits, metamorphic rocks	
Tennantite	$(Cu, Fe)_{12}As_4S_{13}$	Hydrothermal veins	
Enargite	Cu <sub>3</sub> AsS <sub>4</sub>	Hydrothermal veins	
Arsenolite	As <sub>2</sub> O <sub>3</sub>	Secondary mineral formed by oxidation of	
		arsenopyrite, native arsenic and other As	
		minerals	
Claudetite	As <sub>2</sub> O <sub>3</sub>	Secondary mineral formed by oxidation of	
		realgar, arsenopyrite and other As minerals	
Scorodite	FeAsO <sub>4</sub> .2H <sub>2</sub> O	Secondary mineral	
Annabergite	$(Ni,Co)_{3}(AsO4)_{2}.8H2O$	Secondary mineral	
Hoernesite	$Mg_3(AsO_4)_2.8H_2O$	Secondary mineral	
Haematolite	$(Mn, Mg)4Al(AsO4)(OH)8$	Secondary mineral	
Conichalsite	CaCu(AsO <sub>4</sub> )(OH)	Secondary mineral	
Pharmacosiderite	$Fe_3(AsO_4)_2(OH)_3. 8H2O$	Oxidation product of arsenopyrite and other	
		As minerals	

Table 2.2 Major arsenic minerals occurring in nature (Smedley and Kinniburgh, 2002)

Arsenic is often found in hydrothermal sulfide ore deposits and associated with other elements such as gold (Au), silver (Ag), copper (Cu) and uranium (U). Arsenic sulfides such as arsenopyrite are found commonly where tungsten (W) and/or tin (Sn) ore deposits related to granites are seen. Arsenic can also be found in altered zones of mineralized faults and hydrothermal conduits such as feldspatic, argillic and propylitic alteration.

Arsenic is found in very high concentrations in metal oxyhydroxides especially those of iron (Fe), manganese (Mn) and aluminum (Al) mostly in the arseniferous sedimentary aquifers (Jean, Bundschuh, Chen, Guo, Liu, Lin & Chen, 2010). Iron is the fourth most widely found element in Earth's crust and a common component of most rocks and soils. Iron bearing minerals include sulfides, carbonates, hydroxides and oxides. Some minerals contain iron in its reduced ferrous ( $Fe<sup>2+</sup>$ ) state, which is later oxidized to ferric (Fe<sup>3+</sup>) state by weathering of such minerals.

When iron is found in ferrous ( $Fe^{2+}$ ) form in groundwater, it causes high dissolved iron concentrations. Depending on the dissolved oxygen level and pH of water, oxidation rate of iron increases in aqueous solutions. Almost all of the iron found in sedimentary or alluvial materials is in the ferric state. Sediment deposition in lakes or stream beds may turn out to be a source of ferrous iron in local groundwater under reducing conditions (Moss, R., 1990).

Oxidation-reduction potential and pH are important parameters on dissolved iron species and concentration. The oxidation reaction of ferrous ( $Fe^{2+}$ ) iron is given below:

$$
4Fe_{(aq)}^{2+} + O_{2\text{(g)}} + 4H_{(aq)}^+ \rightarrow 4Fe_{(aq)}^{3+} + 2H_2O_{(1)} \tag{1}
$$

Ferric  $(Fe^{3+})$  iron becomes insoluble and precipitates as ferric hydroxide by following reaction:

$$
\text{Fe}^{3+}_{\text{(aq)}} + 3\text{H}_2\text{O}_{\text{(1)}} \leftrightarrow \text{Fe(OH)}_{3_{(s)}} + 3\text{H}^+_{\text{(aq)}} \tag{2}
$$

Manganese is another abundant element in the Earth's crust. Manganese chemistry is similar to iron but there are some important differences. The most important oxidative states of manganese are  $Mn^{2+}$ ,  $Mn^{4+}$  and  $Mn^{7+}$ . Manganic  $(Mn^{3+})$ is unstable in water and decomposes to manganous  $(Mn^{2+})$  ion and precipitates as manganese dioxide  $(MnO<sub>2</sub>)$  by following reaction:

$$
2Mn^{3+} + 2H_2O \leftrightarrow Mn^{2+} + MnO_{2(g)} + 4H^+ \tag{3}
$$

Precipitation of manganese dioxide causes oxidation of manganous. Soluble manganese exists as the reduced manganous  $(Mn^{2+})$  ion in groundwater. Reduced forms of manganese creates quite insoluble precipitates with an oxidation rate slower than iron.

Aluminum is the third most abundant element in the Earth's crust. As a result of low solubility of Al bearing minerals at near-neutral pH, aluminum concentrations in natural waters are typically very low. High concentrations of aluminum in groundwater are strongly correlated with low pH values. Aluminum is found in water in dissolved or ionic form (complexes formed with the hydroxy ions). Mobilization of aluminum in acidic waters ( $pH<5$ ) can be achieved by the dissolution of aluminosilicate and weathering of clay minerals. Gibbsite  $Al(OH)$ <sub>3</sub> mineral usually controls aluminum solubility. Aluminum is mostly found in  $Al^{3+}$  state in waters and precipitates as hydroxides or oxyhdroxides. Aluminum hydroxide formation is given by following reaction:

$$
Al_{(aq)}^{3+} + 3H_2O_{(1)} \leftrightarrow Al(OH)_{3_{(s)}} + 3H_{(aq)}^+ \tag{4}
$$

Arsenopyrite is the most common mineral where arsenic is its major component. Oxidation rate of arsenopyrite depends on pH, temperature and concentrations of chloride or iron (III) sulfate. The following reaction explains arsenopyrite oxidation in water (Henke, 2009):

$$
4\text{FeAsS} + 110_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Fe}^{2+} + 4\text{H}_3\text{AsO}_3^0 + 4\text{SO}_4^{2-} \tag{5}
$$

As shown in the following reaction, Fe(III) is capable of oxidizing inorganic As(III) at very acidic conditions ( $pH \leq 3.5$ ) (Henke, 2009):

$$
H_3AsO_3^0 + H_2O + 2Fe^{3+} \rightarrow H_2AsO_4^- + 3H^+ + 2Fe^{2+}
$$
 (6)

Similar to arsenopyrite, realgar and orpiment are also among the most important arsenic-bearing minerals that create high arsenic levels in natural waters. Oxidation rate of orpiment tends to increase at high temperatures under pH>8 conditions. When dissolved oxygen levels are low, carbonates may dissolve realgar and orpiment.  $HCO<sub>3</sub>$  is less effective than  $CO<sub>3</sub><sup>2</sup>$  in dissolving arsenic from arsenic sulfides, but it is more dominant in near-neutral waters and more responsible of arsenic dissolution. The following reaction could explain the oxidation or orpiment to inorganic As(III) in the aqueous solutions (Henke, 2009):

$$
As_2S_3 + 6O_2 + 6H_2O \rightarrow 2H_3AsO_3^0 + 3SO_4^{2-} + 6H^+ \tag{7}
$$

Under oxidizing and near-neutral pH conditions, inorganic As(III) could slowly oxidize to inorganic As(V) by following reaction:

$$
2H_3AsO_3^0 + O_2 \to H_2AsO_4^- + HAsO_4^{2-} + 3H^+ \tag{8}
$$

Arsenic minerals such as arsenopyrite, realgar and orpiment are stable when there is no oxygen, but are easily broken down by oxidation. Metal oxides do not take arsenic into their structure, but have a great capacity to absorb arsenic onto their surface. Iron oxides are the most important minerals in controlling the occurrence of arsenic in groundwater. In contrast to sulfides, oxides are formed in environments where there are ready sources of oxygen, and conversely breakdown and dissolve in anaerobic environments (Ravencroft, Brammer & Richards, 2009).

The causes of arsenic contamination in groundwater have been attributed to several geophysical, geochemical and biological processes, including oxidation of arsenical sulfides, desorption of arsenic from (hydro)oxides, reductive dissolution of

arsenic–containing (hydro)oxides, release from geothermal waters, and evaporative concentration as well as leaching of arsenic from sulfides by carbonates (Wang & Mulligan, 2006).

Chemical processes such as dissolution/precipitation (i.e., reductive dissolution of Fe oxides and hydroxides, reduction of sulfate and precipitation of pyrite), biological transformations such as (microbial oxidation of organic matter), and physicochemical processes such as adsorption/desorption and ion exchange are the principal processes that are responsible for arsenic release and mobility. Arsenic transport in surface waters can be either in dissolved form (influenced by river/lake sediment-water interactions along the flow path) or in solid form as part of the sediment load of the river. Arsenic is transported predominantly in dissolved form in aquifers, where colloidal transport might also be seen. In the groundwater, dissolved arsenic concentration depends on the groundwater flow field and the geochemical conditions of fluid and solid, which are due to changes along a groundwater flow path (Jean, Bundschuh, Chen, Guo, Liu, Lin & Chen, 2010). The principal geochemical reactions and influencing parameters, which control the arsenic concentrations in groundwater, can be seen in Table 2.3.

Some specific arsenic release/mobilization/transport processes from a geogenic source into groundwater and surface water can explain high arsenic concentrations in many arseniferous aquifers around the world (Ravencroft, 2009; Henke, 2009; Jean, et al., 2010). These release/mobilization/transport processes can be listed as follows:

 Sulfide oxidation in mineralized areas: Oxidation of sulfides, especially of pyrite and arsenopyrite, (by the presence of Fe(III) or exposing to atmospheric oxygen) release arsenic and Fe into the solution or into the other minerals.

	<b>Controlling mineral</b> phases and principal reactions	<b>Controlling arsenic</b> mobility conditions		
	Fe (Mn, Al)	pH; As oxidation state and		
	oxides/oxyhydroxides:	species; presence of ions		
	Adsorption/desorption	competing for adsorption		
	of As	sites; ionic strength;		
		oxygen and $\text{Fe}^{3+}$ , organic		
Oxidizing conditions		acids concentrations		
	Fe (Mn, Al)	(as above)		
	oxides/oxyhydroxides:			
	Precipitation and co-			
	precipitation of As			
	Sulfide minerals:	pH and microbial activity;		
	Sulfide oxidation	oxygen and nitrate		
		contents		
	Fe	Oxidation state of As		
	oxides/oxyhydroxides:			
	Adsorption/desorption			
	and precipitation			
Reducing conditions (no sulfide presence)	Fe	Presence of organic carbon		
	oxides/oxyhydroxides:			
	Dissolution (reductive			
	dissolution)	Presence of organic carbon		
	Sulfide minerals			
Reducing conditions (sulfide presence)	Sulfide minerals:	Sulfide, iron, and As		
	Precipitation	concentrations		

Table 2.3 Principal geochemical reactions and influencing parameters controlling arsenic concentration in groundwater (Jean, et al., 2010)

- As dissolution in deep geothermal reservoirs: Arsenic is released from host rocks of geothermal reservoirs where there is high residence time, high temperature and high pressure together with reducing conditions.
- Formation of secondary arsenic minerals: Metal oxyhydroxides as principal arsenic source are formed by a variety of geogenic processes such as sulfide oxidation, geothermal activities, and generally dissolution/leaching of rocks and minerals followed by precipitation of these secondary minerals.
- Arsenic remobilization from metal oxides and hydroxides:
	- a) Dissolution of metal oxyhydroxides under very acidic conditions: Dissolution of metal oxides/oxyhydroxides in strongly acid environments, such as acid mine drainage, and acidic fumaroles or acidic hot spring deposit environments results arsenic release into the aqueous phase.
	- b) Reductive dissolution of metal oxyhydroxides under reducing conditions: By the presence of organic matter, metal oxyhydroxides could release arsenic that might have sorbed or co-precipitated with the compounds.
	- c) Arsenic sorption by metal oxyhydroxides at high pH and oxidizing conditions.
- Arsenic sorption with respect to clay minerals: Clay minerals are widely found in soils, sediments and weathered rocks that have variety of adsorptive properties. pH effects the adsorption/desorption of arsenic on clay minerals which tend to behave similar to iron oxides.
- Precipitation/dissolution and adsorption processes for calcite: At pH range 7-10 arsenic may be adsorbed or co-precipitated onto calcite.
- Arsenic sorption by other solid surfaces: Arsenic is absorbed onto titanium (Ti) oxides lesser extent than iron oxyhydroxides. Phosphate, sulfate silica and calcium can affect adsorption of arsenic.
- Formation of complexes between humic acids and arsenic species: Anion forming organic acids, such as humic substances, competes with arsenic for adsorption sites on metal oxide surfaces.

The areas with aquifers containing high arsenic levels in groundwater are classified in Figure 2.2 according to specific similarities in geological and climatic hydrogeochemical settings.



Figure 2.2 Classification of groundwater environments prone to arsenic problems from natural sources (Smedley and Kinniburgh, 2002).

### *Anthropogenic Sources*

There are various ways to release arsenic into the environment by anthropogenic activities, which affect the level of arsenic contamination depending on the intensity of the human activity and the distance from pollution sources as well as the pollutant dispersion pattern (Wang & Mulligan, 2006). Metal mining, smelting, recycling,

combustion of municipal solid waste, land application of solid waste/sewage sludge, landfilling of industrial wastes, release or disposal of chemical warfare agents, petroleum refining, and production of pharmaceutical and wastes of construction industry, wastes of pest-control industries and its applications in agriculture and forestry, and combustion of fossil fuels are major anthropogenic sources, which tend to release arsenic into the environment.

Arsenic enters the environment in two steps: (1) extraction from deposits inside the earth and (2) through primary/secondary/recycling processes and the simultaneous gradual dissipation into the environment. Arsenic containing wastes are often produced during the extraction of metals such as copper, gold, nickel, and tin (Wang & Mulligan, 2006). Fine particles selectively eroded from the mining wastes, tailings and slag have the potential to contaminate nearby soils or migrate as sediments in surface waters, greatly enlarging the area affected by the original mining activities. Secondary contamination often occurs in groundwater beneath or down gradient open pits and ponds. Sediments in river channels and reservoirs, and floodplains are also affected by arsenic derived from mining operations (Escobar, Hue & Cutler, 2006).

Combustion of fossil fuels such as coal and petroleum also has an important effect on releasing arsenic into the environment. The amount of arsenic generated from petroleum is relatively small compared with the contribution from coal. Since the 1920s, world arsenic production has increased faster than that originating from the world coal and petroleum industries. In 2000, world cumulative arsenic production from mining was 3.3 million tons and the cumulative global arsenic production from coal and petroleum was 1.24 million tons (Han, Su, Monts, Plodinec, Banin & Triplett, 2003).

Using arsenic compounds as an antibiotic additive in poultry industry may also cause soil and water contamination where the industry settled. Agricultural use of most arsenic compounds as herbicides and pesticides have been banned due to greater understanding of arsenic toxicity and awareness regarding to food safety and

environmental contamination where manufacturing waste and arsenic-laden liquids near manufacturing areas can cause contamination of soil and water bodies.

Water-soluble wood preservatives such as chromated copper arsenate (CCA) and other arsenic compounds result in an accumulation of arsenic in environment. Irrigation with high concentration of arsenic may cause contamination in agricultural areas. Small amounts of very pure arsenic metal are used to produce gallium arsenide, which is a semiconductor used in computers and other electronic applications (Escobar, Hue & Cutler, 2006).

#### **2.3 Toxicity and Health Effects**

Since arsenic has been classified as a human carcinogen, awareness of chronic arsenic toxicity increased worldwide. It is now known that exposure to arsenic causes various adverse health problems including: internal organ cancers, skin lesions, neurological problems, high blood pressure, respiratory and cardiovascular diseases, obstetric problems and diabetes mellitus (Rahman, Ng & Naidu, 2009). Arsenic related adverse health effects depend on dose, exposure period and nutrition status of the exposed population. Exposure to arsenic mostly occurs via ingestion of arsenic contaminated food and water. However, most adverse health effects of arsenic are seen after a minimum of 30-50 year exposure to arsenic contaminant food and water.

The primary toxicity mode of inorganic trivalent arsenite  $(As<sup>3+</sup>)$  is through reaction with sulfhydryl groups of proteins and subsequent enzyme inhibition. On the other hand, inorganic pentavalent arsenate  $(As<sup>5+</sup>)$  does not react as readily as trivalent arsenite  $(As^{3+})$  with sulfhydryl groups, but may uncouple oxidative phosphorylation. Inorganic arsenic  $(As^{3+})$  interrupts oxidative metabolic pathways and sometimes causes inactive enzymes such as in liver mitochondria. Arsenite in vitro reacts with protein-SH groups to inactivate enzymes producing inhibited oxidation of pyruvate and beta-oxidation of fatty acids (Eisler, 2000).

Toxicity of arsenic also depends on available exposure routes, frequency of exposure, biological species, age, gender, individual susceptibilities, genetics, and

nutritional sources (Khan, Owens, Bruce & Naidu, 2009). Long-term exposure to low levels of arsenic in food and water causes adverse effects on human health, which is described by the term arsenicosis. Epidemiological studies show that there is an increased risk of cancers in the skin, lung, liver, and lymph. Furthermore, there is also a strong link that exposure to inorganic arsenicals also triggers cardiovascular diseases and diabetes mellitus. All adverse health effects are dose-related and primarily arise from oral exposure to arsenic, although inhalation of arsenic may also result in certain adverse health effects.

Since the effects of arsenic depend on cumulative exposure, the symptoms are most commonly seen in adults, and because of their lifestyle, in men more than women. Early symptoms are non-specific effects such as muscular weakness, lassitude and mild physiological effects. These are followed by characteristic skin ailments such as changes in skin pigmentation and progressively painful skin lesions, as known keratosis (Villaescusa & Bollinger, 2008).

The clinical presentation of acute As poisoning occurs in two distinct forms: acute paralytic syndrome and acute gastrointestinal syndrome. Acute paralytic syndrome is characterized by cardiovascular collapse (secondary to a direct toxic effect), central nervous depression (caused by vasodilation resulting in hemorrhagic necrosis of both white and gray matter) and death within hours. Acute gastrointestinal syndrome starts with a metallic or garlic like taste associated with dry mouth, burning lips and dysphagia. Violent vomiting may follow and may eventually lead to hematemesis. (Abernathy, Thomasy & Calderon, 2003).

### **CHAPTER THREE DESCRIPTION OF THE STUDY AREA**

### **3.1 General Morphology Of Simav Plain**

Simav Plain is located within the boundaries of the Simav district in Kütahya province of Aegean Region (Figure 3.1). Simav, which is the most western district of Kütahya, is surrounded by Emet to the north, Gediz to the south and Selendi to the west.



Figure 3.1 Location of Simav Plain

The study area is formed at the base of a graben system, which is naturally a closed basin and is surrounded by Ak Mountain to the north, Eğrigöz Mountain to the east and Simav Mountains to the South (Figure 3.1). This graben system was filled by the alluvial sediments of the surrounding mountains. The average elevation of the area is 800 m. To the south of the plain, topography reaches to 1800 m altitude on Simav Mountains.

The Simav Plain was mostly covered by a shallow lake, which was drained in 1960s by the State Hydraulic Works (DSI). Until 1960s, the plain was a semi-closed basin, which was drained to the north in the direction of Dağardı district. Following the drainage activities conducted by DSI, the basin is now drained to the west via the Simav Creek. The drainage project aimed to drain and dry the shallow Simav Lake area and gain new lands for agriculture (Figure 3.2). Within the scope of Simav Lake drainage project, various drainage ditches and channels was built. Finally, the control of the system was provided by a regulator constructed (Figure 3.3) near Boğazköy village to control the flow of Simav Creek.



Figure. 3.2 Satellite view of agricultural lands on Simav Lake area.

Today, the regulator valves are kept open to drain water from the basin, but Simav Lake is partially reformed as a result of heavy precipitation during winter months and groundwater seepage (Figure 3.4). The shallow lake inundates the agricultural lands during winter until accumulated water evaporates and drains by mid May. A snapshot of the Old Simav Lake that partially reforms during winter season is shown in Figure 3.4.



Figure. 3.3 Regulator on Simav Creek near Boğazköy



Figure. 3.4 A snapshot of the Old Simav Lake that partially reforms during winter season

### **3.2 Population and Economy**

According to recent census results, the 2009 population of Simav District, is 71058 (Table 3.1). Of this total, 34803 are male and 36255 are female. While 24799 people (35%) live in Simav district center, 46259 (65%) live in villages. When the populations of past three years are considered (Table 3.1), it is seen that there is a decline in Simav's population, which might be attributed to migration to other cities and large metropolitan areas such as Izmir and Istanbul.

	<b>District Center</b>		<b>Villages</b>		<b>Total</b>				
	Woman	Man	Total	Woman	Man	<b>Total</b>	Woman	Man	<b>Total</b>
2007	12652	13025	25677	25769	24764	50533	38421	37789	76210
2008	12441	12708	25149	24748	23285	48033	37189	35993	73182
2009	12376	12423	24799	23879	22380	46259	36255	34803	71058

Table 3.1 Populations in Simav district (TUIK, 2009).

Population distributions of Simav district by age groups are shown in Figure 3.5. A relatively homogenous distribution in the 0-59 age group is observed. Most of the population is found in the age groups 15-19 and 45-49. The population under the age of 15 is 18.6% and over 60 is 19.4% of the total population.



Figure 3.5 Distribution of population according to age groups in Simav (TUIK, 2009)

The most important sources of income in Simav District and its villages are agriculture and animal husbandry. About 75-80% of the population is involved in farming and animal husbandry. The land area of Simav is composed of 37% arable fields, 23% forests, 8% fruit orchards and 6% pastures (Simav District Governership, 2010). The total number of cattle and sheep in the district are 22507 and 73151,

respectively. Daily milk production is about 40-45 tons, which is distributed in various markets. In Simav district, cereals (lentil, wheat, barley, corn, pea and bean), vegetables (tomato and pepper) and some industrial plants (sugar beet, opium poppy and sunflower) are grown. Besides, walnut, chestnut, plum, apple, pear, peach, apricot, grape, cherry and sour cherry are also produced in the district. In several greenhouses heated with geothermal fluid, tomato, pepper, cucumber, bean and flowers are grown throughout the year. Thermal tourism is also an important source of income for local economy.

### **3.3 Climate and Vegetation**

Meteorological data from Simav Meteorology Station was used to determine the meteorological conditions of Simav Plain and its vicinity. From 1975 to present, observations on many parameters have been made in this station including but not limited to total daily precipitation, total daily open surface evaporation, daily average temperature and daily average relative humidity (DMI, 2010). Simav Meteorology Station is located in city center and within the study area and thus represents the study area very well.

Based on this data set, the mean daily temperature is 11.7°C while the lowest temperature is -11.5°C and the highest is 28.6ºC for the period of 1975-2006. The mean annual precipitation is 783 mm according to observed precipitation data during the 1975-2009 period. In the same period, total annual mean evaporation was recorded to be 846.2 mm. The average daily relative humidity is 65.9%, with a minimum of 24% and a maximum of 98.7% (DMI, 2010).

Based on these values, Simav Plain is considered to be situated at a transition zone between Aegean climate zone and Central Anatolian climate zone. The area is thus cold and rainy in winters; and, hot and dry in summers. Accordingly, the meteorological conditions in Simav Plain are colder and harder than the Aegean Region, and warmer and softer than the Central Anatolian Region. The precipitation is usually in the form of snow in winter and snow on ground can stay for a long time depending on air temperature.

The prevailing climatic conditions of the area triggers land erosion. The hot and dry summers followed by cold and wet winters results in significant sediment transport from highlands to Simav Plain. The rate of this process depends on the seasonal vegetation cover and precipitation amounts as well as the local topography. In particular, the southern slopes of the area have steep grades that create flash floods and high sediment transport. The relatively thick alluvial layer in the plain is a clue for rapid deposition of transported sediments (Gunduz & Simsek, 2007).

### **3.4 Geology of the Study Area**

According to previous studies, study area has five major geological units including: (i) Paleozoic-aged Menderes Metamorphics, (ii) Paleocene-aged Eğrigöz Granite, (iii) Neogene-aged Kızılbük Formation, (iv) Lower Quaternary- aged Basalt; and (v) Quaternary-aged Alluvium as given in Figure 3.6. Schist, gneiss and marble are mainly observed in the metamorphic rocks of the study area that experienced medium to high metamorphism. Magmatic rocks of the area belong to the Paleocene aged-Eğrigöz magmatic complex and mainly consist of granite that is mostly formed by aplite and pegmatite dykes. The Neogene-aged Kızılbük Formation overlies Menderes Metamorphics and Eğrigöz Granite as the primary rock cover of the study area. It consists of claystone, conglomerate, sandstone, agglomerates and tuff. Nasa Basalt is the youngest volcanic formation that is also considered to be the heat source for the geothermal fields of the study area. An alluvium layer overlies these units and forms the uppermost unit in the Simav Graben Plain (Gunduz, Simsek & Hasozbek, 2010).

#### **3.5 Hydrology and Hydrogeology**

The hydrogeology of the study area is governed by two major aquifer systems based on geological formations mentioned above and can be seen in Figure 3.7. The first aquifer is the alluvial surficial aquifer supplying fresh cold water that provides the majority of extracted groundwater for drinking, irrigation and industrial use within the plain.



Figure 3.6 Geological structure of the Simav graben plain.


Figure 3.7 Schematic cross section of the Simav graben plain

This alluvial surficial aquifer is mainly a composition of sedimentary sands and gravels. The aquifer reaches up to 90 m thickness and the biggest amount of extracted groundwater is provided by this aquifer. General groundwater flow is from SE to NW and groundwater depth is quite shallow in the plain. The depths of water supply wells vary between 15 and 90 m, and all irrigation and drinking water demands of a few settlements are supplied from this aquifer. The sediments of old Simav Lake is the best place to observe the general characteristics of this alluvial layer (Gunduz & Simsek, 2007). These sediments originate from different lithological rocks found around the study area and their deposition form the graben plain as a result of sediment transport from the highlands.

The second aquifer is the deep confined aquifer, which is a part of the local geothermal system formed along the major fault lines that pass underneath the Simav graben zone. In this system, hot geothermal waters surface out from the fault line and mix with surface and subsurface waters of the plain. The reservoir rocks of geothermal field found underneath the Simav Plain are compositions of conglomerates, sandstones, limestones, schists and marbles, which belong to Kızılbük Formation and Menderes Metamorphics that supply hot geothermal water.

This system resulted in three major geothermal fields located at Çitgöl, Eynal and NaĢa. Nowadays, these fields are used as thermal spas, hot water supplies for the central heating system of the Simav city center and in greenhouse heating. Because of its high geothermal energy, many large energy companies have an increasing interest in these geothermal fields.

While there are benefits of geothermal areas, there are also some disadvantages. Among those disadvantages, uncontrolled waste geothermal fluid discharge (upon its use in thermal facilities) into surface water resources comes in the first place (Figure 3.8). Under such conditions, hot waste geothermal water has negative impacts on the ecological life and water quality. It is possible to see this situation in the three geothermal fields of Simav.



Figure 3.8 Waste geothermal fluid discharge to surface waters.

#### **3.6 Mining Activities**

As a result of a study that is made by General Directorate of Mineral Research and Exploration (MTA), metallic minerals, industrial raw materials and lignite formations were discovered within the boundaries of the Simav district. During early 1960s, an ore processing facility for the Cu-Pb-Zn mine situated at Dağardı district was operated for copper and lead production near Simav district center. Furthermore, a Sb-mine was operated till 1980s near city center. The mine wastes from these facilities were improperly disposed near city center without any mitigation measures. In addition, a feldspar mine was operated within the district for long years. The mines operated in Simav and ore properties are given in Table 3.2.





# **CHAPTER FOUR MATERIALS AND METHODS**

A multidisciplinary research was conducted in Simav Plain to understand the origin of high arsenic levels in surface and subsurface water resources of the area, to delineate the relations between drinking water quality and observed diseases, and to assess public health risks. To achieve this objective, representative samples from surface and subsurface waters including hot geothermal fluids were collected as part of a field survey and these samples were analyzed using standard techniques. In addition, individual household surveys and oral autopsies are conducted by interviewing local inhabitants and relatives of deceased people to determine the status of public health in the area.

In this chapter, materials used and methods implemented for field studies, laboratory analysis, data interpretations and risk analyses are discussed. The field studies included the analysis of field parameters and the collection of samples from surface and subsurface waters within the scope of a water quality monitoring program. The water samples are collected from different locations that completely represent 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 Dokuz Eylül University Environmental Engineering Department and the analyses of heavy metals and trace elements were performed with inductively coupled plasma – mass spectrometry (ICP-MS) in ACME Laboratories (Canada). Finally, the database created as a result of water quality monitoring program was transferred to a Geographical Information System (GIS) for data visualization and interpretation.

### **4.1 Field Study**

Before commencing field studies, topographic maps and borehole data of the study area were obtained and preliminary GIS datasets were created to set the basis for field survey. The field studies were then conducted in three periods; 25-30 January 2010 (preliminary field surveys and selection of sampling points), 04-09

May 2010 (water quality sampling) 11-25 July 2010 (household surveys and oral autopsies) in Simav Plain located in the Simav District, Kütahya.

Firstly, to see general view of the Simav Plain and to make a preliminary explorations; general baseline information, maps, plans and reports that are related to the study area were gathered from different sources including but not limited to State Hydraulic Works. In this regard, hydrological, geological and morphological structure of the basin and plain were studied. As preliminary exploration of the study area, locations of some springs, fountains, and wells were determined and geographical coordinates (X, Y and Z) were recorded by a handheld GPS device.

### **4.2 Water Quality Sampling**

During field exploration, the locations of sampling points were selected such that a relatively homogenous distribution of sampling points was obtained within the plain to better characterize the quality of surface and subsurface waters with highest possible accuracy. Consequently, a total of 45 sampling points were used in this study. Of these 45 points, 33 represent groundwater samples including production wells drilled in the alluvial surficial aquifer for domestic and irrigational water supply purposes, springs and shallow wells; three represent deep geothermal wells that extract hot geothermal fluid for the three geothermal fields located in the plain; and the remaining nine represent surface waters. Hydrogeochemical analysis of these 45 samples were undertaken to represent not only the overall quality model in the plain but also the general circulation and contamination mechanisms.

Prior to groundwater sampling, wells were purged for a minimum of 15 minutes or until electrical conductivity of the well water stabilized. This purging procedure was omitted for continuously operated water supply and geothermal wells and springs. During sampling, physical parameters (temperature, pH, oxidation-reduction potential, electrical conductivity and dissolved oxygen) were measured in-situ with a multi-parameter probe. Measured field parameters and their explanations are given in Table 4.1

<b>Parameter</b>	<b>Explanation</b>
pH	Negative logarithm of hydrogen activity; $-log[H+]$ .
<b>Oxidation Reduction Potential (Eh)</b>	Oxidation-reduction potential. Expressed as millivolt (mV).
Temperature	Expressed as $^{\circ}C$ .
<b>Electrical Conductivity</b>	Ability to conduct electrical current. Expressed as $\mu$ S/cm.
Dissolved Oxygen	Amount of dissolved oxygen. Expressed as mg/L and %
	Saturation

Table 4.1 Measured field parameter

Following the measurement of field parameters, samples were then collected from each sampling point with polyethylene bottles for laboratory analysis (i.e., 250 mL for the analysis of standard anions and cations, 50 mL for the analyses of heavy metals and trace elements and 50 mL for the analyses of TOC). All 50-mL samples taken for heavy metal and trace element analysis were acidified with nitric acid to achieve a pH value less than 2. For heavy metal and trace element analysis, 17 additional 50 mL samples were taken from random sampling points, which were filtered with 0.45 μm syringe filters in the field prior to acidification to get the dissolved phase of trace elements and heavy metals. Samples collected for TOC analysis were also preserved using sulfuric acid to achieve pH value of below 2.

All samples collected from the field were then stored in portable coolers and transferred to the laboratory where they were kept at 4°C in a refrigerator until the time of analysis. TOC and major anions and cations were analyzed within one week after sampling at laboratories of Dokuz Eylül University Department of Environmental Engineering using high temperature combustion technique for TOC analysis and ion chromatography technique for major anions and cations. The analysis of heavy metals and trace elements were done in ACME laboratories (Canada) using inductively coupled plasma mass spectrometry technique. Finally, the alkalinity measurements were done in laboratories of Dokuz Eylül University Department of Environmental Engineering using standard acid titrimetry method.

The data obtained from field studies and from laboratory analysis were then processed by using ArcGIS 9.3 and Aquachem 3.7 software. All data (primary baseline GIS data, sampling point locations, water quality monitoring results etc.) collected from the study area were gathered in a GIS database. Representative maps

of water quality monitoring results and health risk assessment were produced by using ordinary krigging method that implements an exponential semivariogram. Correlation analyses were made by using SPSS statistical software.

#### **4.3 Health Risk Assessment**

To see the relationship between arsenic and human health (diseases and death causes) in the last five years, individual household surveys and oral autopsy interviews were performed in the study area. In a previous study conducted in the area, high arsenic levels were detected in the drinking water wells of Gölköy and Boğazköy villages (Gunduz & Simsek, 2007). After this study, those wells were abandoned in 2008 and villagers started using new water supplies with less arsenic content. However, the inhabitants of these villages were exposed to arsenic-laden water for many years. According to the results of the previous study, the local people at Gölköy and Boğazköy were exposed to a fairly high arsenic level of 177.2 µg/L. Thus, these two villages were chosen as test villages during the health survey. Öreğler and Demirciköy towns, which has arsenic levels below water quality standard value were then chosen as control villages and were included in this study. Consequently, four settlements were included in the health survey. The total number of surveys to be completed was then calculated based on the following formula:

$$
n = \frac{N\left(Z_{\alpha/2}^2 P(1-P)\right)}{d^2(N-1) + Z_{\alpha/2}^2 P(1-P)}
$$
(9)

where n represents sample size, N represents universe size,  $Z_{\alpha/2}^2$  represents a constant from T tables, P and d represent frequency and deviation.

Individual household survey form used in this study is given in the appendix. The survey included three subsections: (i) basic demographic domains (age, gender, etc.), (ii) mini mental test, and (iii) health status.

Oral autopsy interviews were then made with the relatives of people died in the last 5 year period within the above-mentioned four villages. The oral autopsy was carried out to determine the reason of death and the diseases that the patient suffered before his or her death. The survey form used for oral autopsy interview is given in the appendix. The SPSS statistical software was then used to analyze data collected from surveys and interviews.

The lifetime cancer risk and hazard quotient for chronic arsenic exposure was then calculated using standard U.S. Environmental Protection Agency protocols. Accordingly, chronic daily intake (CDI; miligrams per kilogram per day) was determined by using the equation given below (Markley & Herbert, 2009):

$$
CDI = \frac{C \times IR \times EF \times ED}{BW \times AT \times 365}
$$
 (10)

where C is the arsenic concentration  $(mg/L)$ , IR is ingestion rate (liter per day, EF is the frequency of exposure (days/year), ED is duration of exposure (year), BW is body weight (kg), AT is average time of exposure and 365 is the conversion factor from year to days. The non-carcinogenic hazard quotient (HQ) and lifetime cancer risk were then calculated with equations given below:

$$
HQ = CDI /_{RfD}
$$
 (11)

$$
RF = CDI \times OCSF \tag{12}
$$

where RfD is the reference dose (milligrams per kilogram) for arsenic and OCSF is the oral cancer slope factor for skin cancer (Markley & Herbert, 2009).

## **CHAPTER FIVE RESULTS AND DISCUSSIONS**

This chapter is organized to present the results of the water quality monitoring program and the health risk assessment study conducted in Simav Plain. As it was mentioned in the previous chapter, water quality monitoring of Simav Plain is classified as three major groups: (1) field parameters, (2) major anions and cations and total organic carbon; and, (3) heavy metals and trace elements. The results of the water quality program are grouped in the aforementioned three groups and further subdivided into three categories of (1) surface waters, (2) groundwater and (3) geothermal waters. Locations and descriptions of sampling points are given in Table 5.1.

All data collected within the scope of this study are presented in following sections together with their statistical summaries and comparison with related water quality standards including the Turkish Regulations on Waters for Human Consumption (ITASHY, 2005), Drinking Water Standards of U.S. Environmental Protection Agency (EPA, 2009) and Drinking Water Quality Criteria of World Health Organization (WHO, 2008). The areal distributions of selected parameters are drawn to demonstrate spatial variation of the parameter. The correlations of these parameters with arsenic are provided and their influence on overall water quality is discussed in the following sections. Finally, the risk assessment results of household and oral autopsy surveys are presented.

## **5.1 Groundwater**

In this section, the results of field parameter measurements (temperature, pH, electrical conductivity (EC), dissolved oxygen (DO) and redox potential (Eh)), TOC, alkalinity and major anions and cations as well as the results of trace elements and heavy metals are presented.

Point N <sub>0</sub>	<b>Type</b>	Date	Time	$\mathbf X$	Y	Z	<b>NOTES</b>
P332	Hot water well	07.05.2010	18:38	669398	4334631	788	Nasa hot spring
P333	Surface water	07.05.2010	12:35	659936	4336805	780	Boğazköy regulatory
P334	Well	07.05.2010	12:05	660890	4334896	778	Old Boğazköy Gölköy drinking water well
P336	Well	08.05.2010	11:10	671533	4331628	794	Eynal drinking water well
P353	Well	07.05.2010	20:07	671995	4334031	838	Hüsüm village drinking water storage tank
P354	Well	06.05.2010	13:20	671337	4331231	799	Yeşilova drinking water well
P355	Well	06.05.2010	13:25	671352	4331250	800	Well in Selahattin Bey's garden
P359	Well	06.05.2010	10:00	675512	4329232	826	Gökçeler village drinking water well
P360	Spring	06.05.2010	12:00	674881	4326875	835	Yeşilköy drinking water spring
P361	Well	06.05.2010	09:09	669706	4332465	788	Çitgöl drinking water well
P362	Well	07.05.2010	18:10	668463	4341581	769	Hamzabey village drinking water well
P363	Well	07.05.2010	17:18	665184	4339349	807	Güney drinking water well
P367	Well	07.05.2010	11:40	662617	4333244	789	Gümüssu drinking water well.
P368	Well	07.05.2010	11:55	661976	4333925	795	New Boğazköy-Gölköy drinking water well
P384	Well	07.05.2010	12:20	660072	4336275	785	Boğazköy field
P387	Surface water	06.05.2010	10:15	675417	4329136	816	Catalca Creek
P388	Surface water	06.05.2010	10:40	674054	4329300	817	<b>Balaban Creek</b>
P389	Spring	06.05.2010	11:30	678093	4327819	889	Kalkan village drinking water storage tank Sampling from entrance to storage tank
P390	Well	06.05.2010	12:45	671710	4329870	802	Close to GW-5
P391	Spring	06.05.2010	15:20	670382	4326780	1092	Mehmet Demiray fountain
P392	Well	06.05.2010	16:15	670530	4330886	786	$GW-3$
P393	Well	06.05.2010	16:35	670298	4330157	793	Pumping well in Emine İnan's field
P394	Surface water	06.05.2010	16:50	669240	4331140	793	Drainage channel receiving raw was tewater of Simav district
P395	Well	06.05.2010	17:25	670415	4332373	796	Next to Dokuzgözlü Bridge

Table 5.1 Locations of sampling points, descriptions of.

P396	Surface water	06.05.2010	17:35	670154	4333276	795	Drainage channel next to Citgöl hot spring
P397	Well	06.05.2010	18:00	669982	4334690	791	Next to Nasa hot spring. Cingene hamami location
P398	Surface water	06.05.2010	18:30	667290	4335548	780	Daldırma Creek. Söğütlük location
P399	Well	06.05.2010	18:45	667245	4335040	787	İskele well location.
P400	Surface water	06.05.2010	19:10	665532	4334510	784	Junction of three creeks
P401	Well	06.05.2010	19:25	666632	4332964	790	GW-18
P402	Well	06.05.2010	19:45	668752	4331358	798	Citgöl new drinking water well
P403	Well	06.05.2010	19:55	667936	4330564	788	GW-16. Beyce field
P404	Spring	07.05.2010	09:10	667580	4329279	891	Beyce drinking water storage tank. Sampling from entrance to storage tank
P405	Spring	07.05.2010	09:30	665723	4329725	890	Demirci drinking water storage tank. Sampling from entrance to storage tank
P406	Spring	07.05.2010	10:00	663305	4330871	857	Öreğler drinking water storage tank. Sampling from entrance to storage tank
P407	Spring	07.05.2010	11:10	661816	4331446	835	Caysimav drinking water storage tank. Sampling from entrance to storage tank
P408	Well	07.05.2010	12:55	662628	4335243	785	Gölköy field
P409	Surface water	07.05.2010	13:10	663227	4331749	811	Caysimay Creek
P410	Spring	07.05.2010	16:00	661763	4339722	839	Akdağ drinking water storage tank. Sampling from entrance to storage tank
P411	Spring	07.05.2010	16:15	661272	4340262	873	Akdağ drinking water storage tank. 2. source Sampling from entrance to storage tank
P412	Spring	07.05.2010	17:00	665398	4339515	871	Güney drinking water storage tank. Sampling from entrance to storage tank
P413	Surface water	07.05.2010	17:40	665942	4337774	787	Lake area south of Güney Town
P414	Well	07.05.2010	19:08	670061	4337083	883	Nașa drinking water storage tank. Sampling from entrance to storage tank
P415	Hot water well	07.05.2010	19:20	669953	4333642	798	Citgöl hot spring new water well
P416	Hot water well	08.05.2010	11:00	672472	4332929	810	Eynal hot spring

Table 5.1 (Continued) Locations of sampling points, descriptions of points and quality of sampling points.

#### *5.1.1 Physical Parameters*

The field parameter measurements for 33 groundwater samples were made instantaneously in the field. The results of these measurements are given in Table 5.2. Accordingly, groundwater temperatures ranged between 12.4°C and 23.4°C with an average value of 17.1°C. The well that supplies water to Hüsüm Village (P353) had the maximum water temperature value of 23.4 °C among all other sampling points. Since the village is close to Eynal geothermal field, it is possible that there is a hot water intrusion to this well. On the other hand, springs that supply water to Öreğler (P406) and Beyce (P404) towns had the minimum water temperatures with 12.4°C as these are springs in the Simav Mountains located to the south of the plain.

As seen in Table 5.2, most of groundwater samples vary at a near-neutral pH range of 6.72-7.90 with an average value of 7.35. The maximum pH value of 7.90 was measured at Eynal drinking water well (P336). The minimum pH value of 6.72 was measured in Gümüşsu drinking water well (P367). Groundwater sampling results for pH is all within the allowable range of 6.5-9.5 when compared to water quality standards.

Groundwater sample results for Eh show a range between -123 mV and 192 mV with an average value of 53.95 mV. The maximum value was measured in drinking water supply of Beyce Town (P404), which also has high DO level where oxidizing conditions are dominant. The minimum value of -123 mV, on the other hand, was measured in a well located near Boğazköy (P384), which also had low dissolved oxygen level. Thus, reducing conditions are dominant in this well. Eh distribution map is given in Figure 5.1.

Dissolved oxygen levels in groundwater samples ranged between 12.71-113.04%  $O_2$  with an average value of 59.11%  $O_2$ . The minimum value was measured in a well located near Gölköy village. The maximum value, on the other hand, was measured in drinking water source of NaĢa Town. In six samples, over-saturation was observed where water samples were taken from drinking water storage tank inlet or outlet.

<b>Point No</b>	$T(^{\circ}C)$	pH	Eh(mV)	$EC(\mu S/cm)$	$\overline{DO(mg/L)}$	$\overline{DO(\%)}$
P334	18.90	7.34	44.00	448.00	1.82	21.67
P336	19.60	7.90	87.00	603.00	4.63	56.63
P353	23.40	7.63	169.00	508.00	6.51	84.55
P354	17.60	7.60	130.00	662.00	7.74	90.27
P355	15.70	7.38	152.00	978.00	3.06	34.49
P359	17.30	7.47	103.00	427.00	6.67	76.67
P360	18.70	7.43	111.00	623.00	2.23	26.63
P361	18.70	7.53	95.00	582.00	2.84	33.91
P362	15.60	7.10	145.00	977.00	3.20	35.27
P363	17.10	7.14	$-2.00$	517.00	2.55	29.40
P367	17.40	6.72	$-2.00$	290.00	6.37	73.22
P368	18.00	7.21	$-2.00$	651.00	4.27	49.80
P384	18.70	7.11	$-123.00$	1404.00	2.24	26.85
P389	16.50	7.48	88.00	541.00	9.78	111.47
P390	16.50	7.47	14.00	633.00	2.58	29.41
P391	15.80	7.71	1.00	445.00	8.29	95.29
P392	17.00	7.50	58.00	706.00	5.74	66.18
P393	17.70	7.47	1.00	874.00	2.19	25.54
P395	19.30	7.33	$-5.00$	744.00	1.82	21.73
P397	17.80	6.96	103.00	2127.00	3.09	36.18
P399	19.20	7.52	$-95.00$	737.00	2.88	34.39
P401	20.50	7.39	$-42.00$	660.00	1.54	19.07
P402	21.80	7.56	83.00	629.00	1.27	15.92
P403	15.80	7.01	$-94.00$	515.00	2.46	27.42
P404	12.40	7.42	192.00	147.60	9.24	96.25
P405	13.20	7.43	157.00	170.90	9.95	105.85
P406	12.40	7.44	148.00	212.30	10.32	107.50
P407	15.40	6.83	125.00	143.60	9.40	104.44
P408	18.60	7.27	$-120.00$	334.00	1.08	12.71
P410	15.40	7.16	100.00	70.70	8.98	99.78
P411	14.15	6.89	160.00	87.80	8.14	87.53
P412	14.90	7.25	$-2.00$	37.90	9.25	101.65
P414	14.40	7.78	1.50	476.00	10.40	113.04
Mean	17.13	7.35	53.95	574.60	5.23	59.11
Max	23.40	7.90	192.00	2127.00	10.40	113.04
Min	12.40	6.72	$-123.00$	37.90	1.08	12.71
Std	2.49	0.27	87.97	405.88	3.23	34.83
<b>ITASHY</b>	25	$6.5 - 9.5$	$\bar{\phantom{a}}$	2500	$\overline{\phantom{a}}$	
<b>EPA</b>	$\Box$	$6.5 - 8.5$	$\bar{\phantom{a}}$			
<b>WHO</b>	$\overline{\phantom{a}}$	$6.5 - 8.5$	$\overline{\phantom{a}}$		$\overline{\phantom{a}}$	

Table 5.2 Physical parameters for groundwater of Simav Plain statistical summaries and comparisons with national and international standards



Figure 5.1 Eh distribution map for groundwater of Simav Plain.

Measured EC values ranged from 37.9 μS/cm to 2127 μS/cm with an average value 574.6 μS/cm. The maximum EC value 2127 μS/cm was measured in Cingene Hamamı location (P397). Since this sample point is in Nasa geothermal field, there is a strong possibility that hot waters intrude to this well creating high anion and cation concentrations and high EC values. The minimum EC value of 37.9 μS/cm, on the other hand, was measured in the drinking water supply of Güney Town(P412). Since this settlement supplies its water from mountainous springs, the levels of anion and cation levels are low, which results in low EC values. EC distribution map is given in Figure 5.2.

#### *5.1.2 TOC, Alkalinity and Major Anions and Cations*

The results for TOC, alkalinity and major anions and cations are presented in Table 5.3. Accordingly, maximum TOC concentration of 15.12 mg/L was measured in the sample of Çingene Hamamı location (P397). Anions like nitrite and fluoride concentrations comply with national and international water quality standards at all sampling points and hence are not discussed. The maximum chloride concentration 76.61 mg/L was measured in a sample near Boğazköy (P384). Chloride concentrations of all samples are below the ITASHY standard value of 250 mg/L. The maximum sulfate concentration of 726.71 mg/L was detected in Çingene Hamamı site.(P397) Except two points, all samples are below the standard value 250 mg/L. As this sampling point is located within close vicinity of Nasa geothermal field, it is likely that there is geothermal fluid intrusion to this well.

Similarly, except some sampling points, phosphate, bromide and nitrate concentrations are also typically low. The maximum nitrate concentration 103.03 mg/L was analyzed in the sample from Hamzabey drinking water well (P362). Possible source of nitrate in this point could be the location of the well since it is surrounded by agricultural fields and is very close to the grazing ground of cattle and sheep. The maximum phosphate concentration of 1.65 mg/L was analyzed in the sample from a well near Boğazköy (P384), which is also the grazing ground of cattle and sheep.



Figure 5.2 EC distribution map for groundwater of Simav Plain.

Point N <sub>0</sub>	<b>TOC</b> (mg/L)	HCO <sub>3</sub> (mg/L)	Li (mg/L)	Na (mg/L)	NH <sub>4</sub> (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	$\mathbf{F}$ (mg/L)	$_{\text{Cl}}$ (mg/L)	SO <sub>4</sub> (mg/L)	NO <sub>2</sub> (mg/L)	Br (mg/L)	NO <sub>3</sub> (mg/L)	PO <sub>4</sub> (mg/L)
P334	3.64	265.96	0.19	21.09	0.16	6.42	6.66	71.81	0.21	4.84	25.58	< 0.07	0.03	2.23	0.29
P336	4.49	353.80	< 0.07	12.41	< 0.09	1.47	30.26	86.79	0.22	6.21	48.88	< 0.07	0.04	0.44	0.18
P353	3.65	305.00	< 0.07	13.68	< 0.09	3.11	15.83	76.59	0.21	8.87	13.11	< 0.07	0.04	3.22	< 0.09
P354	2.05	402.60	< 0.07	9.55	< 0.09	1.45	32.47	86.13	0.24	6.02	56.95	< 0.07	0.04	1.16	0.18
P355	5.01	536.80	< 0.07	10.84	< 0.09	3.60	74.36	130.66	0.23	9.60	151.47	< 0.07	0.04	2.80	0.11
P359	2.88	263.52	< 0.07	14.24	0.22	1.51	15.55	60.94	0.28	6.53	18.17	< 0.07	0.04	< 0.23	0.13
P360	2.22	353.80	< 0.07	6.65	&0.09	1.49	42.66	75.22	0.25	3.68	68.26	< 0.07	0.03	0.69	< 0.09
P361	4.53	341.60	< 0.07	16.91	0.36	1.76	25.39	81.22	1.26	7.07	33.96	< 0.07	0.04	< 0.23	0.21
P362	6.68	458.72	< 0.07	40.64	< 0.09	21.54	17.82	160.12	0.50	42.18	56.59	< 0.07	0.06	103.03	0.78
P363	2.57	317.20	0.07	33.20	< 0.09	3.72	15.77	64.51	0.26	14.59	7.36	< 0.07	0.09	5.50	< 0.09
P367	2.93	134.20	< 0.07	9.43	< 0.09	1.60	13.60	34.97	0.22	4.58	28.94	< 0.07	0.04	20.09	0.08
P368	3.34	366.00	< 0.07	11.09	< 0.09	4.45	12.83	124.41	0.24	12.00	47.36	< 0.07	0.04	10.11	0.27
P384	13.49	617.32	0.09	32.40	6.08	18.77	35.33	256.35	0.31	76.61	275.39	< 0.07	0.16	0.23	1.65
P389	3.38	336.72	< 0.07	13.24	< 0.09	2.20	27.92	78.40	0.29	8.46	35.05	< 0.07	0.06	4.31	< 0.09
P390	3.16	414.80	< 0.07	11.79	0.98	1.23	33.36	94.66	0.29	5.31	33.12	< 0.07	0.04	< 0.23	0.16
P391	2.82	305.00	< 0.07	2.51	&0.09	1.30	29.10	65.40	< 0.05	2.97	18.58	< 0.07	0.02	< 0.23	< 0.09
P392	3.30	446.52	< 0.07	10.36	0.48	1.23	38.41	106.14	0.27	10.09	50.82	< 0.07	0.05	< 0.23	0.50
P393	4.26	536.80	< 0.07	26.97	2.68	1.39	37.06	108.85	0.36	32.44	24.81	< 0.07	0.10	< 0.23	0.09
P395	3.55	407.48	0.07	42.41	1.13	3.50	26.57	91.71	0.72	10.27	84.85	< 0.07	0.07	< 0.23	1.59
P397	15.12	800.32	1.32	290.80	< 0.09	39.58	37.25	183.65	4.08	47.96	726.71	< 0.07	0.16	0.24	0.18
P399	3.31	524.60	< 0.07	48.85	5.10	2.09	24.91	88.78	< 0.05	4.24	4.59	< 0.07	0.08	< 0.23	0.22

Table 5.3 TOC, alkalinity and major anions and cations for groundwaters of Simav Plain comparisons with national and international standards

Point No	<b>TOC</b> (mg/L)	HCO <sub>3</sub> (mg/L)	Li (mg/L)	Na (mg/L)	NH <sub>4</sub> (mg/L)	$\mathbf K$ (mg/L)	Mg (mg/L)	Ca (mg/L)	F (mg/L)	$\mathbf{C}$ (mg/L)	SO <sub>4</sub> (mg/L)	NO <sub>2</sub> (mg/L)	Br (mg/L)	NO <sub>3</sub> (mg/L)	PO <sub>4</sub> (mg/L)
P401	3.10	448.96	< 0.07	53.76	1.94	1.71	26.17	65.55	0.26	4.36	8.02	< 0.07	0.06	< 0.23	0.29
P402	2.41	390.40	< 0.07	24.39	0.65	1.48	25.84	84.73	0.25	5.79	27.01	< 0.07	0.04	< 0.23	0.84
P403	4.72	317.20	< 0.07	48.19	5.66	2.34	14.96	39.19	0.66	5.92	0.95	< 0.07	0.11	< 0.23	< 0.09
P404	2.10	82.96	< 0.07	4.97	< 0.09	2.00	< 8.23	< 20.36	0.23	2.33	11.60	< 0.07	0.02	0.31	0.09
P405	2.53	90.28	< 0.07	3.89	< 0.09	2.35	< 8.23	24.24	0.19	2.36	19.21	< 0.07	0.02	0.28	< 0.09
P406	3.09	85.40	< 0.07	4.98	< 0.09	3.98	11.38	< 20.36	0.22	3.00	39.05	< 0.07	0.02	0.50	< 0.09
P407	2.79	43.92	< 0.07	6.46	< 0.09	1.60	< 8.23	< 20.36	0.22	3.14	34.48	< 0.07	0.03	0.81	0.09
P408	3.39	226.92	< 0.07	9.58	2.97	2.82	14.15	45.05	0.32	3.47	3.41	< 0.07	0.04	< 0.23	< 0.09
P410	2.38	41.48	< 0.07	6.52	< 0.09	2.00	< 8.23	< 20.36	< 0.05	3.01	3.24	< 0.07	0.03	0.55	0.33
P411	2.45	43.92	< 0.07	7.15	< 0.09	2.58	< 8.23	< 20.36	< 0.05	2.81	3.16	< 0.07	0.02	1.96	0.26
P412	2.67	14.64	< 0.07	3.38	< 0.09	2.31	< 8.23	< 20.36	< 0.05	2.12	3.95	< 0.07	0.02	0.64	0.14
P414	3.27	312.32	< 0.07	6.93	< 0.09	1.46	16.14	86.50	< 0.05	6.96	14.72	< 0.07	< 0.02	5.36	0.13
Mean	4.59	404.23	0.35	32.34	1.91	5.88	26.07	101.30	0.55	15.45	92.05		0.06	5.07	0.41
Min	2.05	134.20	0.07	2.51	0.16	1.23	6.66	34.97	0.21	2.97	7.36	0.00	0.02	0.23	0.08
<b>Max</b>	15.12	800.32	1.32	290.80	6.08	39.58	76.36	256.35	4.08	76.61	726.71	0.00	0.16	103.03	1.65
St. Dev.	3.40	143.34	0.55	60.62	2.24	9.48	13.99	49.12	0.89	18.80	165.77		0.04	18.01	0.50
<b>ITASHY</b>	$\overline{\phantom{a}}$	$\overline{\phantom{a}}$	$\overline{\phantom{a}}$	200	0.5	$\overline{\phantom{a}}$	50	200	1.5	250	250	0.5	$\sim$	50	$\sim$
<b>EPA</b>	$\overline{\phantom{a}}$	$\sim$	$\sim$	$\overline{\phantom{a}}$	$\overline{\phantom{a}}$	$\sim$	$\overline{\phantom{a}}$	$\sim$	$\overline{4}$	250	250	3.3	$\overline{\phantom{a}}$	44.3	$\sim$
WHO	$\blacksquare$	$\overline{a}$	$\overline{\phantom{a}}$	200	$\sim$				1.5	250	250	$\mathfrak{Z}$		50	$\sim$

Table 5.3 (Continued**)** TOC, alkalinity and major anions and cations for groundwaters of Simav Plain comparisons with national and international standards

Cations like lithium, ammonium and potassium concentrations are typically low. The maximum lithium concentration of 1.32 mg/L was analyzed in the sample of Çingene Hamamı location(P397), which possibly received geothermal fluid inflow. Only maximum sodium concentration (P397) of 290.80 mg/L exceeded the ITASHY standard value of 200 mg/L. The maximum ammonium concentration 6.08 mg/L was measured in a sample near Boğazköy field (P384) where cattle and sheep grazing is done. The maximum potassium concentration of 39.58 mg/L was also analyzed in Çingene Hamamı location (P397) that is under the influence of geothermal fluid. Except for maximum calcium concentration of 256.35 mg/L that was observed in a well near Boğazköy (P384), all calcium values were below the ITASHY standard value of 200 mg/L. The maximum magnesium value of 76.36 mg/L was measured in Hüsüm Village drinking water supply well (P353). Almost all magnesium levels were below the ITASHY standard value of 50 µg/L. The Piper diagram of groundwater samples is given Figure 5.3. Accordingly, groundwater in Simav Plain is mostly of  $Ca-Na-HCO<sub>3</sub>$  water type.

#### Piper Plot For Groundwater



Figure 5.3 Piper diagram for groundwater of Simav Plain.

#### *5.1.3 Trace Elements and Heavy Metals*

Presence of most heavy metals and trace elements in water depend on parameters such as pH, temperature, dissolved oxygen and oxidation-reduction potential as well as their solubility, and presence of some oxyhydroxides. Based on these fundamentals, the results of heavy metals and trace elements are given in Table 5.4. In the study area, arsenic, iron and manganese are predominant in all water types and exceed water quality standards. These parameters are discussed in details in following sections. Parameters such as cadmium, chromium and lead meet water quality standards and are not discussed here. Others are discussed briefly below to provide an overview of ambient water quality in the study area with regards to heavy metals and trace elements.

The maximum aluminum concentration 1114  $\mu$ g/L was measured in a sample obtained from a well located in the vicinity of Beyce Town (P403). In two samples, aluminum values were above the ITASHY standard  $(200 \mu g/L)$ . The maximum boron value of 2170 µg/L was measured in the sample from Çingene Hamamı location (P397). In this sample, fluoride concentration is also high. Possible reason of high boron concentration in this point could be geothermal fluid inflow into this well. Except for one sample, all samples yielded boron concentrations below the ITASHY standard of 1000 µg/L. Copper levels in all samples were below the ITASHY standard value of 50 µg/L. The maximum copper concentration was observed as 8.20 µg/L in Çitgöl drinking water well (P361). On the other hand, the maximum nickel concentration of 15.30 µg/L was measured in a sample taken from the vicinity of Beyce Town (P403). All samples had concentrations below the water quality standard value. Finally, maximum zinc concentration of 101.70 µg/L was measured in the sample of YeĢilköy village (P355). All zinc concentrations were below the ITASHY water quality standard value.

Point No	$\mathbf{Al}$ $(\mu g/L)$	As $(\mu g/L)$	B $(\mu g/L)$	C <sub>d</sub> $(\mu g/L)$	Co $(\mu g/L)$	$C_{r}$ $(\mu g/L)$	Cu $(\mu g/L)$	Fe $(\mu g/L)$	Mn $(\mu g/L)$	Ni $(\mu g/L)$	Pb $(\mu g/L)$	<b>Sb</b> $(\mu g/L)$	Zn $(\mu g/L)$
P334	51	1851.0	57	< 0.05	0.60	0.9	1.2	22211	148.80	< 0.2	4.4	1.86	9.9
P336	<1	6.7	29	< 0.05	0.11	2.3	2.3	<10	104.34	2.7	< 0.1	0.31	1.4
P353	$\overline{4}$	4.1	26	0.05	< 0.02	1.0	2.2	$<$ 10	1.25	< 0.2	0.1	0.07	5.1
P354	14	7.6	31	< 0.05	< 0.02	0.5	0.6	$<$ 10	38.47	< 0.2	< 0.1	0.36	< 0.5
P355	$\tau$	10.8	54	< 0.05	< 0.02	0.6	5.3	<10	23.20	4.7	1.1	0.42	101.7
P359	5	5.3	17	< 0.05	0.10	< 0.5	0.4	61	307.71	< 0.2	< 0.1	0.20	18.4
P360	<1	2.2	68	< 0.05	< 0.02	< 0.5	0.4	<10	< 0.05	0.7	0.8	2.01	1.7
P361	5	42.9	38	< 0.05	< 0.02	< 0.5	8.2	341	163.84	< 0.2	0.2	0.21	6.5
P362	2	64.9	197	< 0.05	< 0.02	< 0.5	2.8	$<$ 10	1.55	< 0.2	< 0.1	0.92	1.2
P363	136	2.3	29	< 0.05	0.06	0.7	2.5	609	30.20	< 0.2	25.6	< 0.05	5.3
P367	154	1.5	6	< 0.05	0.26	1.2	2.5	284	24.85	1.5	0.6	0.06	5.6
P368	$\overline{4}$	9.2	24	< 0.05	< 0.02	< 0.5	0.6	<10	1.26	< 0.2	< 0.1	0.09	1.0
P384	130	231.5	170	< 0.05	< 0.02	0.5	1.4	24	2326.63	< 0.2	0.7	0.09	7.4
P389	16	7.3	14	< 0.05	0.10	< 0.5	1.0	<10	8.03	< 0.2	0.1	0.62	12.7
P390	$\overline{7}$	329.4	29	< 0.05	0.24	< 0.5	2.2	602	1526.02	< 0.2	0.6	0.17	8.0
P391		3.2	12	< 0.05	< 0.02	2.2	0.3	<10	0.29	5.9	< 0.1	0.14	0.6
P392	2	124.2	34	< 0.05	0.10	< 0.5	1.2	651	1949.09	< 0.2	< 0.1	0.11	5.8
P393	701	1070.3	88	< 0.05	1.05	3.0	3.7	8754	2937.77	5.0	1.3	0.14	4.4
P395	$\overline{3}$	475.0	279	< 0.05	0.45	< 0.5	1.3	449	1757.92	0.9	0.7	0.32	23.5
P397	12	77.0	2170	0.10	2.16	1.2	4.3	347	2714.40	4.3	0.1	1.01	4.5
P399		217.2	30	< 0.05	< 0.02	< 0.5	2.0	3291	1689.75	< 0.2	0.1	< 0.05	1.3

Table 5.4 Trace elements and heavy metals for groundwaters of Simav Plain comparisons with national and international standards

Point No	Al $(\mu g/L)$	As $(\mu g/L)$	B $(\mu g/L)$	C <sub>d</sub> $(\mu g/L)$	Co $(\mu g/L)$	$C_{r}$ $(\mu g/L)$	Cu $(\mu g/L)$	Fe $(\mu g/L)$	Mn $(\mu g/L)$	Ni $(\mu g/L)$	Pb $(\mu g/L)$	<b>Sb</b> $(\mu g/L)$	Zn $(\mu g/L)$
P401		270.5	28	0.05	0.15	< 0.5	0.4	959	672.74	< 0.2	< 0.1	0.10	0.8
P402	$\overline{2}$	25.4	32	< 0.05	0.08	< 0.5	0.4	$<$ 10	606.52	0.6	< 0.1	0.14	< 0.5
P <sub>403</sub>	1114	441.8	18	0.45	2.32	5.3	3.0	16331	2656.53	15.3	7.9	0.16	7.9
P404	11	1.6	$\leq$ 5	< 0.05	< 0.02	< 0.5	0.6	$<$ 10	1.44	< 0.2	< 0.1	1.06	0.7
P <sub>405</sub>	26	1.3	6	< 0.05	0.03	< 0.5	0.2	29	0.78	0.2	< 0.1	0.13	0.5
P406	21	1.0	$\leq$ 5	0.18	0.03	< 0.5	3.9	15	0.94	1.9	0.3	0.05	31.6
P407	50	0.8	$\leq$ 5	0.07	0.07	< 0.5	0.9	56	6.62	0.7	0.4	< 0.05	12.0
P408	45	74.5	10	< 0.05	0.03	< 0.5	0.2	4401	532.21	< 0.2	0.2	< 0.05	3.4
P410	59	0.7	$<$ 5	< 0.05	< 0.02	< 0.5	0.3	$<$ 10	1.42	< 0.2	0.1	< 0.05	1.0
P411	23	0.7	$\leq$ 5	< 0.05	< 0.02	< 0.5	0.1	$<$ 10	1.22	< 0.2	< 0.1	< 0.05	0.5
P412	20	0.5	$\leq$ 5	< 0.05	< 0.02	< 0.5	0.3	$<$ 10	0.41	< 0.2	0.3	< 0.05	0.9
P414	3	4.7	23	< 0.05	< 0.02	< 0.5	0.7	$<$ 10	0.85	0.2	< 0.1	0.34	1.8
Mean	84.84	162.64	130.33	0.15	0.44	1.62	1.74	3300.83	632.41	3.19	2.28	0.43	9.26
Min	1.00	0.50	6.00	0.05	0.03	0.50	0.10	15.00	0.29	0.20	0.10	0.05	0.50
<b>Max</b>	1114.00	1851.00	2170.00	0.45	2.32	5.30	8.20	22211.00	2937.77	15.30	25.60	2.01	101.70
St. Dev.	229.63	372.33	412.59	0.15	0.70	1.41	1.79	6293.54	967.30	4.00	5.80	0.53	18.61
<b>ITASHY</b>	200	10	1000	5	$\sim$	50	50	200	50	200	10	5	5000
<b>EPA</b>	200	10	$\sim$	5	$\sim$	100	100	300	50	$\sim$	15	6	5000
WHO	200	10	500	3		50	50	200	400	70	10	20	5000

Table 5.4 (Continued) Trace elements and heavy metals for groundwaters of Simav Plain comparisons with national and international standards

#### *Arsenic*

Being the primary focus of this research, arsenic concentrations in the groundwater samples of the study area ranged between 0.50 µg/L and 1851 µg/L with an average value of  $162.64 \mu g/L$  as shown in Table 5.4. Arsenic distribution map in groundwater of Simav Plain is given in Figure 5.4. Almost half of the samples had higher arsenic levels than ITASHY standard value of 10  $\mu$ g/L as seen from Figure 5.5 (P334 not included). The maximum concentration 1851 µg/L was measured in old Boğazköy-Gölköy drinking water well (P334) that was abandoned in 2008 when a new well was drilled with much lower arsenic levels. Since all proper sampling procedures were not implemented due to site conditions, the value measured in this well should be handled very carefully. However, the same well was previously sampled by Gunduz & Simsek (2007) where they obtained a value of 177.2 µg/L when the well was operative. For this reason, this well has a history of high arsenic levels but the value of 1.85 mg/L is still questionable, as proper well purging procedures could not be performed herein.

As discussed in previous chapter, the form of arsenic in Simav samples was investigated. All arsenic values presented in Table 5.4 are total arsenic levels, which means no filtration was done prior to sample collection. Thus, these values not only include dissolved components but also might contain arsenic in particulate forms. To differentiate between total vs. dissolved forms, some filtered samples were also taken from selected sampling points and filtered from 0.45 µm filters to isolate dissolved form in the eluent. The comparison of arsenic results in these filtered samples with unfiltered samples in the same sampling points revealed that the ratio between dissolved and total arsenic levels in Simav Plain is close to 1, which means that arsenic is mostly in dissolved form in the study area. The dissolved vs. total arsenic percentages are given in the Figure 5.6. It must be noted that there is an experimental error for sample P403, where a ratio of more than 1 was obtained. Considering the sampling problems experienced at P334, the results of this point was excluded when creating Figure 5.6.



Figure 5.4 Arsenic distribution map in groundwater of Simav Plain.



Figure 5.5 Distribution of arsenic concentration in the study and comparison with ITASHY (standard value: 10μg/L) (P334 is not included in this figure)



Figure 5.6 Dissolved vs. total arsenic ratios for groundwater

When high arsenic concentrations measured in this study are examined, it is seen that most of the samples originated from the groundwater samples taken from the alluvial aquifer. As Simav Plain is located in a partially closed basin, deposition of minerals that contain arsenic as the sediment layer could be one of the reasons for high arsenic concentrations in the surface aquifer. In addition to high arsenic levels, seven of these samples (P363, P384, P395, P399, P401, P403 and P408) also had low DO levels and negative Eh values representing reductive conditions.

To understand the dominant arsenic specie in Simav samples, Pourbaix (Eh-pH) diagram is used (Figure 5.7). It is important note, however, that this diagram is typically generated using specific solutions at some specific temperature and pressure values (typically at 1 atm and 25°C), which may not represent the conditions in an actual water sample. Especially in areas where FeS mineral are present, arsenic is predominantly found in arsenite and thioarsenates forms. When the average values of Eh (Eh) and pH in Simav plain groundwater samples are considered (i.e., 53.95 mV and 7.35, respectively), the major dissolved arsenic specie in Simav samples is found to be  $HAsO<sub>4</sub><sup>2</sup>$ , thus, As(V). It must be note, however, that the values are close to the boundary with  $H_3AsO_3^0$ , thus, As(III). When these average values are re-calculated for samples obtained from the center of the plain, one would obtain values of 36.91 mV and 7.36, respectively, which falls in the  $H_3AsO<sub>3</sub><sup>0</sup>$ category. Consequently, arsenic specie in groundwater in central Simav plain is likely to be As(III).



Figure 5.7 Eh-pH diagram for arsenic at 25°C and 1 atm.

Correlations between arsenic and other parameters were calculated by using bivariation method in SPSS platform. For correlation analyses, P334 was excluded due to the problems associated with sampling. Since arsenic is mostly found with metal oxyhydroxides such as iron, manganese and aluminum in sedimentary aquifers, correlation coefficients and significance levels between arsenic and other parameters are given in Table 5.5. According to these correlations arsenic has a negative relationship with Eh (r=-0.43, p=0.05) and DO (r=-0.475, p=0.01), which means that high levels of DO and Eh correspond to low arsenic levels.

On the contrary, arsenic has a strong positive correlation with iron  $(r=0.642,$ p=0.01), manganese (r=0.764, p=0.01), aluminum (r=0.647, p=0.01), cobalt  $(r=0.482, p=0.01)$ , chromium  $(r=0.502, p=0.01)$  and nickel  $(r=0.390, p=0.05)$ . Moreover, arsenic also has positive correlation with some major ions such as bicarbonate ( $r=0.396$ ,  $p=0.05$ ) and ammonium ( $r=0.543$ ,  $p=0.01$ ). It is reported that  $HCO<sub>3</sub>$  could be responsible for arsenic dissolution in near neutral water (Henke, 2009) similar to Simav plain conditions. It is also reported that there is a strong relationship between  $NH<sub>4</sub>$  and arsenic under reducing conditions such as the cases in Bengal and Huhhot Basins (Ravencroft, et al., 2009). At some sampling points in the plain, this condition is observed.

#### *Iron*

In a previous study conducted by Gunduz, Simsek & Hasozbek (2010), the sampling results of local rocks and soils from Simav Plain showed that Fe oxidation exist in both alluvial sediments and metamorphic rocks in the study area. The results of iron concentrations in groundwater samples obtained within the scope of this thesis ranged between 15 µg/L and 22211 µg/L with an average value of 3300.83 µg/L. The maximum concentration of 22211 µg/L was measured in the sample of old Boğazköy-Gölköy drinking water well (P334). The comments made above for arsenic is also valid for iron in this particular well. This value caused a very high average value that is 15 times more than national and international water quality

standards. On the other hand, in almost half of the samples, iron concentrations were measured below the detection limit  $(10 \mu g/L)$  of ICP-MS device.

The comparison of iron levels in groundwater with water quality standards is given in Figure 5.8. Except three samples, all samples with high arsenic concentrations also had high iron levels. The correlation of iron and arsenic (r= 0.642, p=0.01) in groundwater is shown Figure 5.9. As seen from Pourbaix diagram of iron given in Figure 5.10, iron hydroxide is the dominant iron specie in the groundwater samples of Simav Plain. The spatial distribution of iron in Simav Plain is given in Figure 5.11.



Figure 5.8 Distribution of iron concentration in the study and comparison with ITASHY (standard value: 200μg/L) (P334 is not included in this figure)

#### *Manganese*

In this study, manganese concentrations in groundwater ranged between 0.29  $\mu$ g/L and 2937.77  $\mu$ g/L with an average value of 632.41  $\mu$ g/L. The maximum concentration of 2937.77 µg/L was measured in a sample from an alluvial shallow well (P393). This well also has high arsenic levels (1070  $\mu$ g/L) and high iron concentration (8754 µg/L ). As seen in Figure 5.12 manganese concentrations of most samples are above the ITASHY standard value 50 µg/L.

	<b>Correlation coefficient</b>	t	<b>Significance</b>
$T-As$	0.174	0.34	>0.05
pH-As	3.48E-05	0.998	>0.05
Eh-As	$-0.43$	0.014	< 0.05
$EC-As$	0.227	0.125	>0.05
$DO-As$	$-0.475$	0.006	< 0.01
<b>TOC-As</b>	0.142	0.439	>0.05
$HCO3 - As$	0.396	0.025	< 0.05
$Li-As$	$-0.026$	0.889	>0.05
Na-As	0.128	0.487	>0.05
$NH_4$ -As	0.543	0.001	$\sqrt{0.01}$
$K-As$	$-0.016$	0.933	>0.05
Mg-As	0.034	0.851	>0.05
Ca-As	0.225	0.215	>0.05
$F-As$	0.069	0.709	>0.05
$Cl-As$	0.296	$\overline{0.1}$	>0.05
$SO_4$ -As	$-0.031$	0.863	>0.05
<b>Br-As</b>	0.48	0.005	$\sqrt{0.01}$
$NO3-As$	$-0.212$	0.243	>0.05
$PO4-As$	0.225	0.217	>0.05
$AI-As$	0.647	6.31E-06	< 0.01
$B-As$	0.04	0.829	>0.05
$Cd-As$	0.229	0.208	>0.05
$Co-As$	0.482	0.005	$\sqrt{0.01}$
$Cr-As$	0.502	0.003	< 0.01
$Cu-As$	0.72	0.27	>0.05
Fe-As	0.642	7.43E-05	< 0.01
$Mn-As$	0.764	3.49E-07	< 0.01
Ni-As	0.390	0.027	< 0.05
Pb-As	0.034	0.852	>0.05
Sb-As	$-0.131$	0.476	>0.05
Zn-As	$-0.026$	0.888	>0.05

Table 5.5 Correlation coefficient and significance levels between arsenic and other parameters



Figure 5.9 Relationship between arsenic and iron concentrations in groundwater (P334 is not included in this figure)



Figure 5.10 Eh-pH diagram for iron at 25°C and 1 atm.

![](_page_66_Figure_0.jpeg)

Figure 5.11 Spatial iron distribution map in groundwater of Simav Plain.

![](_page_67_Figure_0.jpeg)

Figure 5.12 Distribution of manganese concentration in the study and comparison with ITASHY (standard value: 50μg/L) (P334 is not included in this figure)

Arsenic and manganese have a substantially consistent relationship (r= 0.764, p=0.01) as seen in Figure 5.13. Manganese distribution in Simav Plain is given in Figure 5.14.

![](_page_67_Figure_3.jpeg)

Figure 5.13 Relationship between arsenic and manganese concentrations in groundwater

![](_page_68_Figure_0.jpeg)

Figure 5.14 Manganese distribution map in groundwater of Simav Plain.

#### **5.2 Surface Waters**

#### *5.2.1 Physical Parameters*

The results of field parameters of nine surface water samples are given in Table 5.6. Accordingly, temperature values of surface waters ranged between 15.6°C and 25°C with an average value of 21.02°C. The maximum water temperature was measured in a drainage channel (P394), which received the raw wastewaters of Simav District. The channel also receives waste geothermal fluid that probably increases the ambient water temperature in the channel. The minimum water temperature was measured on Çatalca Creek (P387) located in upstream parts of the plain.

Table 5.6 Physical parameters for surface waters of Simav Plain statistical summaries and comparisons with national and international standards.

Point No	$T (^{\circ}C)$	рH	Eh(mV)	$EC$ ( $\mu$ S/cm)	DO(mg/L)	DO(%)
P333	21.50	7.69	55.00	956.00	3.10	38.87
P387	15.60	8.39	135.00	533.00	9.51	105.98
P388	17.20	8.65	107.00	622.00	11.79	135.93
P394	25.00	7.66	$-1.00$	1077.00	0.60	8.02
P396	22.20	8.15	63.00	644.00	4.17	52.94
P398	23.70	8.00	66.00	841.00	0.86	11.20
P400	21.10	7.84	25.00	721.00	2.40	29.72
P <sub>409</sub>	20.40	8.68	104.00	356.00	8.28	100.98
P413	22.50	8.46	100.00	3310.00	10.23	130.80
Mean	21.02	8.17	72.67	1006.67	5.66	68.27
<b>Max</b>	25.00	8.68	135.00	3310.00	11.79	135.93
Min	15.60	7.66	$-1.00$	356.00	0.60	8.02
Std. Dev.	2.98	0.40	43.22	890.87	4.30	50.56
<b>ITASHY</b>	25	$6.5 - 9.5$	$\overline{\phantom{a}}$	2500	$\overline{\phantom{a}}$	
<b>EPA</b>	$\overline{\phantom{a}}$	$6.5 - 8.5$	$\overline{\phantom{a}}$		$\overline{\phantom{a}}$	
<b>WHO</b>	$\overline{\phantom{a}}$	$6.5 - 8.5$	$\overline{\phantom{a}}$		$\overline{\phantom{m}}$	

The pH range of surface water samples varied between 7.66 and 8.68 with an average value of 8.17 as seen in the Table 5.6. Thus, it could be concluded that surface waters in the Simav Plain show a slightly alkaline characteristic. The maximum pH value of 8.68 was measured in Çaysimav Creek (P409) and the minimum pH value of 7.66 was measured in a drainage channel (P394). When this minimum pH value is compared to the pH values of other surface waters, it probably results from industrial discharges to the drainage channel.

Eh results for surface water samples ranged between -1 mV and 135 mV with an average value of 72.67 mV. The minimum value was measured in a drainage channel of Simav District (P394), which also had very low DO levels demonstrating moderately reducing conditions. The maximum value of 135 mV, on the other hand, was measured in Çatalca Creek (P387), which also had high DO level. In this sampling point, oxidizing conditions are dominant. Eh distribution in surface waters is given in Figure 5.15.

In the study area, measured EC values ranged between 356 μS/cm to 3310 μS/cm with an average value of 1006.67  $\mu$ S/cm. The maximum EC value of 3310  $\mu$ S/cm was measured in the lake area to the south of Güney Town (P413). The minimum EC value of 356 μS/cm, on the other hand, was measured in Çaysimav Creek (P409), which is a point at the foothills of Simav Mountains that has no or little anthropogenic influence and thus has moderately low anion and cation concentrations. EC distribution in Simav Plain is given in Figure 5.16

Dissolved oxygen concentrations ranged between 8.02-135.93%  $O_2$  with an average value of  $68.27\%$  O<sub>2</sub>. The minimum value of  $8.02\%$  O<sub>2</sub> was measured in drainage channel of the Simav District (P394) that received raw wastewater discharge from Simav District with high organic matter. The maximum value of 135.93%  $O_2$ , on the other hand, was measured in Balaban Creek (P388), which is a mountain stream where water is aerated by tumbling over falls and rapids.

![](_page_71_Figure_0.jpeg)

Figure 5.15 Eh distribution map for surface waters of Simav Plain.


Figure 5.16 EC distribution map for surface waters of Simav Plain.

#### *5.2.2 TOC, Alkalinity and Major Anions and Cations*

The results of some of the anions and cations as well as TOC for surface water samples are given in Table 5.7. Accordingly, TOC concentrations in surface waters ranged between 3.68 mg/L and 113 mg/L with an average value of 24.30 mg/L. The maximum value of 113 mg/L was measured in the sample from the lake area to the south of Güney Town (P413).

As seen from the table, anions like nitrite and nitrate concentrations comply with national and international water quality standards. The phosphate and fluoride concentrations are also typically low. The maximum nitrite concentration 0.36 mg/L was analyzed in a channel, which possibly received fresh raw sewage discharge upstream the sampling location (P388). The maximum nitrate concentration of 3.31 mg/L was measured in a sample taken from Balaban Creek (P388). The maximum phosphate concentration of 8.38 mg/L was measured in a sample taken from a drainage channel (P394) that receives wastewaters of Simav District center and wool washing companies as well as inflows of organic matter and nutrients from nearby agricultural areas. Generally, chloride concentrations are all below the standard value of 250 mg/L. Maximum chloride concentration of 101.52 mg/L was measured in a sample from the lake area to the south of Güney Town (P413). Dissolution of chloride compounds and evaporation from shallow water depth could be the reason of high chloride concentration in this sampling point.

The maximum sulfate concentration of 2527.30 mg/L was measured in a sample from the lake area to the south of Güney Town (P413). Except for one sample, all samples are below the standard value of 250 mg/L. The maximum fluoride concentration of 1.95 mg/L was observed in a sample taken from a drainage channel of Simav District (P394). Uncontrolled discharge of geothermal fluid could be the reason for high fluoride level in this sample. Only two of the samples are above the ITASHY fluoride standard of 1.5 mg/L.

Point No.	<b>TOC</b> (mg/L)	HCO <sub>3</sub> (mg/L)	Li (mg/L)	Na (mg/L)	NH <sub>4</sub> (mg/L)	$\mathbf K$ (mg/L)	Mg (mg/L)	Ca (mg/L)	F (mg/L)	$\mathbf{C}$ (mg/L)	SO <sub>4</sub> (mg/L)	NO <sub>2</sub> (mg/L)	<b>Br</b> (mg/L)	NO <sub>3</sub> (mg/L)	PO <sub>4</sub> (mg/L)
P333	16.57	366.00	0.10	53.45	4.05	21.68	33.15	112.57	0.75	17.43	221.42	< 0.07	0.08	< 0.23	1.00
P387	6.04	907.44	< 0.07	10.67	0.35	3.03	28.78	78.42	0.24	7.42	47.64	0.15	0.03	2.95	0.10
P388	4.01	378.20	< 0.07	6.83	0.58	2.95	42.29	84.38	0.22	5.66	61.24	0.36	0.03	3.31	0.23
P394	21.55	519.72	0.28	104.21	10.80	18.47	26.66	78.27	1.95	39.38	91.80	< 0.07	0.07	< 0.23	8.38
P396	22.68	309.88	< 0.07	30.99	0.99	30.19	27.89	54.10	0.48	14.14	81.89	< 0.07	0.07	< 0.23	0.29
P398	24.34	439.20	0.09	47.89	1.93	36.14	32.88	83.13	0.65	16.29	87.10	< 0.07	0.06	< 0.23	0.48
P400	6.81	366.00	0.15	56.33	6.06	12.36	22.17	65.59	1.31	18.13	65.65	0.19	0.04	0.43	3.37
P <sub>409</sub>	3.68	207.40	< 0.07	3.95	< 0.09	2.08	16.74	55.39	0.25	3.26	36.53	< 0.07	< 0.02	0.28	< 0.09
P413	113.00	361.12	0.13	156.32	0.67	14.83	< 8.23	< 20.36	1.04	101.52	2527.30	< 0.07	< 0.02	< 0.23	< 0.09
Mean	24.30	428.33	0.15	52.29	3.18	15.75	28.82	76.48	0.77	24.80	357.84	0.23	0.05	1.74	1.98
Min	3.68	207.40	0.09	3.95	0.35	2.08	16.74	54.10	0.22	3.26	36.53	0.15	0.03	0.28	0.10
<b>Max</b>	113.00	907.44	0.28	156.32	10.80	36.14	42.29	112.57	1.95	101.52	2527.30	0.36	0.08	3.31	8.38
St. Dev.	34.30	198.64	0.07	50.18	3.67	12.20	7.67	18.82	0.58	30.65	815.34	0.11	0.02	1.61	3.04
<b>ITASHY</b>	$\sim$	$\overline{\phantom{a}}$	$\sim$	200	0.5	$\sim$	50	200	1.5	250	250	0.5	$\overline{\phantom{a}}$	50	$\sim$
EPA	$\overline{\phantom{a}}$		$\overline{\phantom{a}}$			٠		$\overline{\phantom{a}}$	$\overline{4}$	250	250	3.3	$\overline{\phantom{a}}$	44.3	
WHO	$\overline{\phantom{a}}$		٠	200				$\overline{\phantom{a}}$	1.5	250	250	3	$\overline{\phantom{a}}$	50	

Table 5.7 TOC, alkalinity and major anions and cations for surface waters of Simav Plain comparisons with national and international standards.

Concentrations of lithium and magnesium are typically low in all samples. The maximum lithium concentration of 0.28 mg/L was observed in the sample taken from the drainage channel of Simav District (P394) that received uncontrolled discharge of geothermal fluid. The maximum magnesium concentration of 42.29 mg/L was measured in a sample from Balaban Creek (P388).

The maximum sodium level of 156.32 mg/L was measured in a sample from the lake area to the south of Güney Town (P413). The reason of high concentrations of most anions and cations in this particular sample could be evaporation from shallow water depth from the lake. However, sodium levels in all samples are below ITASHY standard value of 200 mg/L. Except for two points; all the ammonium concentrations were above the ITASHY standard value of 0.5 mg/L. The maximum ammonium concentration of 10.80 mg/L was measured in a sample taken from a drainage channel of Simav District (P394) that received raw sewage. The high ammonium levels in surface waters are mostly associated with uncontrolled discharges of raw sewage from various settlements within the study area. The maximum observed potassium value of 36.14 mg/L was measured in the sample from Daldırma Creek (P398). Finally, all calcium concentrations are below ITASHY water quality standard of 200 mg/L.

# *5.2.3 Trace Elements and Heavy Metals*

The results of trace elements and heavy metals analysis of surface waters are given in Table 5.8. The sample obtained from the lake area to the south of Güney Town is the most problematic point when all heavy metals and trace elements results are concerned.

Heavy metals such as cadmium, chromium are in compliance of water quality standards. Only one sample exceeded the water quality standards for lead. The observed maximum aluminum concentration of 2896 µg/L was measured in the sample from the lake area to the south of Güney Town (P413) like other metals and elements. Only two samples have values higher than the ITASHY aluminum standard value of 200  $\mu$ g/L. The maximum antimony concentration of 6.55  $\mu$ g/L was

measured in a sample from the lake area to the south of Güney Town (P413). Only in one sample, level was above the ITASHY antimony standard value of 5 µg/L.

The maximum boron value of 758 µg/L was measured in a sample from a drainage channel of Simav District (P394). Fluoride, lithium and sodium concentrations were also high in this sample. Possible reason of high boron concentration could be the discharge of waste geothermal fluid into this channel. All samples were below the ITASHY standard value of 1000  $\mu$ g/L. 21.40  $\mu$ g/L is the measured maximum copper value in a sample from the lake area to the south of the Güney Town (P413) as with other heavy metals and trace elements. Copper levels are below the ITASHY standard value of 50 µg/L. The maximum nickel value of 128.10 µg/L was measured in a sample from the lake area to the south of Güney Town (P413). All the samples were below the ITASHY water quality standard value of 200 µg/L. The maximum zinc value of 39.20 µg/L was measured in a sample from a drainage channel of Simav District (P394). All the samples were below the ITASHY water quality standards.

# *Arsenic*

Arsenic concentrations in surface waters ranged between 4.60 µg/L and 402.80  $\mu$ g/L with an average value of 76.56  $\mu$ g/L in this study. The maximum concentration of 402.80 µg/L was measured in the sample from the lake area to the south of Güney Town (P413). Possible source of high arsenic levels at this locale could be seepage from arsenic rich groundwater. Except for two samples, all samples were found to be above the water quality standards can be seen in Figure 5.17.

The relationship between total arsenic and dissolved arsenic in surface waters is given in Figure 5.18. This result represents the fact that arsenic may mostly be in dissolved form in Simav Plain surface waters.

Point No.	$\mathbf{A}$ $(\mu g/L)$	As $(\mu g/L)$	B $(\mu g/L)$	C <sub>d</sub> $(\mu g/L)$	Co $(\mu g/L)$	$_{\rm Cr}$ $(\mu g/L)$	Cu $(\mu g/L)$	Fe $(\mu g/L)$	Mn $(\mu g/L)$	Ni $(\mu g/L)$	<b>Sb</b> $(\mu g/L)$	Zn $(\mu g/L)$
P333	102	66.8	342	< 0.05	1.87	1.3	3.3	1067	895.58	14.3	1.78	5.1
P387	127	10.3	18	< 0.05	0.15	< 0.5	1.0	51	44.48	0.4	0.53	2.2
P388	18	4.6	44	< 0.05	0.18	< 0.5	1.0	$<$ 10	16.34	1.9	1.14	1.5
P394	184	59.2	758	0.16	0.61	2.0	1.2	642	179.12	5.0	0.68	39.2
P396	769	34.5	184	0.06	1.17	16.3	6.3	868	240.71	6.0	1.23	18.5
P398	302	53.4	271	< 0.05	0.98	1.3	2.2	393	428.56	4.9	1.47	6.4
P400	139	51.5	384	< 0.05	0.42	1.1	3.5	671	176.79	2.7	1.94	9.2
P409	43	5.9	6	< 0.05	0.09	< 0.5	2.0	182	71.09	0.6	0.25	2.8
P413	2896	402.8	643	0.45	10.63	11.9	21.4	7315	3027.32	128.1	6.55	31.9
Mean	508.89	76.56	294.44	0.22	1.79	5.65	4.66	1398.63	564.44	18.21	1.73	12.98
Min	18.00	4.60	6.00	0.06	0.09	1.10	1.00	51.00	16.34	0.40	0.25	1.50
<b>Max</b>	2896.00	402.80	758.00	0.45	10.63	16.30	21.40	7315.00	3027.32	128.10	6.55	39.20
St. Dev.	923.35	124.66	269.66	0.20	3.37	6.70	6.50	2414.38	962.52	41.42	1.89	13.91
<b>ITASHY</b>	200	10	1000	5 <sup>5</sup>	$\sim$	50	50	200	50	200	5	5000
<b>EPA</b>	200	10	$\sim$	5 <sup>5</sup>	$\sim$	100	100	300	50	$\sim$	6	5000
<b>WHO</b>	200	10	500	3		50	50	200	400	70	20	5000

Table 5.8 Trace elements and heavy metals for surface waters of Simav Plain comparisons with national and international standards.



Figure 5.17 Distribution of arsenic concentration in the study and comparison with ITASHY (standard value: 10μg/L)

Considering the average Eh value of 72.67 mV and average pH value of 8.17 in the surface water samples, the dominant arsenic specie was found to be  $HAsO<sub>4</sub><sup>2</sup>$ , so As(V), as seen from Figure 5.19. The arsenic distribution in surface water samples is given in Figure 5.20.



Figure 5.18 Dissolved vs total arsenic ratios for surface waters



Figure 5.19 Eh-pH diagram for arsenic at 25°C and 1 atm in surface waters

*Iron*

In this study, iron concentrations in surface waters ranged between 51  $\mu$ g/L and 7315 µg/L with an average value of 1398.63 µg/L. The maximum concentration of 7315 µg/L was measured in the sample from the lake area to the south of Güney Town. As given in Figure 5.21, only three samples are below the national and international water quality standard of 200 µg/L.

Iron hydroxide is the dominant iron specie in surface water samples as seen in Figure 5.22. Iron distribution in surface waters of Simav Plain is given in Figure 5.23.



Figure 5.20 Arsenic distribution map for surface waters of Simav Plain



Figure 5.21 Distribution of iron concentration in the study and comparison with ITASHY (standard value: 200μg/L)



Figure 5.22 Eh-pH diagram for iron in surface waters.



Figure 5.23 Iron distribution map for surface waters of Simav Plain

# *Manganese*

Manganese concentrations ranged between 16.34  $\mu$ g/L and 3027.32  $\mu$ g/L with an average value of 564.44 µg/L. The maximum concentration of 3027.32 µg/L was measured in the sample from the lake area to the south of Güney Town. As seen in Figure 5.24, most of the manganese concentrations are above the ITASHY standard value of 50 µg/L. Furthermore, arsenic levels were found to be high at points where manganese levels were also high (Table 5.8). Manganese distribution is given in Figure 5.25.



Figure 5.24 Distribution of manganese concentration in the study and comparison with ITASHY (standard value: 50μg/L)



Figure 5.25 Manganese distribution map for surface waters of Simav Plain

# **5.3 Geothermal Waters**

#### *5.3.1 Physical Parameters*

The data collected from three geothermal fields (i.e., Eynal, Çitgöl and NaĢa) for physical parameters are presented in Table 5.9. It must be noted that, all physical properties are measured after the samples are cooled down in glass containers to operating range of multi parameter probes. In the study area, geothermal water from these three fields is currently used in thermal spas as well as domestic and greenhouse heating. However, the temperature of Eynal field also represents suitable conditions for electricity production.

Point No	$T(^{\circ}C)$	рH	Eh(mV)	$EC(\mu S/cm)$	DO(mg/L)	$DO(\% )$
P332	90.00	7.35	217.00	1633.00	4.65	62.37
P415	95.00	7.43	127.00	1819.00	4.29	57.55
P416	160.00	8.92	$-75.00$	2490.00	3.50	46.95

Table 5.9 Physical parameters for geothermal waters of Simav Plain

\*Statistical summaries were not calculated due to insufficient number of data. Comparisons with drinking water quality standards are not given since geothermal waters are not drinkable.

Water temperatures in geothermal fields are measured to range between 90°C and 160°C in the study area, with Eynal field (P416) having the maximum temperature and NaĢa field (P332) having the minimum temperature value. It must be noted that geothermal waters in the study area have the highest temperature when compared to other geothermal fields that exist in the Kütahya Province (Dogan & Dogan, 2007). The pH values of geothermal water samples varied between 7.35 and 8.92, representing fairly alkaline conditions when compared to other geothermal fields in Kütahya Province (Dogan & Dogan, 2007). The discharge of waste geothermal fluids into surface water drainage network of Simav Plain is one reason for obtaining high pH values in some surface water sampling points.

Eh results of geothermal water samples show a range between -75 mV and 217 mV. DO levels also have role on Eh. Based on these results, Eynal geothermal field (P416) has reductive conditions where as oxidizing conditions are dominant in NaĢa and Çitgöl geothermal fields. In this study, measured EC values ranged from 1633 μS/cm (P332) to 2490 μS/cm (P416). These high values are result of high anion and cation concentrations in geothermal water due to high dissolution capacity of high temperature, high pressure waters. EC distribution map for geothermal waters of Simav Plain is given in Figure 5.26. Dissolved oxygen levels in geothermal waters ranged between 46.95(%)  $O_2$  (P416) and 62.37(%)  $O_2$  (P332). Water temperature is effective on DO levels as high temperatures decrease gas solubility in natural waters.

#### *5.3.2 TOC, Alkalinity and Major Anions and Cations*

The anion and cation results for geothermal waters are presented in Table 5.10. Geothermal waters of study area show a typical  $Na-SO<sub>4</sub>-HCO<sub>3</sub>$  characteristic as shown in Figure 5.27 with high fluoride and lithium concentrations.

In the study area, the sample from Eynal geothermal field (P416) has the highest concentrations for lithium (2.09 mg/L), sodium (531.63 mg/L), potassium (60.56 mg/L), fluoride (19.61 mg/L), chloride (76.77 mg/L), sulfate (525.12 mg/L) and bromide (0.35 mg/L). The possible reason of high concentration could be the high temperature of this field with waters being extracted from deeper layers as compared to Çitgöl and NaĢa fields.

As there is not enough data, relationship between arsenic and anions/cations was not made. Furthermore, comparison of anions and cations according to water quality standards was also not made, as geothermal waters are not suitable for drinking purposes.



Figure 5.26 EC distribution map for geothermal waters of Simav Plain

**Piper Plot For Geothermal Waters** 



Figure 5.27 Piper diagram for geothermal waters of Simav Plain

### *5.3.3 Trace Elements and Heavy Metals*

As seen in Table 5.11, arsenic, antimony, boron, iron and manganese concentrations are noticeably high in geothermal waters of Simav Plain. As a result of high pressure and high temperature in geothermal fields, these heavy metals and trace elements could easily dissolve and show high levels in groundwater. Arsenic levels were 30-50 times higher than water quality standard value of 10 µg/L in all samples. As distribution in geothermal waters is given in Figure 5.28. Similarly, boron levels were 2-3 times higher than the ITASHY standard value of 1000µg/L in all samples. Iron levels were high only in Çitgöl geothermal field sample (P415). High arsenic levels in geothermal waters are mostly associated with other trace components, including Li, B, F, Hg, Sb, Se, Th, and  $H<sub>2</sub>S$ . Positive correlations with Cl and salinity have also been reported (Appelo, 2006).

Point No	<b>TOC</b> (mg/L)	HCO <sub>3</sub> (mg/L)	ы (mg/L)	NH (mg/L)	A (mg/L)	Mg (mg/L)	Сa (mg/L)	(mg/L)	Л1 u (mg/L)	SO. (mg/L)	NO <sub>2</sub> (mg/L)	Br 'mg/L	NO <sub>3</sub> 'mg/L	PO. (mg/L)
P332	3.35 J.JJ	585.60	0.97	<0.09	31.04	10.61	65.22	5.05	46.39	347.16	0.78	0.14	0.24	0.10
P415	3.56	624.64	1.39	< 0.09	37.48	<8.23	38.17	11.13	62.52	455.95	0.38	0.18	2.87	13.33
P416	4.62	744.20	2.09	<0.09	60.56	<8.23	$\langle 20.36 \rangle$	19.31	76.77	525.12	< 0.07	0.35	0.23	ຳ 1.41

Table 5.10 TOC, alkalinity and major anions and cations for geothermal waters of Simav Plain.

\* Statistical summaries were not calculated due to insufficient number of data. Comparisons with drinking water quality standards are not given since geothermal waters are not drinkable.

Point	Al	As	В	Cd	U0.	Сr	Ċu	Fе	Mn	Ni	Pb	Sb	Zn
N <sub>0</sub>	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$
P332		311.6	2667	$< \hspace{-0.2em}0.05$	0.08	$< \hspace{-0.2em}0.5$	J.I	20	547.16	< 0.2	0.3	41.87	55 ر.ر
P415	18	363.9	2824	$< \hspace{-0.2em}0.05$	< 0.02	< 0.5	1.4	410	101.15	< 0.2	0.3	23.49	36.1
P416	188	542.9	3784	$< \hspace{-0.2em}0.05$	0.02	$< \!\! 0.5$	1.9	30	34.93	0.7	0.4	27.89	1.4

Table 5.11 Trace elements and heavy metals for geothermal waters of Simav Plain.

\* Statistical summaries were not calculated due to insufficient number of data. Comparisons with drinking water quality standards are not given since geothermal

waters are not drinkable.



Figure 5.28 Arsenic distribution map in geothermal waters of Simav Plain

## **5.4 Health Risk Assessment**

The health risk assessment made within the scope of this study is a cross-sectional epidemiological study. As mentioned in the previous chapter, Gölköy and Boğazköy were selected as the "test" residential areas and Öreğler and Demirciköy were chosen as "control" residential areas. According to census records, 2869 people aged over eighteen live in these four villages, 843 of which live in Gölköy and Boğazköy who were exposed to high arsenic levels until 2008. Of this total population of 2869, 2026 people live in Demirciköy and Öreğler, whose water resources were low in arsenic levels.

The minimum numbers of people to be investigated were then calculated according to the following formula:

$$
n = \frac{N\left(Z_{\alpha/2}^2 P(1-P)\right)}{d^2(N-1) + Z_{\alpha/2}^2 P(1-P)}
$$
(12)

Based on this formula, it is aimed to achieve at least 265 people for Boğazköy and Gölköy and at least 324 people for Demirciköy and Öreğler in total. In this study, N is 843 for Boğazköy and Gölköy, 2026 for Demirciköy and Öreğler;  $Z_{\alpha/2}^2$  is 1.96; P is 0.5 and d is 0.05. During field survey, 202 and 204 interviews were conducted in Gölköy and Boğazköy, respectively, reaching a total of 406 that well exceeded the required minimum of 265. Similarly, 197 and 192 interviews were made in Demirciköy and Öreğler, respectively, reaching a total of 389 that also exceeded the minimum value of 324.

According to statistical results, average age is 55±16.9 and there were no meaningful differences between villagers age distribution (p>0.05) in different villages. Statistical results of the mini mental test showed a low dementia with an average value 22.1±5.7, where there were meaningful differences between villages. While Demirciköy had the highest mini mental test results with  $23.2 \pm 5.4$  (p<0.05),

other villages had mini mental test results that ranged between 21.5±5.9 and 22.1 $\pm$ 5.9. Average value of body weight was 71.0 $\pm$ 13.5 kg and there was a meaningful difference at body weights between villages (p<0.05). Consequently, Öreğler had the lowest body weight with 67.9±14.1 kg and Boğazköy had the highest body weight with  $74.7\pm12.6$  kg.

The distribution of basic disease groups in the entire project area is given in Figure 5.29. According to Figure 5.29, cardiovascular diseases were the mostly observed diseases with 37.7% followed by gastrointestinal system (16.70%) and muscular system (11.10%) diseases. Cancers constitutes 2.6% of all diseases as seen in Figure 5.29.



Figure 5.29 Distribution of chronic diseases seen in Gölköy- Boğazköy and Demirciköy-Öreğler.

Chronic diseases seen in Gölköy and Boğazköy are given in Figure 5.30. Cardiovascular diseases had the highest percentage with 40.7% and cancers had a share of 2.1% as shown in Figure 5.30.



Figure 5.30 Distribution of chronic diseases seen in Gölköy and Boğazköy

Similar distribution was observed in Demirciköy and Öreğler as seen in Figure 5.31. Cancers has a share of 3.1% in these villages, which were higher than the value of Gölköy-Boğazköy.



Figure 5.31 Distribution of chronic diseases seen in Demirciköy and Öreğler

As seen in Figure 5.32, highest percentage was observed in the cancer type of uterus malign neoplasm with 41.20%, which was followed by colon malign neoplasm with a share of 17.80%. All colon cancers were observed in Gölköy.



Figure 5.32 Distribution of cancer types in the villages

The best example for exposure to high arsenic levels is Bangladesh. Over tens of millions of people have been exposed to poisonous levels of arsenic from drinking water. Ahsan and his colleagues (Ahsan, Argos, Kalra, Rathouz, Chen, Pierce, Parvez, Islam, Ahmed, Rakibuz-Zaman, Hasan, Sarwar, Slavkovich, van Geen & Graziano, 2010) conducted a study over 10 tens years in Bangladesh with 12,000 people and they reached following results:

- Risk of dying increased during six years by nearly 70% who had exposed high arsenic levels compared to people with low arsenic levels
- People who drank moderate levels of arsenic were more likely to die from chronic diseases than who drank  $\leq 10 \mu g/L$
- Compared to those exposed lowest arsenic levels  $(\leq 10 \text{ µg/L})$ , those with levels (10-50 µg/L) had a 34% higher risk of death and those with highest levels (150-864  $\mu$ g/L) a 64% higher risk.

A similar risk assessment is made for Simav Plain conditions. Health risk calculation for Simav was made by using parameters given in Table 5.12 Average arsenic concentration in groundwater samples was calculated from analysis results. Ingestion rate was calculated with the results of standard cup method and water diaries that were conducted as a part of the field survey. Average body weight was obtained from the results of the health survey. Exposure duration was chosen as the operation period of old Boğazköy and Gölköy drinking water well, which had arsenic levels of 177.2 µg/L as determined by Gunduz & Simsek (2007). Average time was also calculated with statistical analysis. Based on these values, chronic daily intake was calculated by the following formula and showed in Table 5.12:

$$
CDI = \frac{C \times IR \times EF \times ED}{BW \times AT \times 365}
$$
 (13)

$$
HQ = \frac{CDI}{RfD} \tag{14}
$$

$$
RF = CDI \times OCSF \tag{15}
$$

<b>Parameter</b>	Abbr.	Mean	Demirciköv	Öreğler	Boğazköv-Gölköv New well	Boğazköv-Gölköv Old well
Ingestion rate $(L/d)$	$_{\rm IR}$	1.69	1.69	1.69	1.69	1.69
Concentration $(mg/L)$	$\mathsf{C}$	0.162	0.001	0.001	0.009	0.177
Exposure duration $(y)$	ED.	13	13	13	13	13
<b>Exposure frequency</b> (d/y)	EF	350	350	350	350	350
Body weight (kg)	<b>BW</b>	71	70.5	67.9	72.8	72.8
Average time (y)	AT	55	53.6	56.9	55	55
Reference dose (mg/kgd)	Rfd	0.0003	0.0003	0.0003	0.0003	0.0003
Oral cancer slope $factor*$	<b>OCSF</b>	1.5	1.5	1.5	1.5	1.5

Table 5.12 Parameters used to calculate arsenic exposure risk.

\* US-EPA IRIS database http://www.epa.gov/iris/subst/0278.htm#sumoral

The calculated lifetime risks for having skin cancer were then calculated and given in Table 5.13 for villages where health surveys were conducted and distribution of calculated risk levels for the entire plain were given as a risk map for skin cancer in Figure 5.33. Accordingly, the risk level of skin cancer for the study

area is three orders of magnitude greater than EPA's acceptable risk level, which also means there is a great possibility for internal organ cancers in the study area.

	<b>EPA</b> standard	Mean	Demirciköy	Öreğler	Boğazköy-Gölköy New well	Boğazköy-Gölköy Old well
<b>CDI</b>		8.75E-04	5.58E-06	5.46E-06	4.74E-05	9.32E-04
HQ	$10E + 01$	$2.92E + 00$	1.86E-02	1.82E-02	1.58E-01	$3.11E + 00$
RF(LCR)	1E-06	1.31E-03	8.37E-06	8.18E-06	7.11E-05	1.40E-03

Table 5.13 Calculated values for lifetime cancer risk.

It must be noted that the risks for other organ cancers could not be calculated, as the slope factors for these cancer types are not set by the medical community yet.



Figure 5.33 Risk distribution map for skin cancer groundwater of Simav Plain.

# **CHAPTER SIX CONCLUSIONS AND RECOMMENDATIONS**

This study is conducted to determine the arsenic contamination of groundwater in Simav Plain, Kütahya and to exhibit risks on the human health. To achieve this objective, a water quality monitoring program was conducted and household surveys and oral autopsies surveys were implemented. Within the scope of this study, a total of 45 samples were collected (i.e., 33 of which were from groundwater, nine of which were from surface waters and three of which were from geothermal fields). Samples were then analyzed for various parameters including: physical parameters (i.e., temperature, pH, Eh, DO, EC), major anions and cations, TOC, and heavy metals and trace elements. For health risk assessment, daily water consumptions of local people were calculated via the standard cup method and water diaries; and oral autopsies and individual household surveys were conducted. Based on the result of water quality monitoring and health risk assessment, the following conclusions were reached:

- The water quality monitoring program revealed arsenic concentrations that were 1-100 times higher than national and international standards.
- In groundwater, arsenic mobilization was mostly related to iron compounds present in groundwater. Since  $Fe(OH)_3$  is the dominant specie in groundwater of Simav Plain, reductive dissolution by the presence of iron hydroxides were believed to be the main arsenic mobilization mechanism.
- Arsenic mobilization in surface waters was dependent on various parameters such as sorption by metal oxyhydroxides/oxides, presence of competitive ions and organic matter.
- The main arsenic species is in both in groundwater and in surface water was  $HAsO<sub>4</sub><sup>2-</sup> as As(V).$
- Arsenic was believed to originate mostly from local geological formations. Weathering of arsenic bearing metamorphic rocks could be the main source of high arsenic levels in the alluvial surficial aquifer.
- The most problematic sampling points were Çingene Hamamı (P397) for groundwater samples and the lake area to the south of Güney Town (P413) for surface waters. As Çingene Hamamı sample point was in the immediate vicinity of NaĢa geothermal field, geothermal fluid inflow into the aquifer was believed to be the reason for high levels of several parameters. Furthermore, the lake area to the south of Güney Town sampling point could have high levels because of seepage from groundwater and seasonal evaporation from shallow water depth.
- High levels of various parameters including arsenic observed in surface waters were mostly associated with discharges of waste geothermal fluid from three geothermal fields and domestic sewage discharges from the Simav district center and nearby settlements that are directly made to surface drainage network within the plain.
- When compared to water quality standards, arsenic levels were mostly above where as manganese, iron and most heavy metal and trace elements were below the corresponding water quality standards.
- The health surveys and health risk assessment showed high percentage of various diseases including cancer, which might be related with direct exposure to arsenic contaminated water thru ingestion as well as indirect exposure thru consumption of crops irrigated with arsenic contaminated water. When health risk assessment results were compared to standard values, there is high risk for having internal cancers and other adverse health problems.

To prevent high arsenic exposure via drinking water, the following applications and recommendations are offered:

- In order to better understand the toxicological consequences of arsenic on human health of local people, arsenic speciation should be done by analytical methods.
- A modeling application might be suitable to assess the fundamental arsenic mobilization and transportation mechanisms under various scenario conditions.
- In order to minimize arsenic exposure, operation of deep boreholes and over exploitation from deep wells should be prevented.
- No new boreholes should be drilled in areas with high health risks.
- Waste geothermal fluid should not be disposed to surface drainage network but should be re-injected back to the aquifer.
- Surface waters contaminated with raw sewage and geothermal fluid should not be utilized in agricultural irrigation of edible crops.
- Arsenic removal measures should be implemented in boreholes that exceed the standard value.
- For high arsenic areas, alternative water resources that contain lower arsenic levels should be searched for.

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**APPENDICES**

### DOKUZ EYLÜL ÜNİVERSİTESİ



### **SİMAV OVASI** YERALTI SUYUNDA ARSENİK KİRLİLİĞİNİIN ARAŞTIRILMASI VE İNSAN SAĞLIĞINA OLAN RİSKLERİNİN DEĞERLENDİRİLMESİ **CALISMASI ANKET FORMU**

(TASLAK)

## **ANKET FORMU**

KÜTAHYA 2009



#### Savin Katilimo:

Simav ilçesindeki sağlık sorunlarını tespit etmek amacıyla Dokuz Eylül Üniversitesi öncülüğünde sına ilçesindeki sağlık sorunlarını tespir etmek amacıyla bokuz Eylü Universitesi onculuğunda<br>İşağlık durumları hakkında bilgi almak istiyoruz. Bu amaçla yaklaşık 1 saat sürecek bir anket<br>Sağlık durumları hakkında bilgi al evgrensseines tamamen vesseen vienan saintimingan os sinies tomis somer tagis om vira.<br>Canakkale Onsekiz Mart Üniversitesi Öğretim öğretim elemanları tarafından uygulanmaktadır.

- Bu çalışmada size:<br>1. Hane halkı ile ilgili temel tanımlaycı sorular.
	- ... Hane naiki ile ilgili terrier tarihina yor sololari,<br>2. Hane halki fertleri konusunda sorulari,<br>3. Solsyal ve ekonomik durumunuza yönelik sorulari,
	- Hane halkının sağlık sorunlarına yönelik sorular, 4.
	- Son üç yılda hanenizde meydana gelen ölümler hakkında sorular sorulacaktır. 5.

Bide edilen bilgiler tamamen gizli tutulacak ve üçüncü şahislarla paylaşılmayacaktır. Bilgiler sadece bilimsel amaçlar doğrultusunda kullanılacaktır. Ayrıca bu çalışmayı başlatabilmek için Dokuz Eylül Üniversitesi İnsan Ar üniversiterriz tarafından planlanacak olan izlem çalışmalarında da sağlık durumunuzun takibi amacı yla<br>da size bu adres ve telefon bilgilerinden ulaşılacaktır.<br>Sizden aldığımız bilgiler, Simav halkının sağlık sorunlarının

edilebilmesi amacıyla kullanılacaktır. Ankete katılmak zorunlu değildir ve katılmaya karar verdikten sonra da anketten ayrılabilirsiniz.

asın alan mesteri göyneminenir.<br>Bu çalışma ile ilgili olarak merak ettiklerinizi sormak için, Proje Yöneticisi Dokuz Eylül Üniversitesi.<br>Çevre Mühendisliği Bölümü Öğretim Üyesi Yrd.Doç.Dr.Orhan GÜNDÜZ'e 02324127141 numaral

Dokuz Eylül ve Çanakkale Onsekiz Mart Üniversitesinin işbirliği ile topluma daha iyi sağlık hizmeti sunmanın zeminini hazırlayabilmek için yapılan bu çalışmaya değerli zamanınızı ayınp katkı<br>sağladığınız içn teşekkür ederiz.

Anketör tarafından okundu ( )

Katılımo tarafından Oriaylandı ( ) Redledildi ( )

Tarih: ... ... /........./2009

## SIMAV OVA SI<br>YERALTI SUYUNDA ARSENIK KIRLILIĞININ ARAŞTIRILMASI VE INSAN SAĞLIĞINA OLAN<br>RISKLERININ DEĞERLENDIRILMESI ÇALIŞMASI ANKET FORMU

#### **ANKET KODU:**

Anketör Kodu:.........<br>Anket No:.........

#### TA NIMEAY ICI BILGILER

#### ADRES:



HANE HALKI SORU FORMU

Hane Halki Bilgileri:

9 Bu hane de yaşa yanlar bir aile mi<br>(1) Evet (2) Hayır



#### HANE HALKI BIREYLERININ SA GLIK VE REHA BILITASYON DURUMU

Hane halkı bireylerinden, son bir yıl içerisinde, hekim tarafından tanısı konulmuş akut hastalığı dan birileri var mı?<br>(1) Evet (2) Hayr

Evetse;



Evetse:







Evet i se özürün türünü, nedenini ve süresini belirtiniz.



Bakım ihtiyacı (Yetişkin, 18 yaş ve üstü)<br>Bu yetişkin(ler)'n ne kadar bakıma ihtiyacı var?



Hanenizde bir hastalığa bağlı olarak bakıma ihtiyacı olan çocukluklar var mı? (0-17 yaş.).  $(1)$  Evet  $(2)$  Hayr

Bakım ihtiyacı (Çocuk, 0-17 yaş)<br>Bu çocuk (lar)nine kadar bakıma ihtiyacı var?



HA NEDEKISON ÜÇ YILDAKI ÖLÜM TESPITI

(Ölüm tespit edilen hanelere ölüm nedenlerinin tespiti için ayrıca hekimin görüşmek üzere geleceğini hatırlatınız)

Evetse; Ölüm: Adı, soyadı, ölüm tarihi:



#### HANE HALKI KONUT NITELIĞI ILE ILGILI SORULAR

Evinizde salon dahil (mutfak, banyo ve kiler hariç) kaç oda var?.......................... Evinizde mutfak var mi? (1) Evet<br>Evinizde banyo var mi?<br>KNE of (1) Evet (2) Hayir<br>Eviçinde tuvalet var mi?  $(1)$  Evet (2) Hayn Evinizin tabanı ne ile kaplı? (1) Sert zemin<br>(2) Toprak zemin (3) Karo<br>(4) Beton (5) Parke/Ahsap (6) Diğer...... . . . . . . . . . . Evinizin içme suyunun ana kaynağı nedir?<br>(1) Şebeke suyu (5) Yağmur suyu (samıç) (2) Mahalle çeşmesi(su şebekesine bağlı)<br>(3) Ku'yu suyu ve tulumba (6) Göl ya da akarsu (7) Şişe suyu – pet suyu – damacana<br>(8) Tanker suyu (4) Korumasız kaynak<br>İşme suyunu taşıyarak mi temin ediyorsunuz?<br>İşme suyunu taşıyarak mi temin ediyorsunuz? in Board (\* 1920)<br>19 Evet – Andrej van Amerikaanse voorbrond van die verskip van die stad van die verskip van die voorbrond van<br>19 Even suivanu tasuvarak teminie dii yorsaniz; sui kaynağı evinize ne ka dariuzaktadır? (1) Bahçe içinde<br>(2) Bahçe içinde<br>(2) Bahçe dışında 1 km ya da daha az uzaklıkta (2) banye dişinda 1 km ya da daha az dzakirkia<br>(3) Bahçe dişinda 1 km ya da daha fazla uzaklıkta<br>Kullandığı'nız tuvalet ne tip tuvalettir? (6) Evin dışında açık çukurlu hela<br>(7) Evin dışında kapalı çukurlu hela<br>(9) Diğer (1) Evin içinde, kanalizasyon sistemine bağlı (2) Evin içinde, foseptik çukuruna bağlı 

- 
- 

(2) Evin Iyance, rosepur yawarana başır<br>(3) Evin dışında, kanalizasyon sistemine bağlı<br>(4) Evin dışında, foseptik çukuruna bağlı<br>(5) Evin işinde, açık çukurlu hela<br>Tuvaletiniz evin dışında ise ne kadar uzaklıktadır?



HANE HALKI SOSYAL GÜVENCE SİSTEMİ

HANEDEKI KIŞILEREYÖNELIK SORULAR

Bu bölüm hanedeki herke silçin ayrılayrı uygulanacaktır.

**CALISMA DURUMU** 

Cevaplayana son bir yıl içinde yaptığı işi sorunuz ve söylediği şekilde yazınız. Daha sonra da asıl mesleğini kaydediniz.

(9) Mülk sahibi

(10) Diğer...........................

Son bir yıl içinde geçiminizi sağlayan yaptığınız iş nedir? 



**RISK FAKTÖRLERI** 

1.TÜTÜN

.............

Halen sigara, puro, pipo gibi herhangi bir tütün mamülü kullanılı yor musunuz?<br>(1) Evet hergün (2) Evet hergün değil (3) Hayir

Kaç yıldır tütün ve mamülleri kullanıyorsunuz? 

Hergün tütün mamülleri kullarmaya kaç yaşında başladınız? 

Günde kaç adet sigara ya da diğer tütün ürünlerinden kullanıyorsunuz?

Evinizde aile bireyleri arasında ortak kullanım alanlarında (salon, mutfak vb) sigara içen birileri var mi/var mi ydi?(Birden fazla seçenek i şaretlenebilir.) (0) Hayr kimse içmezdi (d) Fisin<br>(1) Esim<br>(2) Annem<br>(4) Kardeşim<br>(4) Kardeşim

lşyerinizde veya sıklıkla bulunduğunuz ortak kullanım alanlarında (Kahvehane, kantin, yemekhane, kantin, yemekhane, kantin, (1)<br>emekhane,vb)sigaraliyen birilerilvarımı/varımıydı?<br>(1) Evet

Son bira ayda sigara ile ilgili önemli bir sağlık sorununuz oldu mu?<br>(1) Evet (2) Hayr  $(1)$  Evet

<u>2.A.LKOL.</u><br>Şimdiye kadar hiç alkollü içecek içtiniz mi?  $(1)$  Evet (2) Hayn



Son bira ayda alkol ile ilgili önemli bir sağlık sorununuz oldu mu?  $(1)$  Evet  $(2)$  Hayn

#### 3. BESLENME



Yemeklerinizde genellikle ne kadar tuz tüketirsiniz? (0) Tuzsuz yerim<br>(1) Az tuzlu yerim<br>(2) Normal tuzlu yerim<br>(3) Çok tuzlu yerim

Boyunuz ve kilonuzu belirtiniz. 

#### 4. FIZIKSEL AKTIVITE

s. manvast ömnung<br>Simdi size son bir hafta içinde, beden hareketlerine (fiziksel aktviteye) harcadığınız zamanla<br>ilgili sorular soracağım. Lütfen iş yerindeki, ev, bahçe ve tarla işlerinin bir parçası olarak, bir<br>yerden bi

#### Ağır hareket (Güçlü Aktivite)

ngın manenç olaya nenmen<br>Başlayınca bir defada en az 10 dakika süren, ağır kaldırma, kazma, bel balyoz kullanma, hızlı<br>bisiklet sürme, aerobik gibi ağır hareketleri son bir hafta içinde, kaç gün yaptınız? (0) Hayir yapmadım

Yukarıdaki günlerden birini dikkate aldığınızda bu hareketleri;

### 

#### Orta Düzeyde Hareket

en en energies mannen.<br>Yürümek dışında, başlayınca en az 10 dakika süren, hafif taşımalar, normal bir hızda bisiklet<br>sürme veya bahçetarla işleri gibi orta düzey beden hareketleri (fiziksel aktiviteler), son bir hafta içinde, kaç gün yaptınız? (0) Hayr yapmadım

Yukarıdaki günlerden birini dikkate aldığınızda bu hareketleri:

Yürüme i salan.<br>Işte, evde bir yerden yere gitmede veya spor, egzersiz gibi boş vakitleri değerlendirme amaçlı.<br>'yürümeler de dâhil', bir defada en az 10 dakika olarak , son bir hafta içinde, kaç gün yürüdünüz? (0) Hayir yapmadım Yukarıdaki günlerden birini dikkate aldığınızda bu hareketleri; Günde kaç dakika yürüdünüz ?.................................. SAĞLIK DURUMU Genel Sağlık sunan olayını<br>Şulandaki sağlık durumunuz, okuyacağım seçeneklerden hangisi en iyi tanımlar? (5) Çok kötü (1) Çok iyi  $(2)$  lyi  $(3)$  Orta (4) Kötü Son bir ayliçinde kendilişinizi veya evdekilişlerinizi yaparken ne kadar güçlük çektiniz?  $(1)$  H<sub>2</sub>  $(2)$  Haif .<br>(3) Ortal  $(4)$ lleri (5) Çok ileri/

Şimdi bedensel durumunuzla ilgili bazı sorular soracağım. Bu soruları cevaplandırıken, kötü ve iyi<br>günleri de dikkate alarak son bir ayı düşünün. Zorluk diye sorduğum zaman, bu son bir ay içinde bir işi amısın ve amısına sanan ve amasında yapanı sanan sanan sanan sanan sanan sanan sanan sanan sanan sanan sanan s<br>Yaparken daha fazla güç kullanma, acı çekme veya hareketlerde yavaşlama gibi durumları düşünün.<br>(Soruyu okuyunu

Yapam yorum

Haraketlilik Son bir ayiçinde hareket edip dolaşmada ne kadar zorluk çektiriz?  $(1)$  Hq  $(2)$  Haif  $(3)$  Orta  $(4)$ lleri (5) Çok ileri/ Yapam yorum Son bir ay içinde, ener ji gerektiren aktivitelerde ne kadar zorluk çektiriz (bisiklete birme, 3 km koşma ya da tarlada çalışma).<br>Koşma ya da tarlada çalışma).<br>(1) Hiç (2) Haff  $(3)$  Orta  $(4)$  lleri (5) Çok ileri/ Yapam yorum Kisisel bakım  $(1)$  H<sub>2</sub>  $(2)$  Haif  $(3)$  Orta  $(4)$  lleri (5) Çok ileri/ Yapam yorum Son bir ay içinde, üstünüze başınıza bakmada, temiz ve düzgün görünmede ne kadar zorluk çektiniz.<br>(1) Hç  $(2)$  Haif  $(3)$  Orta  $(4)$  lleri (5) Çok ileri/ Yapam yorum Ağn ve rahatsızlık Son bir ayiçinde vücudunuzla ilgili ne kadar ağrı ya da sancı çektiniz?  $(1)$  H<sub>2</sub>  $(2)$  Haif  $(3)$  Orta (4) lleri (5) Çok ileri Son bir ayliçinde vücudunuzla ilgili ne kadar rahatsızlık çektiniz? ..<br>(4) lleri  $(1)$  Hg (5) Çok ileri  $(2)$  Haif  $(3)$  Orta



### DOKUZ EYLÜL ÜNİVERSİTESİ



**SİMAV OVASI** YERALTI SUYUNDA ARSENİK KİRLİLİĞİNİIN ARAŞTIRILMASI VE İNSAN SAĞLIĞINA OLAN RİSKLERİNİN DEĞERLENDİRİLMESİ **CALISMASI ANKET FORMU** 

# **SÖZEL OTOPSİ ANKET FORMU**

KÜTAHYA 2009

### SÖZEL OTOPSI ANKET FORMU















Cevapla yan Adı- Soyadı: \_\_\_\_\_\_\_ \_\_\_\_\_\_\_\_\_\_\_\_\_

GEBELÍK, DOĞUM VE LOHUSALIK DÖNEMİNDE ÖLEN 1549 YAŞ KADINLAR



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Cevapla yan Adı: \_\_\_\_\_\_ \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

L.

### 0.28 GÜN ARASINDA ÖLEN BEBEKLER



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Anket doldurma işlemi bittikten sonra aldığınız bilgiler ve sizin yorumunuz doğrultusunda 1.<br>ve 2. soruları doldurunuz.



Anket doldurulduktan sonra hastane kayıtlarında yer alan TEMEL ve SON ölüm<br>nedenlerini belirtmek üzere bu kısım kopartılarak hastane kayıtlarını inceleyecek<br>anketör (doktor)tarafından doldurulacaktır.

