DOKUZ EYLÜL UNIVERSITY GRADUATE SCHOOL OF
NATURAL AND APPLIED SCIENCES

SPATIAL AND TEMPORAL ASSESSMENT OF GROUNDWATER QUALITY FOR THE NIF MOUNTAIN KARSTIC AQUIFER

by
Rahime POLAT

February, 2009
İZMİR

SPATIAL AND TEMPORAL ASSESSMENT OF GROUNDWATER QUALITY FOR THE NIF MOUNTAIN KARSTIC AQUIFER

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M.Sc. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **“SPATIAL AND TEMPORAL ASSESSMENT OF GROUNDWATER QUALITY FOR THE NIF MOUNTAIN KARSTIC AQUIFER”** completed by **RAHİME POLAT** under supervision of **ASST.PROF.DR. ALPER ELÇİ** 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.

Asst.Prof.Dr. Alper ELÇİ

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(Supervisor)

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(Jury Member)	(Jury Member)

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Prof.Dr. Cahit HELVACI
Director
Graduate School of Natural and Applied Sciences

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SPATIAL AND TEMPORAL ASSESSMENT OF GROUNDWATER QUALITY FOR THE NIF MOUNTAIN KARSTIC AQUIFER

ABSTRACT

This thesis presents a groundwater quality assessment study for the Nif Mountain karstic aquifer, which is located to the southeast of İzmir. The objectives were to present groundwater quality data, provide a spatial assessment of groundwater quality and to implement a statistical evaluation of seasonal alteration of groundwater quality. The study was basically conducted as a four-stage process involving field work and sampling, sample analyses, production of spatial distribution maps of groundwater quality data, and statistical analyses to test significance of temporal changes in groundwater quality and to understand the relationship between different groundwater quality parameters. Groundwater samples were collected from 59 different sampling points in April and September 2006, representing the wet and dry seasons, respectively. Laboratory analyses of major cations and anions were performed. Concentration distribution maps for nitrate, chloride, electrical conductivity (EC) and hardness were generated using a GIS. Moreover, statistical analyses were performed to test the significance of temporal groundwater quality change. The resulting distribution maps showed that groundwater quality in general deteriorates as water travels from the uplands to the plains. Nevertheless, all the investigated groundwater quality parameters were for the most part of the study area in compliance with drinking water standards, with the exception of some occurrences of high concentrations. The temporal assessment using the paired samples t-test and the Wilcoxon Signed Rank tests revealed that the apparent increase in nitrate, chloride and hardness concentrations from the wet to the dry season was statistically not significant. However, the observed increase in EC values was significant. It was concluded that less groundwater recharge in the dry period of the year does not always cause higher concentrations and that other factors such as water circulation times, lithology, quality and extent of recharge and land use also play an important role on the alteration of groundwater quality.

Keywords: Nif Mountain, İzmir, karstic aquifer, nitrate, chloride, GIS, hardness

NİF DAĞI KARSTİK AKİFERİ YERALTI SUYUNUN MEKANSAL VE ZAMANSAL DEĞERLENDİRİLMESİ

ÖZ

Bu tezde, İzmir'in güneydoğusundaki Nif Dağı karstik akiferi yeraltı suyunun kalite değerlendirmesi çalışılmıştır. Yeraltı suyu kalite verilerinin sunulması, yeraltı suyu kalitesinin konumsal bakımdan değerlendirilmesi ve mevsimsel kalite değişiminin istatistiksel değerlendirilmesinin uygulanması çalışmanın amaçlarıydı. Saha çalışması ve örnekleme, örneklerin analizi, yeraltı suyu kalite verilerine ait konumsal dağılım haritaların oluşturulması, istatistiksel analizlerle kalitedeki zamansal değişimin sınanması ve çeşitli yeraltı suyu kalite parametreleri arasındaki ilişkilerin kavranması çalışmanın dört temel aşamalarını oluşturmaktadır. Yaz ve kış mevsimlerini temsilen 2006 yılının Nisan ve Eylül aylarında, 59 farklı örnekleme noktasından yeraltı suyu örnekleri toplanmıştır. Başlıca katyon ve anyonların analizleri laboratuvarda yapılmıştır. Nitrat, klorür, elektriksel iletkenlik (Eİ) ve sertlik verileri için coğrafi bilgi sistemi kullanılarak konsantrasyon dağılım haritaları oluşturulmuştur. Dahası, istatistiksel analizler yapılarak, yeraltı suyu kalitesinin, zamansal değişiminin önemi sınanmaya ve parametreler arasındaki ilişki ortaya konmaya çalışılmıştır. Elde edilen dağılım haritaları yeraltı suyu kalitesinin suyun yüksek yerlerden ovalara indikçe bozulduğunu göstermektedir. Buna rağmen, tüm çalışılan yeraltı suyu kalite parametrelerinin, birkaç istisna dışında, çalışma sahasının büyük bir kısmında içme suyu standartlarını sağladığı görülmüştür. İlişkili örneklemler için t-testi ve Wilcoxon işaretli sıralama testi ile yapılan zamansal değerlendirme sonuçlarına göre nitrat, klorür ve sertlik konsantrasyonlarındaki kıştan yaza görünür artışın istatistiksel açıdan önemsiz olduğu sonucuna varılmıştır. Ancak Eİ değerlerinde gözlenmiş artış önemli bulunmuştur. Yazın azalan yağışlar nedeniyle yeraltı suyu beslenimin daha düşük olmasının her zaman daha yüksek konsantrasyonlara neden olmamaktadır ve sonuç olarak yeraltı suyu çevrim süreleri, litoloji, beslenim suyunun kalitesi ve alanı ve arazi kullanımı gibi faktörlerin de yeraltı suyu kalite değişiminde önemli rol oynamaktadır.

Anahtar Kelimeler: Nif Dağı, İzmir, karstik akifer, nitrat, klorür, CBS, sertlik

CONTENTS

CHAPTER ONE
INTRODUCTION

The increase in population, deterioration of water quality due to pollution, mismanagement of freshwater supplies and also the emerging effects of climate change is expected to lead to critical water shortages for certain regions of the world in the forthcoming years. To conserve this vital resource, more efficient and sustainable use and monitoring of groundwater quality and quantity of existing supplies are required, and better integration of water resources into decisions over land use planning is essential. While the issue of availability of water resources has been globally attracting more and more interest in recent years, it has also become pronounced in the Middle East and the Mediterranean Region, where Turkey is situated. The region has in most parts a semi-arid to arid climate, therefore the water potential in these parts is low. On the other hand, rapidly growing population causes continuous increase in water demand.

Because of surface water resources scarcity in certain regions of Turkey, groundwater is the sole source of water for drinking, domestic, irrigation and industrial use. Groundwater is preferred in areas, where surface water is quantitatively not sufficient to meet the demand or qualitatively not suitable to satisfy standards and quality criteria. Deep ground water is relatively free from pollutants in many places and is usually very suitable for agricultural use and industrial purposes. According to the data reported by State Hydraulic Works [DSI] (n.d.), 14 billion m^3 groundwater constitutes about 13% of Turkey's total consumable water potential. One-third of this potential is represented by karstic aquifers. Although providing more favorable conditions for groundwater recharge as compared to other aquifer types, karstic systems are also more vulnerable to surface-originated contamination. For these reasons, it is important to monitor and assess the spatial and temporal change in groundwater quality, in particular if the karstic aquifer functions as a primary water resource or if it is located upgradient of major water supply wells or reservoirs. Equally important is the hydrogeological characterization of karstic aquifers, however due to their extreme anisotropic and heterogeneous nature, a comprehensive hydrogeological characterization is usually a difficult task.

1.1 Study Objectives

The objectives of this thesis were: 1) to present groundwater quality data for the Nif mountain karstic aquifer system, 2) to provide a spatial assessment of groundwater quality, and 3) to implement a statistical evaluation of seasonal groundwater quality alteration. The aim of the statistical evaluation was basically to test the significance of temporal changes in groundwater quality and to understand relationships between different groundwater quality parameters.

The Nif Mountain karstic aquifer system located in the southeast of the city of İzmir, the third largest city of Turkey, was selected as the study site because the Nif Mountain is considered to be an important recharge source for İzmir’s major water supply systems. Furthermore, groundwater quality of the area was not studied before. The Nif Mountain hydrogeologically recharges the surrounding Bornova, Kemalpaşa and Torbalı Plains (Şimşek, Elçi, Gündüz & Erdoğan, 2008), where intense agricultural and industrial activities take place, as well as the partially protected Cumaovası Plain, which is located within the basin boundaries of the Tahtalı Dam Reservoir, a major water resource of the İzmir water supply system. In this regard, the quality of subsurface drainage originating from Nif Mountain is considered to be an important factor that determines the overall water quality pattern around the İzmir metropolitan area.

1.2 Scope of the Study

The focal point of this study was the spatial and temporal assessment of groundwater quality parameters of the Nif Mountain karstic aquifer. The study was basically conducted as a four-stage process involving (1) field work and sampling, (2) sample analyses, (3) production of spatial distribution maps of groundwater quality data, and (4) statistical analyses to test significance of temporal changes in groundwater quality and to understand the relationship between different groundwater quality parameters. In the first phase of field work, the study site was explored to observe the hydrogeological features and to select groundwater sampling points. In the second phase, samples were collected from 59 different sampling points in April and September of 2006, representing the wet and dry seasons, respectively. A number of analyses in the laboratory, including determination of major cations and anions, were performed. The spatial distributions of certain groundwater quality parameters, namely nitrate (NO_3^-), chloride (Cl^-), hardness and electrical conductivity (EC) representing the general state of groundwater quality were investigated. Distribution maps for these parameters were produced and interpreted. In order to show how the spatial distribution of certain groundwater pollutants changes from the wet winter to the dry summer season, a statistical assessment of the temporal change of contaminant distributions were also done. Data obtained in April and in September of 2006, which roughly marked the end of the wet and dry periods, respectively, was post-processed on a GIS platform in order to assess groundwater quality parameters. Furthermore, in order to clarify whether the temporal change in groundwater quality parameters was significant, some statistical tests were performed on the water quality data. Moreover, the correlation and relationships between groundwater quality parameters were determined. All results were subsequently interpreted in association with the local hydrogeology, lithology and land use of the Nif Mountain and its surrounding area.

CHAPTER TWO
LITERATURE REVIEW

2.1 Groundwater – an Important Component in the Hydrologic Cycle

The continuous circulation of water between ocean, atmosphere, and land is called the hydrologic cycle (Figure 2.1). The hydrologic cycle can be viewed as a major machine on the planet, controlling distribution of water on the earth. Groundwater is one of the major links in the hydrologic cycle. Inflow to the hydrologic system arrives as precipitation, in the form of rainfall or snowmelt. Outflow takes place as stream flow or runoff and as evapotranspiration, a combination of evaporation from bodies of water, evaporation from soil surfaces, and transpiration is delivered to streams both on the land surface, as overland flow tributary channels; and by subsurface flow routes, as inter flow and base flow following infiltration into the soil (Freeze & Cherry, 1979).

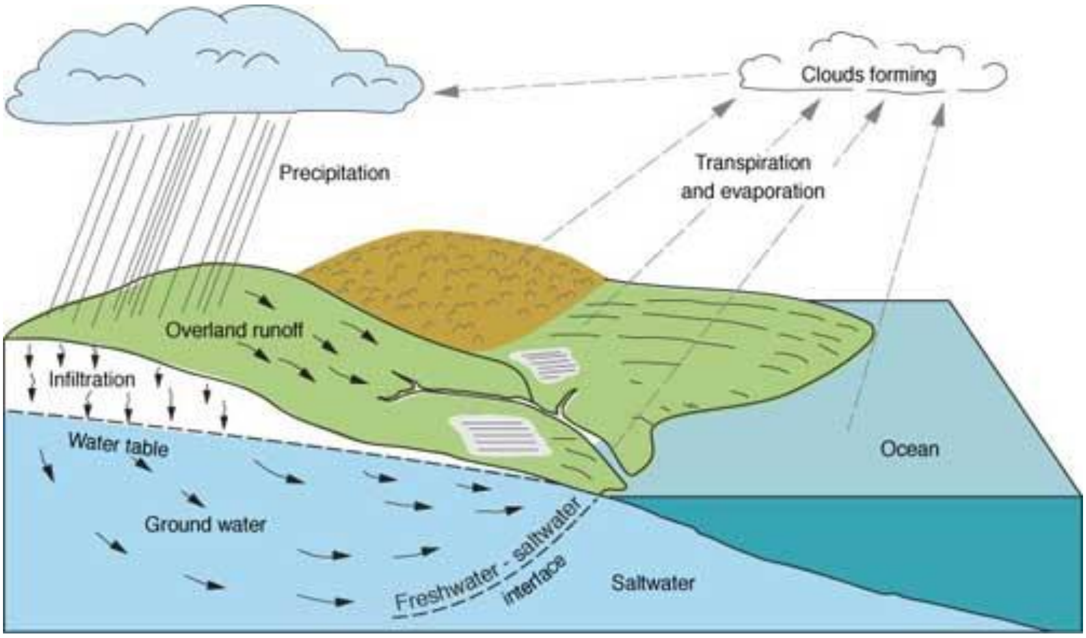

Figure 2.1 Hydrological Cycle (Kansas Geological Survey, 2005)

Excluding the freshwater that is locked up in the form of polar ice caps and glaciers, about 97 percent of the world's freshwater exists in aquifers. Although humans have long known that much water is contained underground, but it is only in the recent decades that scientists and engineers have learned to estimate how much groundwater is stored under ground and its vast potential (U.S. Geological Survey [USGS], 1999).

The total amount of water on the planet is about 1.4 billion km^3, and its distribution among the main global water budget components is listed in Table 2.1 (Maidment, 1993). Of the fresh reservoirs, glacial ice and groundwater are by far the largest. Groundwater and surface water are the two reservoirs most used by humans because of their accessibility. However, for domestic supplies, groundwater often is more important than surface waters. Where surface water is deficient or unsuitable, groundwater is the only water source, particularly in arid and semi-arid regions. It is estimated that almost 80 percent of the world's rural population depends on groundwater for safe water supplies. Furthermore, some 1.5 billion people depend on underground water for their drinking water supply (UNICEF, 2000). Fresh groundwater is about 100 times more plentiful than fresh surface water, but surface water is used more because it is easier to find and less costly to distribute. Also, much of the total groundwater volume is deep in the crust and too saline for most uses (Fitts, 2002a).

Table 2.1 An estimate of the global water budget (Maidment, 1993).

Reservoir	Percent of All Water	Percent of Fresh Water
Oceans	96.5	
Ice and Snow	1.8	69.6
Groundwater:		
Fresh	0.76	30.1
Saline	0.93	
Surface Water:		
Fresh lakes	0.007	0.26
Saline Lakes	0.006	
Marshes	0.0008	0.03
Rivers	0.0002	0.006
Soil Moisture	0.0012	0.05
Atmosphere	0.001	0.04
Biosphere	0.0001	0.003

Increasing demand of water for domestic, agricultural, and industrial purposes, pollution and overexploitation of water resources, periodic droughts and heterogeneous distribution of water resources obligate people to find new prospective resources. While water demand is increasing both in the world and in Turkey, water resources are becoming exhausted and polluted. Many countries will face serious water shortages in the near future. The fact of today's world that 700 million people live in water scarce areas and 1.6 million people lose their lives per year due to the absence of sanitary conditions and clean water, unfortunately justifies this concern (UN News Centre, 2007).

The quality and quantity of ground water are distributed heterogeneously, and once ground water becomes contaminated, the options for cleaning it or finding alternative supplies are very expensive and prospects for replenishing an aquifer may come real in decades, if not longer. Furthermore, excessive withdrawal of ground water can cause drying out of wells and land subsidence. In addition to this deterioration, pollution or mismanagement can deprive future generations from using this vital resource.

2.2 The State of Water Resources and Demand in Turkey

Annual average precipitation in Turkey amounts to 501,000 hm^3 of fresh water. 69,000 hm^3 (13.8%) of this water feeds the groundwater reservoirs; 274,000 hm^3 (54.7%) evaporates from soil, surface waters and plants; 158,000 hm^3 (31.5%) becomes runoff and flows through the rivers and arrives to the seas or lakes. Moreover, 7,000 hm^3 of surface water originates from the neighboring countries. 28,000 hm^3 of the total groundwater recharge returns to the land surface in the form of springs. The total water potential in Turkey, including surface and groundwater, is estimated to be 234,000 hm^3. Due to technical and economical reasons, Turkey can only use 98,000 hm^3 surface water and 14,000 hm^3 ground water yearly from this water potential (DSI, n.d.). According to various hydrogeological studies made to date in our country, the amount of safe groundwater operational reserves is totaling 12,300 hm^3 per year. This reserve was offered to the use of people and by various irrigation systems applied by the State Hydraulic Works (DSİ). The area irrigated with the use of groundwater totaled 445,000 ha as of 2001 (Kartal & Görkmen, 2001*)*.

In terms of the availability of water per capita, Turkey can be defined as a “water stressed” country. Any country with usable water quantity of less than 1000 m^3/year/capita is defined as a water scarce country, and this usually manifests itself in severe constraints on food production, economic development, and production of natural ecosystems (Tomanbay, 2000). The availability of usable water per person in a year is nearly 1,650 m^3 in Turkey (DSI, n.d.). The availability of water per capita in Turkey is only about one fifth of that of the water rich countries of North America and Western Europe (World Wildlife Fund Turkey [WWF], 2007). The Turkish Statistics Institution has estimated Turkey’s population as 100 million by the year 2030 (Turkish Statistics Institution [TURKSTAT], 2008). According to that estimation, the annual available amount of water per capita will be about 1,000 m^3 by

2030 (Nalbantoğlu, 2006). Consequently, Turkey is a water stressed country, having a risk to be a water scarce country.

The Turkish Bank of Provinces (İller Bankası) gives the daily consumption of water in Turkey as 200 liters per capita; however, it is obvious that water demand is increasing in Turkey as in developed countries day by day. Daily consumption of water per person varies in Turkey depending on socio-economic factors. For instance, according to the data of from TURKSTAT (2008), the daily consumption per person is reported as 262 L/day/capita in İzmir, 203 L/day/capita in Çanakkale and 119 L/day/capita in Hakkari.

Access to treated, safe water can be a problem for a particular segment of the population, in Turkey. Nearly 100% of urban dwellers but only 85% of rural residents have access to safe drinking water. Moreover, water supply is also a problem for new residents in peripheral and/or illegally settled areas of Turkey's cities (State Planning Agency [DPT], 1998). Water shortage is not only for rural residents. Today, two important urban cities of Turkey, Ankara and Istanbul face water deficiencies. Unfortunately, water resources mismanagement is apparent. All of these problems express and emphasize the importance of proper evaluation and monitoring of water quantity and quality as essential elements of water management as a whole.

2.3 Background information on groundwater flow and quality

2.3.1 Groundwater Flow

Groundwater occurs in two principal zones beneath the land surface, the unsaturated zone and the saturated zone. In the unsaturated (vadose) zone, pores between the particle grains and the cracks in rocks contain both water and usually air. Though a considerable amount of water may exist in the unsaturated zone; this water cannot be pumped and is not readily available due to the capillary forces holding it too tightly. On the other hand, in the saturated (phreatic) zone, pores and cracks are filled up with water. The upper surface of the saturated zone is referred as the water table. Below the water table, the water pressure is high enough to balance the capillarity forces and to be withdrawn. In generally, saturated water may be referred as groundwater, due to its adequacy for pumping and its usability.

Groundwater is not always accessible, or fresh enough for use without treatment, and it's sometimes difficult to locate or to measure and describe. This water may occur close to the land surface, as in a marsh, or it may be many hundreds of meters below the surface, as in deserts. Water at very shallow depths might be just a few hours old; at moderate depth, it may be 100 years old; and at great depth or after having flowed long distances from places of entry, water may be several thousands of years old (USGS, 1999).

Velocities of groundwater flow are typically low and smaller than velocities of stream flow. The movement of groundwater normally occurs as slow seepage through pore spaces among particles of unconsolidated deposits or through networks of fractures and solution openings in consolidated rocks. Therefore velocities of groundwater flow ranges between the levels of centimeters per day to the levels of centimeters per year. On the other hand, water remains in streams for a relatively short time and the velocities are higher. That is why, stream flow generally are measured in meters per second.

The groundwater flows through in a three type geological media: (1) porous (granular) media, (2) fractured media and (3) the combination of both of them, fractured porous media. In porous media (e.g., sand and gravels, silt, loess, clay and till), groundwater and contaminants move through the pore spaces among individual grains. In fractured media (e.g., dolomites, some shales, granites, and crystalline rocks), groundwater and contaminants move predominantly through the cracks or solution crevices known as impermeable rock. In fractured porous media (e.g., fractured tills, fractured sandstone, and some fractured shales), groundwater and contaminants can move through both intergranular pore spaces and cracks or crevices in the rock or soil. In the case of fractured porous media, and especially when karstification processes occur, fractures contribute as a secondary porosity, adding to the original one. This makes the comprehension of the phenomenon and the characterization of the groundwater flow difficult.

2.3.2 Groundwater Quality

Water is never found in a pure state in nature. Groundwater may contain many constitutes, including organisms, gases, inorganic and organic materials. As a result of chemical and biochemical interactions between groundwater and the geological materials through which it flows, and to a lesser extent because of contributions from the atmosphere and surface water bodies, groundwater contains a wide variety of dissolved inorganic chemical constitutes in various concentrations. It can be viewed as an electrolyte solution, because nearly all its major and minor constitutes are present in ionic form (Freeze & Cherry, 1979).

Groundwater quality comprises the physical, chemical, and biological qualities of ground water. Temperature, turbidity, color, taste, and odor make up the list of physical water quality parameters. Since most ground water is colorless, odorless, and without specific taste, people typically are most concerned with its chemical and biological qualities. Although spring water or groundwater products are often sold as "pure," their water quality is different from that of pure water (Harter, 2003). Various parameters of water quality such as taste, odor, microbial content, and dissolved concentrations of naturally occurring chemical constituents define the suitability of water for different uses.

2.3.2.1 Naturally Occurring Inorganic Solutes

Naturally occurring inorganic chemicals are referred to as dissolved solids. Some dissolved solids may have originated in the precipitation water or river water that recharges the aquifer. A list of the dissolved solids in any water is long, but it can be divided into three groups: major constituents, minor constituents, and trace elements.

Major constituents in groundwater occur in concentrations ranging from 1 to 1000 mg/L. The primary cations are calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^{+}); the primary anions include bicarbonate (HCO_3^-), chloride (Cl^-),sulfate (SO_4^{-2}). The other major constituents are dissolved CO_2 (H_2CO_3) and silica ($SiO_{2\ (aq)}$). The secondary constituents (minor) in groundwater occur in concentrations ranging from 0.01 to 10 mg/l. The secondary cations are potassium (K^+), iron (Fe^{+2}, Fe^{+3}), manganese (Mn^{+2}, Mn^{+3}, Mn^{+4}, Mn^{+5}, Mn^{+6} and Mn^{+7}) and strontium (Sr^{+2}) and the secondary anions are carbonate (CO_3^{-2}), nitrate (NO_3^-), fluoride (F^-), bromide (Br^-). The other secondary (minor) constituent is boron (B).

2.3.2.2 Total Dissolved Solids (TDS) and Electrical Conductivity (EC)

Total mass of dissolved constituents is referred to as the total dissolved solids (TDS) concentration. In water, all of the dissolved solids are either positively charged (cations) or negatively charged ions (anions). The total negative charge of the anions always equals the total positive charge of the cations. A higher TDS concentration means that there are more ions in the water.

Electrical conductivity is directly related to TDS, and can be used as a surrogate parameter that represents the total ion content in the water. With more ions in the water, the water’s electrical conductivity (EC) increases. The TDS concentration in mg/l is approximately 65 percent of the electrical conductivity value in µS/cm or in µmho/cm. For example: 65 mg/l≅100 µmho/cm (Harter, 2003). Generally, EC is proportional with TDS within the range 0 - 50000 µmho/cm (Ateşli, 2002).

At a high TDS concentration, water becomes saline. Water with a TDS above 500 mg/l is not recommended for use as drinking water according to U.S. Environmental Protection Agency [EPA] (2003). Water with a TDS above 1500 to 2600 mg/l (EC greater than 2250 to 4000 µmho/cm) is generally considered problematic for irrigation use on crops with low or medium salt tolerance.

According to the Turkish drinking water regulation (Ministry of Health [MoH], 2005), the acceptable value for electrical conductivity is limited as 2500 µS/cm for 20 ºC. Moreover, the Turkish Water Pollution Control Regulation (Ministry of

Environment and Forestry [MoEF], 2008) was updated in 2008 and the table of water classification, concerning the TDS is presented below (Table 2.2).

Table 2.2 Quality classification of terrestrial water (MoEF, 2008)

	Water Quality Classes			
	I	**II**	**III**	**IV**
Total Dissolved Solids(mg/L)	500	1500	5000	> 5000
Chloride ion (mg Cl^-/L)	25	200	400[a]	> 400

[a] Decreasing the concentration limit may be required, considering the irrigation of sensitive plants against Cl^-

2.3.2.3 Nitrate

Nitrate (NO_3^-) is a widespread constituent in groundwater and surface water. Excessive concentrations of NO_3^- in drinking water can cause adverse health effects for humans, while in surface waters can cause eutrophication. NO_3^- creates the disease known as methemoglobinemia, when it is transformed to nitrite (NO_2^-) in the digestive system. It is also evidenced that when nitrates and nitrites are exposed to amines in the human digestive tract, they may develop nitrosamines, having possible carcinogenic properties (Shuval & Gruener, 1977).

Nitrate in groundwater is of concern not only because of its toxic potential, but also because it may indicate contamination of the groundwater. If the source of contamination is animal waste or effluent from septic tanks, pathogens may also be present. Contamination of groundwater by fertilizers may also indicate the presence of other agricultural chemicals such as pesticides. The source of the NO_3^- may be a clue as to which other contaminants may be present (Sular, 2002).

The mechanisms of natural NO_3^- attenuation in groundwater are dilution, denitrification and plant uptake. Dilution does not remove NO_3^- from groundwater, however. Although denitrification is the primary NO_3^- removal mechanism, it only occurs under certain conditions. Moreover, plant uptake depends on the growth rate of plants. Nitrate is non-volatile and stable under aerobic groundwater conditions.

Therefore, a treatment method must be applied for NO_3^- removal at above exceeded limit levels (Table 2.3).

Table 2.3 Standards and recommended NO_3^- concentrations for drinking water (10 mg/L nitrate-nitrogen (NO_3^-N) = 44.3 mg/L nitrate (NO_3^-))

Standard	**Max. Level**	**Recommended Level**
Turkish Regulation[1]	50 mg/L NO_3^-	25 mg/L NO_3^-
WHO[2]	50 mg/L NO_3^-	25 mg/L NO_3^-
EC Nitrate Directive[3] (EC Drinking Water Directive[4])	50 mg/L NO_3^- (50 mg/L NO_3^-)	25 mg/L NO_3^-
U.S. EPA[5]	10 mg/L NO_3-N	10 mg/L NO_3-N

[1] MoH (2005)
[2] World Health Organization (2006)
[3] European Economic Community (1991)
[4] European Council (1998)
[5] EPA (2003)

2.3.2.4 Chloride

Chloride (Cl^-) is one of the major inorganic anions in water and wastewater. The Cl^- content normally increases as the mineral content increases. It is generally in the form of sodium, potassium, and calcium salts. In many areas, the level of chlorides in natural waters is an important consideration in the selection of supplies for domestic, industrial, agricultural use. Chloride's source in groundwater may be seawater, evaporates, precipitation and atmosphere. Seawater is the source that gives the biggest amount of Cl^- to groundwater. Cl^- concentration in groundwater decreases sharply along the distance from coast. Generally it is low in rainy environments and high in arid zones. In some instances Cl^- in groundwater is geogenic and originates from certain minerals that leach Cl^- to the groundwater flowing through them. Cl^- ions are typically non-reactive and do not participate in redox reactions. They do not sorb on mineral or organic surfaces and do not form insoluble precipitates. Therefore, Cl^- can be used as a tracer in groundwater studies.

Chloride in shallow ground water is also an important indicator of contamination from human sources. Compared to background concentrations, Cl^- concentrations are typically elevated in shallow ground water under urban land use, around septic systems, near waste impoundments and occasionally under agricultural fields. It is common to observe elevated levels near industrial sites, since Cl^- is a daughter product of chlorinated hydrocarbons that are used as solvents in the manufacturing industry. Chlorinated hydrocarbons can biodegrade in the aquifer under certain conditions, thereby yielding Cl^- from the process. According to the Turkish drinking water regulation, the permissible concentration for Cl^- is limited as 250 mg/L. The qualitative classification of terrestrial water with respect to Cl^- is given in Table 2.2.

2.3.2.5 Hardness

One of the most important properties of water is hardness. The reason of hardness of water is primarily the presence of Ca^{+2}, Mg^{+2} and HCO_3^- ions. Hardness in most groundwater is naturally occurring from weathering of limestone, other calcium or magnesium bearing sedimentary rocks and minerals. Hardness can also occur locally in groundwater from chemical and mining industry effluent or excessive application of lime to the soil in agricultural areas.

The hardness of water can be expressed in many ways, one of them being in terms of the amount of $CaCO_3$ or equivalent minerals that would be formed if the water were evaporated. Water is considered soft, if it contains 0 to 60 mg/L $CaCO_3$ of hardness, moderately hard from 61 to 120 mg/L, hard between 121 and 180 mg/L, and very hard if more than 180 mg/L. Hard water is mainly an aesthetic concern because of the unpleasant taste that a high concentration of Ca^{+2} and other ions give to water. It also reduces the ability of soap to produce lather, and causes scale formation in pipes and on plumbing fixtures. Soft water can cause pipe corrosion and may increase the solubility of heavy metals such as copper, zinc, lead and cadmium in water. In some agricultural areas where lime and fertilizers are applied to the land, excessive hardness may indicate the presence of other chemicals such as NO_3^- (Hardness in Groundwater, 2007).

2.3.3 Groundwater Contamination

Groundwater contamination implies solutes dissolved in the water at very high concentrations and also the pathogen bacteria that pose some significant risks to human health or an ecosystem. The fate of groundwater contamination depends on the local hydrogeology, groundwater flow patterns, pore-scale processes and molecular-scale processes. Contamination might spread rapidly within a high conductivity sand lens, or it might diffuse at a snail's pace through low conductivity clay. Some contaminants adsorb onto the surface of aquifer solids moving very little from their source, while others migrate freely with the flowing pore water, sometimes ending up many kilometers. Chemical reactions along the way cause a contaminant to disappear, or worse, appear from apparently nowhere (Fitts, 2002b), like a "chemical time bomb".

Groundwater commonly contains one or more naturally occurring chemicals, leached from soil or rocks by percolating water, in concentrations that exceed drinking water standards. One of the most common water quality concerns is the presence of dissolved solids and chloride. Although not particularly toxic, iron and manganese in greater than the limits can impair the taste of water, stain plumbing fixtures, glassware and laundry, and reduce well-pumping efficiency. Dissolved gases can have a significant influence on the subsurface hydro-chemical environment. They can limit the usefulness of groundwater and, in some cases can even cause major problems or even hazards (Freeze & Cherry, 1979). Examples of possible natural contaminants are trace elements such as arsenic and selenium, radionuclides such as radon, and high concentrations of commonly occurring dissolved constituents.

Anthropogenic sources of groundwater contamination come in a great variety of sizes and shapes. It may be classified as point sources or non-point sources. Leaking underground pipeline or tank, a wastewater lagoon, a septic system leaching field, a spill into a drain at a factory which are examples that are all relatively small. On contrast, non-point sources are larger, broadly distributed sources. Examples of non-point sources include polluted precipitation, pesticides applied to a cropland, and runoff from roadways and parking lots.

Sometimes contamination is introduced to the surface as an aqueous solution such as a septic system effluent or landfill leachate. This is not always the case, though. The source of contamination can be spilled separate liquid phase like gasoline or dry-cleaning solvent. These liquids are usually organic, known by the acronym NAPL, into the water, acting as continuous point source for years. (Fitts, 2002b).

Common sources of human-induced groundwater contamination can be grouped into five categories:

1. Waste disposal practices: Waste disposal practices can take a number of forms. The common forms of this groundwater contamination source are septic systems, landfills, land applications, surface impoundment and waste injection wells. Septic systems are for subsurface disposal of human wastewater, are the rule in more in rural areas not served by sewers and sewerage systems. Wastewater is gathered in a buried septic tank by drainpipes, where solids are settled. For the accumulation, wastewater needs to be pumped periodically. Usually the wastewater flows to a leaching field, in the porous material in the unsaturated zone. This system constitutes several groundwater contamination problems by in a way of exceeding the concentrations of nitrates and nitrites, ammonia, phosphorous, chloride, and organic substances. Landfills are built with elaborate leak-prevention systems, but not many decades ago, we knew the landfills as dumps, and they were nothing more than unlined pits filled with refuse. Poorly designed landfills, leaking liquids or leachates from them, contaminate the surrounding shallow groundwater. Land application of wastewater and sewage sludge is an alternative to conventional treatment and disposal, and is common usage by vegetable industry, petroleum refining, pulp and paper, and the power industry. In many places, solid and liquid wastes are placed or sprayed on the land, commonly after treatment and stabilization (Kırer, 2002). Surface impoundment, including ponds and lagoons, generally consists of relatively shallow excavations that range in area from a few square meters to many square

meters (EPA, 1988). Surface impoundments are used to store, treat or dispose of oil and gas brines, acidic mine wastes, industrial wastes, animal wastes, municipal treatment plant sludge and cooling water. Finally, waste injection wells are used to dispose of some kind of liquid, which are hazardous waste as brines and other waters recovered from oil fields, fluids from solution mining, and treated wastewaters. If the injection well was not isolated from any useful aquifers, the groundwater contamination cannot be prevented.

2. Storage of materials and wastes: Storage of materials is another important source of groundwater contamination. Leakage from underground storage tanks and from pipelines is the growing problem of the groundwater sustainability. The common storage tanks are gas tanks at filling stations, and fuel and solvent storage tanks at industrial facilities. What leaks out of these are organic NAPLs. Corrosion is the most frequent cause for leakage.
3. Agricultural activities: Agricultural activities include several practices that can lead to groundwater contamination: Pesticides, herbicides, and fertilizer application, irrigation and animal waste storage. Pesticides, herbicides and fertilizers are highly toxic organic compounds and quite mobile in the subsurface. Many of these organic compounds biodegrade rapidly, but some are persistent and contaminate groundwater over broad areas. Fertilizer application can cause high NO_3^- concentrations in groundwater, and high nutrient loads in surface runoff. Excessive irrigation causes reaching the contaminants such as pesticides and fertilizers to groundwater easily, and washing the soil minerals to the groundwater. Animal waste is the source of fecal coliforms, nitrates and nitrites, ammonia in the groundwater.
4. Seawater intrusion: Seawater intrusion is a problem of coastal areas. When groundwater is abstracted from near sea aquifers, seawater proceeds into the groundwater and the quality deteriorates with respect to salinity. Seawater intrusion becomes evident, when basically the Cl^- concentration of the groundwater increases over time. However, Cl^- concentration is not an indicator that can be solely relied on, and other geochemical parameters need to be verified.
5. Accidental spills: A large volume of toxic materials is transported by truck and stored in tanks. Accidental spill of the materials are common. Accidental spills

occur in large amounts each year, and these include hydrocarbons, paint products, flammable materials, acids etc. Virtually, no methods are available to quickly and adequately clean up an accidental spill or those caused by explosions of fires (EPA, 1988).

6. Mine wastes: Mining can produce spoils, or unneeded soil, sediment, and rock moved during the mining process, and tailings, or solid waste left over after the processing of ore. These wastes may be piled on the land surface, used to fill low areas, used to restore the land to premining contours, or placed in engineered landfills with leachate-collection systems. Mine wastes can generate leachate as rainwater passes through them. If sulfate or sulfide minerals are present, sulfuric acid can be generated, and the resulting drainage water can be acidic. This is likely to occur with coal-mining wastes, copper and gold ores, and ores from massive sulfide mineralization. Mine-waste leachate may also contain heavy metals and, in the case of uranium and thorium mines, radionuclides. Neutralization of the mine wastes can prevent the formation of acidic leachate and prevent the mobilization of many, but not all, metallic ions and radionuclides. Leachate produced by unneutralized or uncontained mine wastes is a threat to surface and groundwater (Fetter, 1993).

2.4 Karstic Aquifers

Karstic aquifers are an important group of aquifers. The term ‘karst’ is most often used in a geomorphologic sense to describe landscapes that result from dissolution and surface drainage of limestone-carbonate terrains (Kaçaroğlu, 1999). Karst may be also defined as the terrain characterized by the specific surface and underground landforms and features (karens, dolines, ponors, channels, caves, closed depressions, dry valleys etc.) essentially developed in limestone and dolomite and also in other soluble rocks (e.g. gypsum, salt rock, quartzite), by a particular type of groundwater circulation and regime, and by the occurrence of springs that usually have large capacity (Kaçaroğlu, 1999). The size of these porous structures can vary from 1μm to hundreds of meters (Alpaslan, 2001) and these structures increase the occurrences of anisotropy and heterogeneity of permeability at high levels.

Circulation of groundwater in karst aquifers is quite different from water circulation in other aquifer types (non-karstic). In karst aquifers water is being collected in networks of interconnected cracks, caverns, and channels (Huntoon, 1995). Underground channel (conduit) flow is the most important type of water circulation in karst aquifers. In karst aquifers very rapid water circulation occurs (Kaçaroğlu, 1999).

Karst aquifers have specific hydrogeological characteristics that render them highly vulnerable to pollution from human activities. Karst groundwater (the water in a karst aquifer) becomes polluted more easily and in shorter time periods than water in non-karstic aquifers. The pollutants that are introduced in a karst aquifer do not behave like those in granular or in fractured aquifers (Kaçaroğlu, 1999).

The natural attenuation of pollutants in karst aquifers is limited because of the: (1) significant lack of available surface area for adsorption, ion exchange, or colonization by microorganisms, (2) rapid infiltration of water and contaminants restricts the availability of highly volatile chemicals to evaporate, (3) typically thin soil cover and the relatively large secondary voids allow for rapid transport of contaminants, (4) turbulent flow regimes associated with the high flow rates enhances contaminant transport, and (5) lack of sufficient time for time-dependent elimination mechanisms (e.g. bioremediation) to act on contaminants because of the rapid flow-through (Ford & Williams, 1989). Thus, karst aquifers are most sensitive to groundwater contamination. Historically, such problems have been limited to small and rural areas. But recent urbanization of karst terrains has increased the risk and frequency of pollution and has especially increased the need for hydrogeology assessments appropriate to these aquifers (Veni, 1999).

2.5 Investigations and Groundwater Quality Assessment Studies of Karstic Aquifers in Turkey

Karstic aquifers, constituting one-third of Turkey’s aquifers are potential water resources that can fulfill a significant portion of groundwater demand around the country especially in the Mediterranean basin. Intensive karstification is present in almost all regions of the country and both at high altitudes such as over 2,000 m and at low altitudes below sea level (Eroskay & Günay, 1979).

One of the important karstic areas of Turkey is in the Antalya region. The city of Antalya is located in a travertine area, which is highly porous, permeable and karstified. The water for the city of Antalya and some industries is supplied from wells drilled within the travertine aquifer. Some karst springs (e.g. Arapsuyu and Mağara) are also used to meet the water demand. (Günay, Tezcan, Ekmekçi, & Atilla, 1995). On the other hand a sewer system does not exist in the city of Antalya. Sewer system works are not completed and septic tanks are still common in the center of the city. Municipal and industrial waste waters are directly discharged into travertine aquifer. During the tourism season, the population of Antalya increases up to 2 million people. All the domestic wastes of this population are disposed directly into the travertine without any treatment. Intensive use of fertilizers and pesticides in agricultural lands within the travertine area also caused groundwater pollution. Water quality analyses in a study in Antalya showed that groundwater was contaminated by sewage discharge, industrial works, and other activities that created an ever-expending impact to the only available aquifer. The existence of NO_3^- was a clear evidence of pollution, and the contamination was confirmed by the presence of coliform bacteria, which was accounted above 240/100 mL in some wells. NH_3 concentration was above 0.3 mg/L in all of the samples. The levels of the heavy metal concentrations in the samples were low, but they indicated pollution (Karagüzel & Scholz, 1999).

Another example of karst groundwater pollution originating from domestic wastewater can be given from the city of Isparta. The Isparta Plain is an important groundwater basin with a recharge area of approximately 276 km^2 in the southeast corner of Turkey. Analytical results of sampled groundwater indicate that ammonium values range between zero and 0.29 mg/L, nitrite values between zero and 0.05 mg/L and nitrate values between 0.55 and 48 mg/L. High values were obtained in samples within the proximity of the city sewerage system. (Karagüzel & Irlayıcı, 1998)

Another study conducted for the Çesme Peninsula provides a detailed relation between salty water and karstification. Serious saltwater intrusion was detected in the area, especially during the summer season due to seasonal increase in population and overexploitation of groundwater. Karstification is one of the most important factors controlling the extension of the sea water intrusion. Mg^{+2}, Ca^{+2} and HCO_3^- were the main ions for groundwater in the middle of the study area. However, Na^+ and Cl^- became more dominant ions near the coastline. Chloride concentrations in upper aquifer are about 100-200 mg/l; however in some areas contain saline water with Cl^- concentrations reaching up to 4000 mg/l. The proportion of seawater mixing in some water samples attaining 18% (Gemici & Filiz, 2001).

Although there is a number of studies emphasizing the importance of karstic aquifers in Turkey, the groundwater contamination and deterioration of groundwater quality is increasing day by day. “In order to preserve karst groundwater, the hydrogeological and geochemical characteristics of the karst area must be investigated and information on polluting activities and sources must be collected. Then, a comprehensive protection and control system must be developed consisting of the following six components: (1) develop and implement a groundwater monitoring system, (2) establish critical protection zones, (3) develop proper land use strategies, (4) determine the reasonable development capacity of the karst aquifer, (5) control and eliminate when necessary sources of pollution, (6) increase public awareness of the value and vulnerability of karst aquifers” (Kaçaroğlu, 1999).

2.6 Spatial and Temporal Groundwater Quality Assessment Studies

Because of the great importance of groundwater, there are many studies in the world about groundwater quality assessment. For instance, a study by Kannel, Lee & Lee (2008) examined the spatial and temporal variations and factors influencing the management of groundwater along a section of the Bagmati river corridor in the Kathmandu valley (Nepal). Nine locations were sampled in the pre-monsoon and post-monsoon seasons and were of 30 h duration. The pH and dissolved oxygen (DO) were measured in-situ. Moreover, biological oxygen demand (BOD), chemical oxygen demand (COD), total phosphorus (TP), total nitrogen (TN) and trace elements were analyzed using different methods. Subsequently, the data was statistically processed in order to assess the spatial and temporal changes in groundwater quality. The two-tailed t-test was used to examine the difference of groundwater quality (1) from pre-monsoon to post-monsoon and (2) from rural areas to urban areas. The t-test results showed that in rural areas groundwater were less contaminated and had better quality than in urban areas, and the level of organics was higher in the pre-monsoon season, while the level of nutrients was higher in post-monsoon season. Furthermore, a correlation analysis was performed between the quality parameters to obtain interferences as they are affected simultaneously by spatial and temporal variations. The high positive correlation coefficient (0.948) between BOD and COD was explained as they are closely related to the contamination of organic matter. Moreover, COD concentrations showed negative correlation with the DO concentrations because organic matter was oxidized at the expense of oxygen. Positive correlation between BOD and pH was attributed to the fact that the production of ammonia and dissolved inorganic carbon during the decomposition of nitrogen rich organic compounds by bacteria tends to an increase in both the pH and alkalinity. The significant correlation between TN and TP concentrations (0.544) was attributed to groundwater pollution from both point and non-point sources.

Another study was carried out to assess the quality of groundwater for determining its suitability for drinking and agricultural purposes in upland sub-watersheds of Meenachil river, parts of Western Ghats, in Kerala, India (Vijith & Satheesh, 2007). The study area is dominated by rocks of Archaean age, and Charnonckite is dominated over other rocks. Rubber plantation dominated over other types of the vegetation in the area. Though the study area received heavy rainfall, it frequently faced water scarcity as well as water quality problems. Twenty-eight water samples were collected from different wells and analyzed for major chemical constituents both in monsoon and post monsoon seasons to determine the spatial and temporal quality variation. Physical and chemical parameters of groundwater such as pH, DO, total hardness, Cl^-, NO_3^- and phosphate (PO_4^{-3}) were determined. Surface maps were prepared using GIS to assess the quality in terms of spatial variation for September 2004 and January 2005. Comparative assessment of the spatial distribution maps revealed the seasonal fluctuations and the spatial patterns of physical and chemical constituents of the study area. According to the overall assessment of the basin, all the parameters analyzed were below the desirable limits of drinking water standards. The influence of lithology on the quality of groundwater was negligible in this region, and it was found that extensive agricultural practices influenced the groundwater quality of the region.

CHAPTER THREE
DESCRIPTION OF THE STUDY AREA

3.1 General Description

The Nif Mountain karstic aquifer was selected for the spatial and temporal assessment study of groundwater quality. The study area of slightly more than 1000 km^2 is located to the southeast of the city of İzmir (Figure 3.1). The boundaries of the study area were delineated such that groundwater quality representative of the mountain's aquifer system itself and of the surrounding low level plains could be sampled. Being situated within the administrative boundaries of the third largest city and in the vicinity of one of the most industrialized areas of Turkey, the Nif Mountain aquifer is under immense environmental stresses due to residential, agricultural and industrial development. In particular, the fertile agricultural plains are being converted to organized industrial zones or residential lots in Bornova, Cumaovası, Kemalpaşa and Torbalı plains. This transformation is the main reason for the increase in population density in the region. Bornova, Kemalpaşa, Buca, Menderes and Torbalı are among the major counties of İzmir that are situated around Nif Mountain. According to the 2008 census data, about 675,000 inhabitants live within these counties at the lower elevations of Nif Mountain (TURKSTAT, 2008). The population density decreases with proximity to Nif Mountain, where only a few small villages exist on the hillslopes (Elçi, Gündüz, & Şimşek, 2007).

The major anthropogenic facilities multiplying the environmental stress on the study area are industrial. Wastewater, fluid and solid wastes originating in the residential areas and industrial plants pose a significant threat to the aquifer systems of Bornova and Kemalpaşa, which are situated north of the Nif Mountain, in case suitable treatment and disposal conditions are absent. In contrast, the south and southwest of the study area exhibit a relatively protected area character. Furthermore, the airport within the borders of Gaziemir county and some industrial plants located in and around Menderes and Kısık are within the Tahtalı reservoir catchment. Likewise, the east of the study area is used as an agricultural area (Polat, Elçi, Gündüz, & Şimşek, 2007).

3.2 Hydrological Features

Typical characteristics of the Mediterranean climate can be observed in the area with mild, rainy winters and hot, dry summers. Based on the data collected at the Bornova Meteorological Station between 1979 and 2005, the region receives a mean annual precipitation of 594 mm. The highest precipitation amounts are observed in November, December and January, with long-term monthly averages of 100, 120 and 106 mm, respectively. The lowest precipitation values are observed in July and August with long-term monthly averages of 2.3 and 1.8 mm, respectively (State of Meteorological Service [DMI], 2006). During winter months, the precipitation typically occurs in the form of snow around the summit of Nif Mountain (ca. 1,450 m) but no permanent snow cover occurs due to moderate temperatures with a mean above 0°C.

A wide network of streams and creeks developed in and around the vicinity of Nif Mountain as seen in Figure 3.1. Among the most important of these streams, the perennial Hırsız and Gürlek creeks originate from the southwestern slopes of the mountain and later merge to form the Tahtalı stream, which flows through the heavily populated Cumaovası plain. The Tahtalı stream is the major tributary of the Tahtalı reservoir that was constructed in the 1990s to meet the water demand of the İzmir metropolitan Area. The Kapuz and Kestane creeks originate from the northeastern slopes of the mountain and later merge to form the Nif stream, which flows into the industrialized Kemalpaşa plain before merging with the Gediz River. Finally, the Vişneli stream originates from the southeastern slopes of the mountain and is mainly fed by two karstic springs. The Vişneli stream flows into the Torbalı plain, which is considered to be an important agricultural production area and an industrial development region. With long-term mean daily flow values of about 10 m^3/s; the Tahtalı, Nif, and Vişneli streams are important recharge sources for their corresponding underlying surficial aquifers (Şimsek, Elçi, Gündüz & Erdoğan, 2008).

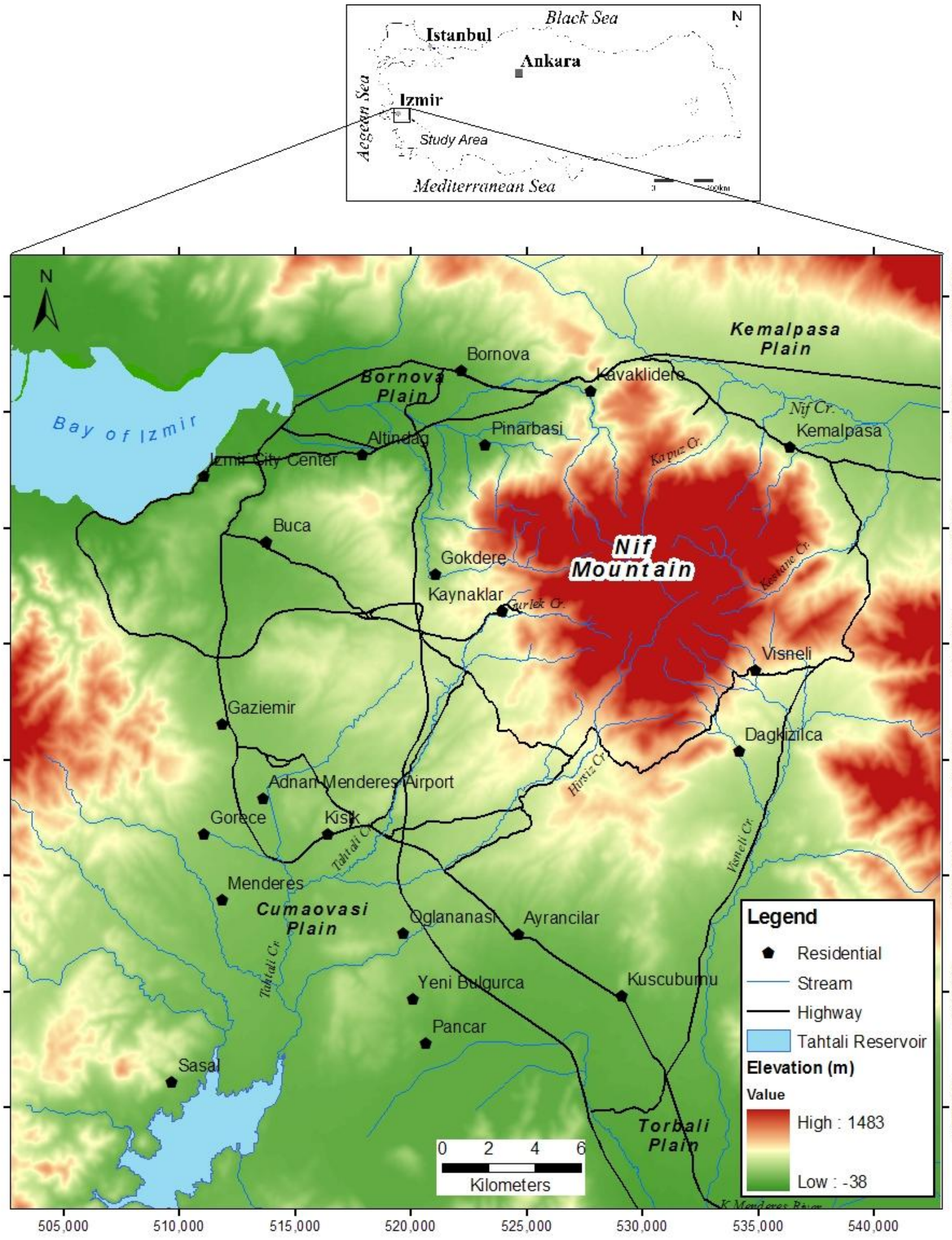

Figure 3.1 General location map of the study area

3.2.1 *Current State of Water Resources in İzmir*

The city of İzmir can be considered as fortunate compared to other metropolitan cities of Turkey with respect to the quantity of water resources. However, it does not mean that the availability of water can sustain forever in spite of the effects of climate change. Today, with İzmir's population of roughly 3,750,000 the domestic water consumption in İzmir can be calculated as approximately 562,500 m^3/day using a consumption rate of 150 L/capita/day. In 1997, the population was 3,114,859 and the domestic water consumption was calculated as 450,000 m^3/day (Atış, 1999). This amount excludes usage for industrial and irrigational purposes. “Due to the large amount water losses in distribution system, the amount of water to be supplied is much larger than theoretical figures. In a study conducted by Dokuz Eylül University, the amount of water loss by leakage is estimated to be 33% (Türkman, Aslan & Yılmaz, 2001). Despite the fact that the study by Atış (1999) foresees that water demand would be roughly 800 hm^3/year by 2040, today it is considered that this amount would be achieved even before that time.

Table 3.1 Distribution of İzmir’s water supply according to the source of water (Gök, 2008)

Source	**2006 (%)**	**2007 (%)**
Balçova Dam	1.76	1.56
Tahtalı Dam	35.92	33.82
Total Surface Water Resources	37.68	35.38
Sarıkız & Göksu Wells	38.64	40.11
Menemen & Cavuşköy Wells	18.37	18.71
Halkapınar & Çamdibi Wells	0.78	0.51
Total Groundwater Resources	62.32	64.62
Total Water Production (m^3)	**215,228,378**	**201,357,705**

The groundwater resources in the İzmir region are abundant and meet nearly 65% of the total amount supplied. Withdrawn groundwater is disinfected by chlorination before fed into the municipal water supply system. Groundwater consumption remained fairly stable in recent years (Fig. 3.2). In addition to this, there are many private wells in the region, which belong to residential areas, industrial and commercial facilities, etc. A significant proportion of these wells are known to be unregistered and illegal.

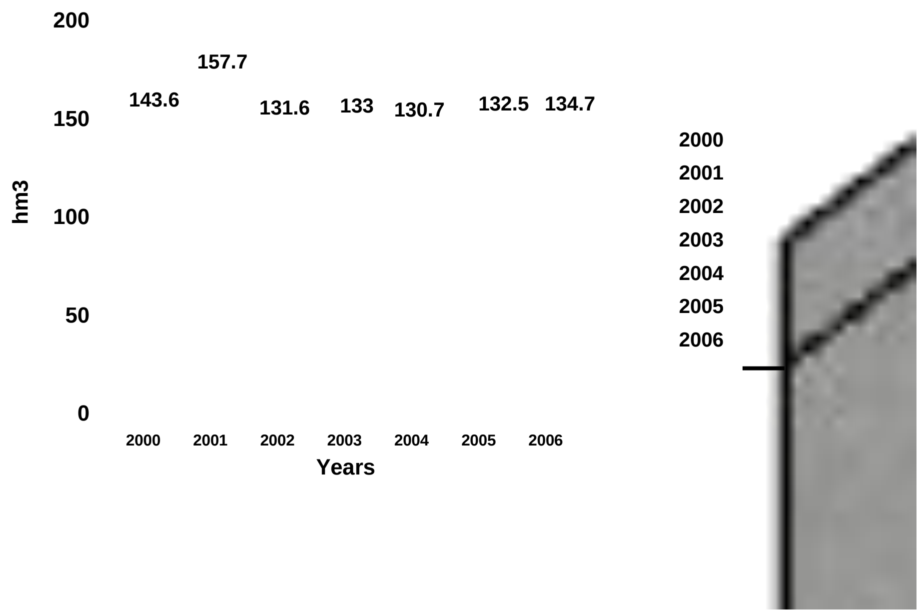

Figure 3.2 Groundwater consumption in İzmir given as hm^3/year (Gök, 2008)

Local studies related to groundwater quality were reviewed by Türkman et al. (2001). Figure 3.3 depicts groundwater pollution cases encountered in areas within the metropolitan borders of the city of İzmir. It can be concluded based on this review and the survey of other current literature presented in this thesis, that up to date groundwater quality studies for the Nif Mountain karstic aquifer could not be found.

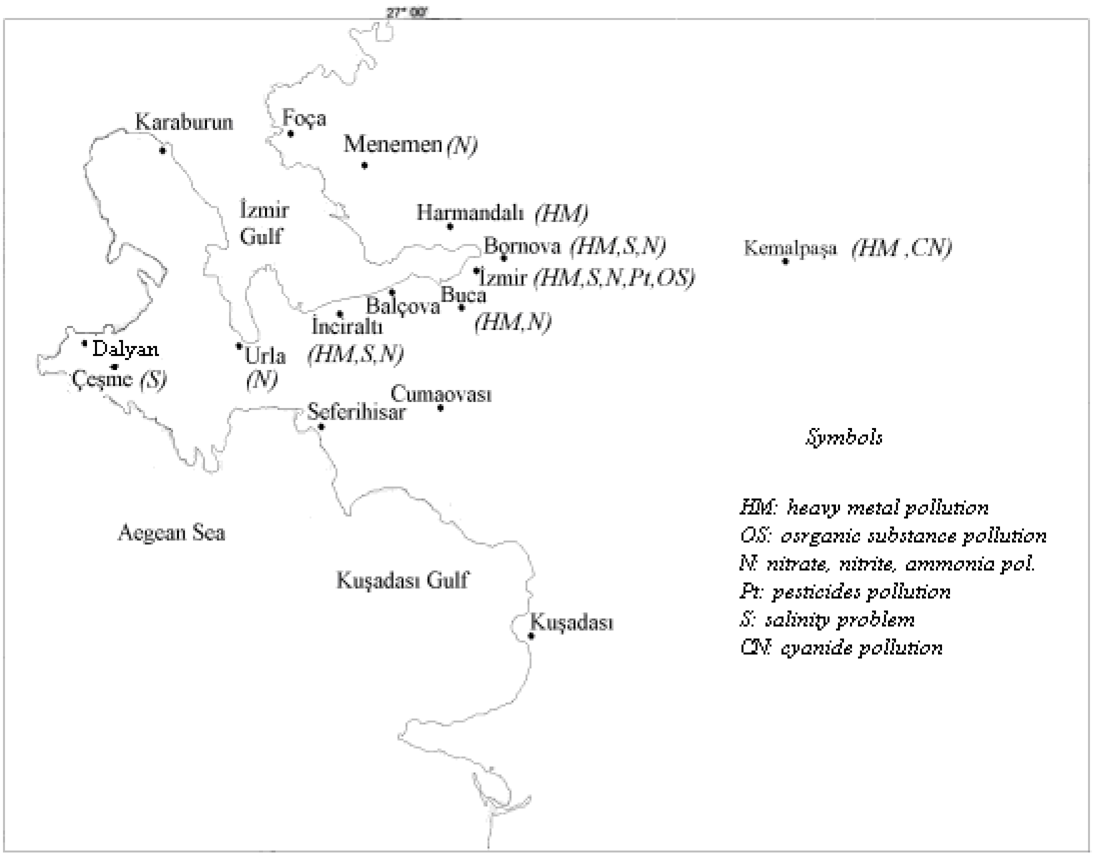

Figure 3.3 Summary of groundwater pollution cases in İzmir region. Letters show pollutants, which exceed the limits for Turkish drinking water standards. (Türkman et al., 2001)

3.3 Hydrogeology of the Study Area

3.3.1 Geological Setting

Basically, four different rock types are observed in and around the study area as seen from Figure 3.4 : (1) the Paleozoic-aged Menderes metamorphics, which mainly consist of schists, (2) the Mesozoic-aged Bornova flysch that mostly contains meta-sandstones, shales, ophiolites as well as the Upper Cretaceous-aged allochthonous limestones, (3) the Neogene-aged conglomerates, claystones and clayey-limestones, which are collectively known as the Vişneli Formation, and (4) the Quaternary-aged alluviums (Elçi et al., 2007). Generally in the Aegean Region and particularly around İzmir; the limestone formations are for the most part allochthonous in nature. They vary in sizes ranging from a few hundred meters up to twenty kilometers inside flysch units (Erdoğan & Güngör, 1992). Within the immediate vicinity of the city of

İzmir, these allochthonous limestone formations are observed at the highest elevation of the Nif Mountain reaching as high as 1,450 m. In addition, these units are also observed to have a thickness of up to 200 m, therefore classifying them as the most significant karstic rock of the region. They are primarily surrounded by flysch formations. Because these flysch formations are considerably less permeable, the karst aquifer system that is recharged from the Nif Mountain is considered to be an important groundwater resource in the region. In this regard, the Nif Mountain hosts a number of large springs with discharge rates exceeding 100 L/s. The majority of these springs outcrop in locales, where the highly permeable allochthonous limestone interfaces with flysch formations. These flysch formations in the Nif Mountain are intermingled with meta-sandstone, shale, ophiolite and serpantinite units. This complex nature of the regional geology influences the hydrogeological properties as well as the geochemistry (quality) of water that flows through them (Şimşek et al., 2008).

The Neogene-aged series lie with non-uniformity over the Bornova Flysch. These Neogene-aged series are collectively named as the Vişneli Formation. The Vişneli Formation mainly consists of a number of rocks including but not limited to conglomerates, sandstones, claystones and clayey limestones (Baba & Sözbilir, 2001). The geological map of the study area shows that the western and southern portions of the mountain are mostly characterized by the Neogene series including conglomerates, sandstones, claystones and limestones (Figure 3.4). Finally, alluvial layers mostly cover the northern and southwestern parts of the study area overlying the Bornova Flysch and Vişneli Formation in the region. The thickness of the alluvial layer ranges from 40 to 120 m in Bornova and Kemalpaşa plains and from 20 to 80 m in Torbalı and Cumaovası plains (Şimşek, 2002).

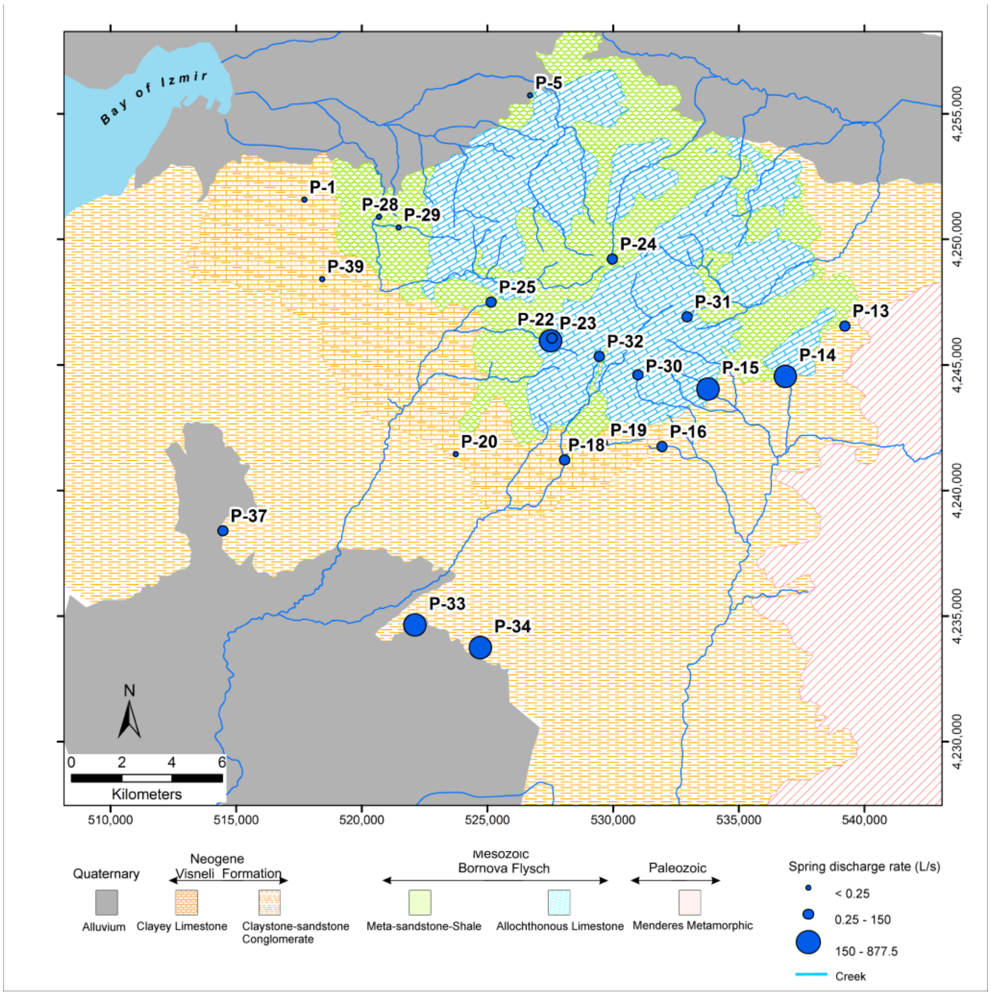

Figure 3.4 Geological map of the study area with discharge rates of major springs (Şimşek et al., 2008)

3.3.2 *Hydrogeological Characteristics*

A detailed assessment of the regional geology and the above-mentioned aquifer systems reveals that the most important water-bearing unit in the study area is the allochthonous karstic limestone aquifer. The Neogene series (conglomerate-sandstone and clayey-limestone) aquifers and Quaternary alluvial aquifer systems are in general of secondary importance for the region, as they have a relatively lower water supply potential compared to the karstic limestone units. In this regard, wells that are drilled in the allochthonous limestone units have been proven to provide significant amounts of water (i.e., as high as 50 L/s from a typical well depth of less than 300 m). It must also be mentioned that all of these aquifer systems are recharged by Nif Mountain via infiltration from surface runoff and horizontal seepage from subsurface interflow.

Simşek et al. (2008) reported that numerous wells are drilled in and around the Nif Mountain area for water supply purposes. Furthermore, the majority of these wells are located below an elevation of 300 m, particularly in lowland areas such as Bornova, Kemalpaşa, Torbalı and Cumaovası plains. These wells are typically drilled in the alluvial, the Neogene conglomerate and the limestone aquifers. Although the depths of these wells are rather variable depending on the aquifer system it is drilled to, wells dug in the alluvial aquifers are generally shallower than 100 m.

The overexploitation of the alluvial aquifers surrounding the study area created significant drawdown in water levels, which in turn resulted in the construction of deeper wells that would penetrate the underlying conglomerate and limestone aquifers. Particularly the wells drilled in the Bornova and Kemalpaşa plains are about 120 to 250 m in depth. For industries that require vast amounts of water (i.e., beverage and brewery industries), wells are drilled in the allochthonous limestone units with depths exceeding 350 m in Bornova and Kemalpaşa plains (Şimşek et al., 2008)

The complex geological structure and the aquifer formations in the Nif Mountain area and its vicinity resulted in the formation of numerous natural springs. These springs can be classified into four major categories depending on the parent rock, the formation mechanism, and the rate of discharge: (1) high-discharge springs that emerge from the outcropping fractures and cracks of allochthonous limestone units, (2) high-discharge springs that emerge from the surface outcrops of conglomerate and sandstone units of the Vişneli formation, (3) medium- to low-discharge springs that are formed at the contact zones of allochthonous limestone and flysch units, and (4) low-discharge springs that are formed at the contact zones of claystone and clayey-limestone units of the Vişneli Formation. Spring discharge rates measured at selected sampling locations are presented along with the regional geology in Fig. 3.4. The high-discharge springs originating from allochthonous limestone units have discharge rates higher than 50 L/s, which can sometimes reach up to 300 L/s depending on the annual precipitation pattern. Typical examples of this category are the Vişneli (P-14 and P-15) and Gürlek (P-22) springs located in the southeast and west of the study area, respectively. The springs with high discharge rates emerging from the conglomerates and sandstone units have discharges in excess of 200 L/s. The seasonal discharge at these locations could occasionally reach up to 1000 L/s during winter and spring seasons when recharge rates are at maximum. These springs usually have larger recharge areas and are observed at lower elevations of the study area. The Oğlananası (P-33) and Ayrancılar (P-34) springs are considered to be typical examples of this category. On the other hand, low-discharge springs originating from the contact zones of Neogene-aged claystone and clayey-limestone units typically have discharge rates less than 1 L/s. The springs in the Altındağ (P-1) and Kırıklar (P-18) region of the study area belong to this category. Finally, the medium- to low-discharge springs that emerge from the contact zones of allochthonous limestone and flysch units have discharge rates that differ considerably and are generally higher than 1 L/s but typically less than 10 L/s. The rate depends on the spatial extent of the limestone interface at the contact zone. Typical examples to this category are Şekeroluk (P-24) and Eşoluk (P-32) springs located in the central portions of the study area. In general, spring discharge rates in the study area decreased on average 65% from April to September based on the comparison of discharge rate measurements in the field (Elçi et al., 2007).

CHAPTER FOUR
MATERIALS & METHODS

This chapter presents the approach taken to assess groundwater quality of the Nif Mountain karstic aquifer. Equipments, laboratory and measurement methods, software etc. used to meet the objectives of this study are also presented in detail.

4.1 Field Work

The field work was implemented in two phases. The first phase was exploratory and its objective was to observe general hydrogeological features of the study area, and explore and select sampling points. In the second phase on-site measurements of several water quality parameters were done and water samples were collected for further analyses in the laboratory.

Groundwater sampling points were selected by marking springs and wells in the study area that were representative of the area’s groundwater quality and that were fairly easy accessible. The aim was also to obtain a fairly homogenous spatial distribution of the sampling points within the study area. Potential sampling points in the study area were marked with a handheld GPS device and miscellaneous properties of the sampling point were recorded. Several other additional details were also noted such as the depth and the average production capacity when the particular point was a well, as well as the mechanism of water outflow and discharge rate in the case of a spring. The final database of sampling points comprised of a total of 59 sampling points consisting of 25 wells and 34 springs. A map depicting the distribution and types of the sampling points is shown in Figure 4.1.

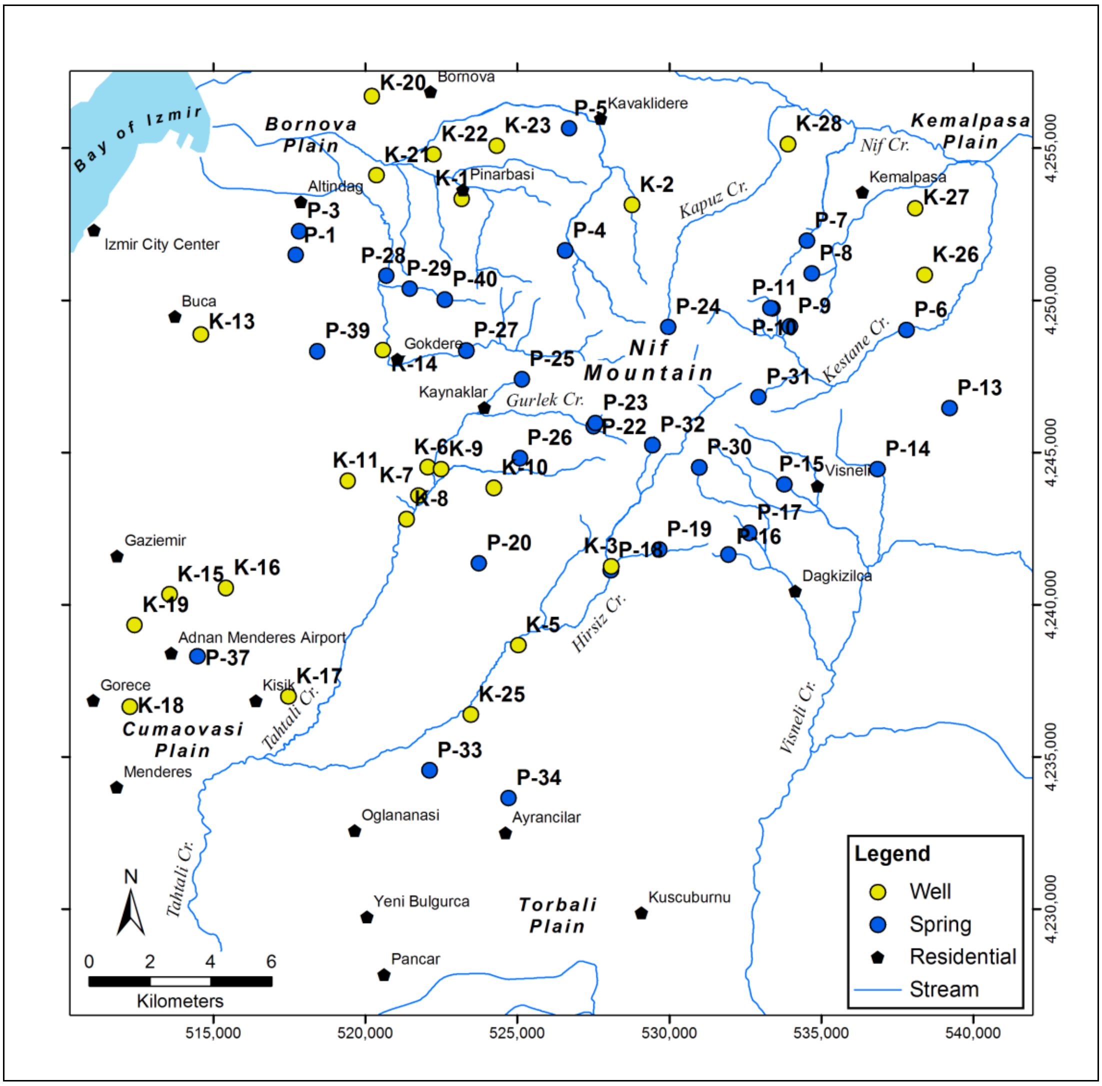

Figure 4.1 Map of study area and locations of sampling points

The collection of groundwater samples, which was the second phase of the field work, was performed in April and September of 2006. These months roughly marked the end of the wet and dry period of the year in the study area. Some basic physicochemical parameters such as pH, EC, water temperature and salinity were measured on-site with portable multi-parameter probes. Dissolved oxygen (DO) was not of interest since the samples were drawn from the surficial aquifer. Only in instances when very high contamination was suspected, DO was measured with the portable multi-parameter probes. For the determination of major ions, water samples were collected in 500-mL polyethylene bottles from each sampling location. Each sampling bottle was rinsed with the sampled groundwater during the sampling. In order to ensure the representativeness of the samples, wells were purged before sampling. The purge volume depended at each sampling point on the borehole volume and roughly 2-3 borehole volumes were pumped out of the borehole before a sample was taken. Bottles were accordingly labeled and stored in portable coolers, and were then transported to the Department of Environmental Engineering's Water Laboratory of Dokuz Eylül University at the end of each sampling day and stored at 4°C in the refrigerator.

4.2 Sample Analyses

In order to determine the groundwater quality parameters, a number of laboratory analyses were performed. On-site measurements of pH, temperature, EC and salinity were done during the sample collection with portable multi-parameter probes that were calibrated with standard buffer solutions. Water samples collected in bottles from 59 sampling points were analyzed for major cations and anions in the laboratory of the Department of Environmental Engineering.

The general job stream of sample analysis was as follows: The 500-mL samples were analyzed for major ions such as Ca^{+2}, K^{+}, Mg^{+2}, Cl^{-}, Br^{-}, NO_3^{-}, nitrite (NO_2^{-}), F, SO_4^{-2} and HCO_3^{-} ions. Of these, only the bicarbonate analysis was performed by a titrimetric method (Standard Methods, 2005); the remaining anions were analyzed by ion chromatography (IC) according to the EPA method 300.1 (Hautman & Munch, 1997).

For the ion analyses, the procedure described in the EPA 300.1 method (Hautman & Munch, 1997) was followed for sampling, preservation, transportation and analysis of groundwater samples. A Dionex ICS-3000 ion chromatography system (IC) setup in the water laboratory of the Environmental Engineering Department of Dokuz Eylül University was used to measure anion concentrations. The system consisted of an autosampler (Dionex AS Autosampler), an isocratic pump (Dionex isocratic single pump SP), a conductivity detector (Dionex CD), anion self-regenarating suppressor (Dionex ASRS ULTRA II-4mm), an anion analytical column (Dionex AS9-HC 4x250 mm) and a guard column (Dionex AG9-HC 4x50 mm). The latter three components needed to be switched with their counterparts, when cation analyses were performed. These were namely the cation self-regenarating suppressor (CSRS ULTRA II-4mm), the cation analytical column (CS12A 4x250 mm) and a guard column (CG12A 4x50 mm).

Prior to the analysis with the IC, water samples needed to be prepared. Firstly, bottles taken out from the refrigerator were rested on the bench to let the sample temperatures reach room temperature. Samples were then filtered through a 0.2 µm PTFE syringe filter (Sartorius Millipore). Samples were filtered to retain suspended solids, so that only dissolved constituents can enter the column in the IC system. Filtrates were injected into special 1.5mL-vials using adjustable volume pipettes without any dilution. Afterwards they were injected into the analytical column via the autosampler and were first analyzed as is without diluting the samples. Samples, which had resulting concentrations outside the calibration range were accordingly diluted for a subsequent re-analysis. For the anion analyses, a 9 mM sodium carbonate eluent and for the cation analyses, an 18 mM methano sulfonic acid (MSA) eluent were prepared. Eluents are the necessary fluids transmitting the injected sample through the analytical column. High purity deionized water (Millipore Systems) was used during the preparation of eluents, dilution of samples and calibration standards.

Calibration standards were prepared from mixed stock solutions that included several ions. In the case of anions, two calibration curves were established with the expectation of a wide range of ion concentrations. Shown in Table 4.1 are the ranges of the calibration curves for each anion. Ranges for each anion depended on its concentration in the stock solution. The lowest calibration standard of each range was taken as the minimum reporting limit (MRL) of the analysis, i.e. samples with ions detected but quantified below this limit were reported as below the MRL. The MRL value for NO_3-, NO_2^-, Cl^-, SO_4^{-2} and Br^- was 0.05 ppm; and for F^- and PO_4^- 0.01 ppm.

Table 4.1 Prepared standards to establish calibration curves

Calibration curve 1 (ppm)			**Calibration curve 2 (ppm)**		
NO_3-, NO_2^-, Cl^-, SO_4^{-2}, Br^-	**F^-**	**PO_4^-**	**NO_3-, NO_2^-, Cl^-, SO_4^{-2}, Br^-**	**F^-**	**PO_4^-**
0.05	0.01	0.1	5	1	10
0.1	0.02	0.2	10	2	20
0.5	0.1	1.0	20	4	40
1	0.2	2.0	30	6	60
5	1	10.0	40	8	80

The IC system was equilibrated for about one hour before sample analysis to attain a stable signal baseline. After the calibration of the system with the calibration standards, groundwater samples were analyzed along with other necessary blanks and solutions that the analysis procedure required. The detected output signals were eventually recorded, post-processed and evaluated by means of the software of the IC system.

4.3 Preparation of Spatial Distribution Maps for Groundwater Quality Data

Groundwater quality data obtained from laboratory analyses results and on-site measurements were tabulated and checked for any errors and inconsistencies. This data was put in a database that was established within a Geographical Information System (GIS) framework in order to create maps for visualization of data and also to interpret the spatial distribution of groundwater quality. Thereby, it was possible to reveal any spatial patterns of groundwater quality for the Nif Mountain karstic aquifer system.

GIS can be described as a collection of computer software and hardware for storing, manipulating, analyzing, and displaying spatial or geographically referenced data. As a visualization tool, GIS allows graphical display of maps, tabular information, statistical summaries, and modeling solutions. As a database, GIS can store, maintain, and update spatial data and associated descriptive information. GIS supports most database functions such as browsing, tabular queries, updating data, and functions supported by commonly used computer software such as spreadsheets and statistical packages. The most significant difference between GIS and other information systems and databases is the spatial nature of the data in a GIS. The analysis functions in a GIS allow manipulation of multiple themes of spatial data to perform overlays, buffering, and arithmetic operations on the data (Engel & Navulur, 1999). GIS-based groundwater studies were concentrated on the preparation of hydrogeomorphological maps, interpretation of lineaments and integrated terrain analysis. Now, GIS is increasingly being integrated with groundwater and surface water quality assessment models. The spatial patterns of chemical constituents are useful in deciding the water use strategies for various purposes. GIS based pattern of groundwater quality can also be used for public health management.

For all the above reasons, GIS was used as a tool to visualize and interpret groundwater quality data. By virtue of a GIS, complex groundwater quality data are shown in an easily understood format, and this served the one purpose of the present study, which was to understand the spatiotemporal variation groundwater quality in Nif Mountain karstic aquifer system and visually represent it. Surfer 8.0 (Golden Software, Inc.) was primarily used in this study as a GIS for visualization of data. However, some maps were generated using ArcGIS 9 (ESRI, Inc.). Maps depicting the locations of sampling points, the topography map and the geological map were generated using this software. On the other hand, spatial distribution maps of certain groundwater quality parameters were produced using Surfer 8.0.

Interpolation with the inverse distance weighting scheme was the primary method in obtaining spatial distributions of the groundwater quality parameters in the study area. Interpolation converts point data, in this case concentration values for each sample point, to an areally averaged quantity. The inverse distance weighting interpolation computes a value for each grid cell using a linear weighting combination of the set of sample points surrounding that cell. “The weight is a function of inverse distance to the observed values. Usually a power of two is adopted for inverse distance, and values greater than two will increase the influence of nearby data” (Engel et al., 1999). Assuming that the concentrations near any sampling point are likely to be closer to the measured concentration at the sampling point, an inverse distance weighting with the power of two was chosen for this study. Interpolated data values resulted in gridded data that was subsequently visualized in the form of contour maps.

A grid resolution of 200 × 200 m was selected for the interpolation process resulting in 136 rows and 151 columns for the entire study area. Before interpolating the concentration data for each groundwater quality parameter, they were tested for normality (see section 4.4.1 for description). For groundwater quality parameters that were not distributed normally, the lognormality condition was checked and the natural logarithm of the concentration values were used as input for the interpolation instead of the raw values. After the logarithms of the data were gridded; the exponential function was applied to convert the results back. For normally distributed data raw values were directly used in the interpolation. The interpolation procedure was implemented for the data of NO_3^-, Cl^-, EC and hardness of each of the two sampling events, therefore resulting in a total of 8 contour maps. By comparing contour maps for both sampling events, a qualitative evaluation of the temporal change in groundwater quality parameters was made possible.

However, in order to better compare the temporal change of groundwater quality, so called classed post maps depicting the percent change for each sampling points were also created. Different post symbol sizes were used to indicate the magnitude of change in percent, whereas different symbol colors were used to show whether there was an increase or a decrease of concentration. The change of concentration was calculated using the following relationship:

$$\text{Change in concentration (\%)} = 100 \times (C_{winter} - C_{summer}) / C_{winter}$$

where C_{winter} and C_{summer} are concentrations for April and September, respectively. Consequently, these classed post maps represented the percent change in concentration of each groundwater quality parameter for each sampling point from the winter (April data) to the summer season (September data).

4.4 Statistical Analysis

Statistical tests conducted in this study had three objectives: (1) to test the normality of each groundwater quality parameter; (2) to confirm whether the temporal change in groundwater quality was statistically significant, and (3) to understand the dependency and relation between groundwater quality parameters. Samples collected from the pre-determined set of sampling points were measured on-site and analyzed subsequently in the laboratory. For each sampling period, wet and dry seasons, samples were collected from the same set of sampling points. However, in September; the samples could be collected only from 57 of pre-determined 59 sampling points, thereby resulting in two missing values for each parameter for the dry season.

In this study, data was analyzed by the statistical package software SPSS 10.0 (SPSS, Inc.). This software is a modular, integrated package for data access, data preparation, reporting, graphics and advanced analysis through statistical techniques. The tests and procedures explained in the following subsections were all executed with this software.

4.4.1 Normality Tests

The normality of the statistical distribution of the NO_3^-, Cl^-, EC, and hardness data were tested by using the One-Sample Kolmogorov-Smirnov test (K-S). It tests the goodness-of-fit for the data and “is used to test the hypothesis that data come from a specific distribution. A minimum sample size of 50 is recommended for use of this test. The K-S test can take one of two forms. A one-sample test can be performed to examine how closely observed probabilities correspond to theoretical probabilities. To accomplish this, the observed cumulative distributions of sample values are compared to a specified continuous distribution function” (McBean & Rovers, 1998) The specified continuous distribution function in this case was the normal distribution.

To find out if the data are normally distributed, the following null hypothesis (H_0) and its alternative (H_S) were formulated. The null hypothesis is accepted if the calculated test statistic is greater than a defined critical value.

H_0: There is no difference between the distribution of the data and the normal distribution.
H_S: There is a difference between the distribution of the data and the normal distribution.

4.4.2 Statistical Analyses to Test Significance of Temporal Change in Groundwater Quality

To compare the data for both sampling periods, from the same sampling points, the paired samples t-test method was used as a parametric test. The precondition to use this test is that the number of samples is greater than 30 for each group, and that the data is normally distributed. This test assesses, if the means of two populations are statistically different from each other. This analysis is appropriate, whenever one wants to compare the means of two normally distributed sets of data.

In the application of the paired sample t-tests, the calculated *p*-value (2-tailed significance) is compared to the significance level α (usually taken as 0.05). If $p< \alpha$ then the null hypothesis that the two groups do not differ is rejected in favor of an alternative hypothesis, which typically states that the groups do differ. As is the case of other parametric tests, the paired samples t-test can be only used under the assumption that the differences between the two sets of data are normally distributed. Therefore, the normality of the temporal differences for the NO_3^-, Cl^-, EC and hardness data was tested using the one-sample Kolmogorov-Smirnov (K-S) test. If the temporal differences were not normally distributed, then an alternative to this test, such as a nonparametric test had to be used. Nonparametric tests are alternatives to parametric tests, in which no assumptions are made about the distribution of the observations. Moreover, the fundamental characteristics of these procedures are that the ranks of the data are used instead of data values themselves. The analyses of data on ranks are a direct parallel of the more traditional parametric methods. The nonparametric procedures require practically no knowledge about the distribution of the population. Thus, in the event that one or more of the assumptions implicit in the t-test are violated (e.g., significant difference between the variances), an alternative class of procedures involving nonparametric analyses may be utilized (McBean & Rovers, 1998). For all the above reasons, the approach taken in this study was that if there was a significant change in the concentrations of other constituents, whose differences were not normally distributed, the Wilcoxon signed ranks test, being the alternative to paired samples t-test, was applied.

4.4.3 Correlation and Regression Analyses

In this part of the study, statistical relationships between the groundwater quality parameters of interest were determined. The statistical importance and degree of dependencies between NO_3^--Cl^- and EC-NO_3^- and EC- Cl^- were examined by correlation analyses. The correlation between two groundwater quality parameters was measured in terms of a correlation coefficient, which indicates the strength and direction of a relationship between two random variables. A number of different coefficients can be used for different studies. The widely used and known Pearson correlation coefficient (r) was used in this study. It ranges from -1 to +1. The closer r is to +1 or -1, the more closely the two variables are related. If r is close to 0, it means there is no relationship between the variables. If r is positive, it means there is a strong and positive relation. If r is negative it means that there is an inverse (negative) correlation. While the correlation coefficient is normally reported as r as a value between -1 and +1, it can be also squared to express the relationship in a different way; the square of the coefficient (or r^2) is equal to the percent of the variation in one variable that is related to the variation in the other. Moreover, the statistical significance of the correlation analysis was also evaluated. For this purpose the following null hypothesis and its alternative were used and a significance level p was calculated. If the significance level was less than a predefined confidence level then the H_0 hypothesis was rejected and it was concluded that the correlation between the two variables is statistically significant.

H_0: The relation between the quality parameters is not considerable
H_s: The relation between the quality parameters is considerable

Although the correlation analysis provided the dependency between two variables, it does not quantitatively describe the relationship or allows one to predict one variable from the other. Moreover, it is not possible to infer any causality. Therefore, regression analysis was warranted and was used in this study. Regression is a technique used for the modeling and analysis of numerical data consisting of values of a dependent variable (response variable) and of one or more independent variables (explanatory variables). The dependent variable in the regression equation is modeled as a function of the independent variables, corresponding parameters (constants), and an error term. The error term is treated as a random variable. It represents unexplained variation in the dependent variable. The parameters are estimated to give a "best fit" of the data. In this study, the best fit was evaluated by using the least squares method

Linear and non-linear regression models were attempted to fit the data. These were linear, second and higher order polynomials, exponential, power and logarithmic regression equations. The coefficient of determination, r^2, which describes the strength of the relationship and the equations of the regression function that illustrated the relationship for NO_3^--Cl^-, EC-NO_3^-, and EC-Cl^- were determined for each model. Regression results were interpreted based on r^2 and the plausibility of the relationship with respect to the interactions between the quality parameters.

CHAPTER FIVE
RESULTS

This chapter presents results of the evaluation and assessment of raw groundwater quality data obtained from field sampling. Well and spring samples collected from the Nif Mountain karstic aquifer system were evaluated and analyzed for several water quality parameters such as temperature, pH, electrical conductivity (EC) , hardness, Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, HCO_3^{-}, Br^{-}, Fl^{-}, Cl^{-}, NO_3^{-} and SO_4^{-2} . Measurement and analyses results are given in the Appendix. However, within the scope of this thesis, the parameters of interest were NO_3^{-}, Cl^{-}, EC and hardness that were further investigated comprehensively.

In order to meet the objectives of the study, obtained groundwater quality data was processed and evaluated in different ways. Firstly, the groundwater quality of the Nif Mountain aquifer system is assessed by presenting basic statistics of data and comparisons with drinking water standards. Secondly, spatial distribution maps for concentrations of the groundwater quality parameters NO_3^{-}, Cl^{-}, EC and hardness of the wet and dry seasons of 2006 are provided. Datasets for each parameter were statistically tested if they with the normal or log-normal distribution. Moreover, percent change maps depicting the temporal differences of the groundwater quality parameters are presented. The results of the statistical tests, paired samples t-test and Wilcoxon signed rank test are shown to further evaluate the significance of temporal change of groundwater quality in the study area. Finally, results of correlation and regression analyses are provided to illustrate the relationship between the water quality parameters and probable causes of contamination.

5.1 General Assessment of Groundwater Quality

A statistical overview of the analyses results with comparison to relevant drinking water quality standards is presented in Tables 5.1 and 5.2. A general characterization of the Nif mountain groundwater quality based only on basic statistics and drinking water standards is presented in this section. Assessment of groundwater quality based on location and sampling time is presented in the next section.

The results show that the temperature (T) of the Nif Mountain groundwater ranges from 8.7 to 22.6 ºC in April and from 11.1 to 26.5 ºC in September, spring samples being more at the lower end of this range. The range of pH values for all samples was 6.46-7.93 in April and 6.62-8.05 in September, implying neutral to weak alkaline waters.

The range of electrical conductivity (EC) for all samples was 212-1583 µS/cm in April, and 243-1780 µS/cm in September, respectively. The broad range is noticeable along with relatively high standard deviations. Furthermore, in both seasons the mean value of EC for well samples is higher compared to the mean EC for spring samples. EC values at all sampling points are in compliance with the relevant Turkish regulation limit of 2500 µS/cm (MoH, 2005).

The hardness values are statistically similar to EC data; they range from 28.2-662.8 mg/L $CaCO_3$ for all sampling points, with mean and standard deviation of 348.41 ± 137.22 mg/L $CaCO_3$ for April and 29.6-639.8 mg/L $CaCO_3$, with mean and standard deviation of 338.54 ± 133.62 mg/L $CaCO_3$ for September, respectively. The mean hardness is as expected higher for well samples, which indicates more dissolution of limestone and other carbonate bearing minerals. The groundwater of the Nif Mountain aquifer can be classified as hard to very hard although there is currently no health-based guideline value.

Table 5.1 Statistical summary of sample analyses results and comparison with drinking water quality standards for April 2006 (wet season)

		Drinking Water Quality Standard		**Wells(N=25)**				**Springs(N=34)**			
	Unit	MoH[a]	EPA[b]	Max	Min	Mean	Std. dev.	Max	Min	Mean	Std. dev.
T	°C			22.60	13.00	17.38	2.29	17.80	8.7	14.05	2.33
pH		6.5<pH<9.5	6.5<pH<8.5[c]	7.84	6.46	7.13	0.28	7.93	6.59	7.35	0.39
EC	µS/cm	2500 (at 20 °C)		1318	486	752.9	195.11	1583	212	555.3	285.0
Hardn.	mg/L			569.4	28.20	380.1	116.08	662.8	122.0	325.1	148.2
Ca^{+2}	mg/L			182.7	9.87	117.8	40.46	248.0	38.68	101.5	51.52
Mg^{+2}	mg/L			45.13	0.88	20.32	9.67	73.62	2.71	17.48	15.19
Na^{+}	mg/L	200		195.2	6.84	39.51	50.98	98.67	2.51	11.55	17.89
K^{+}	mg/L			22.25	0.56	2.85	4.27	7.02	0.29	0.90	1.20
HCO_3^{-}	mg/L			589.0	312	432.0	63.22	719	133	353.6	159.0
Fl^{-}	mg/L	1.5	2[c]or 4[d]	1.22	0.07	0.40	0.29	1.33	0.04	0.20	0.28
Cl^{-}	mg/L	250	250[c]	174.4	6.72	37.89	40.20	148.4	4.29	17.72	24.76
Br^{-}	mg/L			0.49	0.22	0.30	0.06	0.32	<0.05	0.26	0.02
NO_3^{-}	mg/L	50	44.3[d]	164.2	0.19	22.63	32.33	293.8	0.23	12.15	50.27
SO_4^{-2}	mg/L	250	250[c]	89.92	2.09	24.18	20.12	85.09	5.40	19.52	17.19

Table 5.2 Statistical summary of sample analyses results and comparison with drinking water quality standards for September 2006 (dry season)

		Drinking Water Quality Criteria		**Wells(N=24)**				**Springs(N=33)**			
	Unit	MoH[a]	EPA[b]	Max	Min	Mean	Std. dev.	Max	Min	Mean	Std. dev.
T	°C			26.50	14.80	19.42	2.21	23.40	11.10	17.42	3.42
pH		6.5<pH<9.5	6.5<pH<8.5[c]	7.80	6.65	7.19	0.27	8.05	6.62	7.45	0.41
EC	µS/cm	2500 (at 20 °C)		1780	518.0	807.9	268.33	1574	243.0	594.0	291.8
Hardn.	mg/L			639.8	29.60	364.4	122.63	635.3	125.7	319.7	139.9
Ca^{+2}	mg/L			162.6	10.10	110.3	40.59	237.1	41.40	98.84	48.20
Mg^{+2}	mg/L			56.90	1.10	22.03	13.08	73.30	2.70	18.24	15.58
Na^{+}	mg/L	200		187.4	6.20	42.05	52.26	95.60	0.10	12.52	19.45
K^{+}	mg/L			21.10	0.50	2.70	4.49	8.70	0.10	0.95	1.50
HCO_3^{-}	mg/L			595.5	190.5	387.2	83.13	623.7	143.9	348.1	133.8
Fl^{-}	mg/L	1.5	2[c]or 4[d]	0.82	< 0.01	0.24	0.21	1.01	< 0.01	0.14	0.22
Cl^{-}	mg/L	250	250[c]	447.7	6.92	54.8	95.50	111.0	3.77	14.91	20.13
Br^{-}	mg/L			1.51	< 0.05	0.23	0.38	0.16	< 0.05	0.09	0.04
NO_3^{-}	mg/L	50	44.3[d]	344.4	0.88	30.31	69.20	241.0	0.31	10.61	41.73
SO_4^{-2}	mg/L	250	250[c]	256.3	5.07	42.32	55.32	89.29	3.82	17.20	18.01

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[a] MoH (2005)
[b] EPA (2003)
[c] National Secondary Drinking Water Regulation (non-enforceable)
[d] National Primary Drinking Water Regulation (obligatory)

A broad range in values can be observed for major cations. Calcium (Ca^+) concentrations range between 9.87-247.99 mg/L in the wet season and 10.1-237.1 mg/L in the dry season, respectively. Similarly, magnesium (Mg^+) concentrations range from 0.88 mg/L to 73.62 in the wet season and from 1.1 mg/L to 73.3 mg/L in the dry season. For both parameters, the average values of well samples are close to the average values of spring samples in general (Tables 5.1 and 5.2). On the other hand, the mean values of the sodium concentrations for well samples are relatively higher than the mean values of spring wells for both seasons. The mean concentrations for well samples and spring samples are 39.51 mg/L and 11.55 mg/L in the wet season; and 42.05 mg/L and 12.52 mg/l in dry season, respectively. Furthermore, the sodium (Na^+) concentrations in both wet and dry seasons varied from 2.51-195.21 mg/L and 0.1-187.4 mg/L, respectively. According to the Turkish drinking water regulation, the permissible limit is determined as 200 mg/L for the sodium ion, and hence, all of the Na^+ concentrations for the study area comply with this limit. Moreover, potassium (K^+) concentrations range between 0.29-22.25 mg/L and 0.1-21.1 mg/L in wet and dry seasons, respectively. In general, it can be concluded that cation concentrations are lower from groundwater sampled at the springs.

When major anions are concerned, bicarbonate (HCO_3^-) is the predominant ion with concentrations ranging between 133 and 719 mg/L in April and between 143.9 and 623.7 mg/L in September. Fluoride and bromide concentrations on the other hand are extremely lower compared to HCO_3^- concentrations. For both seasons, fluoride and bromide concentrations are not exceeding 1.33 mg/L and 1.59 mg/L, respectively. The current drinking water standard of 1.5 mg/L for fluoride is met for the vast majority of groundwater samples. There are no limits set for bromide in both regulations (MoH, 2005; EPA, 2003).

Chloride (Cl^-) concentrations range from 4.29 to 174.39 mg/L in April and from 3.77 to 447.66 mg/L in September. The permissible limit of chloride is given as 250 mg/L in the drinking water regulation, which is violated at only one well sampling point (K-18). As it is observed for the other parameters, the mean concentrations are significantly higher for well samples. In this case it indicates higher mineral content probably due to contamination. Likewise, SO_4^{-2} concentrations range from 2.09 to 89.92 mg/L and from 3.82 to 256.28 mg/L for the wet and dry seasons, respectively. The permissible limit for sulfate concentration is also 250 mg/L and again except the point of K-18, all of the SO_4^{-2} concentrations are under the drinking water limits.

Nitrate (NO_3^-) is the only groundwater quality parameter that causes occasional non-compliance of limits. The maximum concentration is 164.2 mg/L in well samples and 293.8 mg/L in spring samples, in the wet season. In the dry season maximum concentrations reach higher levels; 344 mg/L for well samples and 240.96 mg/L for spring samples. However, the mean concentrations are considerably lower and they are 16.59 and 18.91 mg/L for the wet and dry seasons, respectively. The permissible limit value for NO_3^- concentrations is given as 50 mg/L in the Turkish regulation. In the wet season, P-3 and K-18 are the sampling points with NO_3^- concentrations exceeding the limit. In the wet season, in addition to these points, K-13 and K-27 exceed the same limit for NO_3^-. Usually, the highest concentrations occur in samples withdrawn from wells drilled in Neogene series formations. These points are also located within residential areas, and it can be concluded that high nitrate concentrations are mostly related with wastewater leakages or agricultural facilities.

Other anions measured but not listed in the Appendix and in Tables 5.1 and 5.2 are nitrite (NO_2^-) and phosphate (PO_4^{-3}). Nitrite was not detected in the wet season for all sampling points. Moreover, in the dry season, except for the value of 1.33 mg/L at sampling point K-28, nitrite was also not detected. The given permissible limit of NO_2^- in the current Turkish regulation (MoH, 2005) is 0.50 mg/L. On the other hand, phosphate concentrations are with one exception (K-26, as 0.70 mg/L) below the reporting limit of 0.1 mg/L for all samples, in the wet season. Furthermore, for the dry season, phosphate concentrations were below the reporting limit, except for points P-7 and K-28, with concentrations of 0.24 and 1.85 mg/L, respectively. There is no limit set for PO_4^{-3} concentrations in the current Turkish regulation.

Consequently, it can be generally observed that groundwater of the Nif Mountain karstic aquifer is of very good quality with respect to current regulations. However, it is evident that the groundwater pollution increases as the water travels from the mountain uplands towards the residential plains. Groundwater from well K-18 and the spring P-3 must not be used as drinking water resource. Moreover, Nif Mountain is located within the basin boundaries of the Tahtalı Dam Reservoir, which is a major component of İzmir's water supply system. In this regard, good water quality of subsurface drainage originating from the Nif Mountain can be considered to be an important factor that will positively affect the overall water quality pattern around the İzmir metropolitan area.

5.2 Spatial and Temporal Assessment of Groundwater Quality Data by Distribution Mapping

To spatially assess the groundwater quality of the Nif Mountain karstic aquifer, spatial distribution maps of certain groundwater quality parameters (NO_3^-, Cl^-, EC and hardness) were prepared for the sampling periods April and September 2006, representing the wet and dry seasons. Moreover, in order to show how the spatial distribution of certain groundwater quality parameters changed from the wet to the dry season, post maps illustrating percent changes of measurement values were also created. However, the groundwater quality parameters were first tested if they statistically fit the normal distribution. This was done to decide whether to use the raw or the natural logarithm of the data in the interpolation process.

5.2.1 Normality Testing Results for Groundwater Quality from each Sampling Period

The normality of the concentration data for NO_3^-, Cl^-, EC, and hardness were tested using the One-Sample Kolmogorov-Smirnov (K-S) test. To find out if the data are normally distributed, a null hypothesis (H_0) and its alternative (H_s) were formulated as follows:

H_0: There is no difference between the distribution of the data and the normal distribution

H_s: There is a difference between distribution of the data and the normal distribution

Presented in figures 5.1 through 5.8 are the histograms for NO_3^-, Cl^-, EC, and hardness data for both sampling periods. These charts provide a qualitative way of assessing the statistical distribution of the data. However, to obtain a quantitative measure of the One-Sample Kolmogorov-Smirnov (K-S) test was performed and its results are summarized in Table 5.3. The *p* values are the asymptotic significance values of the normality (K-S) tests, for the data of each constituent for both sampling periods. These values were compared with an α value of 0.05.

Since *p* values were less than the *α* value for NO_3^- (p=0,000<0.05 in April and p=0,000<0.05 in September), and for Cl^- (p=0,000<0.05 in April and p=0,000<0.05 in September); the null hypothesis (H_0) was rejected and it can be concluded with 95% confidence that the data of NO_3^- and Cl^- for April and September are distributed not normally. As can be seen from the histograms of the data, the distribution is skewed to the right thereby supporting the results of the test. However; for the EC and hardness data, the resulting *p* values were greater than the α value. The *p* values for EC data in April and September and for hardness in April and in September are p=0.802>0.05, p=0.409>0.05, p=0.844>0.05, and p=0.969>0.05, respectively. Therefore, the null hypothesis was accepted and the data of EC and hardness for both seasons may be assumed to be normally distributed with a 5% level of significance. Table 5.4 presents the calculated *p* values to assess the normality of the data for each parameter.

Table 5.3 Results of the One-Sample K-S test for concentration data

	NO_3^-		Cl^-		EC		Hardness	
	April	**Sept.**	**April**	**Sept.**	**April**	**Sept.**	**April**	**Sept.**
N	59	57	59	57	59	57	59	57
Mean	16.587	18.905	26.366	31.697	639.03	684.11	348.410	338.539
Std. Dev.	43.564	55.302	33.467	66.121	267.70	299.27	137.219	133.621
Kolmogorov-Smirnov Z	2.714	2.781	2.037	2.540	0.644	0.888	0.615	0.492
***p* value: Asymp. Sig. (2-tailed)**	0.000	0.000	0.000	0.000	0.802	0.409	0.844	0.969

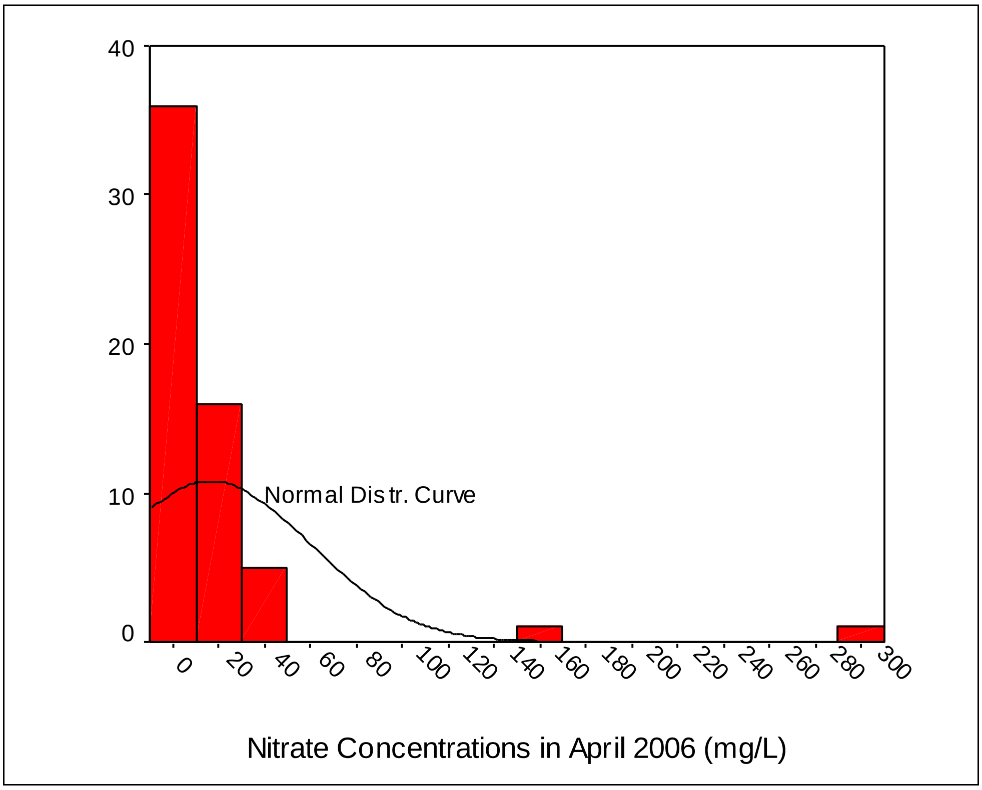

Figure 5.1 Histogram of nitrate concentrations in April 2006

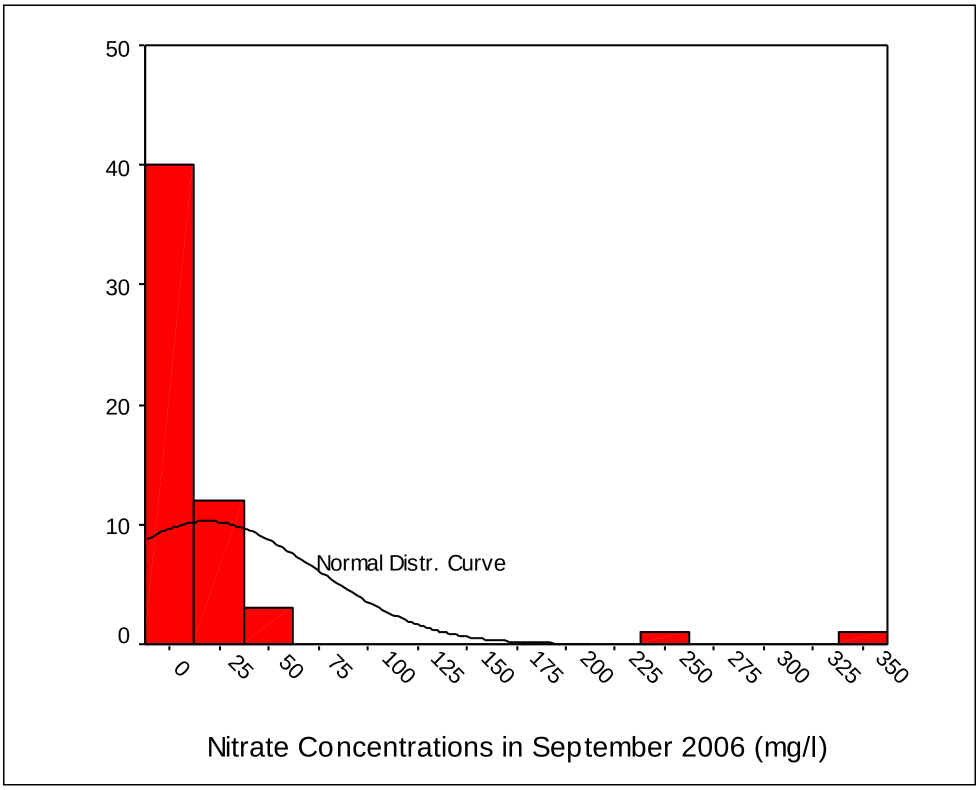

Figure 5.2 Histogram of nitrate concentrations in September 2006

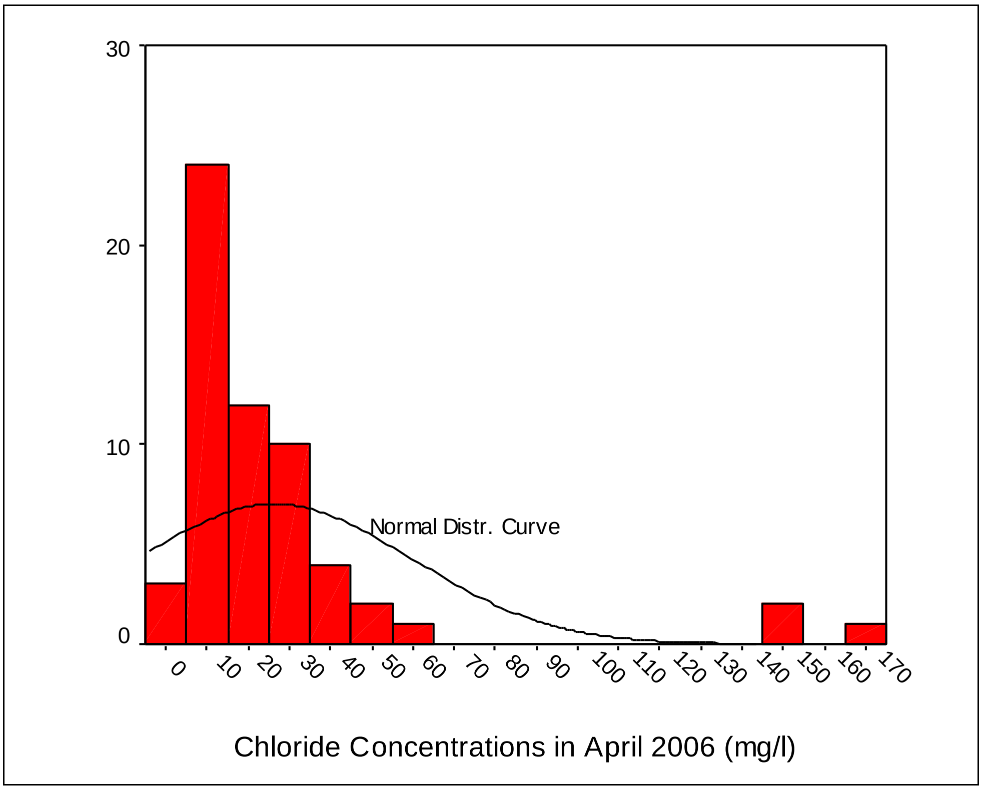

Figure 5.3 Histogram of chloride concentrations in April 2006

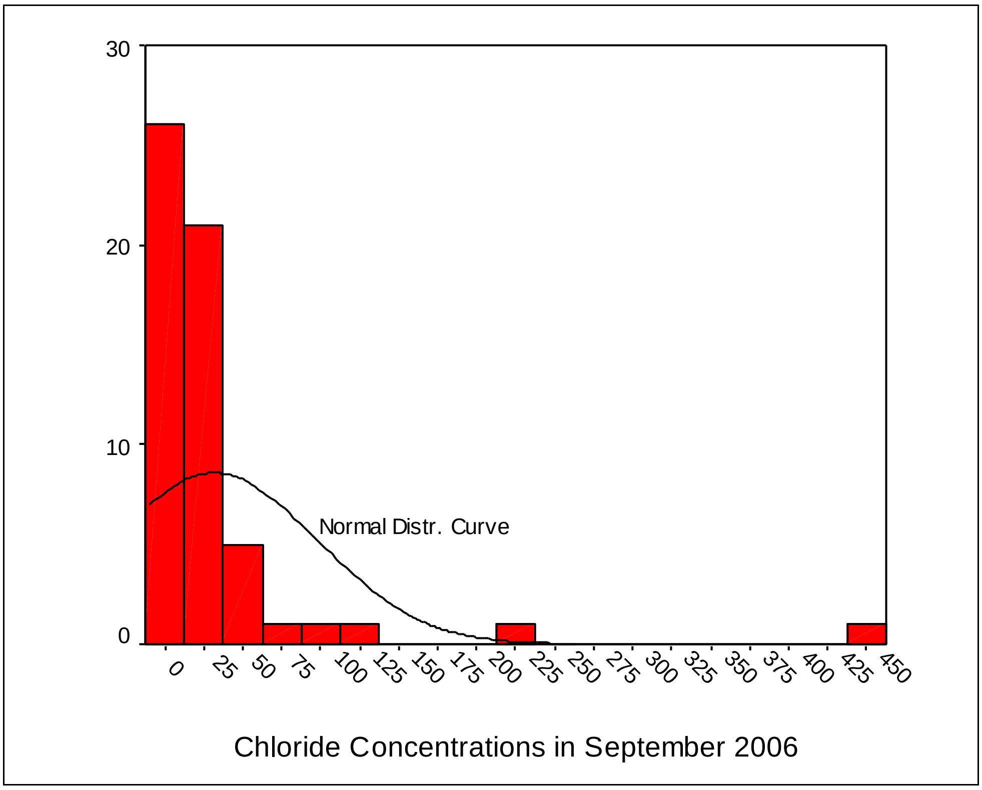

Figure 5.4 Histogram of chloride concentrations in September 2006

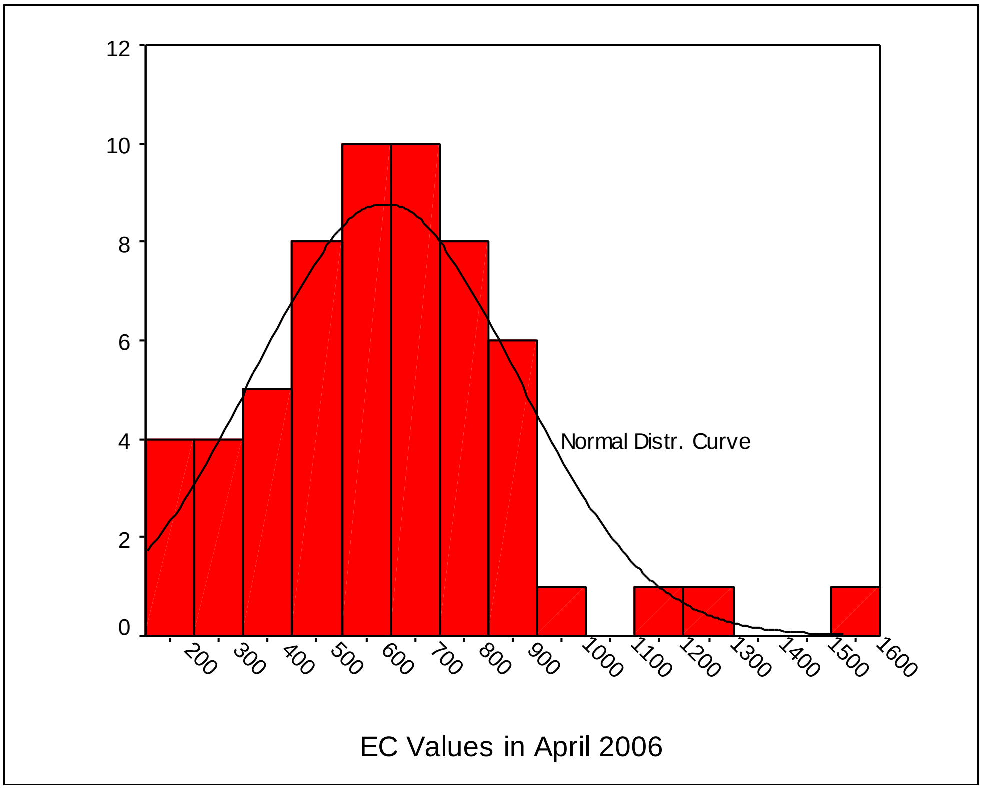

Figure 5.5 Histogram of EC values in April 2006

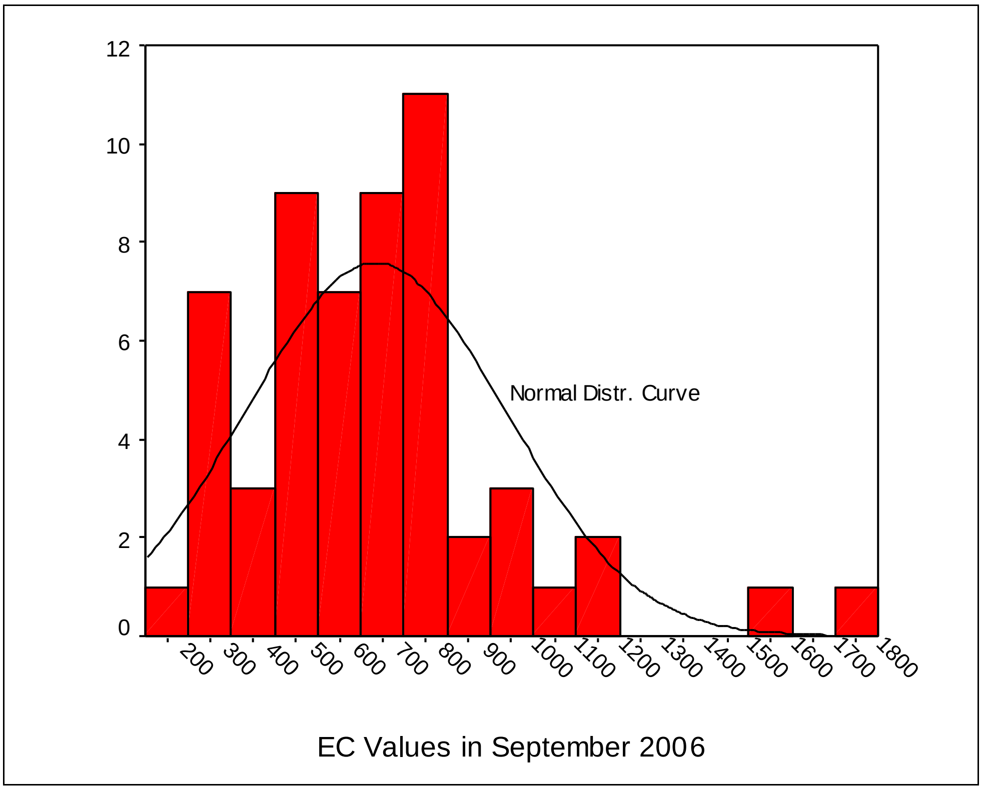

Figure 5.6 Histogram of EC values in September 2006

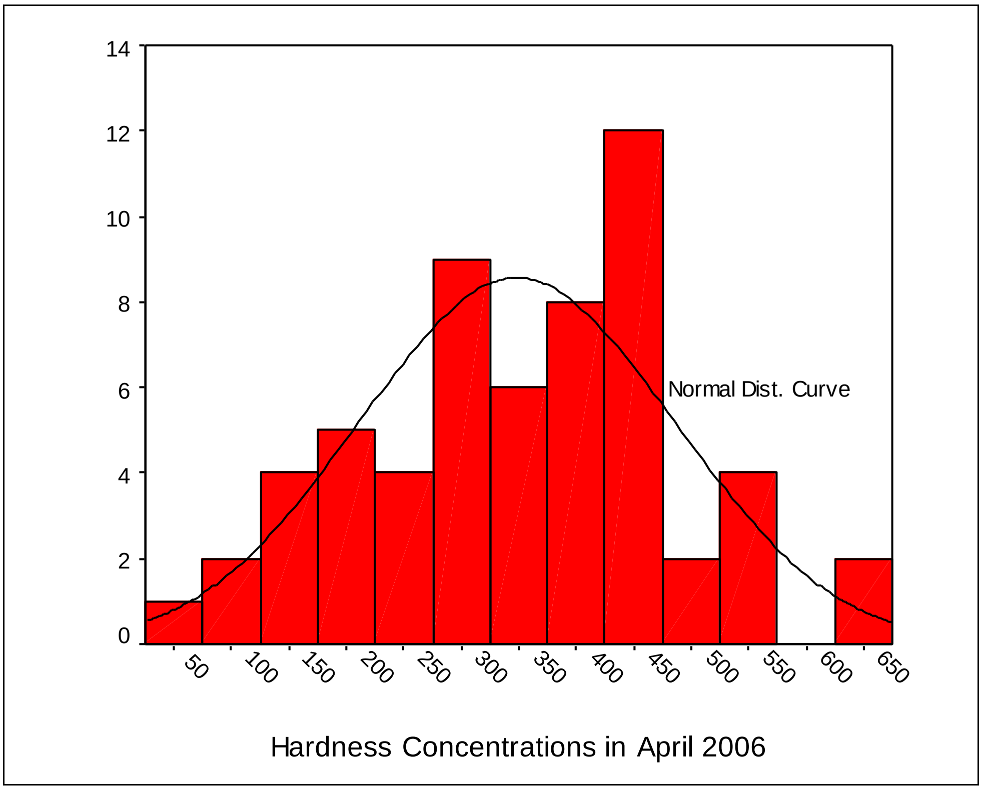

Figure 5.7 Histogram of hardness concentrations in April 2006

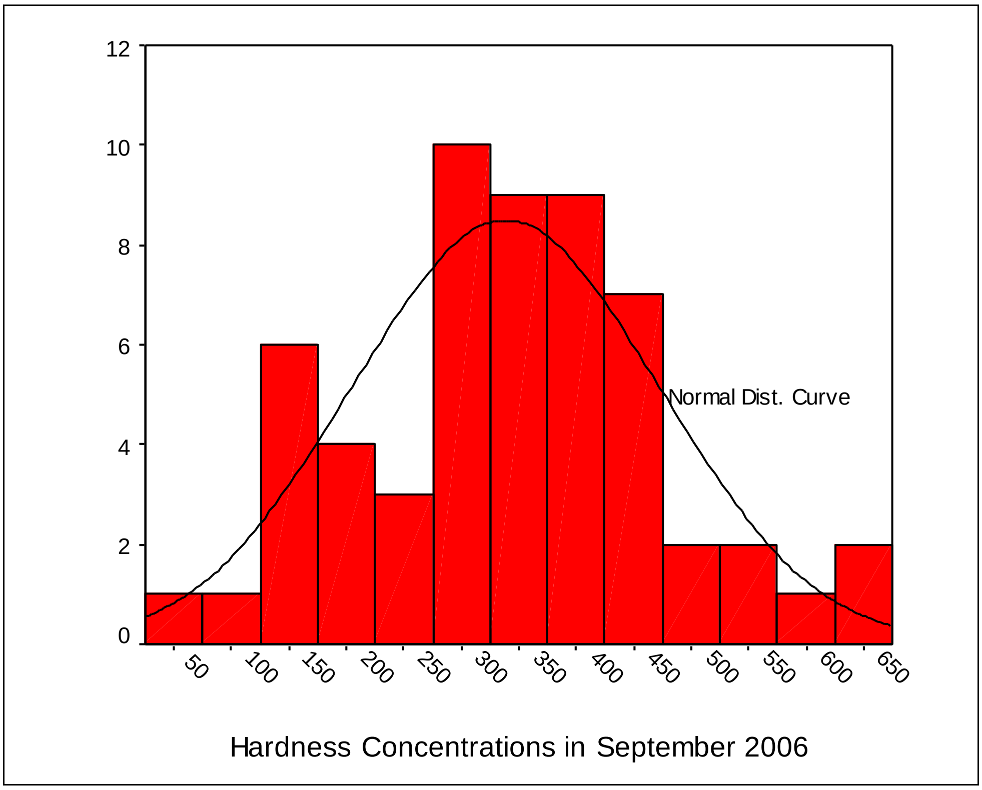

Figure 5.8 Histogram of hardness concentrations in September 2006

Table 5.4 Summary table of the normality of the data

Non-Normal Data	**NO_3^--April**	**NO_3^--Sept.**	**Cl^--April**	**Cl^--Sept.**
***p* values (< α=0.05)**	0.000	0.000	0.000	0.000
Normal Data	**EC-April**	**EC-Sept.**	**Hardness-April**	**Hardness-Sept.**
***p* values (> α=0.05)**	0.802	0.409	0.844	0.969

5.2.2 Testing for Log-Normality of Non-Normal Data

For the data, which are not distributed normally, the log-normality was assessed. Therefore, the natural logarithm (*ln*) of the data was calculated and was subsequently tested for normality by the K-S test. The results of normality tests for the data of *ln* Nitrate and *ln* Chloride in April and in September are given in Table 5.5. The null hypothesis and its alternative were formulated as follows:

H_0: There is no difference between the distribution of the *ln* data and the normal distribution.
H_s: There is a difference between the distribution of the *ln* data distribution and the normal distribution.

Based on the results, *p* values for each K-S test were greater than 0.05, therefore implying that the natural logarithms of the data were distributed normally with 95% confidence. This result was supported by the histograms plotted for the natural logarithms of the raw data (Figures 5.9 - 5.12). Consequently, the raw NO_3^- and Cl^- data for both seasons conformed a log-normal distribution.

Table 5.5 One-Sample K-S Test for logarithmic (ln) data in April & September

		***ln* NO_3^-**		***ln* Cl^-**	
		April	September	April	September
N		59	57	59	57
Normal Parameters	**Mean**	1.1398	1.3074	2.8459	2.7285
	Std. Dev.	1.8909	1.6705	0.8625	1.0358
***p* value: Asymp. Sig. (2-tailed)**		0.273	0.192	0.947	0.747

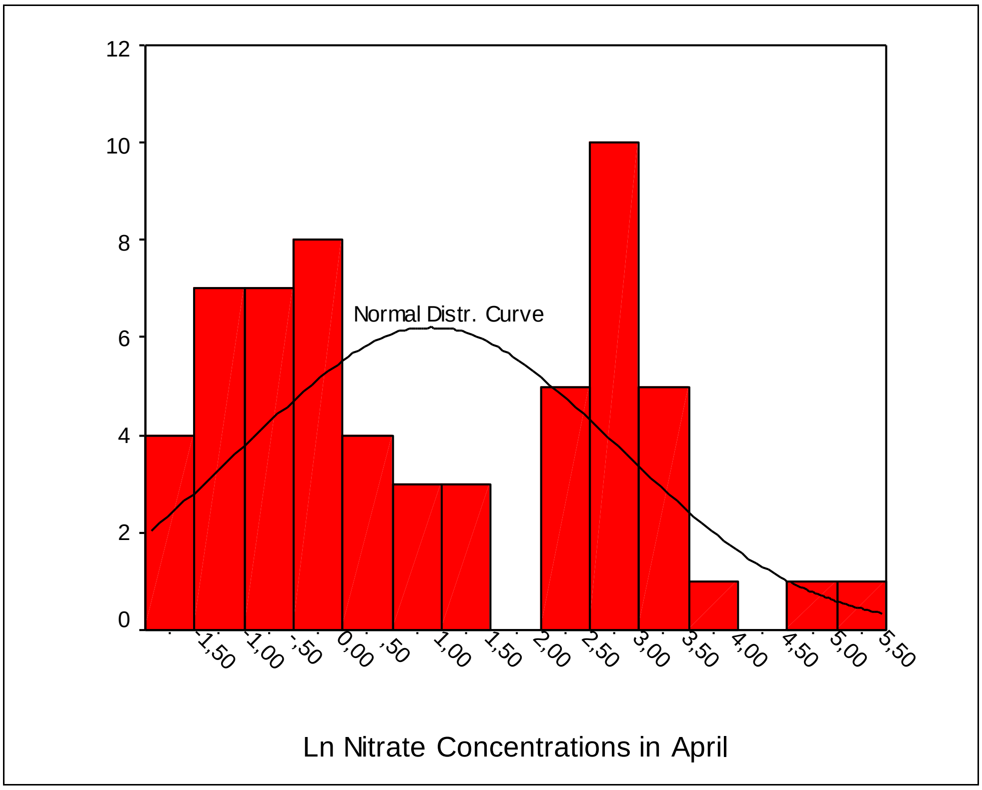

Figure 5.9 Histogram of ln nitrate concentrations in April

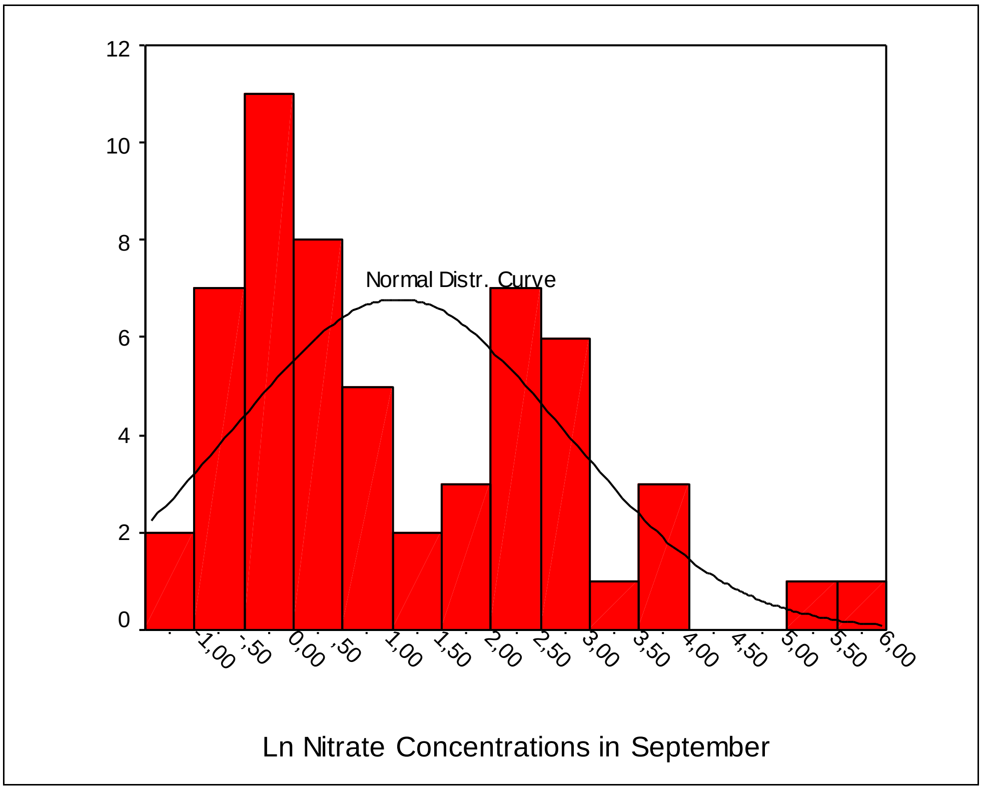

Figure 5.10 Histogram of ln nitrate concentrations in September

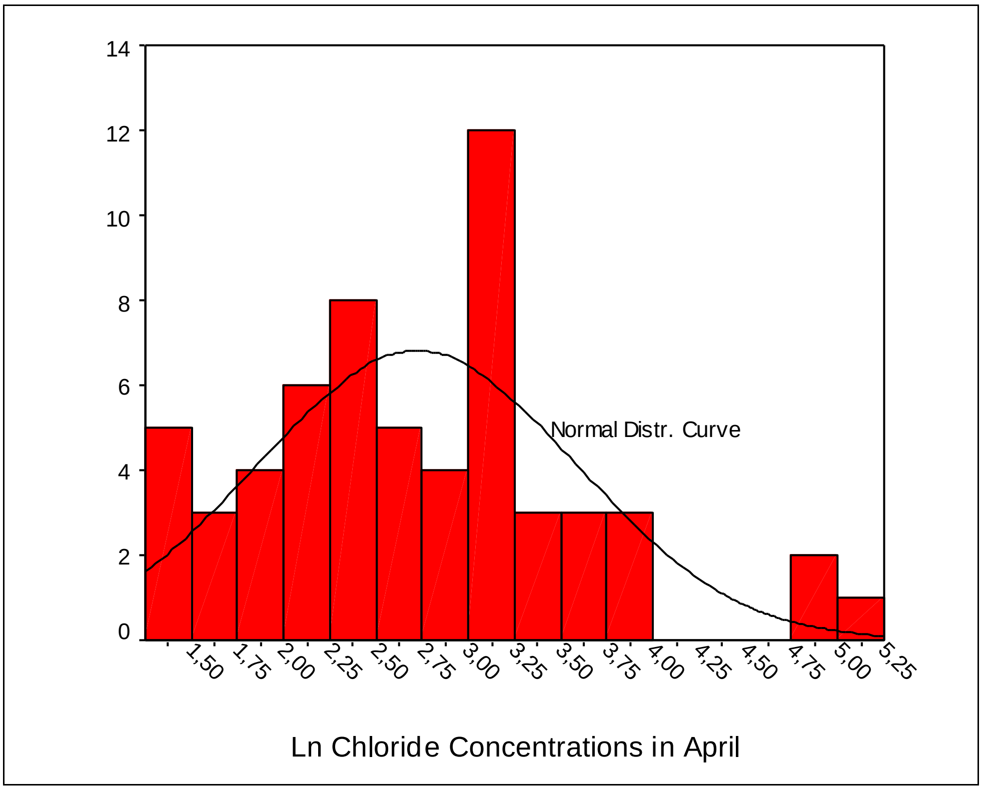

Figure 5.11 Histogram of chloride concentrations in April

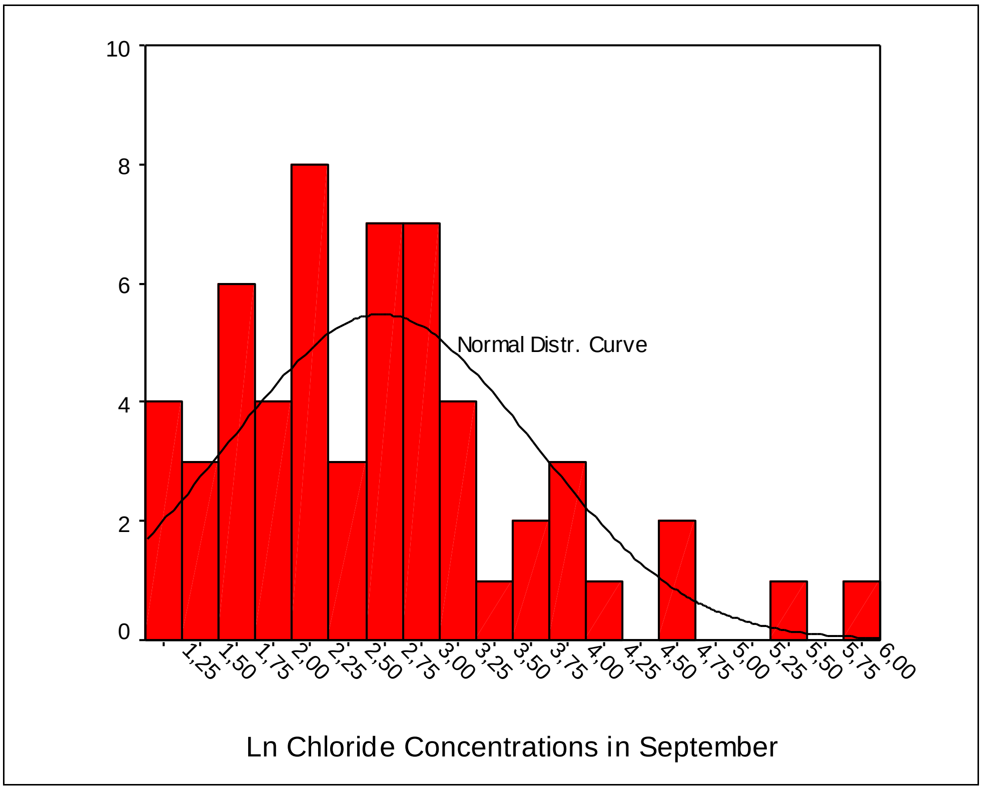

Figure 5.12 Histogram of chloride concentrations in September

5.2.3 Spatial Distribution and Temporal Change Maps

The distribution of NO_3^- concentrations for wet and dry seasons are shown in Figures 5.13 and 5.14. There are sporadic occurrences of high NO_3^- concentrations in certain parts of the study area, e.g. the northwest and southwest corners of the study area, which coincide with dense residential areas. With the exception of the two sampling points in Kemalpaşa (K-28 and K-27); the groundwater in the east of Nif Mountain has nitrate concentration lower than 10 mg/L, almost equivalent to spring water quality closer. Higher NO_3^- concentrations can be seen northwest and southwest of the Nif Mountain.

With respect to temporal change of NO_3^- contamination, increases and decreases occurred sporadically without any concrete spatial pattern, as it is illustrated in Figure 5.15. At about 30% of the sampling points a substantial increase in NO_3^- concentration was observed, whereas at about 35% of the sampled locations a decrease was observed. Moreover, at 35% of all sampling locations, which were mostly springs at higher elevations of the Nif Mountain, NO_3^- concentrations changed less than 0.5 mg/L. More than 25 mg/L increase in NO_3^- concentration occurred in two monitoring wells located close to the industrialized Kemalpaşa plain (K-27), and the Cumaovası plain (K-18), which hosts many farms and greenhouses. The percentage increase values for these points are 110% and 126%, respectively. On the other hand, at two sampling points; K-25 in the south, and P-3 in the northwest (shown as -68% and -18%); NO_3^- concentrations dropped more than 25 mg/L. The maximum increase and decrease occurred at locations K-5 and K-15 with the percentages 268% and -85%, respectively.

The spatial distributions of Cl^- concentrations for each sampling period are depicted in Figures 5.16 and 5.17. It is obvious that water sampled from springs in the mountain had the lowest Cl^- concentrations. The east of Nif Mountain was relatively pristine as well. In contrast, samples taken from sampling points that lie closer to the city center (e.g. northwest of study area) and in agricultural areas (e.g. southwest of study area) had clearly the highest Cl^- concentrations. Nevertheless, with the exception of sampling point K-18, all sampling points were under the drinking water limit of 250 mg/L.

The percent change map demonstrates that the Cl^- concentrations altered randomly from the wet to the dry season (Figure 5.18). At approximately 74% of the sampling points a decrease in Cl^- concentrations from April to September could be observed. Only at 26% of the sampling point a deterioration of groundwater occurred. The extreme was sampling point K-18, located nearby the town Cumaovası. Here the concentrations increased by 194% from April to September and reached a relatively high level of 450 mg/L.

The spatial distributions of EC values for each sampling period are depicted in Figures 5.19 and 5.20. It is noticeable that groundwater from springs in the mountain had the lowest EC levels. Furthermore, a correlation between EC and elevation can be observed; EC was lower in groundwater sampled at higher elevations of the study area and increased towards the plains. This "elevation effect" is typical for areas like Nif Mountain, where the levels of anthropogenic activities and rock water interactions (i.e., shale, ophiolites and clays) increase as groundwater flows down from the uplands. A similar tendency can be also observed for the other quality parameters NO_3^-, Cl^- and hardness. With the exception of K-18, K-22, P-3 and P-5, the EC values at all sampling locations were below 1000 µS/cm in the wet season. In the dry season on the contrary, additional two sample points, K-14 and P-28, also exceeded 1000 µS/cm. Furthermore, a comparison of EC distribution maps with NO_3^- and Cl^- distribution maps revealed an interesting similarity in spatial patterns to some extent. Although, the highest EC values (>1000 µS/cm) coincide with regions of high Cl^- concentrations for both sampling periods, the same is not necessarily valid for NO_3^-.

Figure 5.21 illustrates changes of EC from the end of the wet season to the end of the dry season. An increase in EC values was observed for 43 out of 57 sampling points from wet to dry season. While most of the increase was less than 25% (35 out of 43), a limited number of sampling locations exhibited more than a 25% increase.

This generally increasing trend in EC can be attributed to reduced groundwater recharge related dilution effects during the summer months, and consequently to relatively longer retention time of groundwater within the karstic formation. However, in limited parts of the study area, EC decreased in the summer, e.g. south and southeast of Nif Mountain.

The spatial distribution of hardness of groundwater is shown in Figures 5.22 and 5.23. Figure 5.24 shows the percent change in hardness from April to September. Based on the percent change map, it can be seen that the change in hardness levels was limited and did not changed significantly. The changes for hardness concentrations ranged between a 45% decrease and a 23% increase level. An increase in hardness was observed for 23 out of 57 sampling points from wet to dry season. On the contrary, while most of the decrease was less than 25% (32 out of 34 sampling points), only two of sampling points exhibited more than 25% decrease.

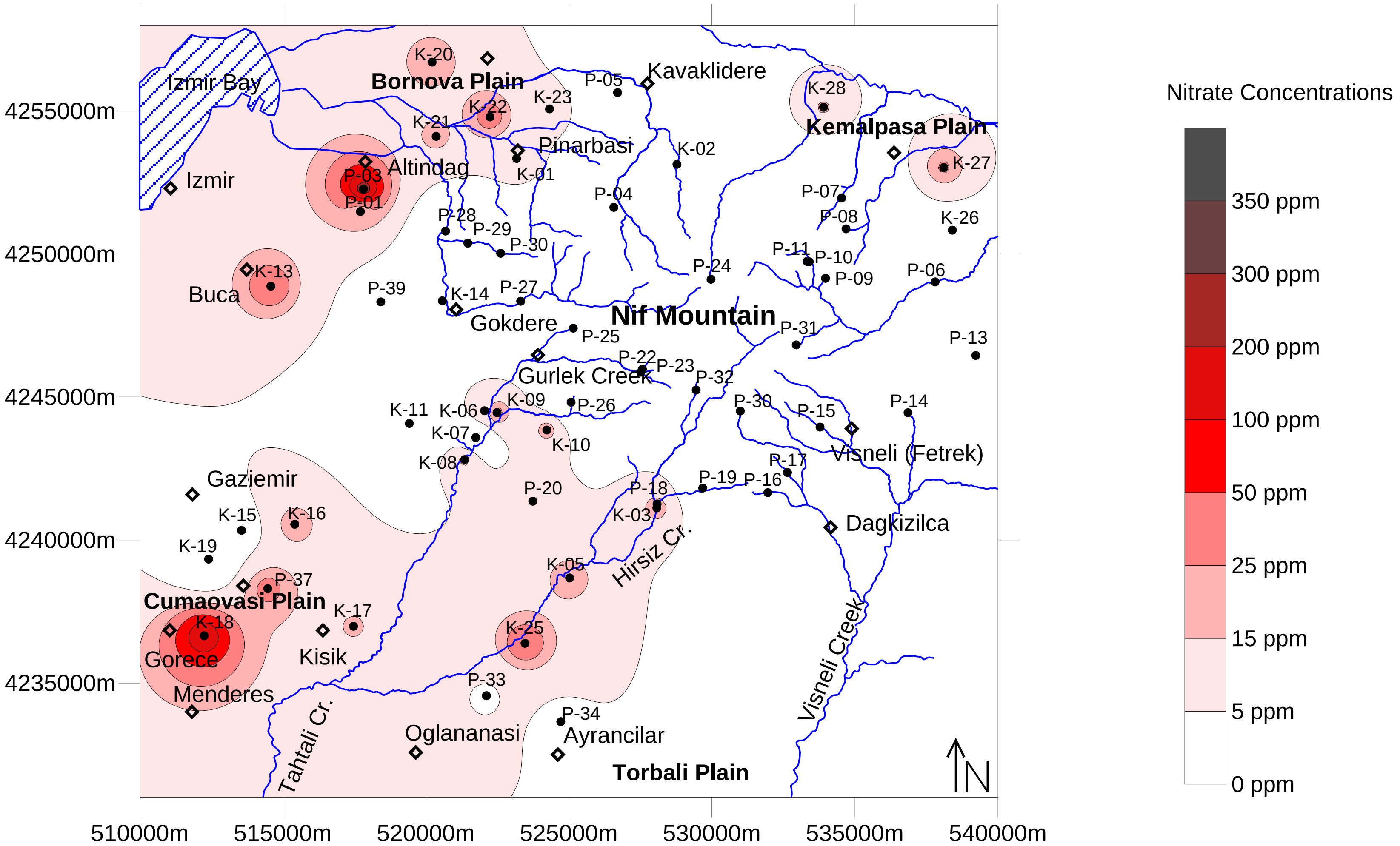

Figure 5.13 Distribution map of nitrate concentrations in April 2006 (P: spring sample, K: well sample).

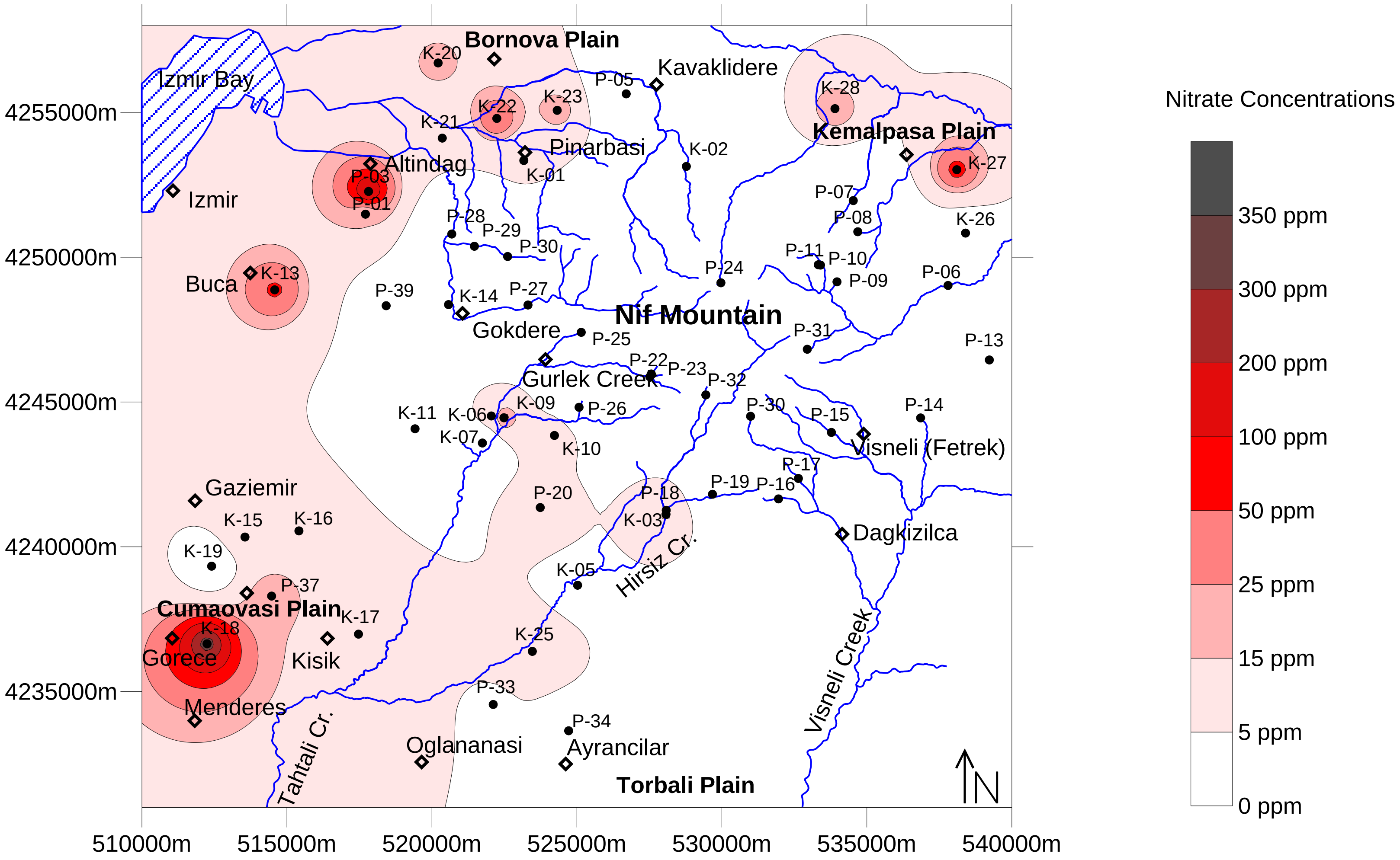

Figure 5.14 Distribution map of nitrate concentrations in September 2006 (P: spring sample, K: well sample).

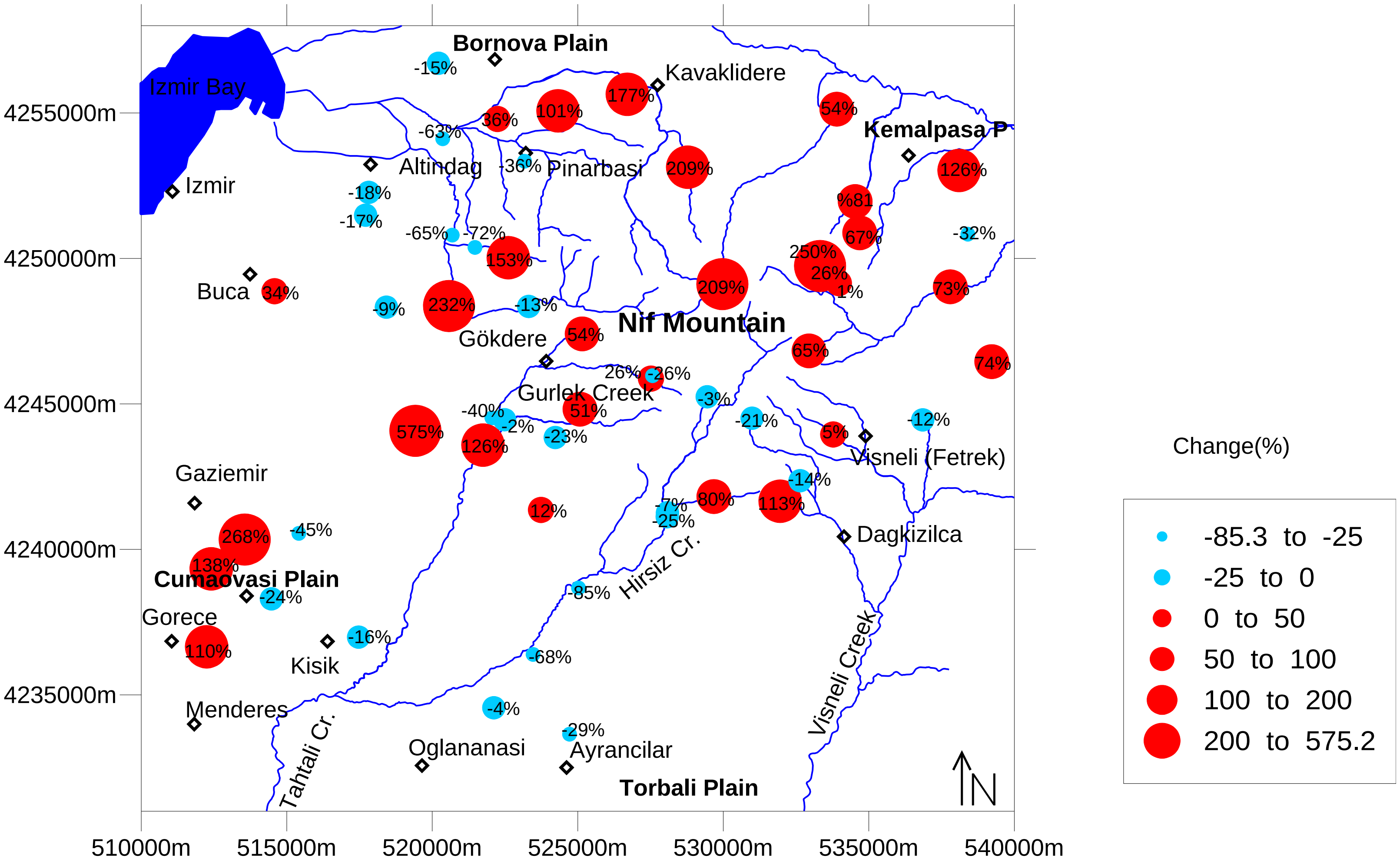

Figure 5.15 Percent change in nitrate concentrations from April to September 2006. Red dots indicate increase in concentration.

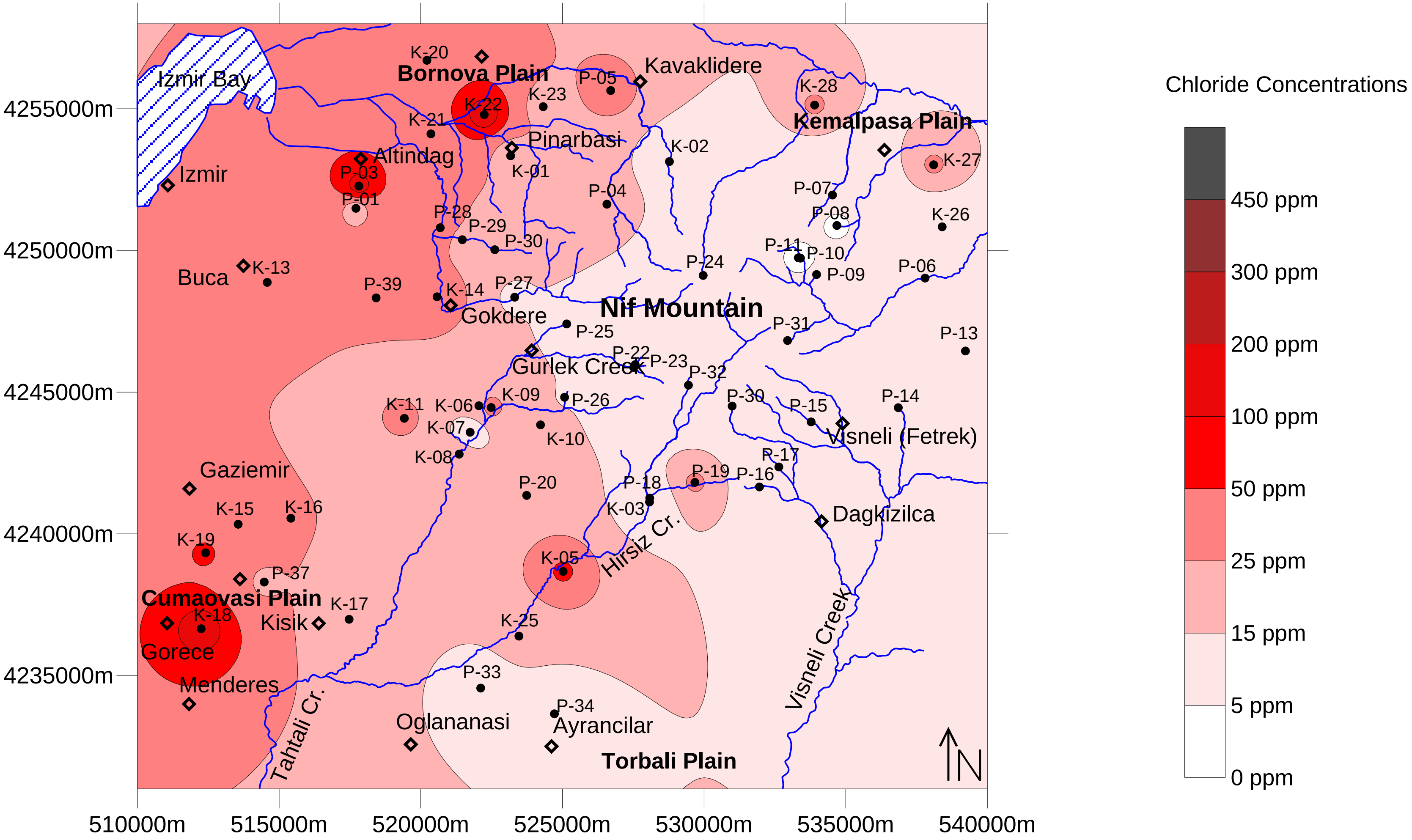

Figure 5.16 Distribution map of chloride concentrations in April 2006 (P: spring sample, K: well sample).

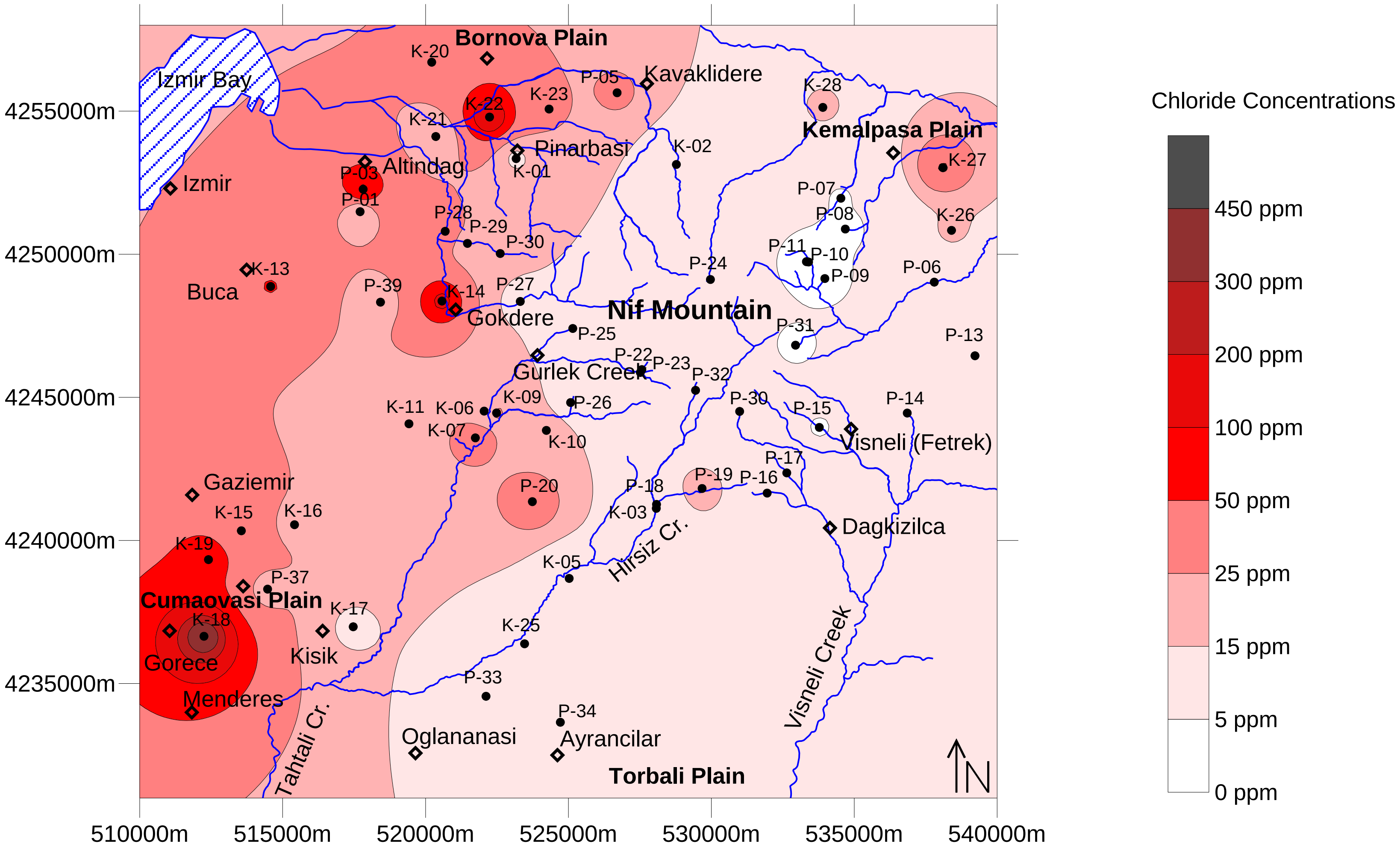

Figure 5.17 Distribution map of chloride concentrations in September 2006 (P: spring sample, K: well sample).

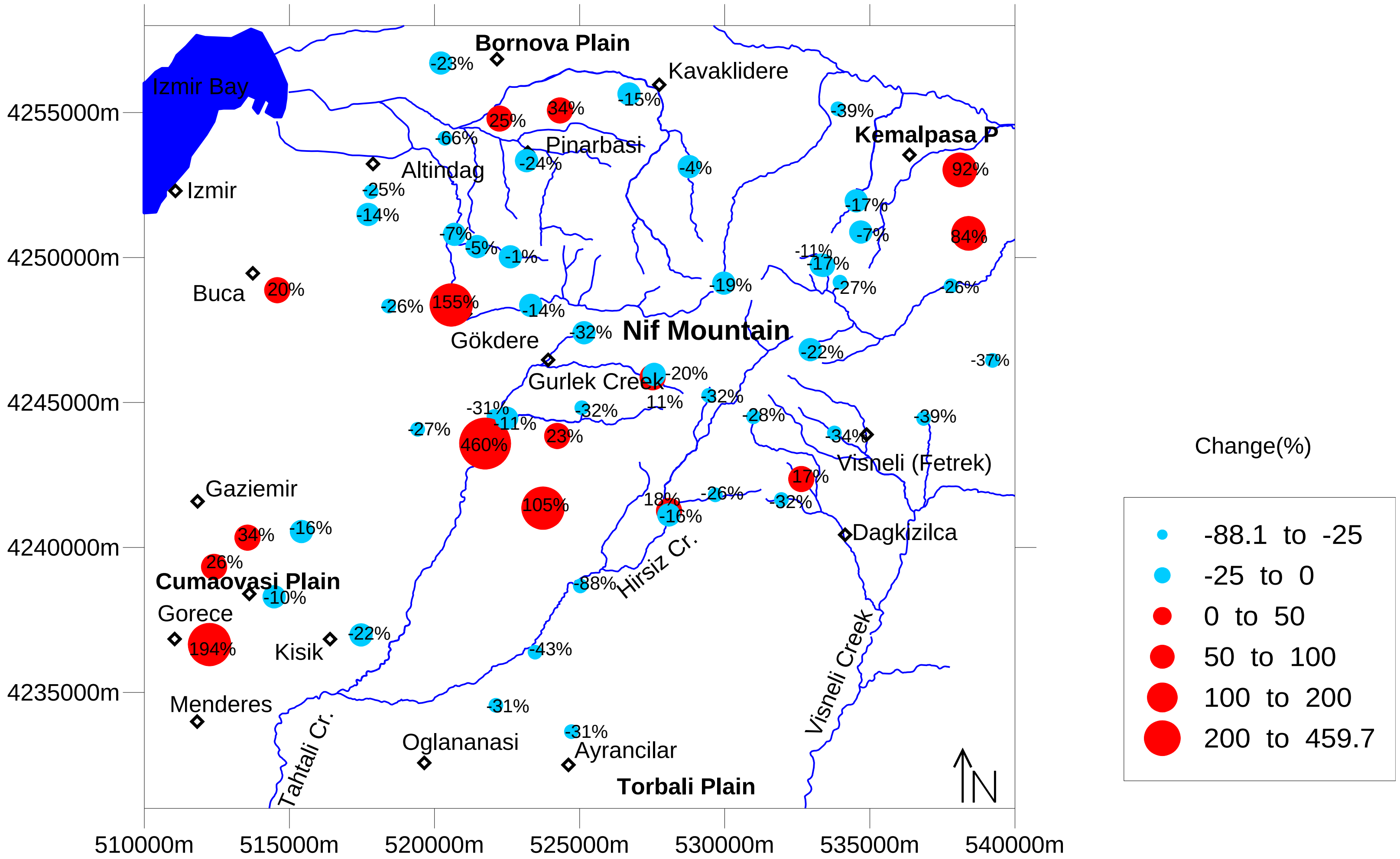

Figure 5.18 Percent change in chloride concentrations from April to September 2006. Red dots indicate increase in concentration.

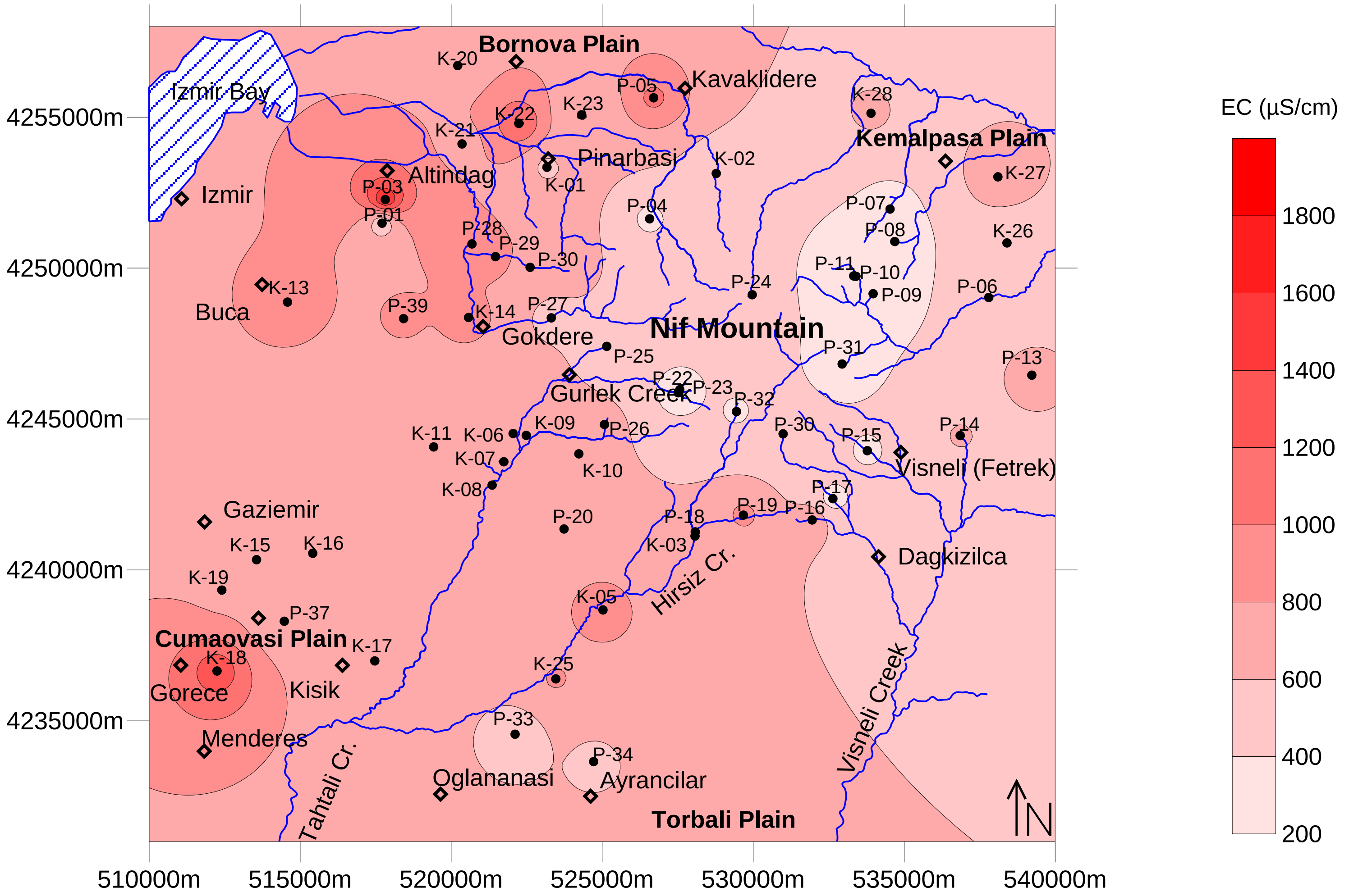

Figure 5.19 Distribution map of EC values in April 2006 (P: spring sample, K: well sample).

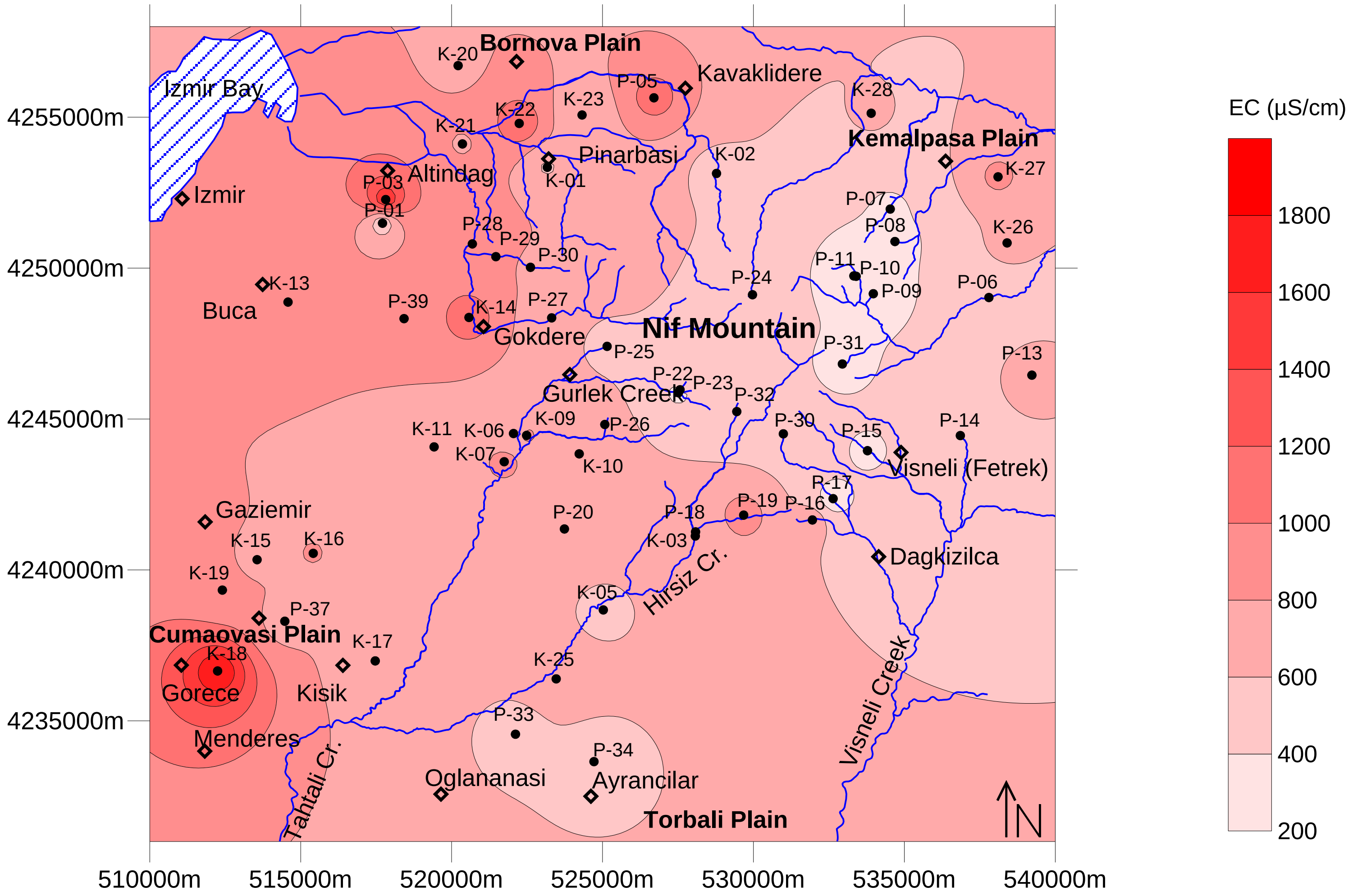

Figure 5.20 Distribution map of EC values in September 2006 (P: spring sample, K: well sample).

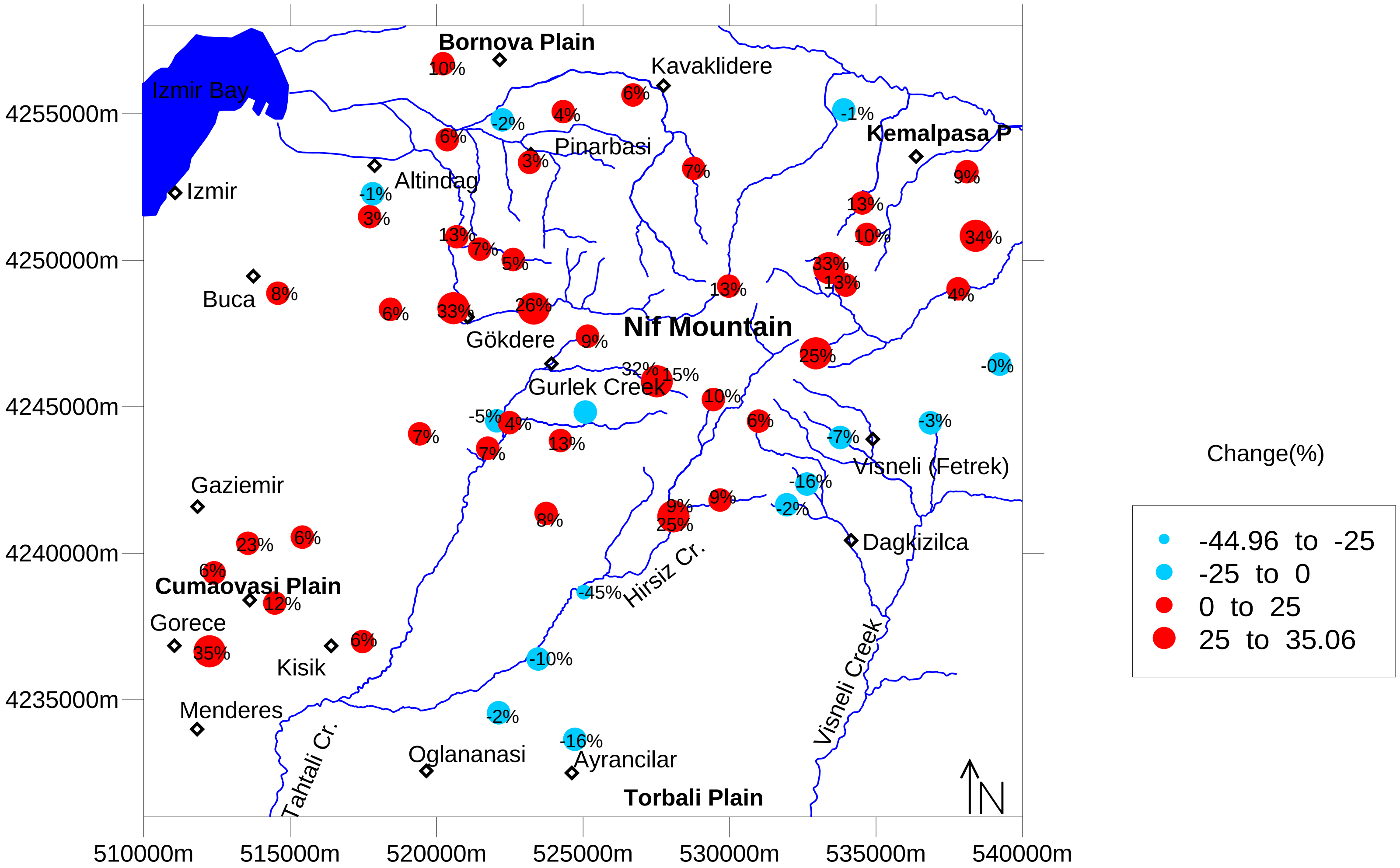

Figure 5.21 Percent change in EC values from April to September 2006. Red dots indicate increase in conductivity.

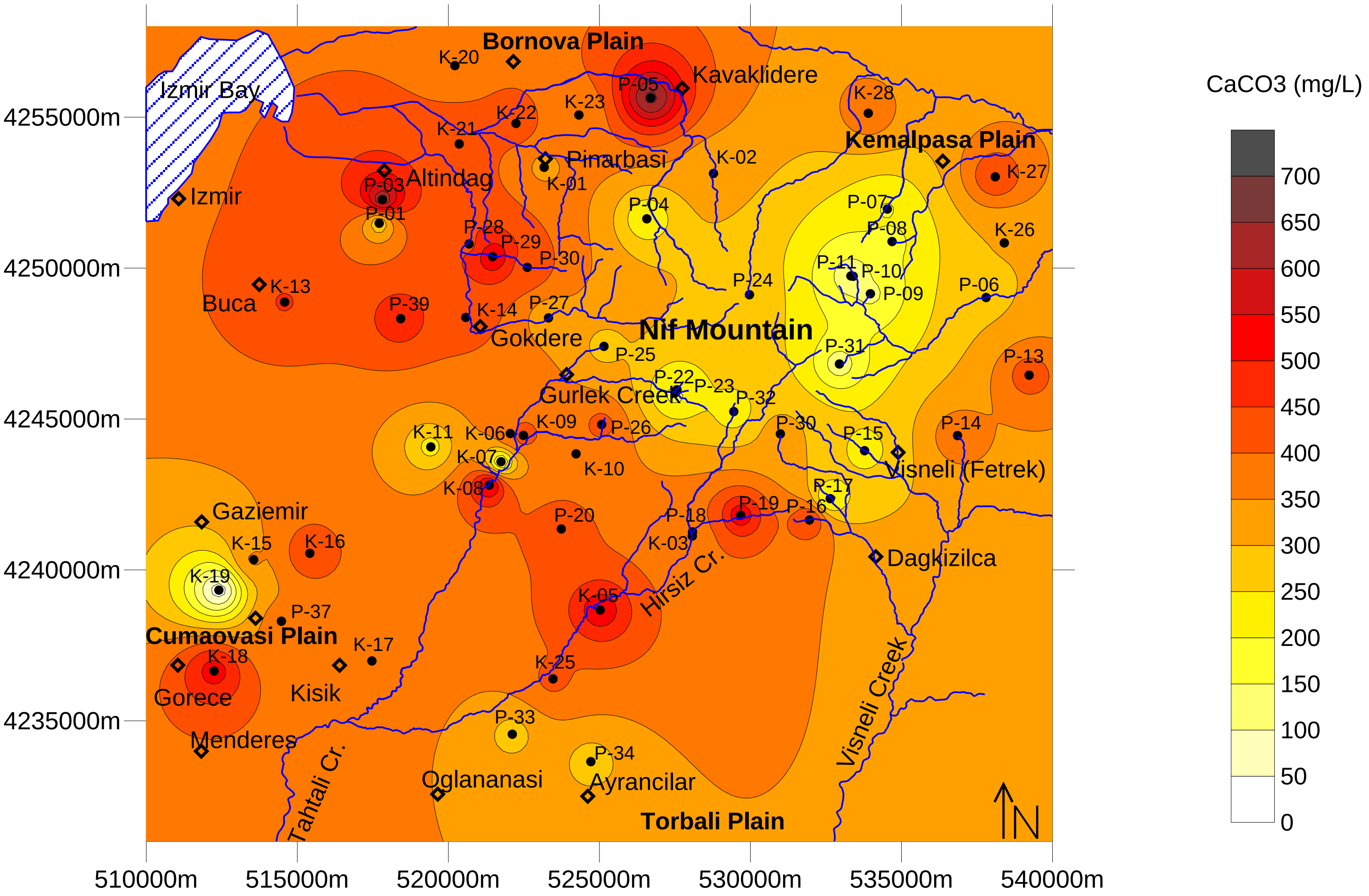

Figure 5.22 Distribution map of hardness concentrations in April 2006 (P: spring sample, K: well sample).

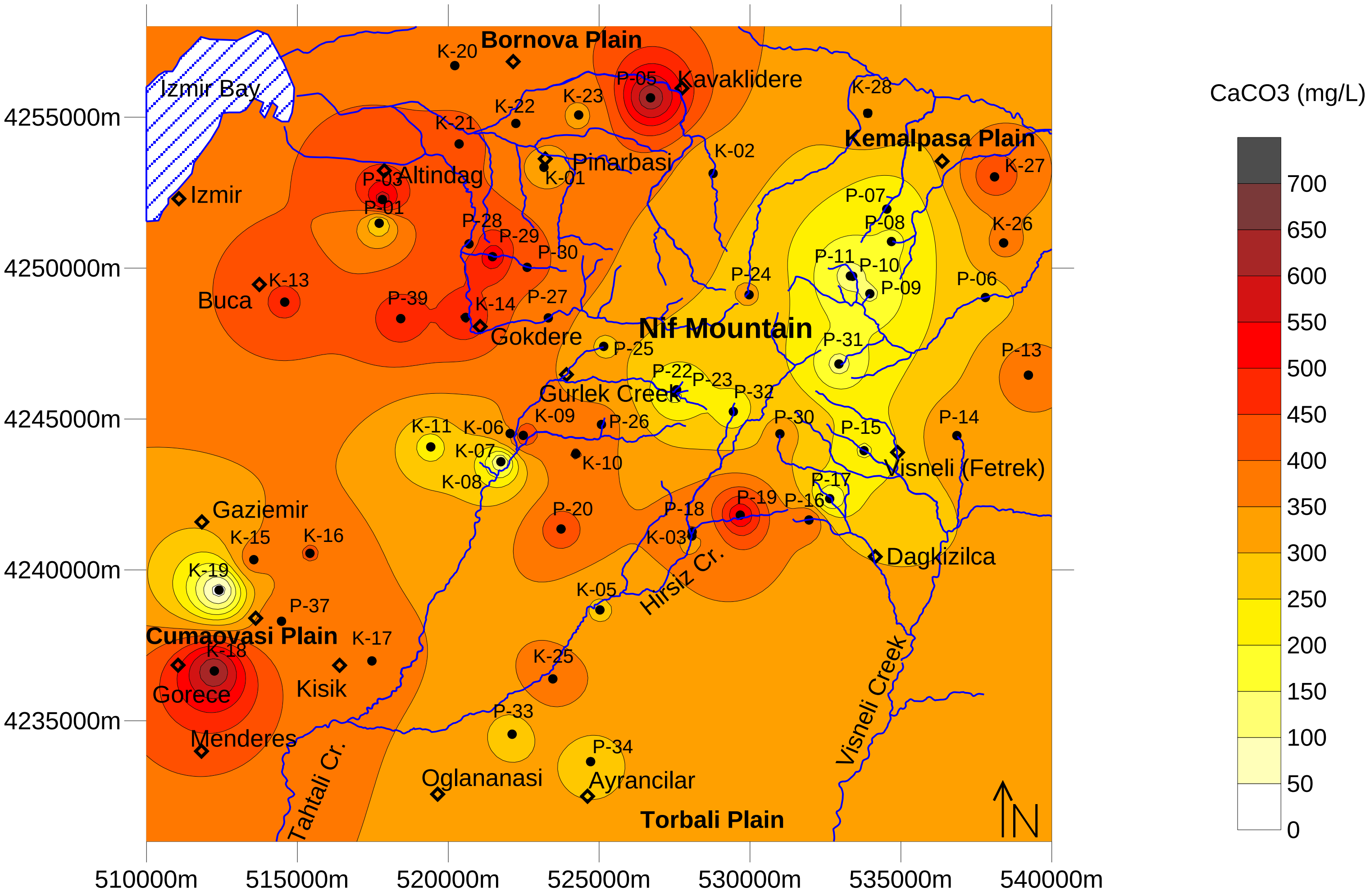

Figure 5.23 Distribution map of hardness concentrations in September 2006 (P: spring sample, K: well sample).

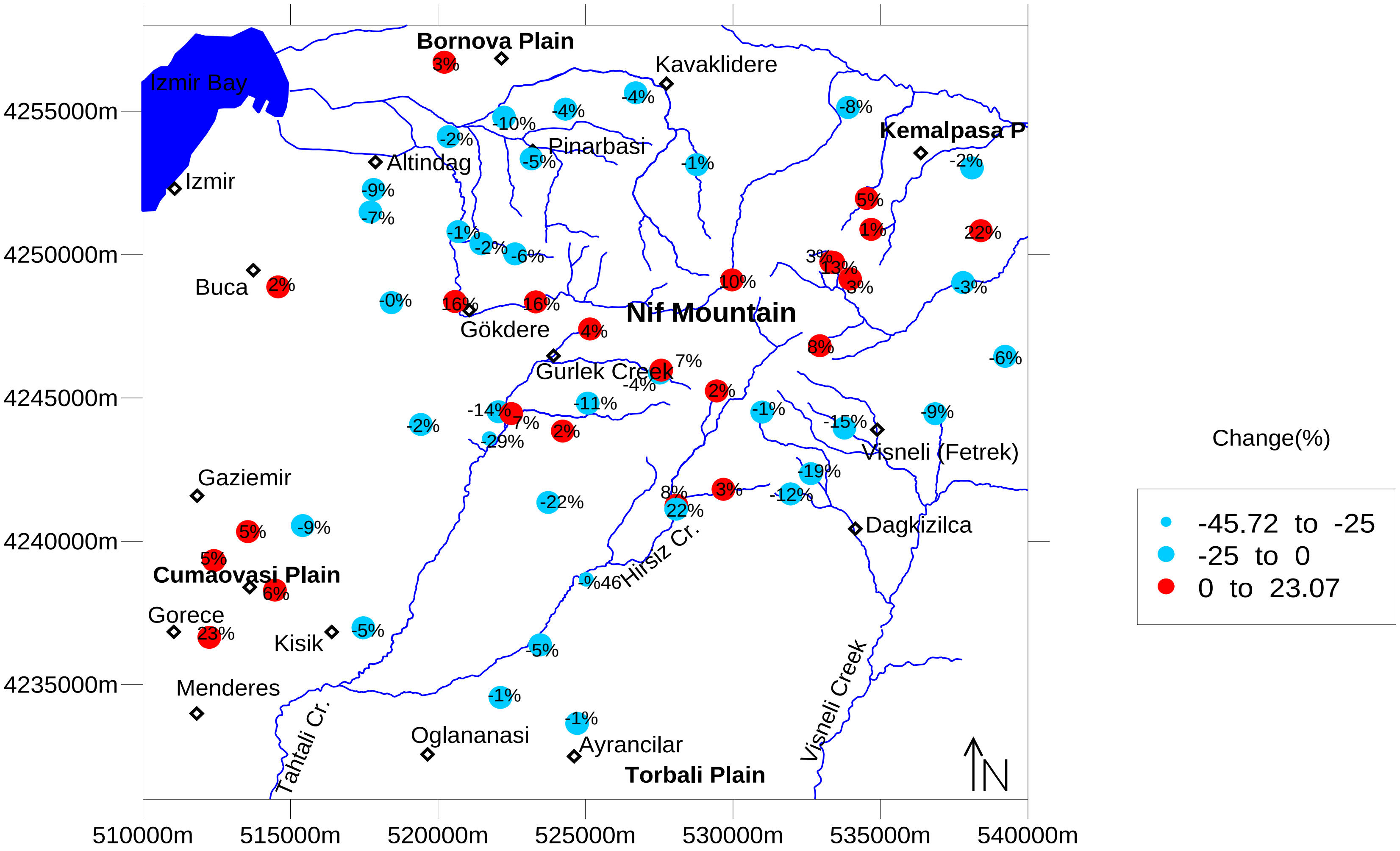

Figure 5.24 Percent change in hardness concentrations from April to September 2006. Red dots indicate increase in concentration.

5.3 Temporal Assessment of Nif Mountain Karst Groundwater by Statistics

5.3.1 Normality Testing for Differences

The paired t-test was applied to test the statistical significance of temporal change of the groundwater quality parameters NO_3^-, Cl^-, EC and hardness. The pre-requirement to use the paired t-test is to have a statistically normal distribution of the differences (d_i) between the two data sets. Therefore, normality of the data was tested using the Kolmogorov-Smirnov (K-S) test. This sections presents the results of this testing. The difference of values between the wet and dry seasons for each quality parameter between data sets was expressed as:

$d_i = x_{1i} - x_{2i}$

where:

x_{1i}: First set of values; data representing the wet season (data of April 2006)

x_{2i}: Second set of values; data representing the dry season (data of September 2006)

To find out whether the differences are normally distributed, a null hypothesis (H_0) and its alternative (H_s) were formulated as:

H_0: There is no difference between the data distribution and the normal distribution.

H_s: There is a difference between the data distribution and the normal distribution.

Table 5.6 summarizes the results of the K-S normality test. The resulting *p* values were compared with a significance level, α (α=0.05). In addition, Figures 5.25, 5.26, 5.27 and 5.28 show histograms of $d_{Nitrate}$, $d_{Chloride}$, d_{EC}, and $d_{hardness}$ for April and September, respectively.

Table 5.6 One-Sample K-S Test for Differences

		$d_{nitrate}$	$d_{chloride}$	d_{EC}	$d_{hardness}$
N		57	57	57	57
Normal Parameters	**Mean**	-2.0728	-5.2612	-42.2281	8.6702
	Std. Deviation	26.2586	42.5839	103.4607	46.3527
***p* value: asympt. significance**		0.000	0.000	0.009	0.240

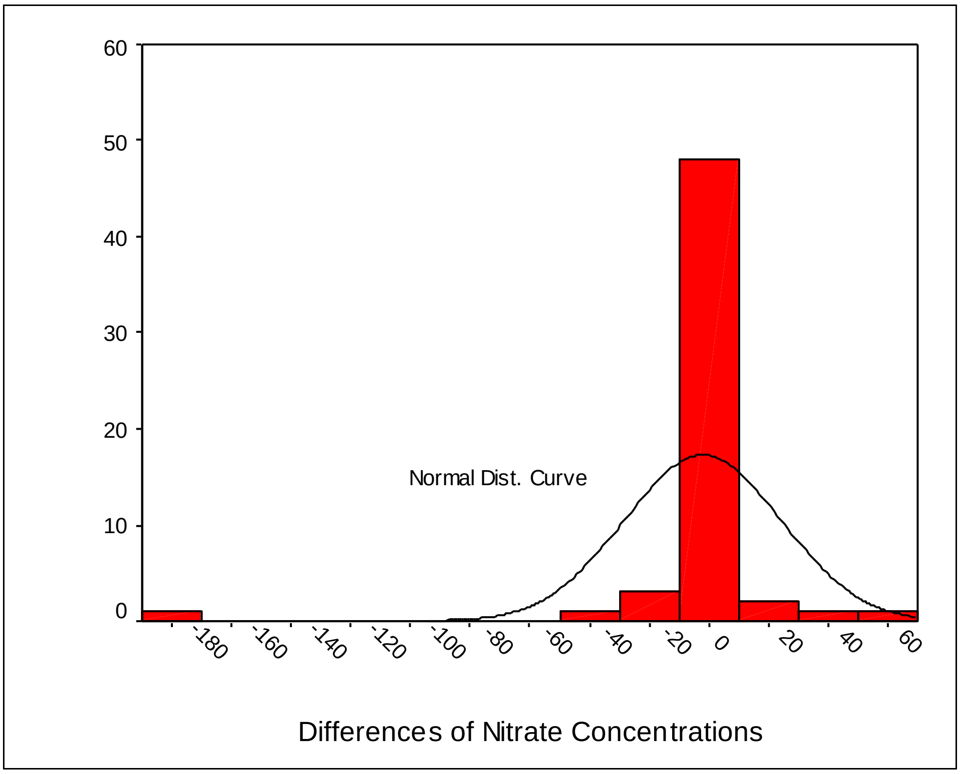

Figure 5.25 Histogram of the differences of nitrate concentrations

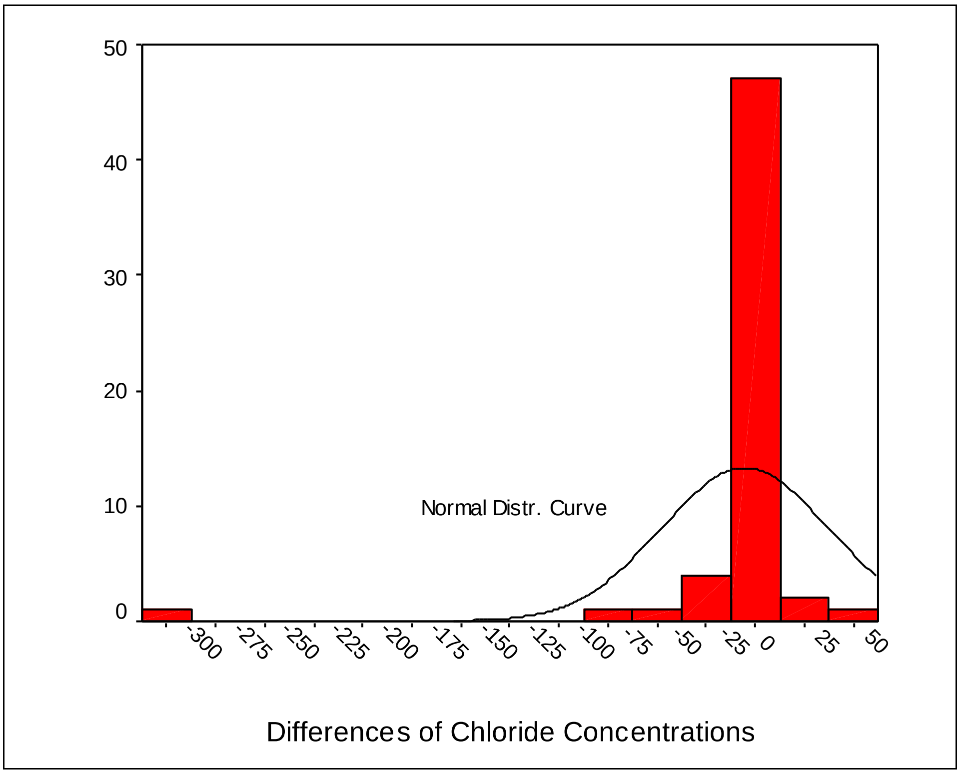

Figure 5.26 Histogram of the differences of chloride concentrations

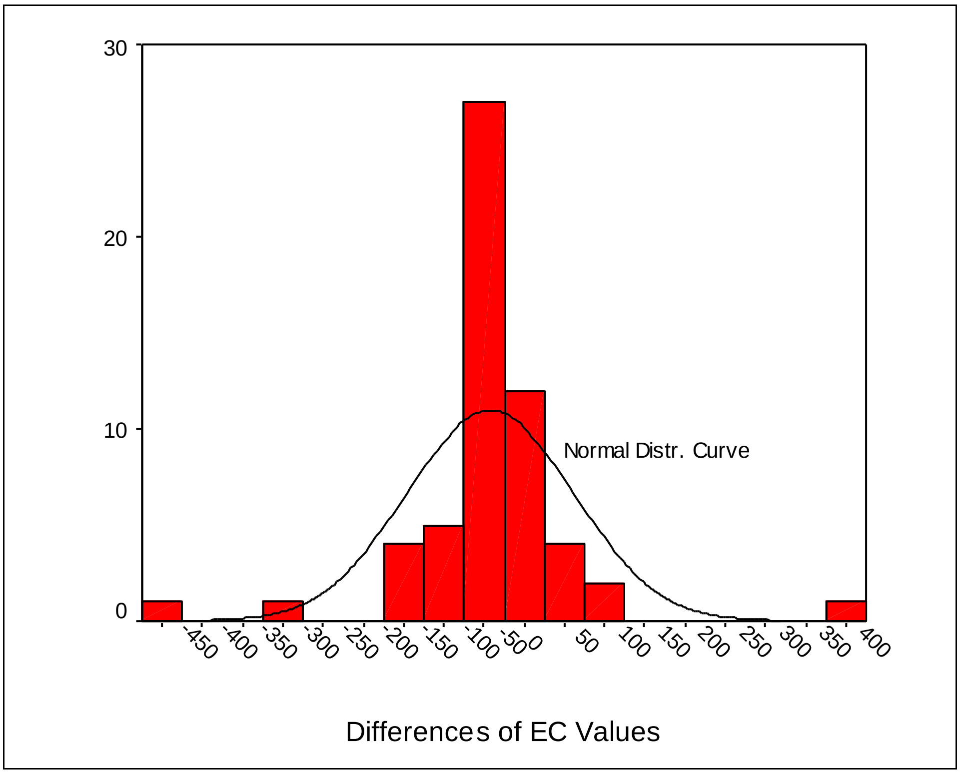

Figure 5.27 Histogram of the differences of EC values

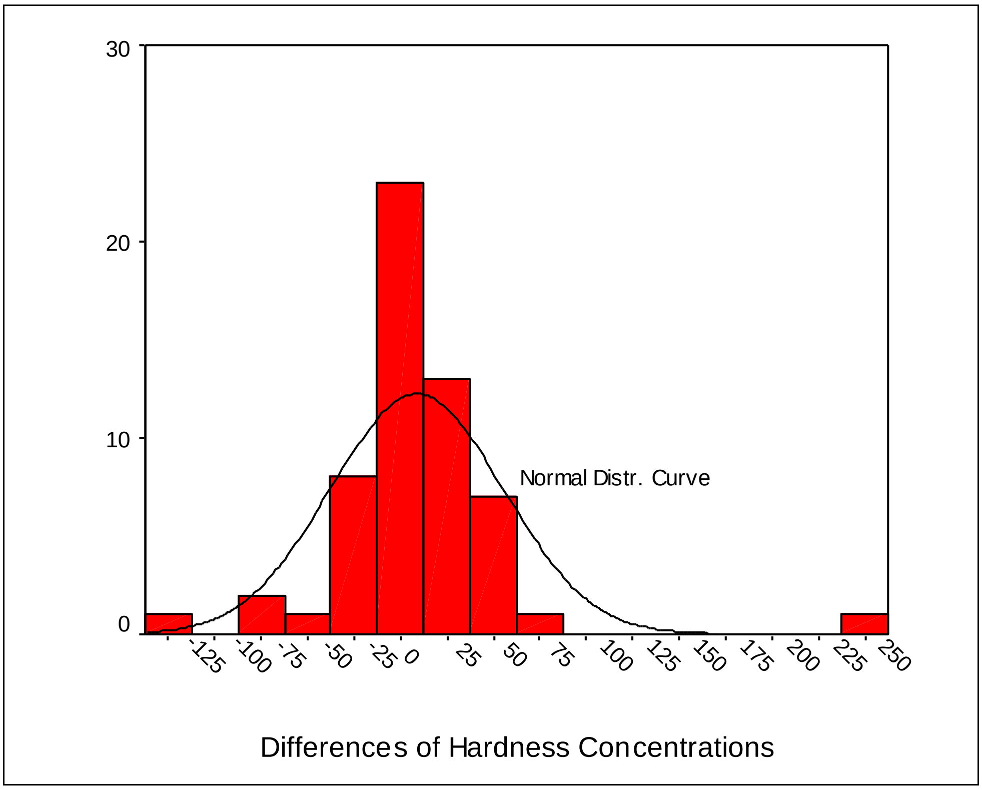

Figure 5.28 Histogram of the differences of hardness concentrations

Since *p* values for nitrate, chloride and EC were less than the α value (for $d_{nitrate}$ p=0.00<0.05; for $d_{chloride}$ p=0.000<0.05, and for d_{EC} p=0.009<0.05), the H_0 (null) hypothesis was rejected and it can be said with 95% confidence that these data ($d_{nitrate}$, $d_{chloride}$ and d_{EC}) distributed not normally. However; for the hardness data ($d_{hardness}$) the *p* value was greater than the α value (p=0.240>0.05). Therefore, the null hypothesis was not rejected and the data of $d_{hardness}$ can be considered to be normally distributed at a 5% level of significance.

According to the normality test results, paired sample t-test can be used only for the hardness data, whose temporal differences are normally distributed. On the contrary, to identify whether there has been a significant difference in concentration of other quality parameters ($d_{Nitrate}$, $d_{Chloride}$ and d_{EC}); a non-parametric test, which is an alternative to the paired t-test must be used.

5.3.2 Paired Samples T-Test

To find out whether the differences are normally distributed, a null hypothesis (H_0) and its alternative (H_s) were formulated below.

H_0: There is no difference between the hardness concentrations in April and September.
H_s: There is a difference between the hardness concentrations in April and September.

Table 5.7 shows the results of paired samples t-test, which was carried out to signify whether there has been a significant change in hardness concentrations from wet season to dry season. These values were compared with a α significance value of 0.05. Since the *p* value is greater than the α value (p=0.163>0.05) the null hypothesis was accepted and it was concluded that there may be no significant difference between the hardness concentrations from April to September with a 95% confidence. Although the mean of the hardness concentrations decreased from 347.2 mg/L to 338.5 mg/L over time (Table 5.8), the decrease is not significant from a statistical point of view based on the test results.

Table 5.7 Paired sample t-test results

Paired Differences	**Mean Std. Dev.**		**Std. Error Mean**	**95% Confidence Interval of the Difference**		**t**	**df**	**p value: Sig. (2-tailed)**
				Lower	**Upper**			
Hardness -April Hardness -Sept.	8.6702	46.3527	6.1396	-3.6289	20.9692	1.412	56	0.163

Table 5.8 Statistics of paired samples

Pair 1	**Mean**	**N**	**Std. Deviation**	**Std. Error Mean**
Hardness-April	347.2	57	134.9	17.9
Hardness-September	338.5	57	133.6	17.7

5.3.3 Wilcoxon Signed Rank Tests

A non-parametric testing method, the Wilcoxon signed rank test, was applied to identify, whether the temporal difference in concentrations of NO_3^-, Cl^- and EC is statistically significant since normality testing for these parameters resulted in non-normal distributions. In general the following null and alternative hypotheses for all three parameters were formulated:

H_0: There is no difference between concentration data in April and in September.
H_s: There is a difference between concentration data in April and in September.

Given in Table 5.9 are results for this test. Negative ranks in this table were assigned to data pairs that represent decreases in concentration from April to September. Positive ranks were assigned to the opposite case. If the data pair happened to be equal then it was assigned as a tie.

The null hypothesis was accepted for the data pairs of NO_3^- and Cl^- as the *p* value was greater than the significance value α. This implies that there may be no statistically significant difference between the parameter concentrations from April to September with 95% confidence. The change in concentrations was not significant from a statistical point of view. The null hypothesis was rejected for the data pair of EC as the *p* value was greater than the significance value α. This, on the contrary, implies that the change in parameter concentrations from April to September with may be significant with 95% confidence.

Table 5.9 Summary of Wilcoxon Signed Ranks test results

		(NO_3^-- Sept.) - (NO_3^-- April)	**(Cl^- - Sept.) - (Cl^-- April)**	**(EC Sept.) - (EC-April)**
Negative Ranks	**N**	27[a]	42[a]	14[a]
	Mean Rank	31.17	25.07	18.50
	Sum of Ranks	841.50	1053.00	259.00
Positive Ranks	**N**	30[b]	15[b]	43[b]
	Mean Rank	27.05	40.00	32.42
	Sum of Ranks	811.50	600.00	1394.00
	Ties	0[c]	0[c]	0[c]
	Z	-0.119[a]	-1.800[a]	-4.509[b]
	p	0.905	0.072	0.000

[a] Based on positive ranks
[b] Based on negative ranks

5.4 Correlation & Regression Analyses Results

Results of the correlation and regression analyses for the data pairs NO_3^- - Cl^-, EC - NO_3^- and EC – Cl^- is presented in this section. Based on the calculated Pearson correlation coefficients it was determined, whether there is a significant relation between parameters. Furthermore, the regression analyses results provided mathematical relationships between water quality parameters.

5.4.1 Relation Between Nitrate and Chloride

The following null hypothesis and its alternative were formulated:

H_0: The relation between the nitrate and chloride is not considerable
H_s: The relation between the nitrate and chloride is considerable

Results of the correlation analysis are given in Table 5.10. The Pearson correlation coefficient (r) was 0.788 for the data pair NO_3^- - Cl^-, and the significance level was $p=0.000<0.01$, then the H_0 hypothesis is rejected. Hence, there was a significant, positive correlation between the nitrate and chloride variables.

Table 5.10 Correlations between nitrate and chloride. Correlation is significant at the 0.01 level (2-tailed).

		NO_3^-	Cl^-
NO_3^-	**Pearson Correlation *(r)***	1.000	0.788
	Sig. (2-tailed)		0.000
	N	116	116
Cl^-	**Pearson Correlation *(r)***	0.788	1.000
	Sig. (2-tailed)	0.000	
	N	116	116

Different type of regression models, e.g. linear, second and higher order polynomials, exponential, power and logarithmic, were attempted to fit to the data. Based on the obtained coefficients of determination the best fit was for a fourth order polynomial ($R^2=0.778$). However, the highest coefficient does not always assure a valid and meaningful relationship. Therefore, the linear regression model was chosen and tested for statistical significance. Figure 5.29 shows the scatter diagram for the data pair and the calculated regression equation with its R^2 value. As a result the regression model can be written as $Cl^-=14.303+0.828*\ NO_3^-$. Furthermore, the calculated p value was less than the significance value α ($p=0.000<0.05$), therefore it can be concluded that the model between NO_3^- and Cl^- is significant.

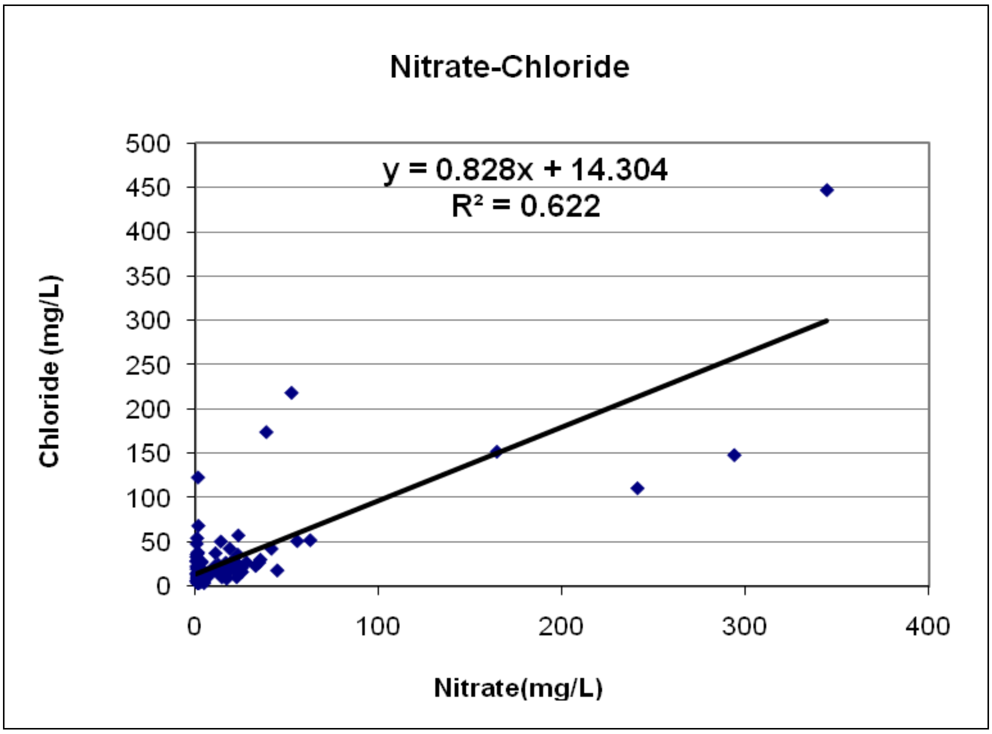

Figure 5.29 Linear regression between nitrate and chloride.

5.4.2 Relation Between EC and Nitrate

The following null hypothesis and its alternative were formulated:

H_0: The relation between EC and NO_3^- is not considerable.
H_s: The relation between EC and NO_3^- is considerable.

Results of the correlation analysis for this pair of datasets are given in Table 5.11. It can be seen that there is a significant, positive correlation between the EC and NO_3^- variables, at the level of r=0,676. Since the significance value is $p=0.000<0.01$, the null hypothesis was rejected, therefore, there was significant correlation between NO_3^- and EC.

Table 5.11 Correlations between EC and nitrate. Correlation is significant at the 0.01 level (2-tailed).

		EC	**NO_3^-**
EC	**Pearson Correlation**	1.000	0.676
	Sig. (2-tailed)		0.000
	N	116	116
NO_3^-	**Pearson Correlation**	0.676	1.000
	Sig. (2-tailed)	0.000	
	N	116	116

The regression curves for the alternative models are shown in Figures 5.31 and 5.32. The coefficients of determination for these polynomial expressions were clearly higher than for the chosen linear regression equation (0.829 for the second order and 0.887 for the third order polynomial). Also, visually these polynomials are a better fit to the data. However, these relationships imply that the EC value may decrease or even remains unaffected (Figure 5.32) with the increase in nitrate concentrations. This is not plausible, nor justifiable from a hydrogeochemical standpoint. It is expected that an increase in ion concentrations result in an increase in EC of the groundwater.

Based on the obtained coefficients of determination the best fit was for a fourth order polynomial (R^2=0.889). However, based on the previous argument, a linear regression model was chosen and tested for statistical significance with the expectation that it would provide a more meaningful relationship between the quality parameters. Figure 5.30 shows the scatter diagram for the data pair and the calculated regression equation with its R^2 value (R^2=0.457). As a result the regression model can be written as $NO_3^- = -60.287+0.118*EC$. Furthermore, the calculated p value was less than the significance value α (p=0.000<0.05), therefore it can be concluded that the model between EC and NO_3^- is significant.

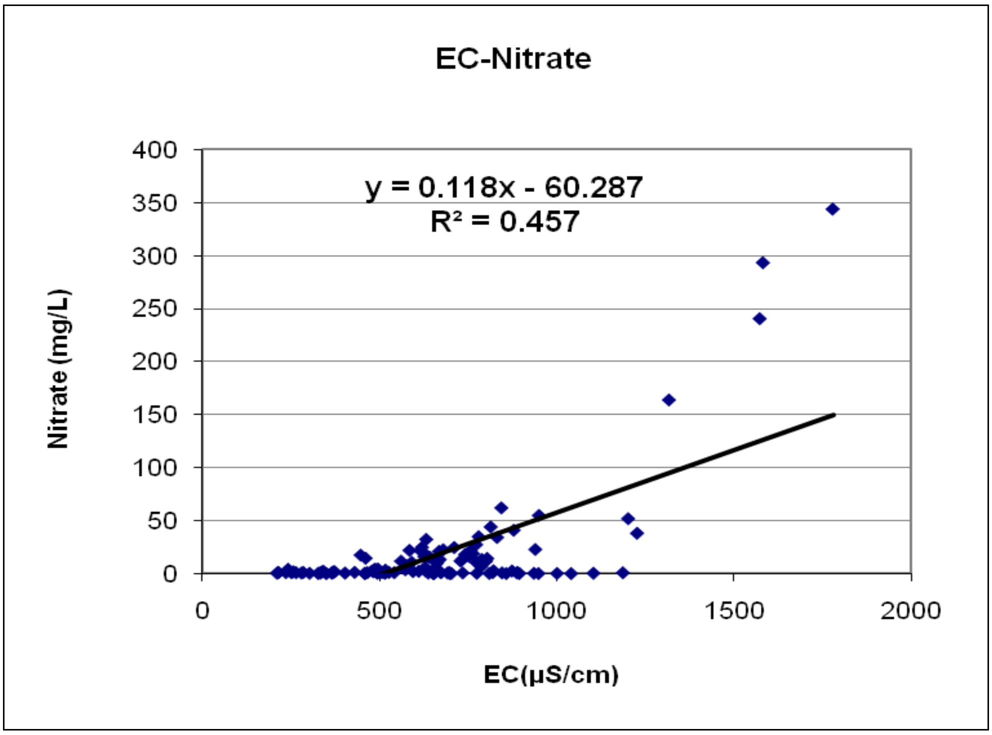

Figure 5.30 Linear regression between EC and NO_3^-

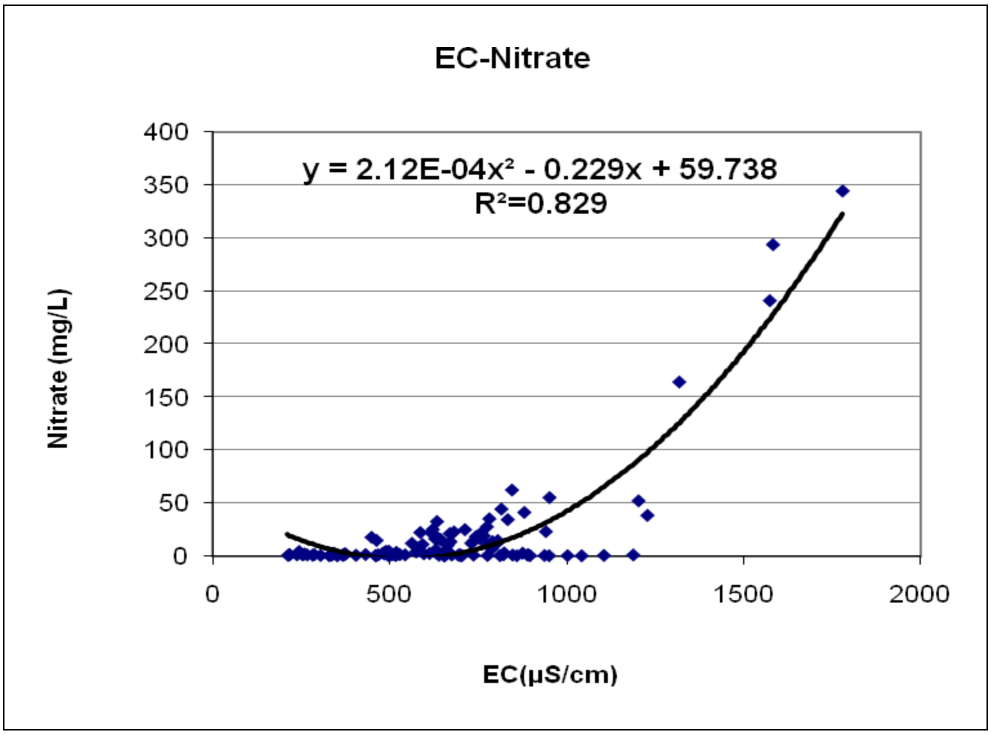

Figure 5.31 Polynomial regression (at the degree of 2) between EC and NO_3^-

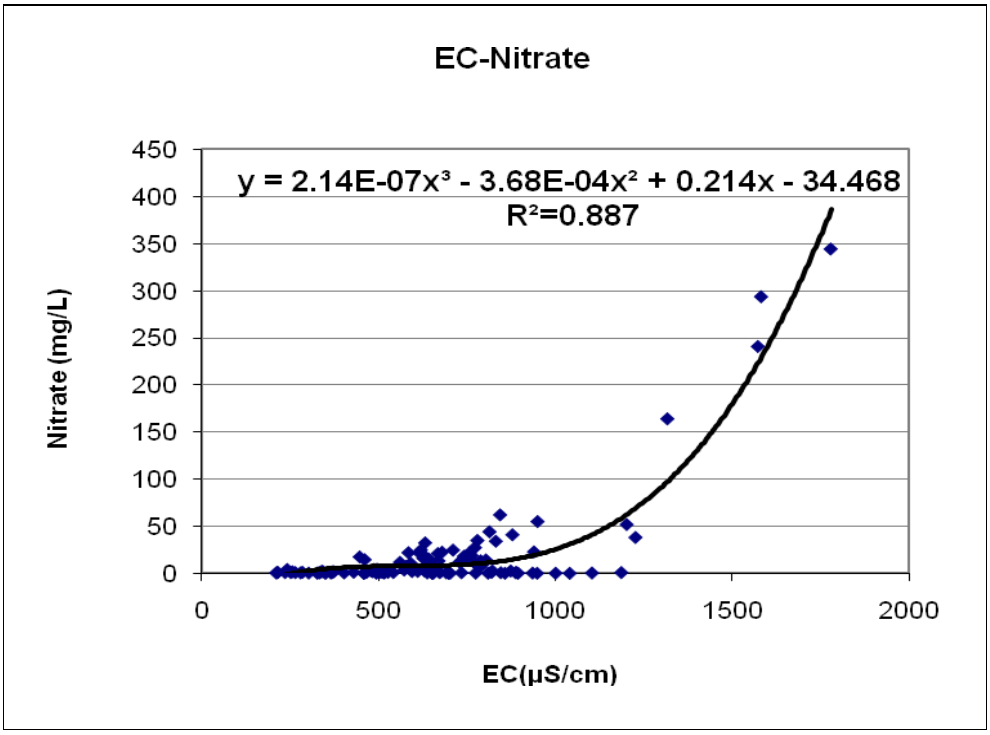

Figure 5.32 Polynomial regression (at the degree of 3) between EC and NO_3^-

5.4.3 Relation Between EC and Chloride

The following null hypothesis and its alternative were formulated:

H_0: The relation between the EC and chloride is not considerable.
H_S: The relation between the EC and chloride is considerable.

Results of the correlation analysis for this pair of datasets are given in Table 5.12. There is a significant, positive correlation between the EC and chloride variables, at the level of r=0,736. Since the significance value is p=0.000<0.01, the null hypothesis was rejected. Therefore, the statistical relation between the EC and chloride is significant.

Table 5.12 Correlations between EC and chloride. Correlation is significant at the 0.01 level (2-tailed).

		EC	Cl$^-$
EC	**Pearson Correlation**	1.000	0.736
	Sig. (2-tailed)		0.000
	N	116	116
Cl$^-$	**Pearson Correlation**	0.736	1.000
	Sig. (2-tailed)	0.000	
	N	116	116

Based on the obtained coefficients of determination the best fit was again a fourth order polynomial (R^2=0.801). However, based on the previous argument and to be consistent, again a linear regression model was chosen and tested for statistical significance. Figure 5.33 shows the scatter diagram for the data pair and the calculated regression equation with its R^2 value (R^2=0.542). As a result the regression model can be written as $Cl^- = -60.305 + 0.135*EC$. Furthermore, the calculated *p* value was less than the significance value *α* (*p*=0.000<0.05), therefore it can be concluded that the model between EC and Cl$^-$ is significant.

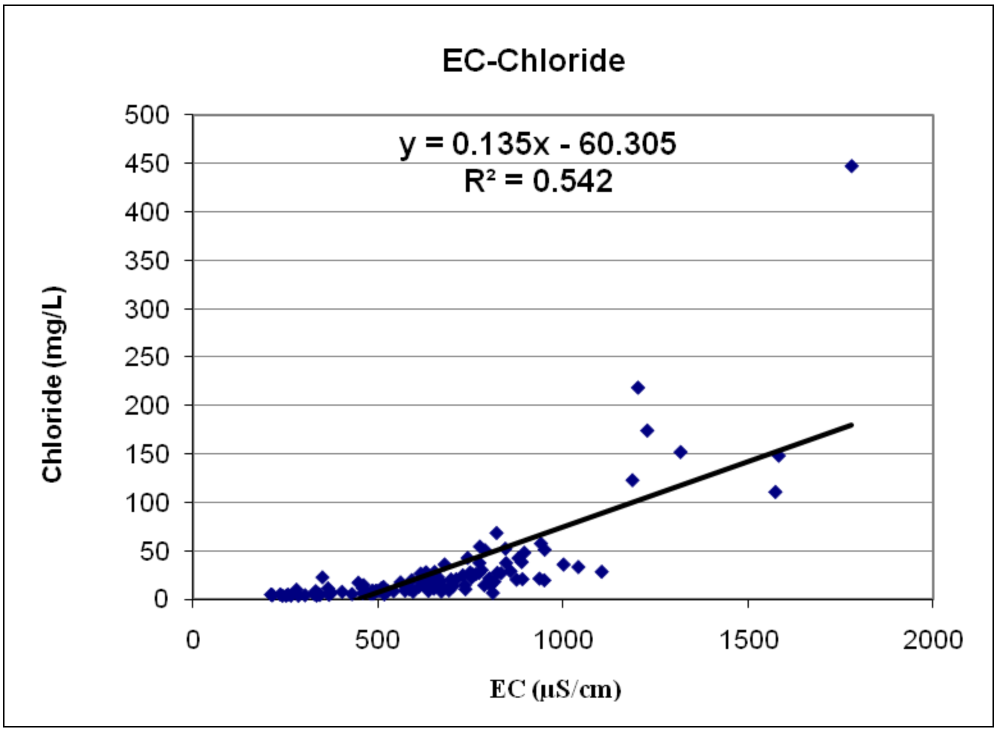

Figure 5.33 Linear regression between the EC and chloride

CHAPTER SIX
DISCUSSION AND CONCLUSIONS

The main objective of the thesis was the spatial and temporal assessment of the groundwater quality of the Nif Mountain karstic aquifer system which is located within the metropolitan borders of İzmir. Moreover, this thesis also presented a general characterization of groundwater quality and investigates the relationships between several quality parameters. Important conclusions could be drawn from the series of statistical tests and mapping that was extensively performed for this study.

The concentration distribution maps of each groundwater quality parameter were illustrated to be able to assess the occurrence of contamination spatially and also temporally. The percent change maps were used to quantify the temporal changes and illustrate them along with their spatial distribution. Furthermore, the paired samples t-test and the Wilcoxon signed rank tests results provided statistical proof of significance. The visual comparison of concentration distribution maps revealed that the spatial distributions for all water quality parameters seemed to be very similar for both seasons. However there were some “hotspots” of contamination, which could be seen in particular for nitrate. These occurrences can be attributed to either dense agricultural activities or to leakage of wastewater in residential area. In dry seasons it can be expected that agricultural activities such as fertilizer application and irrigation increase nitrate pollution. On the contrary, the decrease in nitrate concentrations can be explained by the cease of the contaminant discharge to the aquifer. Alternatively, dilution by surficial or lateral recharge of groundwater is a viable explanation. Natural attenuation mechanisms (e.g. denitrification, plant uptake) are less likely the reason because the groundwater samples were withdrawn from the unconfined aquifer that was in oxidized conditions throughout the entire study period. Plant uptake would be possible, if the water table is very shallow, however that was not the case.

Moreover, intercepting a different character of the groundwater circulation near the sampling point would also affect the contamination. For example, surface-ground water interactions around creeks can significantly affect concentrations in groundwater due to dilution. Although, the temporal evolution of nitrate pollution is more difficult to predict, statistical results underline the fact that the temporal change in nitrate concentrations was not significant. This means that any possible factors that influence nitrate contamination were not substantially dominant or present in the Nif Mountain karstic aquifer. Same conclusions apply for chloride contamination; natural and anthropogenic factors were not there to cause a significant change in groundwater quality with time.

The temporal change in groundwater EC values of the Nif Mountain karstic aquifer was found to be significant. The overall increase in EC values from winter to summer can be attributed to less groundwater recharge and thus slower groundwater circulation. This implies that internal aquifer hydrodynamics and ongoing karstic dissolution processes are more effective in EC occurrence. Furthermore, when EC distribution maps were compared one by one with nitrate and chloride concentration distribution, spatial correlations were noticeable to some extent. However, this correlation appeared to be clearer between the distribution maps of EC and chloride than the distribution maps of EC and nitrate. It was evident from the correlation analysis that the correlation for EC-chloride is higher than for the EC-nitrate data sets.

The spatial distribution of groundwater hardness was relatively homogenous. Temporal changes in hardness were also not very significant. This groundwater quality parameter can be considered as stable that does not seem to be much affected by groundwater recharge and dilution. Carbonate dissolution can be observed widespread in limestone aquifers and in other calcium or magnesium bearing sedimentary rocks and minerals. However, hardness can also occur locally in groundwater from chemical and mining industry effluent or excessive application of lime to the soil in agricultural areas. Therefore, in addition to the continuously ongoing carbonate mineral dissolution processes, anthropogenic sources can also influence the hardness of groundwater.

Regarding the general quality of the groundwater in the study area, the distribution maps of the significant contaminants and the results of the water analyses revealed that the quality of groundwater deteriorates as water travels to the plains from the uplands. This was valid for both sampling seasons. This so-called elevation effect is a direct consequence of the increased levels of anthropogenic activities and rock-water interactions. Spatial assessment of NO_3^- and Cl^- concentrations and EC values also exhibited a dependence on land-use patterns, e.g. higher values in low-populated areas versus higher values at certain hotspots of the studied area. Furthermore, the type of the aquifer was also found to be effective on the overall quality pattern of the water. Especially the water quality in karstic limestone aquifers was generally better than the water quality in the aquifers of the Vişneli and the alluvium aquifers. This finding is related to many factors including but not limited to the type of the formation rock of the aquifer, the mean residence time of water inside the aquifer, the mean altitude of the aquifer as well as the quality and the extent of recharge that the aquifer receives. Moreover, the springs of Nif Mountain, in particular, the high-discharge springs provide significant amounts of high-quality water and thus indicate potential for future use by inhabitants.

It was evident from the study results, that less groundwater recharge in the dry period of the year does not always mean higher concentrations for all groundwater quality parameters. Because water circulation times, lithology, quality and extent of recharge and land use also play an important role on the alteration of groundwater quality. Therefore, in order to better assess the seasonal change of groundwater quality data, more frequent sampling and a detailed assessment with respect to land use patterns is required.

Furthermore, the temporal assessment conclusions will not be changed for NO_3^-, Cl^- and hardness, if we excluded the outlier data points on the basis of an assumed underlying normal distribution. Excluding these outlier values would cause the data distribution resemble the normal distribution and the mean of the different season concentrations of the parameters to be closer. Therefore, the sensitivity of the subsequent temporal tests and the significance value of the tests would increase. This implies that there may be no temporal change for these parameters in the context of elimination of outliers. Furthermore, an outlier exclusion for the regression analysis would probably result in higher r^2 values for some regression models. However, a higher r^2 does not always correspond to a more suited expression that explains the relationship between two variables. Hence, linear regression equations were favored in this study, despite the fact that their r^2 values were lower compared to alternative regression equations.

Finally, groundwater monitoring is required for the Nif Mountain water resources, with taking into account the changes in land use. The unique properties of a karstic aquifer system complicate the assessment of spatial and temporal distribution of groundwater contaminants, and therefore more investigations to explain the dispersion and other hydrodynamics in these systems must be generated. Moreover, karstic aquifers are significant water resources that provide high-quality groundwater in large quantities. With some exceptions our investigations have revealed that the Nif Mountain’s groundwater has a good quality throughout the entire year. However, it seems that the water quality deteriorates day-by-day, as the groundwater water flows from the uplands towards the residential plains. The Nif Mountain karstic aquifer is located partially within the basin boundaries of the Tahtalı Dam Reservoir, which is a major water resource of İzmir’s water supply system. In this regard, the quality of subsurface drainage originating from the Nif Mountain must be considered as an important factor that will affect the overall water quality pattern in and around the İzmir metropolitan area.

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APPENDIX

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Table A.1 Physical and chemical characteristics for well samples collected in April 2006

APRIL 2006 WELLS	**Spatial Coordinates**			**General Parameters**				**Major Cations**				**Major Anions**					
Sample Point	**X (m)**	**Y (m)**	**Z (m)**	**T (°C)**	**pH**	**EC (µS/cm)**	**Hardness (mg $CaCO_3$/L)**	**Ca^{+2} (mg/L)**	**Mg^{+2} (mg/L)**	**Na^{+} (mg/L)**	**K^{+} (mg/L)**	**HCO_3^{-} (mg/L)**	**Fl^{-} (mg/L)**	**Cl^{-} (mg/L)**	**Br^{-} (mg/L)**	**NO_3^{-} (mg/L)**	**SO_4^{-2} (mg/L)**
K-1	523170.63	4253339.7	59	16.1	7.31	562	334.90	108.33	15.71	11.04	1.13	355	0.10	17.61	0.22	11.96	16.82
K-2	528776.42	4253136	280	14.5	7.29	495	310.50	97.47	16.37	6.84	0.56	393.8	0.10	8.88	0.24	0.48	10.29
K-3	528082.02	4241260	388	16.0	7.01	643	409.20	108.78	31.56	9.28	1.72	448	0.07	12.53	0.25	15.49	21.17
K-5	525025.47	4238673.3	250	18.1	6.61	941	538.50	182.69	20.11	22.33	3.00	577	0.09	57.71	0.31	23.00	30.34
K-6	522050.29	4244518.6	212	17.2	7.10	663	395.00	135.48	13.86	13.14	1.85	438.7	0.25	22.87	0.28	10.05	14.38
K-7	521742.7	4243583.9	205	17.0	7.42	811	143.40	30.96	16.08	167.31	5.44	589	0.24	6.72	0.34	0.39	2.09
K-8	521355.73	4242810.3	191	14.8	7.22	765	569.40	128.42	36.22	14.00	2.75	494	0.36	25.94	0.29	18.96	57.74
K-9	522485.08	4244456	244	17.3	7.00	781	427.70	162.53	16.34	13.92	0.64	462.3	0.60	30.43	0.30	35.10	41.09
K-10	524227.09	4243844.9	279	16.1	7.05	669	398.30	117.03	25.84	16.62	1.32	400	0.48	18.46	0.28	21.20	25.55
K-11	519419.62	4244075.3	246	21.3	7.37	654	231.70	42.60	30.49	66.73	22.25	428.9	0.92	28.39	0.30	0.19	14.52
K-13	514580.3	4248873.4	78	19.2	7.30	880	453.30	155.66	15.77	32.42	3.77	437.9	0.31	42.63	0.29	41.13	13.77
K-14	520575.3	4248363.7	173	14.3	7.30	896	434.90	113.86	36.66	54.97	1.21	450.1	0.62	48.31	0.35	0.30	58.82
K-15	513555.13	4240337.9	131	19.4	6.98	631	354.20	117.12	15.07	20.96	1.35	451.6	0.68	28.10	0.28	2.87	6.20
K-16	515415.58	4240549.5	148	17.8	6.85	758	445.10	162.92	9.38	13.26	1.29	493.8	0.56	25.75	0.28	21.80	5.54
K-17	517469.51	4236984.1	139	19.0	7.03	632	384.60	128.06	15.82	11.48	0.93	420.4	0.18	17.03	0.28	16.00	6.02
K-18	512247.34	4236651.1	135	17.0	6.46	1318	519.90	133.96	45.13	89.79	6.14	312	0.21	152.20	0.43	164.20	89.92
K-19	512404.56	4239330.6	130	22.6	7.84	776	28.20	9.87	0.88	195.21	2.70	407.2	0.38	54.61	0.49	0.50	16.82
K-20	520216.13	4256708.8	42	18.5	6.96	681	371.80	121.34	16.80	21.25	2.06	401.6	0.55	30.31	0.33	22.72	12.99
K-21	520358.83	4254113.4	43	16.4	7.17	743	432.40	138.54	21.08	18.70	1.23	420	0.65	42.82	0.27	18.33	24.86
K-22	522239.68	4254792.9	58	18.8	7.35	1228	426.90	126.57	27.00	120.54	1.38	374.5	0.69	174.39	0.30	38.31	39.65
K-23	524322.01	4255072.6	94	21.1	7.28	592	354.00	107.17	21.05	12.80	1.54	392.5	1.22	19.98	0.26	10.92	22.13
K-25	526082.52	4254373.1	140	15.8	7.11	815	409.00	139.07	15.07	16.89	0.97	412	0.17	18.25	0.31	44.30	15.61
K-26	538403.46	4250833.5	252	13.0	7.20	486	300.70	92.25	17.15	7.44	1.51	347.5	0.07	9.16	0.24	3.75	14.73
K-27	538103.29	4253022.9	173	17.6	6.84	774	446.50	156.96	13.34	20.26	3.23	485.8	0.15	27.32	0.27	27.52	28.91
K-28	533900.97	4255130.2	218	15.6	7.10	628	382.40	128.17	15.23	10.52	1.37	406	0.46	26.91	0.26	16.19	14.48

Table A.2 Physical and chemical characteristics for spring samples collected in April 2006

APRIL 2006 SPRINGS	**Spatial Coordinates**			**General Parameters**				**Major Cations**				**Major Anions**					
Sample Point	**X (m)**	**Y (m)**	**Z (m)**	**T (°C)**	**pH**	**EC (µS/cm)**	**Hardness (mg $CaCO_3$/L)**	**Ca^{+2} (mg/L)**	**Mg^{+2} (mg/L)**	**Na^{+} (mg/L)**	**K^{+} (mg/L)**	**HCO_3^- (mg/L)**	**Fl^- (mg/L)**	**Cl^- (mg/L)**	**Br^- (mg/L)**	**NO_3^- (mg/L)**	**SO_4^{-2} (mg/L)**
P-1	517710.72	4251486.2	268	14.4	7.93	448	260.60	99.99	2.71	8.82	0.57	215.6	0.49	17.29	0.29	17.65	57.38
P-3	517817.12	4252270.4	116	17.8	7.43	1583	640.80	238.99	10.81	98.67	7.02	333.5	0.58	148.45	0.27	293.84	85.09
P-4	526781.81	4251761.3	369	12.8	7.76	351	195.90	69.76	5.32	8.56	0.66	193.7	0.51	22.83	0.26	0.23	22.32
P-5	526702.61	4255641.4	194	14.2	6.77	1042	662.80	247.99	10.71	18.28	0.68	719	0.32	33.49	0.32	0.24	33.43
P-6	537800.38	4249025	273	16.6	7.33	467	292.70	92.26	15.21	5.58	0.47	308.6	0.07	8.25	0.24	1.14	8.50
P-7	534532.23	4251955.4	650	12.0	7.60	328	196.50	74.04	2.87	3.67	0.54	224.6	0.05	5.65	< 0.05	0.44	7.91
P-8	534687.58	4250879.7	801	11.4	7.68	304	188.80	65.84	5.97	3.17	0.66	219.6	0.04	4.29	0.23	0.51	6.72
P-9	533970.92	4249150.5	861	10.8	7.80	237	137.60	42.69	7.56	3.76	0.95	167.3	0.05	5.16	0.23	1.04	7.09
P-10	533402.12	4249728.4	954	11.2	7.87	215	126.50	44.64	3.69	3.21	0.65	146.4	0.04	4.61	0.24	1.05	5.68
P-11	533325.97	4249740.3	990	11.5	7.93	216	122.30	43.00	3.65	2.51	0.29	133	0.04	4.35	0.23	1.23	5.40
P-13	539224.85	4246452.4	401	14.7	7.20	675	425.40	113.41	34.62	7.93	0.62	485.6	0.09	12.89	0.25	1.05	16.80
P-14	536854.46	4244450.9	320	16.3	7.10	612	383.50	104.00	30.15	7.64	0.82	442.6	0.11	13.23	0.25	2.35	16.65
P-15	533778.22	4243949.5	421	14.1	7.18	371	228.10	78.44	7.86	3.88	0.29	236	0.05	6.90	0.24	1.86	6.17
P-16	531953.18	4241654.2	515	15.5	7.07	704	456.40	129.15	32.61	7.45	0.38	505.5	0.07	13.62	0.25	0.36	15.90
P-17	532639.37	4242360.4	420	14.8	7.62	333	188.60	57.77	10.81	4.58	0.41	201.6	0.05	8.54	0.24	0.86	8.80
P-18	528073.79	4241121.9	361	14.7	6.93	586	363.90	102.78	26.14	6.98	0.96	400	0.07	10.54	0.25	22.14	19.62
P-19	529676.18	4241815	485	12.3	7.05	859	535.00	139.83	45.74	11.74	0.75	605.3	0.14	29.10	0.26	0.29	25.22
P-20	523737.39	4241355.7	313	15.5	6.94	730	445.90	163.13	9.45	13.18	0.31	457.2	0.11	24.83	0.29	12.11	24.84
P-22	527515.44	4245869.2	619	11.9	7.74	258	155.80	50.63	7.17	3.22	0.31	200	0.05	5.01	0.24	1.92	6.10
P-23	527568.18	4245969.2	653	11.8	7.50	375	232.60	61.36	19.33	3.97	0.52	264.9	0.07	6.90	0.25	1.87	9.98
P-24	529968.4	4249117.3	1102	8.7	7.61	460	276.50	95.14	9.60	4.26	0.56	335.5	0.07	6.43	0.24	0.27	11.43
P-25	525151.6	4247406.2	523	14.0	7.65	460	279.30	80.70	19.10	6.73	0.61	335.7	0.06	11.46	0.25	0.55	12.38
P-26	525075.64	4244818	413	15.6	6.93	656	418.90	94.01	44.80	7.85	0.59	509.9	0.07	14.67	0.26	0.41	18.55
P-27	523314.61	4248350.3	279	13.4	7.25	516	310.60	101.54	13.93	7.89	0.59	347.7	0.07	12.87	0.25	0.71	17.06
P-28	520686.96	4250801	103	15.9	6.92	889	442.90	125.30	31.66	54.61	1.12	585	0.35	38.57	0.31	0.91	48.87
P-29	521466.57	4250378.3	144	15.4	6.62	891	557.20	204.58	11.36	17.11	0.90	598.2	0.09	20.89	0.31	1.10	48.26
P-30	530990.47	4244508	1027	12.4	7.28	511	321.50	103.82	15.19	6.64	0.74	380.8	0.08	11.71	0.24	1.35	13.61
P-31	532945.92	4246821.9	1116	10.7	7.93	212	122.00	38.68	6.19	3.39	0.35	138.6	0.05	5.03	0.24	0.61	9.94
P-32	529447.76	4245245.2	884	13.2	7.65	366	214.10	66.55	11.69	6.21	0.38	218.4	0.05	11.45	0.24	0.73	13.45
P-33	522115.78	4234555.4	138	17.3	6.59	497	284.40	83.35	18.58	5.62	0.59	337.6	0.08	8.73	0.25	4.53	10.14
P-34	524716.99	4233647.5	103	17.3	7.13	574	281.20	81.67	18.82	5.61	0.51	316.2	0.07	8.91	0.25	3.82	9.22
P-37	514473.47	4238298.8	163	17.7	7.10	633	371.00	134.39	8.69	9.44	2.32	337.6	0.81	23.25	0.27	32.51	18.96
P-39	518424	4248325	230	17.3	7.48	823	496.00	77.42	73.62	17.70	2.79	627.3	1.33	27.50	0.29	2.94	17.84
P-40	522613	4250025	274	14.4	7.18	699	438.40	144.99	18.64	12.86	0.70	493	0.48	15.10	0.26	0.34	24.38

Table A.3 Physical and chemical characteristics for well samples collected in September 2006

SEPTEMBER 2006 WELLS	**Spatial Coordinates**			**General Parameters**				**Major Cations**				**Major Anions**					
Sample Point	**X (m)**	**Y (m)**	**Z (m)**	**T (°C)**	**pH**	**EC (µS/cm)**	**Hardness (mg $CaCO_3$/L)**	**Ca^{+2} (mg/L)**	**Mg^{+2} (mg/L)**	**Na^+ (mg/L)**	**K^+ (mg/L)**	**HCO_3^- (mg/L)**	**Fl^- (mg/L)**	**Cl^- (mg/L)**	**Br^- (mg/L)**	**NO_3^- (mg/L)**	**SO_4^{-2} (mg/L)**
K-1	523170.6	4253339.7	59	14.8	7.33	580	317.7	102.2	15.2	10	0.8	346.9	0.05	13.39	< 0.05	7.61	12.57
K-2	528776.4	4253136	280	17.7	7.34	528	306.6	94.6	17.2	6.6	0.5	316.9	0.13	8.53	< 0.05	1.32	15.86
K-3	528082	4241260	388	17.2	7.04	805	443.6	96.6	49.3	12.2	1.4	456	0.11	14.8	< 0.05	14.48	28.72
K-5	525025.5	4238673.3	250	19.4	7.18	518	292.3	78.75	23.1	6.2	0.6	367.7	0.07	6.92	< 0.05	3.39	13.28
K-6	522050.3	4244518.6	212	18.9	6.94	630	341.3	104.9	19.3	15.7	2.1	388	0.23	15.65	< 0.05	6.07	14.78
K-7	521742.7	4243583.9	205	20.7	7.57	847	101.5	21.9	11.4	173.4	4.1	525.5	0.82	37.59	0.11	0.88	27.42
K-9	522485.1	4244456	244	19	7.03	833	456.6	158.5	14.9	14.9	0.5	380	0.07	27.02	0.07	34.32	65.44
K-10	524227.1	4243844.9	279	20	7.08	754	404.9	117.2	27.3	19.2	1.1	390.1	0.11	22.63	0.06	16.41	113.54
K-11	519419.6	4244075.3	246	21.4	7.31	698	227.1	41.6	30	65.1	21.1	412.6	0.54	20.68	0.07	1.31	13.74
K-13	514580.3	4248873.4	78	20	7.35	951	461.6	159.1	15.8	32.7	3.3	409.1	0.22	51.31	0.1	55.16	19.91
K-14	520575.3	4248363.7	173	19.4	7.21	1188	505.8	126.7	46.1	79.5	1.2	452.6	0.51	123.19	0.25	1.01	103.98
K-15	513555.1	4240337.9	131	18.5	7.3	775	373	124.1	15.4	27.7	1	354	0.49	37.68	0.06	10.55	32.3
K-16	515415.6	4240549.5	148	18.7	6.82	802	404.5	161.7	9	12.5	0.8	459.9	0.37	21.71	0.06	11.95	5.07
K-17	517469.5	4236984.1	139	20.7	6.96	671	365.7	121.5	15.2	10.8	1	404.3	0.22	13.22	< 0.05	13.4	5.44
K-18	512247.3	4236651.1	135	18.7	6.65	1780	639.8	162.6	56.9	102.4	11.2	190.5	< 0.01	447.66	0.45	344.44	256.28
K-19	512404.6	4239330.6	130	21.9	7.8	821	29.6	10.1	1.1	187.4	2.9	361.1	0.25	68.6	0.27	1.18	23.72
K-20	520216.1	4256708.8	42	20	6.88	750	382.5	127.4	15.7	22.1	1.7	396.9	0.47	27.93	0.09	19.2	12.31
K-21	520358.8	4254113.4	43	18.8	7.21	788	425.4	136	20.9	19	0.9	461.8	0.06	14.55	< 0.05	6.83	14.64
K-22	522239.7	4254792.9	58	21.9	7.33	1203	382.6	112.8	24.6	116.7	1	292.5	0.05	218.77	0.08	52.05	51.03
K-23	524322	4255072.6	94	26.5	7.6	616	339.8	104.2	19.4	10.5	1.4	303.5	0.13	26.69	< 0.05	21.97	49.37
K-25	526082.5	4254373.1	140	18.8	7.06	737	388.4	103.1	31.9	23	1.2	595.5	0.18	10.46	0.08	14.09	8.36
K-26	538403.5	4250833.5	252	18	7.42	650	365.4	107.7	23.5	12.7	1.8	393	0.03	16.85	< 0.05	2.55	12.79
K-27	538103.3	4253022.9	173	17.6	6.92	845	438.1	154.1	13.1	19.8	2.4	347.7	0.05	52.35	< 0.05	62.26	94.98
K-28	533901	4255130.2	218	17.4	7.11	621	351.3	120.3	12.4	9.1	0.8	287.1	0.44	16.47	1.51	24.98	20.11

Table A.4 Physical and chemical characteristics for spring samples collected in September 2006

SEPTEMBER 2006 SPRINGS	**Spatial Coordinates**			**General Parameters**				**Major Cations**				**Major Anions**					
Sample Point	**X (m)**	**Y (m)**	**Z (m)**	**T (ºC)**	**pH**	**EC (µS/cm)**	**Hardness (mg $CaCO_3$/L)**	**Ca^{+2} (mg/L)**	**Mg^{+2} (mg/L)**	**Na^{+} (mg/L)**	**K^{+} (mg/L)**	**HCO_3^{-} (mg/L)**	**Fl^{-} (mg/L)**	**Cl^{-} (mg/L)**	**Br^{-} (mg/L)**	**NO_3^{-} (mg/L)**	**SO_4^{-2} (mg/L)**
P-1	517710.72	4251486.2	268	16.4	7.8	462	243.6	93.2	2.7	8.4	0.3	227.9	0.13	14.85	0.07	14.68	49.21
P-3	517817.12	4252270.4	116	19.9	7.72	1574	580.1	212.2	12.3	95.6	8.7	338	0.05	110.99	0.16	240.96	89.29
P-5	526702.61	4255641.4	194	21.7	7.46	1105	635.3	237.1	10.7	18.3	0.4	623.7	0.09	28.54	0.1	0.59	28.1
P-6	537800.38	4249025	273	17	7.4	485	283.7	87.3	16	5.2	0.4	324.8	0.06	6.09	< 0.05	1.97	6.04
P-7	534532.23	4251955.4	650	12.7	7.8	369	206.7	77.7	3.1	3.3	0.5	223	< 0.01	4.7	< 0.05	0.79	6.91
P-8	534687.58	4250879.7	801	12.4	7.65	335	190.1	66.9	5.6	2.7	0.3	213.9	< 0.01	4.01	< 0.05	0.86	5.96
P-9	533970.92	4249150.5	861	12	7.65	253	141.7	44.6	7.4	0.1	0.3	168.3	< 0.01	3.77	< 0.05	1.05	5.74
P-10	533402.12	4249728.4	954	13.1	7.86	286	143.5	50.1	4.5	2.6	0.1	164.4	0.07	3.82	< 0.05	1.32	4.5
P-11	533325.97	4249740.3	990	12.3	7.99	243	125.7	43.4	4.2	3.3	0.9	143.9	< 0.01	3.88	< 0.05	4.32	4.52
P-13	539224.85	4246452.4	401	19	7.55	672	398.8	97.3	37.9	6	0.4	417.4	0.04	8.07	< 0.05	1.82	11.28
P-14	536854.46	4244450.9	320	18.1	7.03	596	349.2	89.4	30.7	7	0.9	378.6	< 0.01	8.02	< 0.05	2.07	10.26
P-15	533778.22	4243949.5	421	14.4	7.47	344	193.3	63.2	8.2	3.9	0.3	473.7	< 0.01	4.58	< 0.05	1.95	3.82
P-16	531953.18	4241654.2	515	17.6	6.85	693	399.6	120.3	24.2	7.1	0.3	444	0.04	9.23	< 0.05	0.77	8.53
P-17	532639.37	4242360.4	420	17.5	7.74	281	152.7	47.7	8.2	5.1	0.3	203.9	0.03	10.04	< 0.05	0.74	5.16
P-18	528073.79	4241121.9	361	20.1	6.95	637	283.8	102.1	22.5	6.7	0.6	345.6	0.06	8.81	0.04	16.7	15.48
P-19	529676.18	4241815	485	22.4	6.62	937	548.7	129.4	54.9	12.9	1.3	542.17	0.17	21.48	< 0.05	0.52	35.69
P-20	523737.39	4241355.7	313	19.3	6.9	790	435.5	158.5	9.7	14.3	0.1	456.7	0.25	50.84	0.13	13.5	32.5
P-22	527515.44	4245869.2	619	15.4	7.84	341	148.9	48.5	6.8	3.6	0.4	190.8	< 0.01	5.58	< 0.05	2.41	5.96
P-23	527568.18	4245969.2	653	14.7	7.6	431	250	63.7	22.2	4.5	0.5	279.8	< 0.01	5.51	< 0.05	1.38	9.3
P-24	529968.4	4249117.3	1102	16.5	8	518	305.2	104.5	10.8	6.1	1	337.4	0.05	5.2	< 0.05	0.84	10.64
P-25	525151.6	4247406.2	523	14	8.05	503	290.8	82.4	20.7	7.3	0.5	310	< 0.01	8.76	< 0.05	0.84	10.22
P-26	525075.64	4244818	413	19.9	7.58	639	371.7	81.9	40.7	7.8	0.8	409	< 0.01	9.96	< 0.05	0.61	13.34
P-27	523314.61	4248350.3	279	22.7	7.36	652	360.7	117.3	16.5	9.6	0.7	378.3	0.07	11.02	< 0.05	0.62	13.17
P-28	520686.96	4250801	103	20.1	6.92	1002	438.1	117.8	35.1	73.4	1.5	516.5	0.21	36.04	0.09	0.32	52.01
P-29	521466.57	4250378.3	144	23.4	6.76	950	543.7	197.9	12.1	20	1.1	596.5	0.06	19.77	0.08	0.31	32.24
P-30	530990.47	4244508	1027	17.3	7.13	543	319.6	100.6	16.7	7.4	0.8	349.1	0.05	8.49	< 0.05	1.06	9.82
P-31	532945.92	4246821.9	1116	11.1	8.03	266	131.7	41.4	6.9	3.6	0.3	157.1	< 0.01	3.91	< 0.05	1.01	8.63
P-32	529447.76	4245245.2	884	15.7	7.48	404	218.1	68.4	11.5	7.1	0.8	251.5	0.05	7.79	< 0.05	0.71	9.18
P-33	522115.78	4234555.4	138	22.5	7.44	489	282.1	81.8	19	5.9	0.7	298.5	< 0.01	6.02	< 0.05	4.37	8.03
P-34	524716.99	4233647.5	103	18.9	7.28	480	277.6	79.9	19	5.8	0.6	302	0.04	6.15	< 0.05	2.71	7.05
P-37	514473.47	4238298.8	163	18.8	7.19	712	394	142.2	9.6	10.8	1.8	396.5	0.4	20.84	0.06	24.84	15.07
P-39	518424	4248325	230	18.3	7.75	875	495.1	77.6	73.3	19.5	3	572.6	1.01	20.37	0.07	2.67	17.31
P-40	522613	4250025	274	19.5	6.9	736	412.3	135.4	18.1	18.1	0.9	453.1	0.03	14.94	< 0.05	0.86	22.56