

EVALUATION OF METAL CONCENTRATIONS IN GROUNDWATER
NEARBY SOMA
COAL-FIRED POWER PLANT

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GIUMA SASI

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Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Hüseyin İşçi
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Prof. Dr. Semra G. Tuncel
Supervisor

Examining Committee Members

Prof. Dr. O. Yavuz Ataman (METU, CHEM.) _____

Prof. Dr. Semra G. Tuncel (METU, CHEM.) _____

Prof. Dr. Şahinde Demirci (METU, CHEM.) _____

Prof. Dr. R. Sezer Aygün (METU, CHEM.) _____

Assoc. Prof. Dr. Gülen Güllü (Hacettepe Univ.) _____

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GIUMA SASI

ABSTRACT

EVALUATION OF METAL CONCENTRATIONS IN GROUNDWATER NEARBY SOMA COAL FIRED POWER PLANT

Giuma Sasi

M.S., Department of Chemistry

Supervisor: Prof. Dr. Semra G. Tuncel

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In this work, metal pollution in groundwater near by Soma coal-fired power plant was investigated. Coal combustion results in huge amounts of bottom ash from which metals can originate and migrate to groundwater and pollute it. Forty groundwater samples were collected from water wells in an area near by the power plant to determine 14 metals namely; Na, Ca, K, Mg, Al, Ba, Fe, Zn, Cu, Pb, Cr, Cd, Ni and V. Samples were collected in polyethylene bottles, the pH of the water was measured. Then, the samples were acidified and stored to be analyzed. FAAS, FAES, GFAAS and ICP-AES were used to determine the elements. The results were compared with the WHO, the Turkish and EC guidelines for drinking water quality. Fe concentrations in 12 wells were higher the three guidelines. Zn concentrations in 5 wells were higher than the EC guidelines, but not higher than the Turkish guidelines. Pb concentrations was less than all guilelines but it was relatively high in

8 wells. The other anthropogenic elements were lower than all guidelines but these metals tend to accumulate and they will exceed the guidelines overtime. Enrichment factor calculations showed that the anthropogenic elements were enriched in the regions close to the ash piles pointing out that the ash piles are the main source of these elements. Factor analysis was applied and four main factors of the determined metals were found indicating that the power plant and the ash piles are the main source for the anthropogenic elements.

Keywords: metals, power plant, ashpiles, groundwater.

ÖZ

SOMA TERMİK SANTRALİ YAKININDA YERALTI SULARINDAKİ METAL KONSANTRASYONLARININ DEĞERLENDİRİLMESİ

Giuna Sasi

Yüksek Lisans, Kimya Bölümü

Tez Danışmanı: Prof. Dr. Semra G. Tuncel

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Bu çalışmada, Soma Termik Santrali çevresindeki yeraltı sularında metal kirliliği araştırılmıştır. Kömürün yakılması ile oluşan büyük miktardaki dip külü metallere kaynaklık etmekte ve bu metaller yeraltı sularına geçerek kirliliğe sebep olmaktadır. Santral çevresinde bulunan 40 kuyudan örnekler alınmış ve bu örneklerde 14 metalin (Na, Ca, K, Mg, Al, Ba, Fe, Zn, Cu, Pb, Cr, Cd, Ni ve V) tayini yapılmıştır. Polietilen şişelerde toplanan ve pH değeri ölçülen örnekler asitlendirilerek analiz için saklanmıştır. Elementlerin tayini için Alevli Atomik Absorbsiyon, Alevli Atomik Emisyon Spektrometresi, Grafit Fırınlı Atomik Absorbsiyon Spektrometresi ve Inductively Coupled Plasma-Atomik Emisyon Spektrometresi (FAAS, FAES, GFAAS ve ICP-AES) teknikleri kullanılmıştır. Elde edilen sonuçlar WHO (Dünya

Sađlık Örgütü) ve EC (Avrupa Birliđi) yönergelerinde verilen sınır deđerlerle karşılaştırılmıřtır. Oniki kuyuda tespit edilen Fe konsantrasyonu, her iki yönergedeki deđerden yüksektir. Beř kuyuda gözlenen Zn konsantrasyonu, EC yönergesinden yüksektir. Pb konsantrasyonu her iki yönergedeki sınırdan düşük olmasına rađmen 8 kuyuda gözlenen deđerler, diđerlerine oranla daha yüksektir. İnsan kaynaklı diđer elementlerin konsantrasyonları yönergelerdeki deđerlerden düşüktür, fakat birikme eğilimi olan bu metallerin konsantrasyonları zamanla sınır deđerleri geçecektir. Zenginleşme faktörü hesaplamaları, kül yığınlarına yakın bölgelerde tespit edilen insan kaynaklı elementlerin konsantrasyonlarının zenginleştiđini göstermiřtir. Bu da söz konusu elementlerin kaynađının bu kül yığınları olduđunu kanıtlamaktadır. Elde edilen veri setine faktör analizi uygulanmıř ve insan faaliyetlerinden oluşun elementlerin kaynađının termik santral ve kül yığınları olduđunu gösteren beř faktör tespit edilmiřtir.

Anahtar Kelimeler: Metaller, yeraltı suyu, elektrik santrali, kül yığınları

To My Wife, Children and Brothers

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CHAPTER 1

INTRODUCTION

1.1. Groundwater Pollution

Groundwater pollution, often due to anthropogenic activities is a worldwide problem. Such contamination of groundwater resources potentially poses a substantial risk to local resource users and to the natural environment. Assessing risk involves identifying the hazard associated with a particular occurrence, action or circumstance and determining the probability of that hazard occurring (Al-Busaid, 2001).

There are three categories in recognizing the threat from environmental hazards: hazard to people (e.g. death, disease), hazard to property (e.g. damage or destruction) and hazard to the environment (e.g. loss of biodiversity) (Smith, 2001).

Pollution hazards result from the overlap of environmental, technological and social processes. In the case of groundwater pollution, the environmental factors controlling the hazard (and accordingly the risk) are the rates of progression of the polluted plume and the remediation of pollution through processes of precipitation, adsorption or

attenuation. Technological processes of the hazard invariably pertain to the source of pollution and the characteristics of that source (i.e. the process of pollution generation and the nature, concentration and volume of pollutants produced). Social factors include the action of individuals or communities that increase their exposure and their susceptibility to the hazard (Crosbois and Meybeck, 2005).

As to the nature of pollutants, metals are considered to be very dangerous pollutants to groundwater. They are known to cause serious human health problems and environmental damage (Tamasi and Cini, 2004).

1.2 . Sources of Metals

There are two sources of metals: Natural and Anthropogenic. Natural sources include decay of rocks and earth layers that contain metal compounds and fossil fuels and volcanic eruptions (Goodarzi and Muki, 2000). Anthropogenic sources are: combustion of fossil fuels, mining and smelting operations, processing and manufacturing industries and waste disposal including dumping, release of domestic waste and scrap metal handling (Brown and Peak, 2005).

Coal combustion is one of the most important processes that produce metals which can pose a pollution potential to the environment and groundwater in particular. Once released to the environment, metals can remain for decades, increasing the likelihood of human exposure (Sandroni and Clare, 2003).

1.3. Coal Fired Power Plants as Source of Metals

Coal fired power plants are very important source of metals to the environment. In addition to gases and fly ash emitted from these plants, the solid waste (known as the bottom ash) is a major source for metals. Bottom ash is considered a very important source of metals to groundwater (Santoyo and Surendra, 2000).

The presence of bottom ash deposits derived from coal combustion processes in a power plant could be a major source of metallic pollutants. Metals such as (Na, K, Ca, Ba, Al, Mg, Fe, Cu, Zn, Pb, Cd, Cr, V, and Ni) can have their origin from bottom ash. These metals may migrate to groundwater aquifers and pollute them resulting in a harmful effects to the environment and public health (Özturk and Yilmaz, 1999).

1.4 . Leaching Characteristics of Solid Waste From Coal Power Plants

Use of low quality coals with high ash content in power plants results in huge quantities of both fly and bottom ashes to be disposed off. A main problem related to coal ash disposal is the metal content of the residue. In this regard, experimental results of numerous studies indicate that metals especially toxic trace metals may leach when ashes are in contact with water and contaminate groundwater. The extent of the metals in ash depends on both the mineralogy and particle size distribution of the coal being burnt and combustion temperature. Although the extent of the metals in the ash can be optimized by controlling the particle size and combustion temperature, such procedures

could be very costly. Furthermore, since the coal mineralogy is generally constant for a given coal deposits, not much can be done to control the metal content of the ash. However, leaching of metals to groundwater from ash can be prevented by adequate waste disposal techniques. The leached metals from ash may lead to environmental, health and land-use problems (Baba and Kaya, 2004).

1.5 . Environmental and Health Effects of Metals

Many metals are natural components of the earth's crust. They can not be degraded or destroyed. Metals especially heavy ones are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down or excreted. The ecosystem is affected if groundwater is polluted by metals because groundwater is used for irrigation. High metal content of water is known to affect growth and yield of the crops (Costa and Rydin, 2001) Trace amounts of metals are common in water, and these are normally not harmful to human health. In fact, some metals are essential to sustain life. Calcium, magnesium, potassium, and sodium must be present for normal body functions. Copper, iron, manganese, selenium, and zinc are needed at low levels as catalysts for enzyme activities. However, drinking water containing high levels of these essential metals, or toxic metals such as aluminum, arsenic, barium, cadmium, chromium, lead and selenium may be hazardous to human health.

People are exposed to pollution from groundwater directly by drinking or indirectly by consuming crops irrigated by polluted water (Ekpo and Ibok, 1999).

- **Aluminum**

Aluminum is the most abundant metal in the earth's crust and therefore is likely to be present at some level in most ground waters. The correlation of aluminum consumption to nervous system disorders is currently being researched (Lamley and Stewart, 1989).

- **Barium**

Barium at high doses can cause damage to the heart, blood vessels, and nervous system (Lamley and Stewart, 1989).

- **Cadmium**

Cadmium may interfere with the metallothionein's ability to regulate zinc and copper concentrations in the body. Metallothionein is a protein that binds to excess essential metals to render them unavailable. When cadmium induces metallothionein activity, it binds to copper and zinc disrupting the homeostasis levels. Cadmium is also known to cause kidney damage (Charlesworth and Lees, 1999).

- **Calcium**

Calcium is necessary for good health. Drinking water containing calcium may provide a significant portion of the required daily intake to prevent such ailments as osteoporosis, hypertension, and cardiovascular disorders (Lemley and Stewart, 1989).

- **Chromium**

Low-Level exposure to chromium can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and damage to circulatory and nerve tissue. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium (Boucher and Dorata, 1986).

- **Copper**

Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation (Morrison and Ellis, 1990).

- **Iron**

The human body has the ability to store iron; however, too much iron in the body may be linked to heart diseases, cancer and diabetes (Charlesworth and Lees, 1999).

- **Lead**

Lead is known to cause serious conditions such as anemia, brain damage and kidney failure. And, because of size and charge similarities, lead can substitute for calcium and included in bones; children are especially susceptible to this effect (Ekpo and Ibok, 1999).

- **Magnesium**

Magnesium is quickly expelled from the bodies of healthy humans. People with kidney disease, however, may suffer from hypertension, confusion, muscle weakness, and coma (Woodruff, 1990).

- **Nickel**

Small amounts of nickel are needed by the human body to produce blood cells, however, in excessive amounts, it can become mildly toxic. Short-term over exposure to nickel is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart and liver damage, and skin irritation (Morrison and Ellis, 1990).

- **Sodium**

Sodium at normal intake levels is beneficial to healthy adults. However, people with heart disease or hypertension should reduce sodium intake to lower the blood pressure (Morrison and Ellis, 1990).

1.6. Scope of this Work

As stated in section 1.4, the use of coals with high ash content in power plants results in huge quantities of both fly and bottom ash from which metals can leach to groundwater. Soma Power Plant consists of three units, they burn about 41000 tons/day of coal with an ash content of 40%, so the plant is producing 16400 ton/day of ash (Karayigit and Gayer, 2000).

Forty groundwater samples were collected from near by Soma Power Plant to be analyzed for Na, Ca, K, Mg, Ba, Al, Fe, Zn, Cu, Pb, Cr, Cd, Ni and V in order to:

1. Evaluate the concentrations of these metals in the water wells near by Soma Power Plant.
2. Evaluate the environmental impact of the power plant.
3. Determine the water quality with respect to the EC, the WHO and the Turkish guidelines for drinking water quality.

1.7. Literature Review

There are some studies about the determination of metals in groundwater, coal, ash and soil near coal fired power plants.

1.7.1. Related research in Kütahya, Turkey

N. Öztürk and Y. Yılmaz (1998) studied trace elements levels in drinking water near Tunçbilek Coal-fired Power Plant in Kütahya, Turkey. They analyzed groundwater samples collected from eight sampling points to determine the concentrations of eight metals (As, Hg, Pb, Cd, Cu, Cr, Fe and Zn). They aimed to evaluate metal pollution levels in these samples to ascertain the water quality for human consumption using the European Community (EC) and the World Health Organization (WHO) guidelines.

Öztürk and Yılmaz found that the concentrations of Cd, Hg, Pb and Zn are within the EC and WHO guidelines. But, although the concentrations of Cr and Fe were below the concentrations specified by both guidelines, they were very close to them. The concentration of As was higher than that specified by both guidelines in two samples and very close to them in the rest of the samples.

They concluded that the elevated concentrations of Cr, Fe and especially As could be a result of leaching from the ash ponds of the power plant. They recommended that

periodic sampling should be conducted for continuing evaluation of the possible trend in concentrations of metals overtime.

1.7.2. Related research in Mugla, Turkey

Alper Baba (2001) studied the concentrations of twenty three trace elements and seven major elements in ash and soil samples near Yatagan Coal-fired Power Plant in Mugla, Turkey. He analyzed fifteen bottom and fly ash and nine soil samples to determine twenty three trace elements (Ag, As, Ba, Be, Bi, Cd, Co, Cu, Cr, La, Mn, Mo, Ni, Pb, Sb, Sn, Sr, Ti, V, W, Y, Zr and Zn) and seven major elements (Al, Ca, Na, K, Mg, Fe and P) in order to evaluate the effect of coal combustion and the residue produced from it on soil and hence on groundwater, plants, animals and humans.

Baba found that toxic trace element concentrations exhibited an increase in the order: fly ash> bottom ash> soil, which indicated that Yatagan Power Plant polluted the surface soil in the Yatagan plain. The concentrations were the highest close to the disposal site and decreased with distance.

Baba recommended that better disposal techniques be implemented to avoid subsurface contamination.

1.7.3. Related research in other countries

1.7.3.1. Mexico

E. Santoyo and Surendra Verma (2000) studied the effect of a coal fired power plant on the groundwater in Mexico. They analyzed fifteen water samples collected from around ash piles of a power plant to determine Pb, Cu, Cd, Co, Zn and Ni.

Santoyo and Verma found that the concentrations of Cd in nine samples and the concentration of Ni in one sample were higher than the guidelines of WHO. The concentration of Pb in the samples was close to WHO guidelines. The concentrations of other elements were lower than the WHO guidelines.

They concluded that the elevated concentration of Cd, Ni and Pb could have resulted from ash deposits and recommended that further studies be conducted to monitor the metal concentrations in groundwater near this power plant.

1.7.3.2. Canada

F. Goodarzi and P. K. Muki (2000) studied the possibility of metal leaching from coal seams to groundwater in the Sydney Basin, Nova Scotia, Canada. They analyzed 25 drinking water samples collected from various locations in the Sydney area to determine the concentrations of 7 major elements (Na, K, Al, Ca, Mg, Fe and Zn) and 13 trace elements (Mn, As, Ba, Be, B, Cd, Cr, Co, Cu, Ni, Pb, Se and V). They used the

guidelines of health and welfare Canada (1996) to assess the quality of the drinking water.

They found that the concentrations of eight samples have higher concentrations in Mg and two samples have higher concentrations of Pb than the guidelines. Most samples have slightly elevated concentrations of Cu and Zn but within the recommended guidelines. Water samples were found to have low concentrations of all other elements determined.

Goodarzi and Muki concluded that these metals may have leached from the coal seams within the Sydney Basin.

1.7.3.3. Italy

Gabriella Tamasi (2003) studied trace elements levels in drinking water in Siena and Grosseto districts, South Tuscany, Italy. She analyzed twelve groundwater Samples to determine the concentrations of twelve metals (Al, As, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pd). She aimed to evaluate metal pollution levels in these samples to assess the quality of the drinking water for human consumption in comparison with the Maximum Allowable Concentration (MAC) set by the Italian Ministry of Health.

Tamasi found that the concentration Al, V, Mn, Co, Ni, Cu, Zn, Cd, and Pb are below the MAC. The concentration of Fe in eight samples was higher than the MAC. The

concentration of As in one sample was higher than the MAC and lower than the MAC, but relatively high in the rest of the samples.

She recommended that the elevated concentrations of As and Fe are of great risk to human health and should be dealt with. And there is a need to increase the number of sampling sites in order to monitor the water quality more effectively. She concluded that the elevated concentrations could be due to human activities in that area.

1.7.3.4. Portugal

C. Costa and C. Jesus Rydin (2000) studied the concentrations of four metals (As, Hg, Pb and Zn) in the soil and groundwater in Estarreja, Portugal. Estarreja is an industrial area. They analyzed ten water and soil samples in order to evaluate the effect of the industrial activities on soil and groundwater and hence on plants, animals and humans.

They found that the concentrations of these metals in the soil were higher than the EC guidelines. Much higher concentrations were found in the sediments and in water streams several kilometers away from the pollution source. They also found that the concentration increased with depth reaching groundwater.

They recommended that further studies should be conducted covering a wider and deeper area and more samples.

1.7.3.5. Zambia

C. J. Von der Heden and M. G. New (2000) studied the levels of ten elements (Al, Fe, Mn, Cd, Co, Cr, Cu, Ni, Pb and Zn) in four ground water samples in order to evaluate the quality of the drinking water in Copperbelt, Zambia. They aimed to assess the risk to the environment and public health posed by the contamination of groundwater due to human activities.

They found that the concentrations of Co, Ni and Zn were high in the water samples. The concentrations of the other elements were within the WHO guidelines.

They concluded that groundwater pollution poses great risk to public health in the region. They recommended that further research and remediation should be carried out.

CHAPTER 2

EXPERIMENTAL

2.1. Sampling

2.1.1. Sampling Location

Sampling area is in the vicinity of Soma Coal-Fired Power.

2.1.2. Sampling Strategy

Soma power plant is a coal-fired plant. The ash produced from coal combustion is transported by mixing ash with water and pumping the mixture to an area about three km away from the plant and is being deposited there. The huge ash piles cover an area of about 3 km². Forty groundwater samples were taken from forty different wells which belong to the local residents. The pumps used by the residents to get the water out were used to take the samples. The pumps were run for about 15 minutes before taking the samples to washout any pollutants and leached metals. The samples were taken from the south, southeast and southwest of the ash piles because there were no residents in the other directions and thus there was no way to get groundwater. The ash piles can be a

source for metals to groundwater aquifers. This water is used for drinking and irrigation purposes. Water wells have almost the same depth about 8 m deep and the distance from the ash ponds varied from 1 km to about 5 km. Fig 2.1 shows a map of the town of Soma with the sampling points on it. Fig 2.2 shows a topographic map of Soma. Samples were collected in 500 ml high density polyethylene bottles. These bottles were washed with distilled water and then soaked in 30% (V/V) technical grade nitric acid for twenty four hours. Then, they were filled with 30% (V/V) Merck 65% purity nitric acid and left overnight. Bottles were then rinsed with deionized water ten times. This was done to avoid contamination because the concentrations of most metals in groundwater were expected to be in the trace level. Then the pH of the samples was measured. The pH was between 6.7 and 7.2. The samples were then acidified by adding 1% (V/V) Merck 65% purity nitric acid. Samples were then stored to be analyzed later.

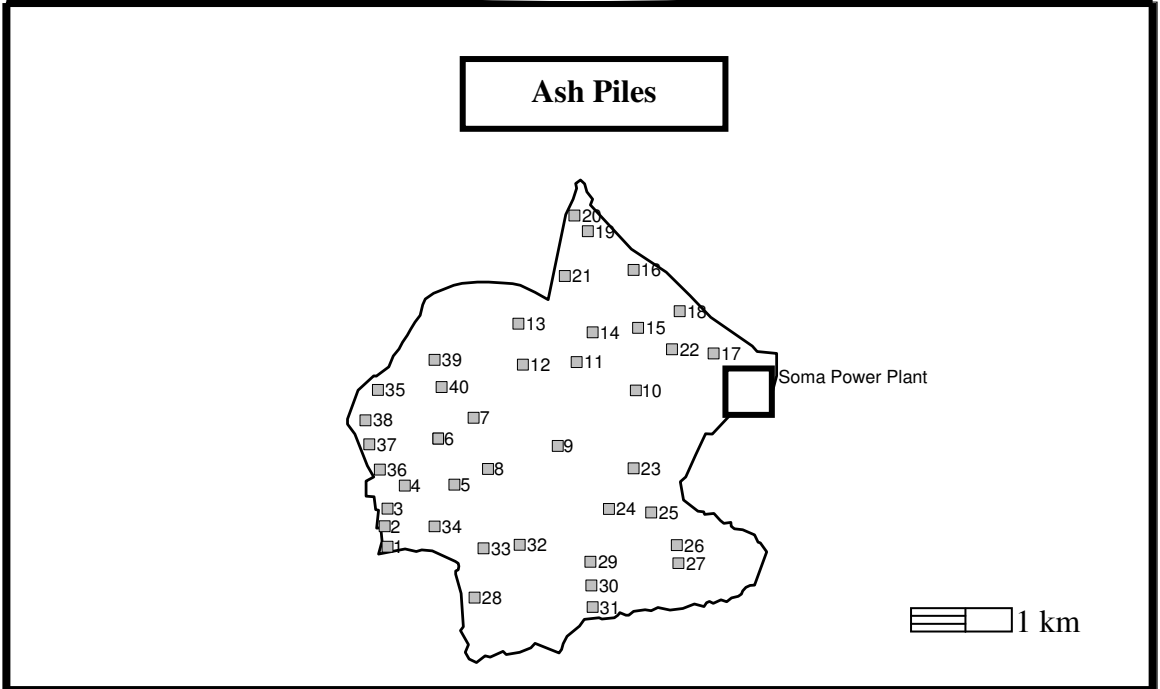


Fig 2.1 Map of Soma showing the sampling points

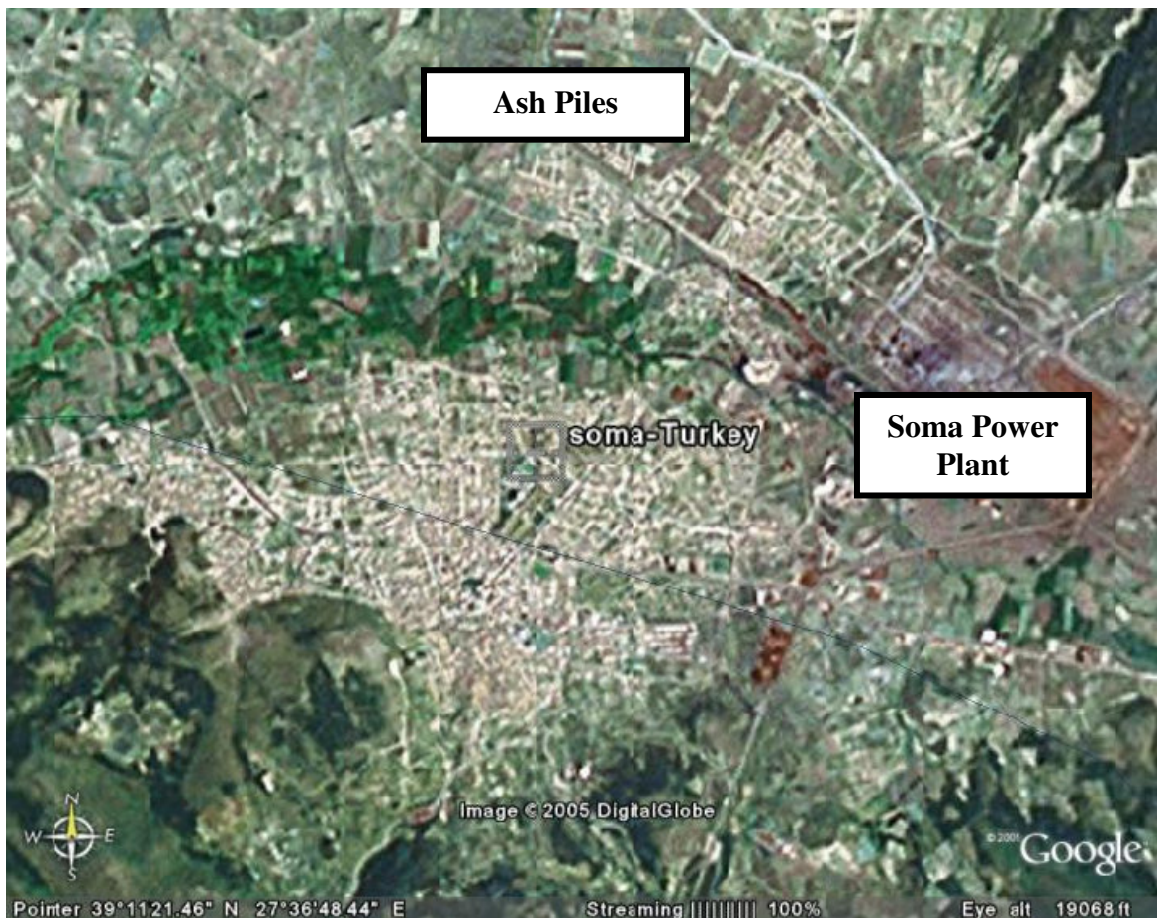


Fig 2.2 Topographic map of Soma

2.1.3. Reagents and Water

For metal determination of environmental samples it is essential that ultra-pure water is used for the preparation of standards, samples and blanks. A Barnstead ultra-pure water system was used for deionization of mono-distilled water, with four cartridges; two for ion removal, one for organic and one for particulate matter removal. The produced deionized water finally had a resistance of 18.3 M Ω . All acids used were MERCK suprapure grade in order to prevent contamination.

2.2. Analytical Techniques and Methodologies Used

2.2.1. Flame Atomic Absorption and Emission Spectrometers

Flame Atomic Absorption Spectrometer (FAAS) is a standard laboratory analytical tool for metals. The metal is extracted into a solution and then vaporized into a flame. A light beam with a wavelength absorbed by the metal atoms of interest passes through the vaporized sample. The emission wavelength and absorption wavelength of any metal (atomic vapor) perfectly match and so, Hollow Cathode Lamp (HCL) of the metal in question is used as a light source in FAAS technique. The monochromatic light intensity attenuated by the analyte atoms at the flame is proportional to its amount and the attenuation is monitored by a photomultiplier tube and Beer's law is applied to quantify the amount present (Öztaş, 2001).

In flame emission spectrometry, the metal is extracted to a solution and then vaporized in a flame. The metal is excited by heat to an upper electronic excited state. When the metal returns to the ground state, it emits light. The wavelength of the light emitted is characteristic of the species that emits it, and the emission intensity is proportional to the concentration of the species present.

Mg and Cu were determined using (FAAS). Na, Ca and K were determined using (FAES). A Perkin Elmer 1100B model atomic absorption spectrometer was used for FAAS and FAES analyses. The instrumental parameters for the FAAS and FAES optimized for the elements are shown in Table 2.1 These parameters had been optimized

by previous researchers (Öztaş, 2001). Since Ca is relatively difficult to be excited by air/acetylene flame, nitrous oxide/acetylene flame was used in the determination of Ca since it gives a higher temperature than air/acetylene flame.

Before starting the analysis, the instrument was allowed to warm up for about thirty minutes. Then the light path was adjusted to obtain maximum sensitivity. Hollow Cathode Lamp (HCL) was used as a light source in the FAAS. The sample aspiration flow rate was 6-8 ml/min. The sensitivity check was performed by standard solutions with concentrations specified by the manufacturer. Aqueous calibration was used for the construction of the calibration curve of the above mentioned elements, except for Cu where standard addition method was used.

Table 2.1. Analytical Parameters for the FAAS and FAES Techniques

Element	Mg	Cu	Na	K	Ca
Technique	FAAS	FAAS	FAES	FAES	FAES
Flame	A/Ac	A/Ac	A/Ac	A/Ac	N. Ox/Ac
Lamp Current, mA	8	13	–	–	–
λ , nm	285.2	324.8	589.1	766.5	422.7
Slit Width, nm	0.7	0.7	0.2	0.7	0.2
Air Flow, ml/min	9.0	9.5	9.5	8.5	9.5
Acetylene, ml/min	3.0	2.2	3.7	3.0	
N. Ox, ml/min	–	–	–	–	4.5

A: Air, Ac: Acetylene, N. Ox: Nitrous oxide

2.2.2. Graphite Furnace Atomic Absorption Spectrometer

Graphite Furnace Atomic Absorption Spectrometry (GFAAS) has long been used as an analytical method for the determination of trace metals in environmental and biological samples due to its reliability, sensitivity, low detection limits and relatively low cost.

GFAAS is a very sensitive technique and trace metals with concentrations as low as $\mu\text{g/l}$ can be determined accurately (Topal, 2000). For this reason, in the groundwater samples, Pb, Cr, Cd, V and Ni were determined using GFAAS because they were at trace levels. In this work, a Perkin Elmer 1100B model, with HGA 700 electrothermal atomizer, graphite furnace atomic absorption spectrometer was used to determine the concentration of the above mentioned trace metals.

With electro thermal atomizers, a discrete sample is deposited, and the atomizer is electrically heated to produce a transient cloud of atomic vapor. The absorption of the light emitted by the Hollow Cathode Lamp by this atomic vapor is probed to determine the amount of analyte in the sample by applying Beer's law. Instrumental settings for each element are shown in Table 2.2.

Table 2.2. Parameters used in GFAAS Analysis

Element	Cd	Pb	Ni	V	Cr
Graphite tube type	uncoated	uncoated	p-coated	p-coated	p-coated
λ , nm	228.7	283.3	232.0	318.4	357.8
Slit Width, nm	0.7	0.7	0.2	0.7	0.7
Injection Volume, μ l	30	30	30	30	30
Lamp Current, mA	8	11	21	20	29

Commercial electrothermal atomizers are relatively small, electrically heated tubular furnaces. The furnace is usually a graphite tube that is 1 cm to 3 cm in length and 3 to 8 mm in diameter. The position of the furnace assembly is adjusted so that the light beam from the source passes through the graphite tube. A hole in the tube allows typical 5-50 μ l of blank, sample, SRM or standard solutions to be injected manually with a pipette or automatic injector. Each end of the graphite is connected to a high-current programmable power supply through water cooled contact. Typically the furnace is heated in four stages, in which the temperature of the furnace is progressively increased by passing larger current through the atomizer tube. The first step is the drying step, in which a sufficient current causes the temperature to rise to 90°C. It is maintained there for few seconds. Then the temperature is increased to 130 °C and maintained for also few seconds. In this step, the solvent is evaporated leaving a solid residue in the furnace. The temperature is optimized to evaporate the solvent as rapidly as possible without

spattering. The second step is the ashing step, in which the temperature is raised to 700-1600 °C, and maintained for few seconds. In this step, organic matter in the sample is ashed and converted to CO₂ and H₂O, and volatile inorganic components are vaporized. The third step is the atomization step. Here the current is increased to raise the temperature to 1600-2550°C and maintained there for few seconds. In this step, the analyte is vaporized and atomized to produce atomic vapor that is probed to the source. The final step is the cleaning step in which the temperature is raised to 2665°C and kept there for few seconds. In this step the analyte is cleaned from the tube for the next analysis.

During the analysis of refractory and carbide forming elements like Ni and Cr, memory effects from graphite tube were observed. When the concentrations of Ni and Cr are high, they are deposited at the colder regions of the graphite tube and appear as a memory effect during following injections. Using additional cleaning step in the temperature program of the instrument for about 5 seconds after the completion of all temperature program steps solved this problem. The current and duration of each step can be adjusted so that the conditions are optimized for each element, type of sample, and sample size. Typically the whole sequence takes 45-90 seconds (Crouch, 1988). The temperature program used for this work is shown in Table 2.3. These parameters were optimized by previous researches (Topal, 2000).

The carrier gas used in this analysis was Ar and during the drying, ashing and cleaning steps, the internal gas flow rate was 300ml/min. The role of the Ar is to drive the

unwanted materials out of the tube as well as providing inert atmosphere; therefore the gas flow was cut off during the atomization step.

Table 2.3. Temperature Program for GFAAS for the Trace Element Determination

Element	Step	Drying 1	Drying 2	Ashing	Atomization	Cleaning 1	Cleaning 2
Cd	Furnace temp., °C	90	130	700	1600	2000	
	Ramp time, sec.	5	10	10	0	2	
	Hold time, sec.	15	10	25	6	5	
Cr	Furnace temp., °C	90	130	1600	2500	2550	2650
	Ramp time, sec.	5	10	15	0	2	2
	Hold time, sec.	15	20	20	5	5	4
Ni	Furnace temp., °C	90	130	1400	2500	2550	2650
	Ramp time, sec.	5	10	10	0	2	2
	Hold time, sec.	15	15	25	5	5	4
Pb	Furnace temp., °C	90	130	750	1800	2100	
	Ramp time, sec.	5	10	10	0	2	
	Hold time, sec.	15	15	25	5	8	
V	Furnace temp., °C	90	130	1200	2650	2650	
	Ramp time, sec.	5	10	10	0	2	
	Hold time, sec.	15	15	25	7	5	

When a new pyrocoated graphite tube was first used, it has been conditioned using a special temperature program given by the manufacture in order to obtain maximum analytical and mechanical lifetime. The temperature program for conditioning a new pyrocoated graphite tube is given in Table 2.4.

Table 2.4 Temperature Program for Conditioning of Pyrocoated Graphite Tubes

Step	Furnace Temp. °C	Ramp time, Sec.	Hold time, sec.
1	2650	60	2
2	20	1	20
3	2650	10	10
4	20	1	20
5	2650	10	10
6	20	1	20
7	2650	10	10

2.2.3. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

When analysis is based upon the atomic emission principle, there is a distinct advantage in using a high temperature source. By doing so, chemical bonds can be broken down and their problems are overcome. At this time, a high degree of excitation and ionization can be achieved. In this way, good selectivity and sensitivity for elemental analysis may

be obtained (Alusine, 2001). Over the last 25-30 years, spectroscopic sources based upon the use of high temperature plasma have been developed to fulfill this role. The presence of ions and electrons in the gas enables energy to be transferred to the plasma by electromagnetic induction process. ICP-AES is now a mature technique for multi-element analysis capable of determining many elements. ICP is formed within the confines of three concentric glass tubes or plasma torch. Each tube has an entry point, with those of the intermediate (plasma) and external (coolant) tubes being arranged tangentially to that of the inner tube, where the latter consists of a capillary tube through which aerosol is introduced from the nebulizer/ spray chamber. Located around the outer glass tube is a coil of copper tubing through which water is circulated. The power input to the ICP is achieved through this load or induction coil and is typically in the range of 0.5-1.5 kW at a frequency of 27 or 40 MHz. The input power induces an oscillating magnetic field, of which lines of forces are axially oriented inside the plasma torch and follow elliptical paths outside induction coil. In order to initiate the plasma, the carrier gas valve is opened and a spark is then provided momentarily from a Tesla coil, which is attached to the outside of the plasma torch. Instantaneously, the spark, which is a source of electrons, causes ionization of the carrier gas (argon). This process is self-sustainable, so that argon, argon ions, and electrons now co-exist within the confines of the plasma torch, and can be seen protruding from the top in shape of a bright white luminous bullet.

The first function of the high temperature plasma is desolvation. This removes all solvents in the sample usually leaving the sample as microscopic salt particles. The next step involves decomposing the salt particles into a gas of individual molecules

(vaporization) that are then dissociated into atoms (atomization). Once the sample aerosol has been desolvated, vaporized and atomized, the plasma has excitation and ionization functions. While the exact mechanism for excitation and ionization in the ICP are not yet fully understood, it is believed that most of the excitation and ionization take place as a result of collisions of analyte atoms with energetic electrons.

ICP-AES Leeman Labs Direct Reading Echelle Spectrometer was used in this study. It is equipped with Hilderband nebulizer and a dual view (radial and axial viewing torch). In this work, ICP-AES was used to determine Al, Zn, Fe and Ba. All of these elements were detected in the axial mode.

The optimized instrumental parameters used in the analysis are shown in table 2.5. These parameters were optimized by previous researchers in our group (Alusin, 2001).

Table 2.5. Optimized Instrumental Parameters used for ICP-AES

Parameter	Optimized Value
RF Power	1.1 kW
Argon Flow Rate	0.3 LPM
Nebulizer Pressure	45 psi
Pump Rate	1.4 ml/min
Coolant Flow Rate	18 LPM

2.2.4. Calibration of Instruments

Calibration of instruments requires the establishment of a relationship between signal response and a known set of standards. By measuring the signal of a series of standard solutions of known concentrations, it is possible to construct a graph which can be used to determine the concentrations of elements in the unknown samples by presenting a sample of unknown concentration to the instrument and interpreting the signal. When working with environmental samples, standard addition technique is usually used.

When applying standard addition method, standards must be prepared within the linear portion of the calibration graph and a reagent blank is used to establish the base line. In case of aqueous standard, water is used to establish the baseline.

2.2.5. Blanks

Contaminations, frequently observed, are due to systematic or random introduction of non-negligible amount of analyte during different steps of the analysis. They result from reagents and materials utilized or from ambient air; they become the most troublesome as concentrations to be determined are low. Arising from reagents, the contamination values are generally reproducible from one sample to another (systematic error). Other contamination sources, more easily avoidable, are random and variable errors. It is necessary to evaluate the possible global contamination by several representative blanks and to consider them in the calculation of results. On the other hand, it is also necessary

to clearly distinguish contamination due to sampling and sampling storage from those associated with preparation and measurement stages (Hoenig, 2001).

Field blanks are prepared from deionized water samples that were placed in bottles and taken to the sampling site and back to the laboratory.

2.3. Data Quality Control and Assurance

Before we statistically interpret data, the quality of such data must be documented by estimating the detection limit, accuracy and precision of the methods and instruments used to obtain such data. It is only after a good detection limit (a detection that is less than the concentration of the sample with the lowest concentration), a good accuracy (usually with a relative error less than 10%) and a good precision (usually with relative standard deviation less than 10%) have been obtained that one can confidently use statistical tools to interpret the data. In this study, the quality of the data was tested by detection limit, accuracy and precision. An elaboration of these tests is given below.

2. 3.1. Detection Limits

The detection limits of the instruments were calculated using the intensities of the blanks. The 3s-detection limit was calculated using equation 3.1 below. Table 3.1 gives a summary of the calculated detection limits. The concentrations of some elements in some samples were below the detection limits and they were not used in the statistical evaluation of the data.

$$DL_{3s} = 3 s / m \dots\dots\dots 4.1$$

Where: DL_{3s} is the 3s-detection limit, 's' is the standard deviation of the blank signal and m is the slope of the calibration curve.(Skoog,1998)

As shown in Table 2.6, ICP-OES is a very sensitive technique for Zn a D.L of 0.002 mg/l was obtained. GFAAS technique for Cd gave a D.L of 0.082 µg/l.

Table 2.6. Detection Limits for the instruments used in the analysis

Element	Instrument	Detection Limit	Element	Instrument	Detection Limit
Na	FAES	0.07	Zn	ICP-AES	0.01
Ca	FAES	0.06	Ba	ICP-AES	0.01
K	FAES	0.02	Pb*	GFAAS	0.30
Mg	FAAS	0.01	Cd*	GFAAS	0.08
Cu	FAAS	0.02	Cr*	GFAAS	0.25
Al	ICP-AES	0.08	V*	GFAAS	0.53
Fe	ICP-AES	0.03	Ni*	GFAAS	0.78

*Units are in µg/l , others are in mg/l

2.3.2. Accuracy Check

The closeness of an experimental result to the true result is known as its accuracy, which is defined in terms of relative error and hence can only be estimated. As the aim of the

measurement is to estimate the true result, accuracy is the most important quality. Accuracy can never be determined exactly because the true value of the quantity can never be known exactly. Standard reference materials (SRM) are often used to check the accuracy of an instrument or methodology. This is often a material or a substance, of which one or more properties of which are sufficiently well established to be used for calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. SRMs are certified to specific chemical or physical properties, and are issued with certificates that report the result of the characterization and indicate the intended use of the material (Trahey, 1992)

In this work, before starting any analysis, the accuracy of the instrument and method was tested using three types of standard reference materials; GSP-2, STM-1 and NIST1640. Materials used in the preparation of GSP-2 was collected by the US Geological Survey from the Silver Plume Quarry, which is located approximately 800 meters west of Silver Plume, Colorado. GSP-2 is a medium grained hypidiomorphigic-granular rock consisting essentially of quartz, plagioclase, microcline, biotite and muscovite. STM-1 was collected by the U.S. Geological Survey from a sill that underlies Table Mountain which is approximately 60 km northwest of Eugene, Oregon. The rock sample was light to medium gray and had a glassy luster. The material was polycrystalline and very fine to fine grained having a very pronounced rachitic texture. NIST1640 is composed of natural fresh water collected from Clear Creek, Co. which has been filtered and stabilized with nitric acid at a concentration of 0.5 mol/l. Element concentrations were determined by cooperating laboratories using a variety of analytical methods. Recommended values are listed in tables for case of reference.

In this work, 0.3 g of GSP-2 and STM-1 was digested using the microwave program shown in table 2.7 with an acid mixture of nitric (65%) and hydrofluoric (40%) acids in the ratios of 6:1. This was diluted to 50 ml after digestion. These solutions and NIST1640 were analyzed by FAAS, GFAAS and ICP-AES for the element to be determined before and during the analysis of the real samples. Values obtained were compared with certified values. Table 2.8 shows the found and true concentrations of elements determined in this work.

Table 2.7 Optimized Microwave Program used for Digestion of SRM

Step	Time (min)	Power (W)
1	6	250
2	6	400
3	6	650
4	6	250
5	5	Ventilation

If the % error is less than 10, the method is considered accurate enough to carry out the analysis (El- Agha, 2000). In this work, the method used for Zn was the most accurate, and the method used for Na was the least accurate method.

Table 2.8. The comparison of the values obtained with SRM certified values

<i>Element</i>	<i>Found Value Average ± SD</i>	<i>Certified Value ± SD</i>	<i>% Error</i>	<i>RSD</i>	<i>Number of Replicates (N)</i>
SRM (GSP-2)					
K	4.68 ± 0.17	4.48 ± 0.12	4.44	3.65	9
Na	2.22 ± 0.19	2.06 ± 0.07	7.98	8.43	9
Al	8.40 ± 0.38	7.88 ± 0.11	7.00	5.70	9
*Zn	119 ± 3.5	120 ± 10	-1.02	2.98	9
*Cu	40.0 ± 0.91	43.0 ± 4.0	-6.30	2.26	9
SRM (STM-1)					
Fe	5.40 ± 0.30	5.22 ± 0.10	3.47	5.58	9
Ca	1.07 ± 0.03	1.09 ± 0.06	-1.83	3.49	9
*Pb	16.8 ± 0.43	18.0 ± 1.8	-6.48	2.53	9
Mg	0.105 ± 0.02	0.100 ± 0.02	5.15	1.57	9
*Ba	525 ± 17	560 ± 60	-6.27	3.30	9
SRM (NIST 1640)					
*Cr	39.7 ± 1.46	38.6 ± 1.60	2.93	3.69	9
*Cd	23.7 ± 0.82	22.8 ± 0.96	4.17	3.45	9
*V	13.7 ± 0.44	13.0 ± 0.37	5.48	3.21	9
*Ni	26.3 ± 1.17	27.4 ± 0.80	-4.04	4.47	9

*Units are in µg/g, the rest are in wt%

2.3.3. Precision and Relative Standard Deviation

Precision probably is the most quoted terms in analytical chemistry. Precision is defined as the closeness of a group of individual results to each other. Precision is most frequently quantified in terms of standard deviation. Even when measurements are carried out under closely standardized conditions, some variability among replicates will occur. Distinction is often made between repeatability and reproducibility. The former refers to variations when replicate measurements are made under closely standardized conditions in the same place in a short time scale. The later applies when time and place and other conditions may differ substantially, but the method remains the same (Alusine, 2001). In this work, repeatability is reported, as replicate measurements were made in the same place in a short time. Standard deviation is the most important precision indicator. It is often quoted in the form of the percent relative standard deviation (%RSD) which was calculated using equation 4.2

$$\%RSD = (s / m) \times 100 \dots\dots\dots 4.2$$

Where: s is the standard deviation and m is the arithmetic mean. Table 2.9 shows the %RSD values obtained in this work.

The lower the %RSD, the more precise the method is. The precision of the method is usually accepted if the %RSD is less than or equal 10 (Öztaş, 2001).

As shown in the table below, the methods are precise enough for the analysis of the samples. The method used for Mg was the most precise one, and the method used for Na was the least precise method.

Table 2.9 Percent Relative Standard Deviation of Generated Data

Element	% RSD	Element	% RSD
Na	8.43	Zn	2.98
Ca	3.49	Cu	2.26
K	3.65	Pb	2.53
Mg	1.57	Cr	3.69
Ba	3.30	Cd	3.45
Al	5.70	Ni	4.47
Fe	5.58	V	3.21

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Overview of the Data

3.1.1. Concentrations of Metals Found in the Water Samples

In this study, 40 samples of groundwater collected from 40 different wells near Soma power plant were analyzed to determine 14 metals. Table 3.1 shows the concentrations found in the water samples.

As shown in Table 3.1 and on Figures 3.1 – 3.14, Na, Ca, K and Mg have high concentrations because they are crustal elements. Al is also a crustal element but it is sparsely soluble in water, so its concentration is much less than the other crustal elements. Fe and Zn are anthropogenic elements, but they show high concentrations in some wells.

Table 3.1 metal concentrations found in the water samples

Well	Na	Ca	K	Mg	Ba	Al	Fe	Zn	Cu	Pb*	Cr*	Cd*	Ni*	V*
1	9.00	101	1.59	26.0	0.218	0.640	<D.L	<D.L	<D.L	0.410	0.950	<D.L	0.77	1.94
2	66.0	120	1.90	92.0	0.344	0.640	0.038	0.003	<D.L	3.38	1.74	<D.L	3.46	3.10
3	36.0	79.0	5.11	55.0	0.233	0.660	0.320	0.117	0.024	0.820	1.11	<D.L	3.46	14.5
4	35.0	120	4.64	18.0	0.153	0.640	0.410	0.027	0.026	1.48	7.31	<D.L	2.10	2.50
5	38.0	207	14.30	16.0	0.220	0.630	0.183	0.000	0.034	1.31	0.830	<D.L	1.73	2.61
6	49.0	174	3.52	23.0	0.251	0.413	5.869	0.210	0.049	3.79	6.42	0.10	5.10	6.50
7	40.0	208	9.83	18.0	0.155	0.660	0.39	0.084	0.022	1.33	0.760	<D.L	3.33	<D.L
8	43.0	263	6.54	15.0	0.183	0.720	0.482	0.029	<D.L	1.23	0.620	<D.L	2.35	<D.L
9	34.0	263	1.55	28.0	0.235	0.660	0.499	0.548	0.019	1.41	0.270	<D.L	4.57	<D.L
10	13.0	255	2.43	23.0	0.116	0.610	<D.L	0.004	0.030	1.28	1.27	<D.L	4.10	<D.L
11	12.0	146	4.08	36.0	0.152	0.700	0.124	0.073	0.040	1.95	1.07	<D.L	3.83	2.83
12	35.0	198	5.01	56.0	0.315	0.730	0.211	2.642	0.045	2.20	0.840	<D.L	3.33	3.72
13	47.0	196	1.83	31.0	0.67	0.650	0.205	0.289	<D.L	1.77	2.38	<D.L	3.21	2.28
14	46.0	251	1.38	38.0	0.235	0.890	0.271	0.172	<D.L	0.72	2.23	<D.L	3.95	11.5
15	102	257	2.73	65.0	0.190	0.660	0.197	0.038	<D.L	1.79	1.37	<D.L	2.47	6.10

Table 3.1 Cont.

16	18.0	130	1.27	57.0	0.150	0.650	1.366	2.248	0.019	4.89	6.51	0.35	2.35	10.3
17	27.0	179	10.74	55.0	0.063	0.640	2.502	0.129	0.027	1.66	5.25	<D.L	1.98	12.8
18	32.0	250	14.89	50.0	0.111	0.620	0.085	0.922	0.032	1.36	0.67	0.17	1.98	8.83
19	9.0	246	1.13	63.0	0.186	0.650	2.106	0.586	0.038	6.20	1.68	<D.L	2.59	14.5
20	9.0	279	2.27	72.0	0.079	0.630	0.030	<D.L	0.040	2.64	0.73	<D.L	3.70	8.28
21	6.0	194	2.74	49.0	0.280	0.680	0.186	1.618	0.051	1.07	1.80	0.11	1.98	3.72
22	44.0	167	6.05	47.0	0.245	0.720	0.279	1.354	<D.L	5.20	7.82	0.20	2.35	6.28
23	11.0	179	1.48	35.0	0.112	0.700	0.081	0.004	<D.L	<D.L	0.75	<D.L	2.22	1.16
24	38.0	285	0.71	65.0	0.150	0.640	0.224	0.078	<D.L	<D.L	0.81	0.10	1.60	3.28
25	47.0	311	1.87	27.0	0.083	0.630	0.268	0.030	<D.L	<D.L	<D.L	<D.L	1.98	1.39
26	23.0	163	9.44	61.0	0.170	0.810	1.380	0.265	0.024	0.87	1.16	<D.L	2.84	3.17
27	20.0	149	8.57	73.0	0.198	0.630	0.030	0.045	0.036	<D.L	0.56	<D.L	4.57	1.94
28	26.0	317	2.19	16.0	0.054	0.630	<D.L	<D.L	0.038	<D.L	<D.L	<D.L	2.47	<D.L
29	70.0	169	10.32	70.0	0.115	0.670	0.262	0.090	0.035	<D.L	0.76	<D.L	2.59	0.61
30	30.0	172	8.17	33.0	0.212	0.760	0.964	0.147	0.039	0.31	1.27	<D.L	5.19	1.10
31	18.0	157	4.13	70.0	0.73	0.950	1.882	0.391	<D.L	4.41	2.31	0.43	3.21	1.00
32	16.0	175	1.87	18.0	0.222	0.640	0.038	0.013	<D.L	<D.L	0.35	<D.L	2.47	<D.L
33	19.0	286	15.41	25.0	0.105	0.640	0.066	0.024	<D.L	<D.L	0.27	<D.L	2.59	1.00
34	17.0	198	1.92	39.0	0.109	0.700	0.89	0.059	0.019	0.79	0.34	<D.L	4.20	<D.L

Table 3.1 Cont.

35	11.0	202	1.74	34.0	0.133	0.790	0.413	0.133	<D.L	0.59	0.89	<D.L	2.35	0.72
36	20.0	220	1.09	40.0	0.245	0.640	0.070	0.412	<D.L	<D.L	0.59	<D.L	2.47	2.60
37	15.0	153	1.09	48.0	0.135	0.750	6.728	2.632	0.412	4.13	4.48	0.24	9.26	17.52
38	23.0	154	2.02	25.0	0.164	0.660	0.053	0.041	<D.L	<D.L	0.41	<D.L	2.59	<D.L
39	12.0	216	1.37	22.0	0.142	0.640	0.981	0.014	0.022	0.51	0.52	<D.L	3.95	<D.L
40	27.0	152	1.73	21.0	0.153	0.630	<D.L	<D.L	0.023	<D.L	<D.L	<D.L	1.98	<D.L

*Units are in µg/l, others are in mg/l

3.1.2. Summary Statistics of Generated Data

Table 3.2 shows concentrations statistical summary which includes minimum, maximum, arithmetic and geometric means, arithmetic standard deviation, and median.

High standard deviations of the anthropogenic samples show that the variability in concentrations of metals is also high. These fluctuations are not unusual, because environmental data is generally log-normally distributed, due to presence of real high concentrations. Arithmetic mean of the samples is small number of results that are high in magnitude. Thus, data population in environmental studies is better characterized by either probability distributions or geometric mean or median concentrations of species. Crustal elements are usually normally distributed and represented by arithmetic mean.

Table 3.2 Summary Statistics of Generated Data

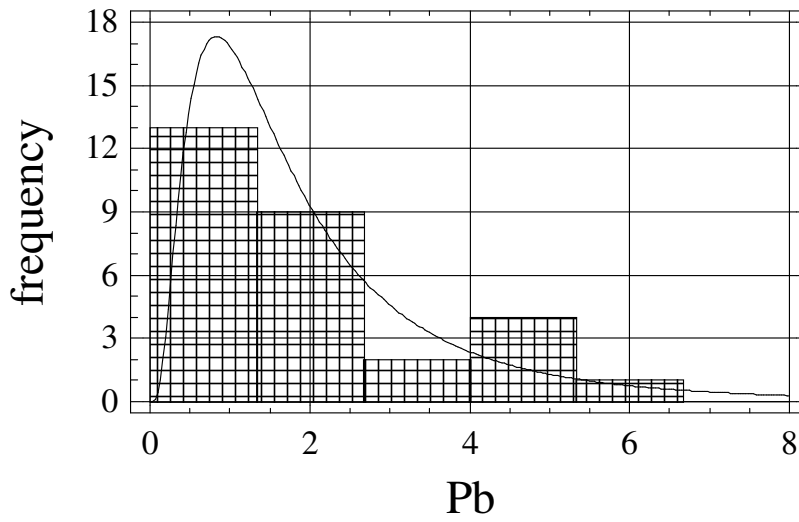
Element	Minimum	Maximum	Average	Standard Deviation	Geometric Mean	Median
Na	6.00	70.0	30.0	20.0	24.5	26.5
Ca	79.0	317	201	58.0	192	197
K	0.710	15.4	4.25	4.14	3.14	2.35
Mg	15.0	92.0	41.0	20.0	37.0	41.0
Ba	0.036	0.327	0.150	0.070	0.140	0.140
Al	0.413	0.951	0.674	0.550	0.669	0.650
Fe	0.030	6.73	0.790	1.50	0.250	0.220
Zn	0.003	2.64	0.440	0.740	0.110	0.120
Cu	0.019	0.051	0.030	0.010	0.024	0.025
*Pb	0.305	6.20	2.05	1.60	1.54	1.41
*Cr	0.230	7.82	1.70	1.89	1.10	0.920
*Cd	0.095	0.435	0.210	0.120	0.190	0.190
*Ni	1.61	9.26	3.14	1.38	2.52	2.59
*V	0.610	17.5	4.95	4.55	3.31	3.06

* Units are in $\mu\text{g/l}$, others are in mg/l

Kolmogorov-Smirnov (KS) goodness of the fit was applied to differentiate the elements that show log-normal distributions and the ones for which distribution is not log-normal. Lead has a highly right-skewed distribution in the data set. Elements Cd, Zn, V, Fe, Cu, Cr, and Ni have similar distributions with that of Pb. Distributions of Ca, Ba, Na, Mg, K and Al are more symmetrical indicating that elements may have different distributions. The frequency distributions of Pb and Ca are shown in Fig. 3.1.

In KS statistics a KS goodness of fit test which divides the range of the variables into non-overlapping intervals and compares the number of observations in each class to the number expected based on the fitted distribution is first used, then Kolmogorov-Smirnov test computes the maximum distance between the cumulative distribution function of the assumed log-normal distribution. Finally computed maximum distance is compared with the theoretical value for log-normal distribution (Önel, 2004). Based on KS test, elements Pb, Cd, Zn, Fe, Cu, Cr, V, Ni, and Pb show log-normal distribution with 95% confidence but Ca, Na, K, Mg, Al and Ba show normal distribution as a result of the test as predicted from the frequency.

Histogram for Pb



Histogram for Ca

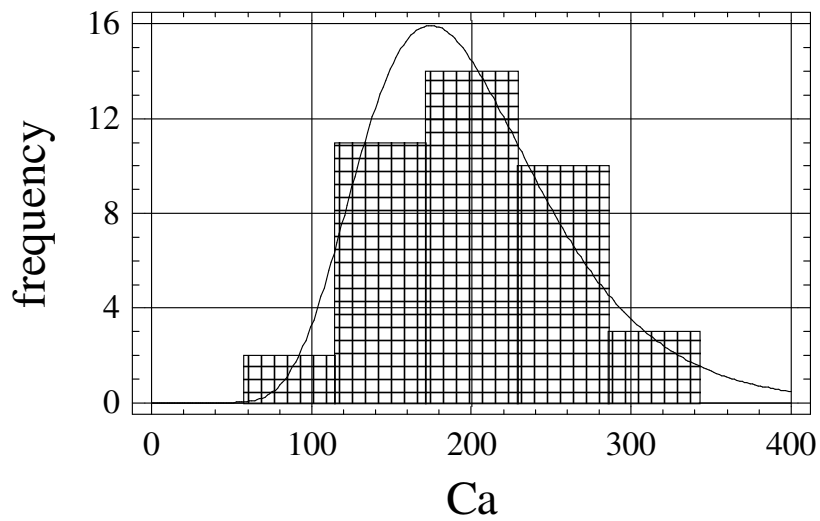


Fig 3.1 Frequency distribution of Pb and Ca

3.1.3. Comparison with Literature Values

Table 3.3 shows a comparison between the maximum metal concentrations obtained in this study and those obtained in other cities, the world health organization (WHO) and the EC guidelines.

As shown in the table below, the maximum Fe concentration in this work is the highest among all others. It is much higher than the WHO and the EC guidelines. It is higher than both guidelines in 12 samples. The maximum Fe concentration in Italy is also high, but it is lower than this work.

Pb maximum concentrations are lower than Kutahya and lower than the WHO and EC guidelines, but it is relatively high.

Cr concentration is lower than Kutahya and lower than the WHO and the EC guidelines.

Al maximum concentration in this work is higher than the other studies but lower than the WHO and the EC guidelines. It is lower than the WHO and the EC guidelines in all samples.

All other elements are lower than the WHO and the EC guidelines.

Table 3.3. Comparison with Literature Values

Elem.	This work ^a Max.	This work Med.	Mexico ^b	Kütahya Turkey ^c	Tuscan Italy ^d	WHO Guidelines for Drinking Water Quality 1993 ^e	EC Guidelines for Drinking Water Quality 1980 ^f	ITS Guidelines for Drinking Water Quality ^g
Na	102	26.5	–	–	–	–	–	–
Ca	317	197	–	–	–	–	–	–
K	15.4	2.35	–	–	–	–	–	–
Mg	92.0	41.0	–	–	–	–	–	–
Ba	0.330	0.140	–	–	–	2.00	–	–
Al	0.950	0.650	–	–	0.413	1.00	1.00	–
Fe	6.73	0.220	–	2.24	4.93	0.300	0.200	0.300
Zn	2.64	0.120	2.54	1.12	1.89	3.00	1.00	15.0
Cu*	50.0	25.0	63.0	26.0	24.0	1000	2000	1500
Pb*	6.20	1.41	6.80	5.41	2.45	10.0	10.0	50.0
Cr*	7.82	0.920	–	45.0	0.800	50.0	50.0	–
Cd*	0.430	0.190	14.0	0.310	0.300	3.00	5.00	5.00
Ni*	9.26	2.59	10.4	–	11.3	20.0	20.0	–
V*	17.5	3.06	–	–	11.5	50.0	50.0	–

* Units are in µg/l, others are in mg/l

^aThis Work

^bSantoyo and Surendra (2000)

^cÖztürk and Yılmaz (1998)

^dTamasi 92003)

^eWHO Guidelines (1993)

^fEC Guidelines (1980)

^gInstitute of Turkish Standards (maximum permissible level)

3.1.4. Graphical Representation of the Concentrations found in the Samples

Figures 3.2 through 3.15 show the well number vs. concentrations found in each sample.

-Fig 3.2 shows the concentration of Na in the groundwater wells. Na is a crustal element; therefore the concentrations in most wells are close to the average. Only wells No. 2 and 29 are much higher than the average and wells No. 1, 19 and 21 are much lower than the average.

-Fig 3.3 shows the concentrations of Ca in the water wells. Ca is a crustal element which comes mainly from soil. As shown on the figure, concentrations of Ca are close to the average in most wells. Wells No. 25 and 28 are about one standard deviation (S.D.) above the average. Wells No. 1 and 3 are about two standard deviations below the average.

-Fig 3.5 shows the concentrations of K in the wells. K is a crustal element; therefore most wells are not far from the average. But there are six wells which are about four standard deviations higher than the average. So, the data is better represented by the geometric mean.

-Fig 3.4 shows the concentrations of Ba. Wells No. 2, 12, 21, and 36 are about 5 standard deviation above average, and wells No. 10, 13, 17, 18, 20, 23, 25, 28, 33 and 34 are around 5 standard deviation below the average. This is typical for an anthropogenic element.

-Fig 3.6 shows the concentrations of Mg in the water wells. Wells No. 2 and 27 are about 2 standard deviations (S.D.) above the average, and wells No. 5, 8, 28 and 32 are about 2 standard deviations below the average.

-Fig 3.7 shows the concentrations of Al in the groundwater wells. Al is considered an element which comes from natural sources mainly soil. As shown on fig 3.6 the concentrations in all wells are very close to the average. This indicates that Al can be taken as an element that comes only from soil.

For all crustal elements, the average and the geometric mean are close to each other. And the average gives a good representation of the data.

-Fig 3.8 shows the concentrations of Fe in the water wells. Four samples are below the detection limit of the instrument. Wells No. 6 and 37 are about 5 standard deviations above the average. Wells No. 17 and 19 are about 2 standard deviations above the average. There are 28 wells which are about 1 standard deviation below the average. So, the geometric mean gives a better representation of the data.

-Fig 3.9 shows the concentrations of Zn in the water wells. 8 samples were below the detection limit of the instrument. Wells No. 12, 16 and 37 are about 5 standard deviations above the average. Wells No. 21 and 22 are about 2 standard deviations above the average. 24 wells were much below the average. This is typical for an element which comes mainly from anthropogenic sources. Therefore the geometric mean gives a better representation of the data because about 30 wells are close to the G.M.

-Fig 3.10 shows the concentrations of Cu in the groundwater water wells. 17 wells are below the detection limit of the instrument. Wells No. 6, 12 and 20 are about 3 standard deviations above the average. Many wells are about 1 standard deviation below the average. Cu is an anthropogenic element, therefore it is better represented by the geometric mean.

-Fig 3.11 shows the concentrations of Pb in the water wells. 11 samples are below the detection limit of the instrument. Wells No. 16, 19, 22, 31 and 37 are about 3 standard deviations above the average. Many wells are about 1 standard deviation below the average. The data is better represented by G.M. because Pb is an anthropogenic element.

-Fig 3.12 shows the concentrations of Cr in the wells. 3 samples are below the detection limit of the instrument. Wells No. 6, 16 and 22 are about 3 standard deviations above the average. There are about 28 wells which are about 1 standard deviation below the average. The data is better represented by the geometric mean which is typical for an anthropogenic element.

-Fig 3.13 shows the concentrations of Cd in the water wells. Cd is an anthropogenic element. Cd concentrations are relatively low. 28 samples are below the detection limit of the instrument. Wells No. 16 and 31 are about 2 standard deviations above the average. Five wells are below the average. Therefore the geometric mean gives a better representation of the data.

-Fig 3.14 shows the concentrations of Ni in the water wells. Ni is an anthropogenic element. Well No. 37 is about 5 standard deviations above the average. The other wells are close to the geometric mean, so the geometric mean gives a better representation of the data which is typical for environmental data.

-Fig 3.15 shows the concentrations of V in the water wells. Wells No. 3, 17 and 37 are about 2 standard deviations above the average. 11 wells are below the detection limit of the instrument. Most wells are close to the geometric mean. So the geometric mean represents the data better than the average which is typical for an anthropogenic element.

Well No. 37 is high in all anthropogenic elements. This well is quite far from the ash piles. So there could be another source close to this area.

The above trend is typical for anthropogenic elements in which the source in this case is the ash ponds, and the elements are filtered by the soil layers in some wells and enriched in other wells depending on the nature of the soil and the distance from the ash ponds.

In general, crustal elements do not show long variation from one well to another, but anthropogenic elements do.

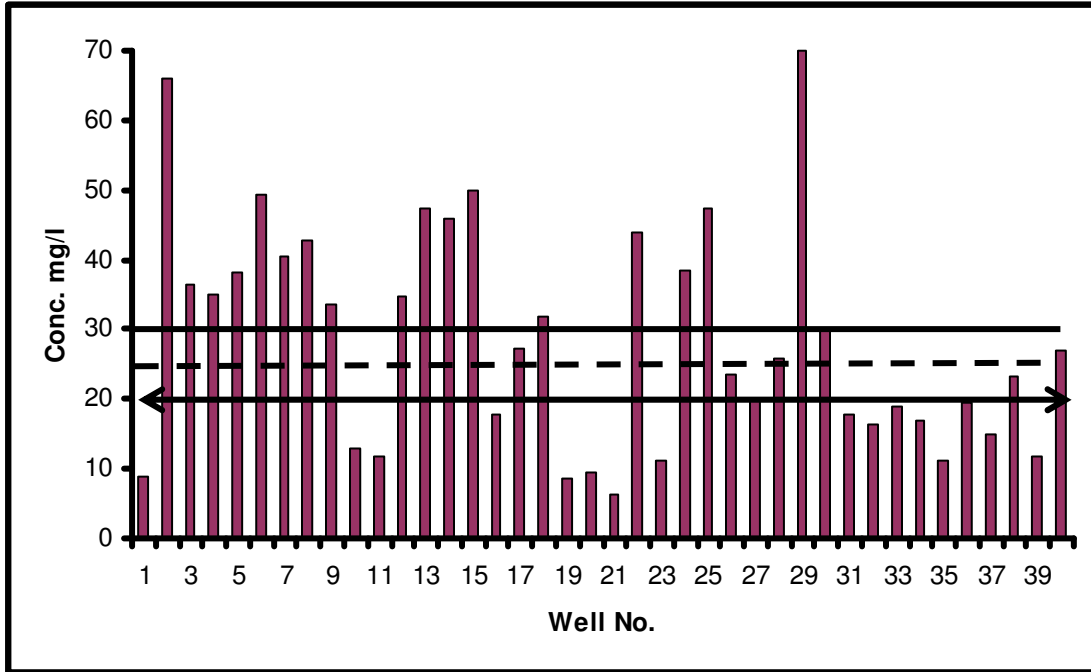


Fig 3.2 Na conc. in the water samples

— Ave. - - G. M. ↔ S.D.

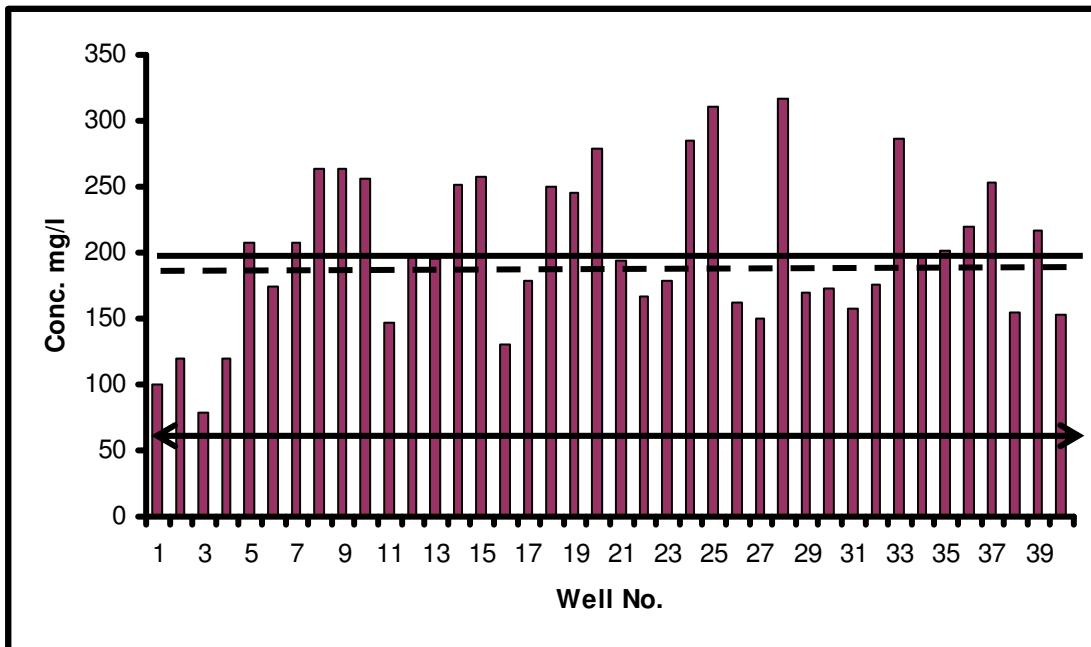


Fig 3.3 Ca conc. in the water samples

— Ave. - - G.M. ↔ S.D.

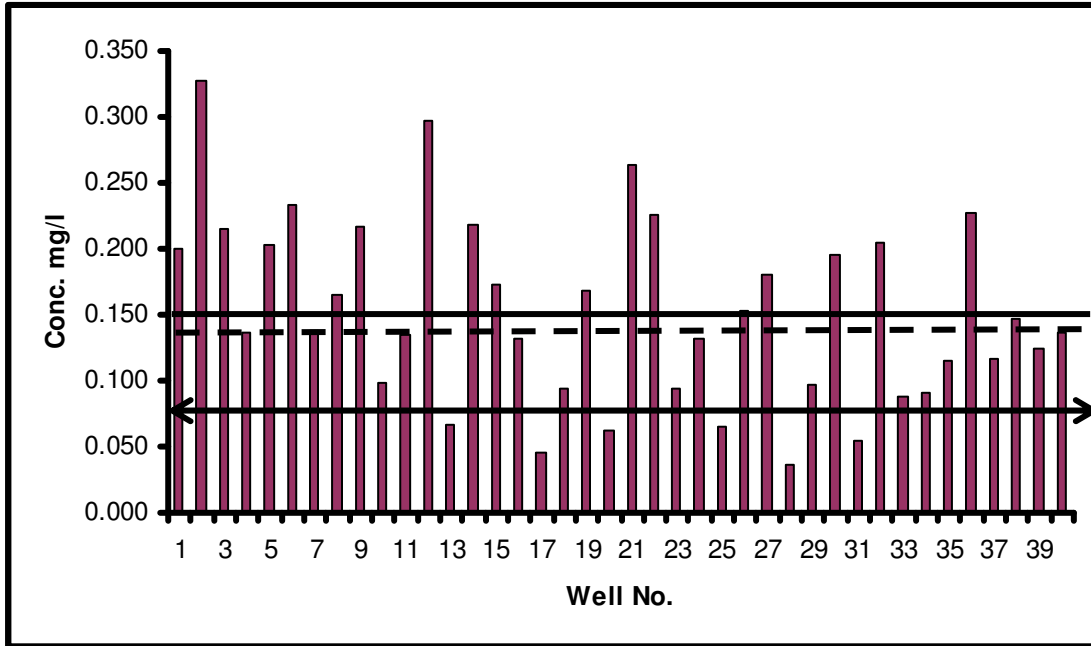


Fig 3.4 Ba conc. in the water samples

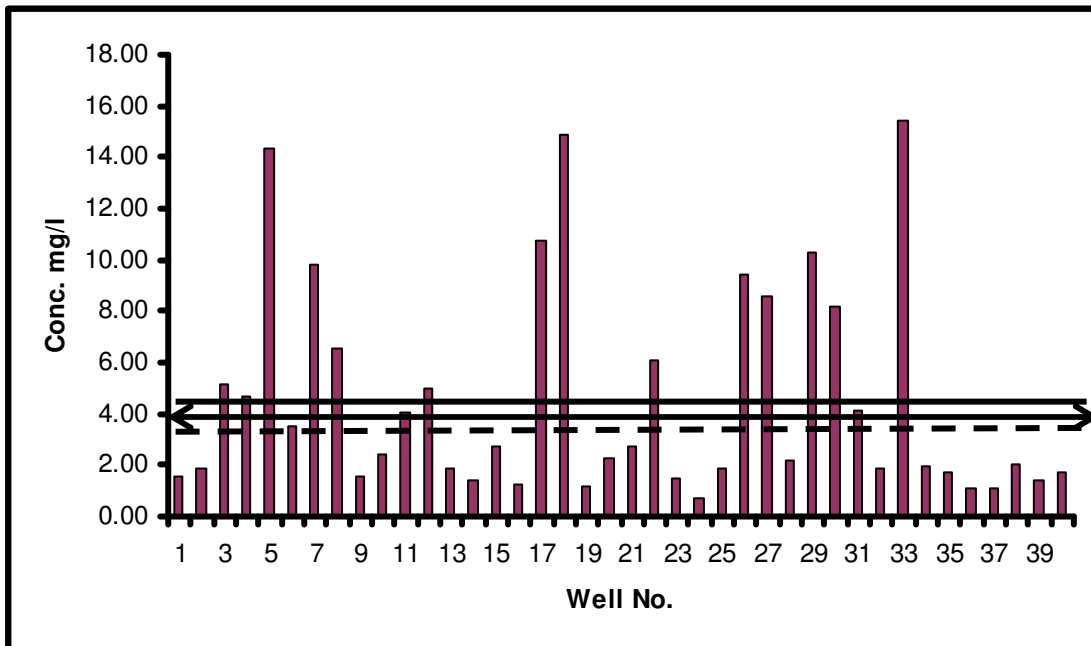
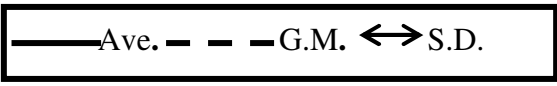


Fig 3.5 K conc. in the water samples



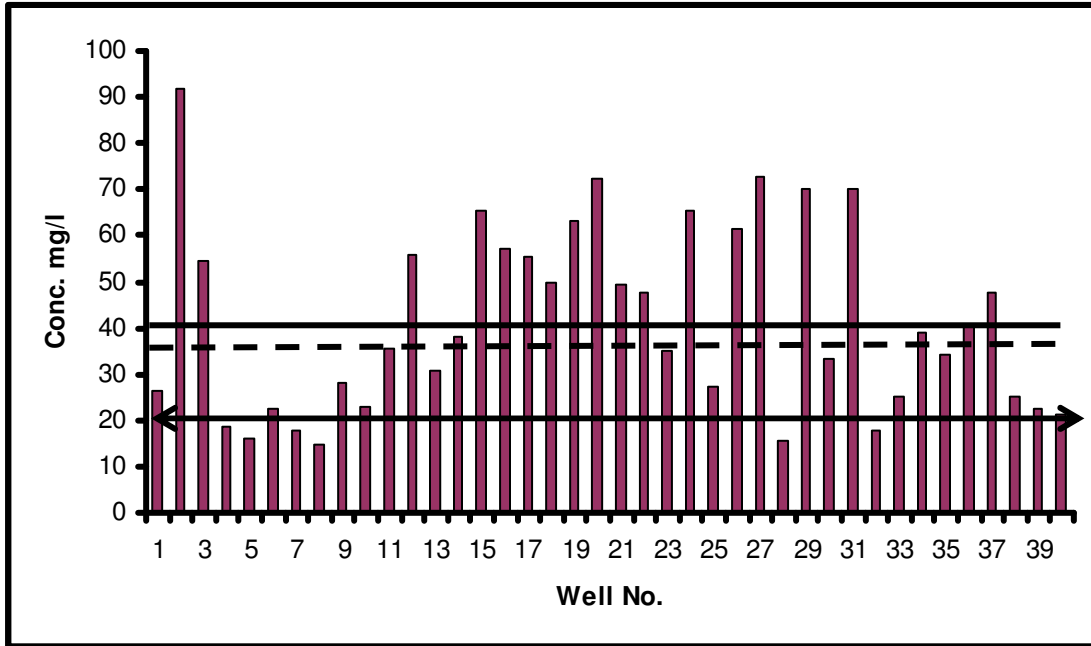


Fig 3.6 Mg conc. in the water samples — Ave. - - G.M. ↔ S.D.

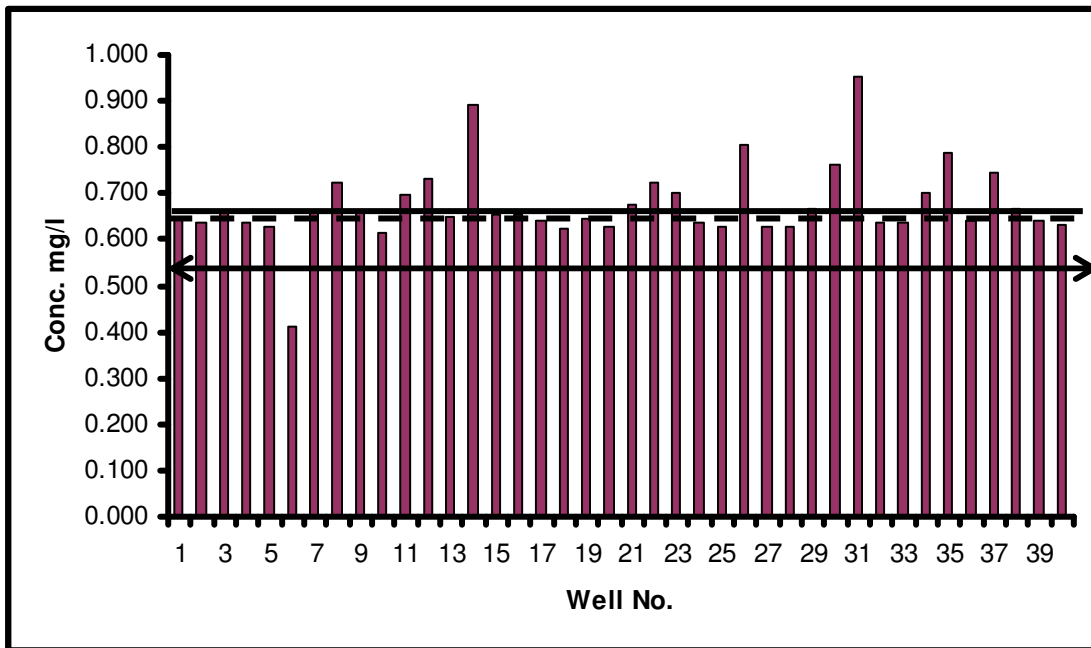


Fig 3.7 Al conc. in water samples — Ave. - - G.M. ↔ S.D.

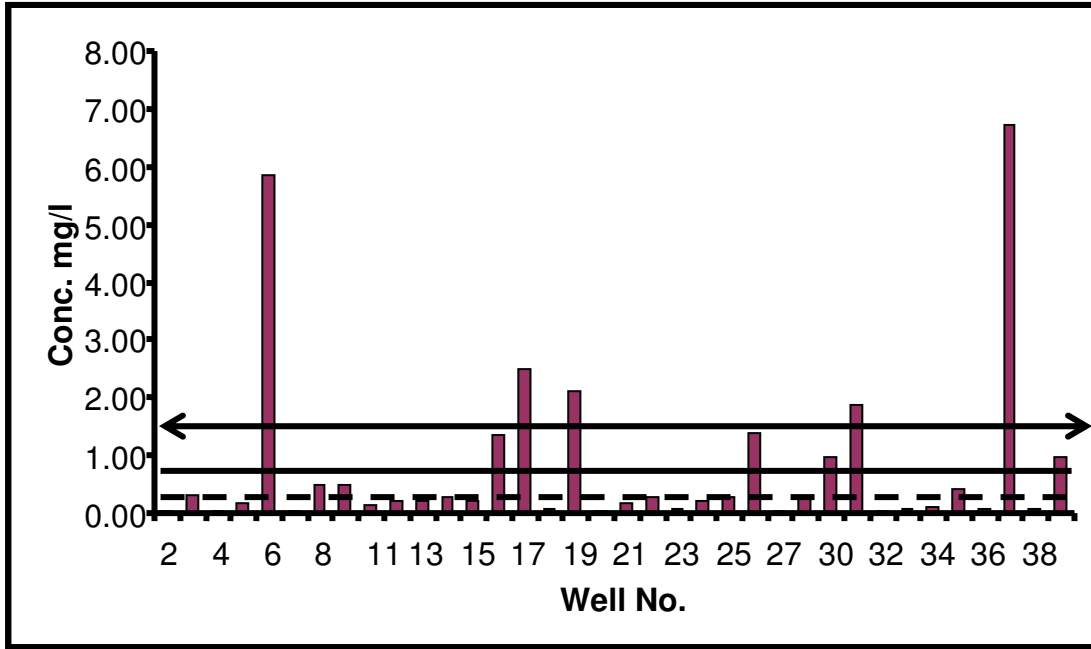


Fig 3.8 Fe conc. in water samples

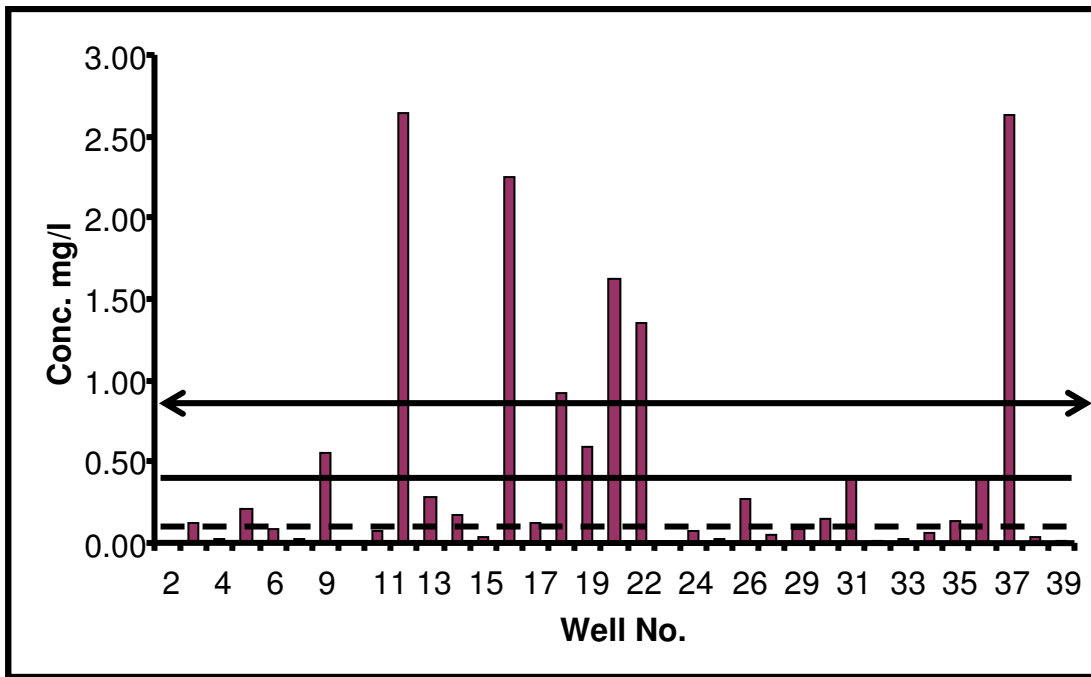
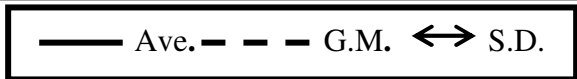
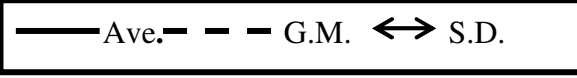


Fig 3.9 Zn conc. in water samples



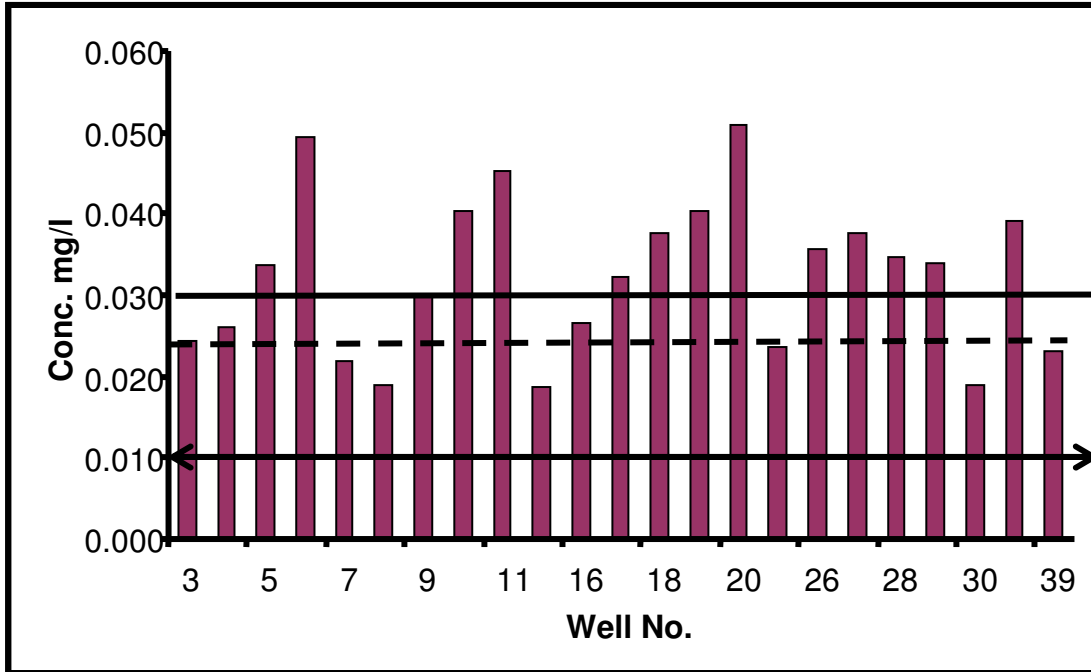


Fig 3.10 Cu conc. in water samples

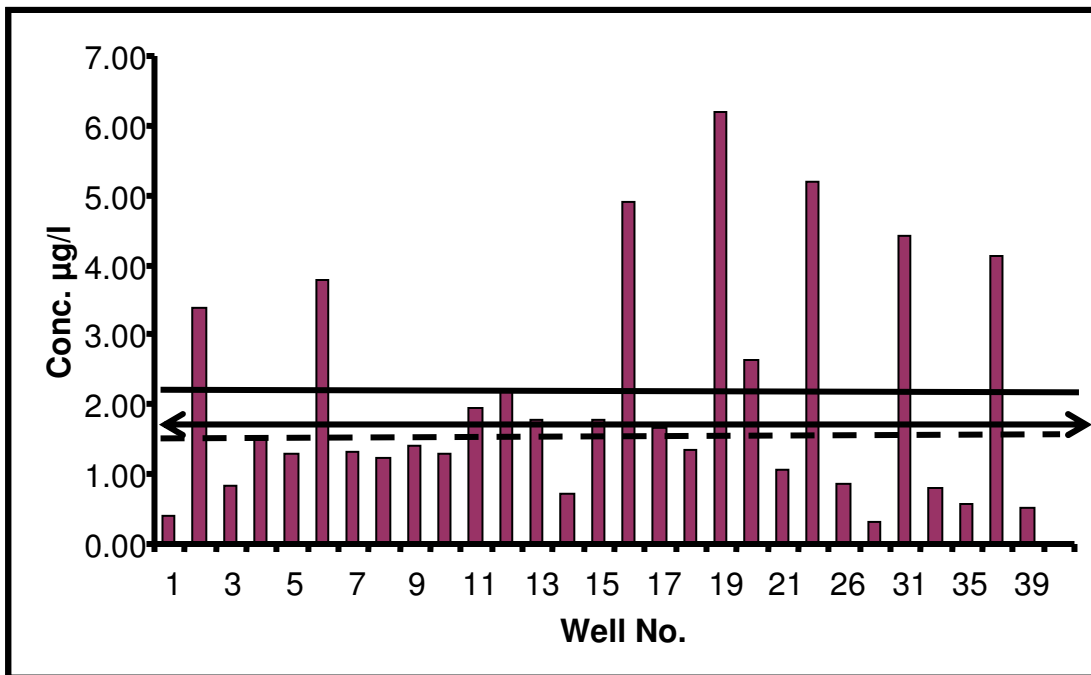
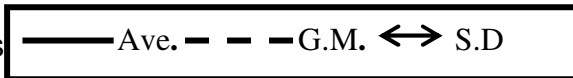
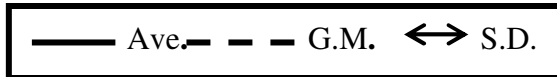


Fig 3.11 Pb conc. in water samples



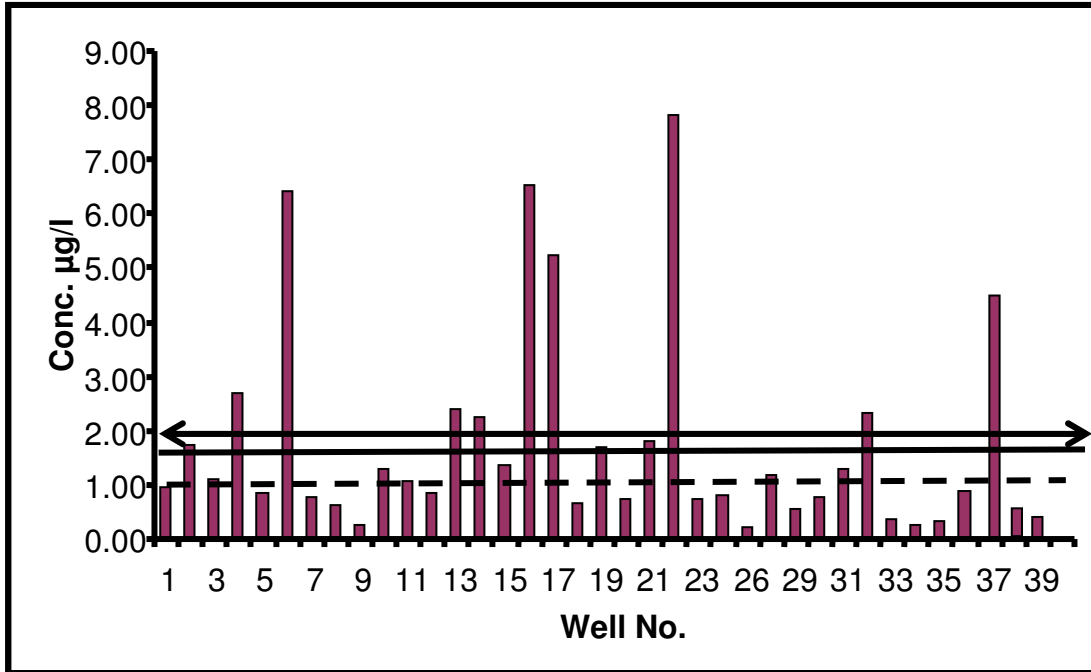


Fig 3.12 Cr conc. in water samples

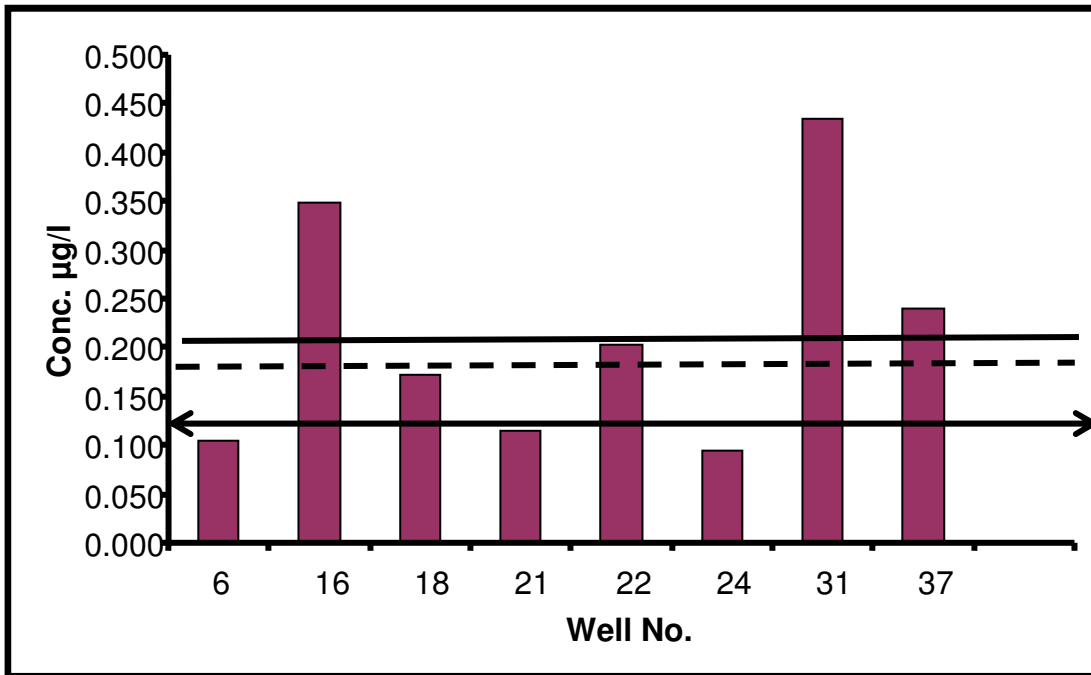


Fig 3.13 Cd conc. in water samples



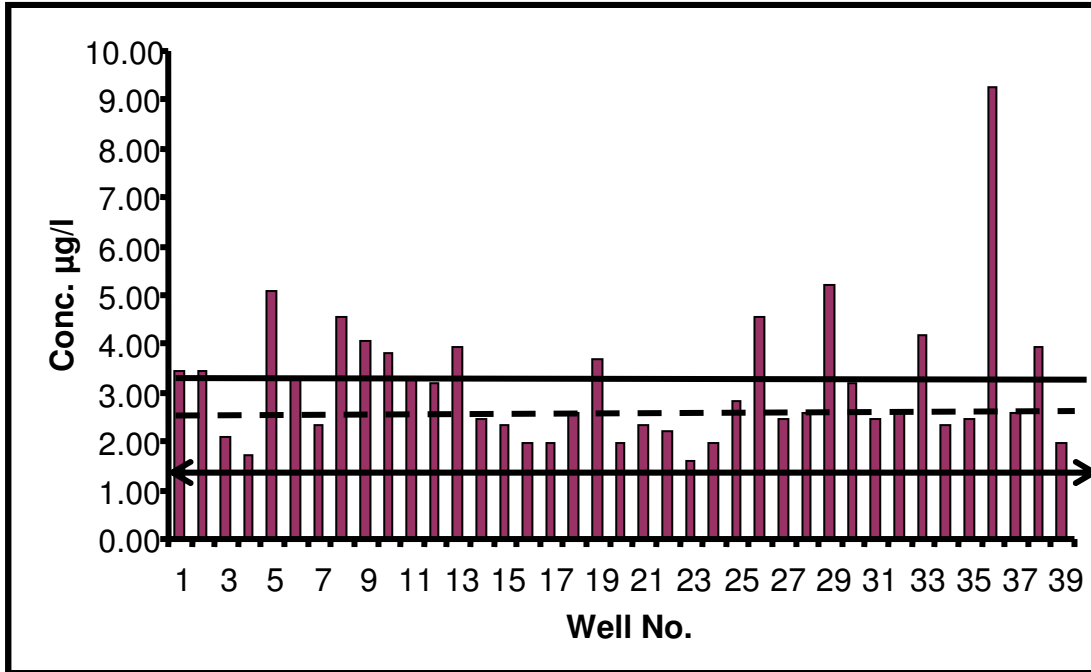


Fig 3.14 Ni conc. in water samples

— Ave. - - - G.M. ↔ S.D.

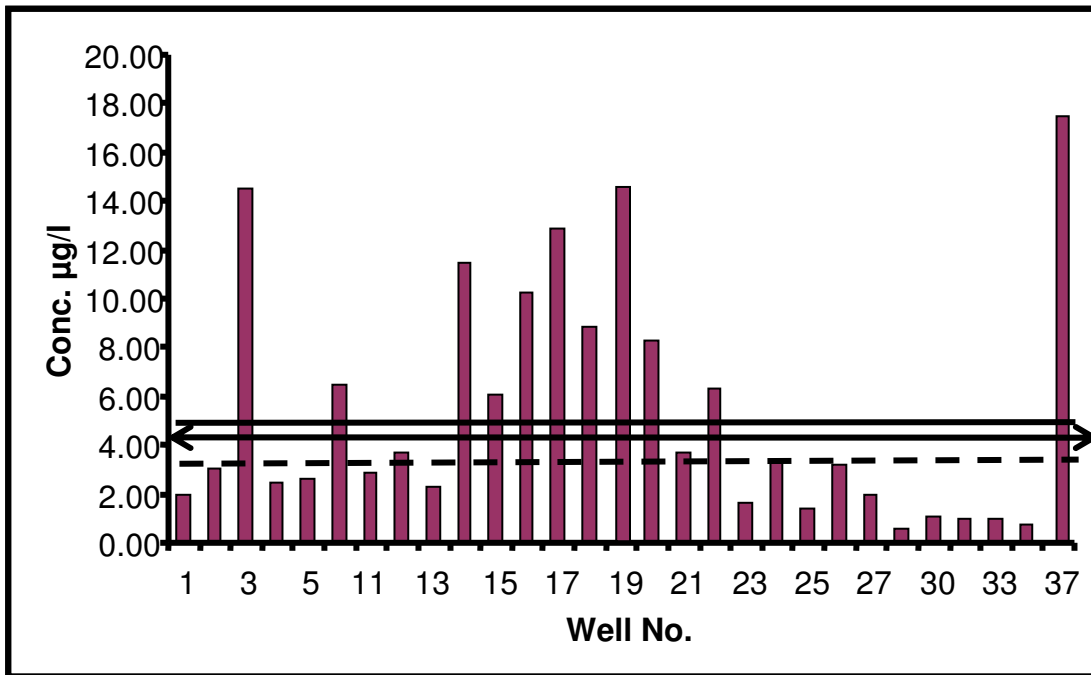


Fig 3.15 V conc. in water samples

— Ave. - - - G.M. ↔ S.D.

3.1.5. Spatial Distribution of the Concentrations of the Elements

The sampling points were grouped depending on the distance from the ash piles in four regions, northeast, northwest, southwest and southeast of the ash piles, the main source of the pollution. As shown on Fig 3.15. Wells No.11, 14, 15, 16, 17, 18, 19, 20, 21 and 22 are in the northeast region, wells No. 6, 7, 12, 13, 35, 36, 37, 38, 39 and 40 are in the northwest region, wells No. 1, 2, 3, 4, 5, 8, 28, 32, 33 and 34 are in the southwest region and wells No. 9, 10, 23, 24, 25, 26, 27, 29, 30 and 31 are in the southeast region.

-Figures 3.17 through 3.21 show the average concentrations of the crustal elements in the four regions. The concentrations of the crustal elements are close to each other in the four regions which indicate that the source of these elements is mainly natural.

-Fig 3.22 shows the average concentrations of Ba in the four regions. Ba is an anthropogenic element but the average concentrations are close to each other which may be explained as the element travels with the flow of water to all wells evenly.

-Figures 3.23 through 3.30 show the average concentrations of the anthropogenic elements in the four regions. The north east region has the highest average concentration for all anthropogenic elements. This region is the closest to the ash piles and to the power plant which indicates that these metals are originated from the ash piles.

The northwest also has high average concentrations but lower than that of the north east region. This region is also close to the ash ponds but the flow of the groundwater is not directly toward this region that might be the reason for lower concentrations of the N. E. In the S. W. and S. E. regions, concentrations are much lower than those of the other two regions. These regions are quite far from the ash ponds. Therefore the metals might have been filtered out by the soil layers or precipitated down, thus the concentrations were lowered in these regions.

On the figures, the \pm standard deviations are also shown. Given results indicate that the concentrations of an element are not very different from each other in a given region which means that the wells which are close to each other have almost same concentrations.

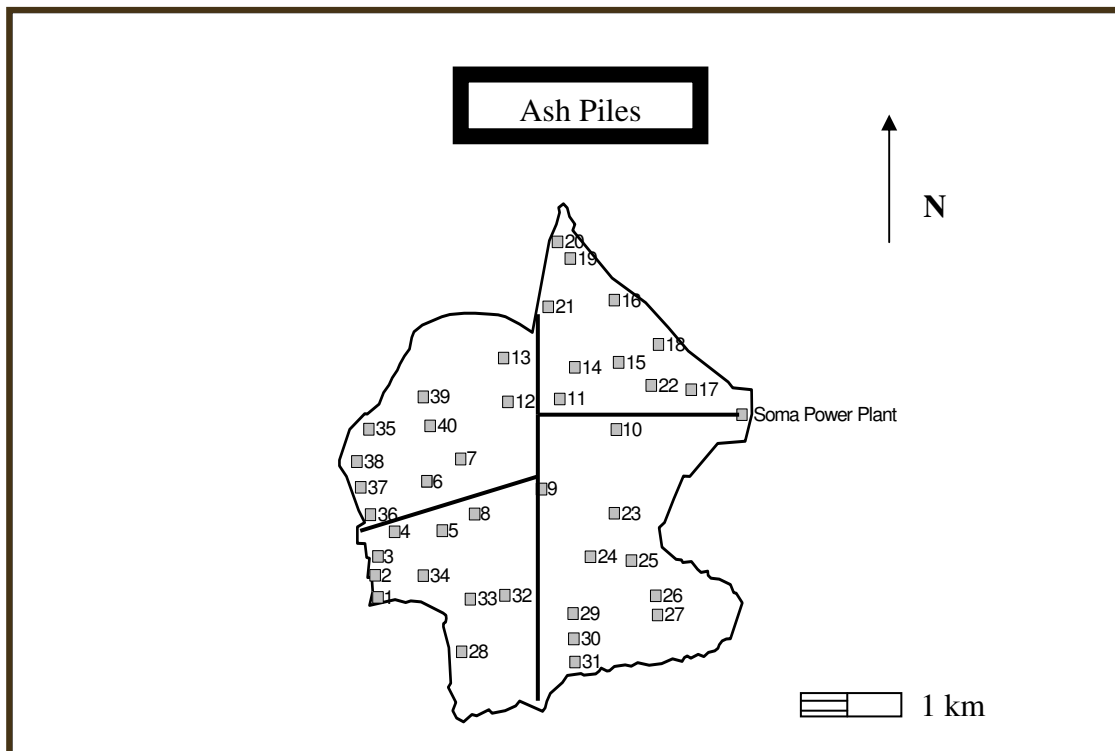


Fig 3.16 Map of Soma showing the grouped regions

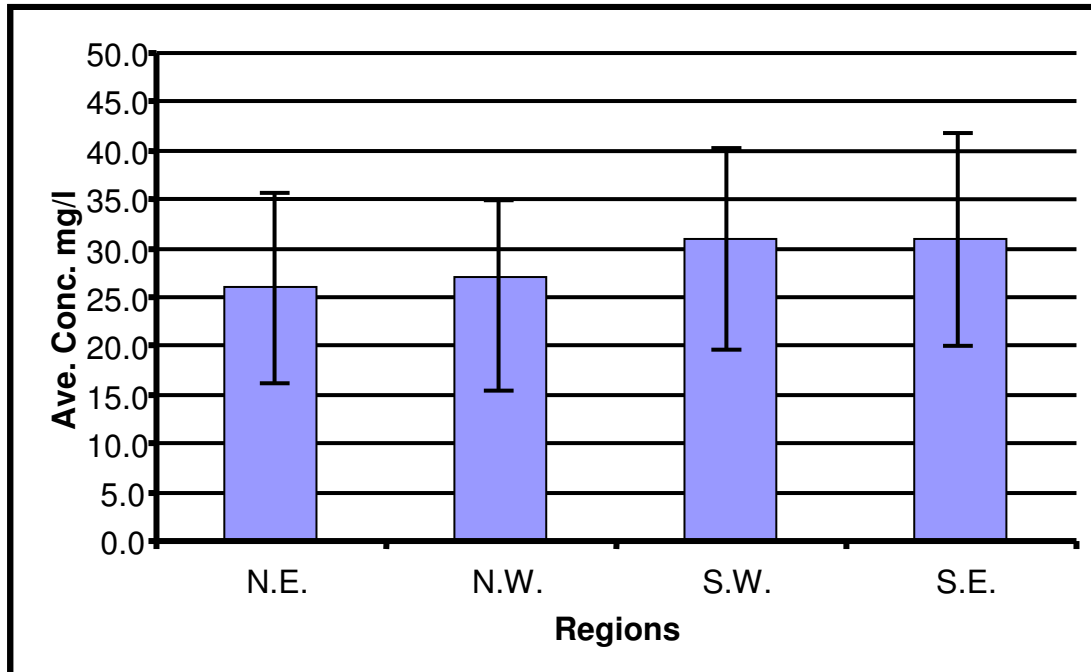


Fig 3.17 Grouping of Na

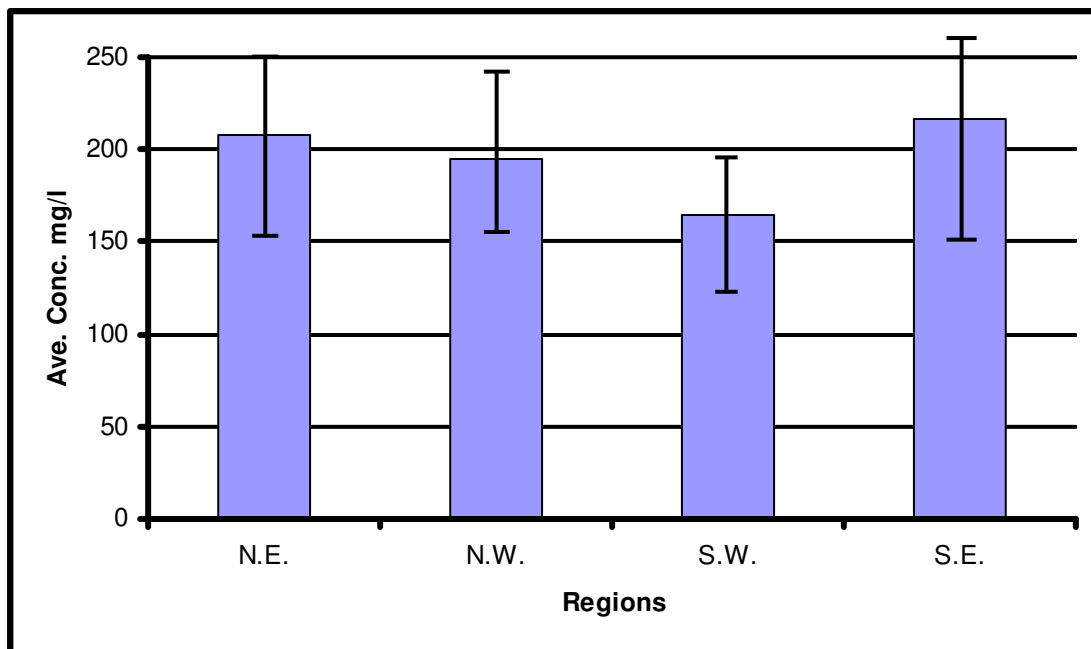


Fig 3.18 Grouping of Ca

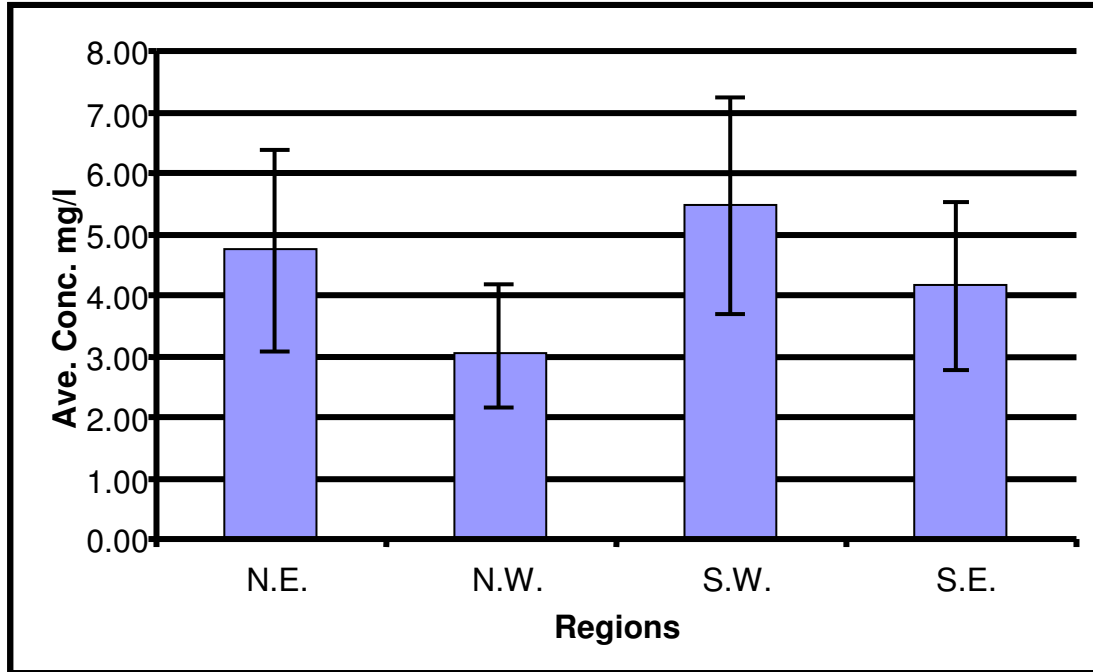


Fig 3.19 Grouping of K

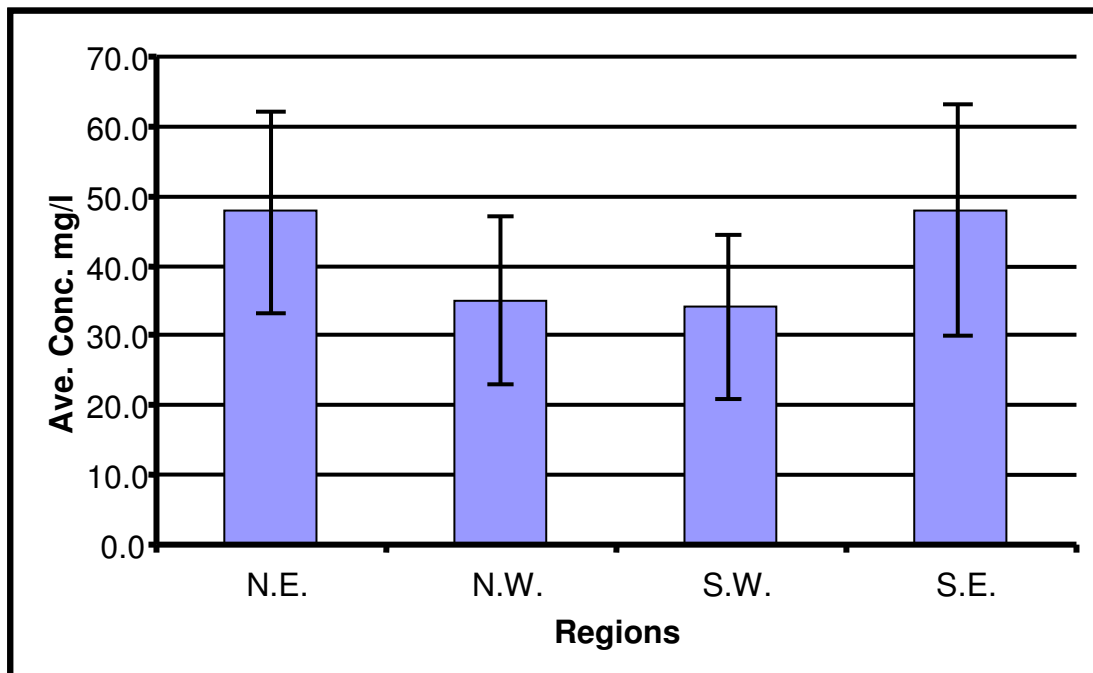


Fig 3.20 Grouping of Mg

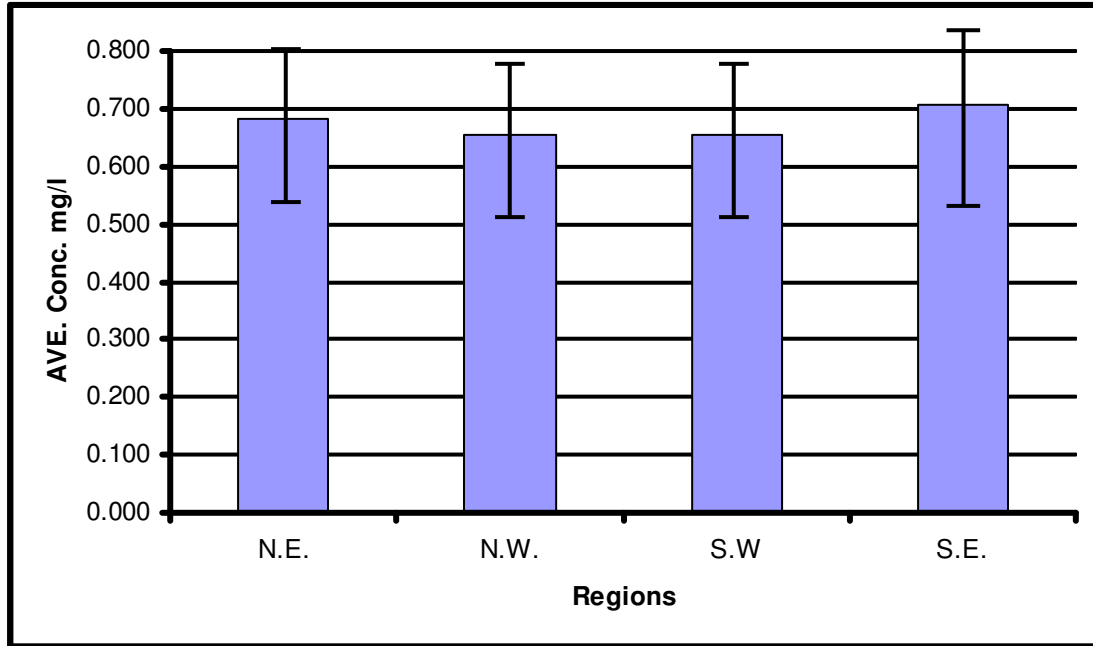


Fig 3.21 Grouping of Al

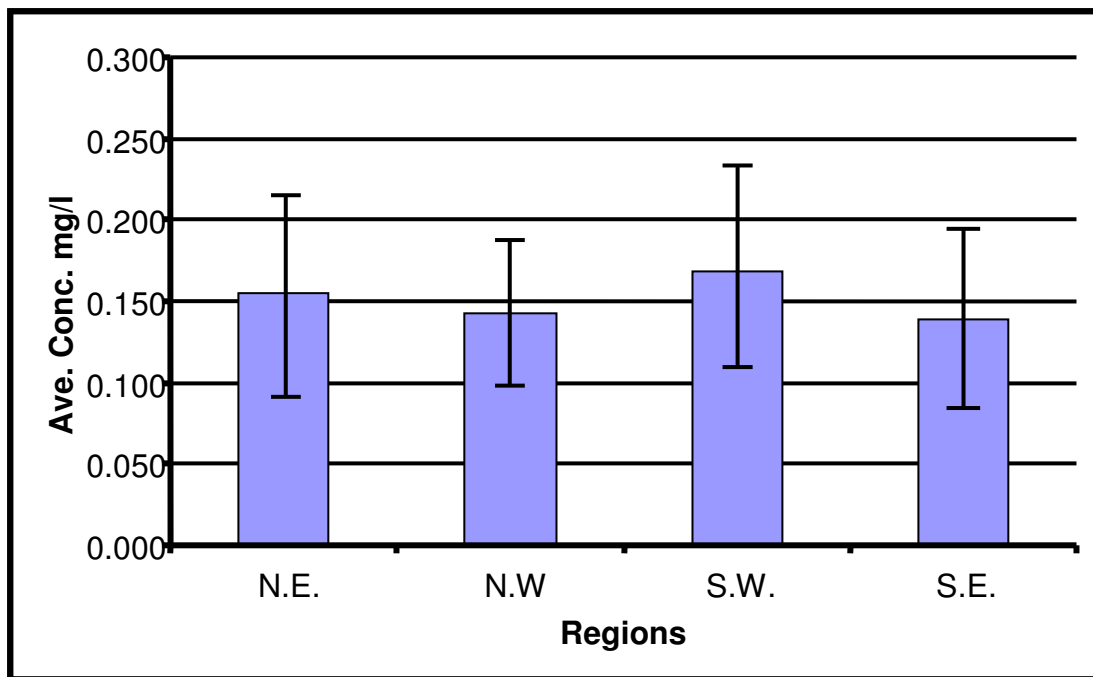


Fig 3.22 Grouping of Ba

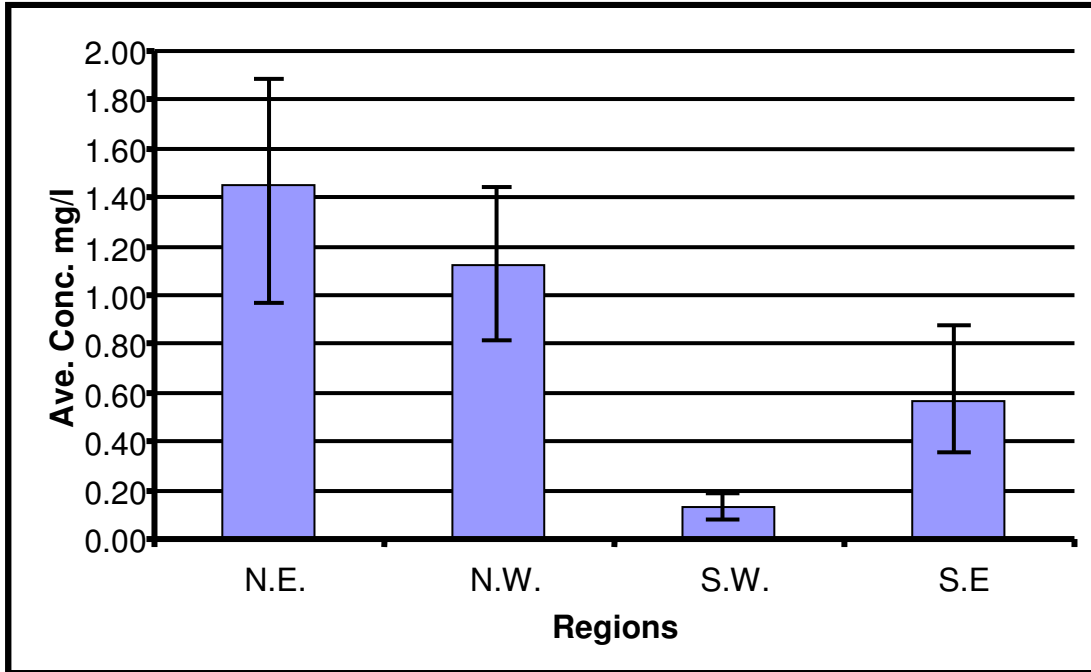


Fig 3.23 Grouping of Fe

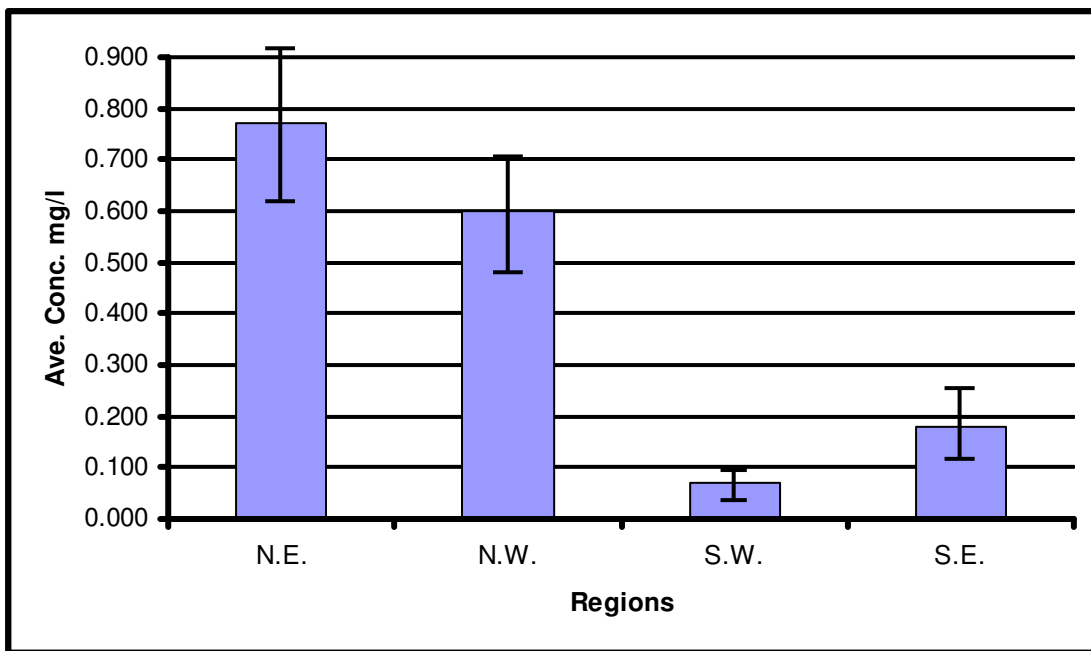


Fig 3.24 Grouping of Zn

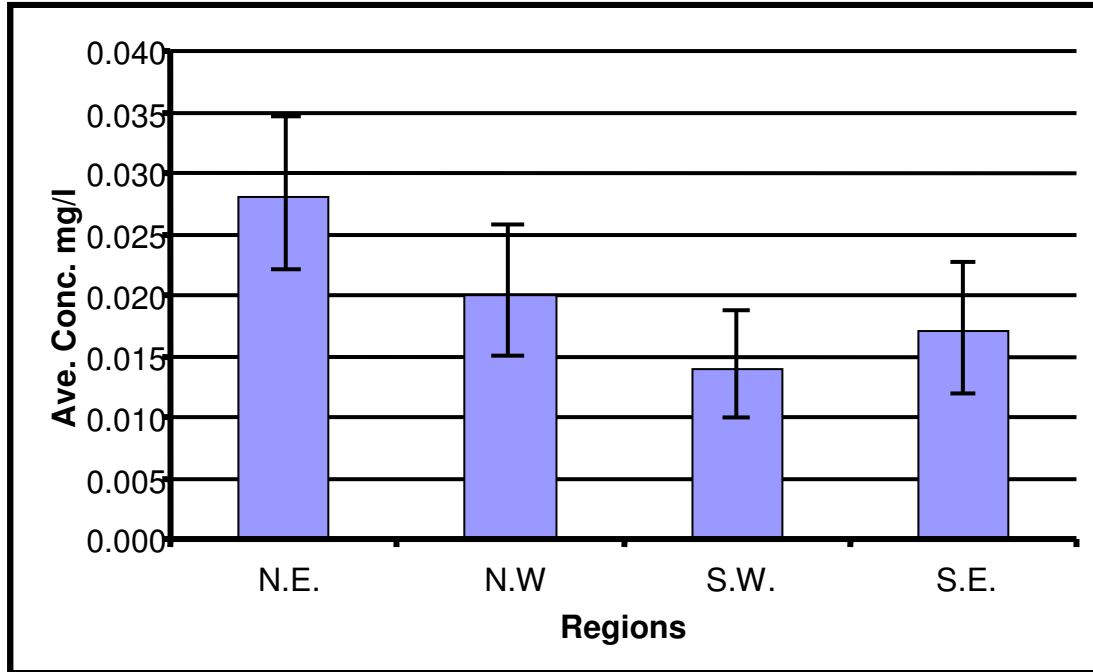


Fig 3.25 Grouping of Cu

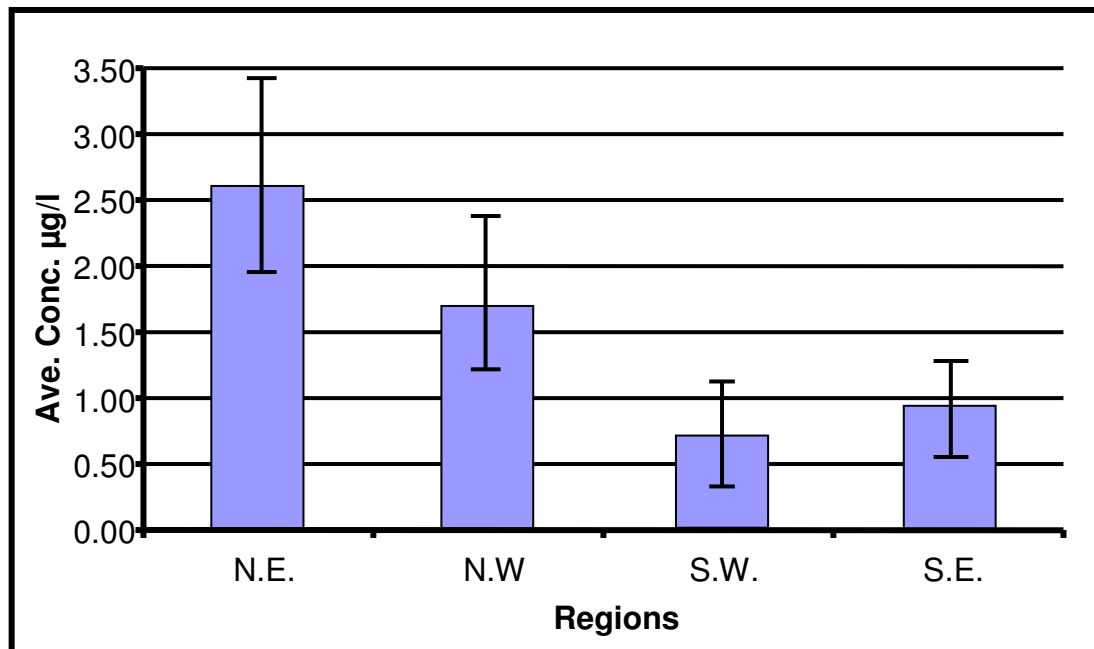


Fig 3.26 Grouping of Pb

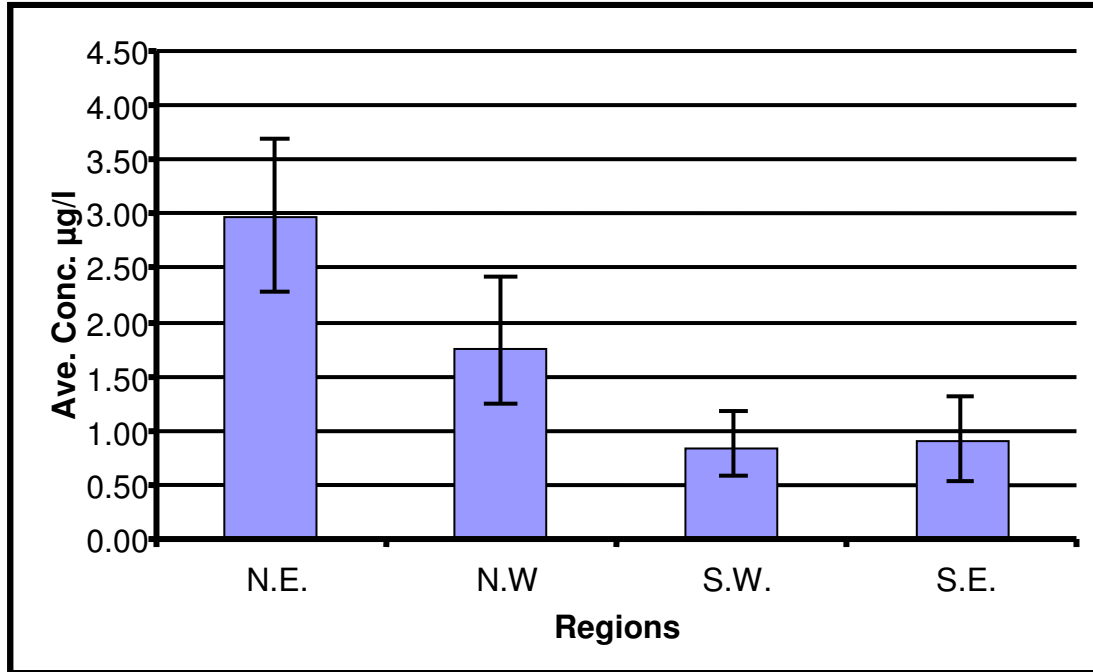


Fig 3.27 Grouping of Cr

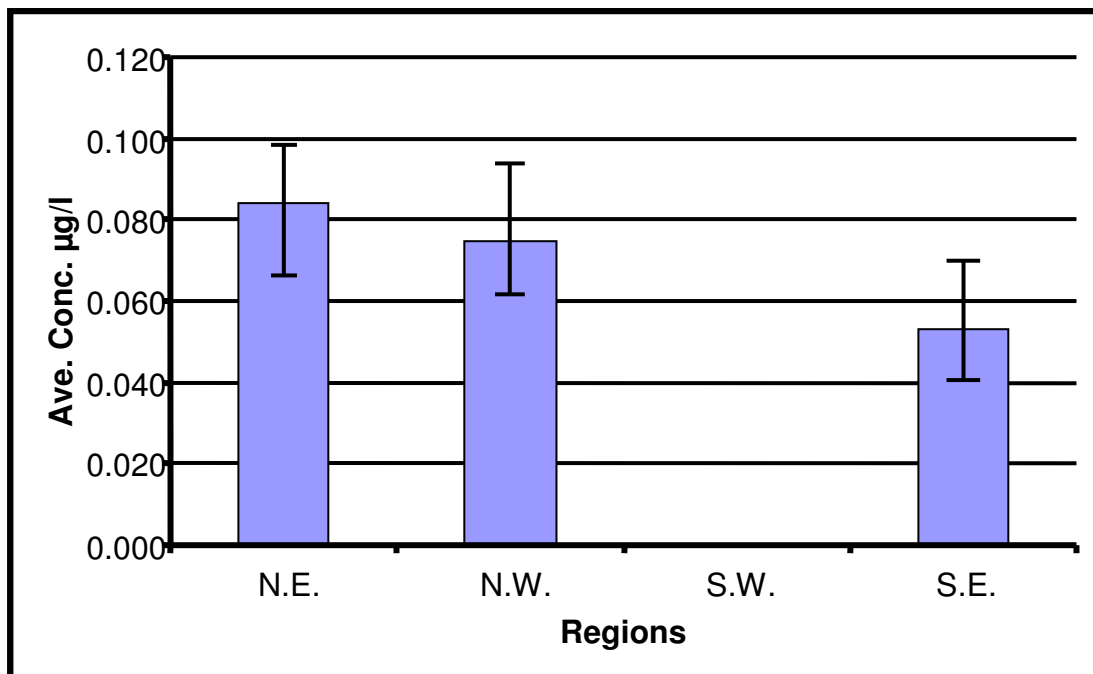


Fig 3.28 Grouping of Cd

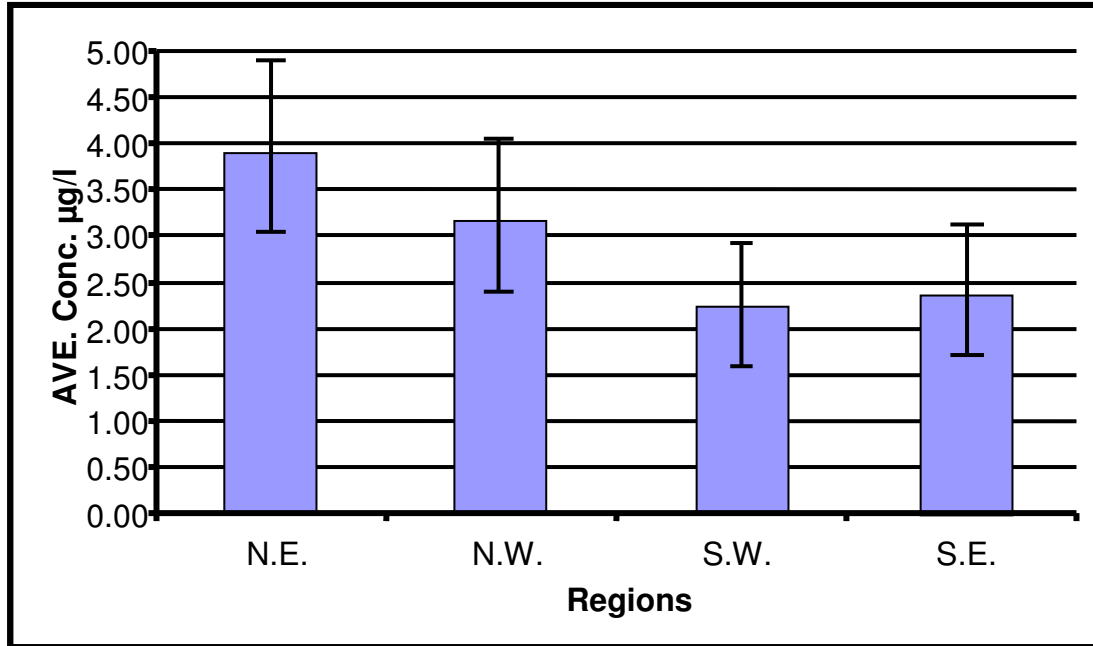


Fig 3.29 Grouping of Ni

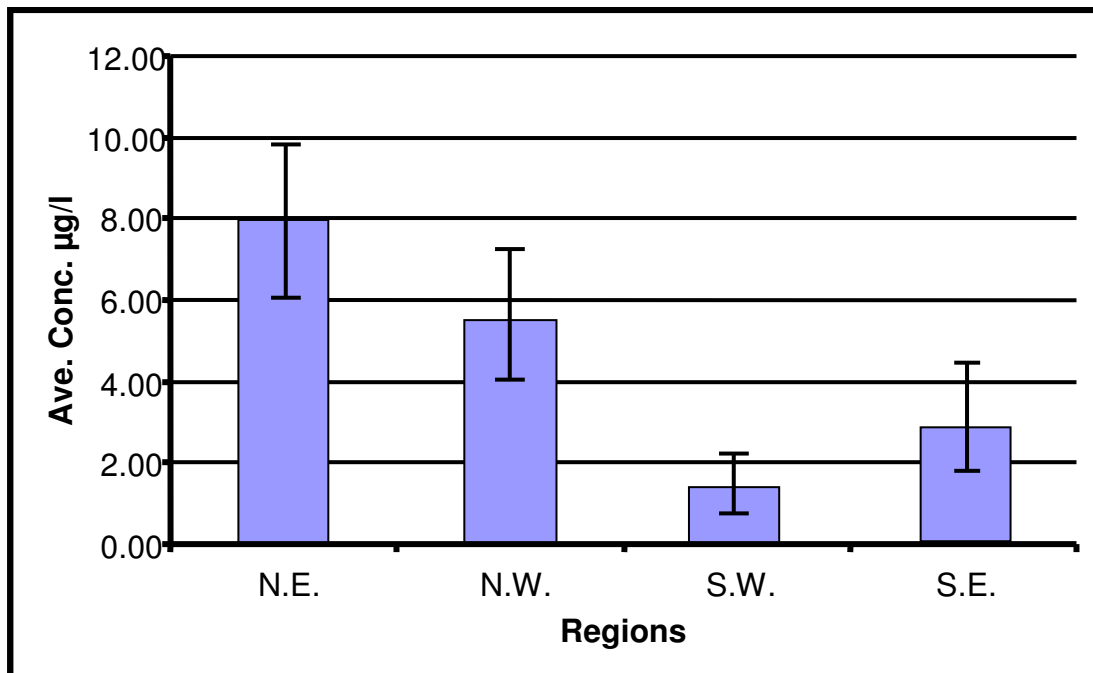


Fig 3.30 Grouping of V

3.2. Distribution of Metals

Contour maps (Fig 3.31 to 3.44) show the distribution of the metals in the groundwater. The distribution of a metal in groundwater depends upon the solubility of the metal compound, the pH, the composition of the soil, the geochemistry, the hydrogeology and the path of the flow of the groundwater (Desboeufs et al., 2000).

-Fig 3.31 shows the distribution of Na. Na concentration is quite high in the whole area because it is a crustal element. Na has the highest concentration in the area around the well No.15.

-Fig 3.32 shows the distribution of Ca. The soil in Soma area is plentiful of CaCO_3 , therefore the concentration of Ca is high in all wells. The highest concentration appears around the well No. 28.

-Fig 3.33 shows the distribution of K. K is a crustal element but its compounds are moderately soluble in water, therefore its concentration is not high. The highest concentration appears around the well No. 3.

-Fig 3.34 shows the distribution of Mg. Mg is also a crustal element and its compounds are moderately soluble in water. Therefore its concentration in the water samples is relatively high ranging from 15 – 95 mg/l. The highest concentration appears around the well No. 3 to the southwest of the ash piles.

-Fig 3.35 shows the distribution of Ba. Ba is an anthropogenic element and its compounds are moderately soluble in water. The high concentrations of Ba appear around wells 14, 21 and 22 which are close to the ash piles, and around wells 12 and 19 which are midway from the ash ponds. So, Ba may have originated from the ash and migrated to the groundwater.

-Fig 3.36 shows the distribution of Al. Al is a crustal element, and its compounds are sparsely soluble in water. The highest concentration of Al is around well No. 31 of 0.950 mg/l. The concentrations of Al range from 0.413 – 0.950 mg/l. Concentrations are close to each other which imply that this element comes from crustal sources.

-Fig 3.37 shows the distribution of Fe in the water wells. Fe comes from anthropogenic sources and its compounds are sparsely soluble in water. It can also come from natural sources. There are three wells that have high concentrations of Fe. These are wells No. 6, 17 and 37 that have concentrations of 5.87, 2.5 and 6.73 mg/l respectively. This is relatively high. So, Fe might have leached from the ash ponds and from the power plant area and got dissolved in groundwater. The variation of the distribution of the element depends on the pH, the hydrogeology and the composition of the soil. The soil may cause the metal to be adsorbed on the soil and hence extracted from the liquid phase. This depends on the hydrogeology and the geochemistry of the groundwater reservoir.

-Fig 3.38 shows the distribution of Zn in the water. Zn is an anthropogenic element. Its compounds are sparsely soluble in water. The highest concentration of Zn appears in well No. 37 (2.63 mg/l). The concentrations in wells No. 12, 16, 19, 21 and 22 were also

high. These wells are close to the ash piles. So, the high concentration of Zn might be a result of leaching of this from the ash to the groundwater.

-Fig 3.39 shows the distribution of Cu in the groundwater. Its compounds are moderately soluble in water. In general Cu concentration is not high. The highest concentration appears in the wells No. 11, 12, 13, 14, 19, 20 and 21 which are close to the ash piles. So, Cu might have leached from the ash piles and migrated to the groundwater.

-Fig 3.40 shows the distribution of Pb in the groundwater. Pb is an anthropogenic element and its compounds are moderately soluble in water. The high concentrations of Pb appear in wells No. 15, 16, 19, and 20 which are the closest to the ash piles. The concentrations range from 4.98 – 6.20 $\mu\text{g/l}$. This is relatively high. This might be a result of the leaching of this toxic element from the ash piles to the water.

-Fig 3.41 shows the distribution of Cr. Cr is an anthropogenic element and its compounds are moderately soluble in water. The high concentrations appear in the wells No. 13, 14, 15, 16, 17, 22 which are close to the power plant and the ash piles and in the wells No. 4 and 6 which are relatively far from the ash piles and the power plant. Cr could have leached from the ash piles and migrated to the water.

-Fig 3.42 shows the distribution of Cd in the groundwater. Cd is an anthropogenic element and its compounds are moderately soluble in water. The high concentrations of Cd appear around wells 15, 16, 17, 19 and 22 which are very close to the ash piles. So, Cd might have leached from the ash piles to the groundwater.

-Fig 3.43 shows the distribution of Ni. Ni comes from anthropogenic sources, and its compounds are moderately soluble in water. The high concentrations of Ni appear in the wells 9, 10 and 14 which are close to the ash piles. This high concentration could be a result of leaching of Ni from the ash piles.

-Fig 3.44 shows the distribution of V. V is an anthropogenic element. Its compounds are moderately soluble in water. The high concentration of V appear in wells 14, 15, 16, 17, 18, 19 and 20 which are very close to the ash piles. This suggests that V had leached from the ash piles and migrated to the groundwater.

In general, all trace elements show high concentration around well 37 to the southwest of the ash piles, but quite far from them. This suggests that there might be another source in that area.

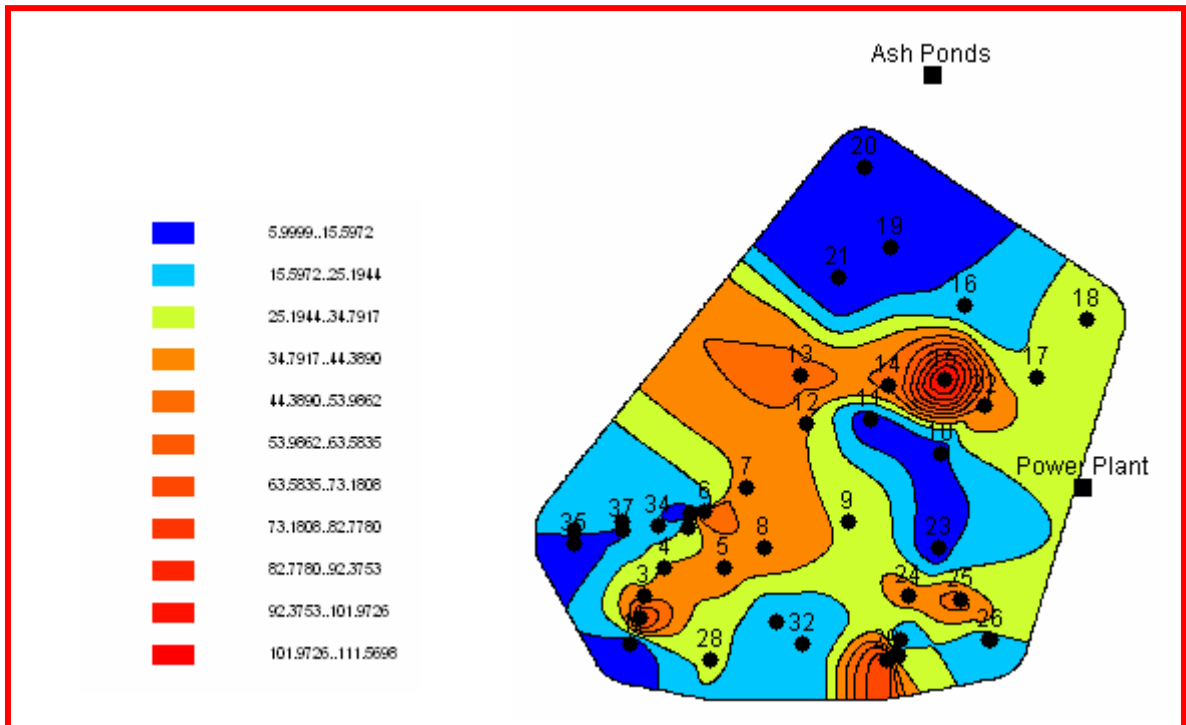


Fig 3.31 Na Distribution mg/l

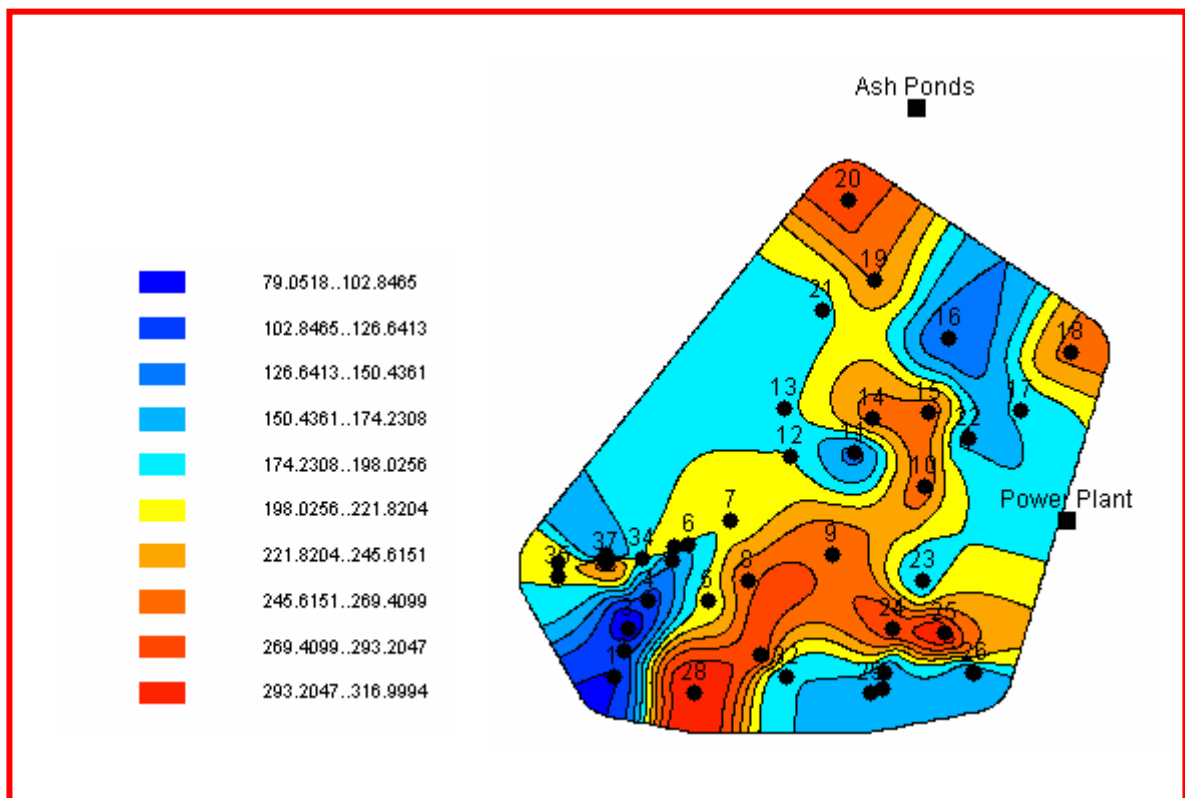


Fig 3.32 Ca Distribution mg/l

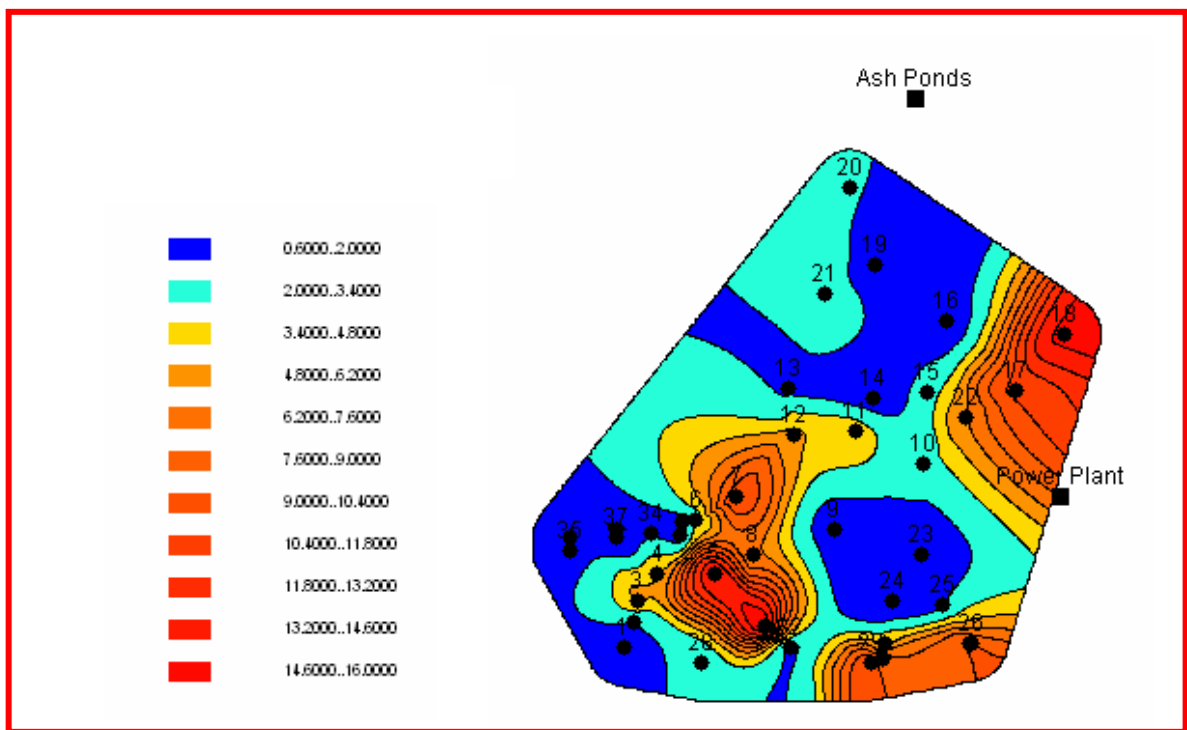


Fig 3.33 K Distribution mg/l

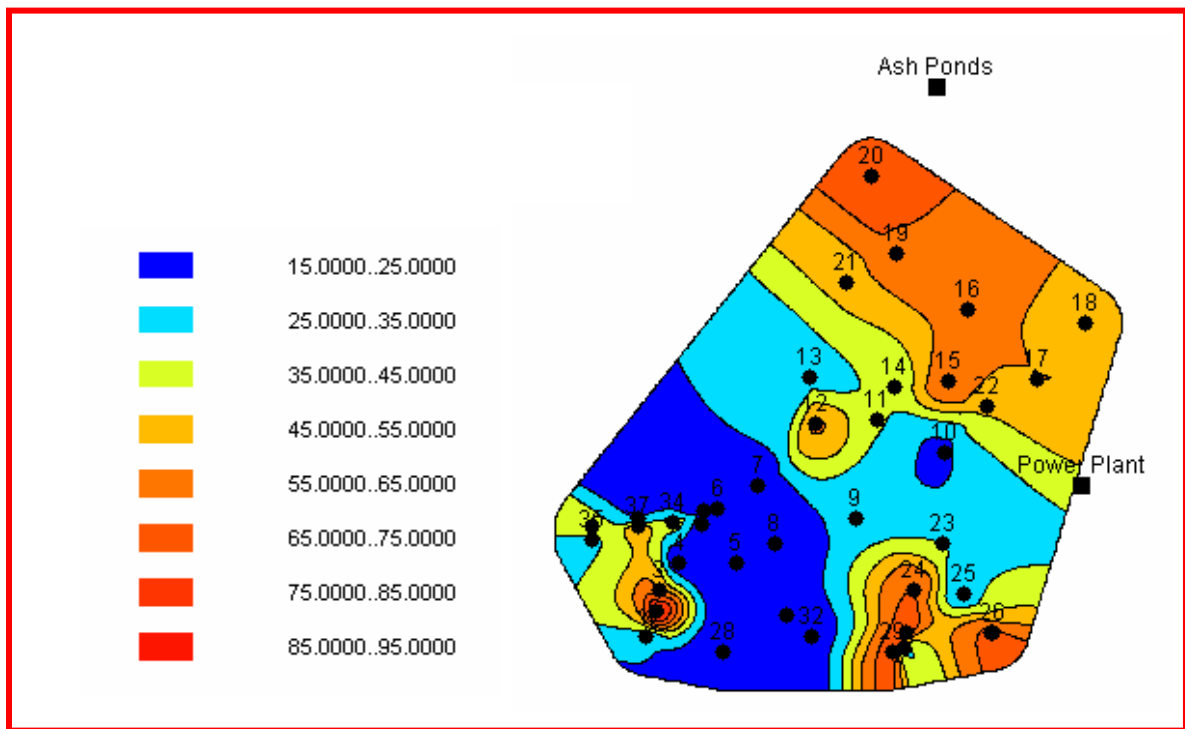


Fig 3.34 Mg Distribution mg/l

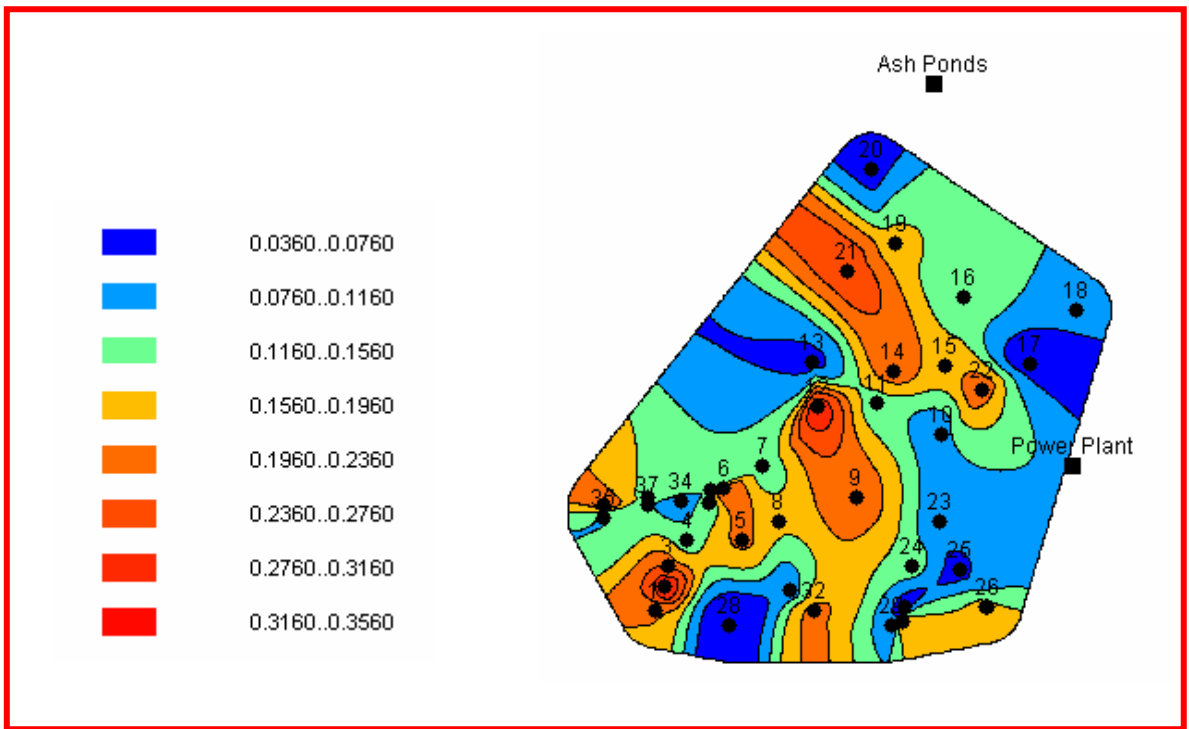


Fig 3.35 Ba Distribution mg/l

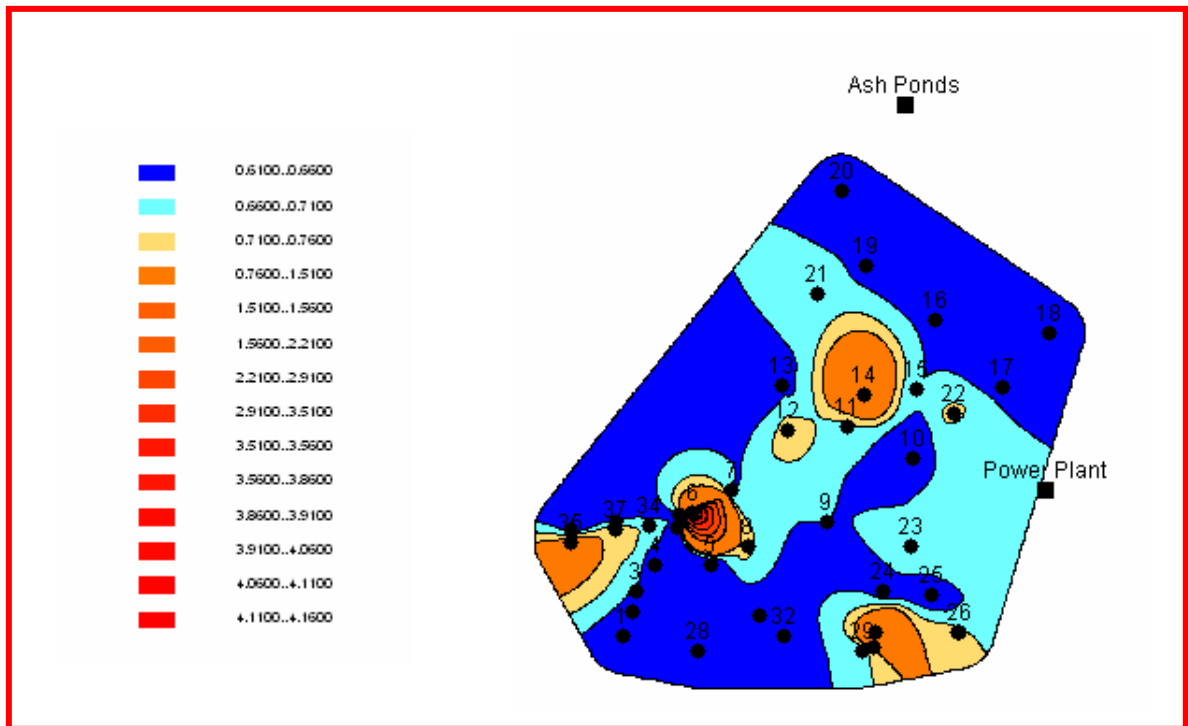


Fig 3.36 Al Distribution mg/l

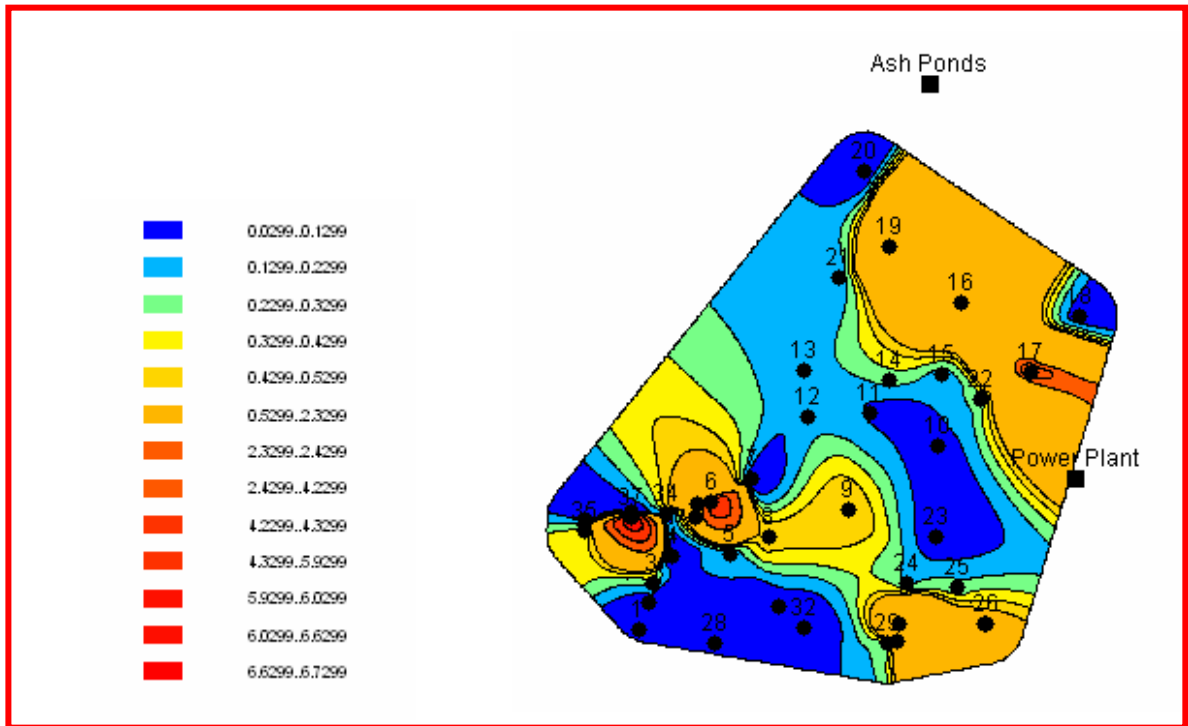


Fig 3.37 Fe Distribution mg/l

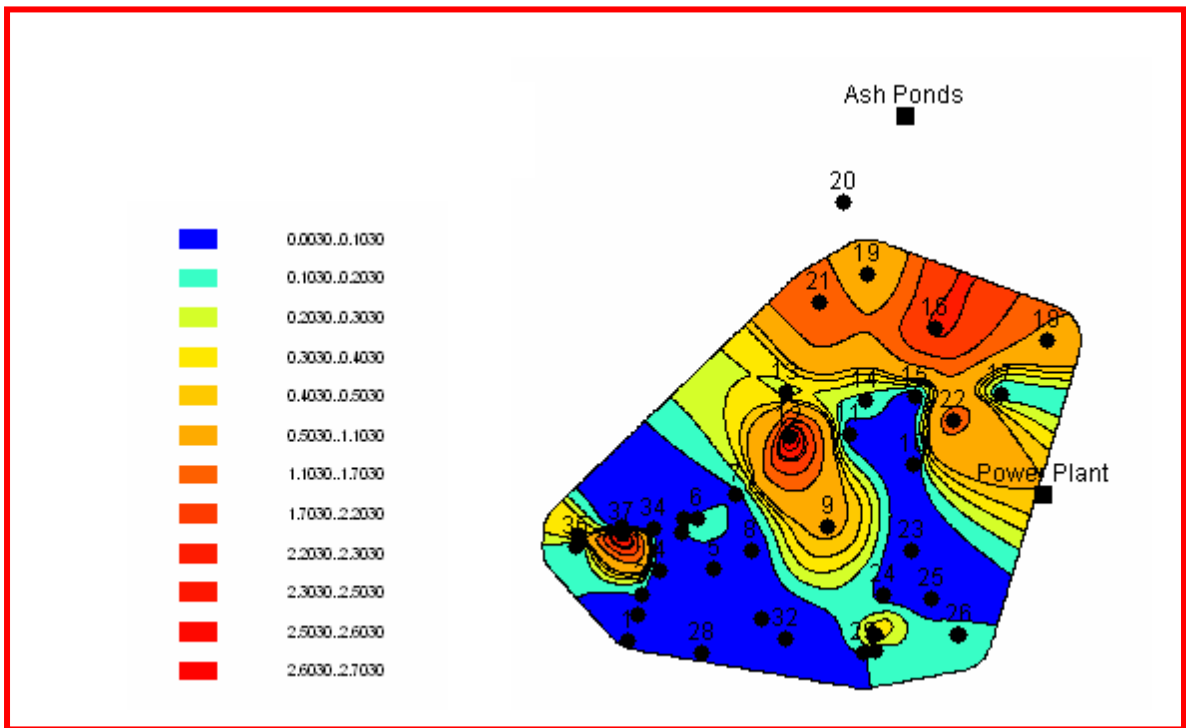


Fig 3.38 Zn Distribution mg/l

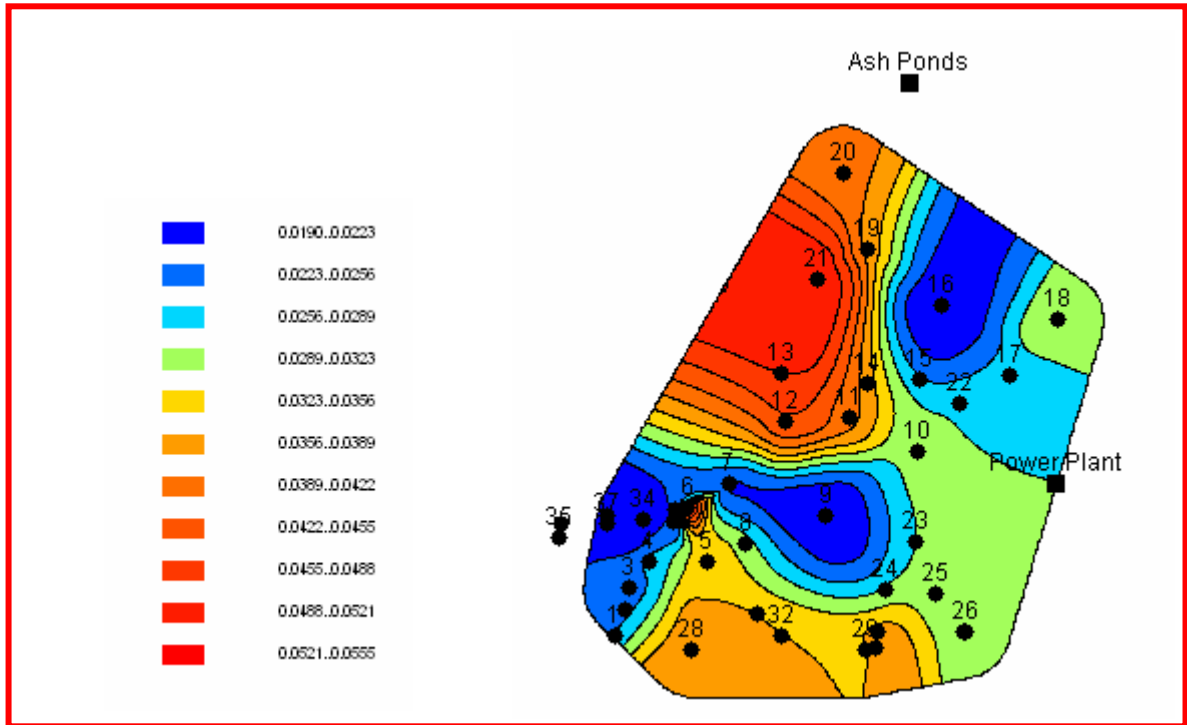


Fig 3.39 Cu Distribution mg/l

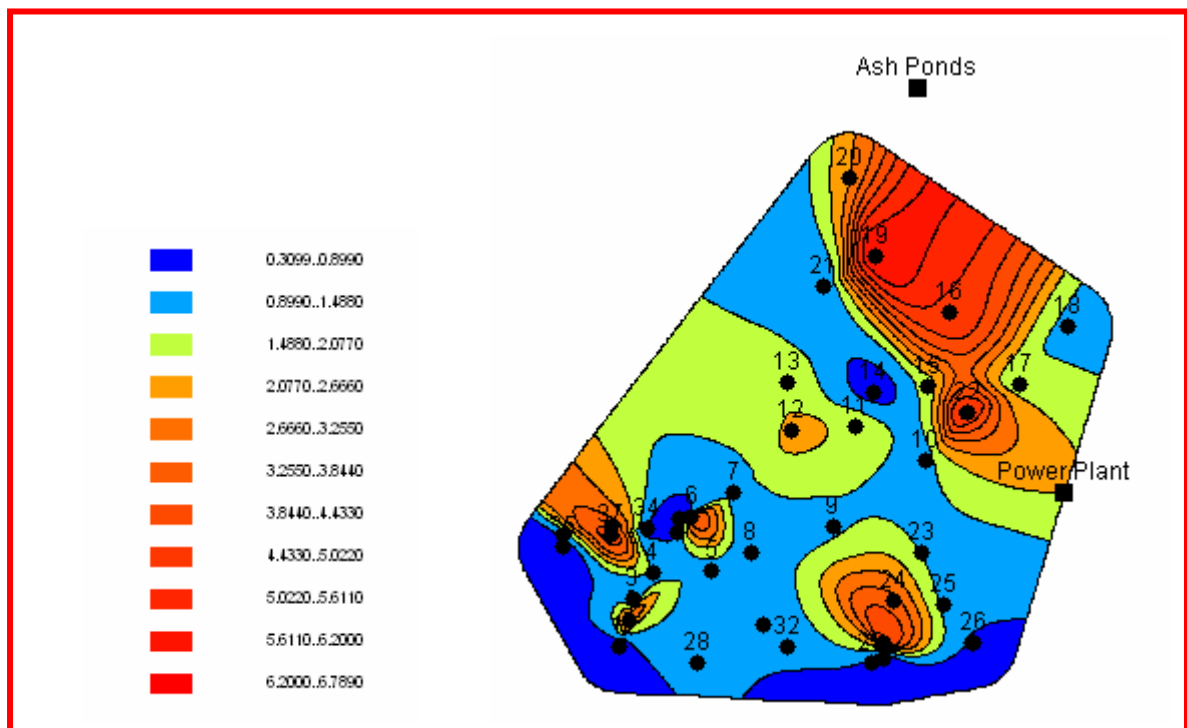


Fig 3.40 Pb Distribution mg/l

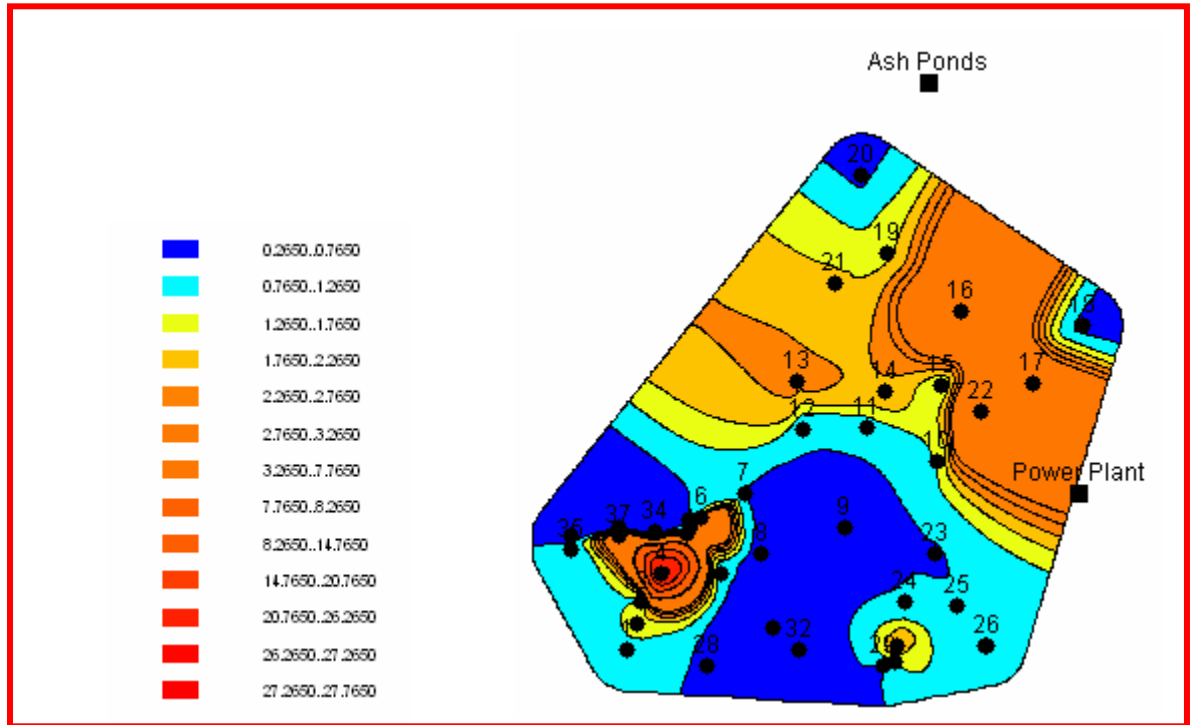


Fig 3.41 Cr Distribution $\mu\text{g/l}$

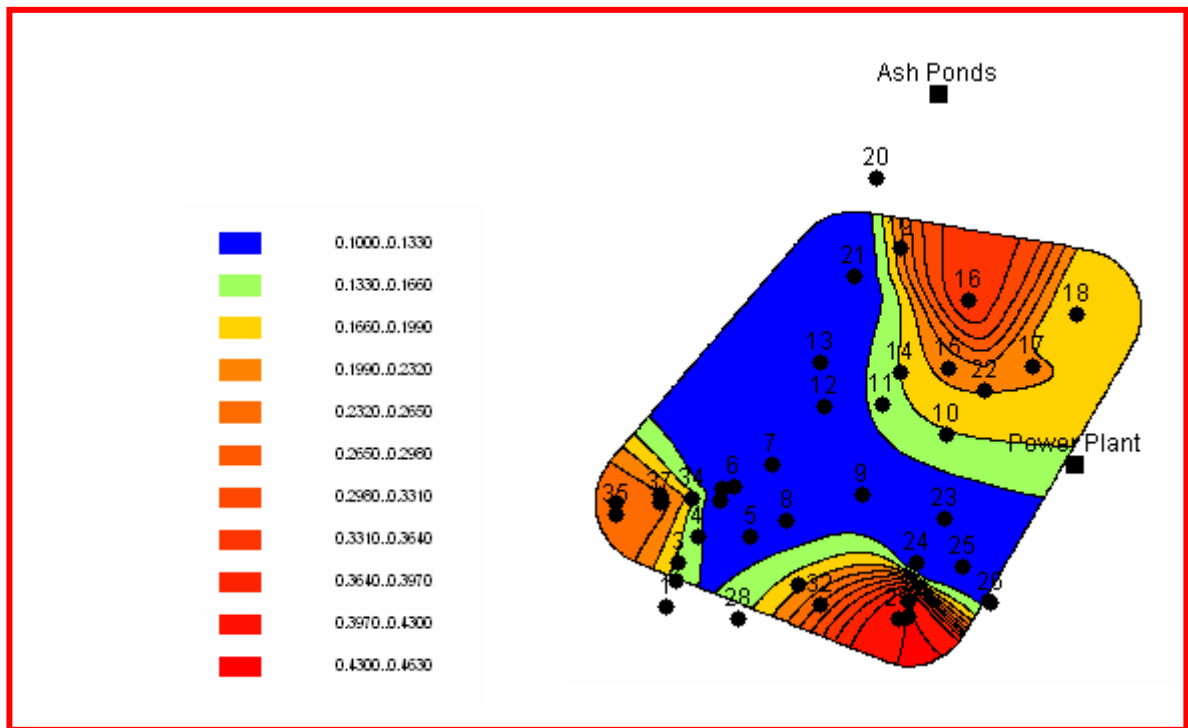


Fig 3.42Cd Distribution $\mu\text{g/l}$

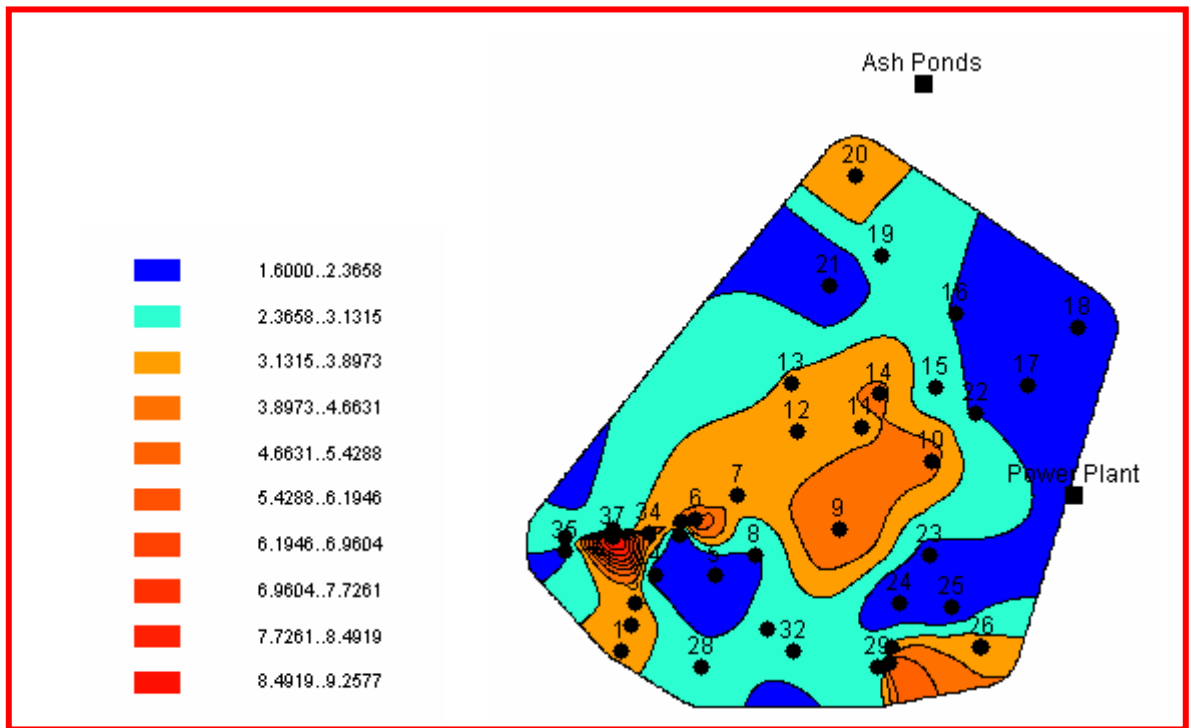


Fig 3.43 Ni Distribution µg/l

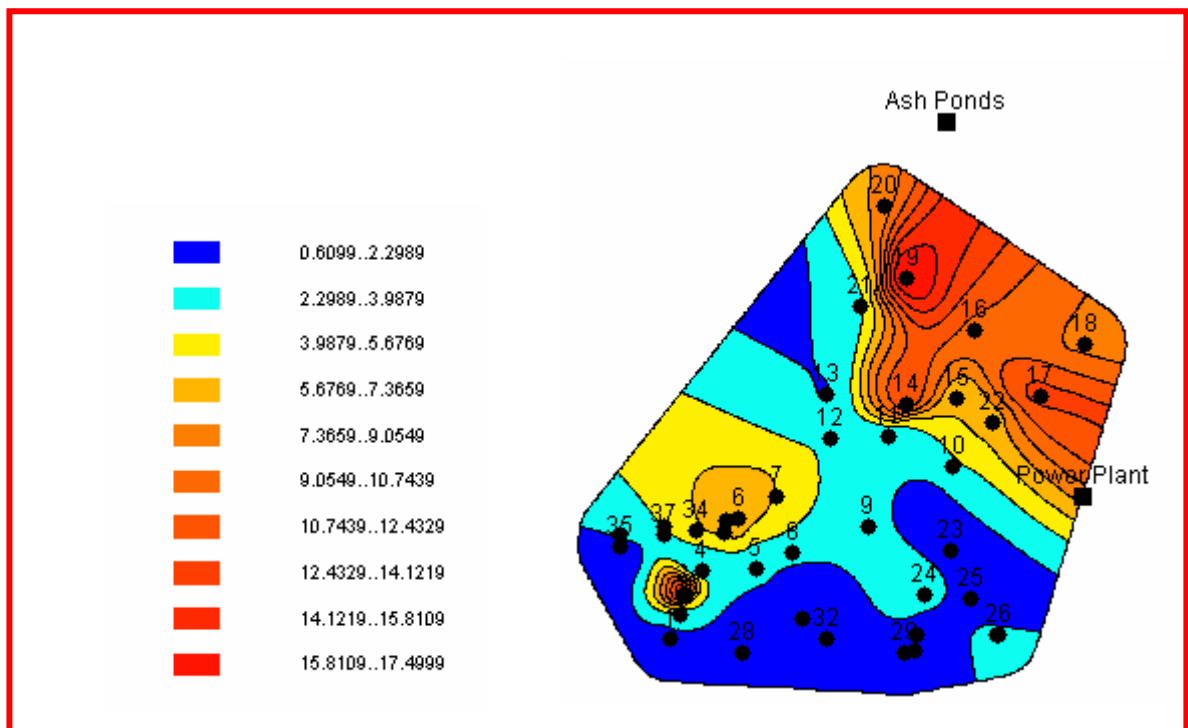


Fig 3.44 V Distribution µg/l

3.3. Enrichment Factors of Elements in the Water Samples

Enrichment factor is double normalization of elemental concentration in order to estimate enrichment with respect to a given matrix, usually soil. First, the ratio R_{sample} is calculated by dividing the concentration of an element X in a sample (e.g. Fe) by the concentration of a normalizing element Y from the same sample. The normalizing element is the one whose presence is attributed to a known and single source. Generally Al is selected as a normalizing element. The normalization eliminates any sample to sample variation in crustal material loading. Next, R_{sample} is divided by the average natural crustal ratio of the same two elements, R_{crustal} ;

$$(EFX)_{\text{sample}} = \frac{R_{\text{sample}}}{R_{\text{crustalaverage}}} = \frac{(X/Y)_{\text{sample}}}{(X/Y)_{\text{crustalaverage}}} \dots\dots\dots 3.1$$

When EFC is close to unity for any element X, this element may have a crustal source. Elements with enrichment factors less than 10 are not considered to be enriched in the sample, because variations in crustal compositions can account for such enrichments. However, elements with crustal enrichment factors greater than 10 are considered to be enriched (Gaga, 2004).

The reference element in crustal enrichment factor calculations should be a typical non-volatile lithophile element which has high abundance in crustal material. It should not have any other source than crustal material. Other than Al, Ti, Si and Sc are used in crustal enrichment factor calculations. The crustal composition was obtained by Mason (1966).

In this study, Mason's crustal elements to aluminum values were used as a reference. The metal concentrations to aluminum concentrations ratios were calculated and enrichment factors were obtained. Fig 3.44 shows the average enrichment factors of the elements.

It can be seen from the figure that Ba, Zn, Cu, Pb and Cd are enriched indicating anthropogenic origin. Fe, Cr, Ni, and V are considered not enriched. Na, Ca, K and Mg have high E_{Fc} but these metals are crustal elements so they can not be considered as coming from anthropogenic origin.

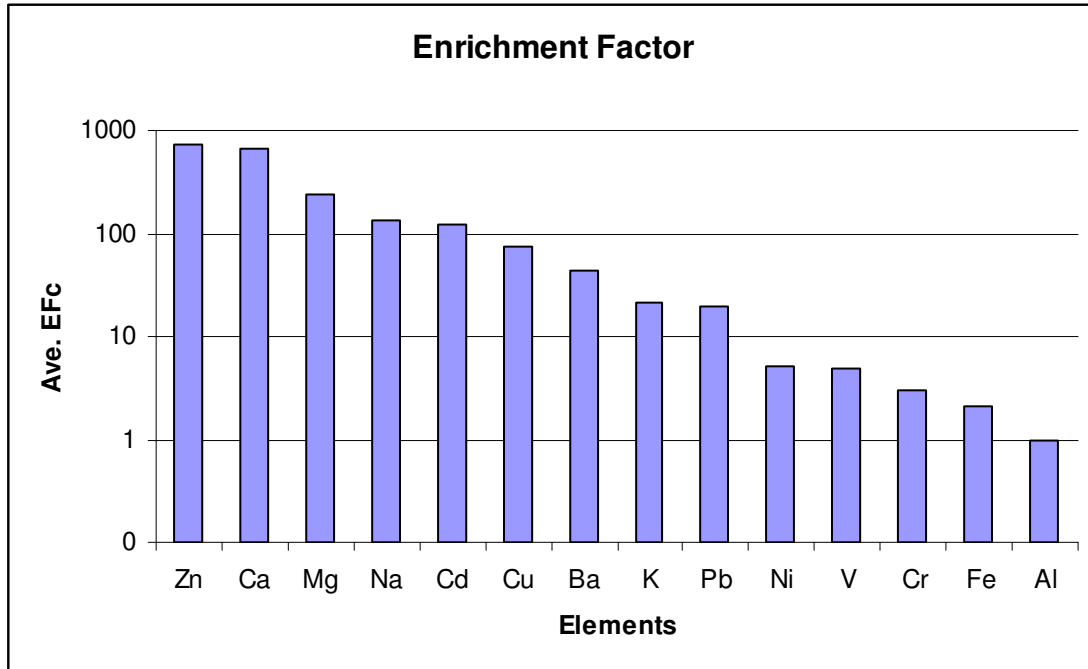


Fig 3.45 Enrichment Factor of Elements

3.4. Grouping of the Enrichment Factors

The average enrichment factors of the elements in the four regions were calculated. That is in the north east, northwest, south east and south west of the ash piles.

Figures 3.46 through 3.52 show the average enrichment factors vs. the regions. As expected, there is not much variation in the enrichment factors of the crustal elements among the regions. But, for the anthropogenic element, the enrichment factors in the north east and northwest regions are higher than 10 which means that all of these elements are enriched in these two regions. So, there is an anthropogenic origin for these elements. This trend is typical because these two regions are close to the ash piles.

For the southeast and southwest regions, Cu, Cd and Zn are enriched but less enriched than the other two regions. The rest of the anthropogenic elements are not enriched in these two regions. This indicates that the concentrations of these elements decrease as you go away from the ash piles. So, the ash piles are a source for these metals.

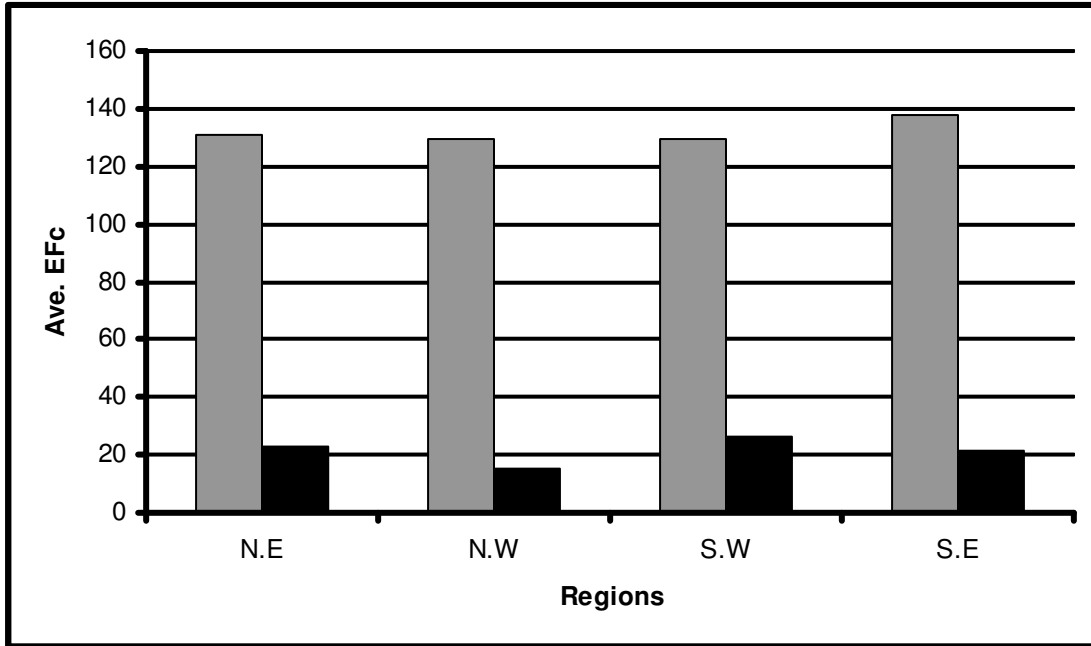


Fig 3.46 Enrichment Factors of Elements

Na  K 

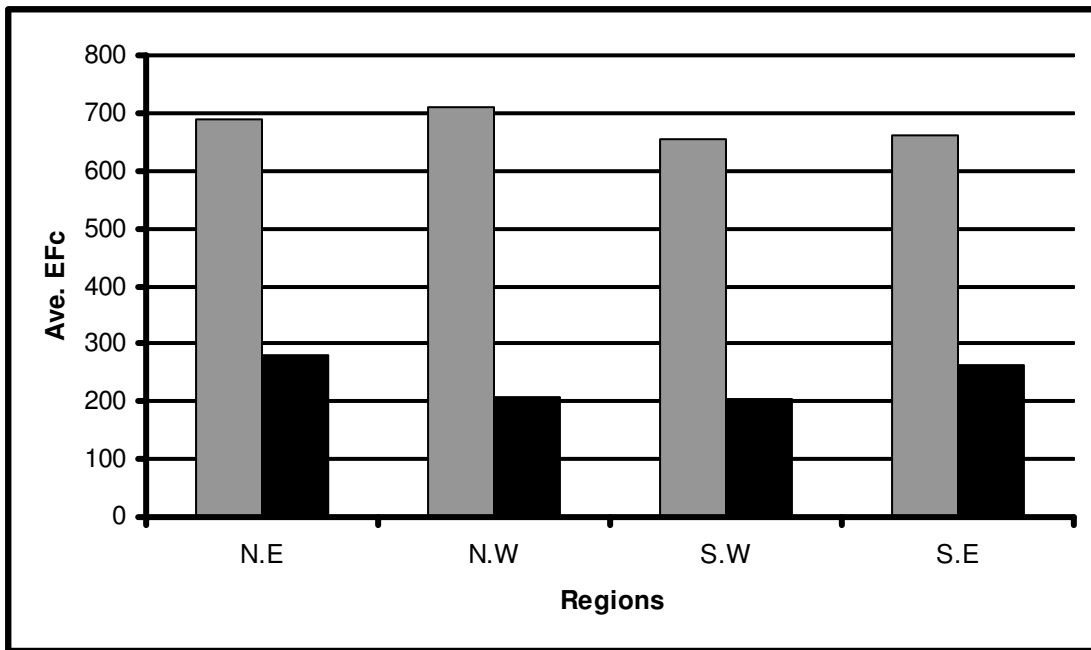


Fig 3.47 Enrichment Factors of Elements

Ca  Mg 

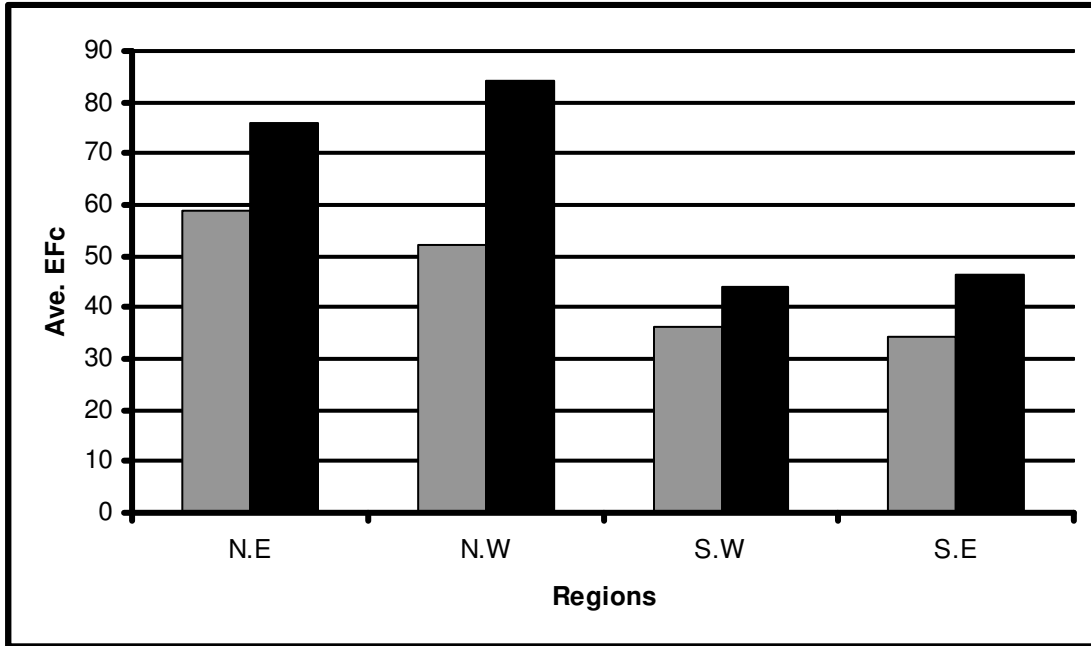


Fig 3.48 Enrichment Factors of Elements

Ba  Cu 

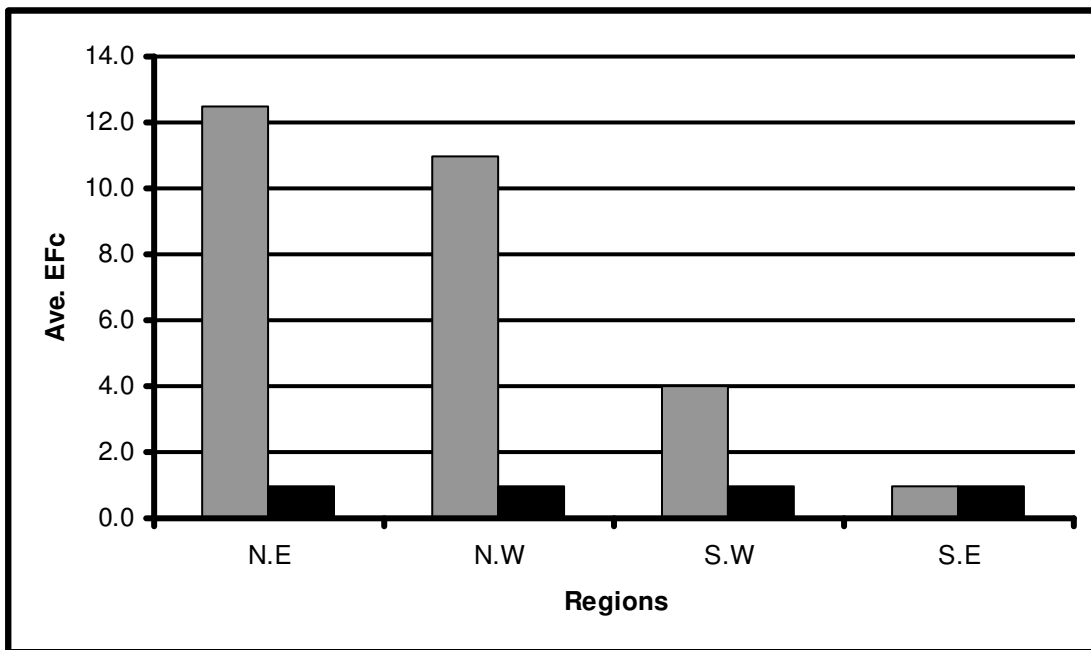


Fig 3.49 Enrichment Factors of Elements

Fe  Al 

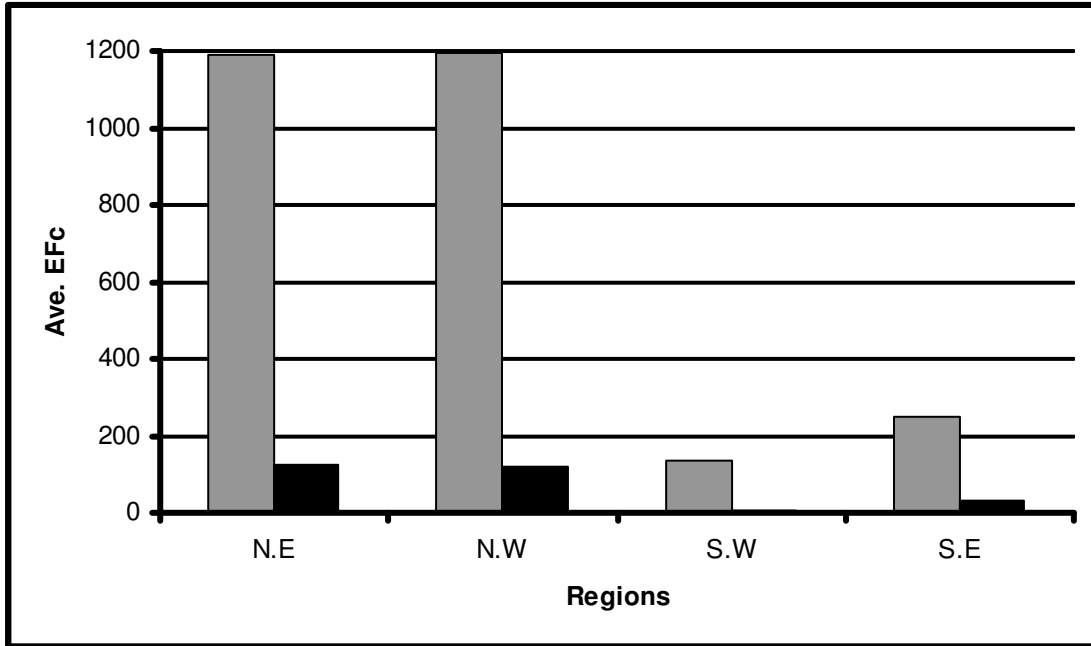


Fig 3.50 Enrichment Factors of Elements

Zn Cd

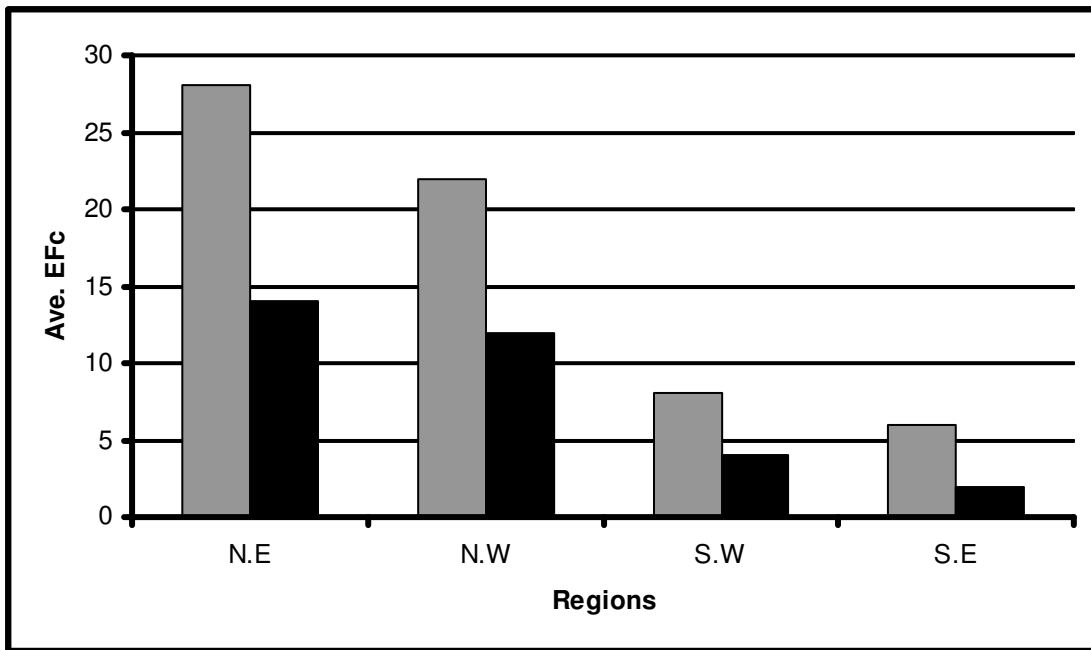


Fig 3.51 Enrichment Factors of Elements

Pb Ni

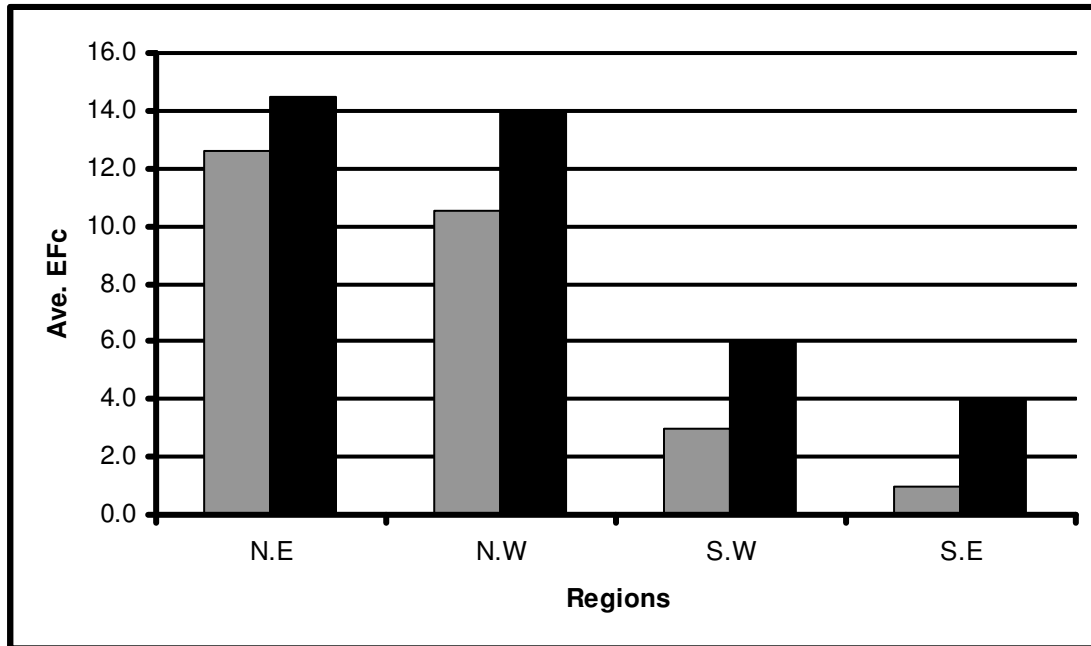


Fig 3.52 Enrichment Factors of Elements

Cr  V 

3.5. Factor analysis

Multivariate statistical methods such as factor analysis have been frequently applied in environmental pollution studies with the aim of identifying possible sources of pollution and to determine the elemental composition of these sources as well as the contribution of each source to the total pollution level.

The major goals of factor analysis are 1) to determine the number of factors needed to describe the experimental data satisfactory and 2) to determine the matrix of factor loadings.

If the data set of elemental concentrations determined at N observations for a total of n elements, the concentration of the j-th element (j=1.....n) at the i-th sampling site (i=.....N) is denoted by x_{ij} , the data set is transformed to standardized variables z_{ji} by

$$z_{ji} = (x_{ji} - \bar{x}_j) / \sigma_j \dots\dots\dots 3.2$$

Where \bar{x}_j and σ_j are the mean of the data and standard deviation of the measurement for the element j respectively. Concentrations of all elements in each sample are normalized. This normalization gives each element equal weight in the factor analysis regardless of its average concentration. This normalized concentration, z_{ji} has a mean value of 0 and a variance of 1.

The z_{ji} is then assumed to be a linear sum of m common factors (emission sources) , with $m \leq n$, which account for the correlations between the variables, and a unique contribution which is specific of each individual sampling site.

In factor analysis the number of factors m is decided by the eigenvalues cutoff. As the cutoff value decreases, m increases. One of the serious drawbacks in factor analysis is the selection of this cutoff value which in turn governs the value of m . On the selection of the cutoff value, there is no universally applicable method for establishing m and it is necessary to discard a number of small eigenvalues. Generally, eigenvectors with eigenvalues greater than 1 are more signal than noise and should be kept in the model. Eigenvectors with eigenvalues less than 0.5 have more than twice as much noise as signal and must be eliminated from the model. The total variance explained by the factors is also important in the reduction of the number of factors. At least 70% of the total variance must be included in the analysis. (Karakaş, 2000)

We have obtained four factors which explain 74.589% of the total variance as the result of factor analysis. Elements with factor loading greater than 0.450 should be considered in the analysis. (Gaga, 2004) Results of factor analysis are shown in Table 3.4.

Factor 1 which explains 25.624% of total variance is loaded with Fe, Zn, Cu, Pb, Cr, Cd, Ni and V is obviously an anthropogenic factor which means that these elements originated from an anthropogenic source which in this case is the ash piles.

Factor 2 which explains 18.943% of total variance composed of elements Ca, Al and Fe represents a crustal factor which in this case is the soil.

Factor 3 which explains 16.719% of total variance is loaded with Mg indicating that there is a specific source for Mg which might be some layers of the soil.

Factor 4 which explains 13.843% of total variance is loaded with Na and K represents a crustal source which is the sea.

So, from the factor analysis, there is an anthropogenic source for the pollution, which in this case are the ash piles indicating the effect of the power plant on the environment.

Table 3.4. Varimax Rotated Factor Matrix

Element	Factor 1	Factor 2	Factor 3	Factor 4
Na				0.799
Ca		0.891		
K				0.605
Mg			0.575	
Al		0.871		
Fe	0.692	0.461		
Zn	0.765			
Cu	0.644			
Pb	0.762			
Cr	0.839			
Cd	0.591			
Ni	0.843			
V	0.726			
Eigen Value	3.587	2.652	2.265	1.938
Variance	25.624	18.943	16.179	13.843
Total Variance	74.589			

CHAPTER 4

CONCLUSION

In this study, forty groundwater samples were collected from water wells near by Soma power plant in order to evaluate the effect of the power plant and the ash piles on the groundwater.

Samples were collected in polyethylene bottles; their pH was measured, acidified and analyzed using FAES, FAAS, GFAAS and ICP-AES.

GFAAS gave low detection limits for trace metals and ICP-AES gave low detection limits for Fe, Zn, Al and Ba.

The crustal elements did not show high variations from one well to another, but the anthropogenic elements did. Fe concentrations in 12 wells were higher than the WHO, the Turkish and EC guidelines and Zn concentrations in 5 wells were higher than the EC guidelines. Zn concentrations were not higher than the Turkish guidelines. Pb concentrations in 8 wells were high but not higher than the guidelines. The other anthropogenic elements were within the guidelines. But, metals tend to accumulate in

groundwater and if no action is taken, after some time the concentrations of these metals will exceed the guidelines.

Enrichment factor calculations showed that all the anthropogenic elements were enriched in the northeast and northwest regions of the sampling area which are close to the ash piles indicating that these elements had originated from the ash piles. So, the anthropogenic metal concentrations decrease as you go away from the ash piles.

Factor analysis calculations showed that one factor was loaded with anthropogenic elements which imply that there is an anthropogenic source for these metals which in this case are the ash piles.

Soma residents are at risk because they drink the groundwater and use it for irrigation. This water is polluted with Fe and Zn and there are some amounts of the other anthropogenic elements which will accumulate over time. So, correction steps should be taken to overcome the problem of the ash disposal and save the health of the residents.

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