٢٥٦٣٥

ASSESSMENT OF THE POTENTIAL IMPACTS OF FUGITIVE DUST FROM SEYİTÖMER (KÜTAHYA) COAL-FIRED POWER PLANT FLY ASH DISPOSAL AREA

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
THE MIDDLE EAST TECHNICAL UNIVERSITY

BY

AYŞEGÜL HAMZAOĞLU

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE
IN
THE DEPARTMENT OF ENVIRONMENTAL ENGINEERING

SEPTEMBER 1998

for the memory of my father,

Mehmet Emin Hamzaoğlu

Approval of the Graduate School of Natural and Applied Sciences

Prof. Dr. Tayfur Öztürk
Director

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

Prof. Dr. Celal F. Gökçay
Head of the 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. Coşkun Yurteri
Co-Supervisor

Prof. Dr. Gürdal Tuncel
Supervisor

Examining Committee Members

Prof. Dr. Gürdal Tuncel

Prof. Dr. Coşkun Yurteri

Assoc. Prof. Dr. Kahraman Ünlü

Assoc. Prof. Dr. Ülkü Yetiş

Assoc. Prof. Dr. Nilgün Güleç

ABSTRACT

ASSESSMENT OF THE POTENTIAL IMPACTS OF FUGITIVE DUST FROM SEYITOMER (KÜTAHYA) COAL-FIRED POWER PLANT FLY ASH DISPOSAL AREA

HAMZAOĞLU, Ayşegül

M.Sc., Department of Environmental Engineering

Supervisor: Prof.Dr. Gürdal TUNCEL

Co-Supervisor: Prof.Dr. Coşkun YURTERİ

September 1998, 112 pages

Seyitömer coal-fired thermal power plant (SCTPP), with four units each having a capacity of 150 MW, was constructed in the province of Kütahya to supply energy for the north-west Anatolian region. The fly ash generated from these units has been deposited in an ash dam located 2.5 km from the power plant.

Fugitive dust, either from coal yard or from ash disposal area, creates problems like visibility and deposition on the lands nearby. Hence, the scope of this study is to assess the potential impacts of SCTPP fly ash by mathematical modeling. For this purpose, "receptor modeling" approach and a computer based model were studied in parallel. The results of the two models were compared in order to determine the dispersion of the fugitive dust from plant.

During this study, 22 aerosol and 40 soil samples were analyzed for the elements Na, Mg, Al, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb with a combination of flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS).

As a result of this study, the deposition and dispersion of the fugitive dust from plant were predicted and the values were compared with the ground-level concentrations given in literature. In this regard, the impacts of fugitive dust will be assessed and necessary precautions will be proposed if needed.

According to the results of this study, it is observed that the soil composition is severely differs from the average soil composition near the power plant and ash disposal site indicating that the sources have serious impacts within the their vicinity. However, 5 - 6 km away from the sources, the affect of sources sharply decreases.

Key Words: Air Pollution, Fly Ash, Trace Elements, Receptor Modeling and Factor Analysis

ÖZ

SEYİTÖMER (KÜTAHYA) KÖMÜR İŞLETMESİ VE ELEKTRİK SANTRALI'NIN UÇUCU KÜL DEPOLAMA SAHASINDAN KAÇAN TOZLARIN ÇEVREYİ ETKİLEME POTANSİYELİNİN BELİRLENMESİ

HAMZAOĞLU, Ayşegül
Yüksek Lisans Tezi, Çevre Mühendisliği Bölümü
Tez Danışmanı: Prof.Dr. Gürdal TUNCEL
Yardımcı Tez Danışmanı: Prof.Dr. Coşkun YURTERİ

Eylül 1998, 112 sayfa

Herbiri 150 MW kapasiteli dört üniteden oluşan Seyitömer kömür kaynaklı elektrik santralı (STS), kuzey-batı Anadolu'ya enerji sağlamak amacı ile Kütahya ili sınırlarına kurulmuştur. Ünitelerden çıkan uçucu kül santrale 2,5 km uzaklıktaki depolama alanına taşınmaktadır,

Kömür sahalarından ve kül depolama alanından çıkan tozlar görüş mesafesini azaltma ve yakın çevredeki alanlarda birikme gibi problemler yaratmaktadır. Bu sebeple, bu çalışmanın amacı, STS'deki küllerin potansiyel etkilerinin bir matematiksel model ile belirlenmesidir. Bu amaçtan yola çıkarak, reseptör ve dağılım modelleri ile paralel olarak çalışılmıştır. Her iki modelden elde edilen sonuçlar birbirleri ile karşılaştırılmış ve toz emisyonunun dağılımı belirlenmeye çalışılmıştır.

Bu çalışma süresince, 22 adet aerosol ve 40 adet toprak örneklerinde alevli atomik absorbsiyon spektrometresi ve grafit fırın atomik absorbsiyon

spektrometresi ile Na, Mg, Al, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Cd ve Pb elementleri analiz edilmiştir.

Sonuç olarak, santral kaynaklı tozların birikme ve dağılım konsantrasyonları belirlenmeye çalışılmış ve bulgular literatürdeki değerler ile karşılaştırılmıştır. Bu bağlamda, tozun etkileri belirlenmiş ve gerekli tartışmalar yapılmıştır.

Çalışma sonucunda elde edilen bilgilere göre, termik santral ve kül depolama alanı yakınlarındaki toprak kompozisyonunun belirgin bir şekilde değişmiş olduğu gözlenmiştir. Bu da kirletici kaynaklarının yakın çevrelerinde etkili olduğunun belirtisidir. Ancak, kaynaklardan 5-6 km kadar uzaklaşıldığında, bu etkilerde büyük bir düşüş görülmektedir.

Anahtar Kelimeler: Hava Kirliliği, Uçucu Kül, Eser Elementler, Reseptör Modellemesi ve Faktör Analizi

ACKNOWLEDGEMENT

My deep appreciations are for my advisor Prof.Dr. Gürdal Tuncel and my co-advisor Prof.Dr. Coşkun Yurteri for their great encouragement, guidance and suggestions during this study.

I am also very grateful to Mr. Turan Karakaş, Mr. Omer El-Agha, Mr. Ozan Devrim Yay, Ms. Nilgün Güvenç and Ms. Sinem Atgın for their helps during the experimental analyses and to technicians Ms. Aynur Yıldırım and Mr. Ramazan Demir for equipment supply. Thanks to Mr. Emre Kaya during my ISCST runs and any kind of computer knowledge and to Ms. Öznur Oğuz for MAPInfo drawings.

I would also like to thank to TEAŞ, especially SCTPP Administration and officers working there and Mr. Cem Çakıroğlu for his helps in supplying knowledge about SCTPP.

I extend my sincerely thanks to my room mates Ms. Başak Erdoğan and Ms. Gülnur Tumbat as well as Mr. Baton Begolli and other friends both in and out of the department.

My deepest gratefulness is for my mother, sister, other parents and family Korur for their endless patience during this study.

My special thanks are to my dear Serkan Korur not only he was with me in every second during this study, but also for planning to share his rest of life with me.

TABLE OF CONTENTS

ABSTRACT ..... *iv*
ÖZ ..... *vi*
ACKNOWLEDGEMENT ..... *viii*
TABLE OF CONTENTS ..... *ix*
LIST OF TABLES ..... *xii*
LIST OF FIGURES ..... *xiii*

1. INTRODUCTION 1

2. LITERATURE SURVEY 4
    2.1. General 4
    2.2. Ash 5
        2.2.1. Disposal of Ash 7
        2.2.2. Particulate Matter 9
    2.3. Source Apportionment Studies 12
    2.4. Dispersion Models 14
        2.4.1. ISCST Model 15
        2.4.2. Fugitive Dust Emissions 17
    2.5. Receptor Models 18
        2.5.1. Factor Analysis 22
        2.5.2. Enrichment Factors of the Elements 26

3. SEYITÖMER THERMAL POWER PLANT 29
    3.1. About the Case Study 29
    3.2. Seyitömer Coal-Fired Thermal Power Plant 29
    3.3. Ash Disposal in SCTPP 33

3.4. Meteorology of the Region..... 34
3.5. Summary..... 36

4. MODEL APPLICATIONS AND EXPERIMENTAL METHODS..... 40
4.1 ISCST Approach..... 40
4.1.1. Study Area..... 40
4.1.2. Model Application..... 40
4.1.3. Model Inputs..... 43
4.1.3.1. Area Sources..... 43
4.1.3.2. Point Sources..... 44
4.2. Receptor Modeling Approach..... 46
4.2.1. Sampling..... 46
4.2.1.1. Collection of Aerosol Samples..... 46
4.2.1.2. Collection of Soil Samples..... 47
4.2.2. Preparation of Samples for Analyses..... 49
4.2.2.1. Preparation of Aerosol Samples..... 49
4.2.2.2. Preparation of Soil Samples..... 50
4.2.3. Analyses of Elements in Aerosol and Soil Samples..... 50
4.2.3.1. FAAS and FAES Measurements..... 50
4.2.3.2. GFAAS Measurements..... 51
4.2.4. Data Quality Assurance..... 52
4.2.4.1. Blank Samples..... 52
4.2.4.2. Sample to Blank Ratios..... 52
4.2.4.3. Analyses of SRMs..... 54
4.2.4.4. Detection Limits..... 56

5. RESULTS AND DISCUSSION..... 58
5.1. Calibration of the Model..... 58
5.2. Sensitivity Runs..... 58
5.3. State of Pollution in Seyitömer Region..... 59
5.3.1. Average Concentrations of Elements..... 59
5.3.2. Levels of Pollutants in Seyitömer Region..... 64

5.3.2.1. Aerosol..... 64
5.3.2.2. Soil..... 66
5.3.3. ISCST Predictions..... 69
5.3.4. General Evaluation..... 74
5.4. Distribution of Elements in Soil..... 76
5.5. Enrichment Factors..... 84
5.6 Relative Contributions of Stack and Fugitive Dust Emissions..... 90
5.6.1. Model Predictions..... 90
5.6.2. Factor Analysis..... 95

6. CONCLUSIONS AND RECOMMENDATIONS
FOR FUTURE WORK..... 100
6.1. Conclusions..... 100
6.2. Recommendations for Future Works..... 103

REFERENCES..... 104

LIST OF TABLES

Table		Page
2.1	Coal-Fired Power Plants in Turkey	6
2.2	Thermal Power Plants and Ash Disposal Techniques in Turkey	9
2.3	Houston Aerosol Source Categories	26
3.1	Technical Characteristics of SCTPP	31
3.2	Data During the Operation Phase of SCTPP	33
4.1	Characteristics of Ash in the Disposal Area	44
4.2	General Characteristics of the Stacks	45
4.3	Size Distribution of Particles at Exit of Electrostatic Precipitators	45
4.4	Technical Specifications for Hi-Vol Sampler	46
4.5	Operation Parameters in FAAS and FAES	53
4.6	Operation Parameters in GFAAS	53
4.7	Sample to Blank (S/B) Ratios	54
4.8	Concentrations of Standard Reference Materials	56
4.9	Detection Limits for Elements	57
5.1	Parameters Used in Four Scenarios	59
5.2	Experimental Results of Soil Samples	61
5.3	Experimental Results of Aerosol Samples	62
5.4	Assessment of Soil Pollution Classes	68
5.5	Annual Ground Level SPM Concentration Estimates	70
5.6	Hourly and Daily Ground Level SPM Concentration Estimates	72
5.7	Hourly and Daily Ground Level SO_2 Concentration Estimates	74
5.8	VARIMAX-Rotated Factor Loading and Corresponding Source Type	97

LIST OF FIGURES

Figure		Page
2.1	Particle Deposition in the Different Areas of the Respiratory Tract in Dependence of the Mean-Diameter of the Particles	11
3.1	Map of the Region	30
3.2	Layout of SCTPP	32
3.3	Conveyors Used for Ash Disposal	35
3.4	Ash Disposal	35
3.5	Wet Disposal Site Applied in SCTPP	35
3.6	Wind Rose of SA Between Years 1927-1990	36
3.7	Hourly Wind Roses of SA During March, 1996	37
4.1	3-D Digitized Topographical Map of SA	42
4.2	Soil Sampling Points	48
4.3	Percent Blank Contributions in Samples	55
5.1	Comparison of Four Scenarios	60
5.2	Frequency Histograms of Al and Pb	63
5.3	Comparison of Aerosol Samples with Different Studies	65
5.4	Comparison of Soil Samples with Different Studies	67
5.5	Annual SPM Concentration Estimates	71
5.6	Annual SO_2 Concentration Estimates	75
5.7	Distribution Plots of Al and Fe Concentrations	79
5.8	Distribution Plots of Cd and Cu Concentrations	80
5.9	Distribution Plots of Zn and Pb Concentrations	81

5.10 Distribution Plots of Cr and Ni Concentrations..... 82
5.11. Annual SPM Deposition from Stacks and Ash Disposal Site..... 83
5.12 Enrichment Factors of Elements in Soil..... 85
5.13 Enrichment Factors of Elements in Aerosols..... 86
5.14 Enrichment Factor Distributions of Cd and Zn..... 87
5.15 Enrichment Factor Distributions of Cr and Pb..... 88
5.16 Enrichment Factor Distributions of Cu and Ni..... 89
5.17 Area to Stack Ratios of Annual SPM Concentration Estimates..... 91
5.18 Stack to Area Ratios of Annual SPM Concentrations Estimates..... 92
5.19 Area to Stack Ratios of Annual SO_2 Concentration Estimates..... 93
5.20 Stack to Area Ratios of Annual SO_2 Concentration Estimates..... 94
5.21 Distribution of Factor Scores..... 99

CHAPTER 1

INTRODUCTION

In recent years, rapid increase in industrialization and population resulted in increasing energy demand. Increased utilization of coal and fossil fuels (which are the most common energy sources) caused high emissions of trace elements to the ambient atmosphere and directly led to environmental pollution.

In Turkey, most of the coal-fired thermal power plants use low quality lignites. Thus, the major waste of power plants is ash whose amount depends on ash percent in coal and the combustion technology and efficiency. The amount of ash in coal is generally 20% or more (Ferraiolo et al., 1990).

Ash generated in coal-fired power plants can be categorized as "bottom ash (slag)" and "fly ash". The refractive inorganic fraction of coal residue (bottom ash) is usually coarser and heavier than fly ash due to the agglomeration of granules and consists of approximately 15-40% by weight of the total ash (Egemen, 1993). The relative amounts of fly and bottom ashes depend to a large extent on the firing method and the type of combustion chamber (Environment Canada, 1980).

Nowadays, identification and quantification of aerosol sources in the atmosphere is receiving a major attention. Collection and analysis of particle samples provide the necessary data for the problem of resolving a series of complex mixtures into its components. One of the frequently used methods are receptor models. Chemical mass balance (CMB) and factor analysis (FA) are the common tools of

receptor models. If all the sources and their composition profiles are identified, the CMB becomes a multiple regression methodology. If a series of samples were analyzed without any knowledge about the source profiles, it is useful to use FA first.

In addition to the receptor models, dispersion models are used to quantify the pollutants on the receiving environment. Within this scope, Gaussian plume model is the most frequently used tool.

In this study, receptor and dispersion models were compared. The mathematical tools of receptor models were adapted to the measured levels of atmospheric trace elements and major ions together with the parameters to apportion the sources in Seyitömer coal-fired thermal power plant, Kütahya. The preliminary steps are FA and enrichment factors (EF) which are the two qualitative approaches.

The computer model used in the scope of dispersion models is the well-known Industrial Source Complex-Short Term (ISCST). The ground-level concentration (GLC) values of SO_2 and both GLC and deposition values of suspended particulate matter (SPM) emitted both from stacks and ash disposal area were calculated. The predictions were compared with the FA results and necessary discussions were done.

The aim of this study is to assess the impacts of the fugitive dust from Seyitömer coal-fired thermal power plant (SCTPP) ash disposal area. Source apportionment study of the region was carried out with three possible sources; (i) fly ash deposition from stacks, (ii) fugitive dust emission from the disposal site, and (iii) crustal dust blown by wind. Two parallel studies, ISCST runs and FA was done. Within this intention, dust emissions from ash disposal site were modeled. Additionally, soil samples were taken from the vicinity of the plant and analyzed.

First chapter of this thesis includes the introduction part explaining the aim and scope of this study. Second chapter includes different global studies carried out

related to this subject. The background information can be achieved from this chapter.

Third chapter gives some details about SCTPP. The topographical and meteorological characteristics of the selected study area were explained here.

Sampling techniques, instrumentation and the analytical techniques used were discussed in the fourth chapter. During this study, 22 aerosol and 40 soil samples were analyzed for the elements Na, Mg, Al, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb using a combination of flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS). Blank values and detection limits of the analytical methods as well as the results of data quality assurance were also given in this chapter.

The results obtained from these two parallel studies were thoroughly explained in the fifth chapter. A discussion of sources and signatures of pollutants were also presented.

The sixth chapter of this study includes concluding remarks and some suggestions for further research on this subject.

CHAPTER 2

LITERATURE SURVEY

2.1 General

Environmental pollution due to trace elements attracted increasing attention item in few decades. As a result of industrial activities, energy generation and vehicular traffic, the levels of these pollutants in the environment have increased significantly (Pacyna, 1986a). Fossil fuels, especially coal, are the major sources of energy for the countries which have increasing energy demands (World Bank, 1979; Wilson, 1980; UN, 1981; Häefe, 1981; Pacyna, 1986b). Hence utilization of these sources generates the major potential environmental pollution problems in the vicinity of industrial regions.

The most important energy resources in Turkey are lignite and hydrology. Hence, most of the large-scale coal-fired power plants (13 out of 18) use local lignites with low calorific value and high ash content (approximately 35%). The names, number of units, energy productions and efficiencies of these power plants are given in Table 2.1.

The use of coal for electricity generation has resulted in important environmental problems. SO_x, NO_x and total solid particulate (TSP) emissions from low stacks result in high levels of pollutants close to plants, local air pollution problems and hazardous high SO_2 levels. Later power plants were built outside urban areas. Stack height increased up to 600 m in order to prevent regional acid pollution problems.

The wet acid deposition is commonly called acid rain. Acidity represents the baseline for comparing the pH of rainwater which can also be altered by SO_2 or NO_x oxidation products. Gaseous SO_2, NO_2, and HNO_3 and acid aerosols are deposited when they contact and stick to the surface of water bodies, vegetation, soil and other minerals. If surfaces are moist or liquid, the gases can go directly into solution and hence the acids are formed that fall in the form of acid rain (Stern et al., 1984).

Although environmental problems related to stack emissions from power plants are well documented, problems caused by bottom ash did not attract similar attention due to its local nature.

The use of lignite with high ash content (typical for coal burned in Turkish power plants) has potential impacts on environment. For instance, stack emissions may cause acidification of the receiving bodies (i.e. soils or surface waters). On the other hand, ash deposited in dump areas may leach heavy metals including selenium (Se), arsenic (As), lead (Pb), zinc (Zn) and nickel (Ni) which can be toxic for soils as well as surface and ground water resources (Egemen, 1993).

Fugitive dust emissions from disposal sites, which is the topic of this study, did not attract sufficient attention as an environmental problem mainly because ash disposal areas are remediated minimizing fugitive emissions. However, since remediation procedures are not common in Turkey, fugitive dust emission from disposal sites is a significant environmental problem for the population living around the power plants. As an example, in 1993 the annual fly ash amount in Turkey was approximately 12 million tons (Özbayoğlu, 1994).

2.2 Ash

Ash is the major by-product of coal-fired power plants formed by the combustion of the inorganic solid portion of the residue (Egemen, 1993). Ash content of coal

generally varies with the geologic and geographic factors (i.e. it changes from bed to bed) of the coal deposits. The amount of bottom ash formed depends on the composition of coal, the design parameters of power plants and the combustion efficiency (Environment Canada, 1980). It may reach 20% or more, usually not exceeding 5% (Ferraiolo et al., 1990).

Table 2.1. Coal-Fired Power Plants in Turkey

Power Plant	# of Units	Capacity (MW)	Efficiency (%)
Afşin-Elbistan	4	1,360	47.7
Çatalağzı-B	2	300	68.1
Çayırhan	2	300	65.5
Kangal	2	300	61.5
Kemerköy	3	630	Not known in 1995
Orhaneli	1	210	Not known in 1995
Seyitömer	4	600	90.2
Soma-A	2	44	110.3
Soma-B	6	990	71.6
Tunçbilek-A	3	129	-
Tunçbilek-B	2	300	77.0
Yatağan	3	630	64.6
Yeniköy	2	420	83.1
TOTAL	**36**	**6,213**	**56.6**

Ash generated in coal-fired power plants can be categorized as "bottom ash (slag)" and "fly ash". The refractive inorganic fraction of coal residue (bottom ash) is usually coarser and heavier than fly ash due to agglomeration of granules and consists of approximately 15-40% by weight of the total ash (Egemen, 1993). The relative amounts of the fly and bottom ashes depend to a large extent on the firing method and the type of combustion chamber (Environment Canada, 1980).

2.2.1 Disposal of Ash

Large quantities of bottom ash formed during the operation of power plants have to be disposed. Three different methods are available for disposal:

1. Dry landfilling
2. Ponding (commonly used in developed countries)
3. Marine disposal (commonly used in Turkey)

Selection of ash disposal technique depends on some site-specific factors such as acceptability of the technique, effluent standards and market demand for ash as well as land and water availability.

(i) *Dry Landfilling of Ash:* In landfilling method, the ash generated is disposed on the land with a proper topography such as a valley located close enough to the power plant. In this method, ash is carried to the site in a dry storage bin generally by means of air pressure. Ash is wetted to 10-20% moisture by weight to improve handling characteristics and hence the fugitive dust emissions during transport to disposal site are also avoided. The major factors to be considered for the selection of an ash landfill site is: (a) dispersion of ash in the vicinity of landfills due to wind erosion, and (b) the leachate due to atmospheric precipitation. On the other hand, there are some disadvantages of ash landfills such as limited availability of land with proper topographic features, reaction of the population and high capital costs required for a safe disposal site (Egemen, 1993).

(ii) *Ponding of Ash*: The ponding of ash generally requires developed technology as the ash is being processed before it is disposed. In this approach toxic elements in ash are leached by treating ash with water for an extended period of time, such as 24 hrs (Environment Canada, 1980). The water may be made acidic to speed up leaching. The wastewater, after leaching, may be recycled back to the power plant for reuse. Ponds, in

which this process is carried out, can be either an intermediate step before landfilling or they may serve as ultimate sink. At the end of their operational periods, these disposal ponds should be reclaimed (i.e. drying and covering the sludge with soil) (Egemen, 1993). The amount of water required generally ranges from 5 to 167 L kg^{-1} of ash (Chu et al., 1980). Due to high area requirements and water quality deterioration of waters used, ponds are not preferred in Turkey.

(iii) *Marine Disposal*: The method involves discharging of ash to a nearby sea as slurry. In many European countries and Canada, ocean disposal of ash is forbidden due to its potential environmental impacts particularly on the bottom flora (Egemen, 1993).

In Turkey, there are 18 thermal power plants among which 13 are coal-fired (12 lignite and one anthracite), two are natural gas-fired, three are fuel-oil-fired and two are diesel-fired. According to the information taken from Turkish Electricity Company (TEAŞ), the fuel types and the ash disposal techniques of the power plants are given in Table 2.2.

As can be seen from the table, the ash originated in Afşin-Elbistan thermal power plant is disposed back to the empty mines that the coal is drilled. Marine disposal technique is used only in Çatalağzı power plant. Recently, most of the power plants in Turkey use the method of wet disposal of ash to dams. Uncontrolled ash disposal technique, however, is also one of the most widely used methods. With this intention, a small portion of the ash generated from the power plants is evaluated and most of the ash is disposed to the fields near the power plants. However, due to fugitive dust emissions from the dump sites, this technique creates problems such as visibility reduction, deposition on nearby agricultural lands, breakdown of machinery and equipment as well as health problems related to the respiratory system. Hence, it can be concluded that, dust can be categorized as particulate matter and is a serious potential source of pollution near the thermal power plants having an uncontrolled ash disposal.

Table 2.2. Thermal Power Plants and Ash Disposal Techniques in Turkey

Power Plant	Fuel Type	Ash Disposal Technique
Afşin-Elbistan	Lignite	Filling Empty Mines
Çayırhan	Lignite	Wet Disposal to the Ash Dam
Kangal	Lignite	Uncontrolled Land Disposal
Kemerköy	Lignite	Wet Disposal to the Ash Dam
Orhaneli	Lignite	Wet Disposal to the Ash Dam
Seyitömer	Lignite	Uncontrolled Land Disposal
Soma-A	Lignite	Wet Disposal to the Ash Dam
Soma-B	Lignite	Wet Disposal to the Ash Dam
Tunçbilek-A	Lignite	Uncontrolled Land Disposal
Tunçbilek-B	Lignite	Uncontrolled Land Disposal
Yatağan	Lignite	Wet Disposal to the Ash Dam
Yeniköy	Lignite	Wet Disposal to the Ash Dam
Çatalağzı-B	Anthracite	Marine Disposal
Ambarlı	Natural Gas	-
Hamitabat	Natural Gas	-
Ambarlı-Hopa	Fuel-Oil	-
Aliağa	Diesel	-
Teko	Diesel	-

2.2.2 Particulate Matter

Particulate matters (PM) are the materials that may adsorb chemicals such as toxic trace elements and mutagenic organic material. Since some of these particles can penetrate to lungs, and can stay there for a period of time, adsorbed toxic and mutagenic material on these particles can cause health deterioration. Carcinogens, due to their external and internal surface area, increase their penetration rate into the lungs or prolong their residence time there and enhance the effect of the adsorbed agents. Certain size fraction of these particles also serve as condensation nuclei for water and other vapors to produce cloud droplets in which gases such as SO_2 may be absorbed as acids (Stern, 1977).

Particulate emissions during coal combustion and their chemical composition depends on:

1. affinity of elements for pure coal and mineral matter
2. physico-chemical properties of elements and their concentrations in coal
3. combustion conditions
4. emission control devices used in power plants (i.e. electrostatic precipitators)

Incomplete combustion of fossil fuels is the major source of PM in the respiratory system. In polluted air, particles range from 0.001 to 10,000 μm. In general, controlled combustion produces particles in the 0.1-10 μm range (Stern, 1977).

In this study, the term "fugitive dust" is used for the dust resuspended from disposal sites via wind action together with the crustal dust. Some portion of this fugitive dust is inhalable. Particles having less than 10 μm aerodiameter size[1] can pass from upper respiratory tract, while less than 2.5 μm aerodiameter size can penetrate deep to the lower respiratory tract. Parts of the respiratory tracts and the deposition fractions of the particulate matters are shown in Figure 2.1. It is a well-known fact that, particles ≥10 μm are retained in the eye, skin and hair (called head) during normal respiration (15 L min^{-1}). On the other hand, the deposition of monodisperse aerosols in the head during inhalation via nose is essentially 100% for particles ≥10 μm (when respiration rate is 30 L min^{-1}) (Miller et al., 1979). Deposition of particles <2 μm is small in the upper respiratory tract since these particles are not retained in the upper parts of the respiratory system and they can penetrate to lungs directly. In addition to mutagenic effect of fine particles, toxic elements and mutagenic organic material adsorbed on these particles can also cause health effects.

[1] *diameter of a unit density sphere having the same terminal settling velocity as the given particle*

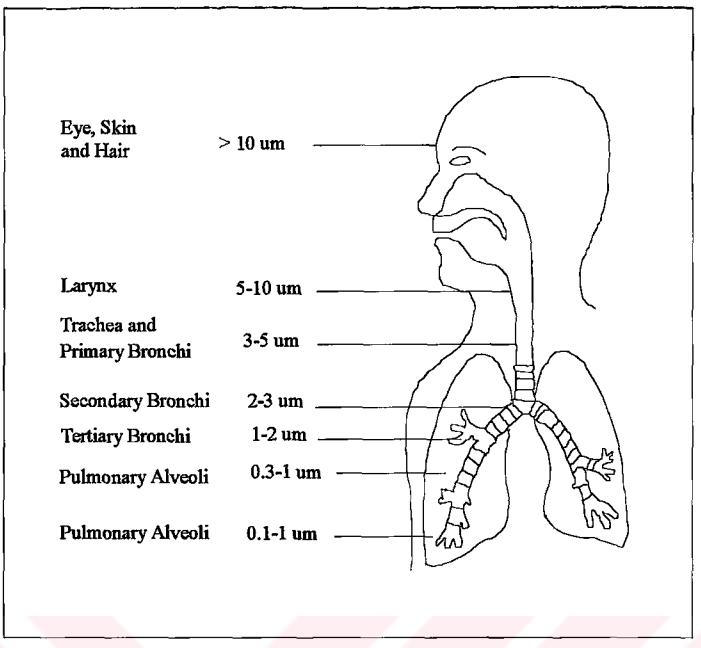


Figure 2.1. Particle Deposition in the Different Areas of the Respiratory Tract in Dependence of the Mean-Diameter of the Particles (Baumbach, 1996)

Fly ash particles are composed of stable or compounds that are usually not considered directly toxic in concentrations found in ambient air. However, fly ash does contain excess toxic and mutagenic material due to adsorption of these species from gas phase onto fly ash particles.

Fly ash particles are toxic and mutagenic when inhaled. In addition to respiratory intake, fly ash particles bearing toxic elements such as Cd, V, Ni, Hg, and Mn can be taken orally if they accumulate on fresh vegetables growing close to a power plant (Stern, 1977).

An additional effect of the fly ash particles was recognized in recent years. When these particles are emitted from stack, small size fraction can be transported over long distances and deposited to the lakes and closed seas. Deposition fluxes of toxic elements to marginal seas such as the Black Sea, or the Mediterranean Sea

is shown to be comparable to their riverian fluxes (Hacısalihoğlu et al., 1992; Al-Momani et al., 1995).

The particle mass measured in ambient air is a mixture of particles coming from variety of sources. The farther the measurements are made, the more sources contribute to measured particle mass.

To take any regulatory action to reduce particle load at any locality (rural, urban and industrial), these sources contributing to the particle mass and their contributions must be determined. The process used for this purpose is called source apportionment. There are two approaches for source apportionment: (a) source oriented approach, which includes emission inventories as well as dispersion modeling, and (b) receptor oriented approach, which is called receptor modeling.

In this study, the comparison of these two models was carried out, and the details are given in the following sections.

2.3 Source Apportionment Studies

The levels of the trace elements and the ions in the atmosphere are diverse over the earth's surface, depending on the particular contributing sources and the other topographical and meteorological conditions. There are difficulties in comparing results from different studies that were done at different time and places, because of the factors that can influence the actual levels measured. The details of the sampling time, the period over which the measured trace element and ion levels were determined and the year when the work was done are necessary for making any comparisons (Yaaqub et al., 1991).

As discussed above, there are two types of mathematical models used to apportion the aerosols measured at a receptor site to its likely sources:

1. Source oriented approach
2. Receptor oriented approach

The source oriented receptor modeling approach is based on real time measurements of certain natural traces in the atmosphere and includes statistical treatment of the generated data set. In rural source apportionment studies, data interpretation is supplemented by backtrajectory modeling and in urban and industrial regions it is supplemented by surface wind sectoring.

The advantages of source oriented dispersion modeling is that it is easy to perform, does not require extensive measurements, can be applied over wide areas and can be used as frequently as one wishes.

The disadvantages, on the other hand, are: (a) they include fairly extensive assumptions, (b) they use parameters with poorly known values (such as dry deposition velocity) and, (c) they require extensive meteorological information which is not always available at the study site. Because of these assumptions and poorly known constants, results are at best approximate.

The receptor modeling approach was developed as an alternative to the source oriented dispersion modeling (Gordon, 1988). Source modeling uses source emission inventories, simulates atmospheric transport (dispersion modeling) and reactions, ground-level concentrations and deposition fluxes of pollutants.

Receptor models, on the other hand, start with observed ambient airborne particle concentrations at a receptor and seek to apportion the observed concentrations between several source types based on the knowledge of the compositions of the source and receptor materials using elemental composition of collected particles and multivariate statistical techniques (Henry et al., 1984). In recent years, receptor oriented models or receptor models have been employed to identify major source types of airborne PM and estimate their contributions to particulate mass (Cheng and Hopke, 1989).

The advantage of receptor modeling is that it does not include any assumption and poorly known parameters. In this regard, the results are very accurate. Various inter-calibration exercises have shown that the source contributions can be determined within 5% accuracy using different receptor oriented techniques.

The disadvantage is the concern of extensive field measurements that are difficult and expensive.

The brief description of the approaches in the models is given below with their commonly used mathematical tools.

2.4 Dispersion Models

Dispersion models are commonly used to predict the environmental impact of an emission source (Henry et al., 1984). Since the application of these models is easy and instruments are cheap, they are frequently preferred by the researchers.

Since the input data used in the dispersion models is permanent, the models can be used as frequent as possible. The application area of the models are larger compared to the area used in sampling. Additionally, the output obtained from the models can be used in the regulatory action.

Even if the results obtained from dispersion models were accurate, the source emission inventories upon which they rely are not (Gordon, 1988). The deposition of dust particles predicted by the models is not reliable since the size distribution is the major factor in deposition and it can only be known by sampling. The reliability of the results obtained from models is depended on the accuracy of input data. For instance, it is generally impossible to find a meteorological station within the study area, and the meteorological data are taken from 20-30 km away whose data representation for the study area is doubtful. Although the real values of most parameters are not known, they are used in the model.

Within this intention, the results of the dispersion models should be compared with the sampling at the site and a kind of calibration should be achieved for the accuracy of the study. Calibration is a kind of adjustment of results and different tools can serve for this purpose.

In this study, a receptor model was applied and using the results of the model, calibration of the predictions obtained from the dispersion modeling was carried out. The dispersion model used in this study is explained below.

2.4.1 ISCST Model

Industrial Source Complex-Short Term (ISCST) computer model is developed by the USEPA and frequently used for the air quality studies. The basic concept of the ISCST model is similar to that of the steady state, straight-line Gaussian plume equation. The model combines various dispersion model algorithms for pollutant sources such as stack and fugitive emissions. The details of the model formulations are given in the ISCST Manual (EPA, 1992b).

The four input sets used by the model are:

1. Meteorological data
2. Source data
3. Receptor data
4. Control data

1. Meteorological data: This data set consists of hourly wind speed and direction, ambient air temperature, Pasquill stability class, mixing height, wind profile exponent and potential vertical temperature gradient (optional) values (EPA, 1992a). Basic meteorological parameters are usually obtained from meteorological stations preferably at the study area and secondary parameters, such as stability classes, mixing heights, are calculated by pre-processors.

2. Source data: Deposition and concentration can be evaluated for more than 200 pollution sources. Variety of pollutants including sulfur dioxide (SO_2), nitrogen oxides (NO_x), suspended particulate matter (SPM) and carbonmonoxide (CO) can be modeled. The model is capable of dealing with multiple sources which are categorized as point, volume and area sources. These different source types are explained below:

- Releases from stack and isolated vents are referred as "point" sources. The input data for the point source algorithms include point emission rate, release height above ground, stack gas exit velocity, stack gas exit temperature and stack inside diameter.
- Releases from a variety of industrial sources, like building roof monitors, multiple vents and conveyor belts are categorized as "volume" sources and the input data needed for this algorithm are volume emission rate, release height (from the center of the volume) above ground and initial horizontal and vertical dispersion parameters (σ_y and σ_z values).
- Releases from storage piles, ash dumping areas, lagoons as well as toxic air release sites are "area" sources. The input data for this category are area emission rate, release height above ground and side length of the square source area. The ISCST accepts only square areas whose sides are oriented north-south and east-west. In order to model irregularly-shaped areas, the area must be subdivided into smaller square areas. (EPA, 1992a)

3. Receptor data: The ISCST model calculates GLC and deposition values at the corner points of a user defined grid system. The coordinates and elevation of the grid corners within the study area are the receptor points. The grid systems used in ISCST can be either in polar or cartesian projection. The quantity of dust emission from the disposal site during the disposal of bottom ash is directly proportional to the volume of the ash. The subsequent deposition calculations are based on the average annual ground-level concentrations (GLC) predicted by the ISCST model at each grid square. (EPA, 1992a)

4. Control data: Program control parameters can be selected by the user among 30 different alternatives. Prediction of either GLC or deposition rates, definition of discrete points other than receptor locations and calculation of concentration values concerning different time intervals are some of the control parameters. More complete listing can be found in ISCST Manual (EPA, 1992a).

2.4.2 Fugitive Dust Emissions

The type of emissions which is of particular interest for this study is fugitive dust emissions. The amount of particulate matter (PM) emissions from storage piles can be calculated using the expression given below (EPA, 1977).

$$E = \frac{0.33}{(PE/100)^2} \tag{2.1}$$

where;

E : emission factor (lb ton^{-1})

PE : an approximate measure for average soil moisture

The so-called Thornthwaite's index for precipitation-evaporation can be determined from total annual rainfall and mean annual temperature. However, rainfall amount needs a correction for irrigation (EPA, 1977).

For PM, the ISCST model uses size distribution information to calculate GLC and deposition values. The size distribution is a crucial component, because settling velocity and surface reflection coefficient depends strongly on the size of particles. In order to obtain the correct size distribution, sieve analysis should be applied to ash samples taken from the area. Mass-mean diameter can then be calculated using Equation (2.2).

$$d = \left[0.25 \times \left(d_1^3 + d_1^2 \times d_2 + d_1 \times d_2^2 + d_2^3\right)\right]^{1/3} \tag{2.2}$$

where;

d_1 : lower bound of the particle-size category

d_2 : upper bound of the particle-size category (EPA, 1992b).

The settling velocity is a function of the mass-mean diameter. A settling velocity of 0.0 means that the plume material does not settle (i.e. the plume centerline remains horizontal even though some of the plume material can be deposited on the ground surface). For particles with a density on the order of 1 g cm^{-3} (in the range of 0.5-10 g cm^{-3}) and diameters less than 80 μm, the settling velocity is calculated as formulated in Equation (2.3).

$$V_s = \frac{2 \rho g r^2}{9 \mu} \qquad (2.3)$$

where;

V_s : settling velocity (cm s^{-1})

ρ : particle density (g cm^{-3})

g : gravitational acceleration (~ 980.6 cm s^{-2})

r : particle radius (cm)

μ : absolute viscosity of air (~ 1.83×10^{-4} g cm^{-1} s^{-1}). (EPA, 1992b)

The reflection coefficient is a function of settling velocity and roughness of the ground surface. A reflection coefficient 0.0 means that the plume material for that settling category is completely removed when it reaches the ground surface and a reflection coefficient 1.0 means that all of the plume material is reflected from the surface without any deposition. (EPA, 1992a)

2.5 Receptor Models

Receptor oriented source apportionment techniques were developed as an alternative for source oriented approach due to uncertainties involved in both emission inventories and dispersion modeling as discussed previously.

These receptor methods have been developed, extensively tested in 1980's, and recommended by USEPA, as an alternative for dispersion modeling in regulatory studies in 1990s. The basic idea is to resolve the observed concentration patterns of atmospheric particles at the receptor site (sampling site) into the contributions from several possible sources (Gordon, 1988).

Although its name includes "modeling", receptor modeling is not a simulation technique. The technique consists of statistical treatment of measurement results, and because of this it does not include any priori assumptions. Since no assumptions are involved, the results of receptor modeling are accurate. The uncertainties of source contributions can be as low as 5% if sufficient number of samples are collected and analyzed with reliable analytical methods.

In receptor modeling certain natural tracers are involved, but these tracers are not added to the source emissions, they exist in emissions naturally. These so called "source fingerprints" should fulfill the following requirements.

The development of receptor-based models has progressed significantly in the last 10 years. In general, the chemical and physical characteristics of ambient gases as well as particles are used in receptor models in order to both identify the presence of and quantify the source contributions to the receptor site. In this modeling, the chemical and physical characteristics must be such that:

1. they should be present in different proportions in different source emissions,
2. these proportions should remain relatively constant for each source type,
3. changes in these proportions between source and receptor sites should be negligible.

The most widely used natural traces that fulfill these requirements are trace elements. The elements do exist in different proportions in emissions from

different source types, their ratios are fairly stable within each source group, and they are conservative, meaning that elemental ratios do not change during transport from source to receptor.

In last few years, organic molecules are also being used in receptor modeling studies. However, the use of organics in receptor oriented techniques is hindered by their known chemistry in the atmosphere.

Although variety of statistical techniques, such as calculation of enrichment factors (Ölmez et al., 1988; Thurston and Lioy, 1987), multiple linear regression (Ölmez et al., 1988; Henry et al., 1984), hybrid receptor model (Gordon, 1988) had been used in receptor modeling, to most common statistical tools are the principle component analysis (PCA) and chemical mass balances (CMB).

The starting point of the most multivariate statistical techniques has been the correlation matrix of the n aerosol properties for m observations (usually over time). These correlations indicate the extent to which ambient properties (e.g. elemental concentrations) vary together from observation to observation. For example, the PCA model assumes that the total concentration of each observed element is made up of the sum of contributions from each of p pollution source components (Thurston and Lioy, 1987).

The basic idea of CMB is that composition patterns of emissions from various classes of sources are different enough that one can identify their contributions by measuring concentrations of many species in samples collected at a receptor site (Gordon, 1988). The model assumes that each element in the receptor site has linear combinations of sources contributing (Yatın, 1994). It is generally preferred to run FA first before the application of CMB in order to identify the sources and then to apply CMB to quantify the contribution of these sources.

The facts that PCA approaches to source apportionment require a minimum of prior knowledge of the sources affecting the monitor and only qualitative

information regarding their properties (e.g. key element tracers) are major advantages of this approach. Moreover, the user is not limited to a single type of property and may include a host of variables helpful in discriminating pollution sources (e.g. meteorological variables) (Thurston and Lioy, 1987). With this intention, if one knows the composition of aerosol particles, the source profiles of dominant sources and the source contribution terms, it is easy to apply a least square fit to the observed concentrations of a set of elements called "marker elements". Marker elements are strong indicators of particles from the individual sources and they are usually non-volatile elements which can be measured reliably in both ambient and source (emitter) samples (Albert and Hopke, 1981).

Multivariate methods usually result in uncorrelated components or factors. In this regard, the potential source profile multicollinearity problems occurred in CMB are greatly reduced. The components, by definition, are independent of one another since PCA derives orthogonal components. However, it is important to note that multivariate methods do have problems with sources having spatially and temporally correlated emissions. Thus, if two different but correlated sources always impact a site at the same time, then multivariate methods will not discriminate them (Thurston and Lioy, 1987).

The basic difference between PCA and CMB is that the multivariate techniques do not rely solely on source inventories to identify/quantify the sources affecting a site during individual sampling periods. Instead, they quantify ambient aerosol property interrelationships (e.g. among elemental concentrations) by analyzing the variations of these properties in a series of samples collected at a receptor site. On the other hand, the chief limitation of PCA is that they require many more observations (samples) than CMB methods do.

Multivariate methods are hypothesis-generating techniques, while CMB methods are complementary hypothesis-testing techniques. This suggests that multivariate and CMB methods might be most efficiently used sequentially, rather than as alternative approaches to source apportionment.

The major advantage of the CMB method is that a researcher knows exactly what the source apportionment model represents, because he/she has chosen the model and its inputs. This option greatly simplifies the interpretation of the model results. The chief limitation in the CMB application is the lack of appropriate elemental profiles for transported aerosols to input into such models (Thurston and Lioy, 1987).

2.5.1 Factor Analysis (FA)

Factor analysis (FA) is the most widely used tool of multivariate analysis. Factor analysis does not need a priori estimates of the number and compositions of components, because it searches the data set for groups of species (the "factors") whose collective variations account for most of the fluctuation of the species included (Gordon, 1988). The objective of FA is to find a minimum number of factors that explain most of the variance of the system. In general, FA has four steps that are described below:

1. The linear correlation matrix for all normalized variables is computed. Variables which do not relate with others can be identified from the matrix and associated statistics,
2. Minimum number of factors, which accounts for most of the system variance, is extracted from correlation matrix. Although the extraction process involves fairly complex vector algebra, the user does not need to know this to apply the technique to a data set. In order to determine the number of factors necessary to represent the data set, factor extraction is done.
3. Factors are transformed in order to make them more interpretable. This process is called rotation.
4. In the last step of regular FA, factor scores, which indicate relative weight of each factor in each sample, are computed for each case. These scores can then be helpful in source strength calculations and in variety of other analysis.

During the extraction step, concentrations of elements in each sample are transformed into normalized standard form expressed as below:

$$z_{ik} = \frac{x_{ik} - \bar{x}_i}{s_i} \tag{2.4}$$

where;

z_{ik} : standardized value of the i-th element for the k-th sample,

i : total number of parameters measured (1,2,3,....,n),

k : total number of observations (1,2,3,....,m),

x_{ik} : concentration of the i-th parameter at the j-th observation,

$\bar{x}_i$: mean value of the i-th parameter,

s_i : standard deviation of the distribution of concentrations of the i-th parameter.

Each standardized value, z_{ik}, has a mean value of zero and a standard deviation, s_i, of one. Hence, it can be easier to take the equal weighting for each element, regardless of its average concentration.

It is important to note that, the multivariate analysis, as proposed in this study, requires sufficient degrees of freedom, meaning that the data set must have more observations than observed variables (e.g. m>n+40) to have stable results (Dzubay et al., 1984). The requirement of extensive measurement program is one of the disadvantages of the FA technique.

In this study, it was assumed that the total concentration of each element consists of the sum of elemental contributions from each j pollution source components. This can be expressed as follows:

$$z_{ik} = \sum_{j=1}^{p} W_{ij} P_{jk} \tag{2.5}$$

where,

j : number of pollution sources (1,2,3,....,p),

W_{ij} : coefficient matrix of the components,

P_{jk} : j-th component's value for observation k.

The above equation can also be expressed in matrix terms as:

$$[P]_{jxk} = [B]_{jxi}[Z]_{ixk} \tag{2.6}$$

where,

$$[B]_{jxk} = \frac{[W]_{jxk}}{L_j} \tag{2.7}$$

and L_j is the eigenvalue associated with P_j (Yatın, 1994).

Generally, FA needs as many components, which are "factors", as possible. However, only a limited number of these uncorrelated components (i.e. four to six) are required to explain virtually all of the variance in data set of original inter-correlated variables. The main purpose in FA is to explain >90% of the system variance with minimum number of components (or factors). Empirically, it has been found that the unrotated factors are generally not interpretable, because they attempt to explain all of the system variance (SPSS Manual, 1990).

Within this intention, a limited number of components which explains at least 80% of the total variance are usually subjected to rotation using a criteria such as VARIMAX (Yatın, 1994; Koutrakis and Spengler, 1987). After the VARIMAX rotation, the resulting components have been found to be more representative of individual underlying sources of variation. This, in turn, results in more interpretable and useful components. The necessity of VARIMAX rotation in analyzing ambient trace element data and air pollution data have been tested and discussed in the literature (Hopke et al., 1980; Tuncel et al., 1985).

Rotated factors and loading of elements in each factor, which is a parameter indicating associations of elements with factors can be used to identify sources. Elemental composition of factors is similar to the elemental composition of sources. If one knows about elemental composition of sources, similarities between elemental composition of factors can be used to identify sources affecting the receptor site (Yatın, 1994).

Dzubay et al. (1984) applied the mathematical and empirical receptor models in a workshop (Quail Roost II). In that study, nine investigators independently applied receptor models to apportion ambient aerosol mass contributions to components from emissions in Houston, TX. The models tested included CMB, multiple linear regression, factor analysis and target transform factor analysis (TTFA). The source categories and marker elements used in source apportionment of Houston aerosols are summarized in Table 2.3 (Dzubay et al., 1984). A logical approach to estimate the source profiles at a specific site would be to use ambient data in a multivariate model (Zelenka et al., 1994).

In general, FA requires no priori estimates of the number and compositions of components, because in FA the data set is searched for groups of factors whose collective variations account for most of the fluctuation of the species included (Gordon, 1988). On the other hand, for accurate results the sample size is preferred to be more than 20 (Dzubay et al., 1984). It must also be noted that, FA cannot be successfully applied to all data sets. Its success depends on the presence of considerable independent sample-to-sample fluctuation of source strengths. However, it is a fact that, the researcher's ability in selecting the species to include in the data set and frequent use of VARIMAX rotation result in successful applications (Gordon, 1988).

Table 2.3. Houston Aerosol Source Categories (Dzubay et al., 1984)

Marker Elements	General Source Category	Specific Source Categories
Na, Cl	Marine	Marine
Al, K, Ca, Mn, Fe	Crustal	Wind erosion of soil Paved and unpaved road dust Construction Limestone crushing and handling Cement Lime kiln Fly ash Slag
Br, Pb, C	Transportation	Non-catalyst vehicles Diesels
Mn, Fe	Steel	Iron and steel production Steel finishing and handling
Cu, Zn, As, Sm, Sb	Non-ferrous metals	
SO_4	Sulfate	Primary emissions Conversion of SO_2 Regional background
NO_3	Nitrate	Photochemical

2.5.2 Enrichment Factors of the Elements

Enrichment factors (EF) are used in order to determine the contribution of crustal and non-crustal sources (Duce et al., 1983). The major natural sources of trace metals and SPM in the atmosphere are soil, sea salt, volcanic dust and gases.

Comparison of trace element concentrations in the atmosphere with the ones in natural sources can provide information about the source contributors are whether

anthropogenic or natural (Galloway et al., 1982; Kuloğlu, 1997). The EF can be expressed as:

$$(EF)_{crust} = \frac{(C/Al)_{sample}}{(C/Al)_{crust}} \qquad (2.8)$$

where;

$(C/Al_s)_{sample}$: ratio of test element to Al concentration in the sample,

$(C/Al_c)_{crust}$: corresponding ratio in soil.

Based on the above equation, the test element is assumed to originate from earth's crust if its EF value is around unity. Elements with enrichment factors greater than 10 are assumed to originate from sources other than soil (Parekh et al., 1989).

Other reference elements and global composition data can be used to determine contribution of other natural sources. For example, Na and global sea water composition can be used to calculate marine enrichment factors if the study area is close to the sea. The EF approach is generally used as a first step in source apportionment studies because the information it provides is limited. EF cannot quantify a source's contribution, it can only provide information if a given element comes from soil or not. It relies heavily on the assumed source composition, which may vary from one location from another, and it is not applicable to complex source mixtures where multiple local sources are contributing to the same element. Usually, in receptor modeling studies the EF calculations and inter-element ratios are preliminary step giving an insight about the characteristic of the trace element data set (Jervis et al., 1975; Yatın, 1994).

Elements whose $(EF)_{crust}$ values are between 10 and 100 are called "moderately enriched elements". These elements do have non-crustal sources, but a significant fraction of their observed concentrations still have an origin from soil. The elements having $(EF)_{crust}$ values higher than 100 are considered to be highly

enriched elements and have the contributing sources to the atmosphere different than the earth crust.

CHAPTER 3

SEYITÖMER THERMAL POWER PLANT

3.1 About the Case Study

In this study, the receptor and dispersion modeling of fugitive dust emissions from an ash disposal site was assessed. With this intention, Seyitömer Coal-Fired Thermal Power Plant (SCTPP) was selected within the scope of case study. It is a fact that, there are serious fugitive dust problems both during and after the ash disposal in SCTPP. The vicinity of the ash disposal site is covered with agricultural areas indicating that dust emissions from the disposal site may have serious implications. The aim of this study is to assess the magnitude of these emissions on the surrounding region. In addition, relative proportions of stack emissions and fugitive dust emissions from disposal site were also investigated.

3.2 Seyitömer Coal-Fired Thermal Power Plant

Seyitömer coal-fired power plant (SCTPP) is located in the Aegean Region. It is approximately 28 km away from Seyitömer Village which is on the northwestern part of Kütahya Province. A map of this region together with the highways is depicted in Figure 3.1.

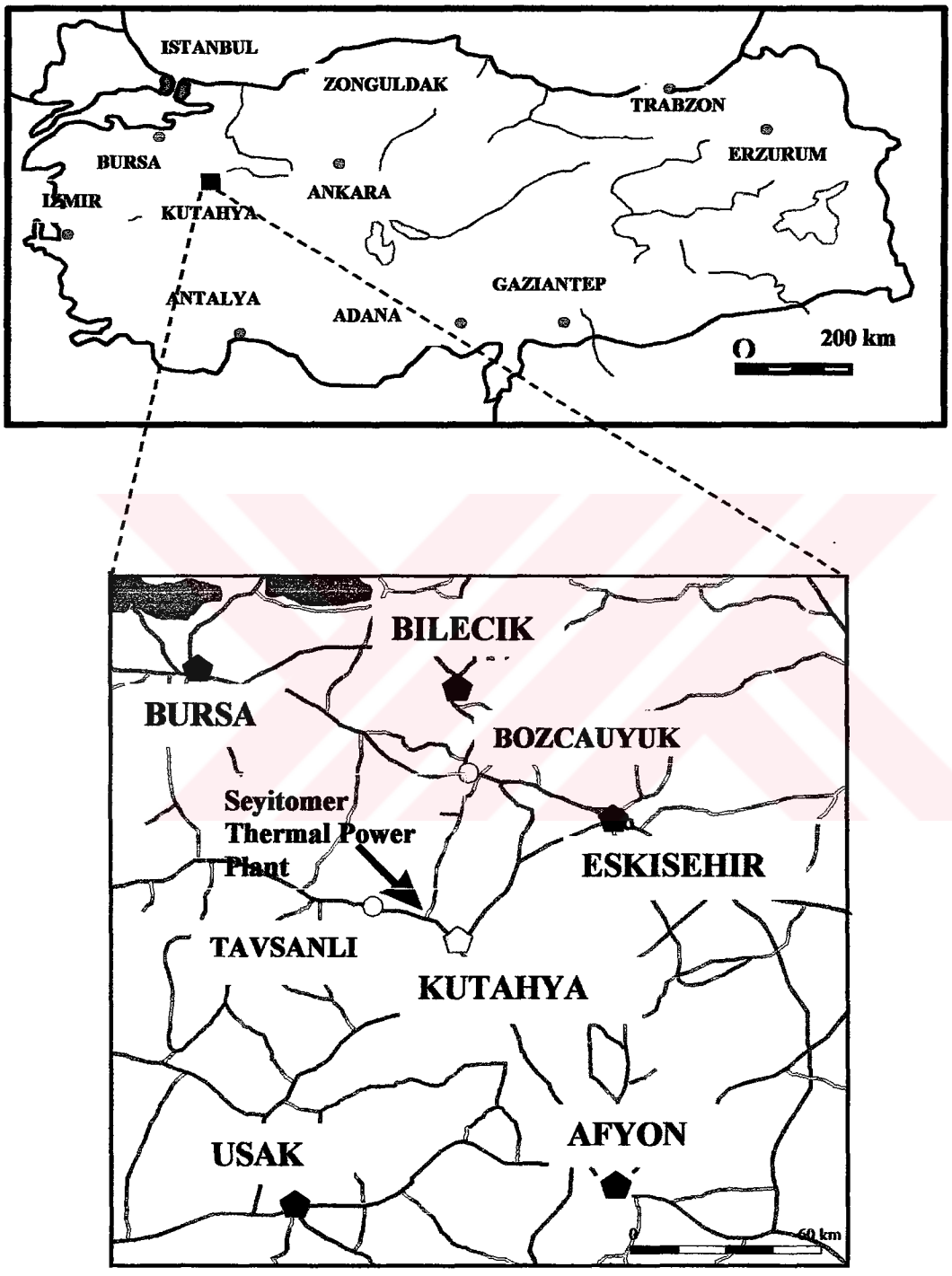


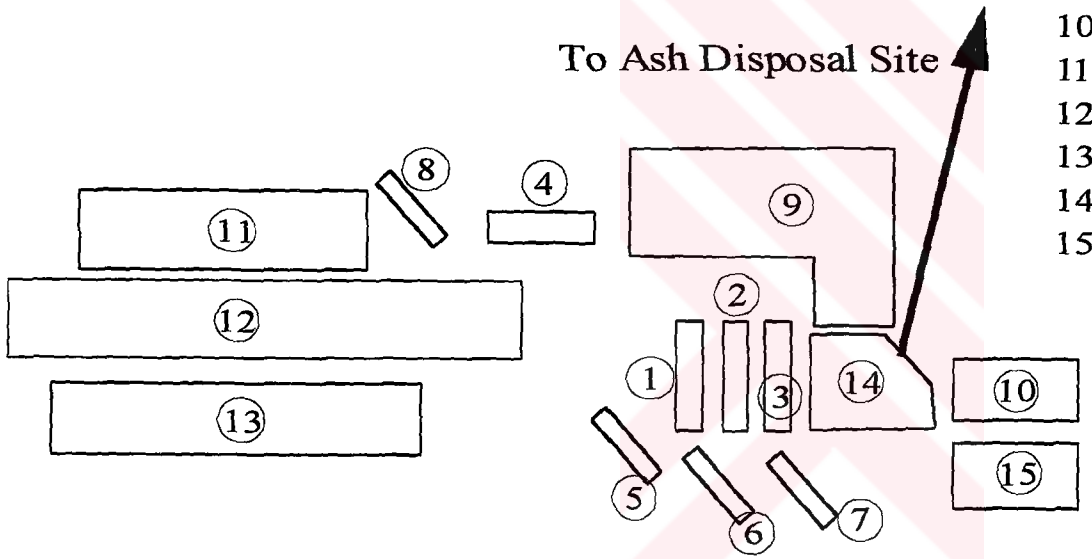
Figure 3.1. Map of the Region

SCTPP was constructed in 1973 to operate using the lignite produced at Seyitömer basin by Turkish Coal Managements (TKİ). The water used in the process is supplied from a reservoir located approximately 13 km away from the plant. In the SCTPP, there are four units with a total capacity of 600 MW (each having a 150 MW capacity). The annual electricity generation of the plant is about 3.6×10^9 kWh which corresponds to 4.5% of the national production. The layout of SCTPP is shown in Figure 3.2.

The plant uses low-quality (calorific value of about 1750 ± 100 kcal kg^{-1}) lignite of Seyitömer basin which has a high ash content (~35%). The daily coal utilization is approximately 20,000 tons (~5.5×10^6 tons yr^{-1}) and about 8,000 tons of ash is generated per day. Each unit in the plant has two electrostatic precipitators with an efficiency of about 98 %. (TEAŞ, 1991) The technical characteristics of the plant with its four units are listed in Table 3.1 and operational data are given in Table 3.2.

Table 3.1. Technical Characteristics of the Plant

Parameter	Unit # 1	Unit # 2	Unit # 3	Unit # 4
Capacity (MW)	150	150	150	150
Start of Operation	1973	1974	1977	1989
Annual Energy Production (GWh)	950	950	950	950
Boiler Efficiency (%)	86	86	87	87
Amount of Feeding Water (t h^{-1})	500	500	450	450
Temperature of Feeding Water (°C)	245	245	245	245
Pressure of Feeding Water (kg cm^{-2})	165	165	165	165
Temperature of Steam (°C)	540	540	540	540
Amount of Steam (t h^{-1})	430	430	420	420
Coal Utilization (t day^{-1})	6,000	6,000	7,200	7,200
Stack Gas Temperature (°C)	150	150	150	150



1- Unit I
2- Unit II
3- Unit III
4- Unit IV
5- Cooling Tower of Unit I
6- Cooling Tower of Unit II
7- Cooling Tower of Unit III
8- Cooling Tower of Unit IV
9- Power Generating Site
10- Wastewater Treatment Plant
11- Coal Deposition Site for Unit IV
12- Coal Deposition Site for Units I & I
13- Coal Deposition Site for Unit III
14- Ash Disposal Facilities
15- Administration Building

Figure 3.2. Layout of SCTPP

T.C. Yükseköğretim Kurulu
Dokümantasyon Merkezi

Table 3.2. Data During the Operation Phase of SCTPP

Parameter	Unit # 1	Unit # 2	Unit # 3	Unit # 4
Annual Energy Production (GWh)	1,033	676	952	1,184
Daily Coal Utilization (t day^{-1})	4,909	4,749	4,700	5,374
Annual Coal Utilization (t $year^{-1} \times 10^6$)	1.6	1.1	1.4	1.8
Efficiency (%)	78.6	51.5	72.5	90.1

The efficiency of the last unit is significantly higher than the others as it is constructed recently and hence the better technology was used during both planning and construction stages.

3.3 Ash Disposal in SCTPP

From the start of the operation, bottom ash have been transported to the ash disposal site which is located approximately 3 km away from the plant by conveyors as shown in Figure 3.3. Figure 3.4 shows the dust emissions during a disposal activity. At the disposal site, ash is disposed from the conveyors at the top of the hill generating a fair haze, particularly during windy days. The ash disposal formed a small hill with a volume of approximately 2.5×10^6 m^3 and a height of about 100 m (TEAŞ, 1991).

In order to minimize the wind erosion, disposed ash piles are being covered with soil intermittently. However, there is always an uncovered area from where fugitive emissions do occur. Wet disposal alternatives were also applied to reduce dust emissions. With this intention, a pipeline was constructed from the plant to the disposal site in order to supply water. Hence, the residues were disposed by means of water into an ash dam situated near the lower slopes of the ash site. However, because of the high rainfall in May 1997, a small portion of the disposal area slipped

(i.e. lower slopes of the dump area contacted with water and deposited ash was subjected to liquefaction) and the residues flowed and covered an area which extends more than 10 km, including agricultural areas (see Figure 3.5). The plant administration is still considering to construct an appropriate ash dam which fulfills the relevant engineering criteria (Hamzaoğlu et al., 1997).

3.4 Meteorology of the Region

Hourly data recorded in 1996 were obtained from Kütahya Meteorological Station operated by the General Directorate of State Meteorological Organization (DMİ). This station is the nearest synoptic station situated within the boundaries of the area taken into consideration where hourly meteorological data are available. Geographically, the station is located at the 39°25′ northern latitude and 29°58′ eastern longitude.

The dominant wind direction obtained from 1996 data is WNW. The wind rose based on long-term average data (between 1927 and 1990) is presented in Figure 3.6 and the hourly wind roses of the region (based on March, 1996 hourly data) are given in Figure 3.7. As can be seen from these figures, when compared with the long-term averages of the same station, 1996 data were found to be typical for the region.

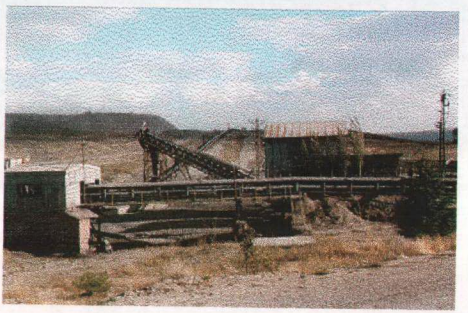


Figure 3.3. Conveyors Used for Ash Disposal

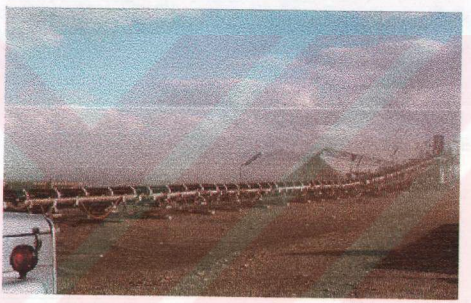


Figure 3.4. Ash Disposal



Figure 3.5. Wet Disposal Site Applied in SCTPP

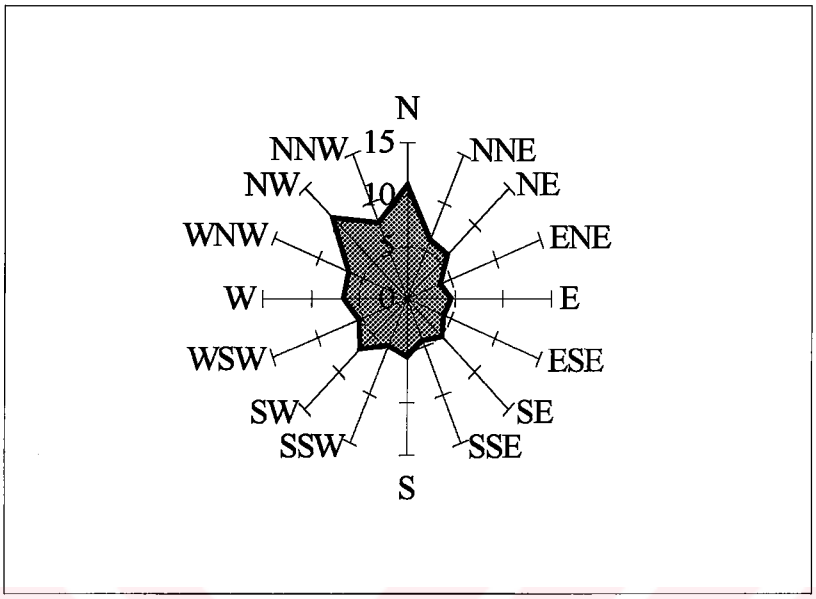


Figure 3.6. Wind Rose of Study Area Between Years 1927-1990

3.5 Summary

Seyitömer coal-fired thermal power plant (SCTPP) is located within the boundaries of Province Kütahya. An uncontrolled ash disposal is applied in the plant. In this study, an assessment of the fugitive dust emissions was carried out. In this regard, there were assumed to be two types of sources. The four stacks of the plant were the source of suspended particulate matter (SPM) and SO2 emissions. On the other hand, the ash disposal area was fugitive dust emission.

In this regard, the ground level concentration (GLC) values of SPM and SO_2 emissions were predicted. On the other hand, the calculated deposition values of SPM from sources were compared with the results obtained from the experimental analyses. Hence, source apportionment studies enable us to have a conclusion about the ash deposition on the agricultural fields located nearby.

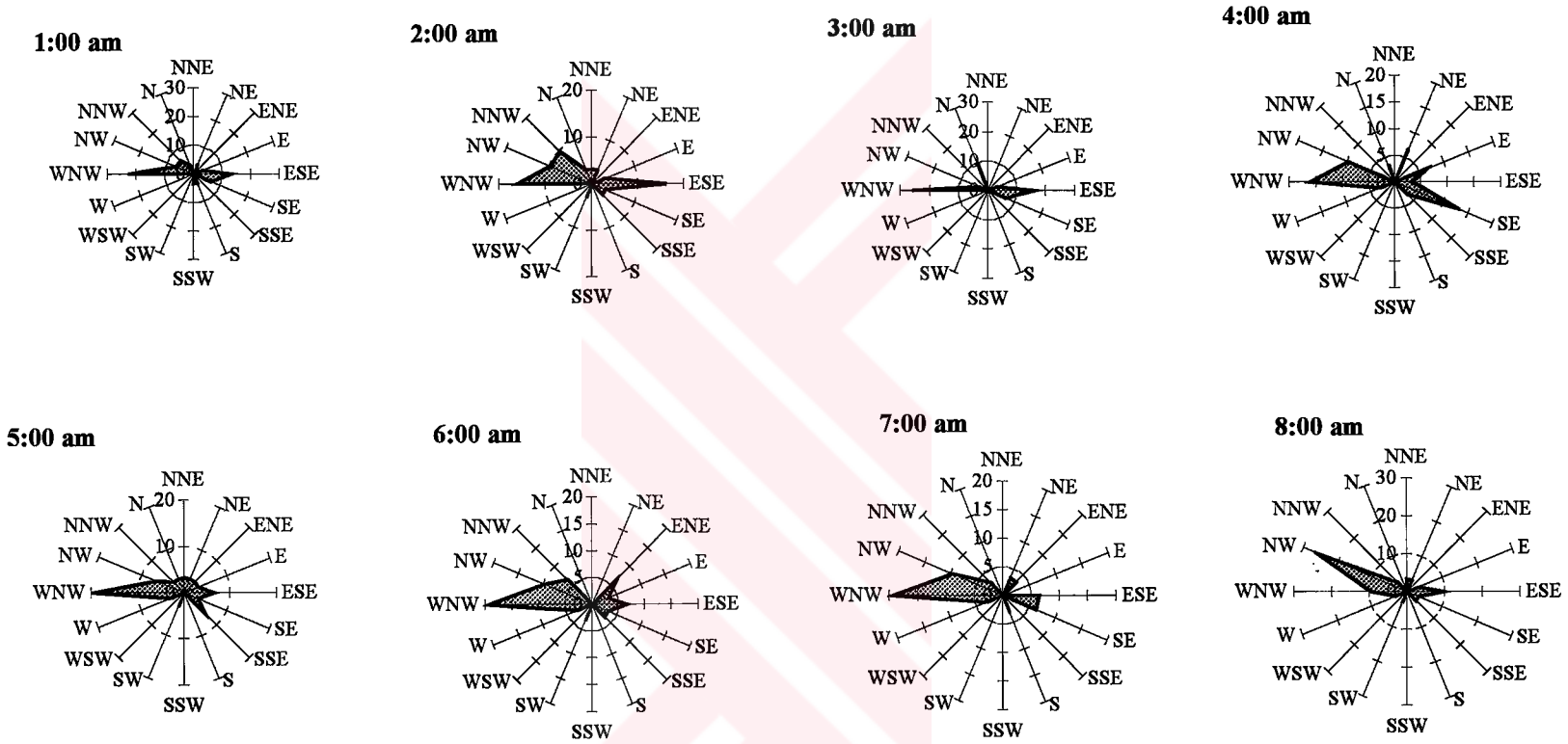


Figure 3.7. Hourly Wind Roses of Study Area During March, 1996

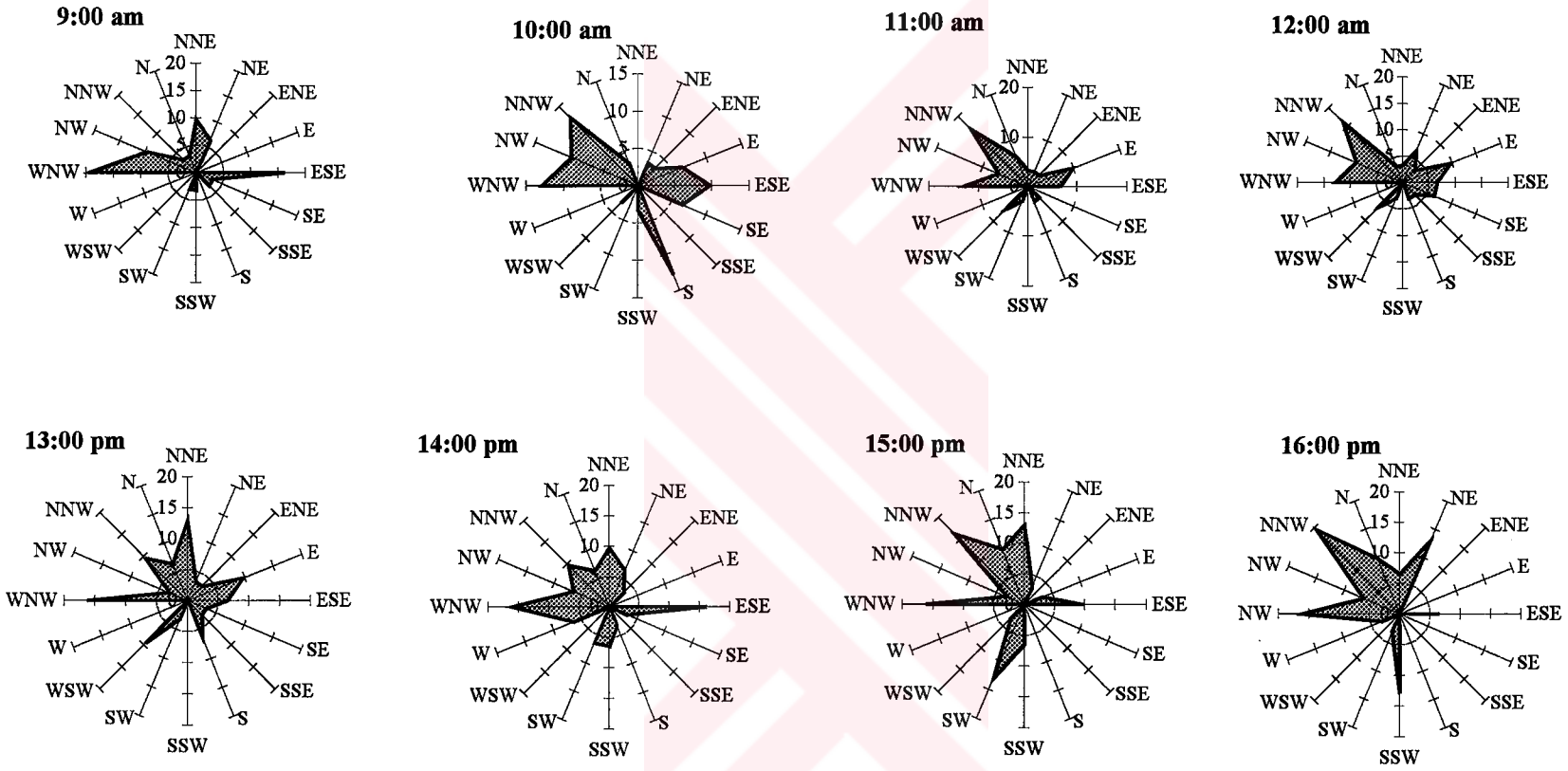


Figure 3.7. Hourly Wind Roses of Study Area During March, 1996 (continued)

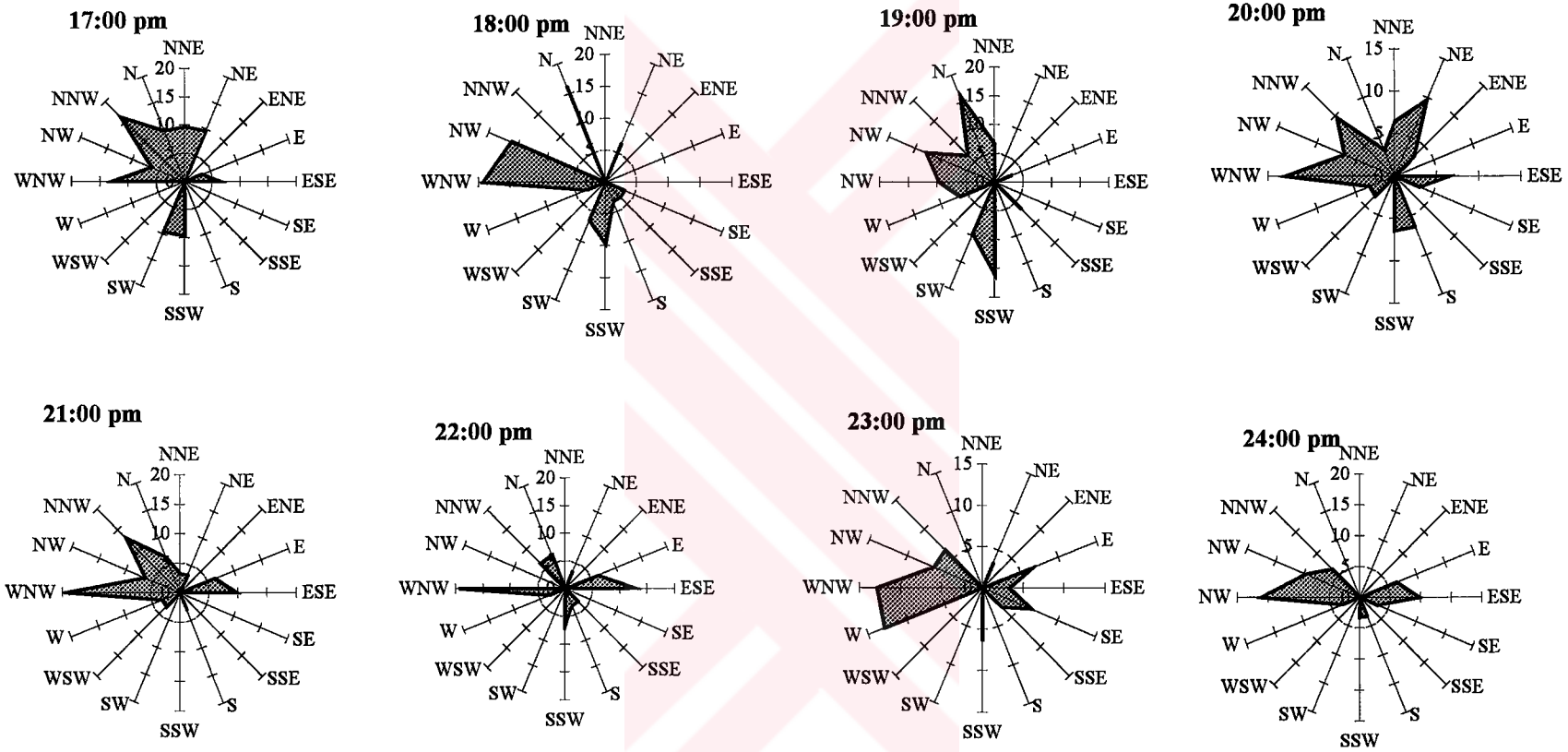


Figure 3.7. Hourly Wind Roses of Study Area During March, 1996 (continued)

CHAPTER 4

MODEL APPLICATIONS AND EXPERIMENTAL METHODS

4.1 ISCST Approach

4.1.1 Study Area

The study area selected for ISCST was defined as a square having the ash disposal area at its center with sides having 10 km distance to the center in north, south, west and east directions. The 3D-digitized topographical map of the study area is shown in Figure 4.1. The topography of the region is not very steep and the general elevation pattern of the study area is around 1,250 m. In the figure, the dashed line shows the boundary of ash disposal site. The solid lines, on the other hand, represent a stabilized road passing through the villages located near the power plant including the village of Seyitömer as well as the ash disposal area. (Hamzaoğlu et.al., 1997)

4.1.2 Model Application

The input data set used for the ISCST model in the context of this study are given below:

Meteorological data: Hourly data recorded in 1996 were obtained from Kütahya Meteorological Station operated by the General Directorate of State Meteorological Organization (DMİ). As discussed in Section 3.3, this station is

the nearest synoptic station situated within the boundaries of the study area. It is also stated in Section 3.3 that the major wind pattern in the region is from WNW according to the hourly data of 1996 (see Figure 3.7). The meteorology input file used in this study was prepared using a pre-processor (REG-308) which calculates the mixing height and the corresponding Pasquill stability classes (for the dispersion calculations) on hourly basis (REG-308, 1990).

Source data: In the model application, there were two types of sources which belong to "area" and "point" classifications. The area source was the ash disposal site which is the origin of fugitive dust emissions. The side length of the square area and release height of the emission above the ground was assumed to be 20 m and 100 m, respectively. The point sources, on the other hand, were the four stacks belonging to the four units of the power plant. The general characteristics of the stacks together with the values used in the model were discussed in the subsequent sections.

Receptor data: A square cartesian grid system (taking the south-west corner of study area as the origin and centering the ash disposal site) was used. The selected system consisted of 40 × 40 grid elements (each with a dimension of 500 m × 500 m) which covers a total area of 400 km^2 (see Figure 4.1). Hourly, daily and annual ground level concentration (GLC) values in each grid element were calculated for the year 1996. On the other hand, the villages Seyitömer, Bozcaüyük, Ayvalı, Andız and Kınık located near the plant and ash disposal area were also taken as the discrete receptor points.

Control data: Ground level concentrations of SPM and SO_2 and deposition values of SPM were evaluated for the air quality near the ash disposal site.

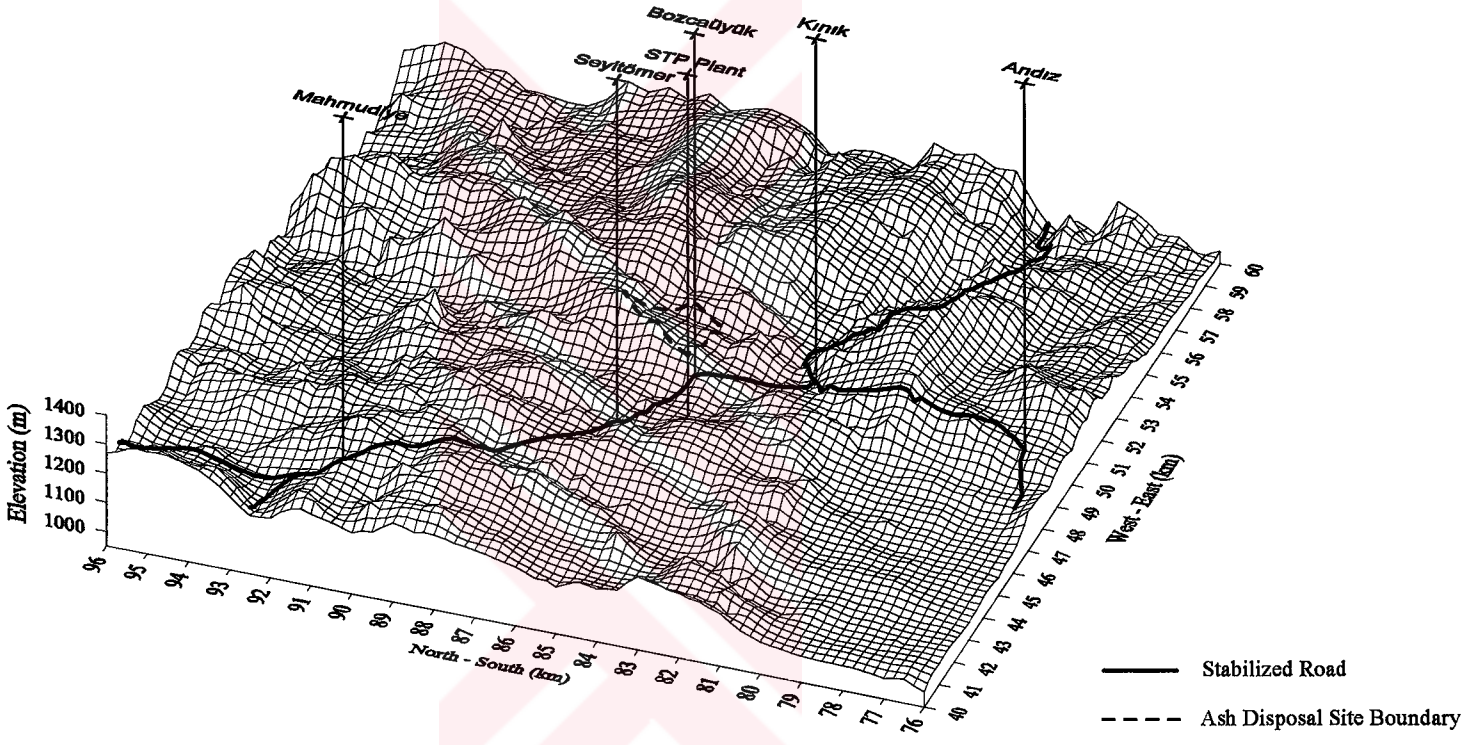


Figure 4.1. 3-D Digitized Topographical Map of the Study Area

4.1.3 Model Inputs

4.1.3.1 Area Source

The fugitive dust emissions from stock piles were compiled using Equation (2.1) as stated in Section 2.4.2. The PE index (I) used in this formula, which is the precipitation-evaporation index, can be calculated using Equation (4.1). The precipitation-evaporation index generally depends on the latitude and longitude of the study area, which determines both the annual precipitation and daily maximum evaporation in the formulation.

$$I = \frac{annual\ \ precipitaion(mm)}{daily\ \ max.\ \ evaporation(mm)} \qquad (4.1)$$

The index (I) was calculated to be 43.43 using the data obtained from the Kütahya Meteorological Station, where the annual precipitation and the daily maximum evaporation values in the region between years 1929-1990 were 564.6 mm and 13.0 mm, respectively (DMİ, 1997).

The fugitive dust emissions that originate from one tone (t) of disposed ash was calculated as 1.75 lb using Equation (2.1). Since ash disposal rate of the plant is 8,000 tons day^{-1} (TEAŞ, 1991), SPM emission rate was found to be 73.565 gr s^{-1}. The emission per unit area, on the other hand, was 0.1839 gr s^{-1} m^{-2}.

Size distribution of ash and settling velocities, reflection coefficients for each size fraction which are important parameters for deposition calculations are given in Table 4.1. Although the size distribution of ash should be determined by sieve analysis, the literature information for size distribution is used in this study, due to reclamation works carried out within the disposal area. Such reclamation work altered the size distribution of ash by mixing some of it with soil.

As can be seen from the table, the mass-mean diameters were 5, 15, 30 and 60 μm; and the corresponding terminal settling velocities and reflection coefficients (R_f) were 0.223, 2.009, 8.038 and 32.151 cm s^{-1}, and 0.90, 0.71, 0.54 and 0.00, respectively.

Table 4.1. Characteristics of the Ash in the Disposal Area

Mass-Mean Diameter (μm)*	**Mass (%)***	**Settling Velocity (V_s) (cm s^{-1})**	**Reflection Coefficient (R_f)**
5	55.5	0.223	0.90
15	16	2.009	0.71
30	9.5	8.038	0.54
60	19	32.151	0.00

* *Evans et al., 1980*

4.1.3.2 Point Sources

Since there are four units in the power plant, this corresponds to the four point sources (i.e. the four stacks) for the modeling exercise. The general characteristics of the sources at the exit of each stack are given in Table 4.2. Note that there exists one electrostatic precipitator (ESP) for each unit.

As can be seen from the table, the most technological unit (it is the last unit) has the least SPM emission (648 gr s^{-1}) due to the high efficiency of ESP (~98%). The source having the highest emission (4,283 gr s^{-1}) is the first unit due to lower efficiency of the ESP in this unit (~92%).

It must be noted that, the SPM emissions used in the model were the worst case scenario. It is reported for the stacks that the SPM emissions from each unit was sampled at the exit of the ESPs and recorded as 15,906; 13,481; 4,346 and 2,105 mg Nm^{-3}, respectively (TÜBİTAK, 1994).

Table 4.2. General Characteristics of the Stacks (TEAŞ, 1991)

Parameter	Unit # 1	Unit # 2	Unit # 3	Unit # 4
Stack Exit SPM Emission (gr s^{-1})	4,283	4,181	1,090	648
Efficiency of ESP (%)	91.5	88.6	97.04	98.19
Stack Exit SO_2 Emission (gr s^{-1})	1,761	2,170	1,487	1,710
Stack Exit Temperature (°C)	155 (428 °K)	156 (429 °K)	165 (438 °K)	179 (452 °K)
Stack Exit Velocity (m s^{-1})	17.82	20.42	13.51	16.73
Density (kg m^{-3})	0.696	0.708	0.692	0.649
Stack Inside Diameter (m)	3	3	3.3	3.4
Stack Height (m)	105	105	105	105
Efficiency (%)	91.50	88.60	97.04	98.19

The SO_2 emissions, on the other hand, were recorded as 6,540; 6,996; 5,931 and 5,552 mg Nm^{-3}, respectively (TÜBİTAK, 1994).

The distribution of mass among size fractions and the general size characteristics obtained at the exit of the electrostatic precipitators are given in Table 4.3. It must be noted that, the density of the particles were assumed as 0.8 gr cm^{-3} during the calculation of terminal settling velocity (V_s) (EPA, 1992b).

Table 4.3. Size Distribution of Particles at the Exit of the Electrofilters (TEAŞ, 1991)

		Mass Size Distribution (%)					
Diameter Range (μm)	**Mass-Mean Diameter (μm)**	Unit # 1	Unit # 2	Unit # 3	Unit # 4	**V_s (m s^{-1})**	**R_f**
63-125	97	31.72	47.62	28.28	39.95	0.0896	0.00
45-63	55	8.40	12.03	10.74	8.60	0.02882	0.00
32-45	39	14.14	7.92	12.50	13.50	0.01449	0.00
0-32	20	38.47	22.17	37.28	20.63	0.00381	0.54

4.2 Receptor Modeling Approach

4.2.1 Sampling

4.2.1.1 Collection of Aerosol Samples

The sampling station was located in Ayvalı Village at approximately 1.5 km to the east of ash disposal site (see Figure 3.1). Ayvalı is the nearest residential area which is downwind from the ash disposal site.

Aerosol samples was collected using a SIERRA-ANDERSEN Model SAUV-10H PM-10, High Volume Sampler, on 20 cm × 28 cm Whatman-41 cellulose filters. The technical specifications of the sampler are summarized in Table 4.4. A preimpector removed particles larger than 10 μm aerodynamic diameter from reaching the filter. Consequently, only particles which are smaller than 10 μm are sampled (PK-10 sampling).

The Hi-Vol. sampler was located in the garden of a residential area in the Ayvalı Village. Although the location was a garden, there were no SPM around. The area was protected throughout the sampling period and power was available all the time. The samples were collected for a total of 22 days between March, 11 and April 1, 1998.

Table 4.4. Technical Specifications for Hi-Vol. Sampler

Parameter	Specification
Flow Rate	1.96 m^3 per hour (69.2 ft^3 per hour)
Flow Rate Stability	Over 24 hours, average flow rate within ± 5% of initial
Filter Media	20 cm×28 cm (8 in×10 in) Whatman-41 cellulose filter
Inlet Collection Efficiency	The inlet has a cut-point of 9.7±0.5 μm over a wind speed of 0-36 km hr^{-1}.

During the sampling period, Whatman-41 filters were used in order to operate the sampler at high flow rate without significant pressure drop due to particulate loading (Güllü, 1996). The flow rate was recorded by a recorder accumulated air volume was determined by a mass flow integrator.

Samples were collected on a daily basis and filters were changed at approximately 15:30 hours every day. During sample-change, the sampler was stopped, the cozette which contains the filter was removed from the sampler and moved to a protected area. The filter was removed from the cozette using plastic forcepts and placed in a polyethylene bag. A fresh filter was placed in the cozette and the cozette was mounted on the sampler. The total airflow during 24-hr sampling was recorded from the mass flow integrator and the sampler was operated for the new sample. During sample-change, operator was asked to wear polyethylene gloves and use plastic forcepts to manipulate filters to minimize the chance of sample contamination.

4.2.1.2 Collection of Soil Samples

Soil samples were collected at the corners of 1 km × 1 km grid elements of a 100 km^2 (10 km × 10 km) grid system which is centered on the ash disposal area of the power plant. The sampling points were tried to be at 1 km distances from each other. Although collection of 100 samples was originally planned, only 40 samples were collected due to poor weather and field condition. The locations of the sampling points are given in Figure 4.2. As can be seen from the figure, 40 sampling points were selected so that they represent the study area. At each sampling point, surface soil samples were tried to be taken with a polyethylene spatula after removing non-soil material such as grass, rocks, etc. During the sample collection, plastic gloves were used to minimize the contamination. The soil samples were stored in the polyethylene bags and the moisture was taken out as they were taken to the laboratory.

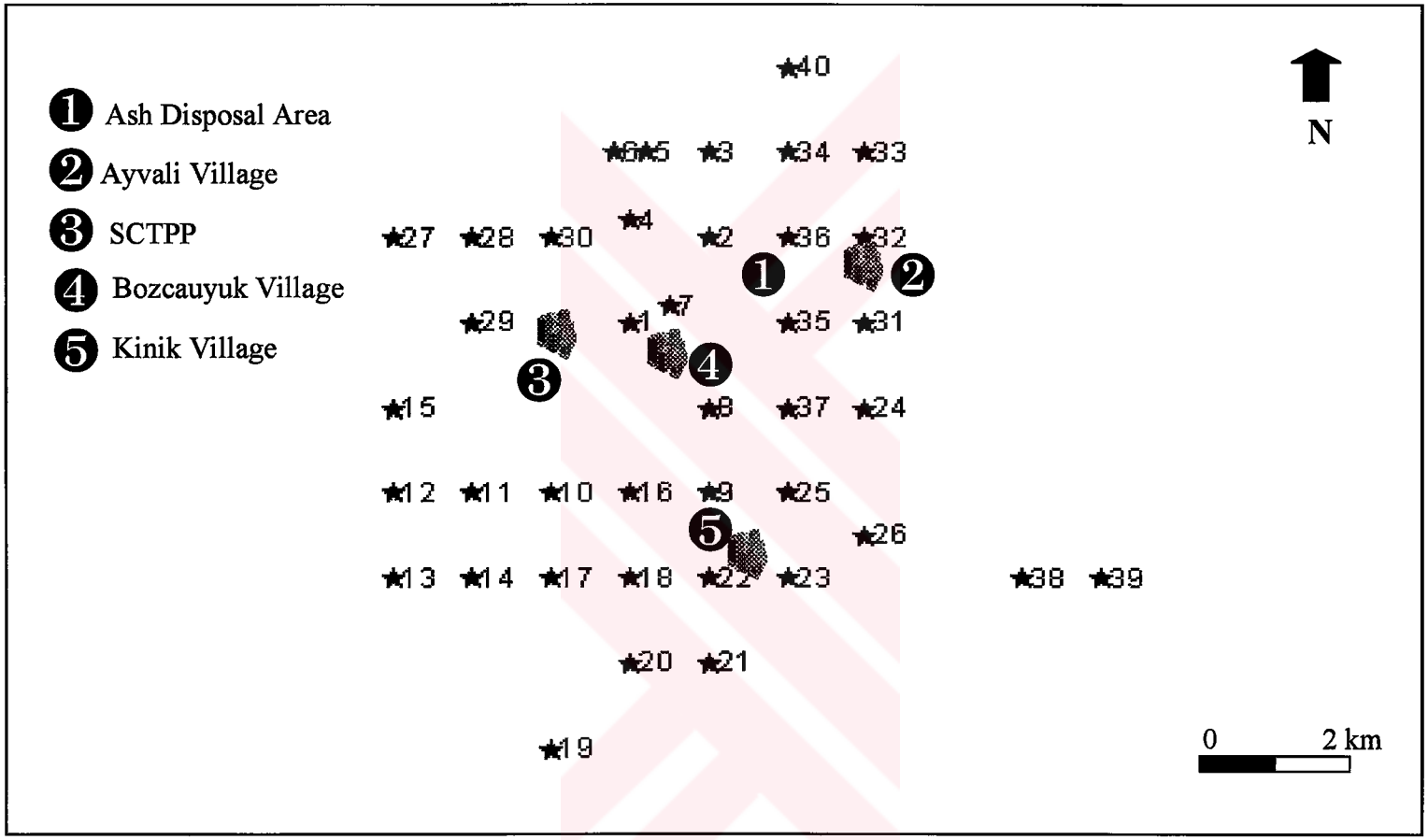


Figure 4.2. Soil Sampling Points

4.2.2 Preparation of Samples for Analyses

4.2.2.1 Preparation of Aerosol Samples

Aerosol samples were analyzed by Atomic Absorption Spectrometry (AAS) for the elements Na, Mg, Al, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb. Filters were first weighted then divided into four-quarter pieces. Each piece was weighted to determine flow through quarter filter. In order to determine the elemental concentrations of aerosol samples by AAS, the elements should be solubilized either by extraction or total acid digestion. In this study, total acid digestion was used. For this, one fourth of the filters were transferred into a 250 mL Teflon beakers, 30 mL of sub-boiled HNO_3 was added and beakers were closed with a Teflon cover. Samples were refluxed for 10 - 12 hours at 130 ± 10°C on a hot plate. After refluxing, the clearness of the solutions were controlled, some more acid (up to a total of 20 mL) was added if the solution was not clear enough and refluxing was resumed for 6 - 8 more hours. Then, covers were removed from the beakers and HNO_3 was allowed to evaporate until its volume reached approximately to 10 µL. Five mL of pure HF was added to destroy the silicate matrix. The beakers were covered again and let to reflux for 6 - 8 hours on a hot plate. At the end of refluxing, the covers were removed and heating was continued until samples reached to near dryness. About 5 mL of concentrated HNO_3 was added and evaporation was repeated until the white fumes of HF were no longer visible. Complete evaporation of HF was necessary, because any HF that remains can damage the nebulizer and other glass or quartz parts of the spectrometer. When HF was completely removed, samples were removed from the hot plate and allowed to cool. The residue was redissolved with the addition of 1% HNO_3 in a 50 mL volumetric flask and diluted to 50 mL with the same 1% HNO_3 solution.

During experiments, special attention was paid to prevent the contamination of samples. With this intention, plastic and Teflon glasswares were soaked in 30% HNO_3 overnight and rinsed several times with double distilled-deionized water.

4.2.2.2 Preparation of Soil Samples

In the laboratory, soil samples were dried in an oven at 60°C for approximately 3 - 4 days. Dried soil was then grinded by hand and homogenized to fine dust using an Agent homogenizer. Homogenized samples were than digested using following procedure. Approximately 250 mg of soil was weighed into Teflon vessels of the high-pressure digestion bombs. Four mL HNO_3 and 1.5 mL HF were added. The vessels were covered and placed in their stainless-steel jackets. Assembled digestion bombs were then placed in an oven of 150°C for approximately 1.5 hours. Then, they were allowed to cool to room temperature and Teflon vessels were removed from stainless-steel jackets and the solution was evaporated on a hot plate near dryness. The residue was re-dissolved with the addition of 1% HNO_3 in a 50 mL volumetric flask and the solution was made to 50 mL with the same solution.

4.2.3 Analysis of Elements in Aerosol and Soil Samples

Elements Na, Mg, Al, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb in a total of 22 aerosol and 40 soil samples were analyzed by a combination of flame atomic absorption spectrometry (FAAS) and flame emission spectrometry (FAES) and graphite-furnace atomic absorption spectrometry (GFAAS).

4.2.3.1 FAAS and FAES Measurements

The aerosol filter and soil samples collected were analyzed for major elements namely Na, Mg, Al, K, Ca, Cr, Mn, Fe, Cu and Zn by FAAS and FAES. A Perkin-Elmer 1100B model AAS was used for the measurements. Only elements including Na and K were analyzed by FAES. Operating parameters of the instrument during FAAS and FAES analyses are given in Table 4.5. All elements

were analyzed using air-acetylene flame except for Al which is measured using N_2O-C_2H_2 flame (because Al forms stable oxides in the flame which can only be broken apart in the higher temperature of the N_2O-C_2H_2 flame).

Before the analyses, AAS was allowed to warm up for approximately 20 minutes. Burner position and Hollow Cathode Lamp (HCL) were optimized for the maximum sensitivity. The solutions were directly aspirated to burner at a 7 - 8 mL min^{-1} flow rate. Standard solutions used for calibration were prepared by necessary dilutions of commercially available 1,000 mg L^{-1} stock solutions (Aldrich). During the measurements, method by standard additions was used. If absorbance value of an element in a sample exceeds the dynamic range for that element, the sample was diluted and re-analyzed (again with method of standard addition).

4.2.3.2 Graphite Furnace Atomic Absorption Spectrometry (GFAAS) Measurements

Graphite furnace atomic absorption spectrometry (GFAAS) was used to analyze for Ni, Cd and Pb for which in samples were too low to be detected by FAAS. A Perkin-Elmer 1100B spectrometer coupled to Perkin-Elmer HGA 700 electrothermal atomization system was used for GFAAS analyses. Deuterium lamp was used to correct for non-specific background absorption. Argon (Ar) was used as the purge gas. During analyses, internal gas flow rate through the graphite tube was 300 mL min^{-1}; however gas flow was interrupted during atomization to increase the lifetime of atoms on the optical path. Parameters used during the GFAAS measurements are summarized in Table 4.6.

In order to achieve the maximum absorption and minimum background, sample volume, ashing, atomization temperature, ramp and hold times were optimized before analyses. If possible, the average absorbance value was held about 0.4-0.6 and if the maximum absorbance value was exceeded, the samples were diluted with distilled-deionized water and re-analyzed.

4.2.4 Data Quality Assurance

4.2.4.1 Blank Samples

In order to keep the sample contamination under control, deionized water, reagents, laboratory blanks and field blanks were regularly analyzed along with samples. These control samples provided information on the level of contamination originating from water, filters and laboratory processes during the analyses.

Field blanks were prepared by placing the filter onto the Hi-Vol. sampler. However, unlike sampler, air was pulled through the field blank filters for only 1 min. Then the field blanks were treated in the same way as the samples. Aerosol filter blanks were the unused clean filters. They were digested and analyzed like aerosol filters. The difference between filter blanks and field blanks, provided information on the contamination due to field operations. Acid blanks consisted of HNO_3 and HF in the same amounts they were used in the samples. Soil blanks, however, were prepared following the same steps done for the samples except no soil sample was put in digestion bombs.

4.2.4.2 Sample to Blank Ratios

The average sample to blank (S/B) ratios of aerosol and soil samples are given in Table 4.7. An illustration of this table is presented in Figure 4.3 and denoted as percent contribution of blank to the samples. It is obvious that the low values in S/B ratio indicate the large uncertainties in the analyses due to high blank values.

As can be seen from the figure, the trends of two graphs are approximately same. Zn has the largest contribution in both soil and aerosol samples with 13.68 and

Table 4.5. Operation Parameters in FAAS and FAES

Parameter	Elements									
	Na	Mg	Al	K	Ca	Cr	Mn	Fe	Cu	Zn
Technique	FAES	FAAS	FAAS	FAES	FAAS	FAAS	FAAS	FAAS	FAAS	FAAS
Wavelength (nm)	589.0	285.2	309.3	766.5	422.7	357.9	279.5	459.4	324.8	213.9
Slit Width (nm)	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Air (mL min^{-1})	9.5	8.0	-	8.5	9.0	8.8	8.0	9.8	9.5	10.4
Acetylene (mL min^{-1})	3.7	2.0	7.7	3.0	3.9	5.6	2.5	2.9	2.2	2.8
N. Oxide (mL min^{-1})	-	-	7.2	-	-	-	-	-	-	-

Table 4.6. Operation Parameters in GFAAS

Parameter	Elements		
	Ni	Cd	Pb
Tube	Pyrolitic Coated	Uncoated	Uncoated
Wavelength (nm)	232.0	228.8	283.3
Slit Width (nm)	0.2	0.7	0.7
Lamb Current (mA)	25	3	9
Sample Volume (µL)	20	20	20

18.34 %, respectively. As a whole, the percent contributions of elements are less than 20% indicating that the results obtained using the current sampling and analytical techniques are reliable. It is obvious that the percent contributions of blanks are small.

Table 4.7. Sample to Blank (S/B) Ratios

Element	Soil Samples		Aerosol Samples	
	S/B	% Blank	S/B	% Blank
Na	69	1.44	8	12.6
Mg	2,638	0.04	189	0.53
Al	1,782	0.06	184	0.55
K	415	0.24	63	1.60
Ca	655	0.15	24	4.12
Cr	140	0.71	18	5.48
Mn	1,110	0.09	84	1.19
Fe	3,878	0.03	395	0.25
Ni	445	0.23	61	1.63
Cu	61	1.65	68	1.47
Zn	7	13.68	6	18.34
Cd	16	6.18	15	6.56
Pb	140	0.71	113	0.88

4.2.4.3 Analysis of Standard Reference Materials

In order to obtain a high accuracy in FAAS and GFAAS measurements, standard reference materials (SRM) were analyzed on a daily basis. Three different SRM's were used from National Institute of Standard and Technology (NIST); namely, geological sample (GSP-1), estuarine sediment (SRM-1646) and Buffalo River Sediment (SRM-2704). Digested SRM's were analyzed every day before starting the measurements and the results were compared with the certified values. During the day, several injections of SRM were carried out to control the variations in the slope of the standard addition curve.

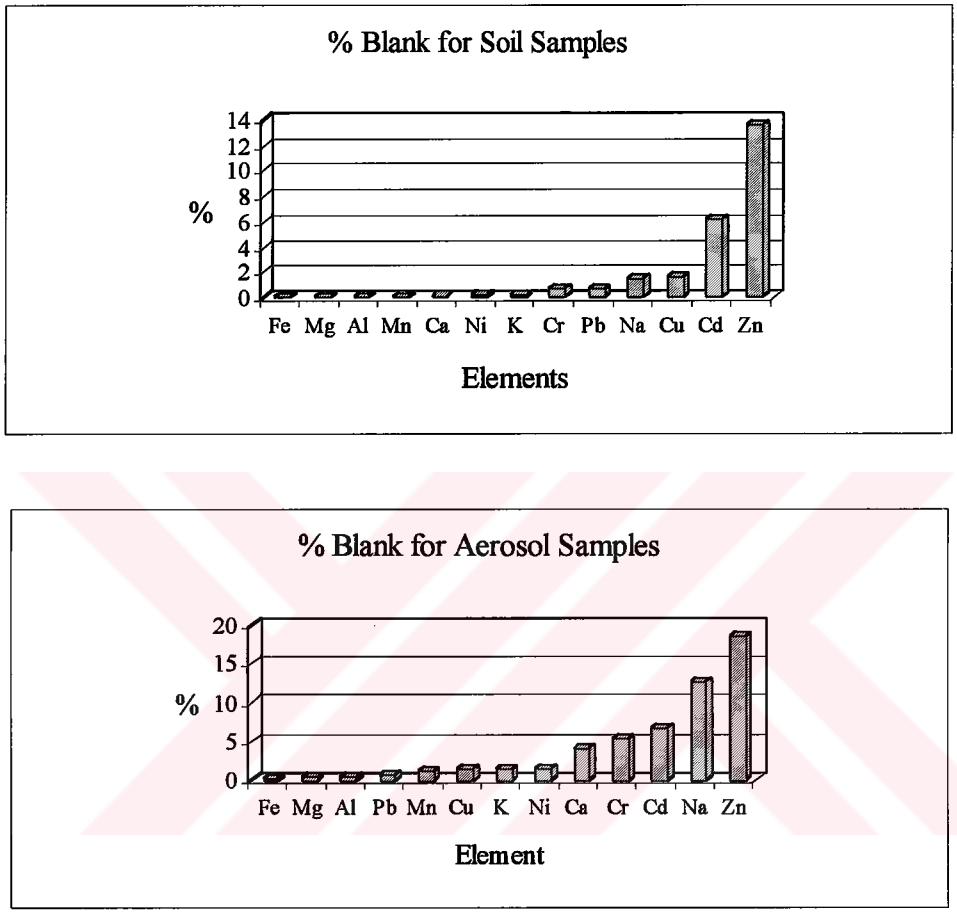


Figure 4.3. Percent Blank Contributions in Samples

The analyses of samples were resumed if the results were within ±10% of the certified values. The analysis results of the three SRM's with their certified values are given in Table 4.8. As can be seen from the table, the observed certified values were in good agreement for most of the elements.

Table 4.8. Concentrations of Standard Reference Materials

		SRM-1464 (GSP-1)		SRM-2704		SRM-1646	
Element	Conc. Unit	NIST Value	Found Average ±SD	NIST Value	Found Average ±SD	NIST Value	Found Average ±SD
Na	%	2.08	2.04±0.17	0.76	0.68±0.1	2	1.95±0.13
Mg	%	0.596	0.61±0.04	1.2	1.17±0.15	1.09	1.05±0.1
Al	%	8.2	8.31±0.21	6.11	6.44±0.26	6.25	6.48±0.22
K	%	4.57	4.54±0.14	2	1.97±0.1	1.63	1.79±0.13
Ca	%	1.46	1.56±0.18	2.6	2.4±0.12	0.83	0.13±0.16
Cr	$\mu g\ L^{-1}$	13	12±3	135	129±2	76	80±3
Fe	%	3.01	3±0.1	4.11	3.9±0.3	3.35	3.3±0.3
Ni	$\mu g\ L^{-1}$	9.8	12±3	44.1	35±6	32	27±3
Cu	$\mu g\ L^{-1}$	34	35.1±1.9	98.6	996±2.1	18	19.4±1.4
Zn	$\mu g\ L^{-1}$	103	115±6	438	464±15	138	152±10
Cd	$\mu g\ L^{-1}$	56	54.45±13.56	3.45	3.35±0.77	0.36	0.34±005
Pb	$\mu g\ L^{-1}$			1,161	166±0.6	28.2	30.3±2.6

4.2.4.4 Detection Limits

Detection limits of elements in AAS measurements depend both on the sensitivity (which is the concentration that is given 0.1 A) and the fluctuation of the background or baseline. In practice, the variability of the blank value determines the detection limits. A common definition of detection limit is "twice the standard deviation of blank measurements" (Güllü, 1996). The detection limits which were calculated using above definition are given in Table 4.9 with the average concentrations observed. As can be seen from the table, the limits are two to three orders of magnitude below the concentrations of elements in the samples indicating that the detection limits were not a source of uncertainty in the

measurements. Note that; Ni, Cd and Pb were analyzed by GFAAS and the rest by FAAS.

Table 4.9. Detection Limits (DL) for Elements

Element	DL (ng L^{-1})	Observed (ng L^{-1})	
		Soil Samples	Aerosol Samples
Na	237	26,939	3,081
Mg	73	234,559	16,810
Al	216	253,032	26,072
K	49	36,781	5,558
Ca	289	362,235	13,440
Cr	9	1,764	230
Mn	5	4,597	349
Fe	189	580,687	59,107
Ni	5	1,554	214
Cu	6	285	321
Zn	17	465	346
Cd	0.3	1.75	1.65
Pb	6	315	255

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Calibration of the Model

Dispersion models are one of the tools used to apportion the sources of pollution. The reason they are frequently used is its easy application. The predictions obtained from these models, however, are not so accurate because of assumptions involved in computations. In this regard, it is necessary to calibrate these models with the experimental results obtained from the analyses of ambient air sampling.

5.2 Sensitivity Runs

In this study, fugitive dust (i.e. SPM) is the pollutant that is investigated. The major input parameter for the SPM is the particle size distribution. Terminal settling velocities and reflection coefficients, which are the important parameters for GLC are calculated using particle size distribution and mean-diameter of particle size classes (see Section 2.4.2).

Another important parameter in the calculation of GLC values is the emission rate. In this study, the worst case scenario was applied for the SPM emissions, whose parameters were discussed in Section 4.1.3. Other scenarios include some changes in the particle size distribution and SPM emission rates. The parameters used in four scenarios are listed in Table 5.1 and the predictions of these scenarios are shown in Figure 5.1.

The influence of particle size distributions and emission rates on calculated GLC's and deposition of particles was investigated using 4 hyphotetical scenarios. These scenarios involve two different size distributions and two different emission rates for the Seyitömer power plant.

Table 5.1. Parameters Used in Four Scenarios

Parameter	Alternative 1	Alternative 2	Alternative 3	Alternative 4
Mean-Diameters of Particles (μm)	5, 15, 30, 60	5, 15, 30, 60	1.5, 3.5, 13.5, 25	1.5, 3.5, 13.5, 25
Total SPM Emissions (g sec^{-1})	10,202	4,022	10,202	4,022

In this table, the SPM emissions were also taken from the report prepared by TÜBİTAK for Seyitömer Power Plant administration (TÜBİTAK, 1994). The particle size distribution, on the other hand, is the one used for conventional power plants and selected using background knowledge. In this study, Alternative 1 represents the worst case scenario having the highest SPM emissions. As can be seen from the figure, the SPM emissions and deposition values were so above the limits stipulated by the Turkish Regulation on Preservation of Air Quality, hence the application of worst case scenario is not a wrong approach.

5.3 State of Pollution in Seyitömer Region

5.3.1. Average Concentrations of Elements

Average concentrations of measured elements in soils and aerosols are presented in Table 5.2 and Table 5.3, respectively. In this table, number of samples (N), arithmetic and geometric averages, arithmetic standard deviations (SD) and median concentrations are included.

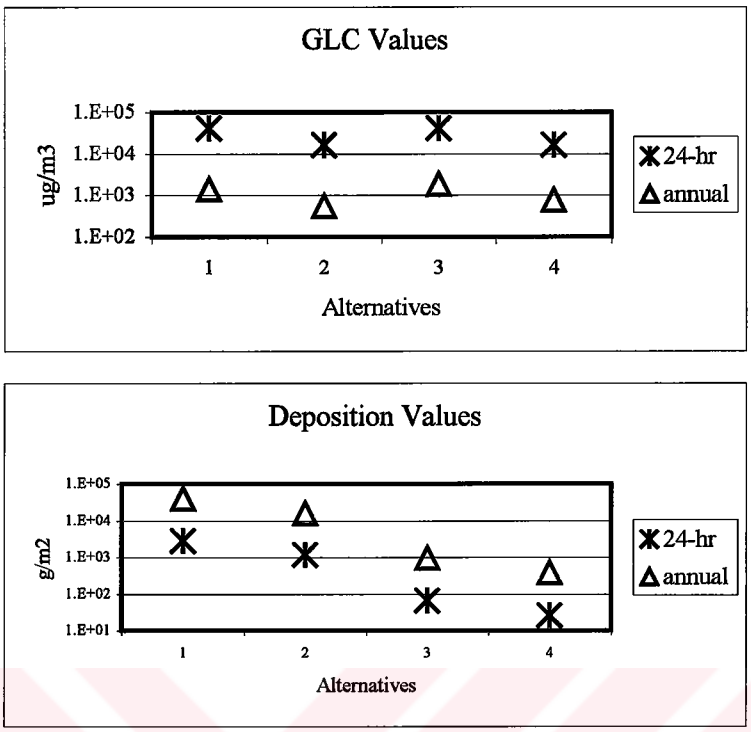


Figure 5.1. Comparison of Four Scenarios

High SD values particularly those observed in aerosol samples do not imply poor sampling or analyses. High SD's in aerosol data indicate variations in meteorological conditions, physical and chemical transformations in the atmosphere, transport and deposition of air mass as well as variations in source strength. In an ucontaminated soil, elements are expected to have similar concentrations and have fairly small SD values.

Although variations in soil data are smaller than variations observed in aerosols, standard deviations shown in Table 5.2 are still fairly high. Such high standard deviations may either imply contamination or variation in soil chemical composition in the study area. As can be seen from Table 5.2, the SD value of Pb is fairly high compared to other elements indicating that the soil is probably contaminated with this element. The frequency distributions are prepared and distributions were tested, using chi-square test for all elements measured in soil.

Two examples of frequency distributions are given in Figure 5.2 for Pb and Al, indicating log-normal and Gaussian distribution respectively. With the exception of Pb and K, elements show Gaussian distribution within 90% confidence interval. Pb and K, on the other hand, showed a log-normal behavior.

Table 5.2. Experimental Results of Soil Samples

Element	N	Avg. Conc.± SD (ppm)	Geo. Mean (ppm)	Median (ppm)
Na	40	5,301±2,095	4,955	4,840
Mg	39	46,820±19,154	43,376	42,908
Al	40	50,491±13,900	48,484	48,720
K	40	7,327±2,991	6,713	7,068
Ca	40	72,222±62,998	49,493	50,806
Cr	40	350±184	303	319
Mn	40	917±243	882	969
Fe	40	115,913±29,161	111,761	120,927
Ni	39	301±164	247	287
Cu	40	56±21	52	55
Zn	40	80±19	78	81
Cd	40	0.32±0.16	0.28	0.29
Pb	40	62.5±99	21	14

Concentrations of elements in clean soil which is not affected from anthropogenic activities are expected to show Gaussian distribution. Smooth curve of this distribution indicates that the elements are equally distributed over the study area which means fairly clean environment. Log-normal behavior, on the other hand, may indicate anthropogenic activities such as deposition of combustion particles from atmosphere or discharges. Based on this simple argument, K and Pb are suspected to have anthropogenic sources affecting their measured concentrations. However, it should be noted that distributions alone cannot be considered as a conclusive evidence on the presence or absence of anthropogenic contribution on observed concentrations of measured parameters.

Additionally, if the arithmetic means are smaller than geometric means and medians, the data set is concluded to be skewed. Skewness is a value to determine the degree of asymmetry of data in a distribution around its arithmetic mean (Güllü, 1996). As can be seen from Table 5.2, the arithmetic means of the elements are comparable with both the geometric mean and median values of elements indicating that the data set is not skewed much.

Table 5.3. Experimental Results of Aerosol Samples

Element	N	Avg. Conc.± SD (μg m^{-3})	Geo. Mean (μg m^{-3})	Median (μg m^{-3})
SPM	22	139.6±78.7	120.96	138.03
Na	22	0.301±0.297	0.227	0.198
Mg	22	1.932±2.489	1.142	1.057
Al	22	3.062±5.512	1.303	0.998
K	22	0.633±0.899	0.389	0.315
Ca	22	4.415±1.586	0.91	0.85
Cr	15	0.025±0.033	0.01	0.01
Mn	22	0.041±0.074	0.018	0.013
Fe	22	6.977±12.822	2.878	1.774
Ni*	22	24.028±48.447	6.853	5.528
Cu	22	0.034±0.008	0.033	0.034
Zn	22	0.031±0.021	0.025	0.024
Cd*	22	0.155±0.098	0.127	0.145
Pb*	22	43.122±93.299	7.923	7.458

* *Values are in (ng m^{-3})*

Unlike in soil, SD values are comparable with or larger than average concentrations of elements in aerosol samples. The histograms and goodness-of fit tests were not performed to aerosol data due to small number of aerosol samples collected. However, large SD values indicate log-normal distribution for most of the elements in atmospheric particles. Log-normal distributions of elements in aerosol data are also confirmed by fairly large differences between arithmetic and geometric averages of elements. Such log-normal behavior may be

either due to anthropogenic contribution on elemental concentrations or due to dependence of concentrations on meteorological parameters, such as mixing height.

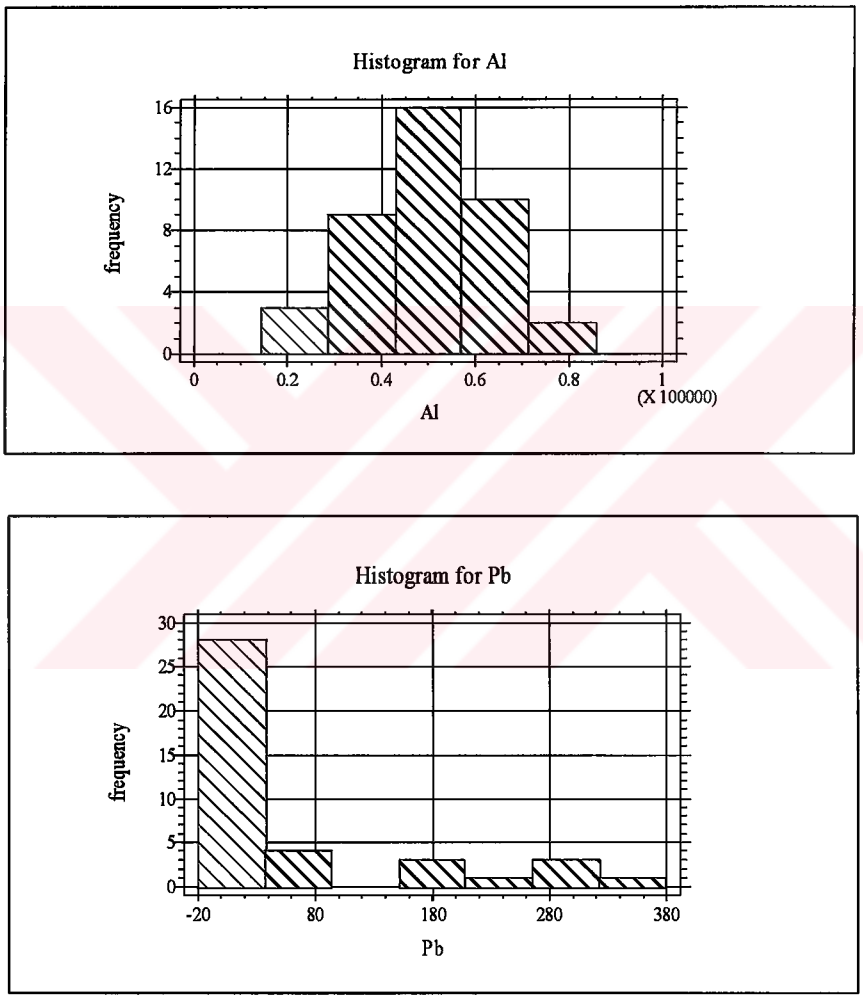


Figure 5.2. Frequency Histograms of Al and Pb

5.3.2 Levels of Pollutants in Seyitömer Region

There are two ways for assessment of the present data and indicate the pollution. One of them is the comparison of the values with the limits stipulated in the regulations and the other is the comparison of the values with the literature values.

In the study area, there are no strong local emission sources except Seyitömer Power Plant. Consequently, a heavy pollution is not expected. It is a possibility to have elevated levels close to the plant and ash disposal area. These levels, however, are not expected to be significant in the whole study area which covers a 20 km × 20 km region. Since heavy pollution is not expected, comparison of measurement results with regulatory standards does not mean too much, because observed concentrations are significantly lower than standards and guidelines. Consequently, the approach used in this study is to compare the measured concentrations with the reported data in the literature for contaminated soils.

Pollution does not necessarily mean concentrations higher than regulatory standards. Modification of soil and air compositions beyond background composition by human activities indicates pollution. Comparison of the obtained data with the data taken from comparable sites in the literature can provide information on the anthropogenic contribution on observed concentrations of elements as well as the extend of the modification of natural composition, if such modifications do exist. The elemental concentrations measured in the study area are compared with the literature data in Figure 5.3 and Figure 5.4 for aerosol and soil samples, respectively.

5.3.2.1 Aerosol

It is important to have some information about the characteristics of the study area before comparison. Since studies do not include all the elements that were

studied on, literature values were taken from various references. A schematic description of this comparison is shown in Figure 5.3. The data used in this figure were obtained from Hungary (Borbely-Kiss et al., 1991), Portuguese West Coast (Pio et al., 1991), Black Sea (Hacısalihoğlu et al., 1992) and Norwegian Arctic (Maenhout et al., 1989).

As can be seen from Figure 5.3, crustal elements Mg, Al, K, Mn and Fe are high compared to literature data. Fairly high concentrations of soil-related elements imply that more dust becomes airborne in the arid study area compared to other parts of the world. This is a fairly common observation and reported in various other parts of Turkey (Al-Momani et al., 1995; Hacısalihoğlu et al., I992).

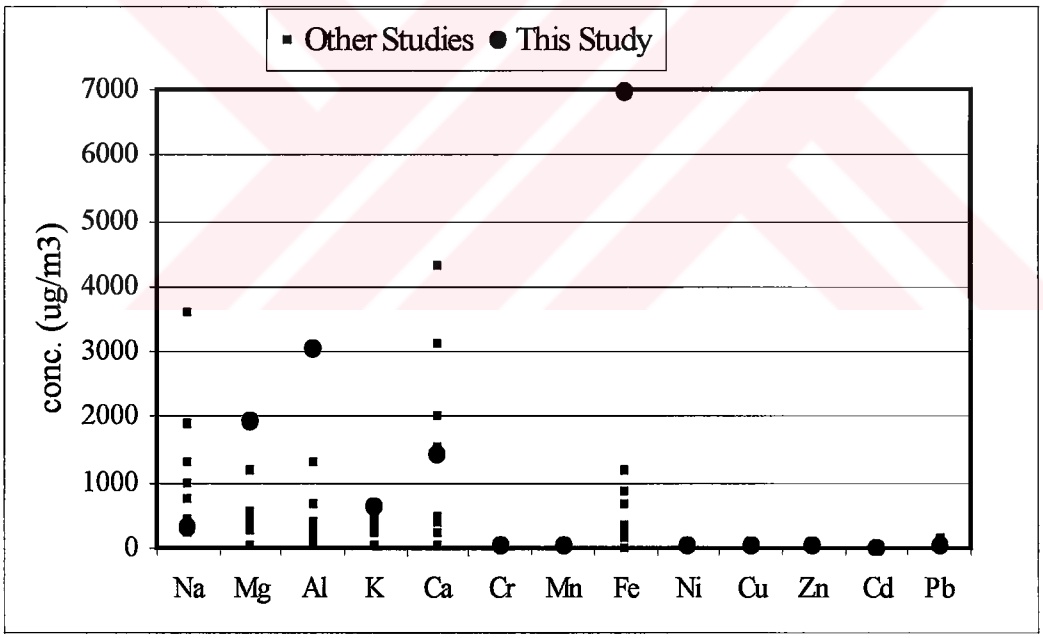


Figure 5.3. Comparison of Aerosol Samples with Different Studies

Concentrations of Cr and Ni are also high compared to the values reported for other locations. High concentrations of these elements can be due to both anthropogenic contribution or unusual composition of soil because Cr and Ni have anthropogenic sources, but their concentration in soil is also high. The only

anthropogenic element that has fairly high concentrations compared to literature data is Pb. Concentrations of other pollution-derived elements Zn and Cu are low. Hence, the atmosphere is not significantly enriched by anthropogenic particles except for Pb.

5.3.2.2 Soil

As discussed in the previous section, soil samples were also compared with different studies and the schematic figure is shown in Figure 5.4. In this figure, the locations of the studies are China (Chen et al., 1991), south-east Kansas City (Abdel-Saheb et al., 1994), Continental Chile and the Antarctic Peninsula (Adriana Carasco and Prendez, 1991) as well as studies of Kabata-Pendias and Pendias (1984), Mason (1986), Fergusson (1990), Aubert and Pınta (1977). Note that, the y-axis in the figure is in log-scale, because the concentrations of elements cover a wide range between 0.1-10^5 $\mu g\ g^{-1}$.

As can be seen from Figure 5.4, concentrations of Na, Al, K, Mn, Cu, Zn, Cd and Pb are comparable with the concentrations reported in the literature suggesting that the soil in the study area is not unusually contaminated by anthropogenic activities. It should be noted that, this conclusion is valid for average levels of these pollution-derived elements in the study area. Their concentration may still be high in certain locations.

Concentrations of Mg, Ca, Cr, Fe and Ni are significantly higher than the values reported in literature. With the exception of Cr and Ni, higher concentrations observed in study area is probably due to soil composition rather than anthropogenic input. Cr and Ni, on the other hand, can be high due to both unusual soil composition or anthropogenic activities. However, it is not possible to differentiate between the two sources simply by comparing the experimental results with literature data.

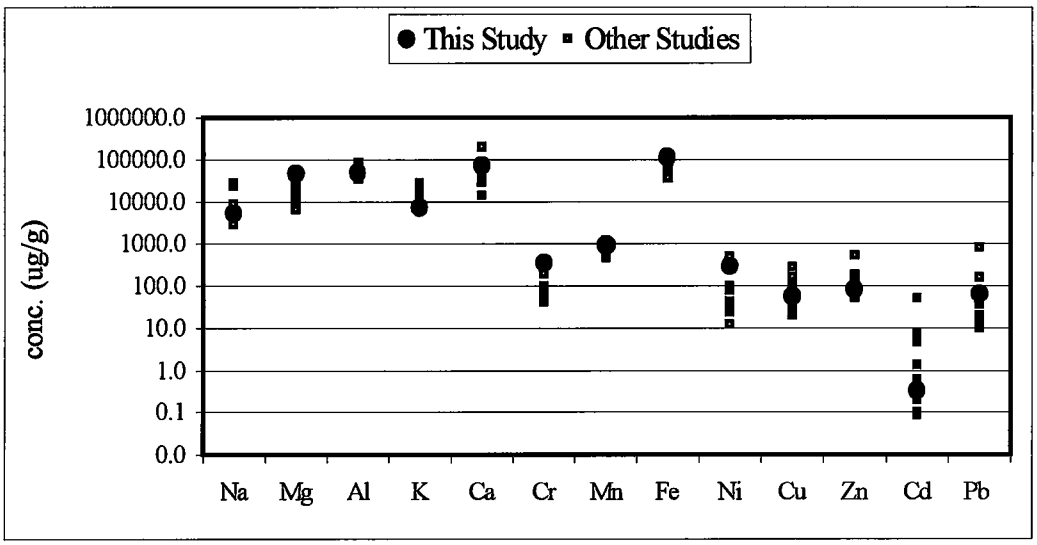


Figure 5.4. Comparison of Soil Samples with Different Studies

As discussed previously, there are two ways for assessing the soil contamination in the Seyitömer region. One is the comparison with different studies, which is already discussed, and the other approach is to compare experimental data with the regulatory standards, guideline and action levels. Regulatory standards for heavy metals in soils are not currently available in Turkey. Natural background concentrations of heavy metals in soil show large variations for various regions throughout the world, rendering to establish a worldwide criterion, a difficult task. Hence, a kind of "guideline levels" should be set for elements in soil in order to assess and classify the soil contamination and reach an evaluation about the pollution status.

Guideline levels depend on several factors including local condition, land use and even author (Kabata-Pendias and Pendias, 1992). Soil contamination classes used in this study were adopted from the data used in different studies (Kabata-Pendias, 1992 and 1995; Rauta et al., 1995a; Rauta et al., 1995b) and are listed in Table 5.4. In this table, only the elements which have known anthropogenic sources, namely Cr, Ni, Cu, Zn, Cd and Pb are included. Pollution has been divided into six classes which are namely; unpolluted (I), slightly polluted (II),

moderately polluted (III), considerably polluted (IV), heavily polluted (V) and extremely polluted (VI).

Table 5.4. Assessment of Soil Contamination Classes (units are in μg g^{-1})

Elements	Pollution Classes						This Study	
	I	II	III	IV	V	VI	Average	Maximum
Cr	30	70	100	300	1000	>1000	350	881
Ni	10	30	50	100	400	>400	301	809
Cu	15	30	50	80	300	>300	56	110
Zn	50	100	300	700	3000	>3000	80	150
Cd	0.3	1	2	3	5	>5	0.32	0.64
Pb	30	70	100	500	2500	>2500	62.5	327

Based on the criteria given in Table 5.4, the soil in the study area is "considerably polluted" with Cr and Ni according to the average values. Since the average concentrations of Cr and Ni exceed the "considerably polluted" level, it may indicate a wide spread pollution by these elements in the study area. The maximum Cr and Ni concentrations measured in the study area, on the other hand, exceeds "heavily" and "extremely" polluted levels, respectively. The levels of pollution by Cr and Ni observed in the study should be taken with a certain degree of sleeptisizm, because fairly high concentrations of these two elements measured in other parts of the country are attributed to mineralogy rather than pollution (Yay, 1998; Güvenç, 1998). Natural enrichment of Cr and Ni in solution will be further discussed in subsequent sections.

Another element for which average concentration measured in this study indicate "moderate" contamination of soil is Cu. The maximum observed Cu concentration indicate that at certain regions in this study area soil may be "heavily" contaminated by this element. Average concentrations of Zn and Pb indicate that soil contamination by these elements is not a wide spread problem in the study area. However, maximum concentrations fall to "moderately" and "considerably" contamination categories for Zn and Pb, respectively. Neither

average nor maximum concentrations of Cd suggest a significant soil contamination by this element.

5.3.3 ISCST Predictions

Comparison of measured aerosol and soil compositions with literature data indicates that the heavy metal contamination is not a wide spread problem in the study area; but soil may be contaminated by heavy metals in certain restricted regions. If such limited pollution does exist, than the power plant and/or ash disposal site may be the sources of pollution as there is no other source for these elements within 20 km of the study area. In the following sections, the role of power plant and disposal site on the observed levels of elements were investigated by studying the distributions of elements and relating those distributions to the power plant and disposal site.

The first step in this investigation is to understand the groundlevel concentrations of particles emitted from the power plant and disposal site in the study area. Although experimental data for GLC of elements is not available (because generation of such data require a very extensive atmospheric sampling program which is key and the score of this study), groundlevel concentrations of particles emitted from the power plant and disposal site were calculated using ISCST simulations. The reasoning behind this was; if the observed limited contamination of soil is due to power plant and disposal site, one would expect high concentrations of elements at the points where the model calculates high GLC and deposition values. In addition, the model simulations provide data on the levels of anthropogenic particles in villages where people are exposed to these particles.

In the model simulations, both the power plant stacks and ash disposal site are included, because total pollution in the region is being discussed. The predicted annual average GLC values of SPM in villages which are considered to be

sensitive areas for SPM (Seyitömer, Bozcaüyük, Ayvalı, Kınık and Andız) are given in Table 5.5. Distribution of annual average atmospheric SPM concentrations is shown in Figure 5.5. Based on the results obtained, the highest long-term estimate (annual average) SPM concentration expected in the study area was predicted about 865 μg m^{-3} in Bozcaüyük Village. Other villages, on the other hand, do not receive an important amount of SPM emissions.

Table 5.5. Annual Ground Level SPM Concentration Estimates

Receptor	Annual GLC of SPM (μg m^{-3})
Source	1,375
Seyitömer Village	10
Bozcaüyük Village	865
Ayvalı Village	15
Kınık Village	80
Andız District	0.85

The long-term (annual average) regulatory standard for SPM currently effective in Turkey is 200 μg m^{-3} and represents an upper boundary limit for the mean annual GLC. When the SPM distribution predicted by the model is compared with these values, groundlevel SPM concentrations comply with the standard in most of the study area. Standard for industrial area is exceeded only in a limited region.

The distribution of ground level SPM concentrations demonstrated that the study area is not heavily polluted with particles emitted from the power plant and ash disposal site, but their influence can be seen at limited locations. The conclusions based on the model results agree fairly well with the conclusions reached by comparing soil and aerosol concentrations of elements with literature data in the previous sections.

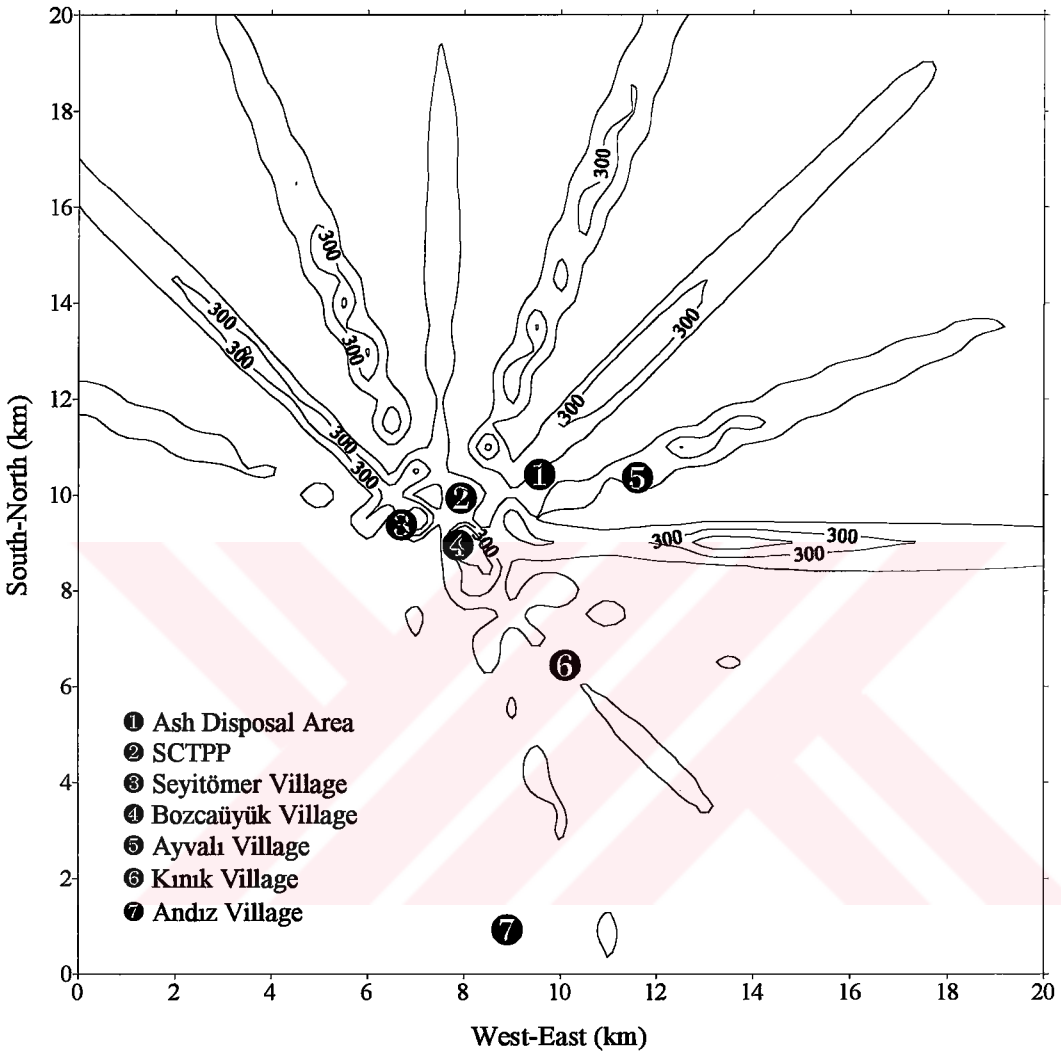


Figure 5.5. Annual SPM Concentration Estimates
(contour are 100, 300, 500, 1000 and 1200 μg m^{-3})

Certain sensitive areas which are the villages in the study area were investigated more thoroughly by the model. There are five villages within the study area among which Bozcaüyük village is the one located closest to the sources under investigation. The long term GLC values of SPM calculated for these villages are given in Table 5.5. Only in Bozcaüyük Village, the SPM is about 865 μg m^{-3}

(approximately a factor of four higher than long-term standard) since it is very close and downwind from the plant. Ground level SPM concentrations in all other villages in the study area are significantly below the long-term standard in the Air Quality Regulation. This finding also confirms our previous conclusion that particulate pollution is not an area-wide problem.

Hourly and daily maximum GLC predicted by the model are given in Table 5.6. The short-term limit (STL) of SPM stated by the Turkish Regulation on the Preservation of Air Quality represents the daily GLC values and should not exceed 400 $\mu g\ m^{-3}$ for industrial areas. When the concentration figures predicted by the model are compared with these values, it is observed that the STL values are violated at locations in the immediate vicinity of the ash disposal site.

Table 5.6. Hourly and Daily Ground Level SPM Concentration Estimates

Receptor	**GLC of SPM($\mu g\ m^{-3}$)**	
	1-Hr	***Daily (24-Hr)***
Source	169,385	40,575
Seyitömer Village	1,880	115
Bozcaüyük Village	88,075	11,220
Ayvalı Village	1,415	300
Kınık Village	21,820	1,975
Andız District	220	40

Daily maximum groundlevel SPM concentrations at Seyitömer village and Andız villages are for below the short-term standard. However, groundlevel SPM concentrations at Bozcaüyük and Kınık villages 11,220 $\mu g\ m^{-3}$ and 1,975 $\mu g\ m^{-3}$, respectively. Both of these values are higher than the short-term standard due to the close proximity of these two villages to the power plant and disposal site. Ayvalı village, on the other hand, approached fairly close to the STL values having a GLC of approximately 300 $\mu g\ m^{-3}$. Although there are no hourly SPM standard in the regulation which can be compared with the maximum hourly

values estimated by the model, very high maximum hourly values were predicted for the same three villages. The comparison of calculated groundlevel SPM concentrations in villages with regulatory standards suggest that all the villages are under the influence of particulate plumes from the power plant and disposal site. The frequencies of these plume incursions determine the concentrations calculated. Only in Bozcaüyük village, impact of plume is frequent enough to exceed long-term standards. In all other villages, plume incursions are infrequent.

The annual SPM predictions found in Ayvalı village can be compared with the SPM data calculated according to the aerosols sampled at the same location. The average SPM concentration in the Ayvalı village is 140 $\mu g\ m^{-3}$ (see Table 5.3), whereas it is approximately 300 $\mu g\ m^{-3}$ based on ISCST calculations (see Table 5.6). These two values are comparable considering the uncertainties involved in modeling. The comparison between model and measurement averages suggest a very broad agreement, but it should not be interpreted any further, because: (i) model calculations are based on meteorological data of the 1996 whereas measurements were performed in 1998, (ii) pooper comparison should be expected if daily values are compared and (iii) the SPM measures includes not only particles emitted from power plant and disposal site, but also resuspended soil particles.

Although the primary concern in this study is the dust and elements associated with it, ground level SO_2 concentrations were also calculated. The ground level SO_2 concentrations (the hourly, daily and annual values) in the villages are given in Table 5.7 and annual average SO_2 concentration plot is plotted in Figure 5.6.

It is interesting to note that annual average SO_2 concentrations are very low compared to long term SO_2 standard which is 150 $\mu g\ m^{-3}$ for residential areas. This difference in the distributions of groundlevel SO_2 and SPM concentrations imply that high annual average SPM concentrations measured in the Ayvalı village may be due to fugitive dust emissions from the ash disposal site rather than stack emissions from the power plant.

Table 5.7. Hourly, Daily and Annual Ground Level SO_2 Concentration Estimates

Receptor	GLC of SO_2 ($\mu g\ m^{-3}$)		
	1-Hr	*Daily (24-Hr)*	*Annual*
Source	3,885	1,020	80
Seyitömer Village	130	5.5	0.05
Bozcaüyük Village	3,310	140	0.7
Ayvalı Village	805	70	1.2
Kınık Village	2,095	270	3
Andız District	525	65	1.4

Short term standard does not exceed in any of the villages, but hourly guideline value in the regulation (900 $\mu g\ m^{-3}$) is exceeded in the Kınık and Bozcaüyük villages and approached to in the Ayvalı village. These villages are impacted by the power plant plume from time to time, but such plume incursions are not frequent enough to affect the daily and annual average values.

5.3.4 General Evaluation

As a result of the ISCST predictions and experimental analyses, trace element levels, GLC values of SPM and SO_2 demonstrate that the study area is not under strong influence of pollution. Certain parts of the region are heavily polluted due to emissions from the power plant and ash disposal site.

Bozcaüyük village is heavily affected from the ash disposal site. The level of particulate pollution in this residential area is very serious and can have health implications. Necessary precautions should be taken and modern ash disposal techniques (such as landfilling or wet disposal) should be considered.

Kınık village is also affected to a certain degree (not as much as Bozcaüyük village) and the impact of the power plant and ash disposal site on the remaining

three villages is not significantly high. Soil trace element levels in the region is low on the average with the exception of Pb.

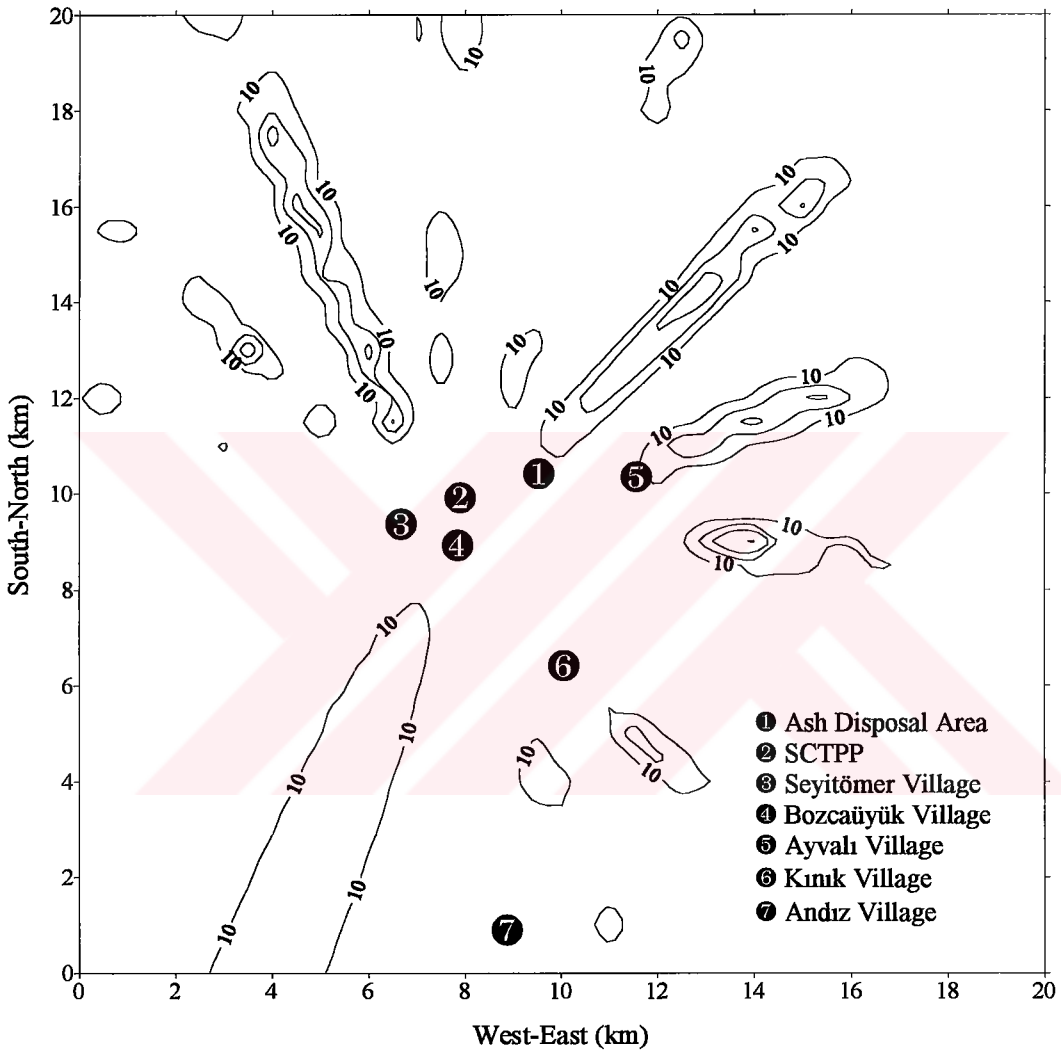


Figure 5.6. Annual SO_2 Concentration Estimates
(contours are 10, 30, 50 and 80 μg m^{-3})

5.4 Distribution of Elements in Soil

Average anthropogenic trace element levels in the study area is low compared to values measured in other parts of the world. However, this does not necessarily mean that the concentrations are low at every point within the region. The distributions of elements measured in this study were investigated in order to understand if certain parts of the study area are polluted by power plant emissions.

The elements that are measured in this study were grouped into the following three classes and distribution of each element was inseparably investigated.

Group 1: This group includes elements Fe, Ca, K, Na, Mn and Al which are the crustal elements. They occur in the aluminasilicate matrix of soil. Their concentrations in the soil are so high. Hence, contribution of anthropogenic sources on their concentrations is generally negligible.

Group 2: Elements Cu, Pb, Cd and Zn are included in this group. Since concentrations of these elements are low in soil, their concentrations can be altered by the contribution of anthropogenic sources.

Group 3: This group consists of elements Cr and Ni. Their concentration in soil is fairly high, but they also have strong anthropogenic sources. The anthropogenic contribution on their soil concentrations can only be detected if such contributions are strong.

Distribution plots of concentrations of Al and Fe, which are typical crustal elements, are given in Figure 5.7. In this study, the distribution plots were prepared by MAPInfo 4.1 program. Interpolation is the procedure used to predict the unknown values with the help of known values at neighboring points which are regularly or irregularly spaced. Many mathematical tools are used for interpolation. Some them are the average of the neighboring values or a weighted average where the weights are inversely proportional to the distance (Aronoff, 1993). In this study, triangulation with smoothing method was used. On the maps,

contour lines are used to portray surface relief as a set of lines that connect points having the same value.

The concentration contours show a gradual change over the study area. There are fairly wide areas with similar concentrations which is a typical distribution pattern for crustal elements. Strong variations may indicate different soil type with slightly different Al and Fe concentrations rather than contamination. Most other crustal elements included in Group 1 showed similar patterns.

Distribution of concentrations of Cd, Cu, Zn, Pb, Cr and Ni are given in Figure 5.8, Figure 5.9 and Figure 5.10. Distribution of Cu resembles the distribution of other soil elements. It is a high probability that there is no influence of plant and disposal site on the Cu distribution in the region. There are some common features for Zn, Cd, Ni, Cr and Pb. There is one location to the north-west of the power plant and the ash disposal site where concentrations of Zn, Cd and Pb are high. This site covers the power plant and the ash disposal site which indicates to the modification of soil composition in this location.

There is another hot spot immediately to the north-east of the power plant and ash site. This is clearly seen in the distribution plots of Cd and Pb, less clear in the distributions of Zn and Ni and not observed in the distribution plot of Cr.

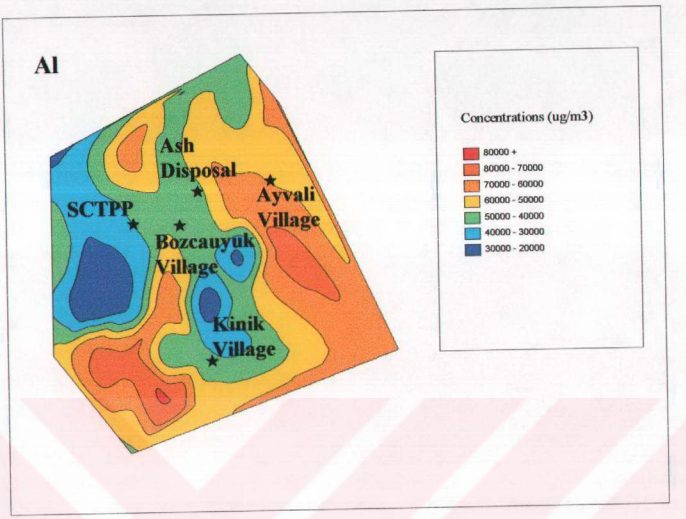
A third common hot spot is located to south-west of the power plant and disposal site. High concentrations of Cd and moderate concentrations of Cu, Ni and Cr are observed in that location.

Distributions of Ni and Cr agrees to a certain extend to the distributions of other anthropogenic elements, but on the other hand particularly Cr show fairly gradually changing distribution which closely resembles soil related elements. Probably the effect of the power plant on observed concentrations of Cr and Ni are limited to the hot spots discussed above and in the rest of the study area, their distribution is determined by the variations in the natural soil composition.

Since there are no anthropogenic activity within 30 km of the power plant, distributions of anthropogenic elements in the study area is determined by the impact of the power plant or the ash disposal site. The hot spots identified from the concentration distributions of anthropogenic elements is fairly uniformly distributed around the power plant and the disposal site which agrees with the annual average wind pattern shown in Figure 3.6. The winds in the region is fairly uniformly distributed among sectors, any obstacle such as small hills where plume can hit and deposits particles can appear as hot spot. Uniform distribution of high SPM concentrations were also predicted by the model calculations as discussed previously.

If the observed enrichments in soil is due to the deposition of particles emitted from the power plant stacks or from the ash disposal site, then the deposition pattern calculated by the model should be in general agreement with the observed distributions of anthropogenic elements.

As discussed in the previous sections, the annual SPM deposition in the study area due to power plant and ash disposal site is calculated by the ISCST and results are depicted in Figure 5.11. The important feature of the deposition pattern calculated by the model is the fairly uniform deposition in all wind sectors, probably due to uniform distribution of winds. This pattern is in agreement with the conclusion reached on the distributions of the concentrations of anthropogenic elements where hot spots are distributed fairly uniformly around the plant which confirms that the observed high concentrations of six contamination derived elements in the study area is due to emissions from the power plant and ash disposal site.



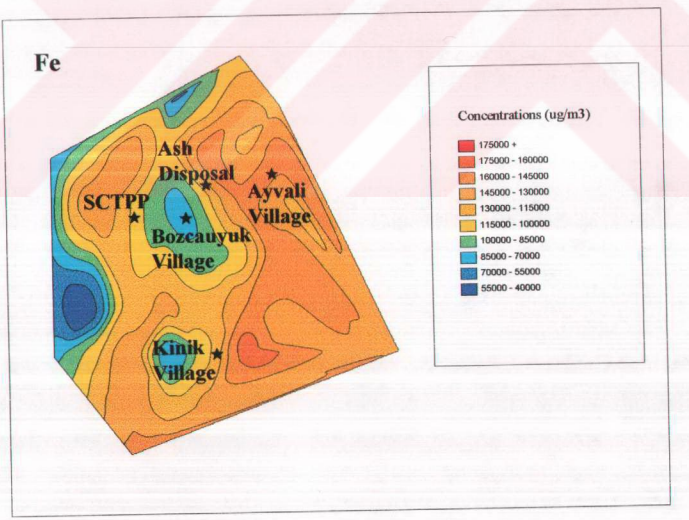
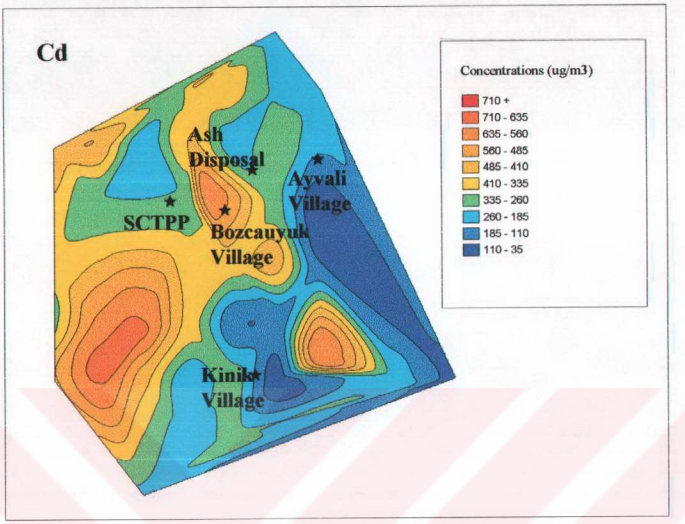


Figure 5.7. Distribution Plots of Al and Fe Concentrations



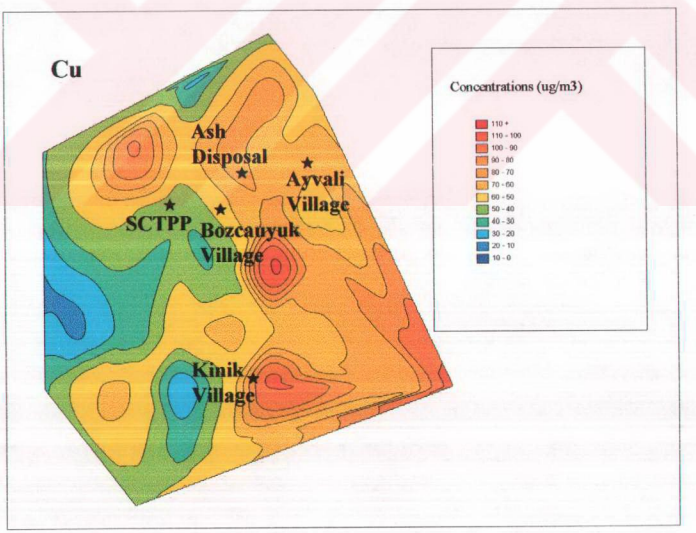


Figure 5.8. Disrtibution Plots of Cd and Cu Concentrations

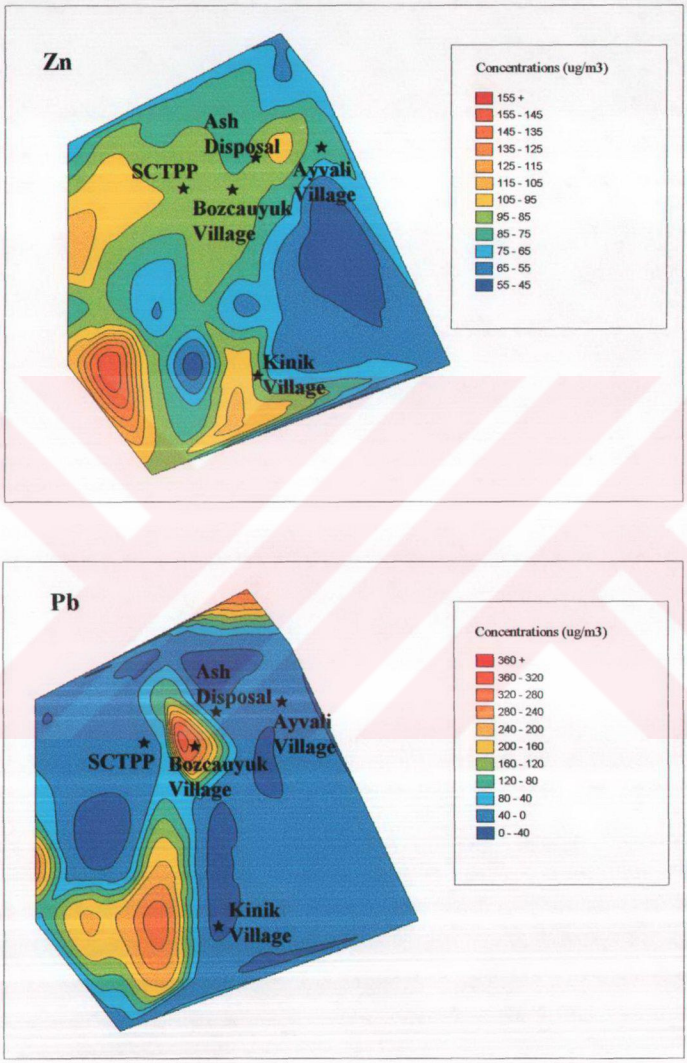


Figure 5.9. Distribution Plots of Zn and Pb Concentrations

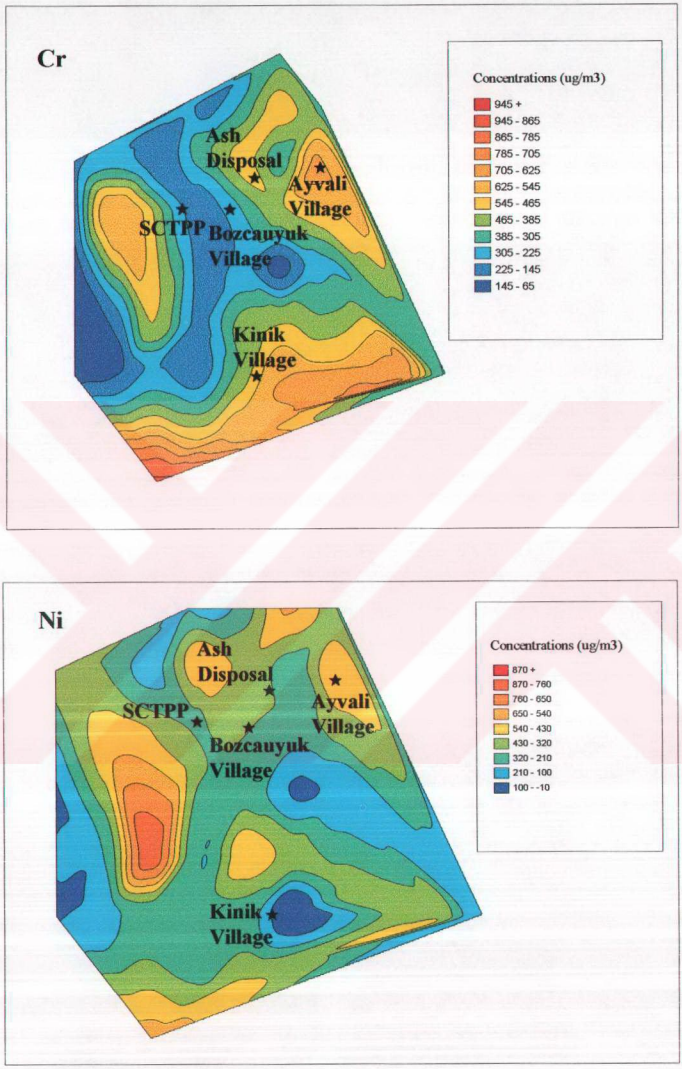


Figure 5.10. Distribution Plots of Cr and Ni Concentrations

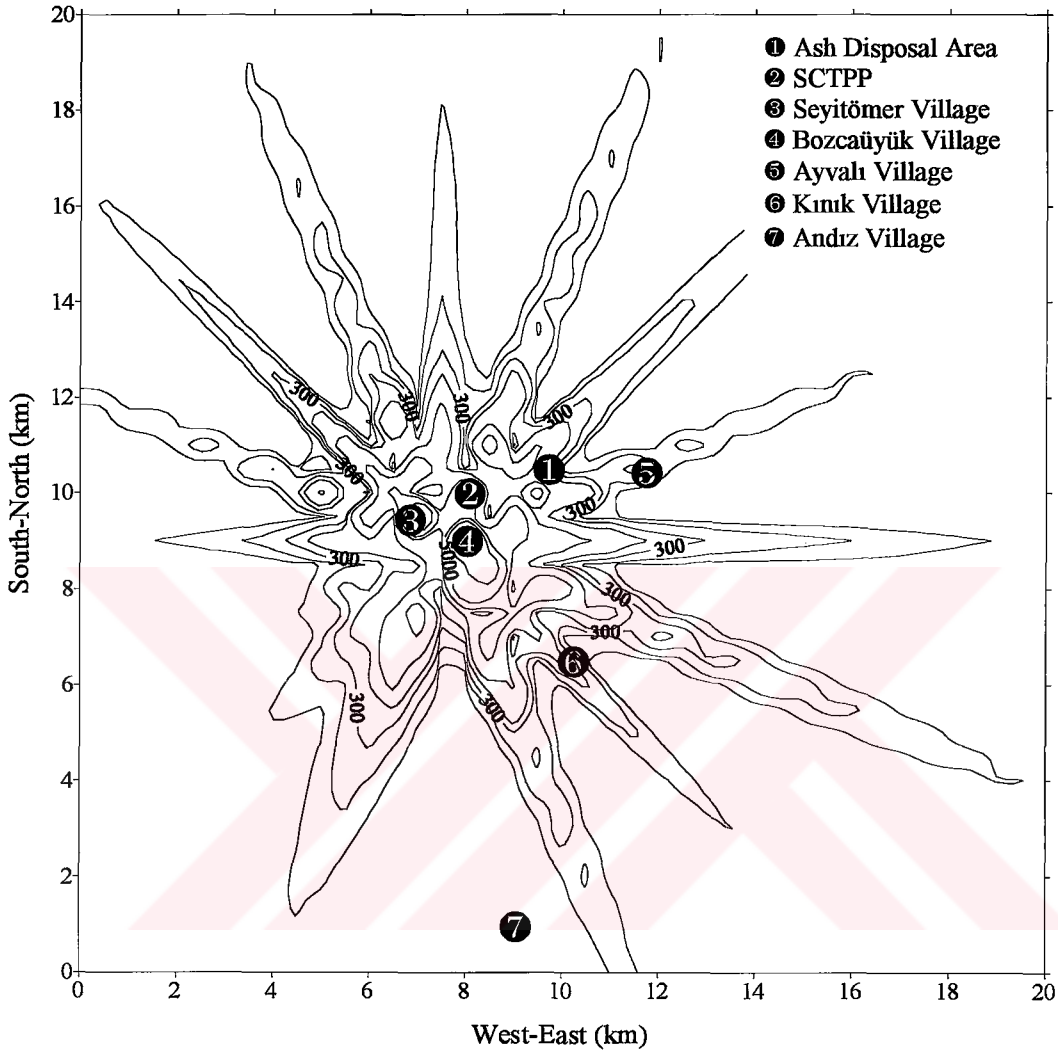


Figure 5.11. Annual SPM Deposition from Stacks and Ash Disposal Site (contours are 75, 150, 300, 500, 1000, 2500, 5000 and 10000 mg m^{-2})

5.5 Enrichment Factors

Soil, seawater and volcanic dusts are the major natural sources of metals in the atmosphere. As discussed in Section 2.5.2, enrichment factors (EF) are used in order to determine the contributions of contamination from natural and anthropogenic sources. Generally, Al or Si and occasionally Ba, Fe or Sc are used as the crustal indicators.

Elements with enrichment factors greater than 5 are assumed to originate from sources other than soil (Parekh et al., 1989). It is a common observation that chalchophilic elements such as Ag, As, Cd, Cu, In, Pb, Sb, Se and Zn are substantially enriched in soil and aerosols. Ni and V are marginally enriched because they can originate from both natural and anthropogenic sources.

In this study, EF values were calculated in order to obtain information on extend of modification in soil composition in the vicinity of SCTPP from expected soil composition due to anthropogenic activities. EF_c values were calculated according to the Equation (2.8) in Section 2.5.2. Al was selected for the reference element.

During the EF_c calculations, Mason's (1986) global average crustal rock composition was used. In fact, Mason soil composition may be significantly different than the soil in Kütahya, however, the data of Mason is the most widely used soil composition. In this regard, necessary discussions were carried out in the subsequent sections.

EF_c values less than 5 are not considered to indicate anthropogenic contribution because of possible differences between Mason's general soil composition and composition of soil in the study area. Average EF_c values of elements are presented in Figure 5.12. Hot spots do not necessarily mean heavy contamination of soil throughout the study area. EF_c values provide information on how much the soil profile in the study area is modified relative to global average soil.

As can be seen from Figure 5.12, only Cr, Pb and Ni have EF_c values higher than 5, indicating a significant modification in soil composition relative to global average soil. Although enrichment values less than 5 also indicate modification of soil composition, it is not certain whether such low enrichments are due to emissions from the power plant and the ash disposal site or due to differences between the local soil and global average soil used in EF_c calculations.

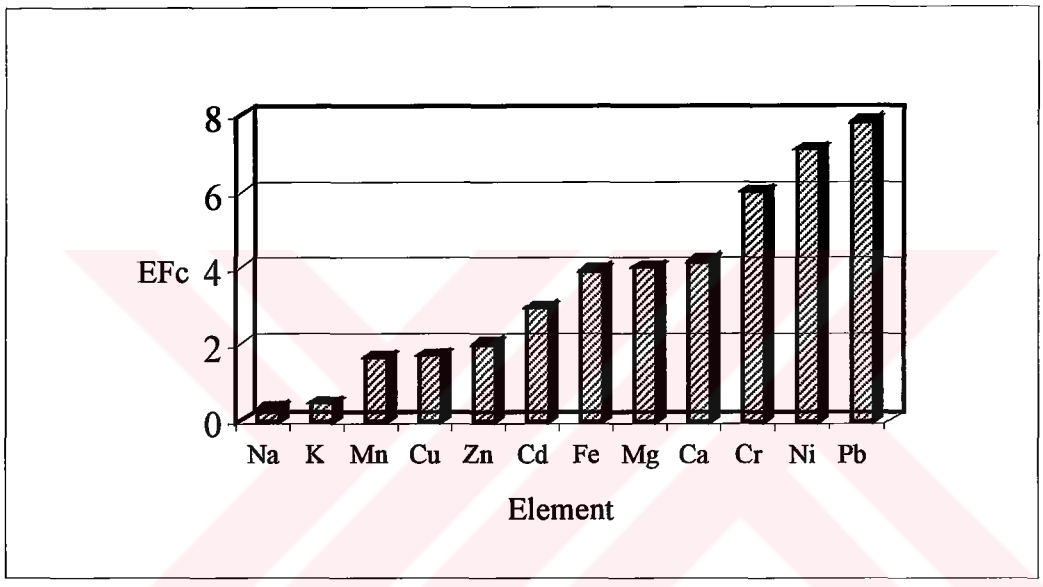


Figure 5.12. Enrichment Factors of Elements in Soil

The average EF_c values of elements in collected aerosol samples are also presented in Figure 5.13. As can be seen from these two figures that EF_c values of crustal elements are not different between aerosol and soil samples, however anthropogenic elements are significantly more enriched in atmospheric particles. It is due to soil-bound, natural component of anthropogenic elements in collected soil samples. Since about 250 mg of soil was digested, there are substantial quantities of anthropogenic elements coming from soil matrix (natural). In the sample, non-crustal (anthropogenic) component must be very high in order to observe enrichment. Since concentration of anthropogenic elements in soil is small and amount of soil is a few micrograms in aerosol samples, the crustal

anthropogenic element concentrations are also small. Consequently, concentrations of anthropogenic elements in aerosols coming from non-crustal sources are much higher than their concentrations coming from soil.

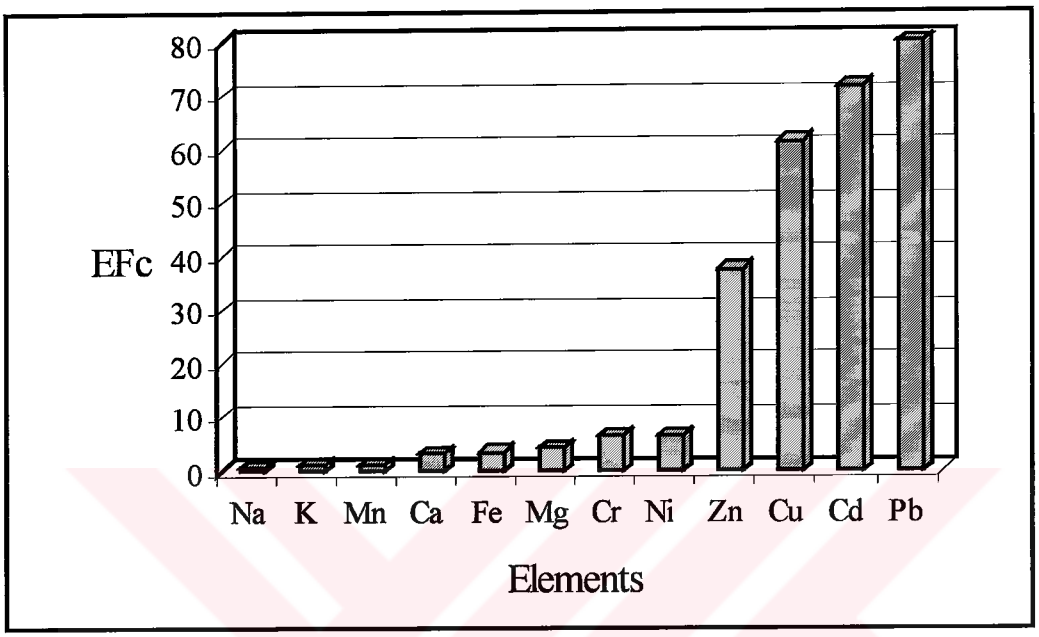


Figure 5.13. Enrichment Factors of Elements in Aerosols

Although the average EF_c values of elements indicate lack of significant changes in soil composition, the EF_c values of anthropogenic elements may be high in certain hot spots. The distribution of EF_c values of anthropogenic elements Cd, Zn, Pb, Cu, Ni and Cr are given in Figure 5.14, Figure 5.15 and Figure 5.16, respectively. As can be seen from the figures, the distributions of EFc values show that the soil composition near the power plant and ash disposal site are seriously different than the average soil compositions. It is clear that, both the plant and the ash disposal site have serious impacts within this small area. However, the degree of this impact sharply decreases 5 - 6 km away from the sources. Additionally, the EF_c distributions of Cr seem to have a wider area indicating a different soil composition rather than anthropogenic factors.

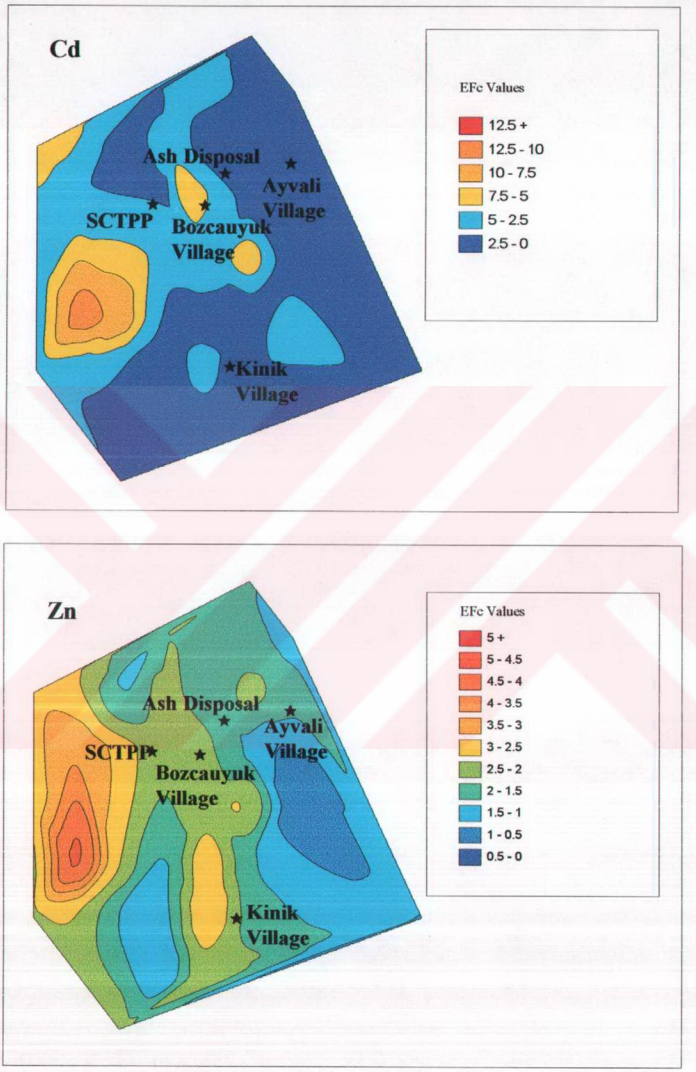
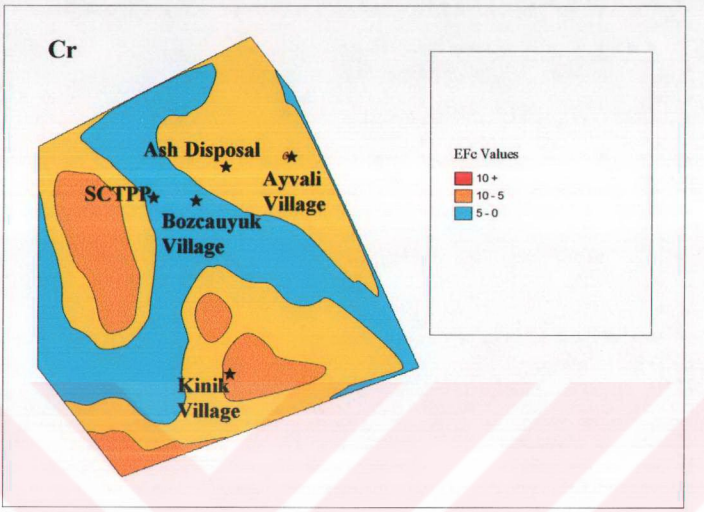


Figure 5.14. Enrichment Factor Distributions of Cd and Zn



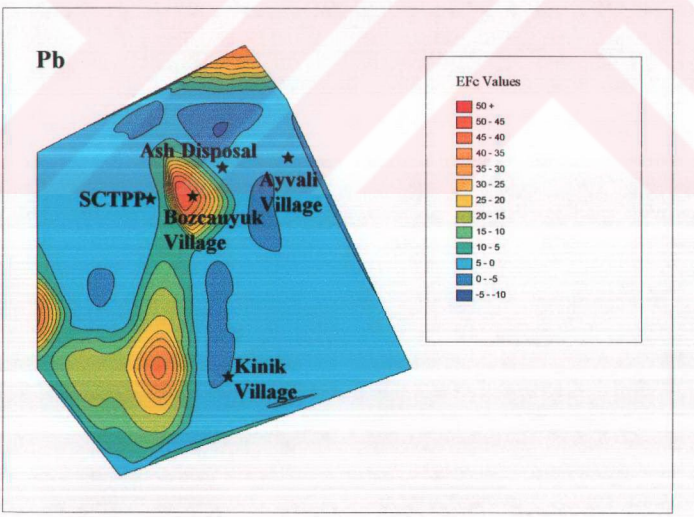


Figure 5.15. Enrichment Factor Distributions of Cr and Pb

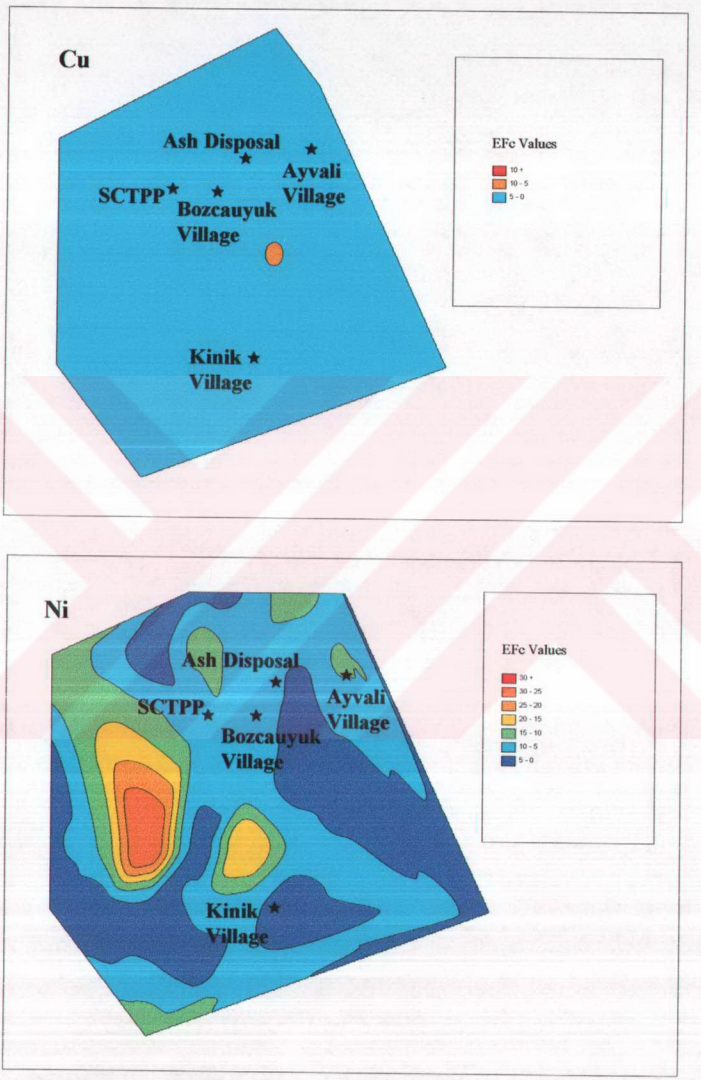


Figure 5.16. Enrichment Factor Distributions of Cu and Ni

5.6 Relative Contributions of Stack and Fugitive Dust Emissions

The discussions carried out in the previous sections include emissions from both stacks and ash disposal site. The contamination in some part of the study area, however, can be due to stack emissions while the other parts due to fugitive dust emissions from disposed ash. Model simulations were used to assess the relative contributions of stack emissions from the power plant and fugitive dust emissions from disposed ash on SPM concentrations and deposition in the study area.

In this section, the sources (i.e. stacks and ash disposal site) were considered separately and their individual contributions to the GLC and deposition was investigated.

5.6.1 Model Predictions

The differences observed in the levels of SO_2 and SPM which was discussed in Section 5.3.2. was a qualitative mean of assessing relative contributions of the power plant itself and the disposal site on pollutant levels in the study area.

The SO_2 is a good marker to separate stack and fugitive emissions, as it is emitted from the stacks but not from the ash disposal site. Very low SO_2 compared to fair SPM concentrations calculated by the model have suggested that the main source of atmospheric particles in the study area is the disposal site rather than power plant itself.

A more quantitative approach was used to assess relative contributions of these two sources on ground-level SPM concentrations and annual SPM deposition. In this approach, annual average SPM concentrations caused by stack and fugitive emissions were separately calculated using the ISCST model and results are depicted in Figure 5.17 and Figure 5.18. Similar computations were also performed for annual SPM deposition. The results of deposition calculations are

given in Figure 5.19 and Figure 5.20. The ratios of the SPM concentrations caused only by the power plant to the concentrations caused by fugitive dust emissions at each grid-point are presented in Figure 5.17 and the inverse of this ratio is presented in Figure 5.18. Consequently, these figures indicate the regions in the study area which are dominated by the power plant and ash disposal site, respectively.

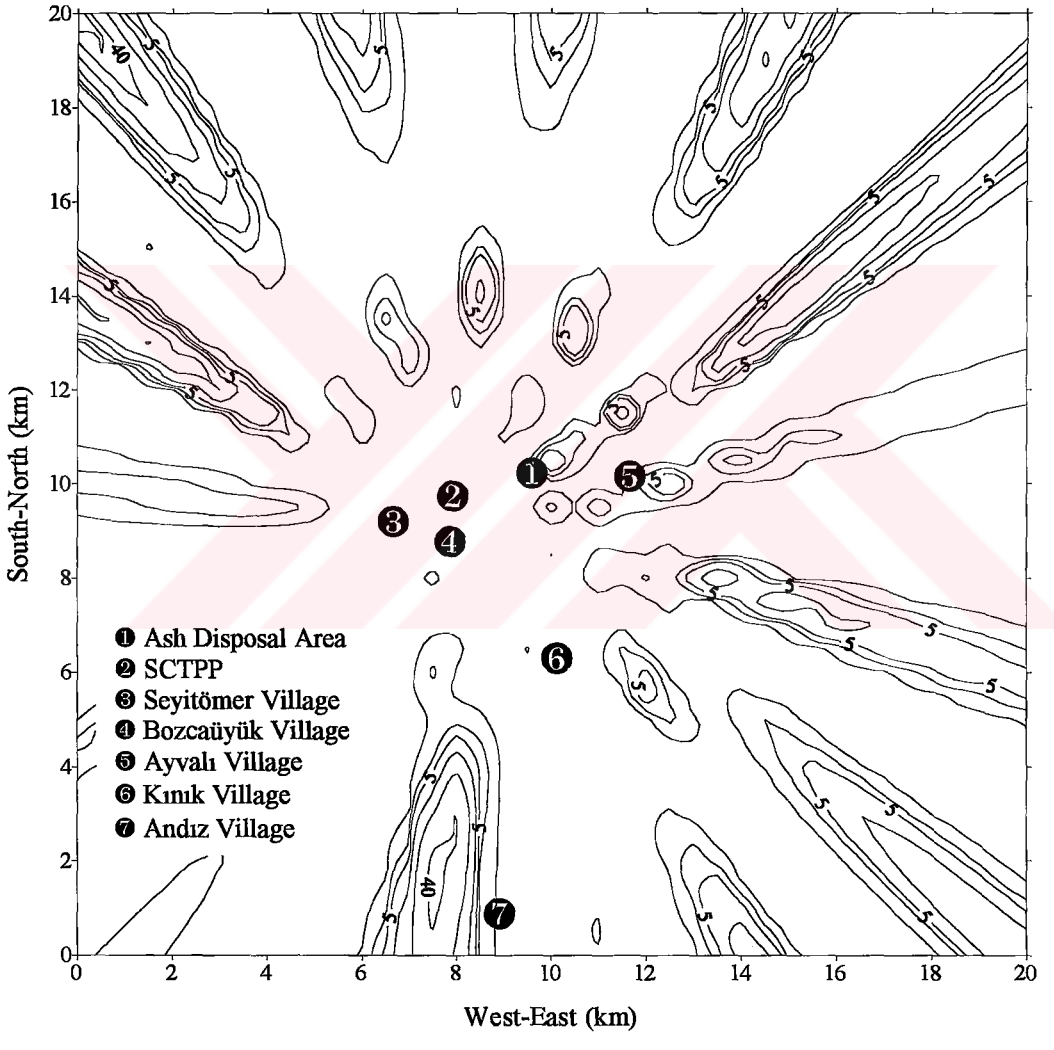


Figure 5.17. Area to Stack Ratios of Annual SPM Concentration Estimates (contours are 1, 3, 5, 10, 20, 40 and 50 units)

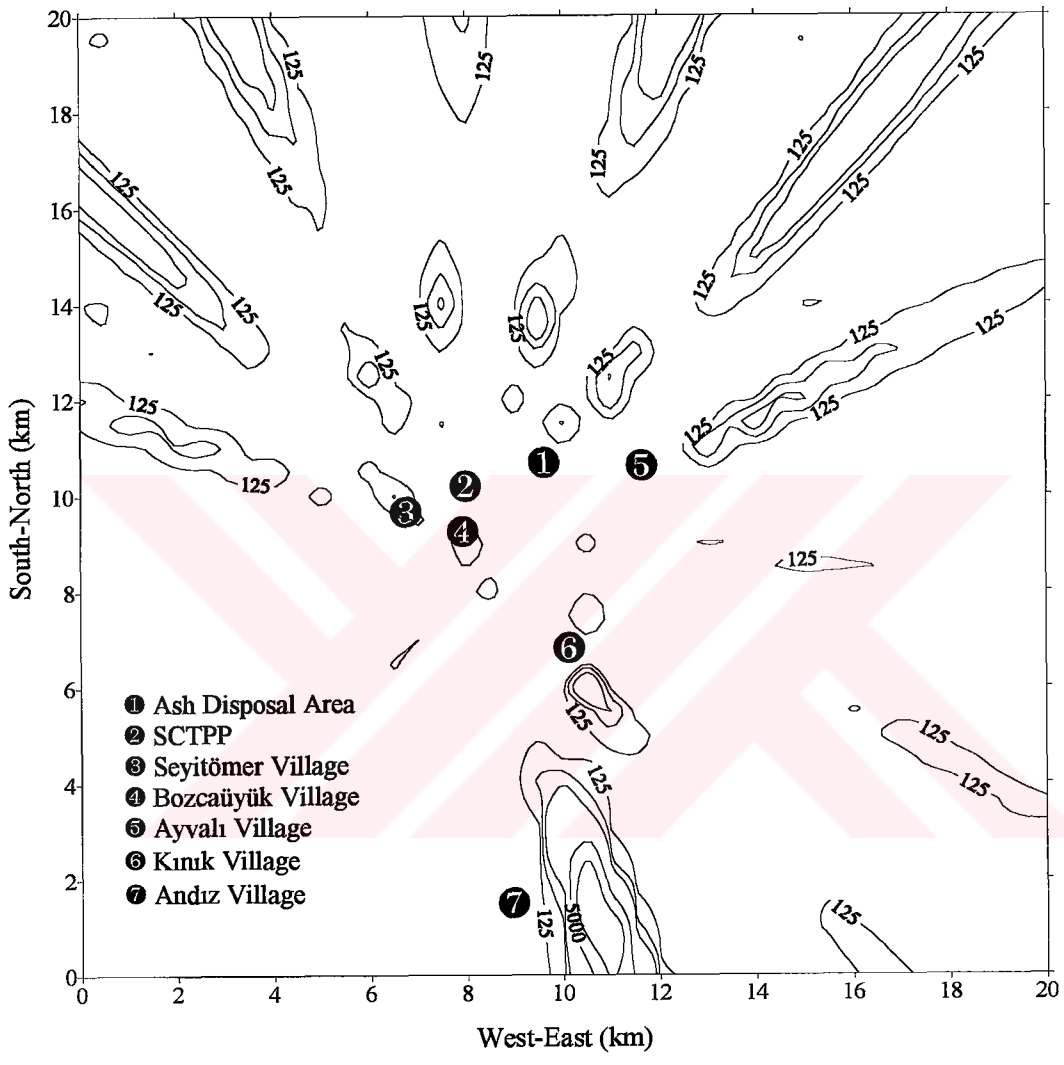


Figure 5.18. Stack to Area Ratios of Annual SPM Concentration Estimates (contours are 125, 500, 1000, 5000 and 10000 units)

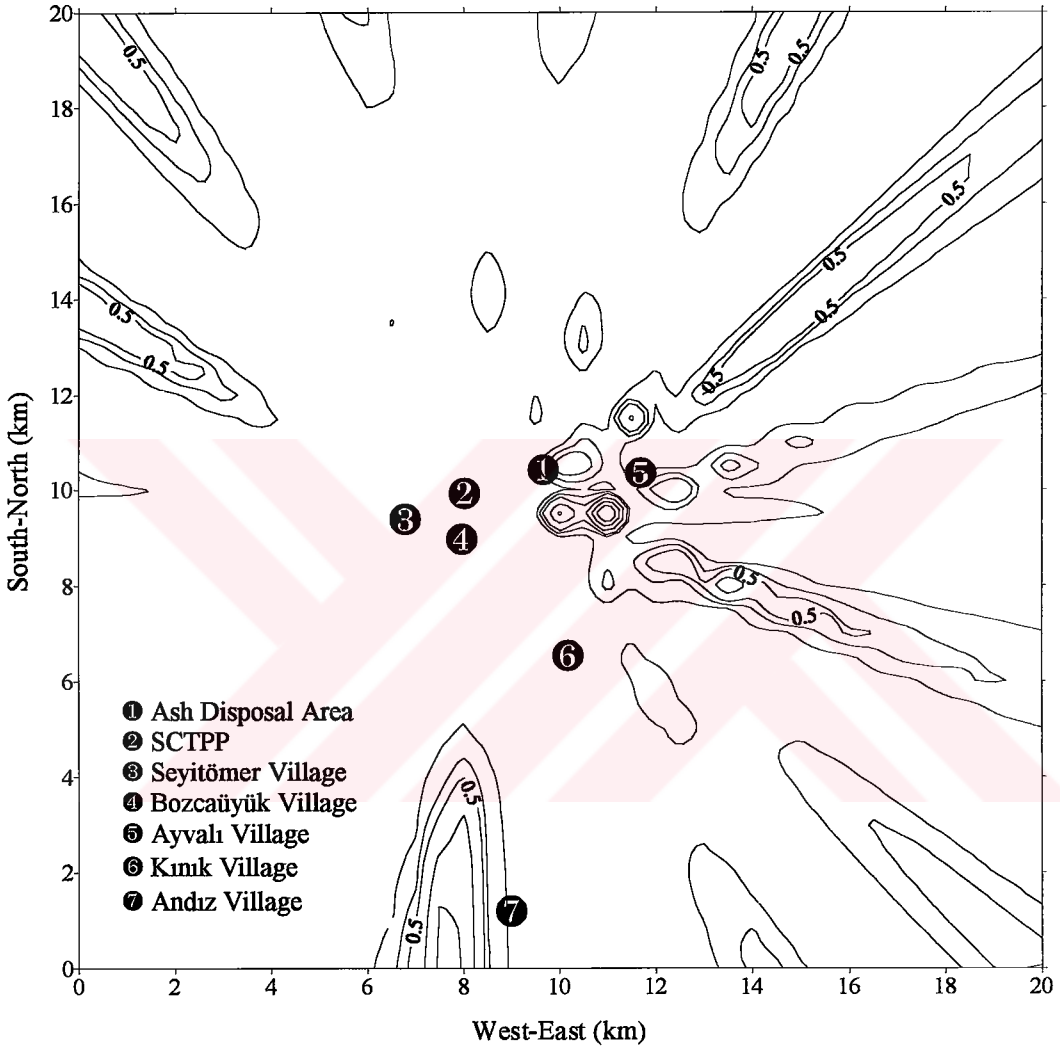


Figure 5.19. Area to Stack Ratios of Annual SPM Deposition Estimates (contours are 0.1, 0.3, 0.5, 1, 1.5, 2 and 3 units)

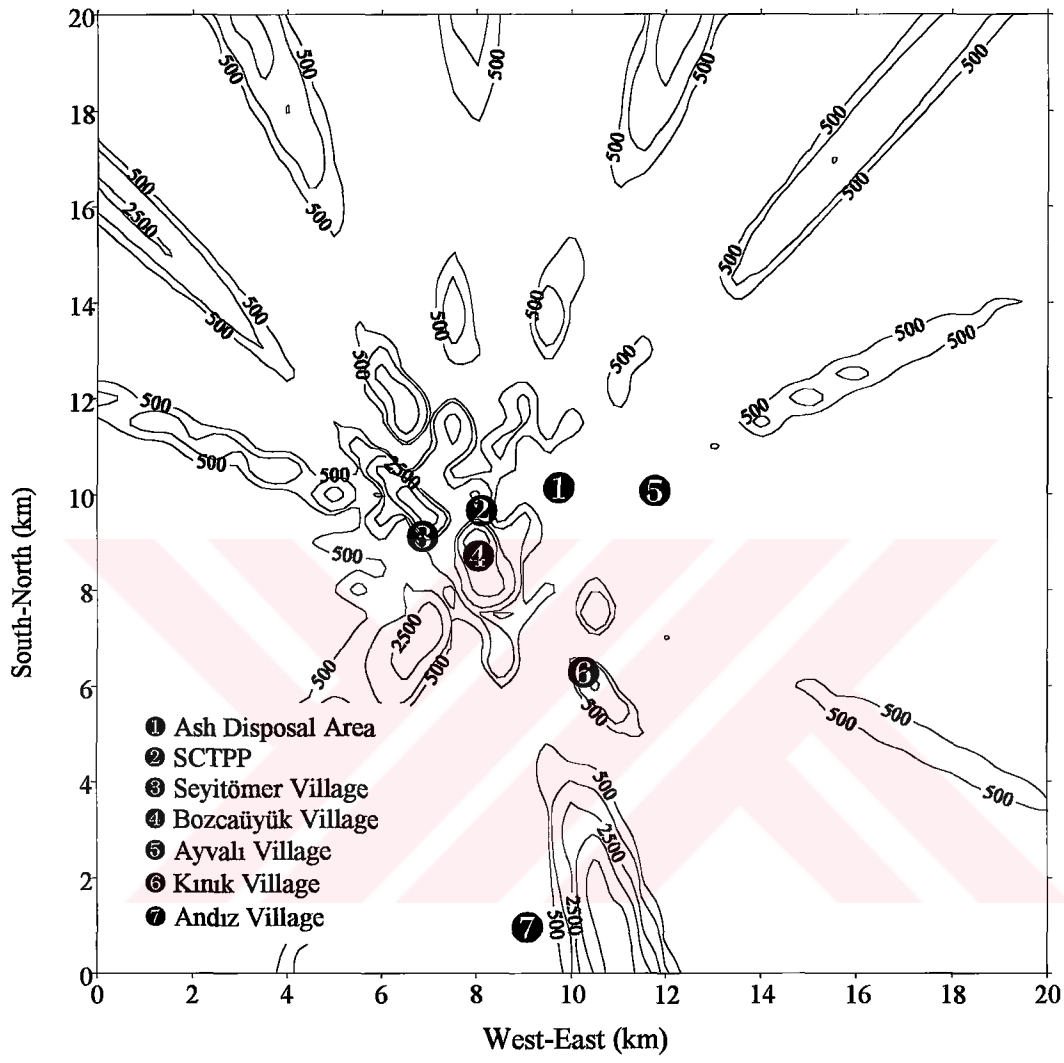


Figure 5.20. Stack to Area Ratios of Annual SPM Deposition Estimates (contours are 500, 1000, 2500, 5000 and 10000 units)

In the plots showing groundlevel SPM concentrations, it is clear that the particle concentrations throughout the study area are dominated by stack emissions, except a small region in the immediate vicinity of the ash disposal site. As can be seen from Figure 5.17, there are regions where contribution of emissions from disposed ash is a factor of 5 higher than the concentrations of stack emissions.

However, these regions are antifact due to poor handling of meteorological data by the ISCST model.

A similar pattern is also observed for deposition. Contribution of stack emissions on total particle deposition in the region is three-order-of magnitude higher than contribution of emissions from ash disposal site. The study area, except for a very small region in the immediate vicinity of the ash disposal site where contribution of two sources affecting, can be isolated using multivariate statistical methods such as factor analysis (FA) and chemical mass balance (CMB). In this study, FA was applied to the soil data set to differentiate between contributions of stack and disposed ash emissions.

5.6.2 Factor Analysis

Factor analysis provides some information about the potential sources of a receptor site by distinguishing groups of elements whose concentrations fluctuate together between the samples as discussed previously in Section 2.5.1. In this regard, the source groups affecting the samples can be determined. By the help of this method, it is easy to determine the number of factors needed to describe the variance of the experimental data and the matrix of factor loading.

In the FA, the factors having eigenvalues larger one are the ones to be discussed on. Factors having zero eigenvalues are considered as irrelevant and the ones less than one indicates that factor contributes less than a single variable. In this study, the lower limit of eigenvalue is selected as unity and three factors have been extracted. Since principal component method was selected, the initial community estimates have been set to assume that all of the variability in the data is due to common factors.

FA was run with three factors and the results of VARIMAX-rotated FA are presented in Table 5.8 and the distribution of factor scores indicating weight of that factor at each sampling point is shown in Figure 5.21. The analysis includes

three factors, because their eigenvalues were greater than 1.0 and these three factors can be explained. It should be noted that elements having factor loadings less than 0.25 (25%) were not included in the table to improve readability. The three factors retained explain 67% of the system variance.

First factor includes Na, Al, Cr, Mn, Fe and Cu and it explains 31% of the system variance. This group is identified as crustal factor since it includes high loadings of soil-related elements. Although Cr is an anthropogenic element, it can be included in the group of crustal elements since it has high concentration in soil and certain minerals which are frequently found in different parts of Turkey contain very high Cr concentrations. The distribution of Cr concentrations in soil closely resemble distributions of crustal elements such as Al and EF_c calculations suggest that Cr is not unusually enriched in soil except at a small area in the immediate vicinity of the power plant and disposal site. All these information and observations suggest that the main source of Cr in the study area is the soil. Moderate Cu loading in Factor 1 is probably due to its low percentage in aluminasilicate matrix of soil and indicate that soil is the main source of Cu in the study area. Since Cu is not enriched in soil in the study area as discussed previously in the text, the soil source for Cu is not surprising. Hence, the first factor represents the main soil type in the region. Distribution of Factor 1 scores which is shown in Figure 5.21 is typical of distribution of soil related parameters as discussed in the previous section.

The second factor represents the anthropogenic component in soil. This factor includes the elements K, Zn, Cd and Pb and explains 21% of the system variance. The distribution of Factor 2 scores is depicted in Figure 5.21. The scores are high in the area which cover both the power plant and ash disposal area and have high values to the north of the study area, indicating the parts of the study area affected by deposition of particles emitted from the power plant and ash disposal area.

Table 5.8. VARIMAX Rotated Factor Loading and Corresponding Source Type

Element	FACTOR 1	FACTOR 2	FACTOR 3
Na	0.36		
Mg			0.60
Al	0.67		
K		0.90	
Ca			
Cr	0.63		0.60
Mn	0.78		
Fe	0.85		
Ni			0.84
Cu	0.49		
Zn		0.79	
Cd		0.51	
Pb		0.48	
PROBABLE SOURCE	Main type of soil	Anthropogenic	Different type of soil
% VARIANCE	31	21	15
TOTAL SYSTEM VARIANCE (%)			67

The third factor includes Mg, Cr and Ni and explains 15% of the system variance. A small loading of Cd is also observed. This probably represents a different soil type enriched by three elements.

Although the factor analysis applied to the data set, and distribution of factor scores have provided valuable information on the element groups and locations of sources affecting elemental composition of soil in the study area, it failed to distinguish contributions of the power plant and ash disposal site. There are two main reasons for this failure:

(i) The stack emissions are the dominating source for observed elements in the study area. The contribution of fugitive emissions from ash disposal site is negligible at almost all sampling points.

(ii) Concentrations of the elements measured are not substantially different in stack and fugitive emissions. If the chemical composition of particles emitted from different sources are sufficiently different, FA can isolate them. For example, two different soil types with different Ni, Mg and Cr content could be identified, but only limited number of elements were measured by the AAS used in this study. Concentrations of these elements were not sufficiently different in stack and fugitive emissions. Due to these two significant factors, the FA failed to distinguish between two source types. Although there were an alternative multivariate statistical approach which is called "Chemical Mass Balance" which is felt to be beyond the scope of this study.

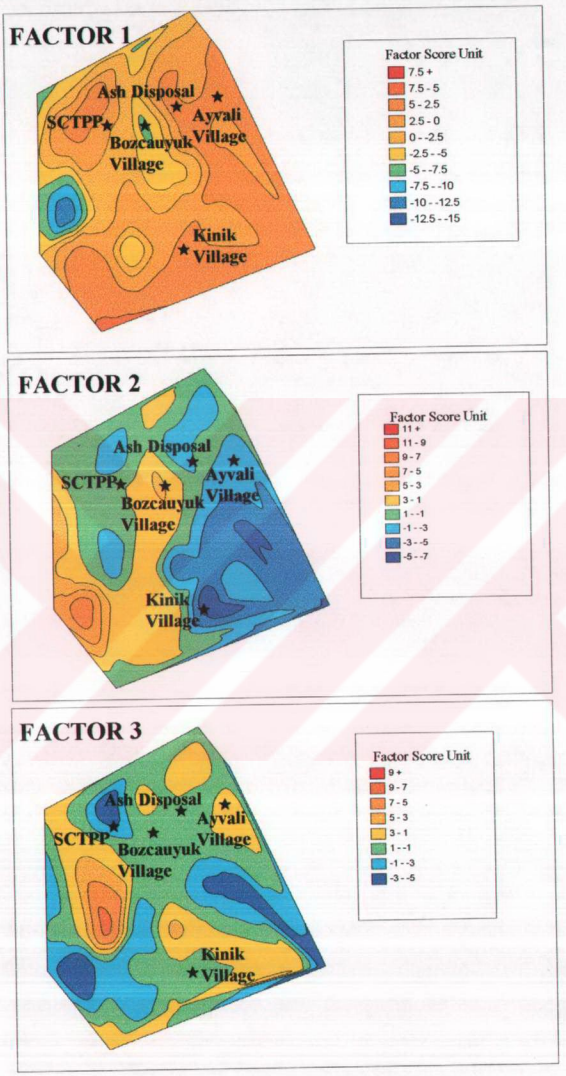


Figure 5.21. Distribution of Factor Scores

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 Conclusions

In this study, air and soil pollution in the 20 km × 20 km area around Seyitömer thermal power plant and ash disposal site is investigated using numerical and experimental techniques. Pollution levels in soil and atmosphere, sources responsible for observed high concentrations and relative contributions of the power plant and ash disposal area on observed concentrations of elements and SPM are studied.

Samples are taken from soil located within the vicinity of the plant and analyzed by atomic absorption spectrometry for Na, Mg, Al, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb, and the results are compared with the data reported in the literature.

Ambient aerosol samples were collected for a period of 22 days (March, 11 and April, 1, 1998). The samples were also analyzed for the same set of elements; namely, Na, Mg, Al, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb. Results of analysis were evaluated to understand general levels of metals in the atmosphere. Measured SPM concentrations from these samples were compared with the ground level concentrations calculated by the ISCST model.

Additionally, with the separate runs carried out in order to assess the contributions of stacks and ash disposal site to the regional pollution separately. The concentrations of measured elements indicate that most of the elements have Gaussian distributions except Pb and K. Based on the discussion that the clean soils are expected to show Gaussian distribution, Pb and K are suspected to have anthropogenic sources affecting their measured concentrations. Unlike in soil, most of the average concentrations of elements in aerosol samples show log-normal (exponential) distribution. Since it is a well-known fact that aerosol data frequently follow log-normal distributions, such a behavior can be either due to anthropogenic contribution on elemental concentrations or due to dependence of concentrations on meteorological parameters like boundary layer and mixing heights.

According to the soil samples analyzed, although it is observed that average anthropogenic trace elements in the study area is low compared to the studies carried out throughout the world, the concentrations are not so low to have an un-skewed soil composition. Based on the FA analysis carried out in this study, there are three groups of elements. The first group consists of crustal elements Fe, Ca, K, Na, Mn and Al. The concentrations of these elements are high in the soil samples and contribution by anthropogenic sources on their concentrations in soil is generally negligible.

Second group has the elements Cu, Pb, Cd and Zn. The concentrations of these elements in soil are low and are thought to be altered by the contribution of anthropogenic sources. Third group includes Cr and Ni as well as crustal elements and believed to represent Cr-rich soil.

In the light of concentration distributions of elements Cd, Zn, Pb, Cr and Ni, the region within the vicinity of the plant and ash disposal site is concluded to be impacted. Some regions on the south-west and west of the sources receive high concentrations of Cd, Zn, Pb, Cr and Ni.

According to the enrichment factors of elements calculated throughout the SA, it is observed that the soil composition severely differs from the average soil composition near the power plant and ash disposal site indicating that the sources have serious impacts within the their vicinity. However, 5 - 6 km away from the sources, the affect of sources sharply decreases.

Comparing the average concentrations of elements with the soil pollution classes, it is observed that the regional soil is heavily polluted with Cr and Ni. The maximum values, on the other hand, show that some parts of the SA are extremely polluted. Zn, Cd and Pb loads are not significant for the SA, since their observed average concentrations correspond to soil pollution Class II. The SA soil has high amounts of Cu deposition and belongs to soil pollution Class IV.

Computer model predictions carried out for 22 days in concern are not similarly distributed with the SPM concentrations calculated from aerosol samples. Annual deposition values estimated by the model (300 $\mu g\ m^{-3}$), on the other hand, are close to the SPM concentrations calculated from aerosol samples (140 $\mu g\ m^{-3}$). The difference is due to the assumptions made by the model and experimental errors faced with during the analyses.

In the light of ISCST predictions, it is observed that the SA is not heavily polluted, but the impacts of the power plant and ash disposal site are seen at limited locations. The discussions of the model estimates agree fairly well with the conclusions reached by comparing atmospheric concentrations of elements with literature values. The villages located nearby, on the other hand, do not receive high emissions of pollutants, namely SPM and SO_2. Only Bozcaüyük village is heavily affected from the ash disposal site. The SPM level in this residential area is serious and necessary precautions should be taken in order to prevent health implications. Kınık village is also affected to a certain degree.

As a result of separate runs of stacks and ash disposal site carried out by ISCST, stacks have more contributions on both GLC and deposition values of SPM. The

stack to site ratios of SPM concentrations increases up to 125 within the vicinity of the sources. The stack to site ratios of SPM deposition values, on the other hand, are much higher reaching to 500 and even to 2500 near the sources.

6.2 Recommendations for Future Works

T.C. YÜKSEKÖĞRETİM KURULU
DOKÜMANTASYON MERKEZİ

The study carried out in the Kütahya station allowed us to understand general features of the atmospheric aerosols, regional soil and their sources. The pollution degree of the regional soil is not much, but the influence of the stacks and ash disposal site cannot be neglected within their vicinity. Necessary precautions should be taken for high SPM emissions received in the nearby villages to prevent the health implications. Within this intention, one method for ash disposal technique is the wet disposal of ash which eliminates fugitive dust emissions.

In the future studies, differentiation between the effects of the stacks and the ash disposal area should be carried out. Since some marker elements for ash disposal site were not considered in the measurement program, the factors found with the FA did not serve for this purpose. A statistical method known as chemical mass balance (CMB) can be applied to the results and a more detailed conclusion can be reached for the sources of pollution in the region.

REFERENCES

Abdel-Saheb, I., Schwab, A. P., Banks, M. K., Hetrick, B. A., 1994, "Chemical Characterization of Heavy-Metal Contaminated Soil in Southeast Kansas", Water, Air and Soil Poll., Vol. 78, pp. 73-82.

Albert, D.J., Hopke, P.K., 1981, "A Determination of the Sources of Airborne Particles Collected During the Regional Air Pollution Study", Atm. Env., Vol. 15, pp. 675-687.

Al-Momani, I.F., Tuncel, S., Eler, Ü., Örtel, E., Şirin, G., Tuncel, G., 1995, "Major Ion Composition of Wet and Dry Deposition in the Eastern Mediterranean Basin", The Sci. of the Total Env., Vol. 164, pp. 75-85.

Adriana Carasco, M., Prendez, M., 1991, "Element Distribution of Some Soils of Continental Chile and the Antarctic Peninsula", Projection to Atmospheric Poll., Vol. 57-58, pp. 713-722.

Aronoff, S., 1993, Geographic Information Systems: A Management Perspective, WDL Publications, Canada.

Aubert, H., Pınta, M., 1977, Trace Elements in Soils, Developments in Soil Science 7, Elsevier Scientific Pub.Company, Amsterdam.

Baumbach, G., 1996, Air Quality Control, Springer-Verlag, Berlin.

Bergametti, G., Dutot, A.L., Buat-Menard, P., Losno, R., Remoudaki, E., 1989, "Seasonal Variability of the Elemental Composition of Atmospheric Aerosol Particles Over the Northwestern Mediterranean", Tellus, Vol. 41B, pp. 363-361.

Borberly-Kiss, I., Bozo, L., Koltay, E., Meszonos, E., Molnar, A., Szabo, G., 1991, "Elemental Composition of Aerosol Particles Under Background Conditions in Hungary", Atm. Env., Vol. 25A, pp. 661-668.

Chen, J., Wei, F., Zheng, C., Wu, Y., Adriano, D.C., 1991, "Background Concentrations of Elements in Soils of China", Water, Air and Soil Poll., Vol. 57-58, pp. 699-712.

Chu, Y.J., Kim, B.R., Raune, R.J., 1980, "Behavior of Coal Ash Particles in Water: Trace Metal Leaching and Ash Settling", U.S. Environmental Protection Agency, USEPA 600/7-80-067, Washington, DC.

Cheng, M.D., Hopke, P.K., 1989, "Identification of Markers for Chemical mass Balance Receptor Model", Atm. Env., Vol. 23, No. 6, pp. 1373-1384.

Chester, R., Nimmo, M., Murphy, K.J.T., Nicholas, E., 1990, "Atmospheric Trace Metals Transported to the Western Mediterranean: Data from a Station on Cap Ferrat", Water Poll. Research Reports (ed. by Martin, J.M., and Barth, H.), Vol. 20, pp. 597-612, Commission of European Communities.

Chester, R., Nimmo, M., Alarcon, M., Corcoran, P., 1991, "The Chemical Character of the North Western Mediterranean Aerosol", Water Poll. Research Reports (ed. by Martin, J.M., and Barth, H.), Vol. 28, pp. 495-504, Commission of European Communities.

Chester, R., Nimmo, M., Alarcon, M., Saydam, C., Murphy, K.J.T., Sanders, G.S., Corcoran, P., 1993, "Defining the Chemical Character of Aerosols from the Atmosphere of the Mediterranean Sea and Surrounding Regions", Ocean. Acta, Vol. 16, pp. 231-246.

Cornille, P., Maenhaut, W., Pacyna, J.M., 1990, "Sources and Characteristics of the Atmospheric Aerosol Near Damascus, Syria", Atm. Env., Vol. 25A., No. 5, pp. 1083-1093.

DMİ, 1997, Spreadsheets of Data Recorded in Kütahya Meteorological Station, (not published), State Meteorological Works (DMİ), Ankara.

Duce, R.A., Arimoto, R., Ray, C.K., Harder, P.J., 1983, "Atmospheric Trace Elements at Enewatak Atoll: 1, Concentrations, Sources and Temporal Variability", Journal of Geophysical Research, Vol. 88, pp. 5321-5342.

Dzubay,T.G.,Stevens, R.K., Balfour, D.W., Williamson, H.J., Cooper, J.A., Core, J.E., Cesar, R.D., Crutcher, E.R., Dattner, S.L., Davis, B.L., Heisler, S.L., Shah, J.J., Hopke, P.K., Johnson, D.L., 1984, "Interlaboratory Comparison of Receptor Model Results for Houston Aerosols", Atm.Env., Vol.18,No.8,pp. 1555-1566.

EPA, 1977, "Compilation of Air Pollutant Emission Factors", U.S. Environmental Protection Agency (EPA), Office of Air Quality Planning and Standards), North Carolina.

EPA, 1992a, "User's Guide for the Industrial Source Complex (ISC2) Dispersion Models, Volume I- User's Instructions", U.S. Environmental Protection Agency (EPA), Office of Air Quality Planning and Standards, North Carolina.

EPA, 1992b, "User's Guide for the Industrial Source Complex (ISC2) Dispersion Models, Volume II- Description of Model Algorithms", U.S. Environmental Protection Agency (EPA), Office of Air Quality Planning and Standards, North Carolina.

Egemen, E., 1993, "Release of Metal Ions from Fly Ash Originating from Coal-fired Power Plants", Master's Thesis, Department of Environmental Engineering, METU, Ankara.

Environment Canada, 1980,"Water Intake, Wastewater Production and Treatment, and Air Pollution Control Technology in Coal-fired Steam-electric Power Generating Stations", Environment Canada, Report No. EPS 3-WP-80-1.

Evans, D.W., Wiener, J.G. & Horton, J.H., 1980, "Trace Element Input from a Coal Burning Power Plant to Adjacent Terrestrial and Aquatic Environments", Journal of the Air Poll. Control Assoc., 30 (5), 567-573.

Fergusson, J. E., 1990, The Heavy Elements: Chemistry, Environmental Impact and Health Effect, Pergamon Press.

Ferraiolo, G., Zilli, M., Converti, A., 1990, "Fly Ash Disposal and Utilization", J. Chem. Tech. Biotech., Vol. 47, pp. 282-305.

Galloway, J.N., Thorton, J.D., Norton, S.A., Volchok, H.L., Mclean, R.A.N., 1982, "Trace Metals in Atmospheric Deposition: A Review and Assessment", Atm. Env., Vol. 16, pp. 1677-1700.

Gordon, G.E., 1988, "Receptor Models", Env. Sci. Tech., Vol. 22, No. 10, pp. 1132-1142.

Guieu, C., 1991, "Apports Atmospheriques a la Mediterranee Nord-Occidentale", These de Doctorat de l'Universite de Paris, 225 pages.

Güllü, G. 1996, "Long Range Transport of Aerosols", Ph.D. Thesis, Department of Environmental Engineering, METU, Ankara.

Güvenç, N., 1998, "Investigation of Soil Pollution in the City of Antalya", M.Sc. Thesis (unpublished), Department of Environmental Engineering, METU, Ankara.

Hacısalihoğlu, G., Eliyakut, F., Ölmez, İ, Balkaş, T., Tuncel, G., 1992, "Chemical Composition of Particles in the Black Sea Atmosphere", Atm. Env., Vol. 26A, No. 17, pp. 3207-3218.

Häefe, W., 1981, Energy in a Finite World: A Global Systems Analysis, Ballinger, Cambridge, Mass.

Hamzaoğlu, A., Kayın, S., Tuncel, G., Yurteri, C., 1998, "Fugitive Dust Modeling: A Case Study for Seyitömer Coal-Fired Power Plant", Proceedings of the Fifth Inter. Symp. On Env., Issues and Waste Manag. In Energy and Mineral Production-SWEMP, May 18-20, Ankara, Turkey.

Henry, R.C., Lewis, C.W., Hopke, P.K., Williamson, H.J., 1984, "Review of Receptor Model Fundamentals", Atm. Env., Vol. 18, No. 8, pp. 1507-1515.

Hopke, P.K., Lamb, E.R., Natusch, D.F.S., 1980, "Multielemental Characterization of Urban Roadway Dust", Env. Sci. Tech., Vol. 14, pp. 164-172.

Hopke, P.K., 1988, "Target Transformation Factor Analysis as an Aerosol Mass Apportionment Method: A Review and Sensitivity Study", Atm. Env., Vol. 22, pp. 1777-1792.

Jervis, R.E., Paciga, J.J., Chattopadhyay, A., 1975, "Characterization of Urban Aerosol and Their Hazard Assessment, by Size Sampling Combined with Inter-Element Ratios", IAES-SM-206/9, pp. 125-150.

Kabata-Pendias, A., 1992, "Trace Elements in Soil of Poland-Occurance and Behavior", Trace Substances in Environmental Health, Vol. 25, pp. 53-70.

Kabata-Pendias, A., 1995, "Agricultural Problems Related to Excessive Trace Metal Contents of Soils", Heavy Metals Problem and Solutions, Environmental Science, Springer-Verag Berlin Heidelberg.

Kabata-Pendias, A., Pendias, H., 1984, Trace Elements in Soils and Plants, CRC Press, Boca Raton, FL.

Kabata-Pendias, A., Pendias, H., 1992, Trace Elements in Soils and Plants, 2nd Edition, CRC Press, Boca Raton, FL.

Koutrakis, P., Spengler, J.D., 1987, "Source Apportionment of Ambient Particles in Steubenville, OH, Using Specific Rotation Factor Analysis", Atm. Env., Vol. 21, pp. 1511-1519.

Kubilay, N., Saydam, A.C., 1995, "Trace Elements in Atmospheric Particulates Over the Eastern Mediterranean; Concentrations, Sources and Temporal Variability", Atm. Env., Vol. 29, No. 17, pp. 2289-2300.

Kubilay, N., 1996, "The Composition of Atmospheric Aerosols Over the Eastern Mediterranean: The Coupling of Geochemical and Meteorological Parameters", Ph.D. Dissertation, METU, Institute of Marine Sciences, Erdemli.

Kuloğlu, E., 1997, "Size Separation and Dry Deposition Fluxes of Particles in the Eastern Mediterranean Basin", M.Sc. Thesis, Department of Environmental Engineering, METU, Ankara.

Maenhaut, W., Cornilla, P., Pacyna, J.M., Vitols, V., 1989, "Trace Element Composition and Origins of the Atmospheric Aerosols in the Norwegian Arctic", Atm. Env., Vol. 23, pp. 2551-2569.

Mason, J., 1986, Introduction to Geochemistry, 3rd Edition, Willey, New York.

Miller, F.J., Gardner, D.E., Graham, J.A., Lee, Jr. R.E., Wilson, W.E., Bachmann, J.D., 1979, "Size Considerations for Establishing A Standard for Inhalable Particles", J. of Air Poll. Control Assoc., Vol. 29, No. 6, pp. 610-615.

Ölmez, İ., Sheffield, A.E., Gordon, G.E., Houck, J.E., Pritchett, L.C., Cooper, J.A., Dzubay, T.G., Bennett, R.L., 1988, "Compositions of Particles from Selected Sources in Philadelphia for Receptor Modeling Applications", J. of Air Poll. Control Assoc., Vol. 38, No. 11, pp. 1392-1402.

Özbayoğlu, F., 1994, "Termik Santrallarda Oluşan Uçucu Küllerin Depolama Sorunları", Enerji ve Çevre Sempozyumu, April 13-15, Mersin.

Pacyna, J.M., 1986a, "Emission Factors of Atmospheric Elements", Offprints from Toxic Metals in the Atmosphere, Edited by: Dr. Nriagu, J.O. and Dr. Davidson, C.I., John Wiley & Sons, Inc.

Pacyna, J.M., 1986b, "Atmospheric Trace Elements from Natural and Anthropogenic Sources", Offprints from Toxic Metals in the Atmosphere, Edited by: Dr. Nriagu, J.O. and Dr. Davidson, C.I., John Wiley & Sons, Inc.

Parekh, P.P., Ghauri, B., Husain, L., 1989, "Identification of Pollution Sources of Anamolously Enriched Elements", Atm. Env., Vol. 23, No. 7, pp. 435-442.

Pio, C.A.,Salguerio, M.L., Nunes, T., 1991, "Seasonal and Air-Aass Trajectory Effects on Rainwater Quality at the South-Western European Border", Atm. Env., Vol. 25A, No. 10, pp. 2259-2266.

REG, 1990, REG-308 MET Pre-Processor, Ontorio Ministry of Environment, Toronto, Canada.

Rauta, C., Lacatusu, R., Carstea, S., 1995a, "Agricultural Problems Related to Excessive Trace Metal Contents of Soils", Heavy Metals Problem and Solutions, Environmental Science, Springer-Verag Berlin Heidelberg.

Rauta, C., Lacatusu, R., Carstea, S., 1995b, "Heavy Metal Pollution in Romania", Heavy Metals Problem and Solutions, Environmental Science, Springer-Verag Berlin Heidelberg.

SPSS, 1990, SPSS (Statistical Package for Social Sciences), Copyright: by SPSS Inc., 444 N. Michigan Avenue, Chicago, IL, 60611.

Sezer, İ, 1988, "İklim ve Vejatasyon Sınıflandırması Konusunda Yeni Bir İndis Denemesi", Coğ. Derg., No. 4, pp. 161-201, İzmir.

Stern, A.C., Boubel, R.W., Turnet, D.B., Fox, D.L., 1984, Fundamentals of Air Pollution, USA.

Stern, A., 1977, Air Pollution-The Effects of Air Pollution, Vol. 2, Academic Press Inc.

TEAŞ, 1991, 4×150 MW Seyitömer Termik Santralı, Türkiye Elektrik Üretim AŞ (TEAŞ), Kütahya.

TÜBİTAK, 1994, "Seyitömer Termik Santralı Elektrofiltre Giriş ve Çıkış Toz ve Gaz Ölçümleri", TÜBİTAK Marmara Araştırma Merkezi, Enerji Sistemleri ve Çevre Araştırma Enstitüsü Raporu, No. 15.3.006.

Thurston, G.D., Lioy, P.J., 1987, "Receptor Modeling and Aerosol Transport", Atm. Env., Vol. 21, No. 3, pp. 687-698.

Tuncel, S.G., Ölmez, İ., Parrington, J.R., Gordon, G.E., 1985, "Composition of Fine Particle Regional Sulfate Component in Shenandoah Valley", Env. Sci. Tech., Vol. 19, pp. 529-537.

UN, 1981, "The Coal Situation in the ECE Region in 1979 and its Prospects", Report ECE COAL, No. 57, United Nations, New York.

Wilson, C., 1980, Coal Bridge to the Future: Report of the World Coal Study, Ballinger, Cambridge, Mass.

World Bank, 1979, "Coal Development Potential and Prospects in the Developing Countries", World Bank, Washington, D.C.

Yaaqub, R.R., Davies, T.D., Jickels, T.D., Millers, J.M., 1991, "Trace Elements in Daily Collected Aerosols at a Site in Southeast England", Atm. Env., Vol.25A, pp. 985-996.

Yatın, M., 1994, "Source Apportionment of Urban Aerosols Using Receptor Modeling Approach: An Application to Ankara", Ph.D. Thesis, Department of Chemistry, METU, Ankara.

Yay, O.D., 1998, "Changes in the Chemical Composition of Soil in Ankara due to the Deposition of Atmospheric Pollutants", M.Sc. Thesis (unpublished), Department of Environmental Engineering, METU, Ankara.

Zelenka, M.P., Willson, W.E., Chow, J.C., Lioy, P.J., 1994, "A Combined TTFA/CMB Modelling Approach and its Application to Air Pollution Sources in China", Atm. Env., Vol. 28, pp. 1425-1435.