TRACE METALS IN AIRBORNE PARTICLES AND THEIR DRY DEPOSITION IN İZMİR

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İZMİR

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We certify that we have read this thesis and "**TRACE METALS IN AIRBORNE PARTICLES AND THEIR DRY DEPOSITION IN IZMIR**" completed by **AYŞE BOZLAKER** under supervision of **PROF. DR. AYSEN MÜEZZİNOĞLU** and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

A series of twenty four dry deposition samples were collected on a surrogate surface between September 2000 and June 2001 in Izmir, Turkey and analysed for trace elements of anthropogenic and crustal origin. Concurrently ambient air samples were taken using a high-volume sampler.

The results show that the average measured Pb, Cr, Zn, Cd, Cu, Ni, Mn, Mg, Al, Ca and Fe dry deposition fluxes were 0.219, 0.0158, 1.9057, 0.0239, 0.1237, 0.1292, 0.1350, 3.1, 23.5, 43.1 and 12.089 mg m^{-2} day^{-1}, respectively.

Particulate phase overall dry deposition velocities calculated using the dry deposition fluxes and ambient concentrations. Average dry deposition velocities calculated using the dry deposition fluxes were 2.837, 1.23, 4.63, 3.62, 1.35, 4.95, 1.23, 0.98, 0.55, 1.46 and 6.15 (cm s^{-1}) for Pb, Cr, Zn, Cd, Cu, Ni, Mn, Mg, Al, Ca and Fe, respectively.

This values were higher than values typically used to estimate particulate trace metal deposition, however they were in reasonable agreement with values determined using similar techniques.

The extent of the anthropogenic contribution was estimated by the degree of enrichment of these elements compared to the average local soil composition. High values (>10) were calculated for Cd, Zn, Pb, Fe, Mg and Ni (anomalously enriched elements-AEEs) and relatively low values (<10) for Cr, Cu, Mn and Ca in dry deposition samples. In aerosol samples, all trace metals were found as non-enriched elements (NEEs).

ÖZET

Havadan yere yağan yirmi dört adet kuru birikim örneği, yapay yüzeyler üzerinde, Eylül 2000-Haziran 2001 tarihleri arasında toplanarak insan faaliyetleri sonucu oluşan ve topraktan gelen ağır metallerin analizi yapılmıştır. Aynı zamanda dış hava örnekleri, bir toz örnekleme cihazı kullanarak alınmıştır.

Analiz sonuçlarına bağlı olarak ölçülen Pb, Cr, Zn, Cd, Cu, Ni, Mn, Mg, Al, Ca ve Fe elementlerine ait ortalama kuru birikim miktarları sırasıyla; 0.219, 0.0158, 1.9057, 0.0239, 0.1237, 0.1292, 0.1350, 3.1, 23.5, 43.1 and 12.089 mg m^{-2} gün^{-1} olarak bulunmuştur.

Partikül fazındaki tüm kuru depolanma hızları, kuru birikim miktarlarının aynı zamanda ölçülen atmosferik konsantrasyonlara bölünmesiyle hesaplanmıştır. Partikül kirleticiler için hesaplanan ortalama kuru birikim hızları sırasıyla Pb, Cr, Zn, Cd, Cu, Ni, Mn, (insan faaliyetleri sonucu oluşan); Mg, Al, Ca ve Fe (toprak kökenli) elementleri için; 2.837, 1.23, 4.63, 3.62, 1.35, 4.95, 1.23, 0.98, 0.55, 1.46 ve 6.15 (cm s^{-1}) olarak hesaplanmıştır.

Yapılan bu çalışmanın sonucunda bulunan bütün bu veriler, partikül fazındaki ağır metallerin kuru depolanmasının tahmininde kullanılan tipik değerlerden genelde büyük olmasına karşın, benzer teknikler kullanılarak hesaplanan değerler ile kıyaslandığında benzerlikler gösterdiği ve dünyanın başke yerlerinde görülen sınırlar içinde olduğu görülmüştür

İnsan faaliyetleri sonucu meydana gelen kirliliklerin katkısının derecesi, yöredeki topraktan havaya gelen elementlerin bileşimi ve topraktaki değerler ile

karşılaştırılarak, bu elementlere ait zenginleştirme faktörleri (EF_{crust}) bulunmuştur. Yapılan hesaplamalar sonucunda kuru birikim örneklerinde; yüksek EF_{crust} (>10) değerleri Cd, Zn, Pb, Fe, Mg ve Ni, (AEEs), ve küçük (<10) EF_{crust} değerleri ise Cr, Cu, Mn ve Ca (NEEs) elementleri için hesaplanmıştır. Dış hava örneklerinde ise tüm elementler için küçük EF_{crust} (<10) değerleri bulunmuştur.

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CHAPTER ONE

INTRODUCTION

Atmospheric deposition, which is commonly classified as either dry or wet, has received a great deal of study over the past decade due to concerns about the effects of deposited material on the environment. Atmospheric deposition is an important mechanism controlling the fate of airborne toxics and their transfer from the atmosphere to natural surfaces (Yi et al., 1997a).

The quantification of dry deposition is difficult due to large spatial and temporal variations and because interactions between the surface and the atmosphere can have large effects on the amount of deposited material. Different kinds of surrogate surfaces including Teflon plates, Petri dishes, dry or diol-coated filters, buckets, pans filled with water, oil-coated glass plates, and greased strips have all been used to measure particle dry deposition (Odabasi et al., 1999). The use of surrogate surface to measure dry deposition is an increasingly important technique that can be used to directly assess deposited material and allows comparisons to be made between measured and modelled data (Yi et al., 1997a).

Dry deposition is a function of the physical and chemical properties of the pollutant, meteorological conditions (temperature, wind speed, atmospheric stability), and surface characteristics (Odabasi et al., 1999). In direct measurements of dry deposition usually an artificial surface is used that simulates as closely as possible the natural surface onto which dry deposition is occurring. The dry deposited material is extracted from the artificial surface for chemical analysis. In indirect methods, air concentrations of the pollutants are measured, and the concentrations are multiplied by measured or literature values of deposition velocities (Golomb et al., 1996).

Analysis of dry fall-out collected on plastic plates have been reported by Herut et al., (2001), Chester et al., (1999) and Odabasi et al., (1999).

Parameters affecting the analytical result include the following: 1) concentration of the pollutant, 2) exposure time, 3) temperature, 4) humidity, 5) velocity of ambient air currents, and 6) variation in concentration (Kettrup, 1991).

The objectives of this study were:

1. To measure ambient trace element concentrations and dry deposition fluxes and to determine their temporal variations,
2. To determine overall dry deposition velocities for particulate trace metals,
3. To calculate the sources of ambient trace elements using their enrichment factors relative to the local soil.

To meet these objectives, a sampling program was carried out between september 2000 and June 2001 in Izmir. The dry deposition fluxes of trace elements (Cr, Cu, Pb, Zn, Ni, Cd and Mn which are primarily of anthropogenic origin and Al, Fe, Ca and Mg which are primarily of crustal origin) were measured directly with a surrogate surface at one location. Concurrently ambient air samples were collected using a High-volume sampler. Particulate trace metal dry deposition velocities were calculated using the dry deposition fluxes and ambient concentrations obtained from the samples. Enrichment factors of trace metals were calculated using the concentration ratio of the trace elements to Al in the air suspended particles and the average ratio in local soil.

Ambient concentrations, dry deposition fluxes, deposition velocities and enrichment factors obtained from experimental studies were evaluated by comparing them to the values reported in the literature.

This study consists of five chapters. An overview and objectives of the study were presented in Chapter 1. Chapter 2 reviews the concepts and previous studies related to

this work. Experimental work is summarized in Chapter 3. Results and discussions are presented in chapter 4. Chapter 5 includes the conclusions.

CHAPTER TWO

LITERATURE REVIEW

2.1 Atmospheric Dry Deposition of Trace Metals

Toxic contaminants of atmospheric origin include heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins and difurans, pesticides and other organic compounds (Golomb et al., 1996).

Atmospheric deposition may be classified as wet or dry. In wet deposition, aerosols and gases are dissolved or suspended in precipitation: rain, snow, hail, fog and mist. Dry deposition of particles occurs by direct impaction and subsequent gravitational settling on land or water surfaces. Wet deposition is the result of washout and rainout. Washout is the process of scrubbing of gases and particles by falling droplets. Rainout is the result of incorporating into cloud droplets of gases and particles, or indeed, cloud droplets forming on particle condensation nuclei (Golomb et al., 1996). Assuming that the present total deposition sampling is representative, atmospheric dry deposition flux can be calculated by subtracting the wet deposition flux from the bulk deposition (wet and dry) flux (Migon et al., 1996).

Estimation of dry deposition is more problematic then wet deposition. Most metals have a relatively short residence time in the troposphere (between a few days and a few weeks), thus they are not well-mixed and their concentrations in the atmosphere and hence in aerosols and rain water exhibit strong spatial and temporal variability.

In comparison between wet and dry deposition fluxes, for most of the metals, the dry deposition is predominant, which is probably due to the permanence of this deposition mode, particularly during the long Mediterranean dry season. In particular, Co, Cu and

Pb are essentially deposited by the dry mode, which represents respectively, 74, 73 and 81% of the total inputs (wet and dry deposition). Pb inputs originating from automotive exhaust may be significantly increased during the summertime (i.e. the dry seasons) in this region, and this could explain the importance of dry inputs. For the case of Co and Cu, the high contribution of the dry deposition mode is presumably due to the relative importance of the lithogenic component for these elements. On the contrary, Cd exhibits a non-negligible wet deposition contribution (50%). This should be due to the high solubility of this element. Despite its non-negligible lithogenic component, Ni is characterised by a predominant wet deposition contribution (Migon et al., 1996).

Dry deposition of particles is determined by meteorological conditions, atmospheric concentrations, surface type/condition and the specific chemical and physical properties of particles. Dry deposition can be conceptualised as a three-step processes: (1) the gas or particle is moved toward the surface by thermally or mechanically driven eddies; (2) it is transferred by diffusion across a thin layer close to the surface where turbulence is absent; and (3) the gas or particle is captured by the surface. In the case of larger particles a second parallel pathway exists; particles are drawn towards the surface by gravity (Pryor & Barthelmie, 2000). The sources of particles and gases are emissions from stationary combustion sources, automobiles, trucks, airplanes and ships, fugitive dust and industrial sources.

The dry deposition has been determined by a number of methods: (i) on the basis of experimental cascade impactor data (Pryor et al., 1999 and Lin et al., 1994); (ii) from theoretical models (Chaster et al., 1999 and Rojas & Grieken, 1993); and (iii) with surrogate surfaces (Yi et al., 1997a and Yi et al., 1997b). The results are very different and hence their comparability is generally invalid, principally owing to a poor knowledge of elemental mass-size distributions and deposition velocities (Migon et al., 1996).

2.2 Dry Deposition Velocity

There are currently a number of models for predicting dry deposition velocities which can be used in conjuction with measured atmospheric concentrations or particle distributions to calculate dry deposition fluxes.

For a given element, experimental atmospheric dry deposition velocity (V_d), (cm s^{-1}) values can be calculated from the particulate concentration (C) as follows:

$$V_d = k \cdot F_d / C ,\qquad\qquad (1)$$

where F_d (dry deposition flux) is expressed in (mg m^{-2} d^{-1}) and C (particulate concentration in air) in (mg m^{-3}) and measured during the same sampling duration as total deposition (i.e. approximately 8h/day). Coefficient (k) leads to the usual units for V_d (Migon et al., 1996). In this study, Eq. (1) was used to calculate the experimental dry deposition velocities.

The calculation of elemental dry deposition velocity is very questionable using theoretical models, as this approach leads to V_d being an underestimation of the real values, whilst experimental processes lead to an overestimation of V_d. The estimation of V_d is generally uncertain, in particular for the case of particles whose size exceeds 10 μm, owing to their very high V_d (Migon et al., 1996).

In addition to the particle size, the deposition velocity depends on particle composition, deliquescence, surface conditions (e.g. land, water or vegetation), and atmospheric conditions (e.g. wind speed, turbulence, temperature and relative humidity).

The elements predominantly found in fine particles have generally lower deposition velocity than the elements mainly associated with coarse particles (Foltescu et al., 1996). For the fine size range (< 2.5 μm) , dry deposition velocity 0.025 cm s^{-1} was selected; for the coarse size range (> 2.5 − 10 μm), dry deposition velocity 0.25 cm s^{-1} was selected by Golomb et al., (1996) to calculate dry deposition flux. Dry deposition velocities were

selected as 1 and 0.1 cm s^{-1} for the non-enriched elements and the anomalously enriched elements, respectively by Chaster et al., (1999) to calculate dry deposition fluxes.

Particles characterised by a specific element will have different size, depending on the way of production and whether it is long or short range transported. Furthermore, there is a strong influence on V_d from meteorological factors, even if the size and other particle properties are the same. Thus, one cannot expect the same V_d for a specific element when measured under different conditions. Nevertheless, if data are collected for a large number of days, during which the conditions change, one can expect that the average velocity will reflect some dependence on physical and chemical properties of the particles in question (Foltescu et al., 1996).

2.3 Particle Size Distribution of Trace Metals

Various techniques can be used to estimate the mass median diameters (MMDs) of the trace metals in aerosols. The most commonly applied technique uses data obtained from cascade impactors.

Particles larger than 0.4 μm are primarily removed by gravitational settling which, in the Stokes region, increases with the square of the particle diameter. Removal of particles < 0.4 μm is governed primarily by Brownian diffusion and, therefore, increases rapidly with decreasing particle diameter (Quinn & Ondov, 1998).

The large particles, which make up only a small fraction of the total mass , dominate the dry deposition flux. For example, Dulac et al., (1989) modeled dry deposition rates from cascade impactor data obtained for the Western Mediterranean. They concluded that: (i) for Al, particles with MMDs > 7.2 μm which represented approximately 10%-40% of the total mass accounted for 90% of the total dry deposition flux; and (ii) for Pb, particles with MMDs > 7.2 μm represented approximately < 10% of the total mass, but accounted for 20% of the dry deposition flux. In terms of the largest particles, those with an MMD of 81μm contributed 35% to the total dry deposition flux of Al, and those with an MMD of 9.5 μm contributed 20% to the total dry deposition flux of Pb (Chester et

al., 1999). Although MMDs calculated from cascade impactor data may describe the particle size distribution in the ambient aerosol, they do not reflect that in the dry deposition resulting from it because this is dominated by large-sized particles. Table 2.1 shows MMDs for the trace metals in dry deposition, calculated from cascade impactor data (n=8), (Chester et al., 1999 and Pirrone & Keeler, 1995).

Lead (a primarily anthropogenic element) was associated with the fine particle mode; however, Ca (a primarily crustal element) was associated with the coarse particle mode as has been found previously (Lin et al., 1994).

The cumulative flux distribution shows that the fine particles (< 2.5 μm diameter) contributed only a small fraction to the dry deposition flux. This finding suggests that coarse particles dominate dry deposition due to their high deposition velocities (Lin et al., 1994).

Table 2.1 Mass median diameters (MMDs) for the trace metals, calculated from cascade impactor data[a].

Trace Metal	MMDs (μm)	
	Cap Ferrat	English Channel
Al	2.78	2.72
Fe	2.46	2.00
Mn	1.98	1.74
Ni	1.82	-
Co	1.55	-
Cr	2.10	-
Cu	1.31	1.48
Zn	1.24	1.60
Pb	0.84	0.75

[a] Chester et al. (1999).

2.4 Dry Deposition Flux

There have been two different approaches to measure and calculate dry deposition. One approach, the surface analysis method, examines contaminant accumulation on the surfaces of interest by using natural or man-made surfaces. The other approach, the atmospheric flux method, includes measurements of contaminant in the atmosphere from which one can estimate the deposition flux. Precise measurements of airborne concentration and micrometeorological data are required in this method. These two methods in part reflect two different definitions of the word "deposition". These definitions are material that is collected by a surface or obstacle that is selected for special consideration (first approach) and the aerial average rate of depletion from the atmosphere to all of the surfaces underneath (second approach), (Bagiroz, 2002).

These methods above, can be used to measure the atmospheric deposition of gaseous and particulate atmospheric toxic contaminants including heavy metals, polychlorinated biphenyls (PBCs), polycylic aromatic hydrocarbons (PAHs), dioxins and dibenzofurans, pesticides and other organic compounds.

Atmospheric dry deposition flux has often been estimated by multiplying a measured airborne concentration by an assumed or modeled deposition velocity. Thus, the magnitude of the chosen deposition velocity has a large influence on the calculated flux. For example, Chester et al., (1999) and Golomb et al., (1996) used this equation to calculate dry deposition fluxes assuming the Vd values.

$$F_d = V_d . C, \tag{2}$$

where F_d is the dry deposition flux of particles (mg m^{-2} d^{-1}), V_d is the overall particle dry deposition velocity (cm s^{-1}) and C is the particle phase air concentration (mg m^{-3}).

One of the reasons for the discrepancy between the estimated and experimental dry deposition fluxes is that deposition velocity is a function of particle size.

2.5 Sources of Trace Elements

There are several mechanisms for emission of trace metals into the air. Some metals are emitted as vapors and by condensation they form secondary aerosols (fumes). Some are emitted as particles from regulated sources in particle form. And some are introduced into the air by means of mechanisms such as reentrainment from less regulated sources as fugitives.

The observed removal of anthropogenic metals during transport to the natural surfaces is primarily due to coarse particles associated with fugitive dust emissions from various sources. Elements predominantly associated with mineral aerosols (crustal origin) have a strong refractory component and they are generally less soluble than elements having an anthropogenic origin (Migon et al., 1996).

Ca and Na associated with the coarse particle mode are originated mainly from sea salt. Mn, Cu, and Fe are neither fine, nor coarse particle elements, and their size distributions can be highly variable, depending on their production source which can be both natural and anthropogenic. This creates a strong impact on deposition velocities. For example the deposition velocity of Cu tends to fluctuate more than the other elements. The principle sources of anthropogenic Fe are soil, steel production and coal combustion; and for Mn soil, wood burning, and regional sulfate (Miller, 1996).

The principle sources of PM_{10} aerosol are distant fossil fuel power plants, wood burning and wind blown dust. The principle sources of non-crustal elements are incinerators (Cd, Cr, Sb, Zn, and Pb), coal (Se), steel (As), oil combustion (V), and possibly motor vehicles (Cd and Pb), (Miller, 1996).

Lead is associated with the fine particle mode and the majority of its compounds have wide-spread industrial applications. For example, it is used in the manufacture of accumulators. Organolead compounds are used as additives in fuel refineries and in the production of pigments as well as anticorrosive materials (Kettrup, 1991).

Chromium is used industrially in the production of steels and alloys. Its hexavalent compounds are used in chromium plating of metals, in the production of paints, pigments, and anticorrosive materials, in the textile, leather and wood preservatives, ceramic industries and as an oxidizing agent in the chemical industry (Kettrup, 1991).

Nickel is mainly used in the production of special steels. In addition, it is used to galvanize metal surfaces. Cadmium and zinc are emitted during municipal waste incineration (Miller, 1996). Zinc bearing aerosols originate from coal-fire power plant emissions, incinerator off-gases, vehicle exhausts, and urban road dust; while atmospheric copper is from coke dust, steel industries, blast furnace, vehicle exhaust, and urban dust (Paode et al., 1996).

2.6 Enrichment Factor

2.6.1 Sources

Trace metals in aerosols are derived from a variety of sources which include the Earht's crust, the oceans, volcanic activity, the biosphere, and a number of anthropogenic processes (e.g. fossil fuel burning, waste incineration, the processing of ores etc.). The degree to which a trace metal in air aerosol is enriched, or depleted, relative to a specific source can be assessed to a first approximation using an enrichment factor (EF_{crust}) (Chester et al., 1999).

The mass of trace elements in a given volume in air derived from crustal and oceanic sources can be estimated from some reference elements such as Al (or Fe), and Na (after correcting for crustal contribution), respectively (Herut et al., 2001). In this study, Al was used to estimate the enrichment factors relative to crustal composition according to the equation:

$$EF_{crust} = (Tr / Al)_{air} / (Tr / Al)_{crust} , \tag{3}$$

where $(Tr / Al)_{air}$ is the concentration ratio of the trace elements to Al in the suspended particles and $(Tr / Al)_{crust}$ is the average ratio in crustal material (Herut et al., 2001).

By convention, an arbitrary average EF_{crust} value of < 10 is taken as an indication that a trace metal in an aerosol has a significant crustal source, and these are termed the non-enriched elements (NEEs). In contrast, an EF_{crust} value of >10 is considered to indicate that a significant proportion of an element has a non-crustal source, and these are referred to the anomalously enriched elements (AEEs); however, when sufficient crustal material is present in the air, the AAEs can switch character and behave as NEEs. Although this is an essentially crude classification, it is useful in interpreting aerosol chemistry (Chester et al., 1999).

2.6.2 Mixing of Anthropogenic and Crustal Aerosol End-Members

The total mass of a certain particulate AEE in a given volume in air (Tr_{air}) is composed of :

$$Tr_{air} = Tr_{crust} + Tr_{antr} , \tag{4}$$

where the subscripts "crust" and "anth" designate crustal and anthropogenic fractions, respectively. Assuming all the Al in the air is of crustal origin;

$$Al_{air} = Al_{crust} , \tag{5}$$

then the mass of Tr_{crust} in aerosol population is given by;

$$Tr_{crust} = Al_{air} . (Tr / Al)_{crust} , \tag{6}$$

Substituting Eqs. (5) and (6) into Eq. (4) we obtain;

$$(Tr / Al)_{air} = (Tr / Al)_{crust} + (Tr_{anth} / Al_{air}), \tag{7}$$

By substituting Eq. (7) into Eq. (3) and rearranging we obtain;

$$EF_{crust} = 1 + (Tr_{anth} / Al_{air}) . (Al / Tr)_{crust,} \qquad (8)$$

Eq. (8) describes a linear mixing between two possible end-members: (a) "clean" crustal-derived particles characterised by $EF_{crust} = 1$ and (b) anthropogenic-derived particles. Within the EF_{crust} vs. $1/Al$ relationship, the slope of the line represents the term $Tr_{anth} . (Al / Tr)_{crust}$ from which Tr_{anth} can be estimated. Thus, polluted samples will exhibit higher slopes than relatively clean samples (Herut et al., 2001).

CHAPTER THREE

EXPERIMENTAL SECTION

3.1 Sample Collection

3.1.1 Description of Sampling Location

The sampling site is located approximately 10 km southeast of Izmir's center and surrounded by a growing coniferous forest. There are also residential areas located approximately 2 km southwest and a highway 0.5 km south of the sampling site. The general layout of the sampling site is presented in Figure 3.1.

3.1.2 Sampling Program and Meteorological Data

Twenty four dry deposition and ambient air samples were taken between September 2000 and June 2001 on the roof of a four-story building located on the Kaynaklar Campus of the Dokuz Eylul University, Izmir, Turkey. Four soil samples were taken at the end of the sampling program. All samples were collected during the daytime and average sampling time was 8 hours. Winter samples were taken on weekend days in order to avoid contamination from the building chimney which is in operation during weekdays. Average sampling volume for air samples was 230 m^3. Samples were exposed only when there was no rain.

Meteorological data was obtained from the meteorological station in Adnan Menderes Airport, Izmir (Figure 3.1). This station is the closest station to the sampling site. The relative humidity values were also obtained from the meteorological station in Güzelbahçe, Izmir (Figure 3.1). A summary of the sampling information (sampling date, sampling duration, sampling volume, and meteorological conditions) is provided in Table 3.1.
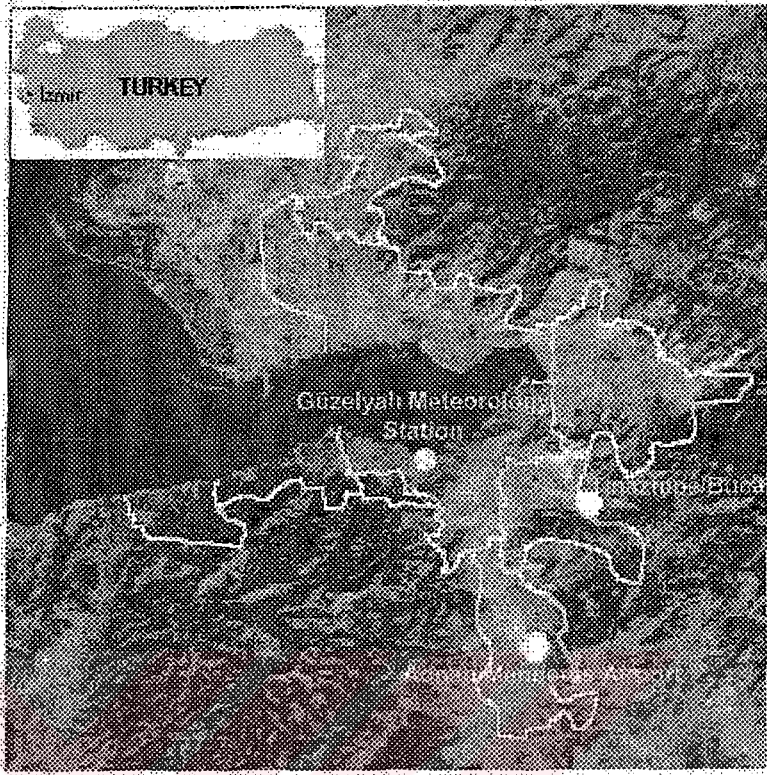
Figure 3.1 General Layout of the Sampling Site.

Table 3.1 Summary of Sampling Information*

Sample No	Date (day)	Sampling Hours	Sampling Time (Min)	Wind Speed (m/s)	Wind Direct (degree)	Relative Hum. (%)	Air Temp. (°C)
1	08.31.00	$09.^{30}-19.^{20}$	530	7.2	307	54.5	28.6
2	09.12.00	$08.^{50}-19.^{05}$	595	8.2	253	72.333	26.8
3	09.18.00	$09.^{15}-17.^{00}$	605	4.1	200	55.545	30.7
4	09.19.00	$09.^{25}-19.^{20}$	595	3.1	177	42	30.3
5	09.21.00	$09.^{10}-19.^{15}$	605	4.6	238	29.833	33.1
6	09.27.00	$09.^{30}-18.^{40}$	515	9.7	170	32.2	22.1
7	10.12.00	$09.^{30}-17.^{00}$	545	3.1	210	38.8	22.4
8	10.20.00	$09.^{30}-18.^{00}$	510	10.7	125	53.0	17.6
9	10.27.00	$09.^{40}-18.^{00}$	520	4.1	170	44.6	18.1
10	11.03.00	$10.^{00}-17.^{50}$	470	2.3	170	51.375	17.6
11	11.22.00	$10.^{00}-16.^{45}$	405	3.1	170	63	17.8
12	11.25.00	$09.^{20}-16.^{35}$	435	3.1	160	62	16.7
13	01.13.01	$10.^{15}-14.^{30}$	255	5.7	170	68.7	10.7
14	01.20.01	$09.^{45}-16.^{30}$	405	7.2	340	60	9.4
15	01.27.01	$10.^{15}-17.^{20}$	495	3.1	150	61.7	8.1
16	02.04.01	$09.^{30}-16.^{30}$	420	2.2	330	68.3	7.5
17	02.17.01	$10.^{00}-16.^{00}$	360	6.2	340	58	12.4
18	03.17.01	$10.^{00}-16.^{50}$	410	3.6	170	57	17.6
19	03.24.01	$10.^{00}-16.^{00}$	360	3.6	340	62.3	18.9
20	04.07.01	$10.^{00}-16.^{55}$	435	5.2	350	74.7	18.2
21	04.26.01	$09.^{15}-16.^{30}$	435	3.1	240	61.7	21.5
22	05.17.01	$10.^{00}-16.^{30}$	390	4.1	280	63.3	25.3
23	05.24.01	$10.^{00}-17.^{30}$	450	10.3	330	64.3	23.7
24	06.07.01	$10.^{00}-17.^{40}$	460	5.2	320	46	26.8

*Wind speed, relative humidity and temperatures were averaged over the sampling period.

3.1.3 Measurement of Dry Deposition Flux and Ambient Particle Concentrations

The particulate phase dry deposition flux was measured using a dry deposition plate. The plate used in this study was similar to those used in wind-tunnel studies. It was made of polyvinyl chloride (PVC) and was 22.2 cm long, 7.5 cm wide and 0.5 cm thick with a sharp leading edge (<10°) that was pointed into the wind by a wind vane. Five deposition plates and strips (378 cm^2 total exposed surface) were used. Each of the plates was covered on top with a Mylar strip (12.8 x 5.9 cm) coated with Apiezon L grease to collect impacted particles. Figure 3.2 shows the top and side view of the dry deposition plate.

Ambient particulate matter samples were collected on 20.3 x 25.4 cm glass fiber using a high-volume sampler.

3.1.4 Sample Preparation

Glass fiber filters were rinsed with 5% nitric acid solution and deionized (DI) water, wrapped loosely with aluminum foil, and dried in an oven at 105 °C for 6-8 hours. Then they were allowed to cool to room temperature in a desiccator for 30 minutes (Bagiroz, 2002; Odabasi et al., 1999).

Mylar was cut into strips (12.8 x 7.5 cm). Then, the strips were rinsed with 5% nitric acid solution and DI water. Cleaned Mylar strips were coated with Apiezon L grease heated on a hot plate using a small paintbrush. The dimensions of each of the greased strip area were 12.8 * 5.9 cm. Strips were mounted on dry deposition plates, and ungreased areas were protected with PVC covers to prevent exposure to deposited material during field sampling (Bagiroz, 2001; Odabasi et al., 1999; Paode et al., 1998; Yi et al., 1997a; Yi et al., 1997b)

High-volume sampler equipment, especially air filter table was cleaned prior to sampling. The Hi-volume sampler was calibrated for flow rates vs. flowmeter readings under laboratory conditions.

Four soil samples were collected at four different points around the sampling site at the end of the sampling program. Samples were taken manually and stored in beakers covered with aluminum foil until the analysis.
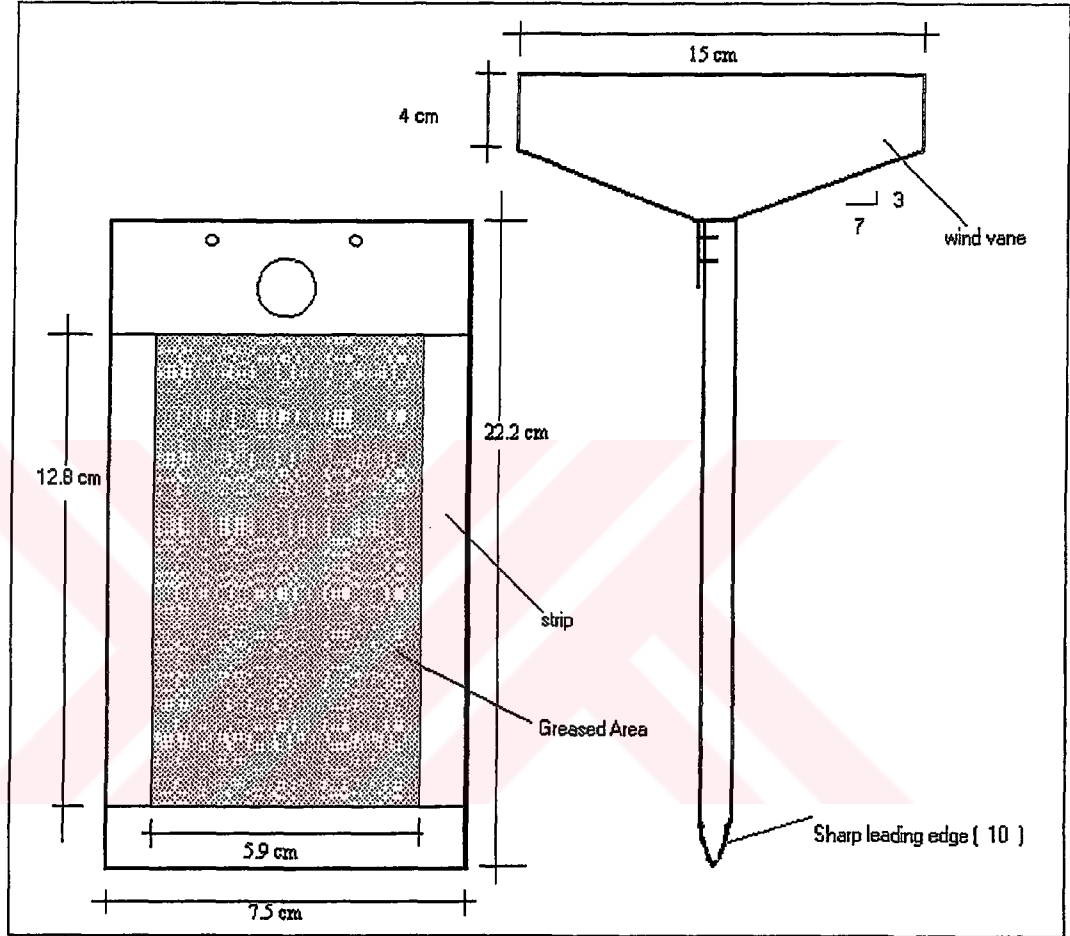
Figure 3.2 Top and Side View of Dry Deposition Plate.

3.1.5 Sample Handling

Cleaned and prepared glass fiber filters and dry deposition plates were transported to the field in their containers without allowing exposure to ambient air. After sampling, filters were wrapped with aluminum foil and placed into an aluminum storage box. The used plates were also placed in the aluminum storage box. Then, storage box covered with its own cover without allowing exposure to air during transport. Samples were brought back to the laboratory and stored in dark at room temperature until they were analysed. Plates were cleaned and placed into their containers until the following sampling.

3.2 Extraction and Analysis

3.2.1 Extraction

All equipment used for sample preparation and extraction were previously washed with detergent, then rinsed with water and soaked in the 5% nitric acid solution for several hours, rinsed with DI water and dried at room temperature before use to avoid any trace metal contamination.

After placing each greased strip into clean 500-mL polyethylene bottles, the strips were rinsed with about 125-mL of 20% nitric acid solution prepared from a stock of 65% (Riedel-deHaen 07006, highest purity). The polyethylene bottles were put into a water shaker for 24 h at 60 °C and 270 rpm to dissolve the particles from the grease into the nitric acid solution. Next, the strips were taken from the bottle and rinsed with a few drops of DI water into the bottle. Then the solution was transferred from the bottle to a clean 250-mL Teflon beaker, the bottle was rinsed with DI water 2-3 times, and the Teflon beaker was placed on a hot plate at a temperature of about 150 °C to evaporate the nitric acid solution until 5-10 mL of solution was left. An additional 20-mL of trace metal grade nitric acid was added to the beaker, and digestion continued until 10-15 mL of solution was left. The digested solution was filtered through filter (598 black ribbon, ashless, S&S Pare Circles Ø125 mm). The filtrates were stored in a clean 100-mL polyethylene bottles in dark until the analysis (Yi et al., 1997b).

The same extraction procedure was applied to the Hi-volume filters. Unused filters and strips from the same batch were extracted in the same way to determine the blank values.

1 g of each of the four soil samples was taken and digested with 125 ml of 25% nitric acid solution in a polyethylene bottles. The same extraction procedures were applied and analysed for trace metals.

3.2.2 Analysis

The strip, filter and soil samples were analysed for the crustal metals (Al, Ca, Fe and Mg) with a UNICAM 939 flame atomic absorption spectrometer (AAS). The other trace metals concentrations which are primarily anthropogenic origin (Pb, Zn, Cu, Cr, Cd, Ni, and Mn) were measured with a VARIAN 220 FS atomic absorption spectrometer with graphite furnace because the expected concentrations in the samples were much lower and a more sensitive method was needed. All trace metal concentrations were determined from respective calibration curves prepared by precisely known concentrations covering the expected ranges.

To prepare the calibration standards, a stock solution of the metal was prepared by dissolving 1 g of the metal from a soluble salt in DI water in a 1L volumetric flask (1g/L) for each trace metal. From this stock solution 1 mL were taken into a 100 mL volumetric flask and diluted with highly purified water (10 mg/L). These calibration standards were freshly prepared from the stock solutions for each series of analysis.

For crustal metal analysis, an acetylene flame AAS (UNICAM 939) was used. After the burner, the fuel gas and the sprayer were adjusted to optimum conditions, the calibration standards and sample solutions were directly sucked and injected into the flame and measured. The results were evaluated from the maximum extinction values for each concentration of the calibration standards.

The other trace metals of primarily anthropogenic origin (Pb, Zn, Cu, Cr, Cd, Ni, and Mn) were measured with a VARIAN 220 FS atomic absorption spectrometer with graphite furnace because of their lower concentration values. The analyses were made at the analytical chemistry department of IZSU, Izmir.

3.3 Quality Control

Background contamination of these metals was routinely monitored using operational blanks (unexposed Mylar strips and filters) that were processed simultaneously with field

samples. The largest amounts found in the dry deposition plate and filter blanks were 0.0391 mg for Ca and 0.4868 mg for Al, among the crustal trace metals. For the anthropogenic origin trace metals the largest amounts found in the dry deposition plate and filter blanks were 0.00731 mg and 0.02145 mg for Zn, respectively.

The limit of detection (LOD, mg) for the trace elements was calculated by repeated analysis of three blank samples. LOD was defined as the mean blank mass plus three standard deviations (Odabasi et al., 1999). LOD and standard deviation values of trace metals in dry deposition and aerosol blank samples were presented in Table 3.2. LODs averaged approximately 3-5% of the levels found in the samples. In general, trace metal amounts in the samples were substantially higher than LODs. Sample quantities exceeding the LOD were quantified and blank-corrected by subtracting the mean blank amount from the sample amount.

Table 3.2 The LODs for trace metals.

Trace Metals	LOD (mg)	
	Dry Dep. (strips)	Aerosol (filters)
Pb	0.0031	0.0011
Cr	0.0012	0.0027
Zn	0.0156	0.0224
Cd	0.0004	0.008
Cu	0.0008	0.0047
Ni	0.0005	0.0033
Mn	0.0003	0.0018
Mg	0.0059	0.9341
Al	n.d.	1.7432
Ca	0.0900	0.7265
Fe	0.0377	0.0322

Some of the samples (at least 15%) were analysed in duplicate. The difference between duplicate analyses was less than 5%. The extraction efficiencies were checked by spiking a known amount of trace metals into the unused greased strips and filters before

extraction. The recovery rate for flame AAS ranged from 96 to 99% and in the case of the graphite furnace AAS from 92 to 94%. As the recoveries were high, no recovery correction was made on samples.

3.4 Calculations

3.4.1 Ambient Air Concentration

Ambient air concentrations of trace metals were calculated as fallows:

$$C \ (mg \ m^{-3}) = m / V, \tag{9}$$

where m is the trace metal mass (mg) in the sample and V (m^3) is the sampled air volume. Trace metal mass (mg) was calculated by multiplying the concentration (mg L^{-1}) of the trace metal in extracted sample by the volume of the extracted sample (mL).

Sampled air volume V (m^3) was calculated using the sampling flow rate (Q, $m^3 \ s^{-1}$) determined from the calibration curve of the high volume sampler (Figure 3.3) and total sampling time (t, s):

$$V \ (m^3) = Q \ . \ t, \tag{10}$$
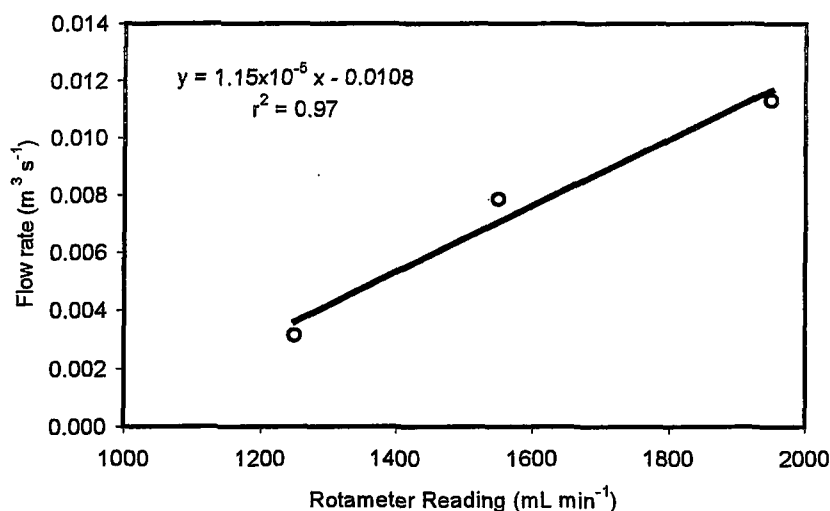
Figure 3. 3 Relationship between sampling flow rate and rotameter reading.

3.4.2 Dry Deposition Flux

In this study, a greased smooth surrogate surface was used to calculate particle dry deposition fluxes. Dry deposition fluxes were calculated by dividing the amount of trace metal deposited per unit area on the experimental plate by the sampling time. Eq. (11) was used to estimate dry deposition flux.

$$F_d = M_d / (A \cdot T), \tag{11}$$

where F_d is the trace metal dry deposition flux (mg m^{-2} d^{-1}), M_d is the particulate trace metal mass (mg), A is the greased strip area (m^2) and T is the sampling time (day).

3.4.3 Deposition Velocity

Particulate phase dry deposition velocities (V_d, cm s^{-1}) were calculated using the dry deposition fluxes measured with dry deposition plate and the ambient air concentrations (Eq. 1).

3.4.4 Enrichment Factor

In this study, equation (3) was applied using the average chemical composition of the soil samples taken around the deposition measurement station. The average mass of Al in soil was used to calculate EF$_{crust}$ values.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Ambient Concentrations

The average trace metal concentrations for Pb, Cr, Zn, Cd, Cu, Ni, Mn, Mg, Al, Ca and Fe were found as 110.79 ± 58.11, 10.46 ± 7.8, 733.38 ± 481.12, 8.43 ± 8.88, 154.2 ± 90.17, 38.99 ± 30.21, 134.92 ± 80.05, 3889.53 ± 1213.78, 145593.55 ± 103028.77, 40201.78 ± 19483.62 and 3438.04 ± 2553.98 in ng m^{-3}, respectively. For this study, the particulate trace metal concentrations in air (ng m^{-3}) were presented in Table 4.1.

Table 4.2 shows the summary of the average atmospheric particulate trace metal concentrations taken from the other studies. Especially, the average airborne concentrations of Al, Ca, Fe and Mg (which are primarily crustal origin) are higher in this study than the values obtained from the other studies shown in Table 4.2.

Ca, Al; Pb, Cu, Mn and Mg, Fe, Zn concentrations had similar seasonal variability (Figure 4.1). Lower concentration values were recorded during winter for Al and Fe while sometimes different temporal variability were observed for the other elements as shown in Figure 4.1.a and Figure 4.1.b.

Table 4.1 Atmospheric concentrations of trace metals in Izmir.

| Sample N.	Pb	Cr	Zn	Cd	Cu	M	Mn	Mg	Al	Ca	Fe
						C, ng/m³					
S1	142.14	19.91	934.59	1.42	176.84	30.78	255.60	5927.54	423853.30	86277.02	9464.91
S2	131.59	24.95	572.83	2.36	115.87	39.29	292.46	4262.42	292937.57	73433.38	7907.97
S3	113.47	14.03	1110.85	n.d.	47.10	17.37	138.64	2270.28	143975.17	24461.71	3015.26
S4	58.84	11.30	891.16	1.95	81.81	17.52	187.06	2315.32	172813.29	28650.37	3473.86
S5	103.49	15.12	508.13	2.52	45.53	33.57	268.26	5173.19	n.d.	40597.93	7745.33
S6	46.44	15.11	563.16	2.73	451.80	43.87	184.02	4109.39	14506.67	56550.06	5823.40
S7	129.86	3.51	330.95	2.14	84.57	35.85	76.98	2799.93	40992.86	34164.62	1266.67
S8	49.64	6.66	500.29	3.01	86.13	30.64	102.84	2600.27	87333.61	32323.34	1343.61
S9	60.64	4.76	245.32	3.24	90.51	29.30	77.18	2110.19	111125.66	14795.91	537.16
S10	118.84	4.85	327.76	8.84	83.20	19.53	100.08	4648.41	111179.60	28081.01	1957.76
S11	192.93	11.21	1343.54	31.83	253.05	44.09	116.77	4884.60	104352.40	55675.35	2895.86
S12	119.14	4.40	543.40	25.30	130.97	31.49	69.68	5102.41	124159.05	37896.91	1661.35
S13	168.26	4.23	518.11	21.59	233.95	135.81	73.08	4813.63	166359.28	26344.56	778.65
S14	35.18	8.34	325.66	21.61	97.63	37.75	63.13	3665.63	138646.40	34817.69	1376.71
S15	57.52	5.04	113.63	n.d.	72.07	16.62	27.68	1951.20	42154.03	14522.03	n.d.
S16	73.60	0.71	222.41	4.11	131.54	22.27	29.77	2114.76	84458.03	14467.34	1078.44
S17	201.29	9.32	602.42	3.42	183.52	99.90	135.77	4067.17	91805.95	49212.19	3865.41
S18	78.54	30.34	1412.32	n.d.	270.01	32.71	96.48	5706.17	31331..21	29108.46	3617.97
S19	202.76	3.88	612.03	9.75	204.99	1752	176.55	5330.40	17951.28	69778.51	3454.31
S20	250.62	22.45	1886.20	10.26	159.66	101.44	312.17	4334.54	120192.62	67601.56	6709.88
S21	52.84	7.06	1488.49	5.63	180.27	30.53	108.04	3975.29	225274.95	30176.95	1782.44
S22	71.99	14.97	1377.12	5.62	221.92	23.15	110.78	3884.00	230080.54	35890.35	2678.51
S23	88.35	0.95	n.d.	7.72	146.59	13.40	75.86	3330.47	n.d.	29333.22	1262.69
S24	111.08	8.03	437.42	2.05	151.32	31.39	159.23	3971.57	n.d.	50682.25	5376.72
Avg.	110.79	10.46	733.38	8.43	154.20	38.99	134.92	3889.53	145593.55	40201.78	3438.04
Std. Dev.	58.11	7.80	481.12	8.88	90.17	30.21	80.05	1213.78	103028.77	19483.62	2553.98
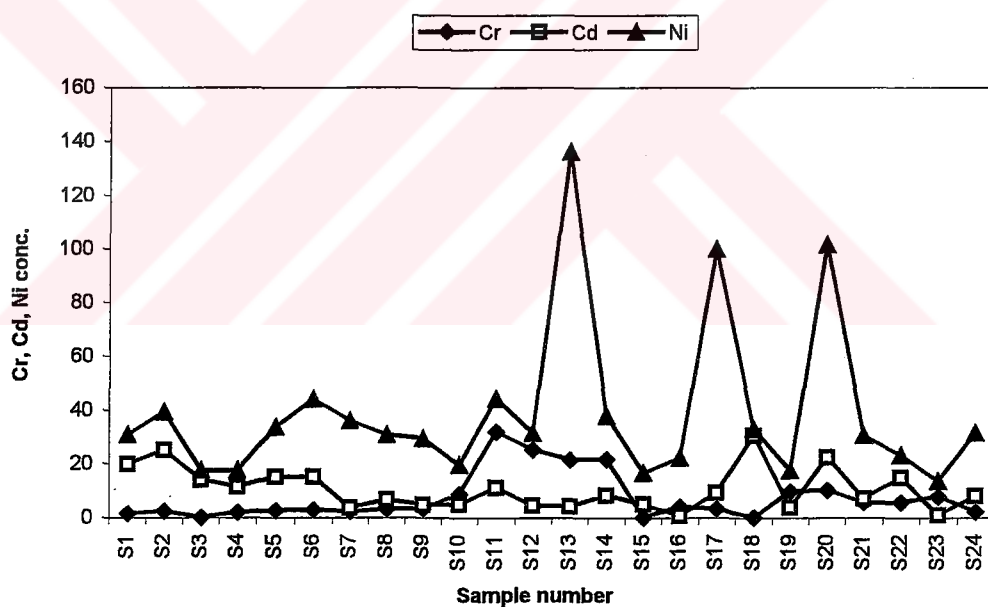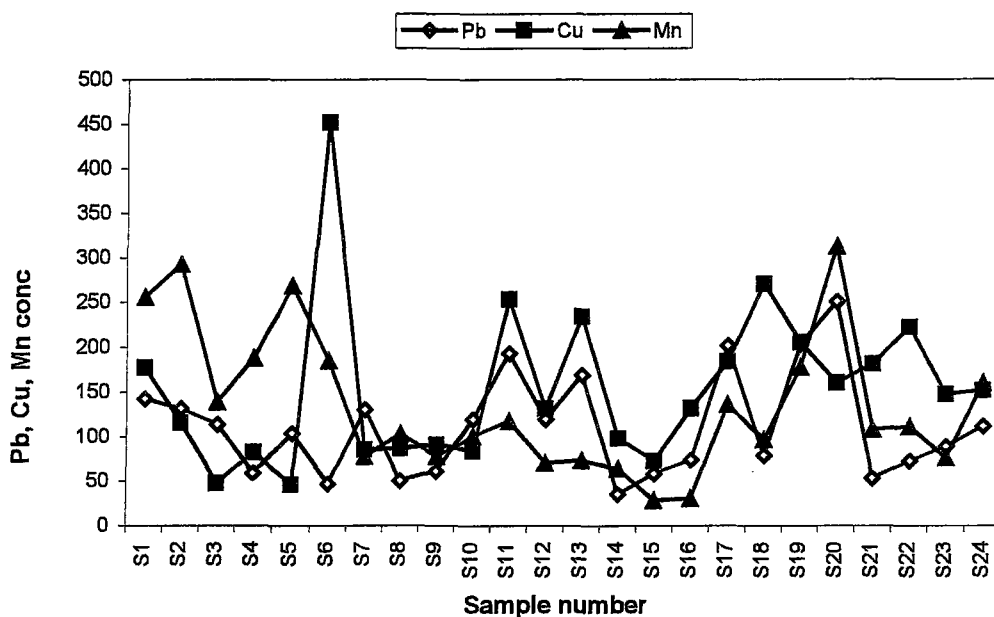
Figure 4.1.a The particle concentrations of Pb, Cu, Mn, Cr, Cd and Ni in air over the different time periods in Izmir.
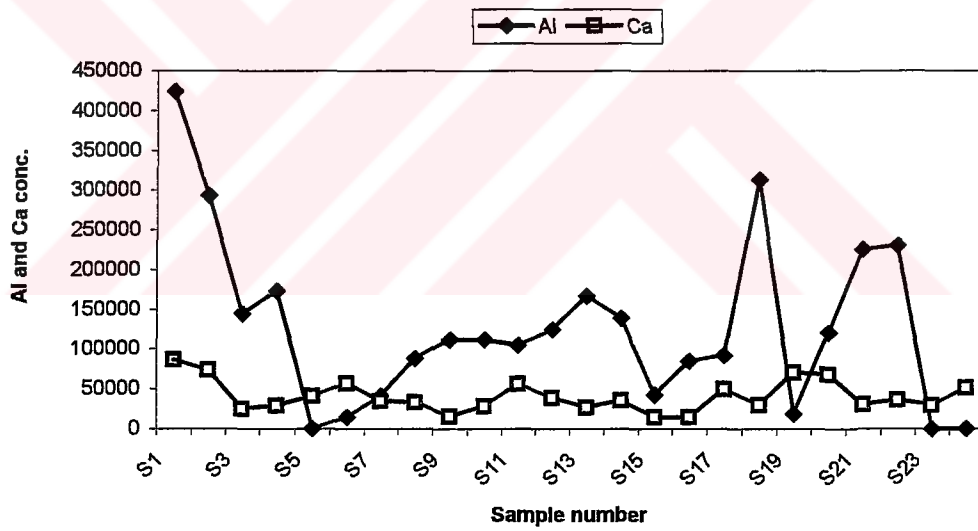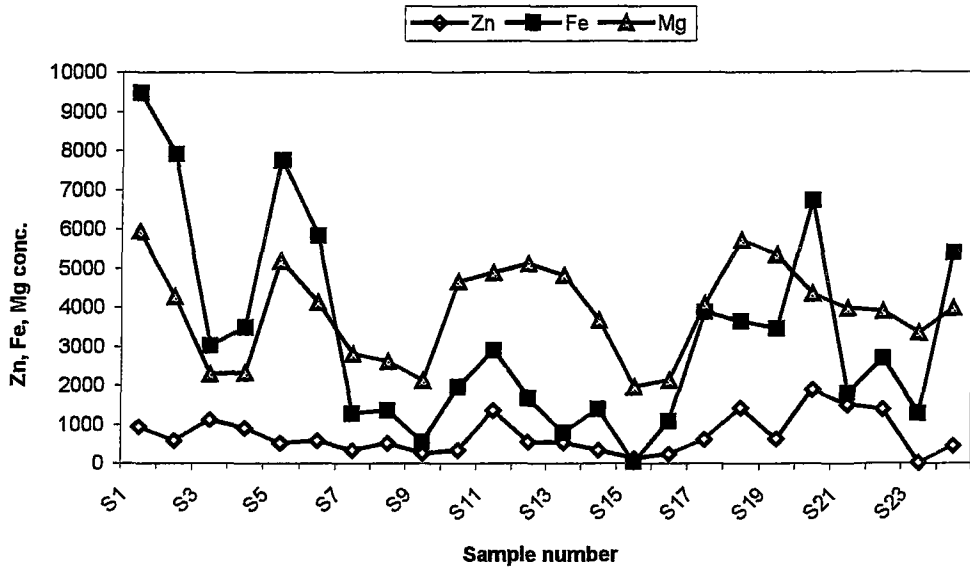
Figure 4.1.b The particle concentrations of Zn, Fe, Mg, Al and Ca in air over the different time periods in Izmir.

Table 4.2 Statistical summary of the average particulate trace metal concentrations in air (ng m^3) taken from other similar studies.

Al	Ca	Fe	Mg	Cd	Cr	Cu	Mn	Ni	Pb	Zn	Location
788	-	685	-	0.23	4.0	7.2	18.1	-	48.9	63.0	M. Michael[a]
865	-	787	-	0.24	2.4	5.7	15.7	-	34.2	89	Northern Israel[a]
685	-	685	-	0.19	8.5	-	12.6	-	30	19	Erdemli Turkey[a]
318	-	275	-	0.7	2.9	5.0	11.0	-	40	41	Europan Coastal Sites[a]
44.2	-	329	-	-	2.7	7.0	12.5	3.36	67.3	51.8	Cap Farrat[b]
167	481	-	182	-	-	4.7	9.0	-	-	-	Lake Michigan[c]
616	1151	589	-	-	1.9	9.9	15.8	0.67	14.3	39	IIT- Chicago[d]

[a]Herut et al., 2001.

[b]Chester et al., 1999

[c]Zufall et al., 1998

[d]Pirrone & Keeler, 1995

4.2 Dry Deposition Flux

Table 4.3 shows the dry deposition fluxes of trace metals measured over the different time periods in Izmir.

The measured average Al, Ca, Fe and Mg fluxes were 23.454 ± 16.8, 43.1 ± 31.5, 12.09 ± 6.97 and 3.10 ± 2.45 (mg m^{-2} d^{-1}), respectively. Since the crustal metals were primarily derived from fugitive dust emissions, it is likely that their sources account for much of the mass flux. Al, Ca and Fe dry deposition fluxes were significantly higher than the flux of Mg. The most probable cause for this difference is that a significant fraction of the flux is due to large particles which have large dry deposition velocities. Figure 4.2 shows the dry deposition fluxes of crustal trace metals measured over the different time periods in Izmir.

The average Al and Ca fluxes were the highest of the other crustal metals possibly because of road/wind-blown dust, the source that accounts for much of the dry deposition flux of these metals.

The measured average dry deposition fluxes for Pb, Cr, Zn, Cd, Cu, Ni, Mn, Mg, Al, Ca and Fe were 0.219 ± 0.213, 0.0158 ± 0.0175, 1.9057 ± 0.8613, 0.0239 ± 0.0294, $0.1237 \pm .0.0903$, $0.1292 \pm .0.1039$ and $0.1350 \pm .0.1815$ (mg m^{-2} d^{-1}), respectively. The average Zn flux was the highest of the anthropogenic metals fluxes. Figure 4.3.a and Figure 4.3.b show the dry deposition fluxes of the anthropogenic trace metals measured over the different time periods in Izmir.

A comparison of the trace metal fluxes from the study with the measurements obtained the other studies was presented in Table 4.4.

Figure 4.2 shows the dry deposition fluxes of the crustal metals measured over the different time periods in Izmir. The fluxes of the crustal elements were at least an order of magnitude higher than anthropogenic elements as shown in Table 4.3.

It has been established by the receptor modelling that zinc bearing aerosol originate from coal-fire power plant emissions, incinerator off gases, vehicle exhaust, and urban road dust; while atmospheric copper is from coke dust, steel industries, blast furnace, vehicle exhaust, and urban dust (Paode, 1996).

Table 4.3 Dry deposition fluxes of trace metals in Izmir (mg m^{-2} d^{-1}).

Samp. N	Dry deposition fluxes									
	Pb	Cr	Zn	Cd	Cu	Ni	Mn	Mg	Al	Ca	Fe
S1	n.d.	n.d.	1.6797	n.d.	0.2475	0.2105	0.2374	2.5853	42.4953	43.6915	11.2799
S2	n.d.	0.0498	1.6805	0.0043	0.3259	0.4296	0.6829	5.1050	23.3460	118.2460	8.7808
S3	n.d.	0.0020	0.9937	0.0061	0.2920	0.0708	0.0567	0.8699	11.2516	21.0786	n.d.
S4	n.d.	n.d.	1.5153	n.d.	0.1504	0.1926	0.0668	0.9470	18.0359	20.5051	n.d.
S5	n.d.	n.d.	0.8760	n.d.	0.1726	0.1782	0.0506	0.7785	15.3236	19.6903	n.d.
S6	0.0885	0.0117	1.7382	0.0091	0.2259	0.2659	0.6026	10.1800	57.0164	n.d.	18.8845
S7	n.d.	n.d.	0.9050	0.0125	0.1023	0.0623	0.0262	3.4238	6.5766	25.4674	2.1482
S8	n.d.	n.d.	1.5990	n.d.	0.1663	0.2134	0.3155	6.9055	3.8360	120.9095	17.8443
S9	0.1339	n.d.	2.7948	0.0011	0.1034	0.0757	0.0439	2.1686	14.4593	21.5745	3.1631
S10	n.d.	n.d.	0.6081	0.0277	n.d.	0.0112	0.0105	1.9798	n.d.	21.0882	13.8546
S11	n.d.	n.d.	n.d.	0.0209	0.0322	0.0135	0.0273	1.6384	n.d.	19.6940	33.9783
S12	0.1220	n.d.	2.1339	0.0027	0.0286	0.0269	0.0226	1.1598	11.6300	25.7893	8.1926
S13	0.8583	n.d.	n.d.	0.0609	0.1525	0.2473	n.d.	8.6740	56.3509	101.1864	n.d.
S14	0.2158	n.d.	1.2388	n.d.	0.0236	0.0794	0.0284	2.4520	29.7213	24.5461	15.0960
S15	0.1301	0.0097	1.4835	0.0194	0.0496	0.0841	0.0868	0.4253	16.2481	15.5320	8.3690
S16	0.0555	n.d.	2.6087	0.0050	0.0430	0.0830	0.0768	3.2361	43.4419	53.8765	9.0163
S17	0.1727	0.0043	2.6702	n.d.	0.0575	0.0722	0.0522	4.0127	40.0959	42.1594	13.7500
S18	0.3255	n.d.	3.3312	0.0230	0.1082	0.0508	0.0121	2.1951	14.9194	15.2728	9.0688
S19	0.0285	n.d.	2.9093	0.1151	0.0426	0.1914	0.0540	2.5742	25.6462	53.6335	17.8284
S20	0.2572	n.d.	2.5767	0.0597	0.1220	0.0526	0.0229	2.3223	5.1983	39.1127	7.4588
S21	0.1393	n.d.	3.0915	0.0111	0.0373	n.d.	0.0947	2.9982	n.d.	33.8399	5.2338
S22	n.d.	n.d.	3.2752	0.0163	0.2301	0.0680	0.1521	1.7992	n.d.	64.2096	14.8631
S23	0.3241	0.0175	0.9730	n.d.	0.0924	0.0565	0.0947	1.7606	10.0424	29.1335	10.5508
S24	n.d.	n.d.	1.2422	0.0105	0.0383	0.2353	0.2885	4.1286	n.d.	61.0750	12.4355
Avg.	0.219	0.0158	1.9057	0.0239	0.1237	0.1292	0.1350	3.10	23.5	43.1	12.09
Std. Dev.	0.213	0.0175	0.8613	0.0294	0.0903	0.1039	0.1815	2.45	16.8	31.5	6.97

Table 4.4 The average dry deposition fluxes of trace metals (mg m^{-2} d^{-1}) reported previously.

Al	Mg	Ca	Fe	Pb	Zn	Cd	Ni	Cu	Mn	Cr	Method	Period	Location
0.034	-	-	0.292	0.0035	0.014	0.0004	0.0025	0.0055	0.0073	0.0034	Bucket type collector	September 1992-September 1993	Nahant and Truro MA[a]
0.189	0.259	0.965	-	-	-	-	-	0.0055	0.0033	-	Dry dep. plate	July 1994-January 1995	Lake Michigan USA[b]
-	-	16.660-17.470	-	0.220-0.240	-	-	-	-	-	-	Water surface and dry dep. plate	May 1994 - September 1994	Commercial and residental, Illinois, USA[c]
-	-	-	-	0.003-0.070	0.004-0.200	-	-	0.007-0.060	-	-	Dry dep. plate	May-July 1994 January 1995	Chicago, Lake Michigan and South Haven, USA[d]
0.170-2.230	0.120-5.320	-	-	0.003-0.070	0.004-0.200	-	-	0.007-0.060	-	-	Dry dep. plate	Summer and fall 1994 winter 1995	Chicago, Lake Michigan and South Haven, USA[e]
0.072-1.704	-	-	-	0.006-0.250	0.010-0.460	0.002-0.005	-	0.020-0.250	-	0.002-0.032	Dry dep. plate	December 1993-October 1995	Urban and non-urban USA[f]
-	-	-	-	0.007	0.114	0.00009	0.0018	0.0044	-	-	Automatic rain collector and filter holder	October 1995-July 1996	Cap Ferrat France[g]
1.362-1.493	-	-	1.1835-1.3589	0.0029-0.0042	0.0054-0.0077	0.00002	-	0.0005-0.0006	0.00003	0.0002-0.00035	Plastic surrogate surface	October 1994-May 1998	Meagan Micheal and Tel Shikmona Israel[h]
0.329-0.381	-	-	0.2411-0.2822	0.0051-0.0058	0.0045-0.0087	-	0.0009-0.0029	0.0006-0.0033	0.0057-0.0108	0.0010-0.00233	Slightly conical surrogate plate	September, October 88 and February, July 1989	Cap Ferrat France[k]
-	-	7.072	-	0.127	-	-	-	-	-	-	Dry dep. plate	June-October 1991	Commercial and residential area,USA[l]
23.454	3.096	43.1	12.09	0.219	1.9057	0.0239	0.1292	0.1237	0.1350	0.0158	Dry dep. plate	September 2000-June 2001	Suburban, Izmir, Turkey[m]

[a]Golomb et al., 1996, [b]Zufall et al., 1998, [c]Yi et al., 1998, [d]Paode et al., 1998, [e]Sofuoglu & Holsen, 1997, [f]Paode et al.,1996, [g]Migon et al.,1996, [h]Herut et al., 2001, [k]Chester et al., 1999, [l]Lin et al., 1993, [m]This study

Figure 4.2, 4.3.a and Figure 4.3.b show the fluxes of trace metals measured over different time periods in Izmir. For anthropogenic metals Mn and Cu dry deposition fluxes had similar seasonal variability. Pb fluxes were higher in winter and spring. These fluxes were lower in winter than during the rest of the sampling periods. Sometimes different temporal varieties were observed for Ca, Fe and Mg. Higher fluxes were recorded during autumn and winter for Fe and Al.

Seasonal variability in crustal elemental aerosol concentrations, which enhanced concentrations (by 2 –3 times) in the summer period has also been noted at collection sites located on the Turkish Mediterranean Coast (Herut et al., 2001). The enhancement was attributed to greater re-suspension of soil particles during the dry summer months and minimum aerosol generation from damp soil surfaces in the winter.
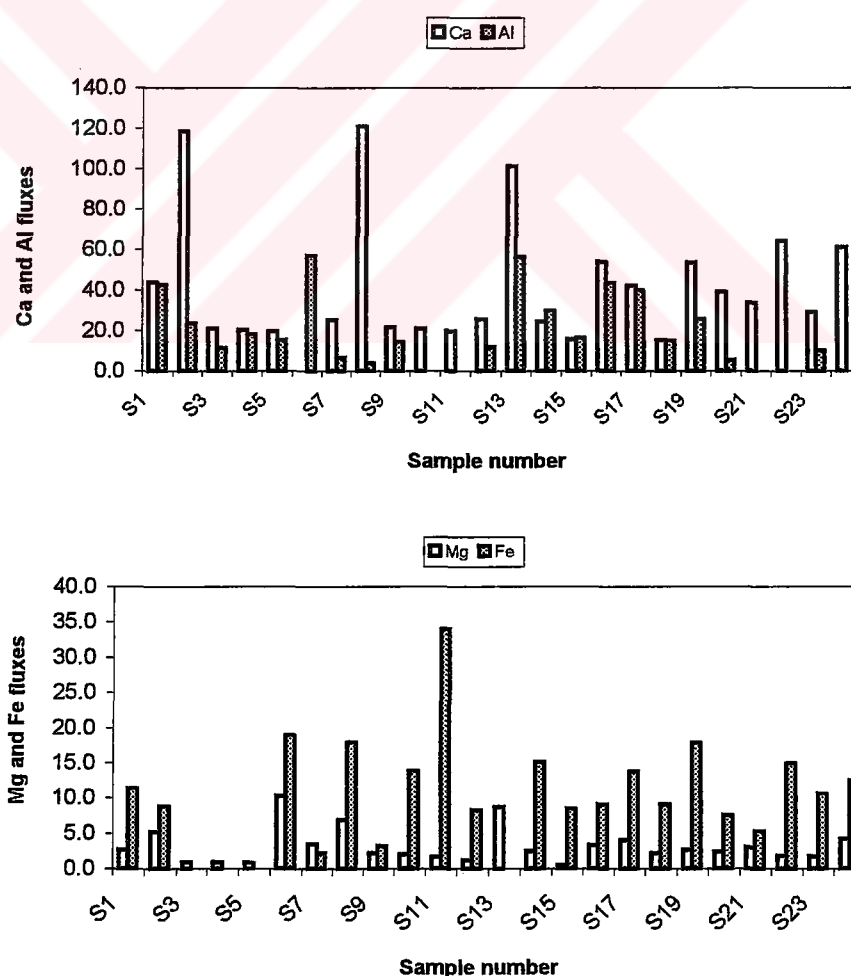

Figure 4.2 Dry deposition fluxes of crustal trace metals (Ca, Al, Mg and Fe) in Izmir (mg m^{-2}d^{-1}).
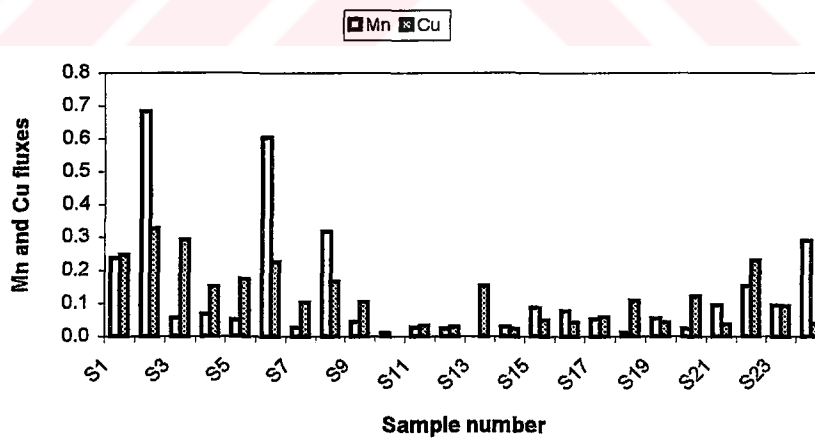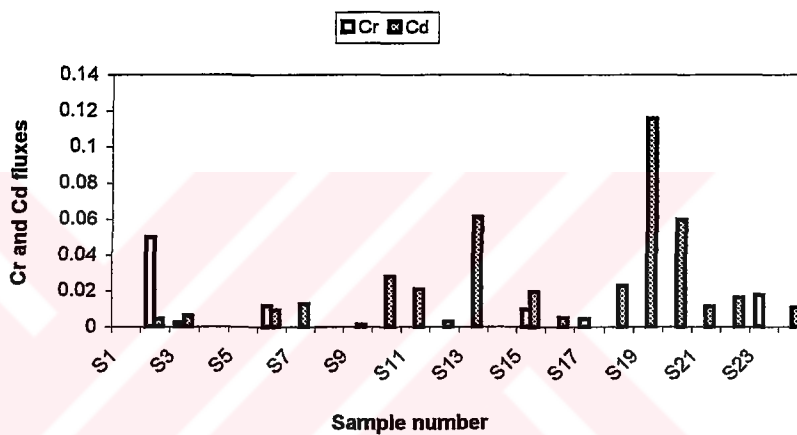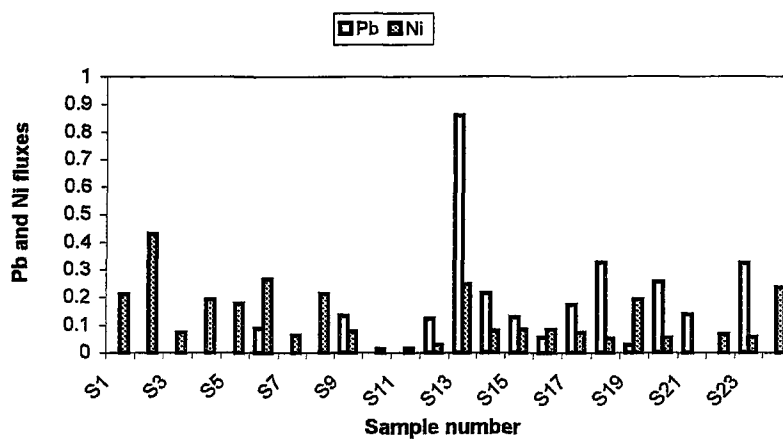
Figure 4.3.a Dry deposition flux of anthropogenic trace metals (Pb, Ni, Cr, Cd, Mn and Cu) in Izmir (mg m^{-2} d^{-1}).
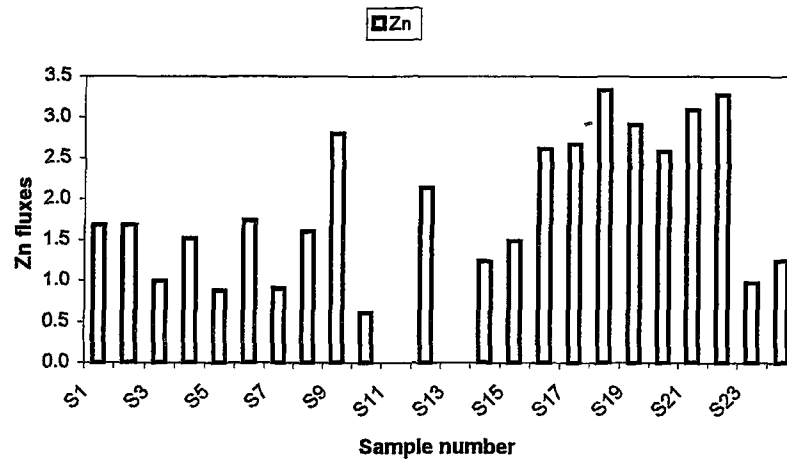
Figure 4.3.b Dry deposition flux of anthropogenic trace metals (Zn) in Izmir (mg m^{-2} d^{-1}).

4.3 Dry Deposition Velocities of Trace Metals

The overall dry deposition velocities of trace metals were calculated by using Eq. (1). All deposition velocities were averaged in order to integrate all the meteorological situations occurring during the sampling. The averaged V_d values were 0.98 ± 0.79, 0.55 ± 1.10, 1.46 ± 1.22 and 6.15 ± 4.35 (cm s^{-1}) for Mg, Al, Ca and Fe which are crustal origin, and 2.84 ± 2.12, 1.2 ± 0.98, 4.63 ± 4.08, 3.62 ± 3.58, 1.35 ± 1.65, 4.95 ± 3.98 and 1.23 ± 1.25 (cm s^{-1}) for Pb, Cr, Zn, Cd, Cu, Ni and Mn which are anthropogenic origin, respectively. The dry deposition velocities of crustal and anthropogenic trace metals were presented in Table 4.5 for this study.

Table 4.5 Dry deposition velocities of trace metals.

Sample N.	Vd (cm s⁻¹)										
	Pb	Cr	Zn	Cd	Cu	Ni	Mn	Mg	Al	Ca	Fe
S1	n.d.	n.d.	2.08	n.d.	1.62	7.91	1.08	0.50	0.12	0.59	1.38
S2	n.d.	2.31	3.40	2.11	3.26	12.66	2.70	1.39	0.09	1.86	1.29
S3	n.d.	0.17	1.04	n.d.	7.17	4.71	0.47	0.44	0.09	1.00	n.d.
S4	n.d.	n.d.	1.97	n.d.	2.13	12.73	0.41	0.47	0.12	0.83	n.d.
S5	n.d.	n.d.	2.00	n.d.	4.39	6.15	0.22	0.17	n.d.	0.56	n.d.
S6	2.20	0.90	3.57	3.87	0.58	7.01	3.79	2.87	4.55	n.d.	3.75
S7	n.d.	n.d.	3.16	6.78	1.40	2.01	0.39	1.42	0.19	0.86	1.96
S8	n.d.	n.d.	3.70	n.d.	2.23	8.06	3.55	3.07	0.05	4.33	15.37
S9	2.56	n.d.	13.19	0.39	1.32	2.99	0.66	1.19	0.15	1.69	6.82
S10	n.d.	n.d.	2.15	3.63	n.d.	0.67	0.12	0.49	n.d.	0.87	8.19
S11	n.d.	n.d.	n.d.	0.76	0.15	0.35	0.27	0.39	n.d.	0.41	13.58
S12	1.19	n.d.	4.55	0.12	0.25	0.99	0.38	0.26	0.11	0.79	5.71
S13	5.90	n.d.	n.d.	3.26	0.75	2.11	n.d.	2.09	0.39	4.45	n.d.
S14	7.10	n.d.	4.40	n.d.	0.28	2.44	0.52	0.77	0.25	0.82	12.69
S15	2.62	2.22	15.11	n.d.	0.80	5.86	3.63	0.25	0.45	1.24	n.d.
S16	0.87	n.d.	13.58	1.40	0.38	4.31	2.99	1.77	0.60	4.31	9.68
S17	0.99	0.53	5.13	n.d.	0.36	0.84	0.44	1.14	0.51	0.99	4.12
S18	4.80	n.d.	2.73	n.d.	0.46	1.80	0.15	0.45	0.06	0.61	2.90
S19	0.16	n.d.	5.50	13.66	0.24	12.64	0.35	0.56	1.65	0.89	5.97
S20	1.2	n.d.	1.58	6.74	0.88	0.60	0.08	0.62	0.05	0.67	1.29
S21	3.1	n.d.	2.40	2.29	0.24	n.d.	1.01	0.87	n.d.	1.30	3.40
S22	n.d.	n.d.	2.75	3.36	1.20	3.40	1.59	0.54	n.d.	2.07	6.42
S23	4.25	n.d.	n.d.	n.d.	0.73	4.88	1.44	0.61	n.d.	1.15	9.67
S24	n.d.	n.d.	3.29	5.94	0.29	8.68	2.10	1.20	n.d.	1.39	2.68
Avg.	2.837	1.23	4.63	3.62	1.35	4.95	1.23	0.98	0.55	1.46	6.15
Std. Dev.	2.12	0.98	4.08	3.58	1.65	3.98	1.25	0.79	1.10	1.22	4.35

Table 4.6 Dry deposition velocities of trace metals reported previously (cm s^{-1}).

Al	Ca	Mg	Fe	Cd	Cr	Cu	Zn	Pb	Ni	Mn	Ref.
-	-	-	-	0.05	-	-	-	0.04	-	-	Migon et al., 96
-	-	-	-	7	-	0.8	5	0.1	0.9	-	Migon et al., 96
-	1.7-2.5	-	0.2	-	-	0.3-2.1	0.8-1	0.2-0.6	0.1-0.6	1.1	Foltescu et al., 96
-	-	-	0.5-7.5	-	-	0.08-1.6	0.05-0.66	1.3	1	0.7-6.4	Foltescu et al., 96
0.11	-	-	0.13	0.25	0.14	0.29	0.16	-	-	0.13	Quinn & Ondov, 98
-	-	-	1.3	-	-	1.3	0.6	0.2	0.5	3.5	Foltescu et al., 94
0.55	1.46	0.98	6.15	3.62	1.2	1.35	4.63	2.84	4.95	1.23	This study.

Reported values for the particulate phase average dry deposition velocities of trace metals were summarized in Table 4.6. In general, the agreement between the calculated velocity values in this study and reported values using similar techniques is good, although velocities are higher than elsewhere. This may be attributed to the deposition sampling techniques. In this study the sticky (greased) nature of the deposition plates assured the accumulation of material without subsequent reentrainment. This might cause higher capture of deposition material and showed more realistic velocities.

4.4 Enrichment Factors of Trace Metals

In the dry deposition samples, high EF$_{crust}$ (>10) were calculated for Cd, Zn, Pb, Mg, Ni and Fe due to their dominant anthropogenic source (representing the group of the so-called anomalously enriched elements - AEEs) and relatively low median EF$_{crust}$ values (< 10) were calculated for Cu, Ca, Cr and Mn (they belong to the non-enriched elements-NEEs). Ni has a minor EF value (9.7) in dry deposition samples. This trace metal behaves as an AEE in dry deposition, but it is characterised as a NEE (EF=0.5) in the aerosol. EF$_{crust}$ values of trace metals in aerosol and dry deposition samples for this study were presented in Table 4.7 and Table 4.8, respectively.

The AEEs (Cd, Zn, Pb, Mg and Fe) are derived from both crustal and anthropogenic compenets, and there are relatively large variations in their EF values in dry deposition samples. For these elements, there were lower EF values (< 10) in aerosol samples.

Cr, Cu, Mn and Ca all behave as NEEs, in both the dry deposition and aerosol samples while Pb, Zn, Cd, Ni, Mg and Fe have higher EF values which behave as AEEs only in dry deposition samples.

In the parent aerosol, all trace metals behave as NEEs. For these NEEs there is generally little variation in their EFs. NEEs are crust-dominated in both types of atmospheric materials.

The sequence of EF_{crust} values were Cd>Zn>Pb>Fe>Mg>Ni>Cu>Ca>Cr>Mn and Cd>Mg>Pb>Zn>Cu>Fe>Ca>Ni>Cr>Mn, in dry deposition and the parent aerosol samples, respectively for this study. A comparison of the EF_{crust} values from the present study with those observed at another Eastern Mediterranean coastal sites was presented in Table 4.9. Fe, Ni, Pb and Cd EF values in dry deposition are higher for this study than for the other studies. The EF values for Zn, Pb, Cu and Ni in aerosol are lower for this study than at Cap Ferrat while Fe, Mn and Cr values are similar.

On the basis of the EF values, the dry deposition has a much more homogenous character than the parent aerosol, presumably because it is dominated by larger-size material having a generally similar composition (Chester et al., 1999).

Enrichment factors for crustal and anthropogenic origin trace metals were presented in Figure 4.4, Figure 4.5.a, Figure 4.5.b and Figure 4.5.c, respectively.

Table 4.7 EF$_{crust}$ values of trace metals in aerosol samples in Izmir.

Sample N.	Aerosol EF$_{crust}$ values										
	Pb	Cr	Zn	Cd	Cu	Ni	Mn	Al	Mg	Ca	Fe
S1	0.618	0.065	0.438	0.158	0.190	0.078	0.058	1	0.951	0.199	0.609
S2	0.827	0.118	0.388	0.380	0.180	0.143	0.096	1	0.990	0.246	0.736
S3	1.451	0.136	1.532	n.d.	0.149	0.129	0.092	1	1.073	0.166	0.571
S4	0.627	0.091	1.024	0.532	0.215	0.108	0.104	1	0.911	0.162	0.548
S5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S6	5.895	1.449	7.710	8.880	14.150	3.228	1.215	1	19.270	3.818	10.941
S7	5.834	0.119	1.603	2.460	0.937	0.933	0.180	1	4.646	0.816	0.842
S8	1.047	0.106	1.138	1.623	0.448	0.374	0.113	1	2.025	0.363	0.419
S9	1.005	0.060	0.438	1.375	0.370	0.281	0.067	1	1.292	0.130	0.132
S10	1.969	0.061	0.586	3.750	0.340	0.188	0.086	1	2.844	0.247	0.480
S11	3.405	0.149	2.557	14.389	1.102	0.451	0.107	1	3.184	0.523	0.756
S12	1.767	0.049	0.869	9.611	0.479	0.271	0.054	1	2.796	0.299	0.365
S13	1.863	0.035	0.619	6.122	0.639	0.871	0.042	1	1.968	0.155	0.128
S14	0.467	0.084	0.467	7.352	0.320	0.291	0.044	1	1.799	0.246	0.271
S15	2.513	0.166	0.535	n.d.	0.777	0.421	0.063	1	3.149	0.337	n.d.
S16	1.605	0.012	0.523	2.296	0.708	0.281	0.034	1	1.703	0.168	0.348
S17	4.038	0.141	1.303	1.757	0.908	1.161	0.142	1	3.014	0.525	1.148
S18	0.462	0.135	0.895	n.d.	0.392	0.111	0.029	1	1.239	0.091	0.315
S19	20.801	0.301	6.771	25.633	5.188	1.042	0.942	1	20.200	3.807	5.245
S20	3.840	0.260	3.117	4.028	0.604	0.901	0.249	1	2.453	0.551	1.522
S21	0.432	0.044	1.312	1.178	0.364	0.145	0.046	1	1.200	0.131	0.216
S22	0.576	0.091	1.189	1.153	0.438	0.107	0.046	1	1.148	0.153	0.317
S23	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S24	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Avg.	2.9	0.2	1.7	5.1	1.4	0.5	0.2	1	3.7	0.6	1.3
Std. Dev.	4.4	0.3	2.0	6.4	3.1	0.7	0.3	n.d.	5.4	1.1	2.5

Table 4.8 EF$_{crust}$ values of trace metals in dry deposition samples in Izmir.

Sample N.	Dry deposition EF$_{crust}$ values										
	Pb	Cr	Zn	Cd	Cu	Ni	Mn	Al	Mg	Ca	Fe
S1	n.d.	n.d.	7.851	n.d.	2.646	5.286	0.535	1	4.139	1.007	7.235
S2	n.d.	2.967	14.296	8.666	6.342	19.641	2.802	1	14.875	4.961	10.251
S3	n.d.	0.252	17.540	25.611	11.789	6.711	0.483	1	5.259	1.835	n.d.
S4	n.d.	n.d.	16.687	n.d.	3.788	11.399	0.355	1	3.572	1.114	n.d.
S5	n.d.	n.d.	11.353	n.d.	5.118	12.413	0.316	1	3.456	1.259	n.d.
S6	2.857	0.287	6.055	7.545	1.800	4.976	1.012	1	12.146	n.d.	9.027
S7	n.d.	n.d.	27.330	89.794	7.066	10.104	0.381	1	35.415	3.793	8.903
S8	n.d.	n.d.	82.789	n.d.	19.699	59.373	7.877	1	122.462	30.871	126.787
S9	17.052	n.d.	38.389	3.569	3.248	5.590	0.291	1	10.203	1.461	5.962
S10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S11	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S12	19.317	n.d.	36.442	10.993	1.118	2.467	0.186	1	6.784	2.172	19.200
S13	28.052	n.d.	n.d.	50.940	1.230	4.684	n.d.	1	10.471	1.759	n.d.
S14	13.370	n.d.	8.278	n.d.	0.361	2.853	0.092	1	5.612	0.809	13.844
S15	14.744	0.827	18.134	56.232	1.387	5.522	0.512	1	1.781	0.936	14.039
S16	2.354	n.d.	11.926	5.414	0.449	2.038	0.169	1	5.067	1.215	5.657
S17	7.933	0.147	13.227	n.d.	0.651	1.922	0.125	1	6.808	1.030	9.347
S18	40.179	n.d.	44.345	72.612	3.296	3.636	0.078	1	10.009	1.003	16.567
S19	2.050	n.d.	22.530	211.771	0.754	7.963	0.202	1	6.828	2.048	18.947
S20	91.126	n.d.	98.449	542.075	10.664	10.807	0.422	1	30.391	7.369	39.108
S21	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S22	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S23	59.437	2.430	19.243	n.d.	4.180	6.002	0.903	1	11.926	2.841	28.635
S24	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Avg.	24.9	1.2	27.5	90.4	4.5	9.7	0.9	1	16.2	3.6	22.2
Std. Dev.	26.9	1.2	25.5	153.9	5.0	12.8	1.8	n.d.	27.2	6.8	30.3

Table 4.9 Statistical summary of the EF$_{crust}$ values of the trace metals.

Al	Ca	Fe	Mg	Cd	Cr	Cu	Mn	Ni	Pb	Zn	Location
1	-	1.2	-	-	6	27	2.9	10	1129	16f[e]	Cap Ferrat[a]
1	-	1.1	-	-	2.7	15	1.6	2.8	114	35[f]	
1	-	2.3	-	228	6.4	21	2.4	-	159	117	Northern Israel[b]
1	-	2.5	-	228	29	-	2.5	-	176	31	Erdemli, Turkey[c]
1	-	2.2	-	1806	21	51	4.6	-	506	146	Europan Coastal Sites[d]
1	0.6	1.3	3.7	5.1	0.2	1.4	0.2	0.5	2.9	1.7[e]	Izmir, Turkey
1	3.6	22.2	16.2	90.4	1.2	4.5	0.9	9.7	24.9	27.5[f]	(This study)

[a]Chester et al., (1999).

[b]Herut et al., (2001).

[c]Herut et al., (2001).

[d]Herut et al., (2001).

[e]In aerosol samples.

[f]In dry deposition samples.
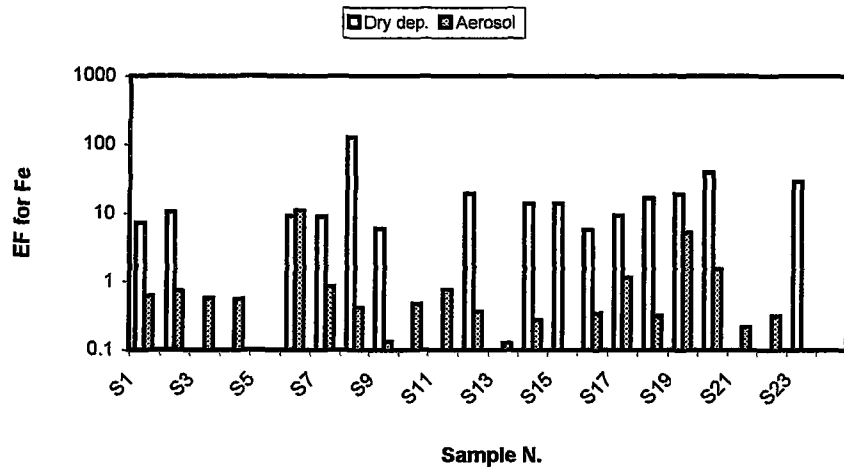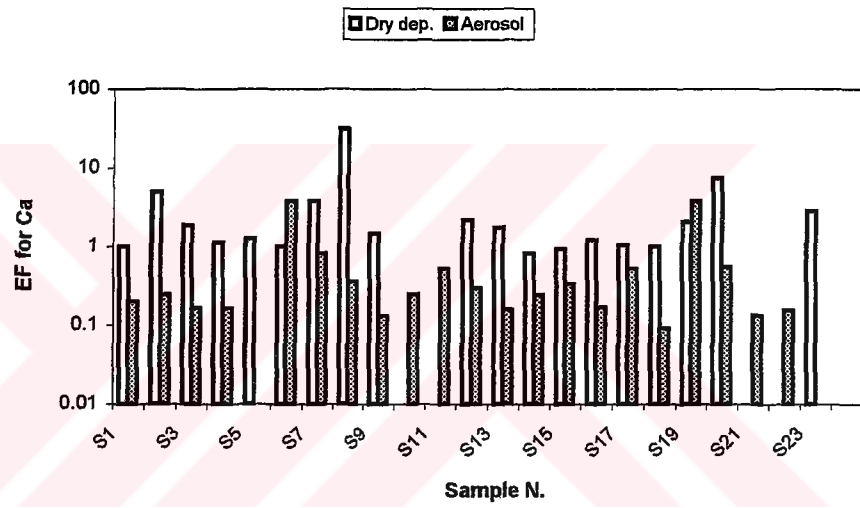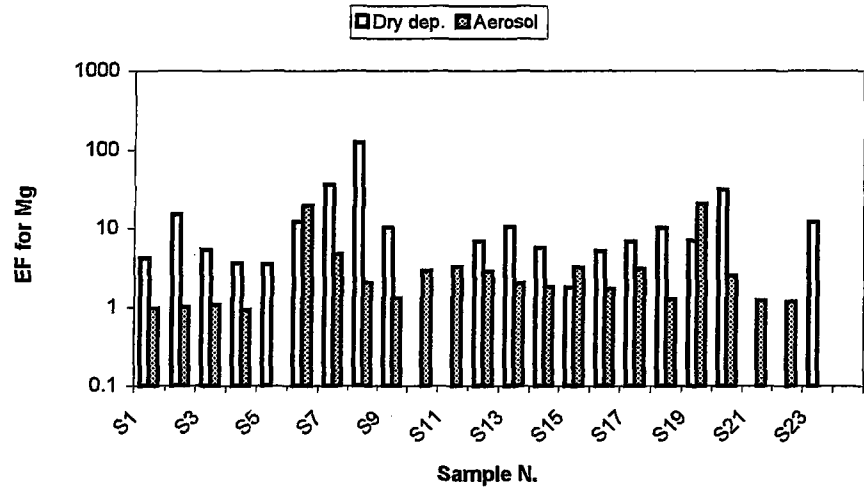
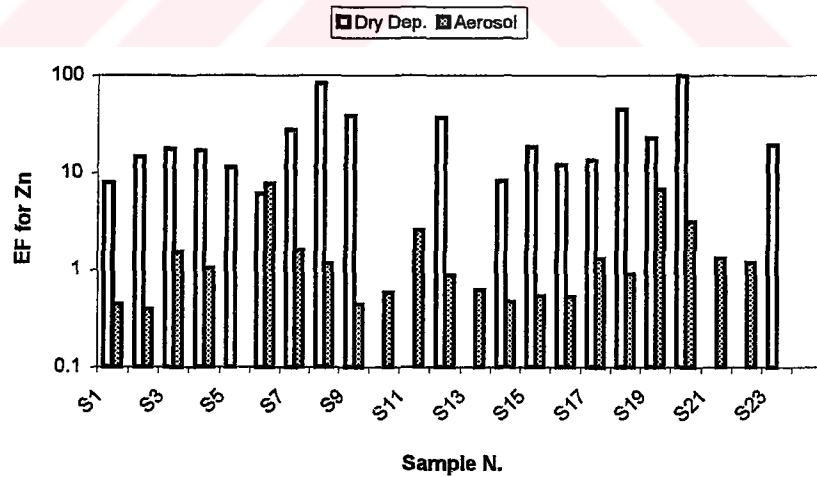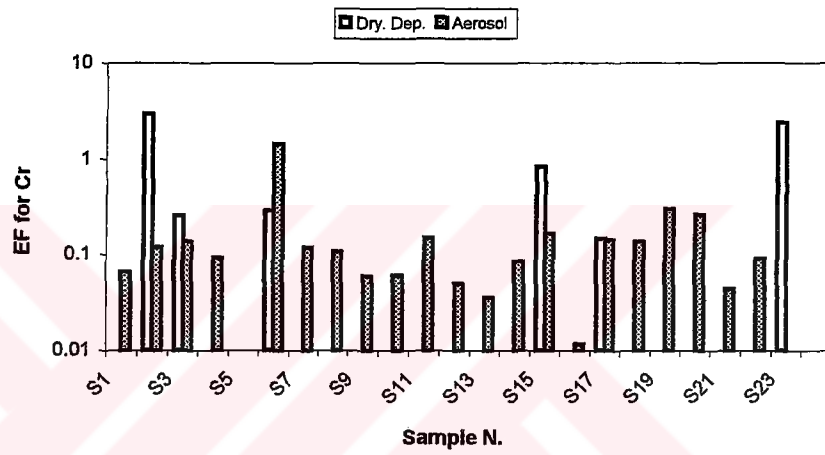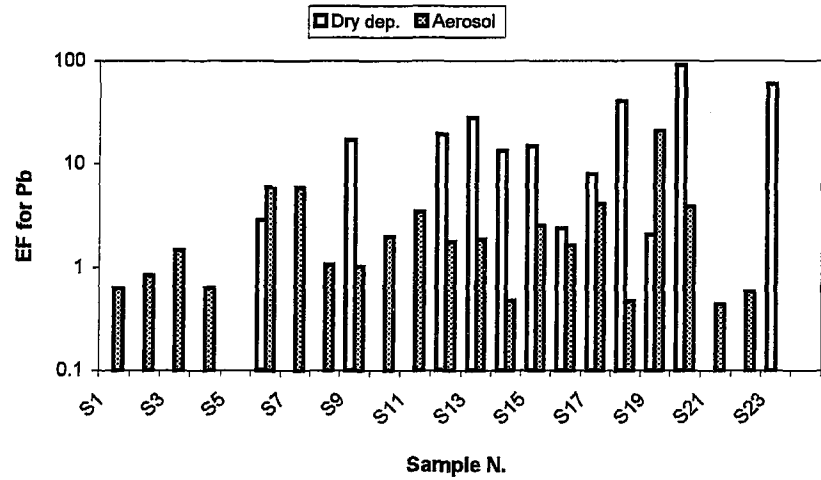**Figure 4.4 EF variations for crustal metals (Mg, Ca, Fe) in Izmir.**

Figure 4.5.a EF variations for anthropogenic metals (Pb, Cr, Zn) in Izmir.

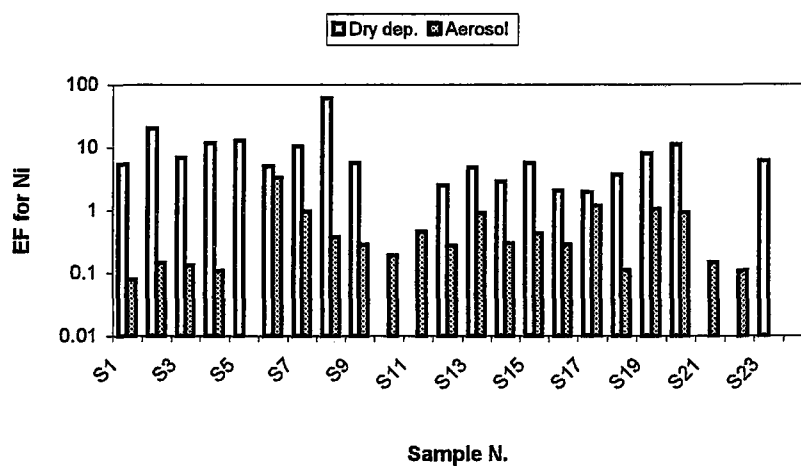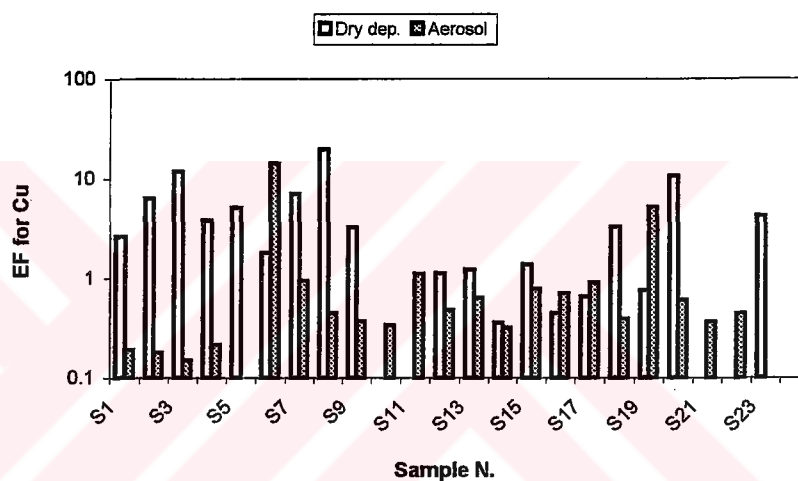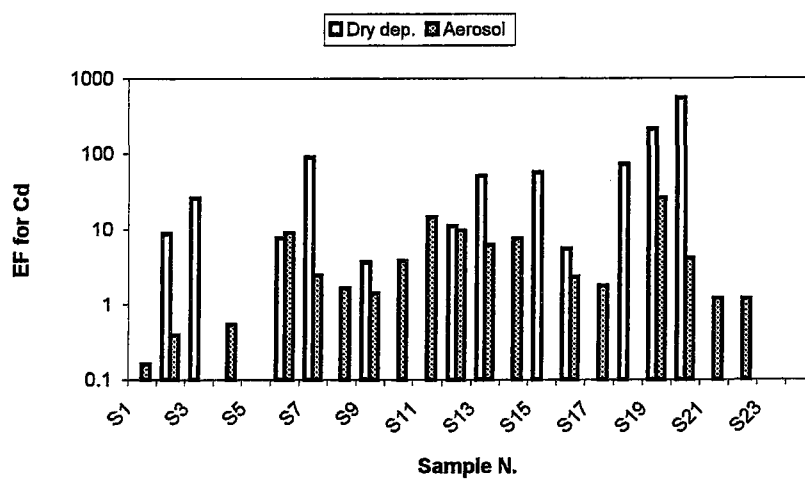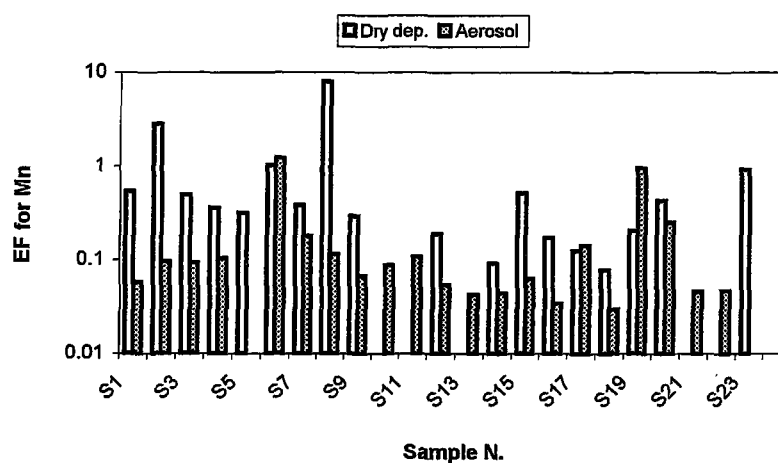Figure 4.5.b EF variations for anthropogenic metals (Cd, Cu, Ni) in Izmir.

Figure 4.5.c EF variations for anthropogenic metals (Mn) in Izmir.

4.5 The Soil Samples

Four soil samples were collected at four different points around the sampling site at the end of the sampling program. The averaged amount of Al in soil was used to calculate EF_{crust} values. Table 4.10 shows the average mass of trace metals for soil samples (mg/g soil sample).

Table 4.10 The average mass of crustal trace metals for soil samples in Izmir.

The average amount of trace metals (mg/g soil sample)										
Al	Ca	Fe	Mg	Pb	Cr	Zn	Cd	Cu	Ni	Mn
37.63	38.393	1.379	0.553	0.02	0.027	0.189	0.0008	0.083	0.035	0.392

CHAPTER FIVE
CONCLUSIONS

The most important conclusions derived from the present study may be summarized as follows:

1. Two main associations of particulate anthropogenic (Cd, Cr, Cu, Mn, Ni, Pb and Zn) and crustal (Al, Ca, Fe and Mg) elements were detected. The composition of Cd, Zn, Pb, Fe, Mg and Ni in dry deposition indicated their dominant anthropogenic origin exhibited by their high EF_{crust} values (>10).

2. Cr, Cu, Mn and Ca all behave as NEEs, in both the dry deposition and aerosol samples while Pb, Zn, Cd, Ni, Mg and Fe have higher EF (>10) values which behave as AEEs only in dry deposition samples. In the parent aerosol, the trace metals all behave as NEEs. For these NEEs there is generally little variation in their EFs. NEEs are crust-dominated in both types of atmospheric materials.

3. The AEEs (Pb, Zn, Cd, Ni, Mg and Fe) are derived from both crustal and anthropogenic sources.

4. Higher concentrations of crustal derived elements (NEEs) and anthropogenic elements (AEEs) were detected at Izmir, Turkey compared to the values obtained from the other studies (Table 4.2).

5. The dry deposition is dominated by primarily crustal origin elements. The fluxes of these elements at least an order magnitude higher than anthropogenic elements.

6. The average Zn and Ca fluxes were the highest of the anthropogenic and crustal metal fluxes, respectively.

REFERENCES

Bağiröz, Ö. (2002). Sulfate Dry Deposition in Izmir, MS Thesis, Graduate School of Natural and Applied Sciences, Dokuz Eylul University, Izmir, Turkey.

Chester, R., Nimmo, M. & Preston, M.R. (1999). The trace metal chemistry of atmospheric dry deposition samples collected at Cap Ferrat: A coastal site in the Western Mediterranean. Marine Chemistry, 68, 15-30

Dulac, F., Menard, P.B., Ezat, U., Melki, S. & Bergametti, G. (1989). Atmospheric input of trace metals to the Western Mediterranean: uncertainties in modelling dry deposition from cascade impactor data. Telus, 41B,362-378

Foltescu, V.L., Lindgren, E.S., Isakson, J., Öblad, M., Tiede, R., Sommar, J., Pacyna, J.M. & Teorseth, K. (1996). Airborne concentrations and deposition fluxes of major and trace species at marine stations in Southern Scandinavia. Atmospheric Environment, 22, 3857-3872

Foltescu, V.L., Isakson, J., Selin, E. & Stikans, M. (1994). Measured fluxes of sulphur, chlorine and some anthropogenic metals to the Swedish West Coast. Atmospheric Environment, 28, 2639-2649

Golomb, D., Ryan, D., Eby, N. & Underhill, J. (1996). Atmospheric deposition of trace metals onto Massachusetts Bay. Atmospheric Deposition to the Great Waters, VIP-72, EPA, 41-47

Herut, B., Nimmo, M., Medway, A., Chester, R. & Krom, M.D. (2001). Dry atmospheric inputs of trace metals at the Mediterranean coast of Israel (SE Mediterranean): sources and fluxes. Atmospheric Environment, 35, 803-813

Kettrup, A. (1991). Analyses of Hazardous Subtences in Air, (Henschler, D.), Volume 1, Germany.

Lin, J.M., Fang, G.C., Holsen, T.M. & Noll, K.E. (1993). A comparison of dry deposition modeled from size distribution data and measured with a smooth surface for total particle mass, lead and calcium in Chicago. Atmospheric Environment, 27A, 1131-1138

Lin, J.J., Noll, K.E. & Holsen, T.M. (1994). Dry deposition velocities as a function of particle size in the ambient atmosphere. Atmospheric Environment, 20, 239-252

McCready, D.I. (1986). Wind tunnel modeling of small particle deposition. Aerosol Science and Technology, 5, 301-312

Migon, C., Journel, B. & Nicolas, E. (1996). Measurements of trace metal wet, dry and total atmospheric fluxes over the Ligurian Sea. Atmospheric Environment, 31, 889-896

Miller, P.E. (1996). Estimation of annual trace element deposition to the Chesapeak Bay watershed. Atmospheric Deposition to the Great Waters, VIP-72, EPA, 63-72

Odabaşı, M., Sofuoğlu, A., Vardar, N., Taşdemir, Y. & Holsen, T.M. (1999). Measurement of dry deposition and air-water exchange of polycyclic hydrocarbons with the water surface sampler. Environmental Science and Technology, 33, 426-434

Paode, R.D., Lu, J., Noll, K.E. & Holsen, T.M. (1996). Long term seasonal and spatial variations in the dry deposition fluxes of anthropogenic and crustal metals measured around Lake Michigan, Atmospheric Deposition to the Great Waters, VIP-72, EPA, 256-261

Paode, R.D., Sofuoğlu, S.C., Sivadechathep, J., Noll, K.E. & Holsen, T.M. (1998). Dry deposition fluxes and mass size distributions of Pb, Cu, and Zn measured in Southern Lake Michigan during AEOLOS. Environmental Science and Technology, 32, 1629-1635

Pirrone, N & Keeler, G.J. (1995). Dy deposition of trace elements to Lake Michigan: a hybrid-receptor deposition modeling approach. Environmental Science and Technology, 29, 2112-2222

Pryor, S.C., Barthelmie, R.J., Geernaert, L.L.S., Ellermann, T. & Perry, K.D. (1999). Speciated particle dry deposition to the sea surface: results from ASEPS' 97. Atmospheric Environment, 33, 2045-2058

Pryor, S.C. & Barthelmie, R.C. (2000). Particle dry deposition to water surfaces: processes and consequences. Marine Pollution Bulletin, 41, 220-231

Quinn, T.L., & Ondov J.M. (1998). Influence of temporal changes in relative humidity on dry deposition velocities and fluxes of aerosol particles bearing trace metals. Atmospheric Environment, 32, 3467-3479

Rojas, C.M. & Grieken, R.E.V. (1993). Comparison of three dry deposition models applied to field measurements in the southern bight of the north sea. Atmospheric Environment, 27A, 363-370

Sofuoğlu, S.C. & Holsen, T.M. (1997). Dry deposition fluxes and mass size distributions of trace elements measured near Southern Lake Michigan. Environmental Research Forum, 7-8, 691-696

Yi, S.M., Holsen, T.M. & Noll, K.E. (1997a). Comparison of dry deposition predicted from models and measured with a water surface sampler. Environmental Science and Technology, 31, 272-278

Yi, S.M., Holsen, T.M., Zhu, X. & Noll, K.E. (1997b). Sulfate dry deposition measured with a water surface sampler: a comparison to modeled results. Journal of Geophysical Research, 102, 19695-19705

Zufall, M.J., Davidson, C.I., Caffrey, P.F. & Ondov, J.M. (1998). Airborne concentrations and dry deposition fluxes of particulate species to surrogate surfaces deployed in Southern Lake Michigan. Environmental Science and Technology, 32, 1623-1628