CHANGES IN THE CHEMICAL COMPOSITION OF SOIL IN ANKARA DUE TO THE DEPOSITION OF ATMOSPHERIC POLLUTANTS

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ABSTRACT

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In this study, trace element levels in Ankara soil were determined by atomic absorption spectrophotometry and instrumental neutron activation analysis. Sampling points included locations within the urban and semi-urban settlement areas of Ankara. However, samples from background locations were also analyzed to differentiate between polluted and unpolluted soils. Two main purposes of this study are to (1) to determine distributions of elements, particularly anthropogenic ones, to investigate at which parts of the city the composition of soil is modified due to pollution, and (2) to investigate the change in the composition of surface soil which is modified by the deposition of atmospheric pollutants. Several methods such as comparison with literature data, statistical analysis, comparison of surface soil with sub surface soil were applied in order to determine the degree of contamination of the surface soil. Crustal enrichment factors were calculated in order to have a numerical expression of the accumulation of trace elements. A multi-variate statistical technique, factor analysis, was applied to the data set in order to assess the major sources which determine the chemical composition of soil in Ankara. Measured trace element composition of surface soil was compared with the surface soil composition statistically derived in a previous aerosol study in Ankara.

Keywords: Atomic Absorption Spectrophotometry, Instrumental Neutron Activation Analysis, Trace Elements, Soil Pollution in Ankara, Enrichment Factors, Factor Analysis.

ÖZ

ANKARA TOPRAĞININ KİMYASAL BİLEŞİMİNİN ATMOSFERİK KİRLETİCİLERİN ÇÖKELMESİNE BAĞLI DEĞİŞİMİ

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Bu çalışmada, Ankara toprağındaki eser element düzeyleri atomik absorpsiyon spektrofotometre ve enstrümantal nötron aktivasyon analizi ile belirlenmiştir. Örnekler genellikle şehir içi yerleşim bölgelerinden alınmakla birlikte, kirlenmiş ve kirlenmemiş toprak ayrımını yapabilmek amacıyla şehir dışındaki bazı noktalardan alınan örnekler de incelenmiştir. Çalışmanın iki amacı bulunmaktadır (1) eser elementlerin, özellikle antropojen kaynaklı olanların, Ankara toprağındaki dağılımlarını belirlemek ve (2) atmosferik kirleticilerin çökelmesi sonucu yüzey toprağının bileşimindeki değişimin incelenmesidir. Yüzey toprağının kirlilik düzeyini belirlemek için literatür değerleriyle karşılaştırma, istatistiksel veri analizi, yüzey ve yeraltı toprağının karşılaştırılması gibi yöntemler kullanılmıştır. Eser elementlerin birikimi ile ilgili sayısal ifadeler elde etmek için toprak zenginleşme faktörleri hesaplanmıştır. Elementlerin miktarlarını belirleyen belli ortak faktörlerin belirlenmesi için faktör analizinden yararlanılmıştır. Yerel toprak bileşimi belirlenerek aerosol eser elementlerinin toprağa bağlı zenginleşmesi ile ilişkilendirilmiş ve daha önce yapılan bir aerosol bileşimi çalışmasının değerlendirmeleri gözden geçirilmiştir.

Anahtar Sözcükler: Atomik Absorpsiyon Spektrofotometre, Enstrümantal Nötron Aktivasyon Analizi, Eser Elementler, Ankara'da Toprak Kirliliği, Zenginleşme Faktörleri, Faktör Analizi.

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INTRODUCTION

1.1 The Composition of Soil

1.1.1 Research on Soil Constituents and Contamination of Soils

Soil may be described as a mixture of inorganic and organic materials ranging from colloids to small particles, containing both dead and living materials, water and gases in variable proportions, and normally in dynamic balance. The main components are: minerals, living and dead organic material, water and air (Fergusson, 1991).

Soil samples are classified according to soil taxonomy and the soil collected from Ankara is generally classified in the group "aridisol" (Haktanır et al., 1995) which indicates soil with relatively smaller contents of water. Such classification is done based mainly on climatic influences and there is a relation between the soil taxonomy and trace element contents. The study by Chen et al (1991) in which soil samples from all around China –which allows for sampling all different soil types- show that lithosols contain the highest concentrations of trace elements and oxisols contain the lowest concentrations. Trace element concentrations in aridisols are between these two structures.

Heavy elements in soils originate either from the weathering of parent material and/or from numerous external contaminating sources. For some elements, such as lead, cadmium and zinc, the levels from contamination often far exceed the levels from natural sources, whereas for the elements such as La, Sm, Eu, etc. which are not used extensively in human activities, natural levels are higher than antropogenic contribution (Fergusson, 1991).

It is the parent rocks that determine soil trace element content. These rocks are the reserve and primary source for these elements. Most often, there is a direct relationship between the respective content of a given element in soils and rocks, in the same type of soil, formed on different rocks (Aubert et. al., 1977). The differences between the rock and soil contents of elements are due to some processes during the formation of soil, contamination from atmospheric deposition, discharges and other similar natural or anthropogenic disturbances (Fergusson, 1991).

Several studies up to now have evaluated soil composition schemes for different soils and some of these schemes have been assumed to be valid for other studies concerned with soil composition. Especially the profile compiled by Mason (1966) has been widely accepted as the general soil composition and used in studies when soil composition is needed.

The concentrations for some particular elements evaluated by different studies are given in Table 1.1.

Table 1.1 Elemental concentrations in soils (μg/g)

	MASON (1966)	Vinogradov (1959)	Vinogradov (1959)	Wedepohl (1968)	Taylor (1972)
		(SED. ROCKS) Shale&clays	Soils	(crustal)	(crustal)
Na	28000	6600	6300	24500	23600
K	25900	22800	13600	28200	20900
Mg	20900	13400	6300	13900	23300
Ca	36300	25300	13700	28700	41500
Al	81300	104500	71300	78300	82300
V	135	130	100	95	135
Cr	100	160	200	70	100
Mn	950	670	850	690	950
Fe	50000	33300	38000	35400	56300
Ni	75	95	40	44	75
Cu	55	57	20	30	55
Zn	70	80	50	60	70
Cd	0.2	0.3	0.5	0.1	0.2
Pb	13	20	10	15	12.5
Sb	0.2	1		0.2	0.2

Studies on soil composition may have different purposes. Chen et al. (1991) analyzed 62 elements in samples from 4095 locations throughout the China in order to evaluate a general soil profile in China and to compare the results with data from other countries while Abdel-Saheb et al. (1994) carried out a study for the chemical characterization of heavy-metal contaminated soil in Southeast Kansas in order to observe the concentrations of some heavy metals and their toxic effects on vegetation. Carrasco et al. (1991) reported the elemental content of soils in continental Chile in relation to their projection to atmospheric pollution. Schirado et al. (1986) analyzed urban soil samples and reported the results in tables differentiating the elemental compositions of polluted and non-polluted soil.

The anthropogenic sources of heavy elements in soils are either primary sources, i.e. the heavy metals are added to the soil as an outcome of working the soil, such as fertilization or secondary sources where heavy metals are added to the soil as a consequence of a nearby activity, such as smelting or aerosol deposition. Primary and secondary sources of heavy elements in soils are listed in Table 1.2.

Table 1.2 Anthropogenic sources of heavy elements in soils (Fergusson, 1991)

Source	Elements
Primary sources	
Fertilizers	Cd, Pb, As
Lime	As, Pb
Pesticides	Pb, As, Hg
Sewage sludge	Cd, Pb , As
Irrigation	Cd, Pb, Se
Manure	As, Se
Secondary sources	
Automobile aerosols	Pb
Smelters	Pb, Cd, Sb, As, Se, In, Hg
Refuse incinerators	Pb, Cd
Mining areas	Pb, Cd, As, Hg
Tyre wear	Cd
Paint (weathered)	Pb, Cd
Marine	Se
Rubbish disposal	Pb, Cd, As, +
Long range aerosol	Pb, As, Cd, Se
Coal combustion	As, Se, Sb, Pb
Chloroalkali cell	Hg

However, it should be noted that although the names primary and secondary sources may lead one to think that the sources listed as primary have greater contamination effect on soil, this is not at all the case for urban pollution of soil since many of the activities listed as primary sources do not take place in urban areas whereas the activities listed as secondary sources have much wider applications and hence cause more extensive pollution in urban areas.

1.1.2 The Change of Elemental Distributions with Depth of Soil

It is important for soil analysis and the related source assessment studies to observe the change of elemental distributions with the depth of the soil. Since it is obvious that the surface soil will be much more affected by external sources compared to deeper sections, it is generally necessary to evaluate the vertical distribution of elements within the soil.

It has been seen by several researches that certain anthropogenic elements such as Pb and Cd decrease to at least half of the surface concentrations when the sample is collected from 15-20 cm depth of soil from the surface (Haktanır et al., 1995; Saur et al. 1994). Saur et al. (1994) mention that low background levels of metals observed in deeper soil sections allow more confidence in the assessment of the enrichment of the upper soil layers resulting from other metal sources i. e., the biological turn-over of mineral elements, or inputs from aerial deposition or agricultural practices.

As a result of these findings, one can make use of the variation of elemental concentrations with depth in differentiating the polluted and non-polluted soil samples.

1.1.3 The Change of Elemental Distributions with Distance to Roads and Highways

The most important single source which substantially affects chemical composition of soil in urban areas is motor vehicles. Since traffic emissions occur at very low level (25-30 cm from ground level), particles and metals attached on them settle down to the ground very quickly. Since this process is almost continous, metal, particularly Pb content of soil around roads are modified substantially.

Although Pb is the best documented element, particulate organics and soot carbon which are emitted from gasoline and diesel powered vehicles are also incorporated in the soil changing its composition. However, studies on these components of traffic emissions are limited.

Many studies such as those by Haktanır et al. (1994), Abdel-Saheb et al. (1994), Agrawal et al. (1981), Majdi et al. (1989), Yaramaz et al. (1983), Yaman (1994), Çakmak et al., and Lau et al. (1982) have shown that there is a significant effect of the proximity of the nearby roads or highways to the sampling point on the concentrations of some elements analyzed, especially those related to vehicle emissions.

Most of these studies have been concentrated on the change of lead concentration – which is the best marker for exhaust emissions- since the use of lead containing gasoline in the light vehicles on the highways causes emissions of lead compounds to the atmosphere which consequently contaminates the nearby soil and the plants (Yaman, 1994). However, other researches investigated behaviours of elements other than Pb pointing out that lead is not the only polluting heavy metal related to traffic load and exhaust emissions and that Cd and Zn which are used in motor oils and tyre vulcanization and Cu and Ni which are emitted by the wear of motor alloys should also be taken into consideration (Haktanır et al, 1995).

The effect of distance to the road changes according to the traffic load and the sampling location. For example, Haktanır et al. (1995) observed a decrease of lead concentration from 124.2 to 24.5 µg/g in 500 m distance to the road and Agrawal et al. (1981) observed a decrease from 275 to 3 µg/g of lead in 100 m distance from the highway while Majdi et al. (1989) observed only a slight decrease of lead concentration with distance from the road (from 18 to 15 µg/g) which was possibly due to the smaller traffic load compared to the studies mentioned earlier.

Because of this certain effect of distance to the road on certain element, any soil study which investigates general profile and distribution of the elements should try to keep the distance of the sampling points a little further to the loaded traffic ways and should try to keep approximately the same distance to the roads at each sampling point.

Besides regular soil samples, Yaman (1994) and Lau et al. (1982), etc. analyzed samples collected from the roadsides of different areas. The content of elements such as Pb and Cd are much higher in road dusts than regular soil samples due to the reasons explained. Therefore the results of road dust analysis are interpreted in separate matrixes from other soil samples because of the great variation of the concentrations of some elements from normal soil composition schemes.

Like roads and highways acting as line sources for some elements, certain facilities such as industries, mines or very heavily populated areas act as point sources for the enrichment of certain elements. Abdel-Sahab et al (1994) studied on soil samples in and around an old mining area in Southeast Kansas and observed that Zn, Pb and Cd concentrations were increased with decreasing distance to the mining area. Davies and Wixson (1997) analyzed and plotted the heavy element concentrations in an old industrial area of Wales. The plots of element distributions clearly show that heavy elements Cd, Cu, Pb, Zn, Co and Ni are concentrated around certain industries.

1.2 Source Apportionment

It has been of interest for some environmental researchers to predict the contributing sources of a local pollution (air, water, soil, etc.) from different sources (air, water, soil, etc.) by using techniques called "Source Apportionment" or "Receptor Modeling". Several methods such as 'chemical mass balances' or 'factor analysis' have been used for such studies.

CMB (chemical mass balance) is based on the assumption that the composition of particles in a sample is a linear combination of the compositions of contributing sources. Since CMB is not used in this study, detailed mathematical information on it is not mentioned here.

The other method of receptor modeling is the FA (factor analysis) which is an example of multivariate analysis. The method for assessing the sources of elements in the soil samples for this study will be FA. Factor analysis has been used in different studies for determining the contributing sources to atmospheric samples (Yatın, 1994; Al-Momani, 1995; Kuloğlu, 1997) or contributing sources to soil samples (Davies, 1997).

Factor analysis is based on the assumption that sample-to-sample fluctuations of elemental concentrations are governed by the fluctuations of the strengths of several common factors. That means that one can observe strong correlations between elements originating from a common source and these elements are grouped in one factor. For example a factor group including the elements Pb, As, Cd, Se can be named as a factor of long range aerosol transport for soil contamination. A factor analysis does not have to (or may not be able to) differentiate the sources in detail such as the sources listed in Table 1.2, and one may extend the factor analysis to a few general groups such as anthropogenic sources, crustal sources, etc.

In factor analysis, the concentrations of all elements in each sample are normalized

$$Z_{'j} = \frac{X_{'j} - \overline{X}}{\sigma_{,}}$$

according to the equation

where

Z_{ij} : the normalized concentration of element i in sample j,

X_{ij} : the actual concentration of element i in sample j,

X : the average concentration of element i in the data set,

σ_i : the standard deviation of the concentration of element i.

In terms of normalized concentrations Z_{ij}, the concentration of each element has a mean value of $Z_I = 0$ and a variance $\sigma_I = 1.0$. Such a normalization gives each element an equal weight in the factor analysis regardless of its average concentration. Then the minimum number of factors that can explain most of the common variance of the system is determined.

The factor model assumes that each of the variables is linearly related to some number of factors so that the values of variable can be expressed as a set of linear equations. The model for the ith variable can be written as

$$X_i = a_{i1}F_1 + a_{i2}F_2 + \ldots.. + a_{ik}F_k + U_{ij}$$

where

F_{ij} : the factors common to all of the variables,

U_{ij} : the unique factor

a_{ij} : factor loadings

The squares of factor loadings a_{ij} indicate the fraction of the observed variance of element i that is accounted for by the variance of the factor j. The sum of the $(a_{ij})^2$

values for an element is the communality h^2 for that element, i.e. the fraction of its observed variance that is accounted for by the variance of common factors. The sum of the $(a_{ij})^2$ values for factor j indicates the total amount of variance explained by that factor. The sum of the total variances for each factor and the sum of the communalities, is the total variance of the system explained by all factors.

1.2.1 Projection of Soil Research to Source Apportionment for Aerosols

Most of the source apportionment studies up to now have been interested in predicting the contribution of different sources to air pollution. In order to use the source apportionment technique, one needs to have knowledge of the composition of the possible contributing sources to the pollution problem of interest.

In most air pollution source apportionment studies, it has been seen that there is at least one soil source (namely surface soil) contributing to the air pollution. In order to make such a prediction one should either have information on the actual composition of the contributing local soil or use a composition scheme that is widely accepted. Since it is generally not possible to have information on actual soil composition, some pre-determined crustal compositions prepared through different studies (e.g. by Mason, Taylor; Wedepohl) have been accepted to be the same as the local contributing soil of interest. This, with no doubt, will cause errors in the results of the source apportionment study -whether little or much.

The impelling force for this study has been the Ph. D. thesis prepared by Mustafa Yatın from Middle East Technical University Department of Chemistry titled "Source Apportionment of Urban Aerosols Using Receptor Modelling Approach: An Application to Ankara". In that study, the aerosol samples to represent the urban air pollution of Ankara city have been analyzed and subjected to source apportionment. In the study, the soil composition has been accepted to be the same as that has been determined by Mason, which is the most widely used scheme and the one that seems to be most fitting to the local soil of Ankara.

In applying the receptor modeling approach for source apportionment, one needs the real emission profiles of the sources to be used as input in CMB (Chemical Mass Balance) calculations. One of the original objections to CMB based receptor modeling for source assessment is that source profiles for every application is not available. In USA, for example, these objections may be no longer valid since a large number of source measurements have been acquired for the major part of USA. However, in Ankara, it is not possible to find any, or at least enough, trace element based source measurement. Then, the only way to use the CMB approach is to create an artificial source data base which must have similar characteristics as the actual present sources in Ankara (Yatın, 1994).

One of the most important findings of Yatın's study was that the surface soil in Ankara had been severely enriched in especially heavy metals from anthropogenic sources. This is concluded by the fact that the portions of these metals with aluminum –which is the best indicator of a soil factor- are much higher than the natural values of these proportions.

An important study, the objectives of which are similar to the objectives of this study, was carried out by Carrasco et al. (1991). In that study, elemental distribution of some soils of continental Chile and the Antarctic Peninsula was analyzed. The aim in establishing the distribution was to get information on local soil and project this to atmospheric pollution source assessment. "In order to get a better determination of the origin of the aerosol, the enrichment factor used as a criterion to establish the origin of trace elements in the atmospheric aerosols should be recalculated based on the local soil."

When the arithmetic means of EF (enrichment factor) values obtained by using terrestrial crust profile prepared by Mason and by using the local soil are compared, a clear difference can be observed.

Table 1.3 EF values compared for terrestrial crust and local soil (Carrasco et al., 1991)

Element	Terrestrial crust	King George Island	Doumer Island (low organic matter content	Doumer Island (high organic matter content)
Ni	21	35	75	42
Cu	333	145	123	12
Zn	904	783	247	21

According to Carrasco et al (1991), when the EF are calculated based on the element concentrations of local soils instead of the values of the terrestrial crust, the assignment of the origin of the elements in the atmospheric aerosol in general remain the same, but in some special cases this assignment should be changed. If the EF values are used to determine the origin of the elements in the atmospheric aerosol in a particular region and the concentration of certain elements in the local soil are very different from concentrations reported in published references, local pollution may be suspected. Then the EF values should be recalculated, based on concentrations found by sampling the local soils, in order to determine the origin of the element of concern in the atmospheric aerosol.

Table 1.4 The enrichment of surface soil with respect to Mason's average earth crust compilation (Yatın, 1994)

EF (Mason) for surface soil					
Element	EF	Element	EF	Element	EF
Hg	0.87	Mg	1.02	Sc	3.96
Cs	0.93	Cl	1.02	As	5.1
V	0.98	Cr	1.04	Pb	114
Co	1	Fe	1.1	Se	139
Na	1	Mn	1.3	Br	252
K	1	Ca	1.37	Zn	305
Al	1	La	1.45	Sb	452
Ni	1.02				

The comment by Carrasco et al (1991) exactly describes the case of Yatın's (1994) thesis where a very enriched profile of soil due to anthropogenic elements was estimated according to Mason's average earth crust compilation as given in Table 1.4.

1.2.2 Source Apportionment for Soils

Although still very little compared to source apportionment studies for aerosols, there is an increasing interest in studies for assessing the sources of the elements in soils.

Different techniques can be useful in source assessment of soil contaminants. One, but quite costly and complex, approach is to make use of detailed physico-chemical analysis. For example, Gulson et al. (1981) used isotopic lead evidence which showed that the vehicle exhausts were the main source. Rabinowitz and Wetherill (1972) and Santos et al. (1993) examined the variations in stable lead isotope to portion the source of lead between vehicle exhausts and smelting.

A cheaper and easier way is the statistical analysis of analytical data. The principal component analysis or the similar factor analysis (Krumbein and Graybill, 1965; Norusis, 1988) have been succesfully used. Factor analysis is a technique in which a complex data set is simplified by creating one or more new variables or factors, where each factor represents a cluster of interrelated variables within the data set (Davies 1997). The elements showing similar correlations are expected to be grouped by FA (factor analysis) resolutions. The purpose of FA is to group the elements with the same variation into the same factor (Yatın, 1994). The elements grouped under the same factor are said to have a common source.Several researches such as Davies and Wixson (1987), Dudka (1992), Sweet et al. (1993), Xhoffer et al. (1991), Davies (1997) used FA to differentiate the sources of trace metals in surface soil into factors as parent rock, soil processes, anthropogenic emissions, airborne emissions, etc.

The scope of the study by Xhoffer et al. (1991) was to assess the sources of individual aerosol particles over the North Sea and the English Channel and to differentiate the soil factors from sea-salt factors. This differentiation is not the scope of a study for inland cities like Ankara but the method used in the mentioned study is of particular interest. In the study, the factor analysıs was enhanced by further cluster analysis. This is done by the observation of the distribution of the factor scores. A similar approach is used in this study by plotting the factor scores over the study area.

Davies and Wixson (1987) made use of factor analysis to differentiate pollutants from other trace metals in surface soils of the mineralized area of Madison county, Missouri, U.S.A. Factor analysis divided the data into three factors. The first and strongest factor (i.e. that explains most of the variance) represents the contamination due to industrial processes and contains elements such as Cu, Ni, Co, Pb and Zn. The second factor loaded by V, Cr, Li, Ba and Be was assigned as the factor representing the weathering residuals. The third factor is composed of Zn, Ba, Sr and Be which are related to local rock type.

Davies (1997) studied the heavy metal contaminated soil in an old industrial area of Wales and identified the sources with statistical data interpretation. Three common factors which explained 74% of the total variance of the data set were extracted. Factor 1 was dominated by Cu, Pb, Zn and organic matter which represented contamination from the waste heaps of the old smelters in the area. Factor 2 was dominated by Mn and pH and there was also some contribution of Cd and Zn. This factor is the soil factor and the interesting result is that Cd and Zn contents of soil are also influenced by soil factors although these elements are generally observed in anthoropogenic contamination factors.

Davies and Wixson (1985) also made use of the isoline plots of soil data to visually relate the pollution to specific sources for supporting the factor analysis. Davies (1997) made a similar use of distribution maps of elements and observed similar distribution patterns for elements that turned out to be loaded under the same factor.

1.3 Objectives and scope of this study

The idea that lead to this work emerged from the aerosol source apportionment study performed by Yatın et al. (1998) in the Ankara atmosphere. Yatın and co-workers, using multivariate statistical tools were able to identify three different soil components in aerosol population and were able to determine the elemental composition of those soil components. The three soil components were identified as surface soil, sub-surface soil and road dust. The difference between surface and subsurface soil was in the concentrations of calchophilic elements such as, Zn, Cd, As, Se which are known to originate from anthropogenic activities such as combustion of fossil fuels. Concentrations of these anthropogenic elements were significantly higher in the surface soil which lead authors to conclude that the surface soil in Ankara is contaminated by pollution-derived elements due to deposition of combustion particles from atmosphere over the years.

This work was initiated to investigate (1) if the surface soil in Ankara is indeed contaminated as proposed by Yatın et al (1998), (2) if so how the pollution of surface soil is distributed over the city, (3) to what extend the natural composition of soil is modified by atmospheric deposition.

Another important objective of the study is to test the soil composition derived statistically from aerosol studies by Yatın et al. (1998), and to estimate how much of the concentrations of anthropogenic elements in Ankara atmosphere originates from combustion and what fraction is due to resuspension of contaminated surface soil.

It should be noted that, the study is not a detailed soil pollution study, because the distance between sampling points are 3 - 4 km's. This work aims to identify polluted regions in the city for more detailed studies (studies with higher resolution) in the future. The study is important because of its spatial coverage.

CHAPTER 2

EXPERIMENTAL

2.1 Sampling

2.1.1 Sampling Points

This study included the metropolitan area of Ankara city and some locations which lie up to few kilometers outside the city boundaries. The sampling points within the residential areas were chosen to examine the level of trace elements and possible contaminations above the expected natural limits and the sampling points outside the residential area were chosen in order to be able to see the difference of the levels of elements between urban and rural locations.

For determining the sampling points, a map of Ankara prepared by the Greater City Municipality of Ankara was divided into grids where each grid element was approximately 3 km x 4 km dimensions. One hundred and twenty points among these grid points were chosen as sampling points. The factors affecting the choice were to be able to take samples representing the whole city as much as possible and to take samples near different emission sources such as roads, industries, railways, small metal processing facilities, and to be able to assess the distribution of metal pollution over the whole city.

However, there were some limitations for taking samples from some desired points. For example, it was not possible to take the sample from a grid point which was in the middle of a military zone in Etimesgut. At some points, it was not possible to take the sample from the exact grid point because of the absence of roads leading to those points, especially in rural areas.

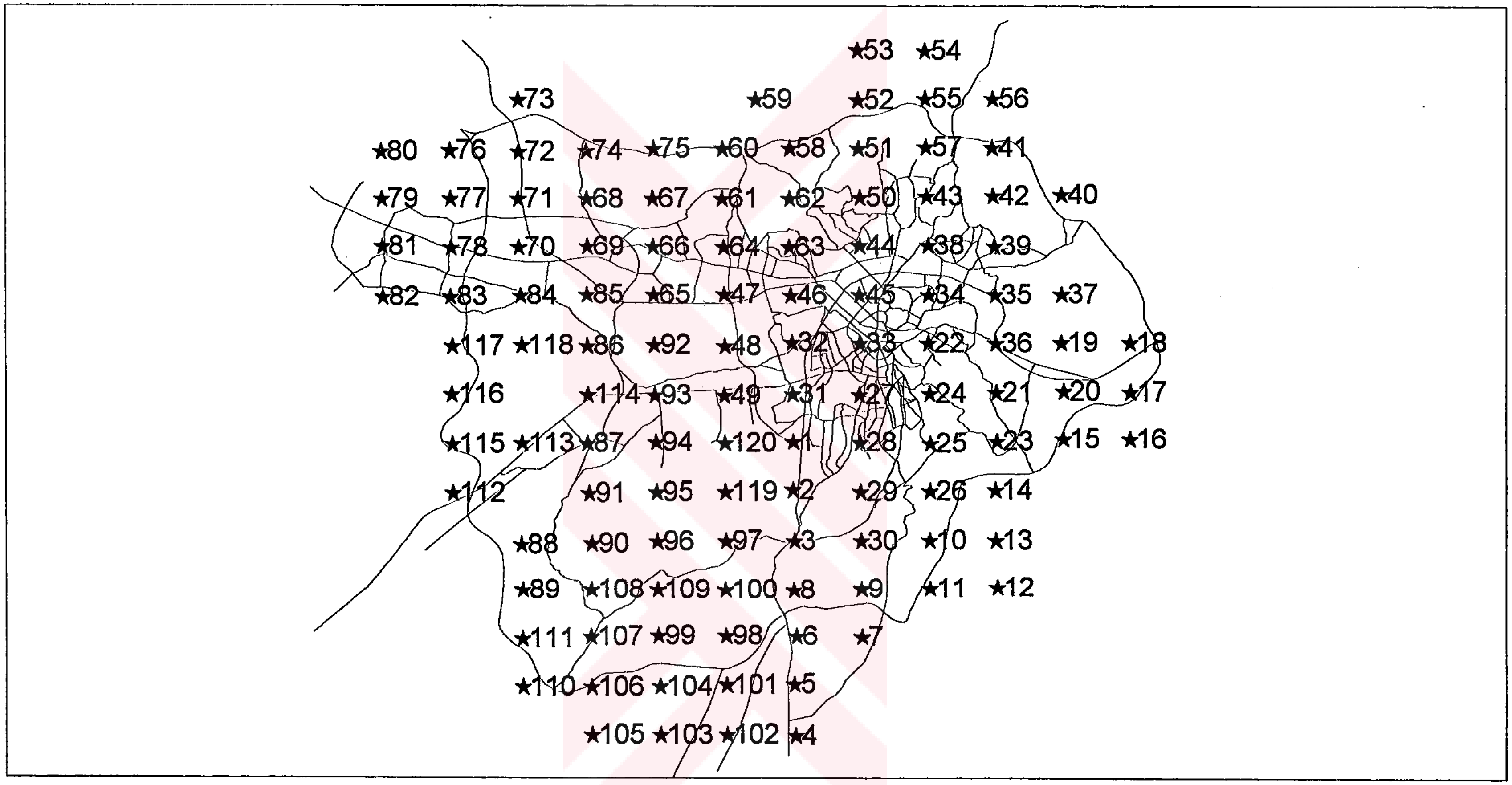


Figure 2.1 Locations of sampling stations

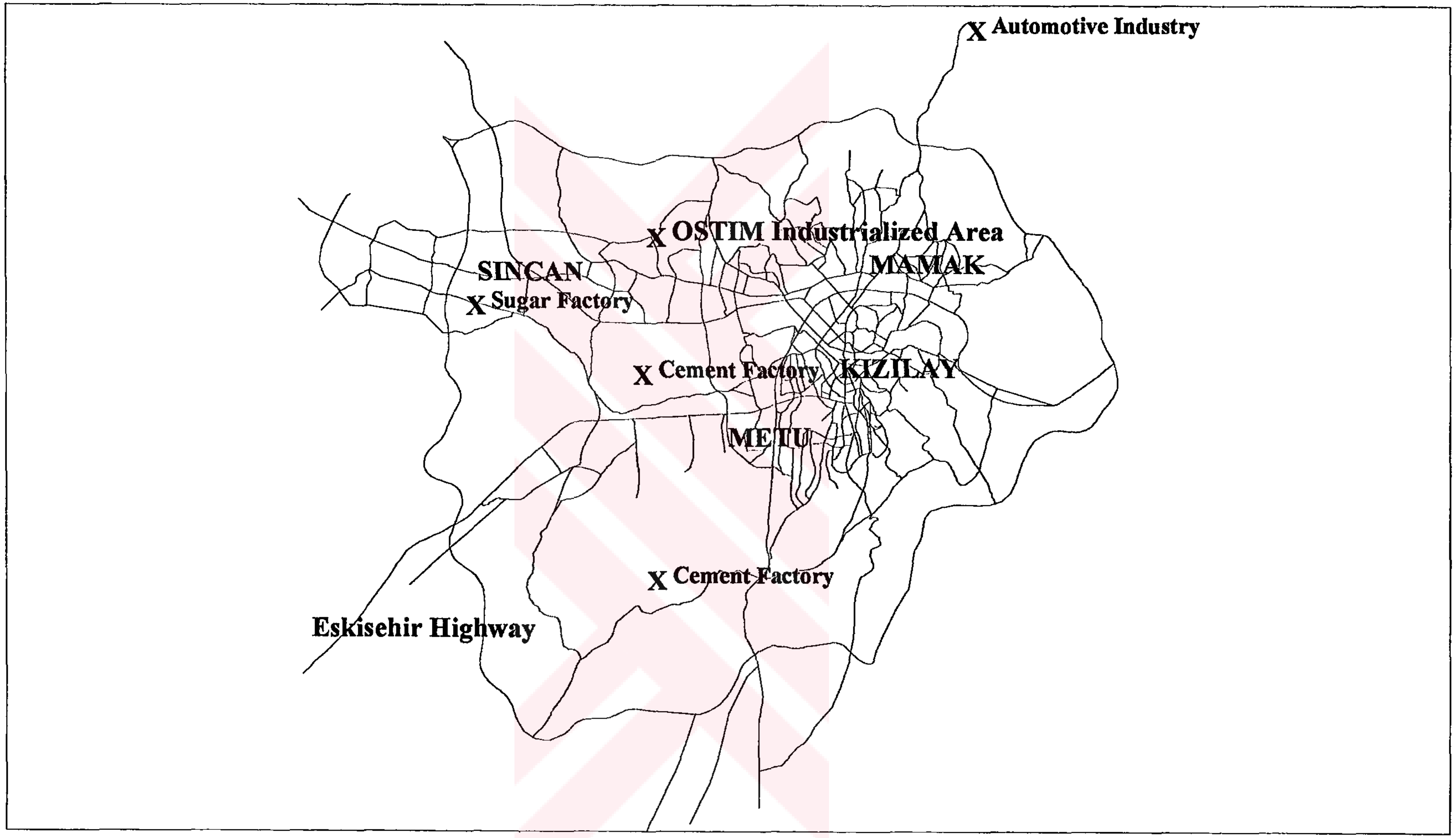


Figure 2.2 Sampling area and major industries and residential areas

Attention was paid to collect the samples at points 20 m from major roads or highways and to keep the same distance where possible because of the known effect of proximity to the highway on certain elements.

Besides these 120 grid points, samples of road dust were collected at 8 points from the roads or highways. The road dust samples were collected at roads near to the grid points.

Finally, core samples were collected at four sites within the city, two from the campus of the Middle East Technical University, one from Güvenpark and one from Dikmen. The aim of the collection of the core samples was to see the variation of the levels of elements with depth.

2.1.2 Collection of Samples

Polyethylene bags were used during the collection of the samples. All the polyethylene bags were washed with dilute (about 5%) nitric acid, distilled water and deionised water subsequently and left to dry in the clean room which was continuously air conditioned. During all stages of sample collection (washing and handling of nylon bags, collection of samples on site and later homogenization of samples), direct handling of the bags and soil samples were avoided and polyethylene gloves were used where necessary.

The samples were collected from about the first top 5 cm of the soil which is generally considered as the top or surface soil. Before collection of the sample, coarse particles like stones and plants were removed and the soil was taken into the bag by a polyethylene spatula or by simple sweeping, especially in the case of the collection of road dust.

The core samples were taken by digging PVC pipes vertically into the soil and collecting the soil trapped within the pipe. The depth of the core sample taken changed according to the hardness and compaction of the soil. Core samples were taken up to about 20 cm depth of the soil. The core samples were later divided into 4 cm portions in the laboratory and collected at separate polyethylene bags.

2.2 Preparation of Samples

2.2.1 Homogenisation of Samples

In the laboratory, the samples were placed in an oven at approximately 60°C for 24 hours to remove the water and present the results on a dry-weight basis before digestion.

Soil samples should be homogenised, i. e. they should be grinded to as small particles as possible and well-mixed so that the resultant sample is representative of the bulk of the sample.

When sampling a mixture of particles of different nature like soil, there will always be minimal amount of variation between the samples due to the fact that the particle composition of each sample will differ (Lame et al., 1993). However, the study of Lame et al. (1993) showed that this error influences the variance only when samples smaller than 10 g are taken. In this study, the amounts of samples collected at the points were far beyond 10 g (approximately 500 g) and the error due to the little amount of sample used for analysis (around 250 mg) was minimized by homogenization.

Before homogenisation, the big particles like stones, foreign material such as glass pieces, pieces of plants were removed from the sample. A RETSCH agate homogenizer was used for this purpose. The samples were then placed in a grinding mill the container of which was made of agate. The use of other containers such as those made of ceramic was avoided since the ceramic material itself can be a source of contamination for the sample. The samples were milled at high speed for about 6 minutes and replaced into polyethylene bags.

2.2.2 Digestion of Samples

After collection and homogenisation of the soil samples, they need to be digested. Since the analysis are made by using atomic absorption spectrophotometry in which only liquid samples are analysed, the soil which is in solid form should be converted to liquid form. This is achieved by dissolving the soils in strong acid solutions under temperature and pressure.

Collected samples were digested using high pressure dissolution vessels known as "digestion bombs" (PARR Co.).

In the sample preparation stage of this study, the reagents used were MERC supra-pure grade concentrated HNO_3 and MERC ultra-pure grade concentrated HF. The amount of the sample to be digested and the amount of the reagents to be used were determined through a series of experiments with different amounts. The amount of the sample to be used which started with 100 mg was reduced to about 25 mg since it has been seen that when 100 mg of sample is used, it can not be dissolved completely due to the small amount of reagent used. The reducing of the sample amount rather than increasing the amount of reagents is preferred since the digestion is used with small-volume containers. The amount of the reagents were firstly 4.5 ml of HNO_3 and 1 ml of HF. However, with these amounts, it has been seen that the silicate matrix of the sample (which is recognised from its white colour) did not dissolve completely. Therefore, the amount of HF, which is known to be more effective in dissolving the silicate matrix, was increased to 1.5 ml and the amount of HNO_3 was decreased to 4 ml. It has been seen that these amounts were adequate for the total dissolution of the samples and the digestion was achieved with these amounts of reagents.

Approximately 25 mg of the sample was placed in the teflon container and 4 ml of HNO_3 and 1.5 ml of HF was added. The teflon container was placed in the steel case and the bomb was placed in an oven which was readily heated up to 150°C. The bomb was left in the oven for about 90 minutes, taken out and allowed to cool to room temperature. After cooling, the teflon container was taken out, its cover was removed and the container was placed on the hot plate at about 100°C. The purpose of heating the solution was to evaporate the HF in the solution which may be destructive for some parts of the atomic absorption spectrophotometer. After evaporating the HF portion, the remaining solution was transferred to a 50 ml high-density polyethylene volumetric flask and diluted to 50 ml by addition of deionised water. General practice is to achieve the dilution by 1% HNO_3 solution in order to keep the sample in low pH but there is no problem in doing this with deionised water since the remaining HNO_3 in the solution makes the sample acidic enough.

After dilution to 50 ml, the samples were kept in polyethylene containers for the analysis. It is important to use polyethylene containers, flasks and pipettes and to avoid using glass equipment during laboratory work since the acidic effect of the solution (especially due to HF) may cause the glass material to dissolve and change the composition of the sample.

2.3 Analytical Techniques

All the samples were analyzed by atomic absorption (AAS) or emission (AES) spectrophotometry for 13 elements. In addition, samples from three points and two core samples (one from the top and one from the bottom of the core) were analyzed by instrumental neutron activation analysis (INAA) for 40 elements. A summary of the analytical techniques used is presented in Table 2.1.

Table 2.1 Analytical techniques used for elements

Measured Element	Analytical Technique
Al, Ca, Cr, Cu, Fe, Mg, Mn, Zn	FAAS
Na, K	FAES
Pb, Ni, Cd	GFAAS
Na, Mg, Al, Cl, K, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, Ga, As, Se, Br, Rb, Sr, Mo, Cd, In, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Yb, Lu, Hf, Au, Hg, Th, U	INAA

2.3.1 Flame Atomic Absorption Spectrophotometry (FAAS) and Flame Atomic Emission Spectrophotometry (FAES)

Among the elements of interest in the study, Al, Ca, Cr, Cu, Fe, Mg, Mn and Zn were analyzed by flame atomic absorption spectrophotometry using a Perkin-Elmer 1100B spectrophotometer.

Air-acetylene flame was used for all elements except for Al. Aluminum was analysed with nitrous oxide-acetylene flame because of its high atomisation temperature.

Parameters used in flame and graphite furnace AAS were optimized before analysis. The positions of the hollow cathode tube, flame burner and graphite tube were adjusted to obtain the maximum absorbance. Similarly, the drying, ashing and atomization temperatures and rates were optimized to achieve the highest absorbance.

The method of standard additions was used throughout the analysis. For this, known concentrations of elements obtained from 100 ppm commercial stock solutions (Aldrich) were added to the sample matrix prepared as a mixture of Ankara and Antalya soils and sediments from the İzmir Bay. The standard addition curve prepared every day was used for measurements throughout the day. According to the extent of the concentration of the element analysed, the sample matrix was used either directly or after dilution. The need for a dilution or not can be observed from the regression value (r) which is desired to be as close as possible to 1.000 and not be less than 0.950.

After calibration, the accuracy standards of measurements were checked by measuring the concentrations of different standard reference materials (SRMs). SRMs are samples with known and internationally accepted concentrations of elements. They are commercially found in solid form and transferred into liquid phase with the same method of the digestion applied to the samples. If the difference between the measured and known values of the SRMs exceed 10%, then it is necessary to repeat the calibration or check for any possible faults with the spectrophotometer.

After all calibrations and checks, the samples were analysed by direct aspiration to the burner and the values were recorded from the monitor of the instrument. The samples with concentration values exceeding the concentration limit beyond which the calibration curve is not linear, the measurement was repeated after dilution. The degree of dilution is decided by trial and the degree of exceeding the linear range and the dilution factor is desired to be as small as possible because the dilution procedure is a certain source of error in measurements.

Na and K were measured by using FAES since Na and K are the most easily excited elements among all other elements and a low-temperature flame is sufficient for Na and K analyses (Black et al., 1965). FAES was experinced with the same instrument as FAAS measurements. The difference in FAES is that there is no hollow cathode lamp and the concentration is estimated by measuring the intensity of the light emitted by the excited atoms whereas the concentrations in FAAS are estimated by the degree of the light absorbed from a known intensity of light by the atoms.

The optimized parameters used in flame AAS measurements are given in Table 2.2.

Table 2.2 Operational parameters used in flame atomic absorption and emission spectrophotometry

Elements	Cr	Al	Mn	Zn	Fe	Ca	Cu	Mg	K	Na
Technique	FAAS	FAAS	FAAS	FAAS	FAAS	FAAS	FAAS	FAAS	FAES	FAES
Wave length (nm)	357.9	309.3	279.5	213.9	248.3	422.7	324.8	285.2	766.5	589.0
Slit width (nm)	0.7	0.7	0.2	0.7	0.2	0.7	0.7	0.7	1.4	1.4
Air (ml/min)	8.8	7.7	8.0	10.4	9.8	9.0	9.5	9.0	8.5	9.5
Acetylene (ml/min)	5.6		2.5	2.8	2.9	3.9	2.2	3.0	3.0	3.7
N. Oxide (ml/min)		5.0								

2.3.2 Graphite Furnace Atomic Absorption Spectrophotometry

Concentrations of Cd, Ni and Pb were determined by using GFAAS because their concentrations were too low to be determined in the flame mode. Such small concentrations are measured by atomisation by very high temperatures which can be achieved by a graphite furnace. GFAAS measurements were done by using the Perkin-Elmer 1100-B spectrophotometer coupled to a Perkin-Elmer HGA 700 electrothermal atomisation system.

Samples were analyzed by the method of standard additions to avoid matrix effect which can be significantly heavy in soil analysis by GFAAS

The optimized parameters used in measurements are given in Table 2.3.

Table 2.3 Operational parameters in GFAAS

Elements	Ni	Cd	Pb
Wavelength (nm)	318.4	232.0	283.3
Slit width (nm)	0.7	0.2	0.7
Lamp current (mA)	25	5	11
Sample volume (μL)	20	20	20

2.3.3 Instrumental Neutron Activation Analysis (INAA)

Five selected samples from the sample set were analyzed by instrumental neutron activation analysis. The purpose of INAA measurements was to be able to compare the results with the data given in Yatın (1994) where the data set was generated using INAA.

Neutron activation analysis uses the production of radionuclides from the elements present in the sample for the identification and quantitative determination of these elements. The samples to be analyzed are irradiated with neutrons in a nuclear reactor. As a result of nuclear reactions, i. e. (n, γ) reactions, between these neutrons and stable isotopes of the elements, radionuclides may be produced. The radiation emmitted by the decaying radionuclides is measured with a γ-ray detector. Decay corrected activity can be calculated by the formula:

$$A_0 = \frac{A\lambda e^{-\lambda t}}{1-e^{-\lambda(t_2-t_1)}}$$

where

A_0: decay corrected count rate at the end of the irradiation

A: measured activity

t_1: time out of the reactor to the beginning of counting

t_2: time out of the reactor to the end of counting

Concentrations of elements in each sample are then determined by comparing the activities of isotopes in samples with those in standard materials which are irradiated together with samples. The unknown element concentrations in the sample can be calculated by using the formula:

$$m_x = m_s \frac{A_S}{A_X}$$

where

m_x: mass of the element in the sample

m_s: mass of the element in the standard

A_X: decay corrected activity of the sample

A_S: decay corrected activity of the standard

For INAA, samples were weighed into polyethylene bags which were heat sealed and placed in sample carriers (rabbits). Rabbits containing samples were irradiated in the Massachusettes Institute of Technology Nuclear Research Reactor in a thermal neutron flux of $1\mathrm{x}10^{13}$ $\mathrm{n.cm^{-2}.sec^{-1}}$. Induced radioactivity was counted using CANBERRA high purity Ge detectors and CANBERRA counting system collected γ-ray spectra were analyzed using a special software designed for analysis.

2.4 Data Quality Assurance

There are several measures to check for the validity of the analytical results. These measures are mainly related to the relations of the sample measurements with the laboratory blanks.

2.4.1 Laboratory Blanks

Although most of the elements measured in this study are in considerably high concentrations in soil, laboratory blanks are still important in trace element analysis in order to check for contamination during laboratory stages.

The preparation of laboratory blanks includes the analysis of reagents used in digestion (i.e. the acids and the deionized water) passed through the same digestion procedure without any sample addition. One blank was prepared for each six samples during this study. The analysis of blanks is important because there is some amount of absorption during AAS analysis due to the non-perfect condition or contamination of the reagents. This contamination is therefore also systematic in all samples and the way to eliminate this effect is to analyze the blanks and subtract their absorbance from those of the samples.

Average concentrations of elements in blanks are given in Table 2.4

Table 2.4 Average blank concentrations and standard deviations (μg/ml)

Elements	Avg. Blank Conc.	Standard Deviation	Elements	Avg. Blank Conc.	Standard Deviation
Al	0.142	0.108	Mn	0.004	0.002
Ca	0.553	0.145	Na	0.389	0.119
Cr	0.013	0.004	Zn	0.064	0.008
Cu	0.005	0.003	Pb	0.006	0.001
Fe	0.150	0.095	Ni	0.007	0.004
K	0.089	0.025	Cd	5.8E-5	6.03E-5
Mg	0.089	0.037			

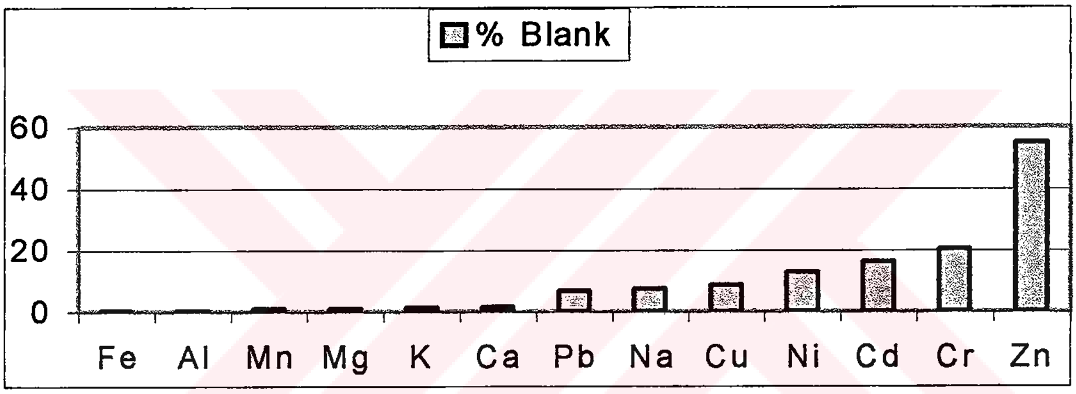


Figure 2.3 Percent contributions of blanks to the measurements

2.4.2 Sample to Blank Ratios

A tool for assessing the uncertainty in the sample measurements is to check for the ratios of sample measurements to blank measurements. Average sample to blank ratios and the percent contribution of blanks on observed concentrations of elements are given in Table 2.5. The percent contribution of blanks to the observed concentrations are also presented in Figure 2.2

Except for Cr Zn, Ni and Cd, the contribution of blanks to all elemental concentrations are smaller than 10% and this implies that the measurements are reliable with the existing laboratory conditions and preliminary sample handling. Low values of sample to blank ratios (i.e. high contribution of blanks) indicate uncertainties in the concentrations of measured species.

For Cr, the percent contribution of blank is significantly larger from the other species (20%) but is still acceptable. The very high blank contribution in Zn measurements indicate that there is some uncertainty in Zn data owing to the blanks.

Table 2.5 Sample to blank ratios and % contribution of blanks to observed concentrations

Elements	Sample to Blank Ratios	Standard Deviation	% Blank
Al	219.36	72.125	0.46
Ca	67.31	62.406	1.49
Cr	4.93	4.444	20.28
Cu	11.32	68.297	8.83
Fe	322.85	160.375	0.31
K	79.28	62.309	1.26
Mg	93.48	40.303	1.07
Mn	107.64	68.275	0.93
Na	13.25	6.841	7.55
Zn	1.82	0.652	54.95
Pb	14.43	51.328	6.93
Ni	7.72	5.19	12.95
Cd	6.17	5.895	16.21

2.4.3 Detection Limits

Detection limits are also calculated to check whether observed values lie below these limits.

The detection limits are dependent on the sensitivity and the fluctuation of the background. The detection limit is defined as the concentration value that corresponds to twice the absorbance obtained from 10 replicate measurements of the blank. Detection limits determined accordingly and the observed concentrations of elements are given in Table 2.6.

Table 2.6 Detection limits and the observed concentrations of elements (μg/l)

Element	Detection Limit	Observed Conc.	Element	Detection Limit	Observed Conc.
Al	0.2152	31.1475	Mn	0.0047	0.4306
Ca	0.2871	37.2223	Na	0.2356	5.1557
Cr	0.0088	0.0625	Zn	0.0163	0.1167
Cu	0.0055	0.0566	Pb	0.0020	0.0865
Fe	0.1882	48.4271	Ni	0.0080	0.0514
K	0.0488	7.0559	Cd	1.206E-4	3.580E-4
Mg	0.0728	8.3197			

CHAPTER 3
RESULTS AND DISCUSSION

3.1 Overview of Data

In this study, the soil samples were analyzed by AAS for 13 elements and by INAA for 40 elements. Average concentrations of elements measured in the study are given in Table 3.1. The table includes both AAS and INAA results. However, it should be noted that AAS data includes data from 119 samples but INAA data includes averages of data from 5 samples. Consequently, INAA data has only information value and does not have much statistical significance. Because of this, only arithmetic mean values are reported for the elements measured by INAA. If an element is measured with both AAS and INAA, the AAS data were used in the table.

Even simple statistical tools can provide indications on the state of pollution in the soil. Assuming that sampling and analytical uncertainties are small, concentrations of elements in the surface soil are expected to be similar and the standard deviations are expected to be small if the soil is unpolluted. Large variations in the concentrations in different samples may indicate high external additions at some sampling points. Although such large variation in soil composition from one sampling site to another may also be due to variation in soil type, large variations in soil type are not expected due to the small size of the study area.

An indication of the skewness of the data is the relation between the arithmetic mean, geometric mean and median concentrations of elements. If the data is normally distributed, all three values (arithmetic mean, geometric mean and median) are expected to be fairly similar, but if the data is skewed, arithmetic mean gets larger than the geometric mean and median (the difference is approximately a factor of 1.5-2.5) while the later two (geometric mean and median) are approximately the same. In Table 3.1, elements Al, Fe, K, Mg, Mn, Na and Ni have similar arithmetic mean, geometric mean and median concentrations indicating that these elements are normally distributed.

However, for elements Ca, Cr, Cu, Zn, Pb and Cd, arithmetic mean concentrations are significantly larger than the geometric mean and median concentrations indicating that the distribution of these elements are skewed. Skewness, although not a conclusive evidence, may indicate anthropogenic perturbations in soil composition as discussed previously.

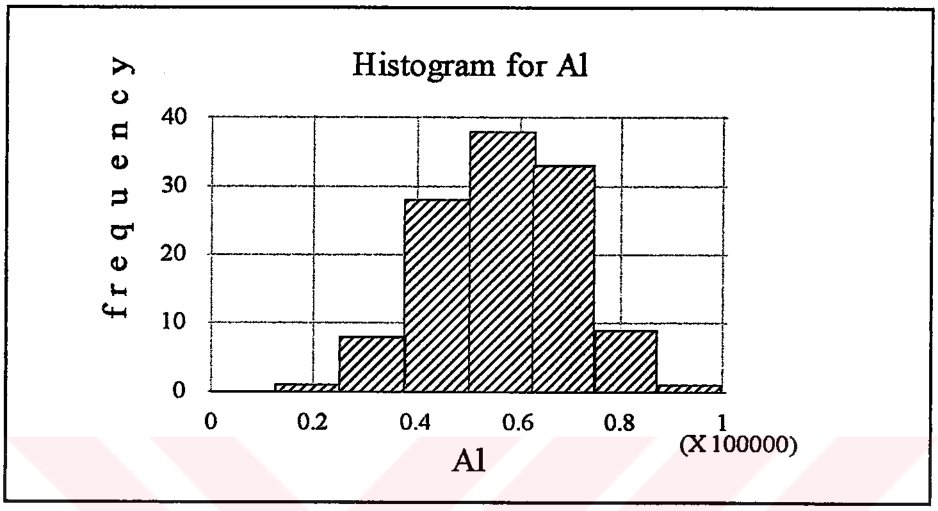
The conclusions derived from statistical tests were visually inspected by drawing frequency histograms for each element and the goodness of the proposed Gaussian or log-normal distributions were tested with chi-square tests. The frequency histogram for Al and Pb are shown in Figure 3.1. The frequency histogram of Al is a good example of elements following Gaussian distribution whereas the frequency histogram for Pb is an example for elements following skewed distribution.

The elements Al, Fe, K, Mg, Mn and Na which follow Gaussian distribution (within 95% confidence interval based on chi-square test) are elements that are involved in the aluminasilicate matrix of the soil. Their background concentrations in soil are quite high, therefore the contribution of anthropogenic sources on their concentrations cannot easily modify the soil composition by these elements. The elements Ca, Cr, Cu, Zn, Pb and Cd, on the other hand, showed skewed log-normal distribution within 95% confidence interval. These elements have relatively small concentrations in soil and anthropogenic input can easily perturb their soil-levels.

The anthropogenic input to surface soil in Ankara can either be discharges containing these elements or deposition from atmosphere. The simple reasoning followed in the previous paragraphs do not allow one to differentiate between the types of input. The discharges are expected to result in unusually high concentrations of some of the elements at the point of discharge, whereas atmospheric deposition is expected to produce more uniform concentrations with higher values at high-emission areas of the city. Contribution of these two different modes of input will be discussed in subsequent sections.

Table 3.1 Summary Statistics of the Measured Species (μg/g)

	N	Arithmetic Mean	Geometric Mean	Median	Minimum	Maximum
Al	118	57000±13000	55300	57300	14800	89400
Ca	114	66900±60600	42300	58000	560	358000
Cr	109	100±100	74	74	13	1000
Cu	119	100±680	32	30	7.7	7500
Fe	119	87900±35000	83400	83000	31000	368000
K	106	13000±11000	10400	12100	2400	88200
Mg	109	15000±5800	14000	14100	4100	43600
Mn	119	770±460	700	670	260	3900
Na	116	8700±4500	7600	8200	970	32000
Zn	119	98±78	81	79	11	620
Pb	118	158±617	46	41	2.4	5900
Ni	116	78±45	67	71	9.9	310
Cd	113	0.58±0.67	0.41	0.41	0.027	5.9
Cl	5	2300±4800				
Sc	5	7.7±3.7				
Ti	5	2800±1600				
V	5	74±34				
Sr	5	450±320				
Co	5	15±12				
As	5	13±8				
Se	5	6.7±7.8				
Br	5	26±52				
Rb	5	58±44				
Mo	5	5.2±5.2				
In	5	1.8±3.7				
Sb	5	1.7±1.6				
Ba	5	460±160				
Dy	5	3.5±1.5				
Cs	5	4.6±6.0				
La	5	25±13				
Ce	5	46±25				
Nd	5	35±33				
Sm	5	3.4±1.7				
Eu	5	0.71±0.16				
Tb	5	0.56±0.43				
Yb	5	1.5±0.87				
Lu	5	0.28±0.15				
Hf	5	3.7±2.2				
Ta	3	3.8±5.4				
Au	5	0.0047±0.0059				
Th	5	7.0±3.3				
U	1	2.0				
Ga	1	5.8				
Hg	5	0.17±0.21				



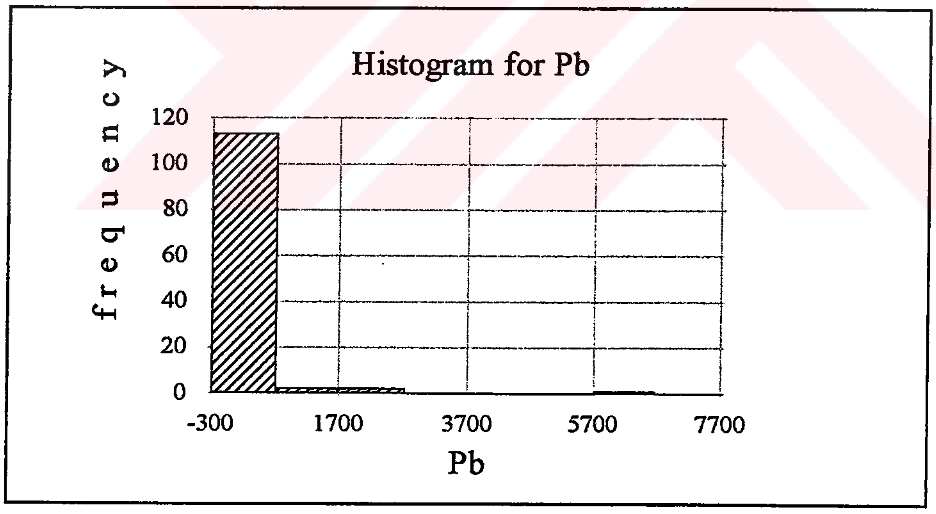


Figure 3.1 Frequency histograms for Al and Pb

3.2 State of the Pollution in Ankara

One of the important components of this study is to understand the pollution level in Ankara soil over a wide area. Various tests each of which produce some information on the current state of the soil pollution have been used. Data evaluation is presented in the following sections. At the end, conclusions obtained in each section is combined to produce the general picture of soil pollution in Ankara.

There are different indicators that show whether the soil in a certain region is polluted or not. This section discusses the state of the pollution of the surface soil in Ankara by making use of several indicators.

Comment on the state of the pollution can be carried out by comparing the results of the study with other studies exhibiting soil compositions for unpolluted or polluted regions. Mathematical interpretations such as enrichment factors and statistical tools (namely the multivariate technique - factor analysis- for this study) are used and discussed in the subsequent sections.

3.2.1 Comparison with Literature

Regulatory standards for soil pollution in Turkey and elsewhere are not available. Although there are some guidelines and action levels, these are for few highly toxic and frequently observed elements. One way to assess the current pollution level of the soil is to compare the data generated in this study with data obtained in other polluted or unpolluted soils given in the literature. In this way, a fairly complete picture of pollution of soil can be obtained for. a variety of elements. Such a comparison is depicted in Figure 3.2.

Since trace element data on surface soil is not very abundant in literature, it was not possible to compile data on different elements from few studies. This was particularly true for elements measured by INAA, because there are few

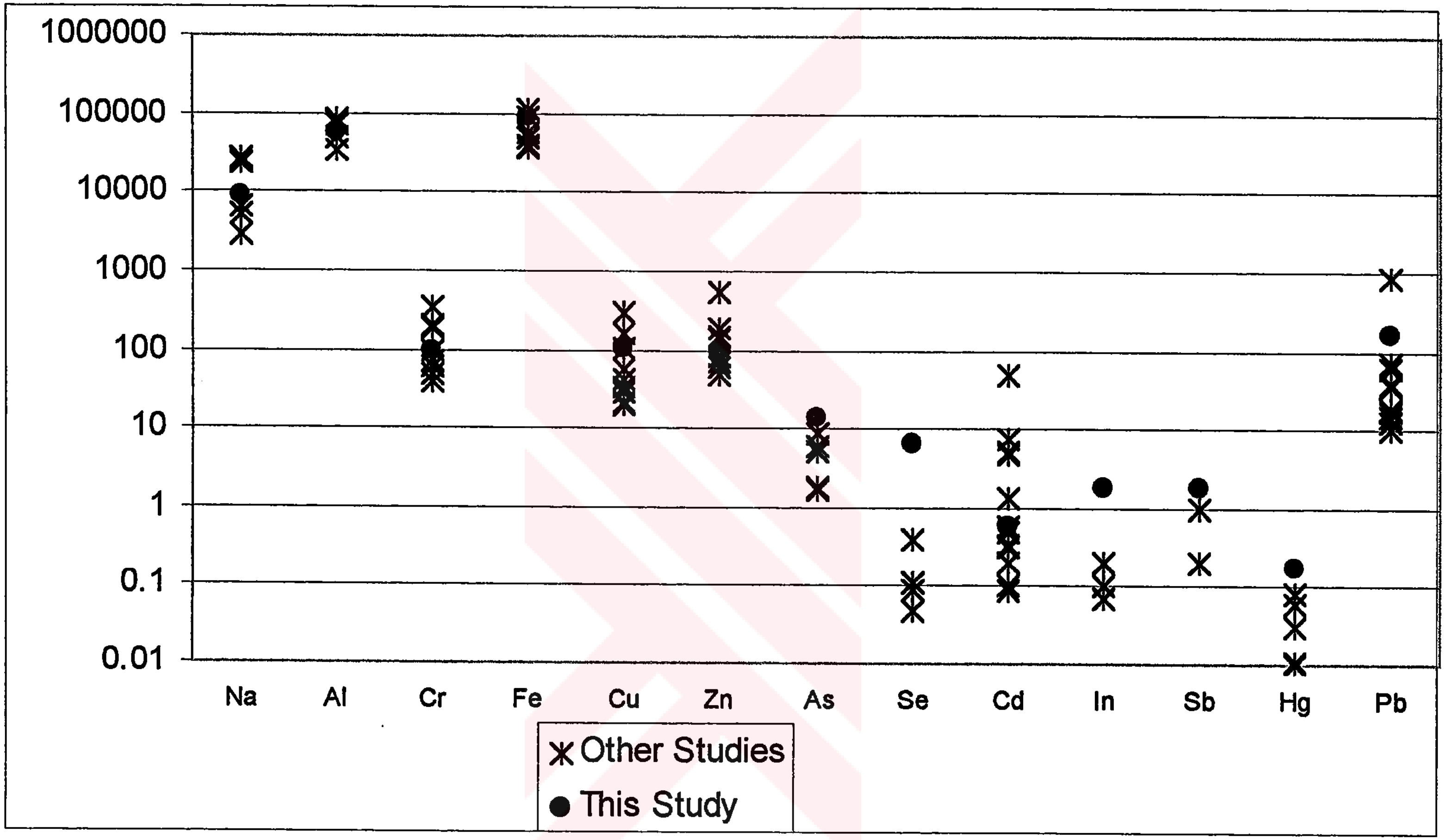


Figure 3.2 Concentrations of elements in this study and other studies (μg/g)

INAA data in the literature. The problem was avoided by using different literature data for different elements.

For this comparison, various types of soils with different degrees of pollution from different parts of the world were used. Background concentrations were obtained from Kabata-Pendias and Pendias (1984) for world range for non-polluted soils, from Mason (1966), from Carasco and Prendez (1991) for continental Chile and Antarctic Peninsula, from Chen et al (1991) for background China soil. Moderately polluted urban soil data were obtained from Fergusson et al (1990) and Aubert et al (1997) for world averages, from Carasco and Prendez (1991) for metropolitan Chile, from Güvenç (1998) for Antalya soil and from Hamzaoğlu (1998) for Kütahya soil. An example for heavily polluted soil was obtained from Abdel-Sahab et al (1994) who carried out their study in an old mining region in USA. The studies of Güvenç (1998) and Hamzaoğlu (1998) were to a some degree affected by copper mining and thermal power plant activities respectively.

Although only 5 samples were analyzed by INAA, elements measured only by this technique, such as As, Se, Hg and Sb, are included in the figure. Although the INAA data are too small to be used in statistical data treatment, the INAA data do provide fairly reliable information on the general levels of these elements in Ankara and can be used in this comparison. For the elements measured by both INAA and AAS, the AAS data for that element was used in the figure due to better statistics of the AAS data set.

Concentrations of Na, Al and Fe in Ankara are comparable with literature values for polluted and unpolluted soil. These elements are part of the soil structure and pollution does not affect their concentrations, neither in Ankara nor anywhere else.

Copper, Cr, Zn, As, Se, Cd, In, Sb, Hg and Pb are pollution derived elements. Their concentrations are likely to be determined by anthropogenic activities such as discharges from specific points or deposition from atmosphere. Among these, Zn, Cr, Cu and Cd have comparable concentrations with literature. Concentrations of all other pollution derived elements, namely As, Se, In, Hg, Sb and Pb, in Ankara soil are higher than corresponding concentrations reported for other urban areas on the world. This is a first indication that soil in Ankara is enriched and probably polluted by toxic elements. This is particularly true for As, Se, In, Sb, Hg and Pb. For these elements, the level measured is one of the highest values reported for urban areas.

3.2.2 Average Concentrations of Different Soils

Another approach to identify the pollution in the city is to compare data generated from sites far from pollution sources such as rural areas with data generated in the expected polluted region.

If the soil in Ankara is polluted, then one would expect a significant difference in the concentrations of pollution derived elements in the stations at the rural area far from settlement and industrial areas, where the influence of anthropogenic activities are minimum, and stations at heavily populated or industrialized districts of the city.

The average concentrations of selected elements in background and polluted stations are given in Table 3.2

The average concentrations of elements in unpolluted stations in the table are produced by averaging the data obtained in a set of 14 stations which are located at the outerskirts of the study area. The average concentrations in polluted stations are obtained by averaging the data from 9 stations which are located in the most heavily populated districts of the city such as Kızılay or districts with nearby industrial activities or heavy traffic load. The locations of these two groups of stations are presented in Figure 3.3.

Concentrations of elements which occur in the alumina structure of the soil and hence usually are not easily affected by external sources are not much different in background and urban sites in the study area.

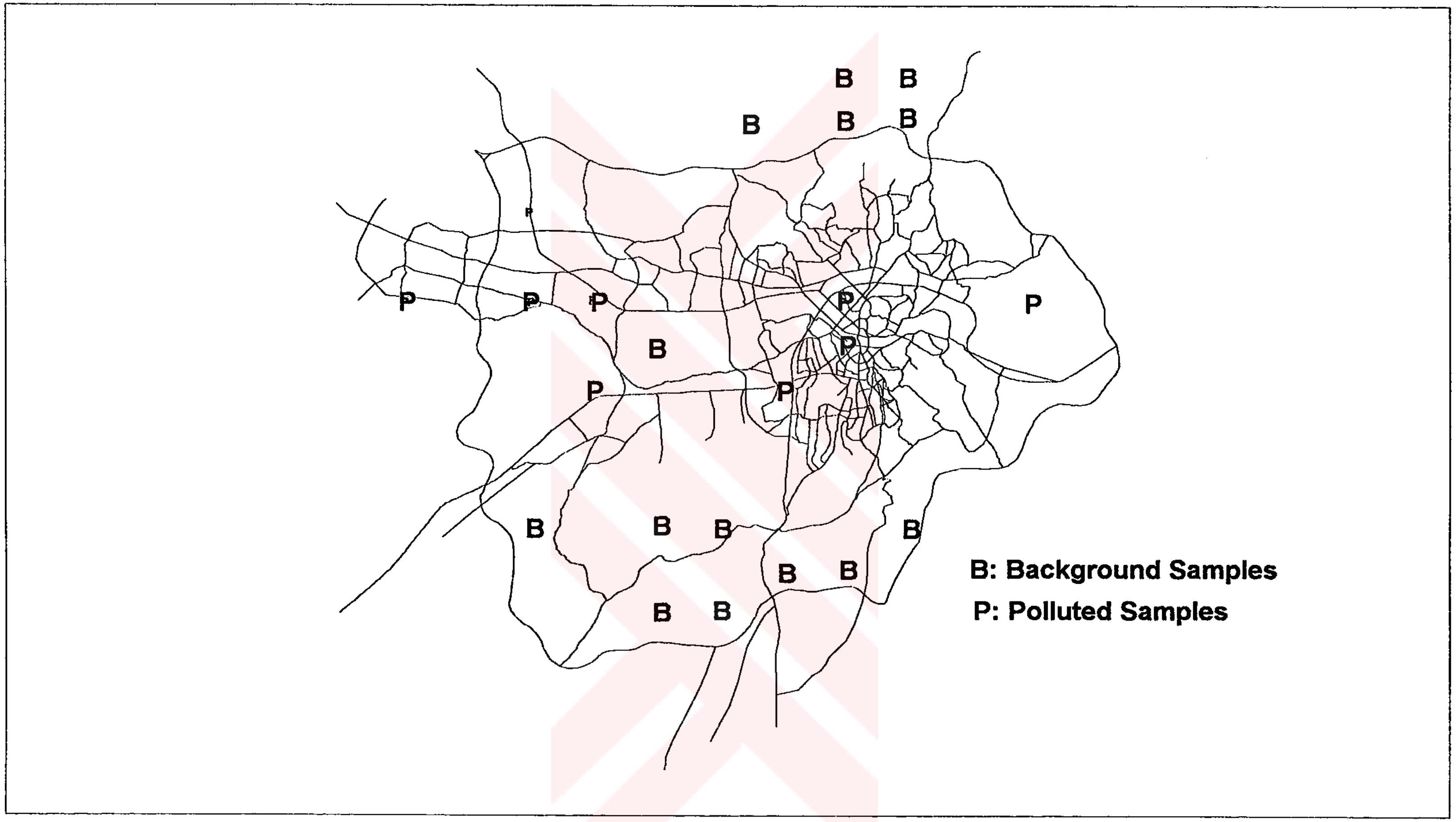


Figure 3.3 Different station groups

Concentrations of pollution-derived elements, which are generally affected by man-made sources, are approximately a factor-of-two higher in polluted regions of the city compared to the concentrations measured in rural parts. There is a significant concentration gradient between polluted and unpolluted regions which is an additional indication that pollution is a function of intensity of human activities.

Unlike other anthropogenic elements, Pb levels in central parts of the city are not different from the Pb levels measured in unpolluted rural stations. This is expected because Pb in soil is generally due to emissions from motor vehicles. Motor vehicle emission is an areal source which is distributed more homogeneously over the city compared to the other elements.

Table 3.2 Average concentrations of anthropogenic elements in unpolluted and polluted stations (μg/g)

	Background	Polluted
Cr	95±58	232±342
Cu	35±13	53±67
Zn	64±25	167±124
Pb	73±77	72±68
Cd	0.45±0.21	0.76±0.53

3.2.3 Vertical Distributions of Elemental Concentrations

Vertical profiles of elements is another indication of anthropogenic contribution to surface soil. One would expect fairly uniform vertical profiles of elements which are not affected by anthropogenic input. Concentrations of elements with anthropogenic sources, on the other hand, are expected to show a gradient with lower concentrations in the deep soil. Four core samples were collected from different parts of the city. Collected cores were 20 cm deep sliced into 4 cm thick sections. Each section were analyzed for the same suit of elements with the bulk surface samples.

The vertical profiles for Al, Pb, and Cd are given in Figures 3.4, 3.5 and 3.6. Aluminium is chosen as an example for crustal elements which does not change with depth of soil. Elements such as Al, Fe,K, Mn and Ni are dominant in soil factor and anthropogenic sources do not significantly cause the enrichment of these elements on the surface. This can be observed from the relatively homogenous profile of Al in the vertical distribuiton.

Pb and Cd are typical anthropogenic elements and their enrichments are mostly related to traffic load. The expected decrease in the concentraions with increasing depth of soil can only be seen for these elements although not consistent in all core samples. The distributions for Güvenpark samples are, however, exceptions. The expected decrease of concentrations with depth cannot be observed in any samples at this location. The reason for this is most probably that Güvenpark is a central and recreational location and the soil is frequently disturbed for planting or other activities. Since the soil is disturbed by dredging or digging the vertical profile has changed and the deeper parts do not necessarily contain undisturbed background soil.

For Pb, the decrease with depth can be observed in Dikmen sample and the profile is most striking in one of the METU samples where the decrease most significant after 10 cm from the surface. The other METU sample exhibits a decrease with depth which is disturbed by the sudden increase at the deepest section. The reason for the increase at the deep section is interesting and need to be explained by further studies.

The reason for Pb and Cd being at higher concentraions at the surface than the deeper sections is certainly the deposition of Pb and Cd emitted to the atmosphere from human activities (especially vehicle emmissions for Pb) to the soil surface.

For Cd, a perfect profile with decreasing concentrations with depth can be seen for the Dikmen sample where the Cd concentration decreases from 900 ng/g at the surface to 200 ng/g at the deepest section. It is interesting to see a

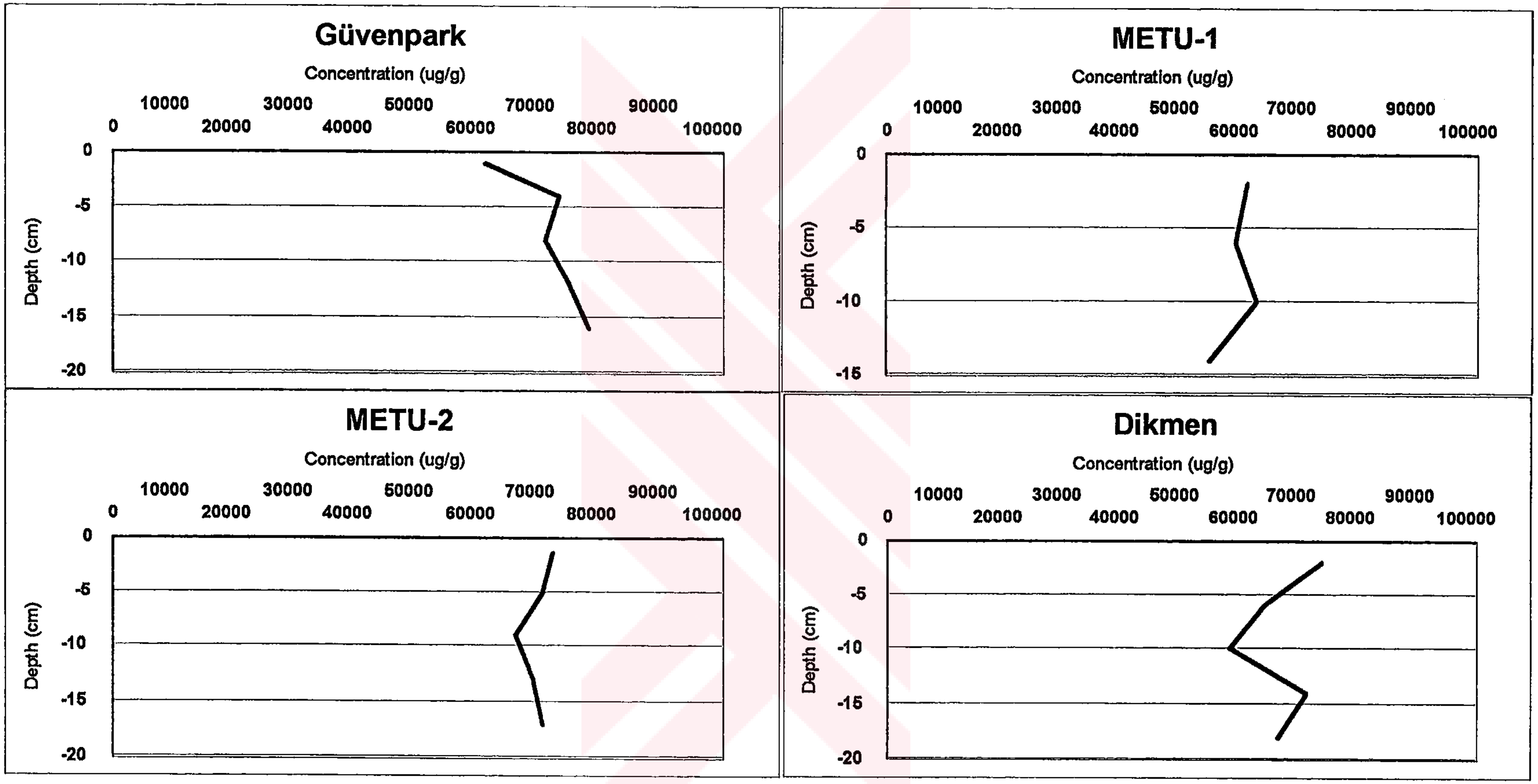


Figure 3.4 The vertical distribution of Al

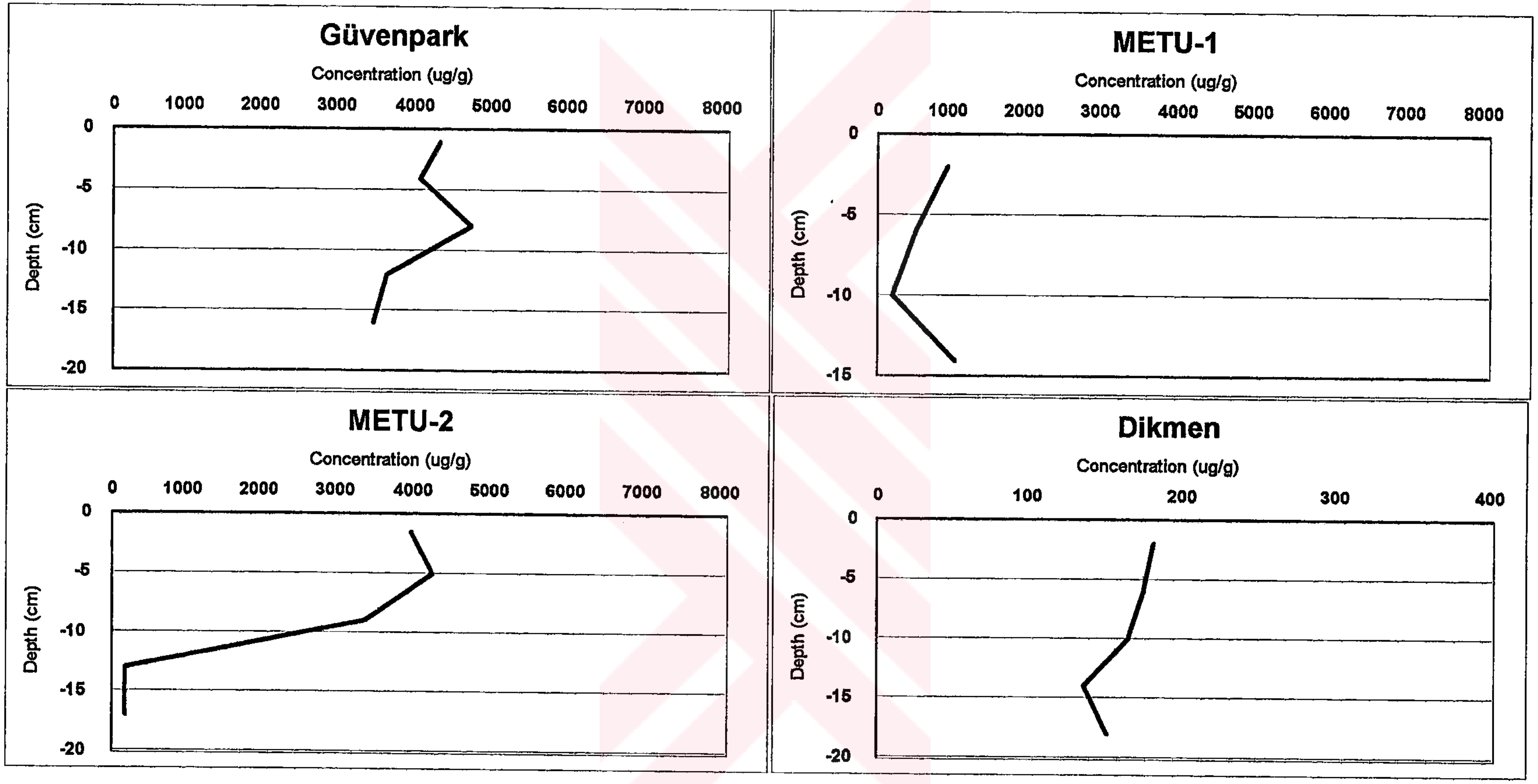


Figure 3.5 The vertical distribution of Pb

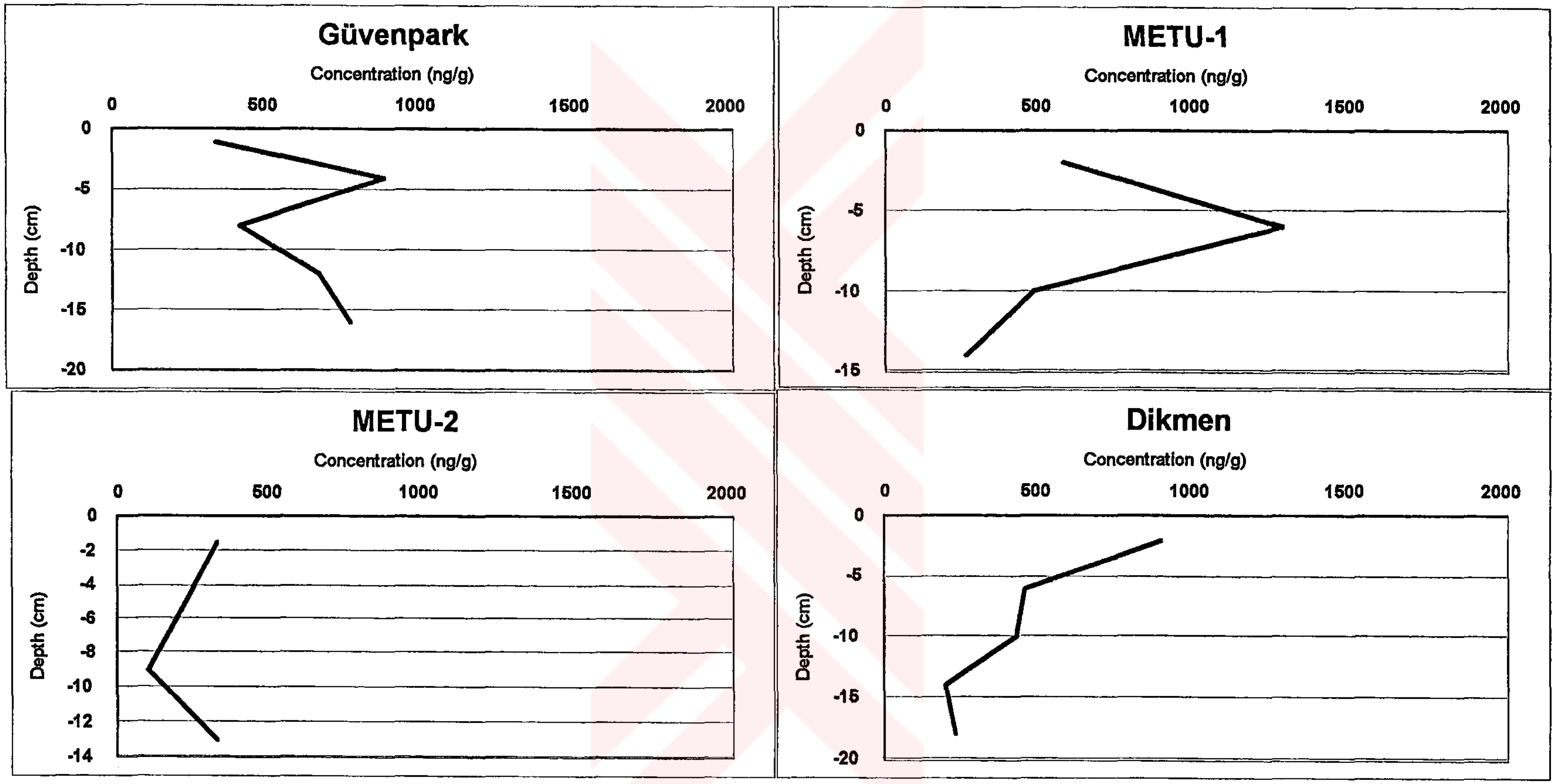


Figure 3.6 The vertical distribution of Cd

trend opposite to that of Pb for one of the METU samples. The Cd concentration decreases systematically at the first 10 cm from the ground but it rises up to the surface values whereas the Pb value had dramatically decreased at the same section. This may lead one to conclude that the effect of crustal origin is more significant for Cd than for Pb. For the other METU sample, a good decreasing profile can be observed after some 8 cm. The lower concentration of the uppermost part can be explained, though, since the first 8 cm can still be considered as the surface soil and the highest concentration can be seen at the second section by the effect of infiltration of the elements to this depth with the effect of rain water.

In general, it can be stated that the chosen depths of core samples have not been adequate since the soil can be vertically mixed within this range. Further studies on vertical distribution of elements should choose greater depths for core samples.

Above discussions on concentrations of anthropogenic elements compared to values reported in other urban areas, difference between concentrations measured in rural parts of the study area and at intensive settlement areas and vertical profiles of elements have indicated that the soil in Ankara, particularly in regions with extensive human activities are polluted. However, these discussions do not provide information on whether pollution is a widespread phenomenon or whether it is limited to certain areas around point or area sources and whether the chemical composition of soil is modified. If the soil composition is modified, it should be determined whether it is modified at certain places or all around the city. The answers to these questions are given in the following sections.

3.2.4 Distribution of Elements in Ankara

Ankara is not an industrial city and there are not many point sources that can cause the enhancement of concentrations in soil. Observed increase in the concentrations of elements in soil is probably due to local human activities such as traffic and residential heating. Consequently, concentrations of elements in soil is expected to be high in area with high population density. This is shown in Figure 3.7 where the variation of Zn concentrations along east-west and north-south transects are plotted. The highest Zn concentrations are observed in central parts of the city which is a circle that extends from Konya-Samsun highway on the west, Oran on the north and Çankaya on the south. Concentrations of other pollution-derived elements are also high within the same circle. This polluted area includes the most heavily populated districts of the city, but it does not include any serious industrial activity. This confirms that the pollution by heavy metals in the city of Ankara is due to the settling of particles emitted from residential heating and traffic.

Although the variation of concentrations along transects indicate that the central residential area in the city is the most heavily polluted part of the city, it does not provide information on the distribution of pollution in other parts of the city. More detailed information was obtained by interpolating the results of measurements at 120 points.

The interpolation was carried out by using the GIS software Mapinfo Professional (Mapınfo Co.). Among the available interpolation techniques, the technique of triangulation with smoothing was chosen. With this option, the software draws virtual triangles between all neighbouring sampling points in a given range and carries out the interpolation within those triangles. The results of the interpolation are saved in grid files which contain concentration data for many more points within the sampling area. The grid file then can be converted to distribution maps with different options of the software. Although there are various techniques for presentation of interpolation results, the maps presented in this study were prepared by contours of concentrations which are believed to be the best way of presenting distributions.

The distributions of Al, Ca, Cd, Cr, Cu and Pb are given in Figures 3.8, 3.9, and 3.10 respectively.

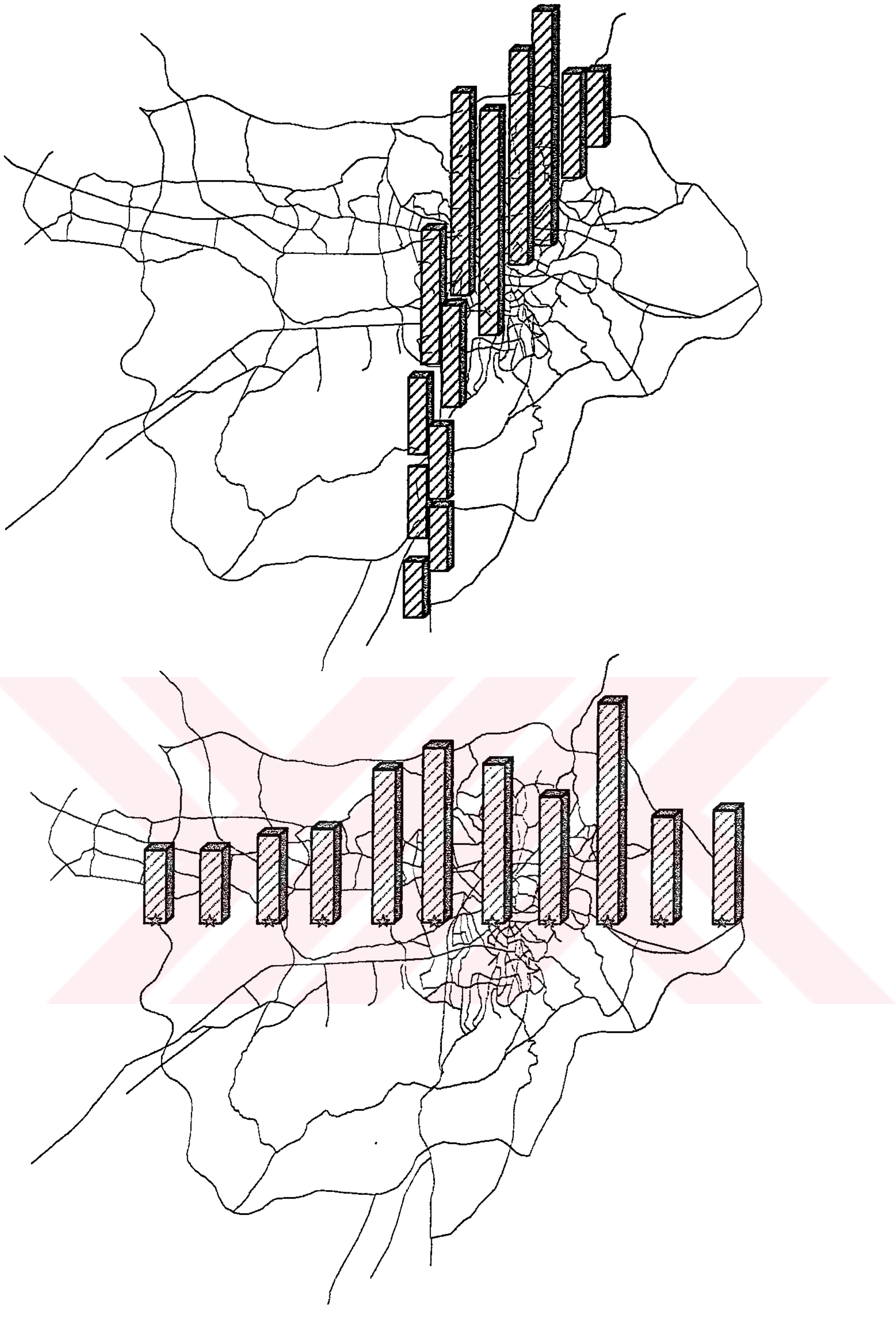


Figure 3.7 Variation of Zn concentration along north-south and east-west transects

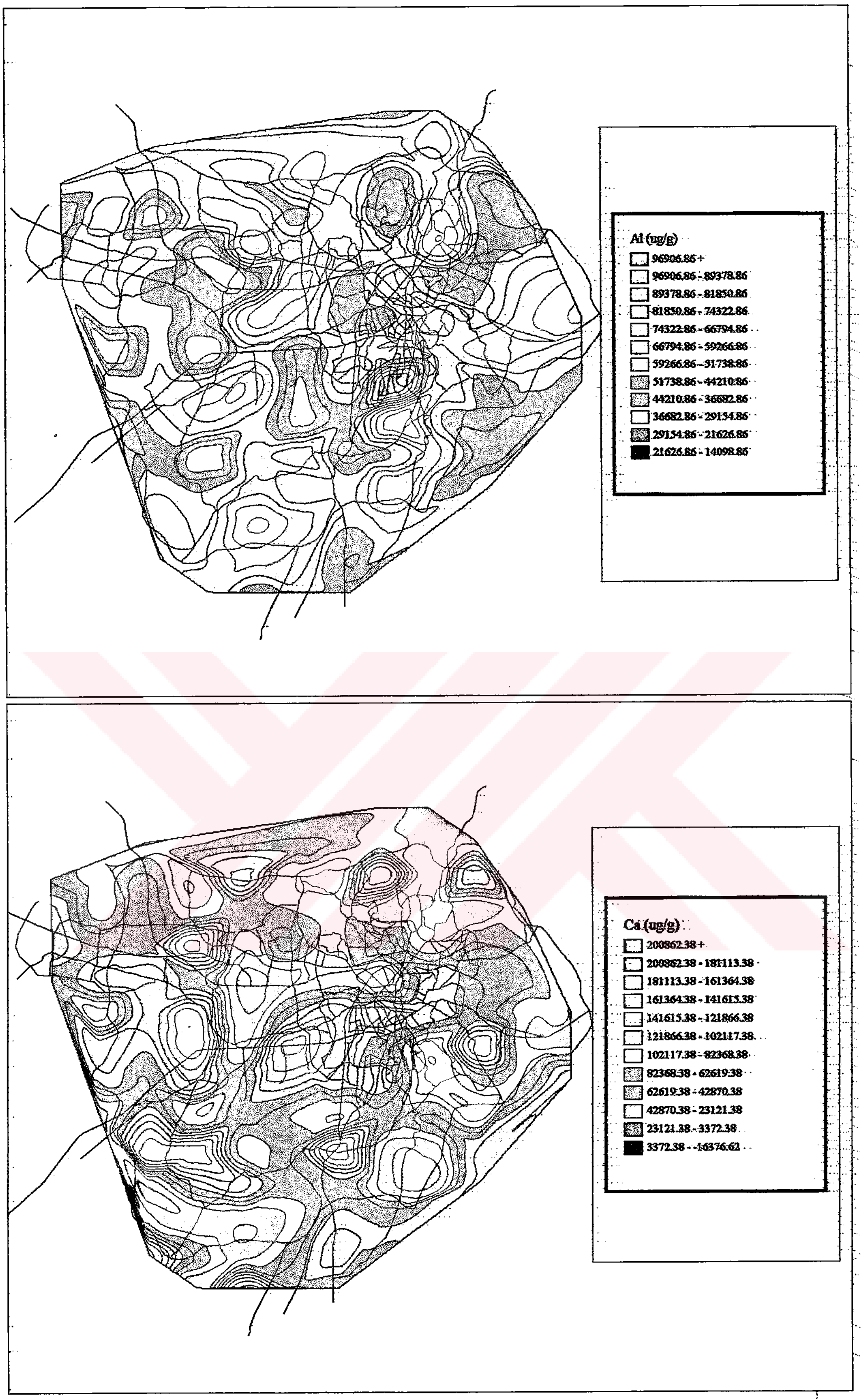


Figure 3.8 Distribution of Al and Ca

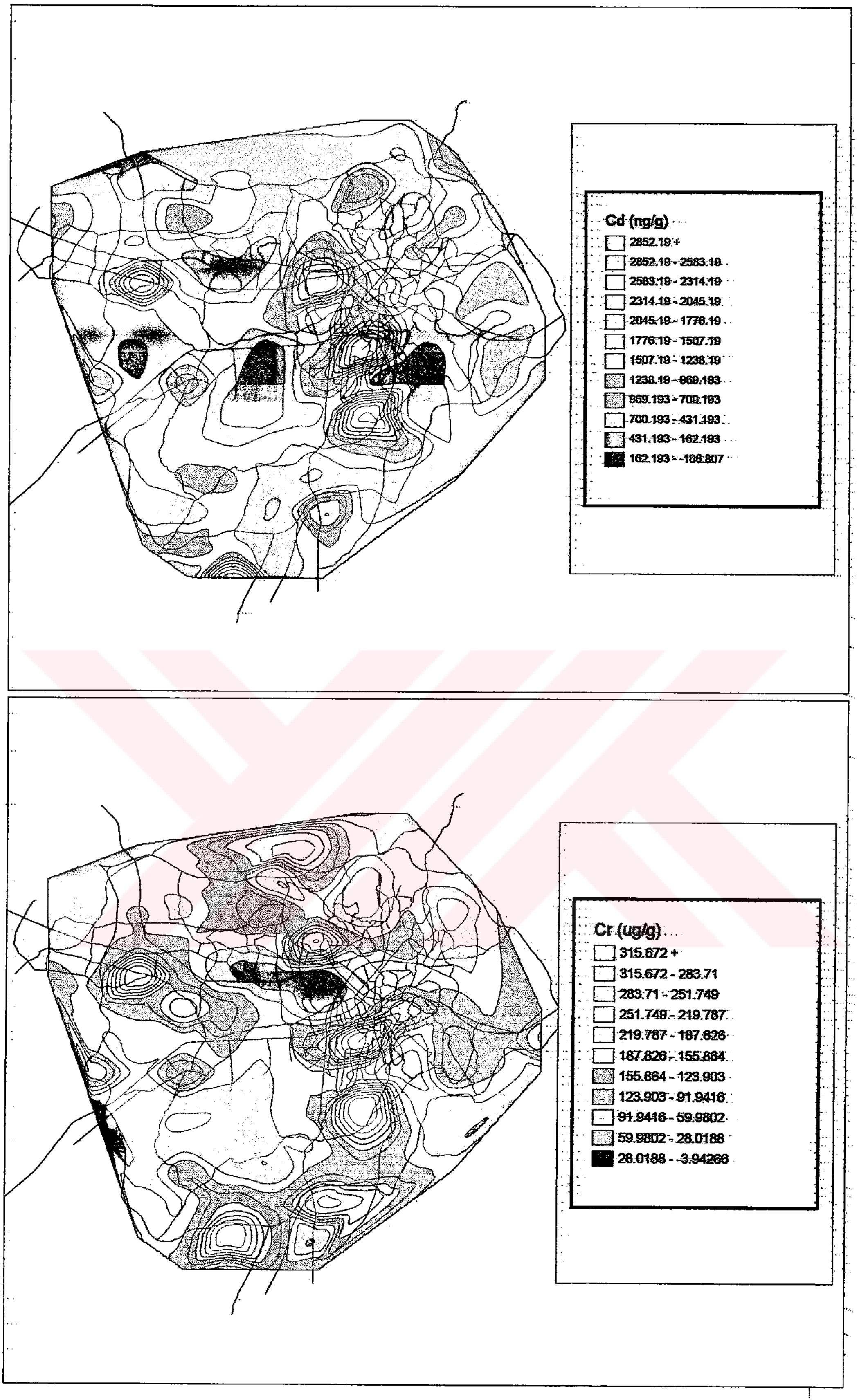


Figure 3.9 Distribution of Cd and Cr

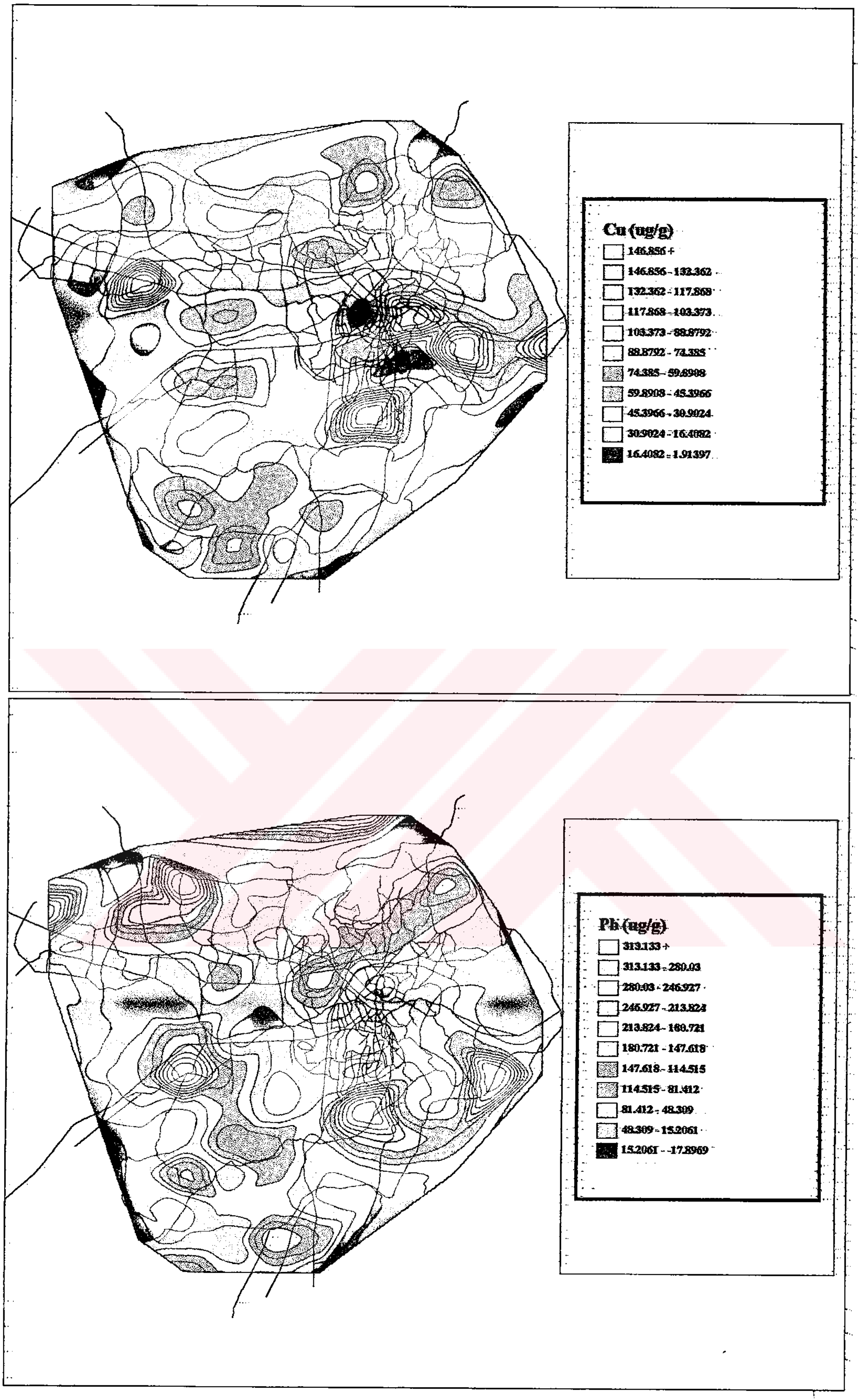


Figure 3.10 Distribution of Cu and Pb

Al and Ca are natural elements, i.e., they occur in the aluminasilicate matrix of the soil. Their concentration in soil are so high that it cannot be easily altered by anthropogenic activities. Their distributions are expected to be fairly uniform. This is observed for Al where the concentrations do not change significantly from one place to another and slight variations indicate different soil composition rather than anthropogenic contribution.

The distribution of Ca is slightly different. The distribution is uniform throughout the city but at two points at both sides of the Eskişehir highway. These two hot spots coincide with two cement factories at those locations. The increase at those points are probably due to the effect of the cement industry. Ca rich soil is used in cement production and deposition of stack emissions result in the observed high concentrations around the cement industry. Although Ca is a crustal element, the observed high concentration is due to an anthropogenic activity.

There are some common features in the distributions of anthropogenic elements Cd, Cu, Pb, Zn, Cr and Ni.

Concentrations of pollution-derived elements are higher in the heavily populated central parts of the city. Especially for Zn, Cd, Cr, Mn and Ni, it can be seen that concentrations are higher in the densely populated districts such as Çankaya, Dikmen and lower sections of Mamak. Concentrations are fairly low in the regions with low population density. For example, sites beyond Hacettepe University and METU are scarcely populated and the lowest concentrations for most of the anthropogenic elements are measured in these locations. Close relation of concentration distributions of elements with population density and lack of similar relation with industrial activities suggest that the deposition of emissions from residential heating is the dominant source of anthropogenic elements in surface soil. This conclusion agrees with the aerosol and precipitation studies performed in the same region. Besides the general high concentrations in these populated regions, three common high concentration spots for the anthropogenic elements were observed. The first of these hot spots occurs at the north-west part of the city which is under the effect of emissions from the nearby industrial areas such as Ostim industrial region.

The other high concentration location for all of the measured pollution-derived elements and for some of the crustal elements is located at the Dikmen district of the city and the third one is located at the northwest of the study area. The hot spot which lies to the northwest of the study area is around the sugar manufacturing plant and in the industrial district of the city where high concentrations are expected. However, the hot spot located to the south of the city (approximately in Dikmen district) cannot be related to any significant nearby source. This spot is probably due to a certain discharge of a polluted waste at the very sampling point or due to contamination during analytical procedures. However, this hot spot can still be of interest for further studies for determining the source of the high concentrations of elements.

The distribution of Pb is slightly different from distributions of other anthropogenic elements. High Pb concentrations were observed throughout the city, not necessarily only at districts with high population density. This is probably due to the area nature of the motor vehicle emission and the difference between the traffic and the population density pattern in Ankara.

3.2.5 Pollution Classes of Elements

Another way to assess the state of pollution of the local soil is to compare the actual concentrations with regulations or guidelines. However, as stated earlier, there are no such regulatory standards for Turkey or any place else. Therefore, the possible way to assign the guidelines is to compile acceptable levels determined in other studies for soil examples with different pollution levels.

Pollution classes assigned as unpolluted , slightly polluted, moderately polluted, considerably polluted, heavily polluted and extremely polluted for the anthropogenic elements Cd, Cu, Ni, Pb, Zn and Cr have been created for this study by making use of data taken from studies around the world Kabata-

Pendias, 1992 and 1995; Kabata-Pendias et al., 1992 and 1993:; Council Directive EC, 1989; Rauta et al., 1995; Lacatusu et al., 1991 and 1992; Code Practice GB, 1989). The pollution classes for concentration intervals for anthropogenic elements are given in Table 3.3

Table 3.3 Pollution Classes for anthropogenic elements (concentrations in µg/g)

Elements	Pollution Class					
	Unpolluted	Slightly polluted	Moderately polluted	Considerably polluted	Heavily polluted	Extremely polluted
Cd	0.3	1	2	3	5	>5
Cu	15	30	50	80	300	>300
Ni	10	30	100	200	400	>400
Pb	30	70	100	500	2500	>2500
Zn	50	100	300	700	3000	>3000
Cr	30	70	100	300	1000	>1000

The distribution of elements around the city according to these classes are also presented in Figures 3.11, 3.12 and 3.13. for Cd, Cu, Ni, Pb, Zn and Cr.

According to the above classification, the figure shows that most parts of the city are either unpolluted or slightly polluted in Cd. However, in the central and populated districts of the city such as Kızılay and Çankaya, and around Sincan –which is closer to industrial districts-, the soil is moderately or even extremely polluted.

The dominant pollution class for Cu is "moderate" in most parts and the levels reach considerable or heavy pollution in some parts. The heavily polluted spots are similar to those mentioned for Cd and higher pollution levels occur at the same locations for other elements presented in pollution class figures.

For Ni and Cr, most parts are moderately or considerably polluted, and there are only a few heavily polluted points.

When Zn is of interest, the soil is considerably or heavily polluted in populated districts and around industries such as the sugar plant at the north-

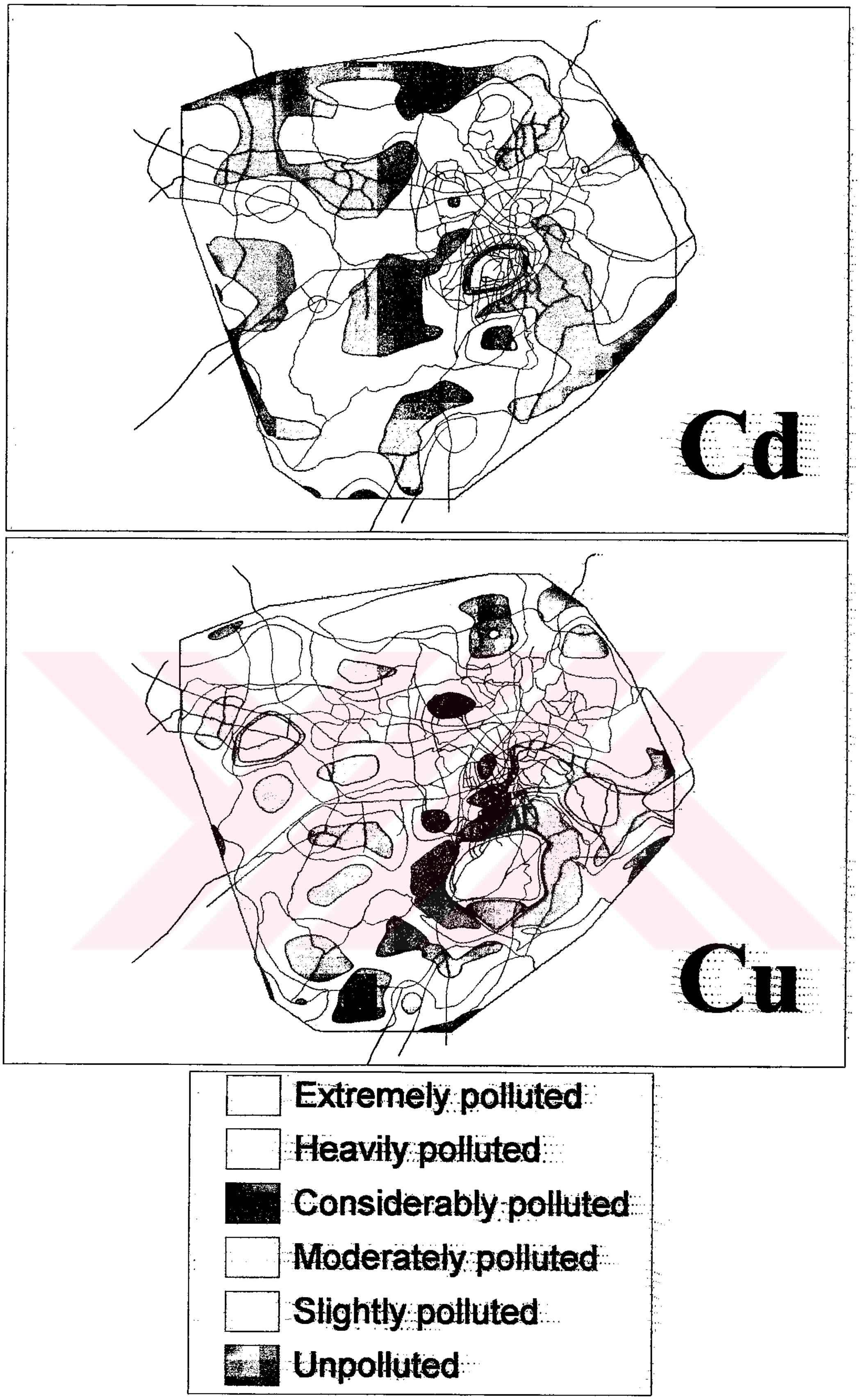


Figure 3.11 Pollution levels for Cd and Cu

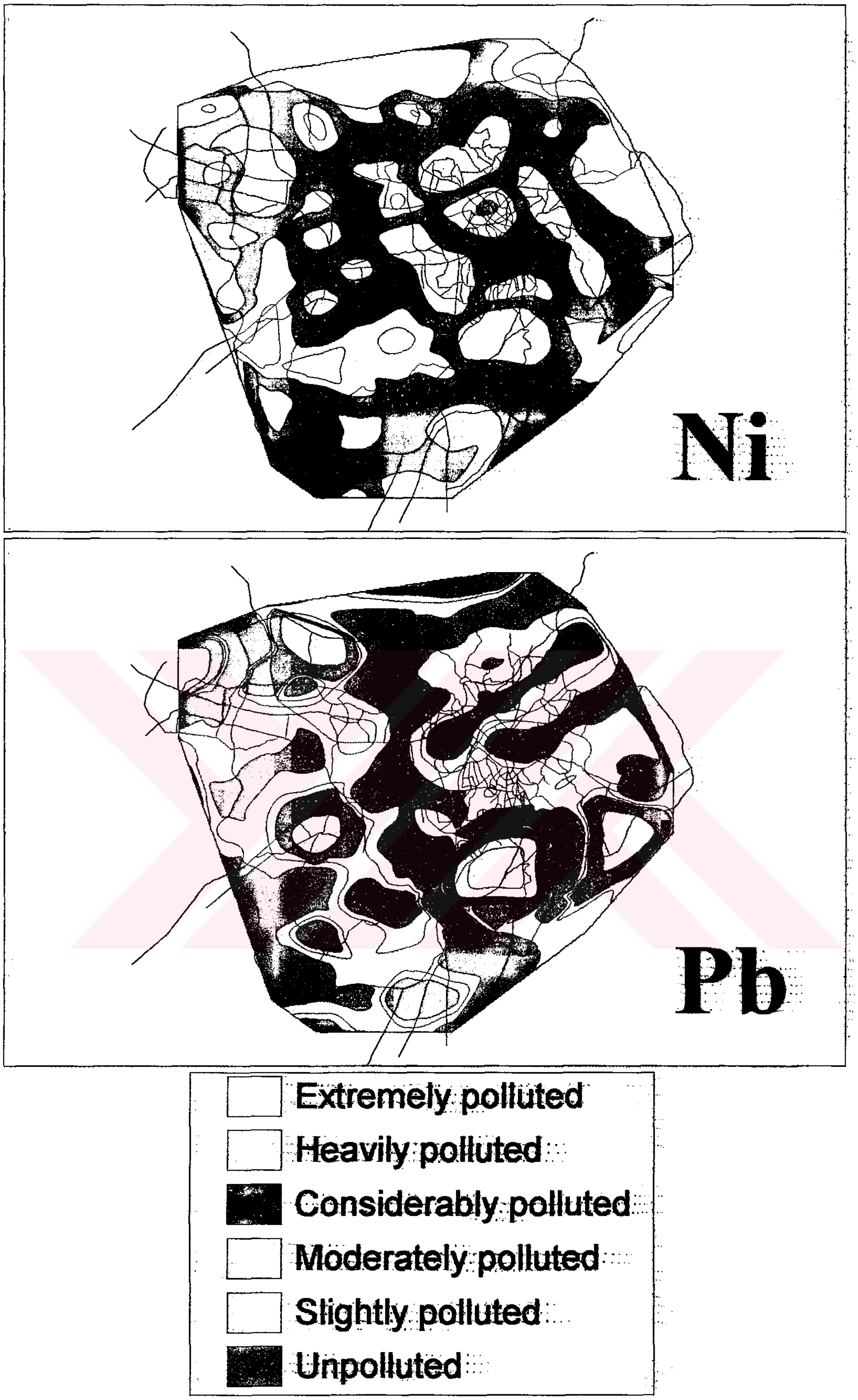


Figure 3.12 Pollution levels for Ni and Pb

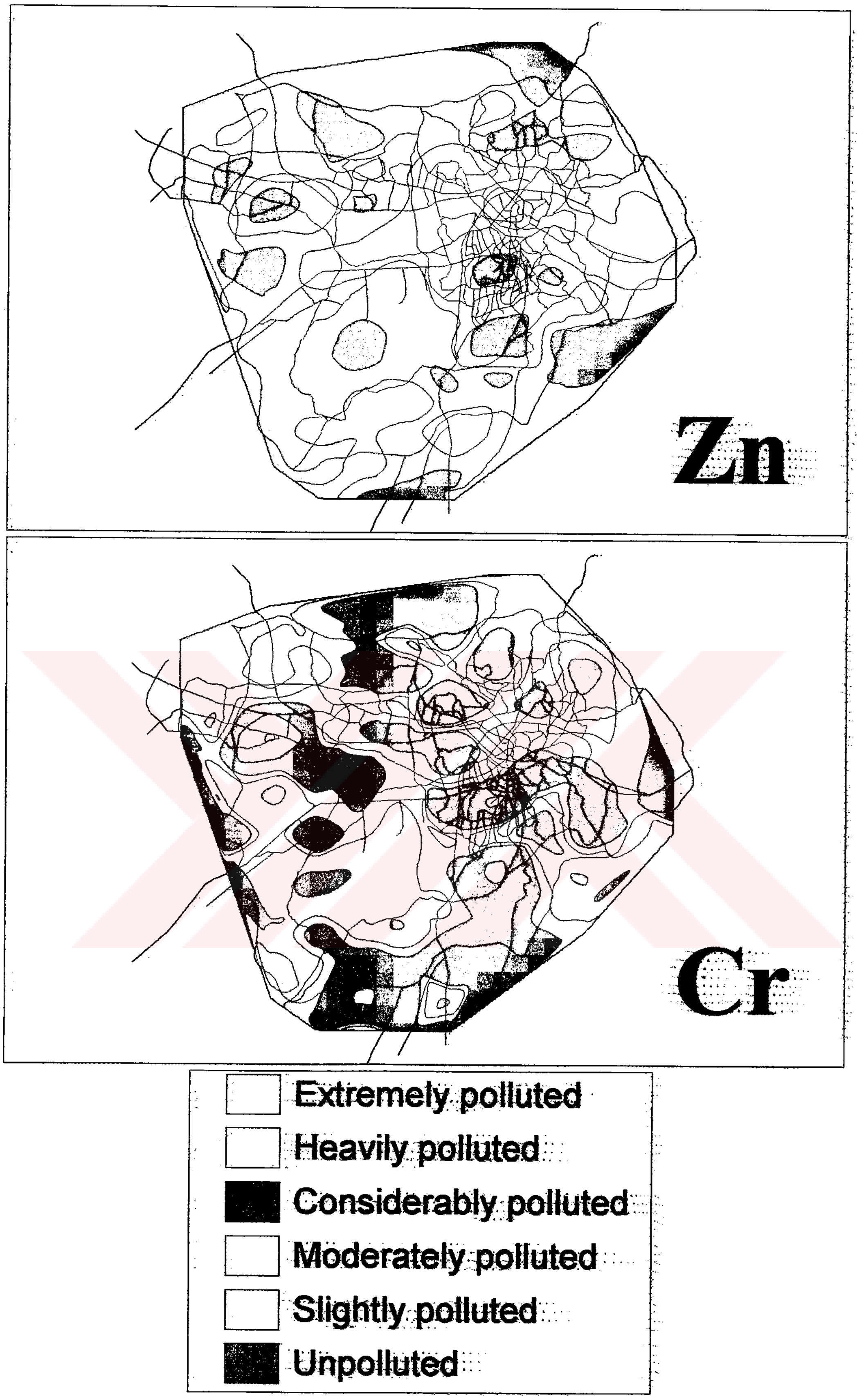


Figure 3.13 Pollution levels for Zn and Cr

west. The remaining districts, which are relatively have smaller population densities, are either slightly polluted or unpolluted.

For Pb, the pollution is more widespread within the city and polluted sections can be observed in different parts of the city which reach heavily polluted state at certain parts.

3.2.6 Crustal Enrichment Factors

The discussion on the distribution of concentrations, comparison with literature all give information on the possible contribution of human activities on soil concentrations of elements but they do not provide information on whether the soil composition is substantially altered by the action of humans. Although comparison with limits do provide such information, the guideline values for elements are generally so high that compliance with the guidelines can give a false impression that the soil composition is not modified. But if the soil composition is modified and deposition to the surface continues, then levels that require some action may be reached in the future.

The measured concentrations have been compared with accepted clean soil composition to assess if the anthropogenic activities in Ankara have modified soil composition. For this purpose, crustal enrichment factors (EF_c) of elements were calculated and distribution of EF_c within the city were investigated.

The enrichment factor (EF) is a double normalization technique which can be computed using the following expression;

$$(EF)_{source} = \frac{(C_i/C_n)_{sample}}{(C_i/C_n)_{source}}$$

where C_n is the concentration of the normalizing element, and C_i: is the concentration of the element whose enrichment is to be determined.

The normalizing element is the common reference element in the source according to which the enrichment will be determined. For crustal enrichment, Al is the common reference element because its concentration in soil is high. There is no common anthropogenic Al source which can modify soil and Al is an element which can be easily measured with a number of analytical techniques. Other reference elements such as Fe, Si and Sc can also be used in EF_c calculations.

The crustal enrichment can be expressed as the ratio of an element in the sample to Al in the sample compared with the ratio of the same element in the reference soil composition to Al in the reference. The most widely expected and used soil profile used as reference for crustal enrichment is Mason's (1966) earth crust compilation. Mason's compilation has been prepared through background analysis of soil from different places and is widely accepted as the composition of earth crust. Mason's compilation was also used in this study as a reference unpolluted soil in enrichment factor calculations. The levels of elements of interest in Mason's compilation were listed in Table 1.1.

If the only source of a measured element is earth's crust, then its EF_c is expected to be unity. An EF_c value higher than unity indicates that the soil has been enriched with some other external source than the crustal origin. However, it is the general practice to consider elements with EF_c value higher than 10 as enriched, because the soil composition generally changes from one location to the other and the slight changes in the ratios of elements can be in relation to this spatial change of the original soil but variations are not expected to be larger than a factor of 5 or 10 (Parekth et al. 1989). It can be stated that elements with EF_c values less than 5 are at background levels, elements with EF_c between 5 and 10 are moderately enriched and elements with EF_c greater than 10 are highly enriched by anthropogenic sources.

The average EF_c's of elements are shown in Figure 3.14. The figure includes all the elements measured by both INAA and AAS. EF_c values for Na, K, Mg,

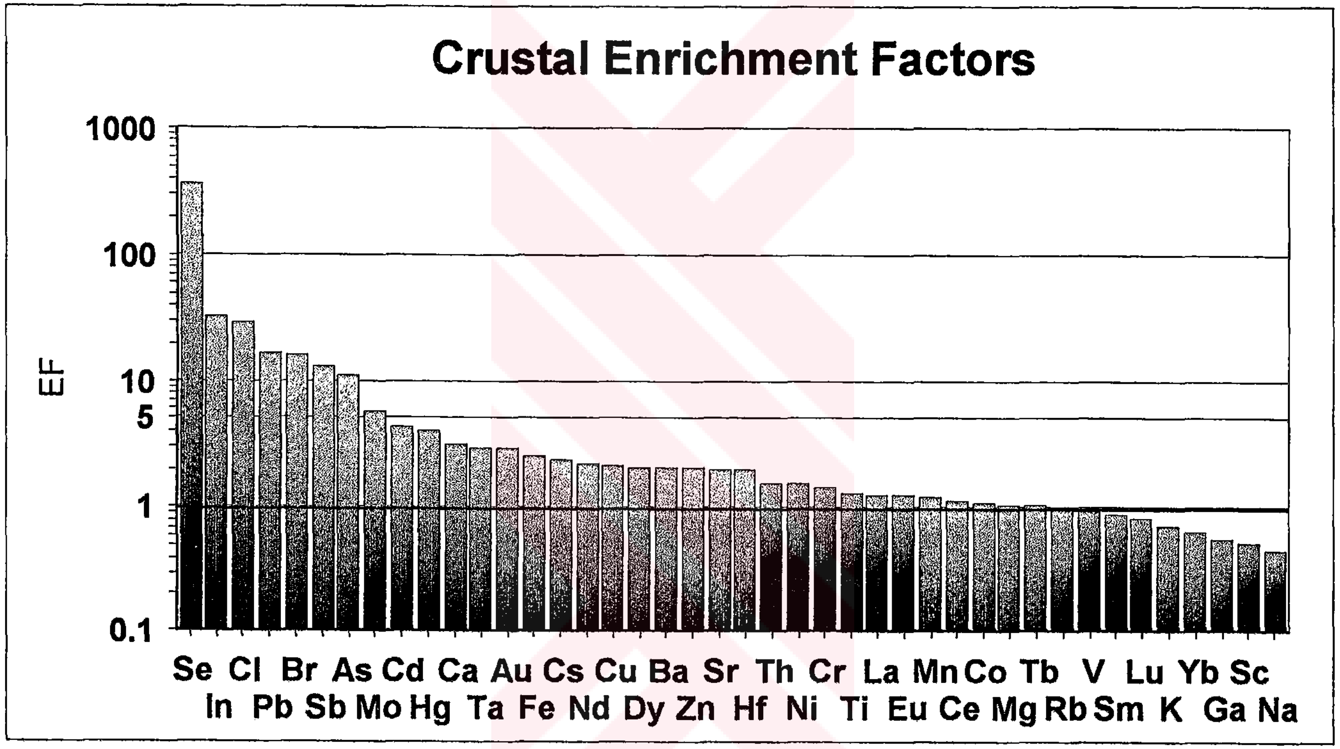


Figure 3.14 Crustal enrichment factors of elements

Mn, Cr, Ni, Zn, Cu, Fe, Ca, Cd and Pb have been calculated by using analytical results of 120 samples and the EF_c values in the figure are representative for the enrichment of these elements in the city. The remaining elements have been analyzed by INAA for only 5 samples and have information value but have only limited statistical significance.

Elements with $EF_c<5$ include all crustal elements as expected. Cu and Zn also have $EF_c<5$ indicating that these elements are not substantially enriched throughout the city but they might be enriched in certain districts.

Anthropogenic elements Mo, As, Sb, Br, Pb, Cl, In and Se are significantly enriched indicating substantial modification of soil composition by these elements due to human activities. Elements Pb, Br and Cl are known to be enriched in motor vehicle emissions (Ondov et al, 1982). Cd, although not as enriched as these elements, is also an indicator of pollution related to traffic because it is a product of tyre wear from vehicles (Haktanır et al, 1995). Elements As, Sb and Se which are also enriched in Ankara surface soil are markers for coal combustion. Based on these arguments, depositions of emissions from motor vehicles and coal combustion are the main sources of soil contamination in Ankara. This conclusion agrees with the conclusion of Yatın (1994) and Kaya and Tuncel (1997). Yatın's study assigned residential coal combustion and motor vehicles as sources for the enrichment of the pollution-derived elements in aerosol samples. It is evident that settling of the aerosol particles contaminated by these two factors also enrich the surface soil with the same elements.

Besides the average EF_c's discussed up to now, the distributions of EF_c's at sampling points are also important because they provide information about whether the soil modification is a common phenomenon throughout the city or whether it is confined to certain areas. The elements which are not substantially enriched in the average may have EF_c values larger than 5.0 in certain areas.

Distributions of EF_c's of elements Cu, Zn, Cd, Pb, Cr, Ca, K and Fe within the city are given in Figures 3.15, 3.16, 3.17 and 3.18.

Potassium and Fe are crustal elements and their enrichment factors are less than 5.0 for all points in the city and its surroundings.

For Zn and Cu, average EF_c's were less than 5 and they were assumed not to be enriched by human activities. However, the distributions of the EF_c's of Cu and Zn indicate that Cu and Zn content of the soil is modified significantly at certain points in the city. For Zn, the slight modification in soil composition is observed in the central part of the city suggesting that residential heating is the main source for the enrichment of Zn. Crustal enrichment factors of Cu do not indicate a significant modification in soil composition in most parts of the city but soil composition is modified at two points. One in Dikmen district and the other one around the sugar production plant.

Enrichment of soil in Pb due to anthropogenic activities in Ankara appear as a more serious problem because modification of soil composition according to this elements is more widespread throughout Ankara. The area wide enrichment of Pb agrees with the earlier conclusion that Pb concentration is more uniformly distributed throughout the city. Now it is obvious that uniform distribution of concentrations is accompanied by fairly uniform deviation from normal soil composition. Like Pb, soil composition in Ankara is modified substantially for Cd in many parts of the city. Similar behaviors of Pb and Cd in their and EF_c distributions may be either due to the presence of large number of sources which can enrich soil by Cd or due to enrichment of Cd in motor vehicle emissions owing to the wearing of tyres.

Calcium is a crustal element, but the distribution of EF_c is different from distributions observed for other soil related elements. In most of the study area, EF_c for Ca is less than 5 as expected. In fairly large areas, EF_c is between 5 and 10. Since it is difficult to explain enrichment of Ca by any anthropogenic activities over such a wide area, observed slight enrichment can be attributed to variation in soil composition. However, at two points around

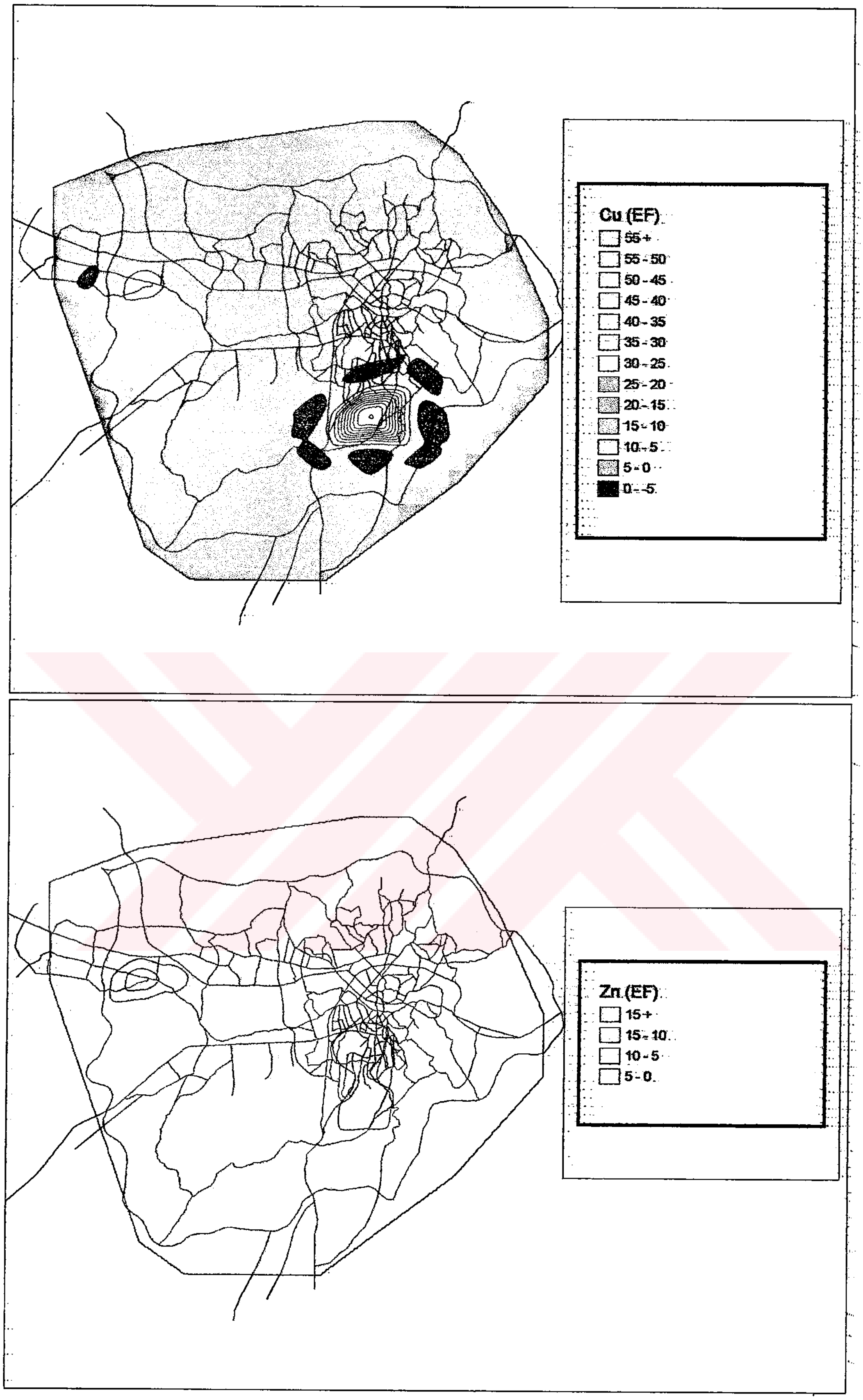


Figure 3.15 Distribution of crustal enrichment factors of Cu and Zn

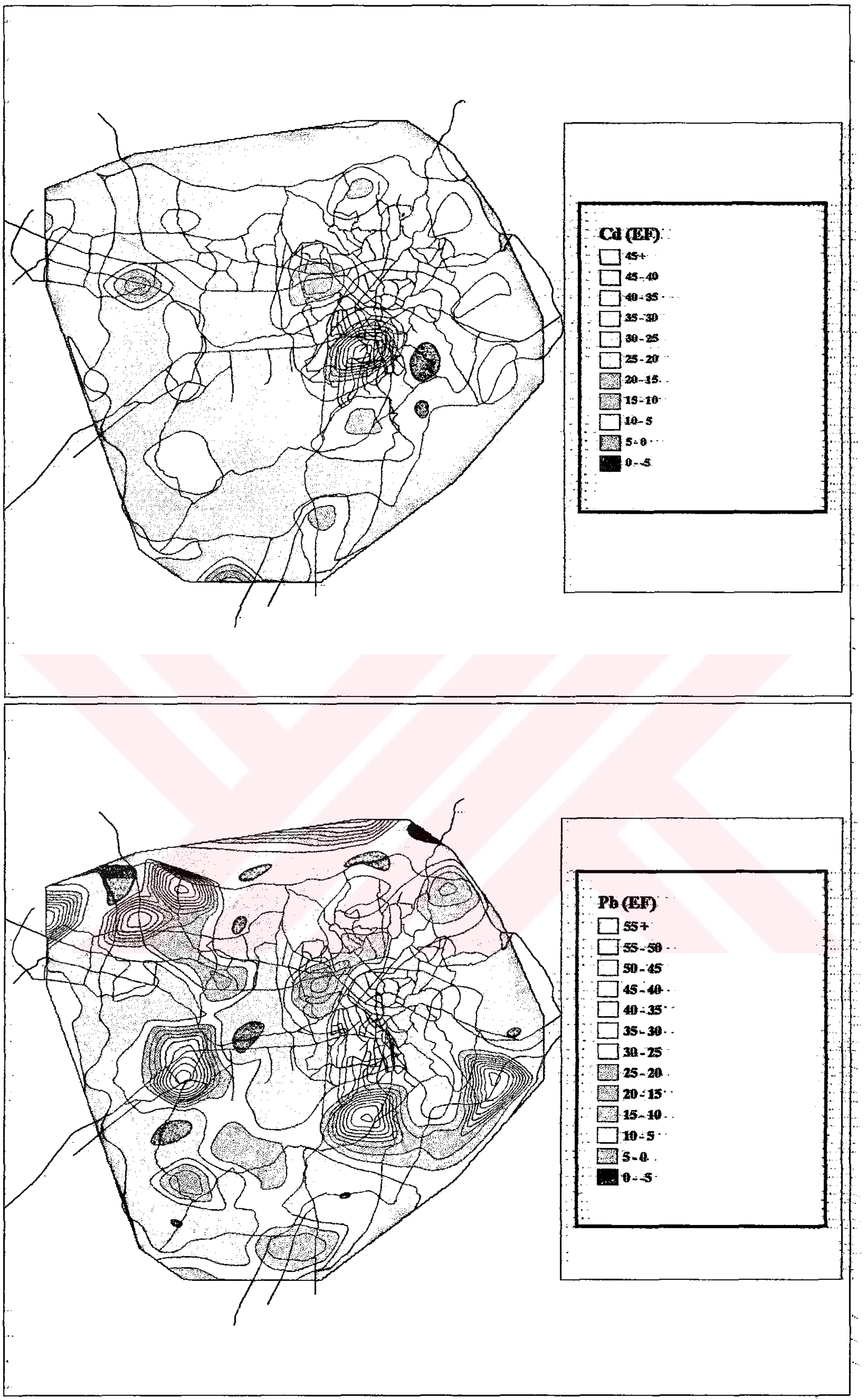


Figure 3.16 Distribution of crustal enrichment factors of Cd and Pb

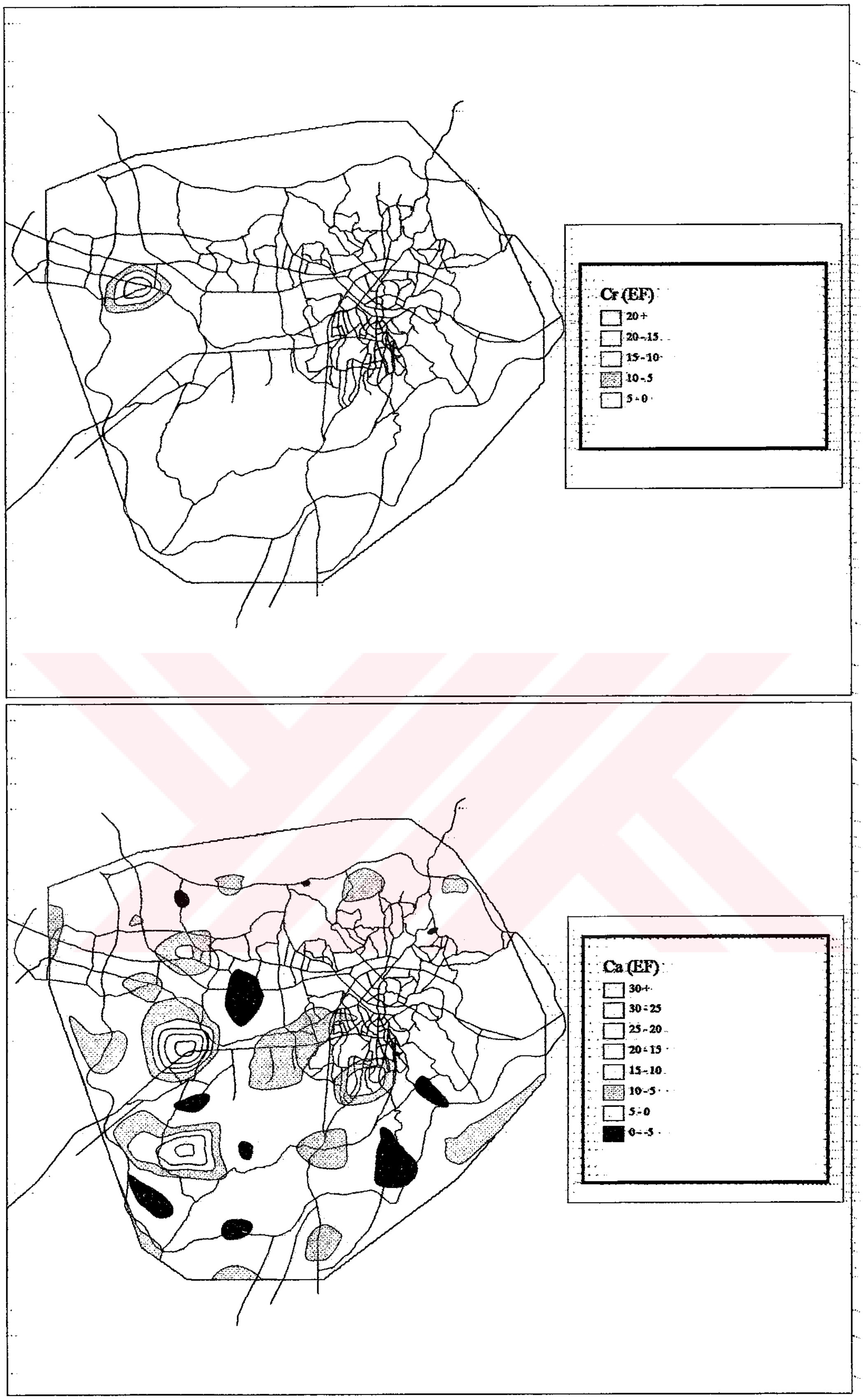


Figure 3.17 Distribution of crustal enrichment factors of Cr and Ca

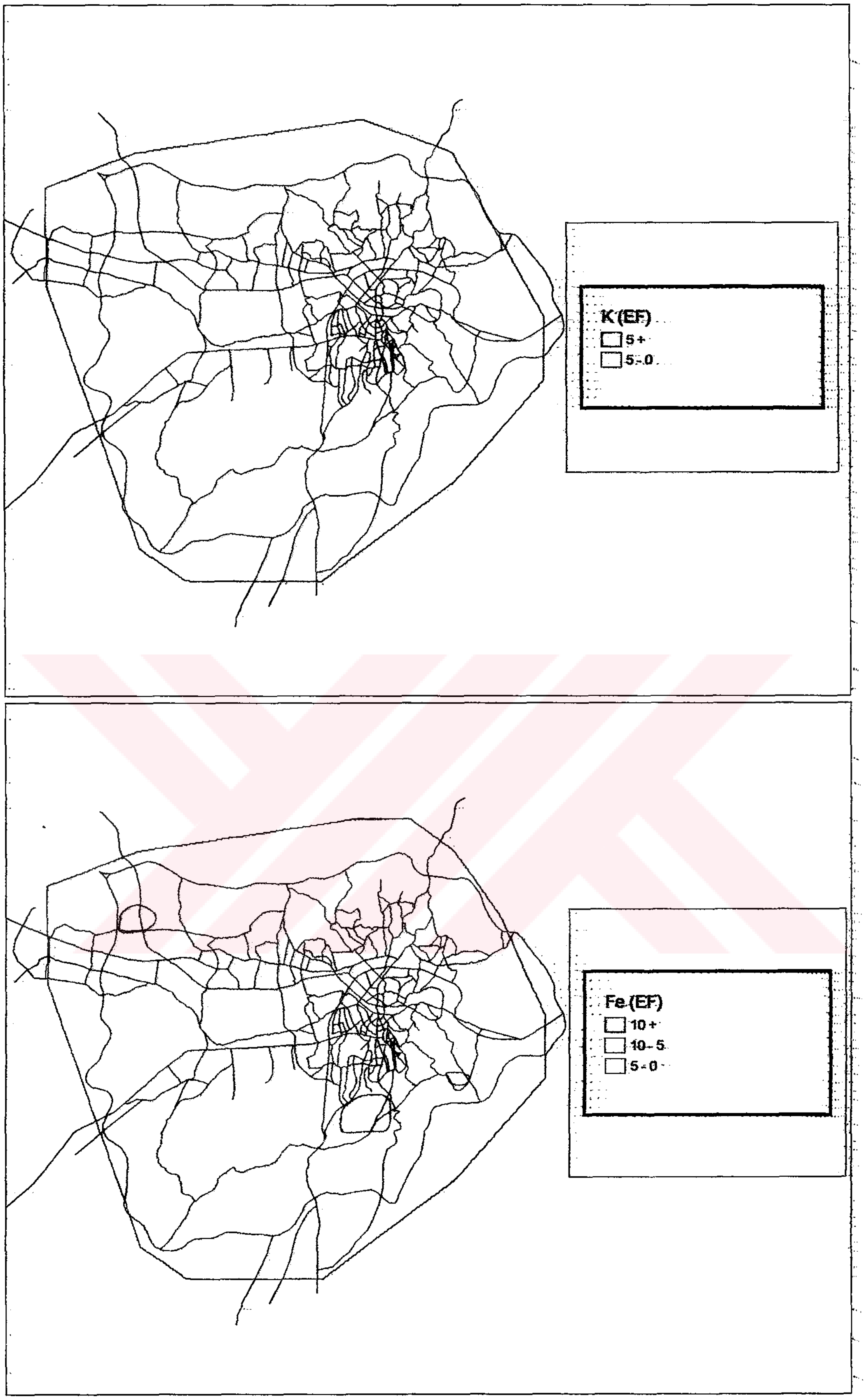


Figure 3.18 Distribution of crustal enrichment factors of K and Fe

two cement factories, EF_c values reach 30 which cannot be explained by variations in soil composition. Obviously, the cement factories do modify the composition of soil by Ca around them.

3.2.7 Factor Analysis

After using different tools such as comparison of data with literature and pollution classes, observation of common tendencies on distribution maps and EF_c calculations, it is now known which elements have unusually high concentrations in soil and where in Ankara these hot spots are located. Although there are some indications that motor vehicles and space heating are the sources of observed enrichments, it is not certain whether observed high concentrations are due to one common source or a result of a combined effect of many sources. A multivariate technique called "factor analysis" was applied to the data set to understand sources affecting observed concentrations of elements.

As discussed previously in Chapter 1, FA groups elements depending on their common variances. Common variances of elements in soil indicate elements with the same distributions which indicate relative position of sources.

Since the FA excludes samples with missing data points, it is generally necessary to fill the missing data in the data set with a suitable method. There are a variety of methods to fill in the missing data points for samples most of which are due to values below detection limits. All of these methods generate numbers which are close to the actual value. However, it should be noted that none of these methods can generate true measurement results. As the number of missing points in a data set increase, the uncertainty in the conclusions reached increases. To minimize the uncertainty, the elements which have missing values with a portion larger than 10% of the total set were not included in the FA exercise. The missing values of elements in the AAS data set used in this study were mostly due to values below detection limit and fairly low in number. Consequently, no matter which method is used in filling the data, FA results did not change significantly. In this study, the missing data for any element was filled with the lower quartile (i.e. the concentration value below which 25% of the existing concentrations lay) value for that element (Al-Momani, 1995). Therefore, the resulting data set included 119 concentration values for all 13 elements. The INAA data were not included in the FA exercise because data were available for only 5 samples.

After filling the missing data, factor analysis was applied to data by using STATGRAPH software for the first time and the resultant factors, factor loadings and factor scores were examined. The program calculates eigen values for 13 factors (which is the number of variables) but extracts only the factors with eigen values greater than or equal to 1. This treshold value for factor extraction can be manually changed but this default option was used in this study because it is the general practice to extract factors with eigen values greater than 1. The factor loading shows the weight of an element within each factor, i.e. elements with large factor loadings (generally values above 0.250 are considered as large) are said to be included in the related factor and to originate from the same common factor.

Before accepting the results of the factor analysis, factor scores should be examined. Factor scores indicate the weight of each factor in each sample. The samples with very high factor scores (i.e. greater than 7) or very low factor scores (i.e. smaller than –7) are deleted from the data set and the factor analysis is repeated with the new data set. The reason for deleting those elements is that they are so effective in one factor by themselves that the factor is determined largely by those few samples and does not adequately represent the general variance related to the general data set.

The results of the FA exercise is given in Table 3.4. Most of the system variance is explained by 5 factors with eigen values greater than 1. These 5 factors together explain 65% of the total system variance. The table shows the factor loadings for different elements in factor groups. Only factor loadings greater than 0.20 are included in the table because factor loadings less than this value do not allow for including an element in a factor group.

Table 3.4 Varimax Rotated Factor Matrix

Elements	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Al		0.42	0.58		
Ca				0.26	
Cr	0.82				
Cu	0.28	0.41		0.53	
Fe	0.34	0.67	0.39		
K		0.68			0.34
Mg	0.65	0.21			0.25
Mn		0.60			
Na			0.75		
Zn	0.25			0.74	
Pb					0.83
Ni	0.86				
Cd				0.73	0.37
Eigenvalue	3.03	1.85	1.43	1.10	1.09
% Variance	23.28	14.25	10.99	8.43	8.42
Cumulative % Variance	23.28	37.52	48.51	56.95	65.37

The first factor is loaded with Cr, Cu, Fe, Mg, Zn and Ni. This composition includes anthropogenic elements such as Cr, Cu, Zn and Ni, but also soil related elements such as Fe and Mg. Such composition suggests a soil which is enriched with anthropogenic particals. A similar composition was also recognized in the aerosol population in Ankara and was attributed to surface soil whish is enriched by anthropogenic particles resulting in the deposition of space heating emissions over the years. The distribution of factor 1 scores is given in Figure 3.19. In the figure, it is seen that the factor scores are greater at settlement areas such as Kızılay or Dikmen, and smaller at rural locations. The only exception is the spot on the north near to the express highway. The spot at that point cannot be explained but may be due to transport of emissions from nearby settlement areas to the north of the study area such as Pursaklar.

The second factor is loaded with Al, Cu, Fe, K, Mg and Mn. These are the elements in the soil structure. The third factor is loaded with Al, Fe and Na. This is also a soil factor. The existence of two soil factors can be explained with the existence of two different soil types in Ankara. Further comment on these two soil factors is possible by observing the factor score distribution plots. Distributions of Factor 2 and Factor 3 are given in Figures 3.19 and 3.20. It can be seen that Factor 3 has a much more homogenous distribution

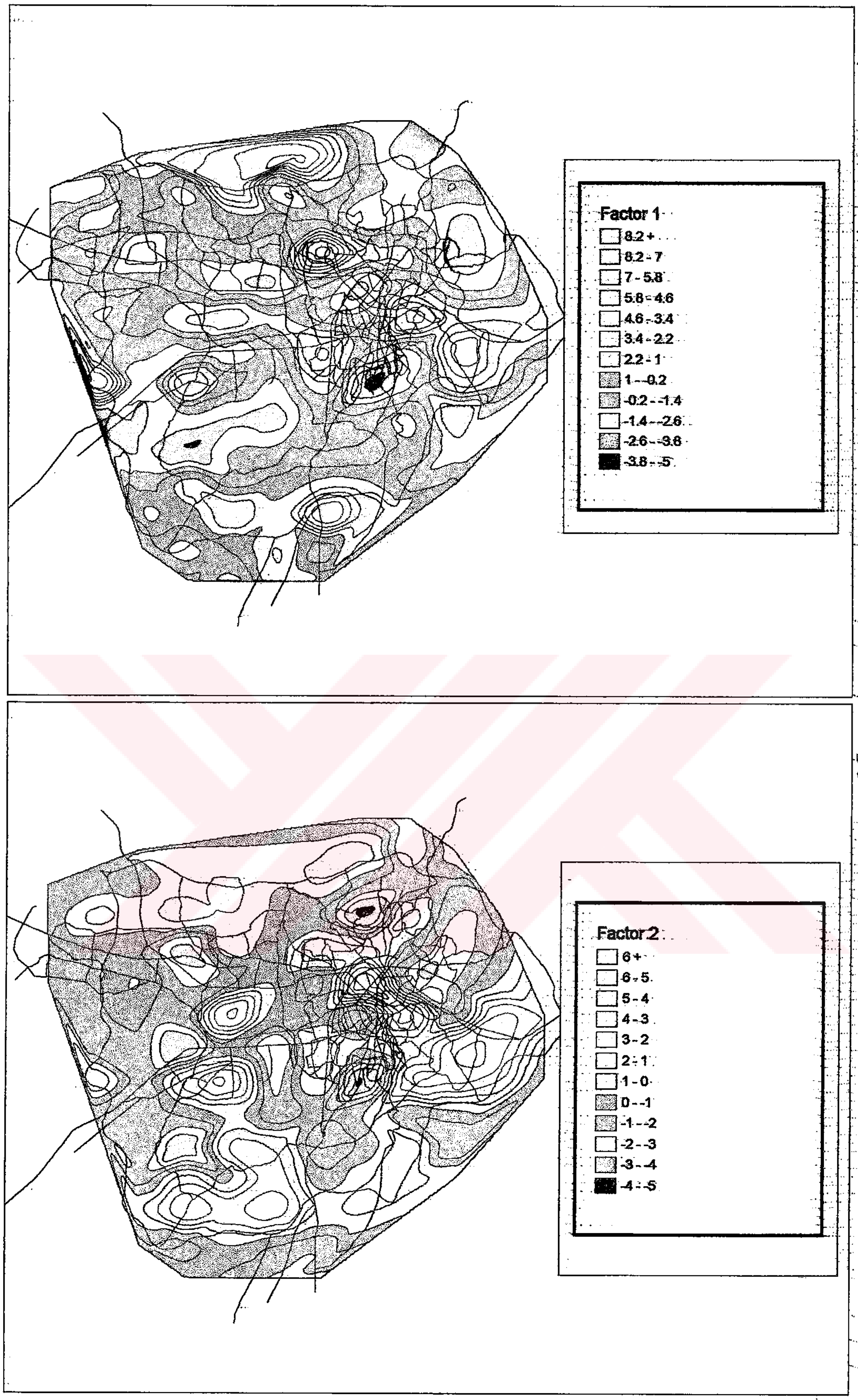


Figure 3.19 Distribution of factor scores for Factor 1 and Factor 2

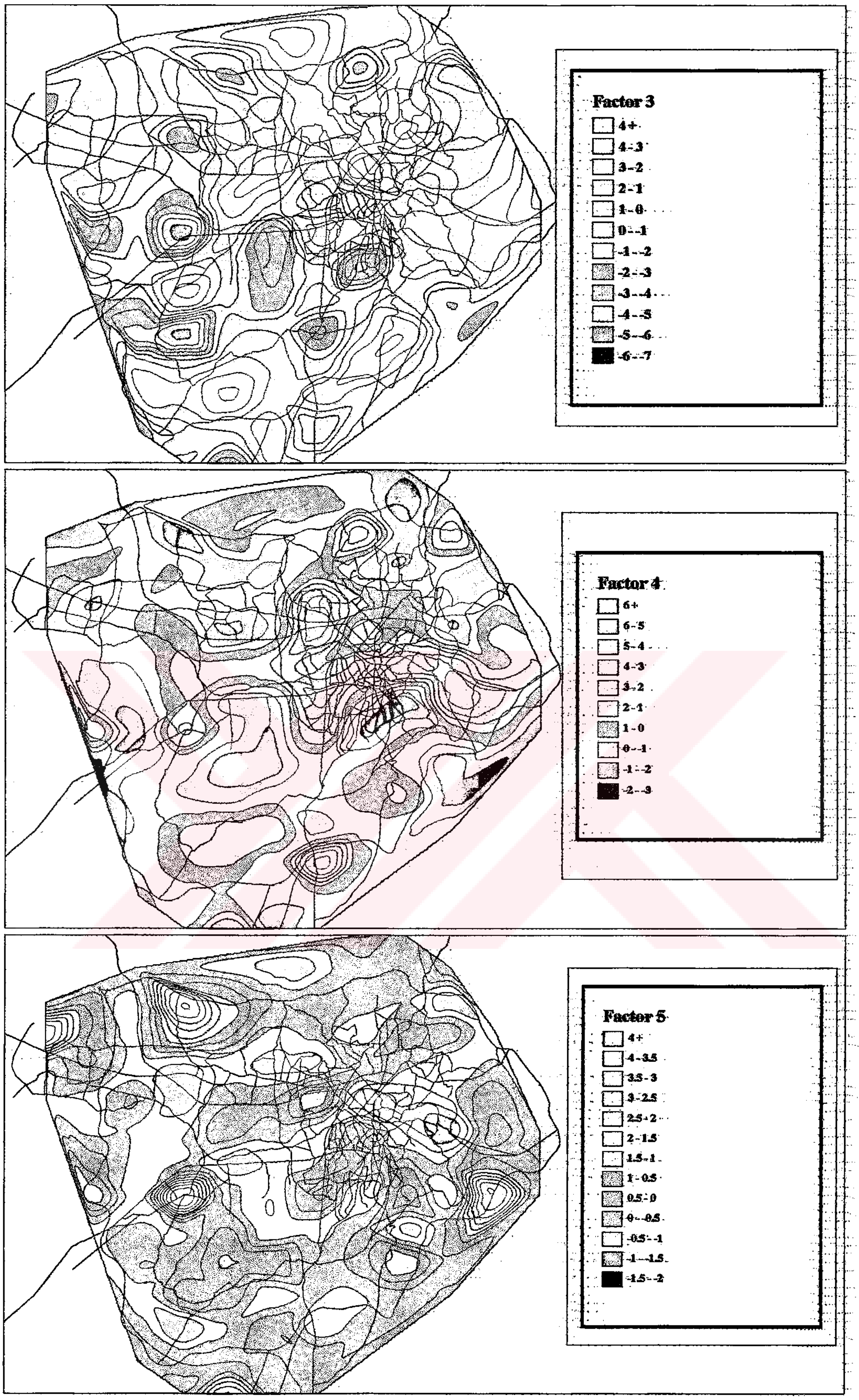


Figure 3.20 Distribution of factor scores for Factor 3, Factor 4 and Factor 5

with positive factor scores whereas the distribution is different for Factor 2. These distributions suggest that Factor 3 represents the dominating soil type in Ankara, whereas Factor 2 is a different type dominant in certain parts of the city.

The fourth factor is loaded with Ca, Cu, Zn and Cd which is another anthropogenic factor. Distributions of factor scores of Factor 4 is depicted in Figure 3.20. Factor 4 scores are high in areas with high population density but not significantly high in industrial areas located to the northwest of the city suggesting a residential heating source.

The fifth factor is loaded with Pb, Cd, K and Mg. This is certainly a factor representing the pollution effect due to traffic. Lead is the best marker for motor vehicle emissions and has a large factor loading in this factor. The loading of Cd into this factor is due to tyre wear from vehicles. Cd is used in the vulcanization process during tyre production. The distribution of factor scores for Factor 5 are given in Figure 3.20. The distribution of factor scores closely resemble the distribution of Pb concentrations.

It should be noted that the hot spots discussed earlier are not observed in the factor score distribution figures because such extremely polluted samples have been excluded from the factor analysis. The reason for this exclusion is that such samples have extremely high factor scores and prevent the overall matrix from representing common sources correctly.

3.3 Confirmation of Aerosol Soil Component

As stated earlier, one of the objectives of this study is to review the aerosol soil component derived in Yatın's (1994) study, where the aerosol composition in Ankara was subjected to factor analysis and six common factors were used to explain sources contributing to the aerosol population. Three of these factors were identified as soil factors; namely surface soil, sub surface soil and salted road dust. The source profiles (ratios of elemental concentrations to that of Al) for each factor was calculated with statistical methods and type of soils were identified by comparing the X/Al ratios in these profiles with X/Al ratios in Mason's average crustal compilation

The most straight forward approach for checking the validity of the profiles, and the related enrichments, estimated by Yatın is to compare the real X/Al ratios of elements determined in this study, with the X/Al ratios estimated by Yatın. This comparison is done for all three soil components (surface soil, sub surface soil and road dust) since this study presents data for all these three groups of soil. The surface soil data is obtained from the average of the surface soil samples, the sub surface soil data is obtained from the lower sections of the core samples and the road dust data is obtained from analysis of actual road dust samples.

Figure 3.21 represents the measured values of X/Al ratios of elements in the surface soil versus the values statistically derived by Yatın With few exceptions, surface soil composition measured in this study agrees fairly well with the soil composition derived by statistical treatment of aerosol data. The similarity is striking considering that the surface soil profile in Yatın's work was derived purely by statistical procedures. However, there are some differences between the two soil compositions. Statistical soil is more enriched with Br and Sb and surface soil composition measured in this study is more enriched with Cl and Hg. All of these elements where differences were observed are measured by INAA in only 5 samples. Ability of these 5 samples for representing the soil in Ankara is questionable. This may be the reason for observed differences between statistical soil and this study.

Figure 3.22 represents the measured values of X/Al ratios of elements in the subsurface soil versus the values statistically derived by Yatın. The similarity of values is also striking in this figure. Although Ce, Sb and Mg seem to be more enriched in the actual soil and Hg, Br, Cl and Zn in statistical soil, the differences are generally not more than a factor of 10. The only exception is Hg where the difference is much higher. This difference can be explained by the fact that Hg was analyzed for only one sample.

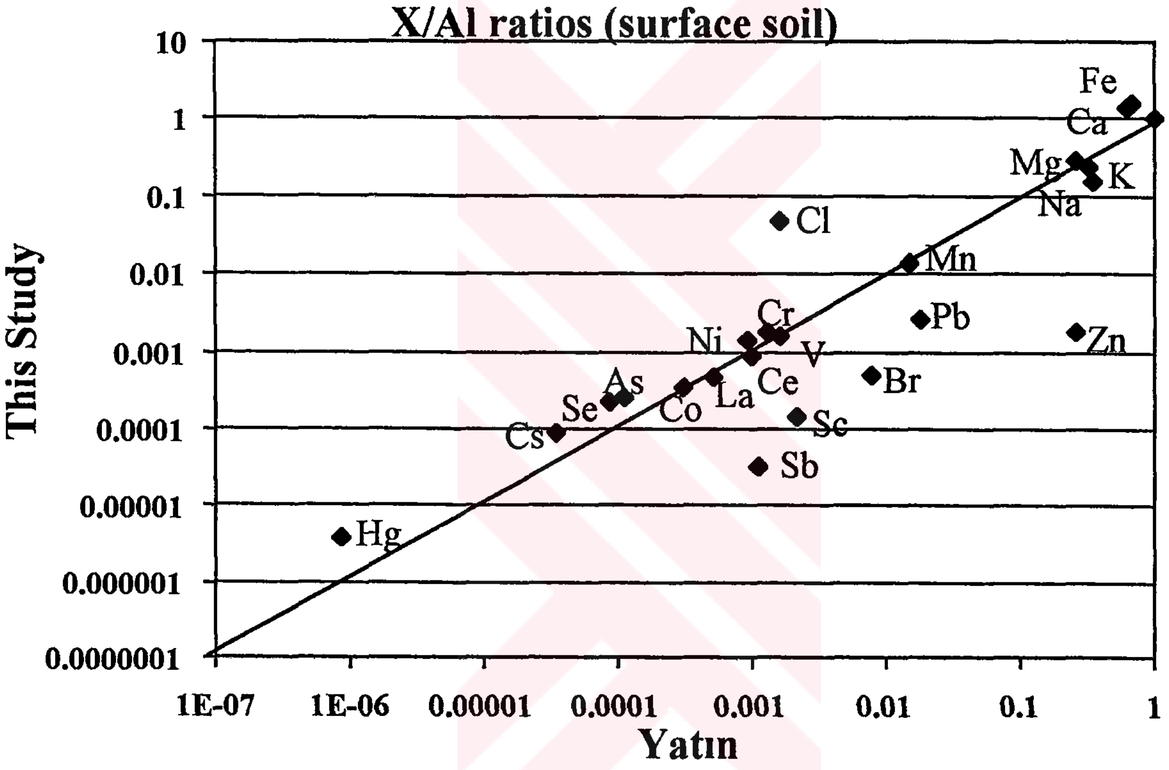


Figure 3.21 X/Al ratios in Yatın and this study for surface soil

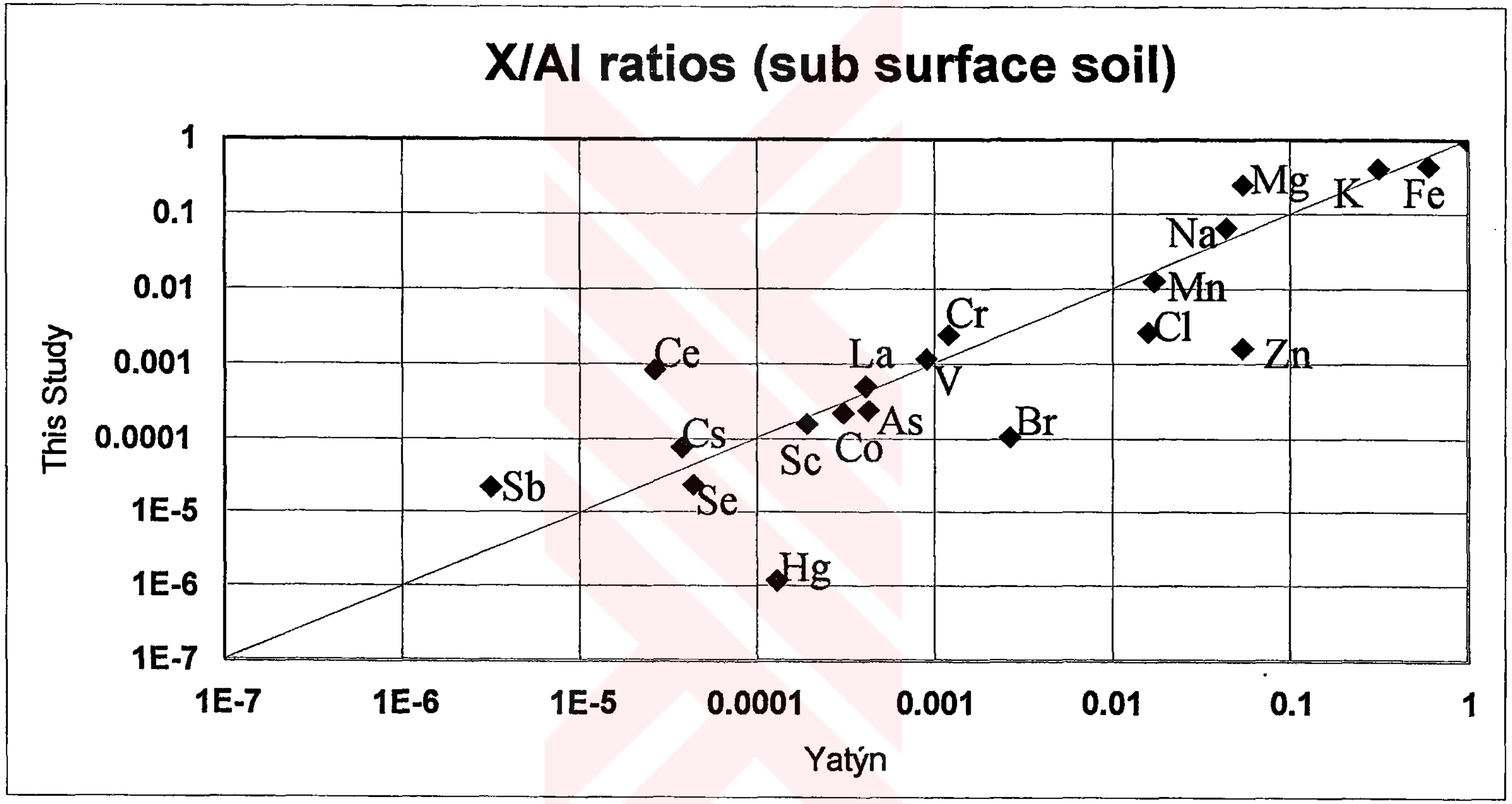


Figure 3.22 X/Al ratios in Yatın and this study for subsurface soil

The road dusts in this study were measured only by AAS, therefore the comparison of measured and statistically derived road dust profile is limited to seven elements only. In Figure 3.23, it can be seen that although concentrations of Na, Mn and K agree fairly well, there are significant differences in the concentrations of Ni, Pb and Ca, indicating that road dust composition derived by Yatın (1994) can only roughly approximate the actual road dust composition in Ankara.

The last step in the aerosol soil component confirmation of Yatın's study is the calculation of soil enrichment of aerosol particles. The soil enrichment factors for Yatın's data were calculated first by using Mason's average earth crust compilation. The calculation is the same as defined for soil enrichment with Mason's compilation. That is, the X/Al ratios in aerosol samples are divided by the X/Al ratios in Mason's compilation. This calculation depends on the assumption that the total enrichment of aerosols is by the soil factor. The soil enrichment factors for the aerosols are then re-calculated by the local soil data obtained in this study. The difference is that the local soil X/Al ratios are used as the normalizing data.

The comparison of calculations of aerosol enrichment by the soil factor calculated by Mason's data and the data from this study are presented in Figure 3.24.

It is evident from the figure that the compared EF values are quite similar for typical soil elements such as Ni, K, Mn, Na, Mg, Fe and rare earth elements such as Eu, Sm, La, but the EF values for pollution-derived elements such as Se, Pb, Br, Sb, Hg, As and Cd are much higher when calculated by using Mason's compilation. The reason for this is Mason's compilation represents the undisturbed soil composition while the local soil has been contaminated by external sources, especially by deposition of atmospheric particles. Naturally, true enrichments of elements in atmospheric particles are the ones calculated by using soil data obtained in study. Large differences in the EF_c values of elements such as Se, Br, Pb, As, Cl etc. clearly demonstrate that a

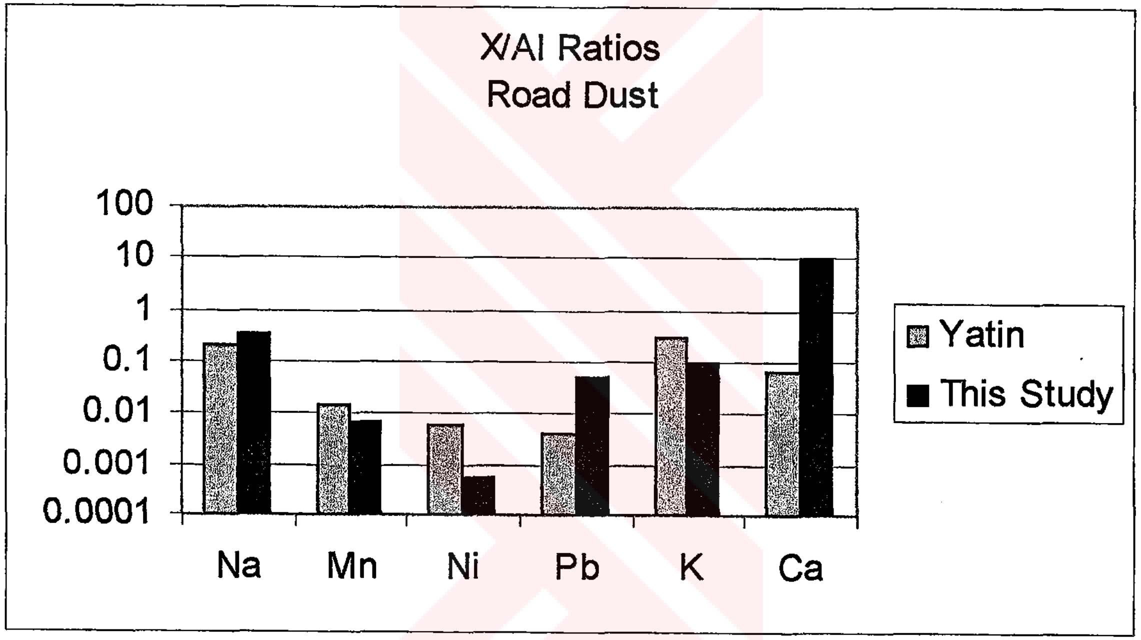


Figure 3.23 X/Al ratios in Yatın and this study for road dust

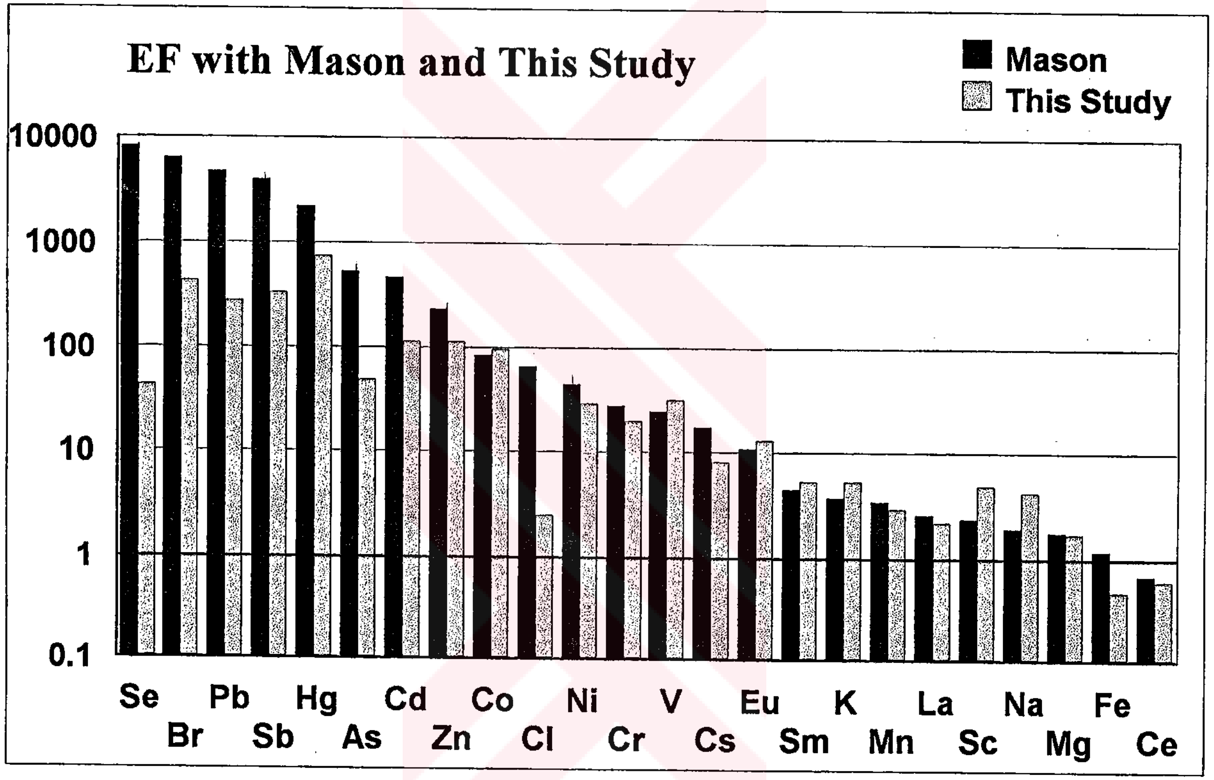


Figure 3.24 Crustal EF calculated for aerosols with Mason's compilation and local soil

significant fraction of the observed concentrations of these elements in Ankara atmosphere originate from resuspended surface soil which is contaminated by these elements. The difference between the EF values for the pollution-derived elements shows that there are different factors that determine the levels of anthropogenic elements in aerosol samples and the similar values for Ni, K, Mn, Mg, Na, Fe and rare earth elements show that the these elements are generated by mainly soil factors in the atmosphere and the effect of anthropogenic activities are much smaller.

CHAPTER 4

CONCLUSION

In this study, surface soil samples from 120 locations in the city of Ankara were collected and the trace element concentrations were analyzed by atomic absorption spectrophotometry and instrumental neutron activation analysis.

The results of the study showed that soil composition in Ankara has been modified with the contamination from anthropogenic activities. The pollution derived trace element contents have increased for years because of the deposition of atmospheric particles. The levels for elements which are not extensively used in human activities and present in the natural composition of soil have not changed.

In the study, crustal enrichments of elements have been calculated and their distributions were plotted. The figures show that there are locally enriched areas for anthropogenic elements within the city. These locations are the districts with high population density or districts with industrial activities, indicating that the sources for the enrichment of the anthropogenic elements are emissions from space heating and industrial emissions. Besides these regionally polluted areas, another source of pollution turns out to be the exhaust emissions from motor vehicles which exhibits a more widespread distribution over the study area.

Besides surface soil samples, core samples from different locations were also analyzed in order to observe the vertical distribution of trace element concentrations in the soil. It can be seen that crustal element levels do not change with depth while the anthropogenic element levels decrease with increasing depth. This is an indication that the surface soil is enriched in these elements by the deposition of atmospheric pollution.

Factor analysis was applied to the data set to find out the common sources that modify the soil composition. Five factors were extracted two of which were soil factors and the other three were anthropogenic factors.

Another objective was to confirm the results of an earlier study carried out by Yatın (1994) for aerosol particles in Ankara. In that study, enrichment factors were calculated for aerosol data and the soil composition was statistically derived by chemical mass balance calculations. The analysis of actual soil composition in this study showed that the soil composition derived by Yatın was correct for most of the elements. The enrichment of aerosols with soil factors were recalculated by using the actual soil data and compared with the earlier results. These comparisons showed that the enrichments and soil compositions were correctly predicted with the exceptions of some of the anthropogenic elements. It is seen that the enrichment of these elements in the atmosphere is through an indirect process. The anthropogenic elements are firstly deposited on the surface soil and the surface soil subsequently becomes a source for the enrichment of aerosol by the resuspension of the elements which are blown from the surface soil to the atmosphere.

CHAPTER 5

RECOMMENDATIONS FOR FUTURE WORK

Although this study gives general information on the soil composition in Ankara, the fact that the distance between sampling locations is large leads to poor detail on the change of distributions within special areas of interest. Later studies need to be concentrated on detailed analysis of regions which turn out to be polluted districts. This study showed that the central locations like Kızılay or industrial locations such as around the sugar factory are enriched in anthropogenic elements. These areas can be of interest for examining the elemental distributions in surface soil.

The results of the core sample analysis showed that the surface soil is frequently disturbed in urban areas. Therefore, later studies are to be carried out by collecting deeper core samples in order to differentiate better between polluted surface soil and background concentrations in undisturbed soil.

The recalculation of enrichment factors for an earlier aerosol study showed that the enrichments in aerosols by soil factors are different when actual local soil data is used instead of another reference. Therefore, later aerosol studies which are interested in enrichment by soil factors should make use of local soil data where avilable.

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