BIOMONITORING OF ATMOSPHERIC POLLUTANTS AT WESTERN ANATOLIA

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ABSTRACT

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The first biomonitoring network in Turkey was set up in Aegean Region. Lichen Xanthoria parietina was chosen as biomonitor organism.

The techniques of INAA and ICP-AES were used to determine 40 elements in 234 lichen samples.

The two lichen species were examined for their accumulation capacities by using ANOVA at 95% confidence level. It was found that the accumulation capacities of two lichen species were different for the elements Ca, Cl, Cu, Pb and Zn.

The concentration results in three lichen species and tree bark were compared with the results of bulk deposition samples in order to obtain a quantitative knowledge. The quantitative relation was obtained for the elements Cr, V, Mn, V and Zn and ions Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ in Xanthoria parietina. Other lichen species and tree bark were also suitable for obtaining quantitative information.

Concentrations of elements were comparable with literature data, except for As with a concentration of 4.2 ppm which is a factor of 2-8 higher than other data. Concentration data were used to get the pollution distribution maps of the region for about 19 elements. The pollution effect of Aliağa region, urban industrial areas and power plants (Soma and Yatağan) was seen clearly on the concentration distribution maps and crustal enrichment factor maps. Selenium was the most enriched element with respect to soil in all regions. These results were also supported by the results of factor analysis which result in four major sources namely dirty soil, Aliağa, urban and industry and power plants. Quantitative impact of each source to elemental concentrations at Aegean Region was estimated by using Absolute Factor Score-Multiple Linear Regression (AFS-MLR) method. Most part of the region is under the influence of Aliağa source. The concentrations of Fe, Mn, Sb, Cr, Cu, Pb and Zn were coming mostly from Aliağa region especially from iron steel plants. The concentrations of elements As, Hg, Sb and Pb are very high around İzmir reflecting the effect of both urbanization and industry. The concentrations of Se and Hg are higher in the power plant region and in industrial areas in İzmir, Kemalpaşa and Manisa.

The modelling results of deposition agreed well with the results of lichens quantitatively around two important pollution sources: Yatağan and Soma power plants.

Keywords: Biomonitoring, atmospheric pollution, lichens, Aegean Region, elements, distribution maps, Factor Analysis, source quantification, AFS-MLR, INAA, ICP-AES

ÖZ

BATI ANADOLU'DAKİ ATMOSFER KİRLETİCİLERİNİN BİYOMONİTÖR YÖNTEMİ İLE İZLENMESİ

Yenisoy Karakaş, Serpil
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Türkiye' de ilk biyomonitör izleme ağı Ege Bölgesi'nde kurulmuştur. Liken Xanthoria parietina biyomonitör organizma olarak seçilmiştir.

234 liken örneğindeki 40 elementi belirlemek için INAA ve ICP-AES teknikleri kullanılmıştır.

İki liken türünün toplama kapasiteleri ANOVA kullanılarak %95 güvenirlik seviyesinde incelenmiştir. İki liken türünün toplama kapasitelerinde Ca, Cl, Cu, Pb ve Zn elementleri için farklılıklar bulunmuştur.

Üç liken türü ve ağaç kabuğundaki konsantrasyon sonuçları ile toplam çökelme örneklerindeki sonuçlar kantitatif bilgi elde etmek için karşılaştırılmıştır. Xanthoria parietina'daki elementler Cr, V, Mn, Cd, Zn için ve iyonlar Cl^-, NO_3^-, SO_4^{2-}, NH_4^+ için kantitatif bir ilişki elde edilmiştir. Diğer liken türleri ve ağaç kabuğu da kantitatif bilgi elde etmek için uygun olarak bulunmuştur.

Likenlerdeki elementlerin konsantrasyon değerleri, 4.1 ppm konsantrasyonla literatürdeki verilerden 2-8 kat fazla olan As hariç, literatürdeki verilerle karşılaştırılabilir düzeydedirler. Konsantrasyon verileri 19 element için bölgedeki kirlilik dağılım haritalarını elde etmek için kullanılmıştır. Aliağa bölgesinin, şehir-sanayi bölgelerinin ve termik santrallerin (Soma ve Yatağan) etkileri konsantrasyon ve toprağa göre zenginleşme faktörleri haritalarından açıkça görülmektedir. Bütün bölgede toprağa göre en fazla zenginleşen element selenyumdur. Bu sonuçlar dört temel kaynak yani kirli toprak, Aliağa, şehir-sanayi alanları ve termik santraller sonucu veren faktör analizi sonuçları ile de desteklenmiştir. Her kaynağın Ege Bölgesi'ndeki element konsantrasyonlarına kantitatif etkisi Mutlak Faktör Skor-Çok Değişkenli Lineer Regrasyon (MFS-ÇLR) methodu kullanılarak tahmin edilmiştir. Bölgenin büyük bir kısmı Aliağa kaynağı etkisi altındadır. Demir, Mn, Sb, Cr, Cu, Pb ve Zn elementlerinin konsantrasyonları özellikle Aliağa bölgesinde demir-çelik fabrikalarından gelmektedir. Arsenik, Hg, Sb ve Pb elementlerinin konsantrasyonları şehir ve sanayiyi yansıtan İzmir civarında çok yüksektir. Selenyum ve Hg konsantrasyonları ise termik santraller, İzmir, Kemalpaşa ve Manisa'daki sanayi alanlarında yüksektir.

Çökelme modellemesi ile likenlerdeki sonuçlar iki kaynak bölgesi olan Yatağan ve Soma termik santrallerinde kalitatif olarak uyumludur.

Anahtar Kelimeler: Biyoizleme, atmosfer kirlenmesi, likenler, Ege Bölgesi, elementler, dağılım haritaları, Faktör Analizi, kaynak belirlenmesi, MFS-ÇLR, INAA, ICP-AES

To my mother, my father and my daughter

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TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

TABLE

LIST OF FIGURES

FIGURE

CHAPTER 1

INTRODUCTION

1.1. Air Pollution and Biomonitoring

Interest in the effects of atmospheric particulates on health has increased in the last 10 years on the basis of evidence that this type of pollution is an important factor for respiratory illness and death (Monaci et al., 2000). In most cities and industrial areas, airborne metals are not routinely monitored with fully or semi-automatic gauges commonly used in current pollution monitoring programs, owing to elevated costs and technical difficulties. This is a grave drawback because vehicular traffic and industrial emissions, which are great sources of fine particulate and airborne metals in urban and industrialized environments, have risen dramatically in recent years.

To complete the information on trace element deposition obtained from automatic gauges, increasing attention has recently being paid to plants, tree bark, needles and other organisms as passive biomonitors. Biomonitoring, in a general sense, is the use of properties of an organism or a part of it to obtain information on certain quantity in a certain part of the biosphere. The relevant information in biomonitoring programs using plants or animals is commonly deduced from either changes in the behaviour of the monitor organism (species composition or richness, ecological performance, morphology) or from the concentrations of specific substances in the monitor tissues (Sloof, 1993). The second approach will be used in the content of this thesis.

This reliable, versatile and inexpensive method can assist decision-makers on the subject of health and environmental protection against potentially hazardous trace elements. Providing a high density of sampling points, biomonitors are very effective for tracing maps of airborne metal contamination in polluted environments (Monaci et al., 2000).

The oldest written report on indicator plants appeared more than 400 years ago. But the career of the term "bioindicator" in biological literature did not start earlier than the end of the 1960s. However there are few earlier publications. The earliest known to the author is that of Clements (1920).

Many authors use "bioindication" and "biomonitoring" more or less as synonyms (Markert, 1993). The only difference is that indication seems to be more spontaneous and active while monitoring is continuous and passive (the indicator does something, the monitor is used to do something. To use an everyday-life comparison: The difference between bioindication and biomonitoring is the same as that between a photograph and a film). Although data provided by physical and chemical monitoring are indispensable for evaluating the changes of the environment, the application of an ideal biomonitor can show several advantages compared to the use of direct monitoring techniques (Kucera, 1994; Sloof, 1993).

- the concentration of pollutants in the monitor organism is often higher than in the system to be monitored. This may facilitate accurate sampling and analysis which are very difficult at the low levels occurring in many compartments of the environment;
- sampling of the organism used as a biological monitor is in general easier than most direct sampling procedures and no long-term use of expensive sampling equipment is required;
- most organisms reflect external conditions averaged over a certain time, depending on e.g. the biological half life of a specific substance in that organism. This is important when monitoring levels may change rapidly in time;
- concentrations of pollutants in organisms may give insight into the bioavailability of that pollutant. This information may be as relevant as the absolute concentrations in a certain part of the environment;

- biological monitors are already present in the environment and monitoring continuously.

There are some demands on an ideal accumulative biomonitors (Pacyna and Otter, 1989; Markert,1993; Kucera, 1994).

- abundant occurrence in the area of interest
-suitable accumulation rate
-no sensitive reaction to the substance to be accumulated
-general toxitolerance
-no seasonal differences in availability and applicability
-no seasonal differences in accumulation ability
-existence of a correlation between accumulation and input to the ecosystem
-independent uptake of local conditions
-average element concentrations over a suitable time period as a result of integrated exposure over a time period
-no or little uptake from sources other than atmospheric so low background concentrations
-no loss (reinsertion) of substance to be monitored
-easy sampling and sample preparation
-element accumulation to concentration levels accessible by routine analytical techniques.
-finally nonspecialists must be able to recognize the biomonitor organism readily in the field. Species distinguished by gross morphological characters and which are not likely to be confused with any others of a superficially similar appearance will consequently be the most satisfactory.

Some species are accumulators or even hyperaccumulators, while others are excluders. To detect low concentrations of heavy metals in the environment, hyperaccumulators are best suited. In highly polluted areas species with a lower accumulation rate will give better differentiation. The ideal accumulative biomonitor is a species, in which internal concentrations accurately reflect external concentrations.

As heavy metals very rarely occur as the only pollutants, but generally combined with other harmful substances, especially SO_2, the ideal accumulator of heavy metals should be rather toxitolerant, in particular SO_2-tolerant. That is why for reasons of comparability, only species having their ecological optimum in the ecosystem under investigation should be considered (Markert, 1993).

1.2. Sources and Transport of Trace Elements in the Atmosphere

Particles in the atmosphere, ranging in size from about 500 μm down to molecular dimensions (0.005 μm), are made up of an amazing variety of materials and discrete objects and may consist of solids and liquid droplets. They can contain 80-90% of inorganic material and the remainder consists of organic compounds and biological debris. They are frequently referred as particulates although particulate matter is a much more correct term. The term aerosols refer to particulate matter in the colloidal size range (Manahan, 1979).

One of the major characteristics of particles in the atmosphere is particle size. The nucleation (aitken) range consists of particles with diameters less than 0.08 μm that are emitted directly from combustion sources or secondary aerosols formed from gaseous species. In polluted areas, the lifetimes of particles in the nucleation range are usually less than one hour, because they rapidly coagulate with larger particles or serve as nuclei for cloud or fog droplets. The accumulation range consists of particles with diameters between 0.08 and ~2 μm. These particles result from the coagulation of smaller particles emitted from combustion sources, from condensation of volatile species, and from finely ground dust particles. The nucleation and accumulation ranges comprise the fine particle or $PM_{2.5}$ size fraction. Particles larger than 2.5 μm are called coarse particles. Coarse particles result from grinding activities and are dominated by material of geological origin. Pollen and spores, ground-up trash and leaves are also included in the coarse fraction. An upper limit of 10 μm is often attached to the coarse range to correspond to the US health standard for suspended particles. The mass concentration of all particles with diameter less than 10 μm is often termed PM_{10} size fraction. The coarse size fraction is practically limited by gravitational settling, since most particles larger than ~30 μm fall out of the atmosphere very close to the point at which they are emitted (Finlayson-Pitts and Pitts, 1986). There are major classes of air pollutants: primary and secondary pollutants. Primary pollutants are directly emitted from their sources to the air (e.g. sulfur dioxides, carbon monoxide, particulate matter, Pb, hydrocarbons and nitrogen oxides). They can undergo chemical reactions in atmosphere and produce new substances, which are called secondary pollutants (such as ozone, sulfuric acid, nitric acid, organic pollutants).

Trace elements are in the category of the primary ones and introduced into the atmosphere from both natural and man-made sources. Crustal material from wind-blown dust, bubble bursting over the ocean, forest fires, volcanoes and biogenic emissions are the most common natural sources of the particles in the atmosphere. Terrestrial dust is generally in the large size range (>2 μm diameter) and is primarily composed of crustal elements including silicon, aluminum, iron, sodium, potassium, calcium and magnesium (Finlayson-Pitts and Pitts, 1986). Arid and semiarid areas are major continuous sources of the crustal material. Particles are generated at the surface of the ocean by the bursting of bubbles and some of these are carried inland. They, too, tend to be large, more than 50% having the diameters >3 μm. Their chemical composition includes the elements found in seawater (primarily chlorine, sodium, sulfate, magnesium, potassium and calcium) and organic materials, perhaps including viruses, bacteria. Biological emissions of particles may occur from plants and trees; additionally, volatile organics such as terpenes may react in the air to form small particles. Volcanic eruptions are highly variable in the size range of 0.01 to 66 μm with emission ~6 x 10^6 metric tons. Wildfires also produce significant particulate matter, most of it in the respirable size range from ~ 0.1 to 1 μm. Elemental carbon and organics from the majority of these particles, with some minerals also being present.

A variety of man-made sources release both particulate and gaseous material into the atmosphere. These include the combustion of fossil fuels, including such additives as the lead in gasoline, the roasting of ores from refining metals, waste incineration, the processing of crustal materials for manufacturing cements, the production of chemicals, agricultural utilization and numerous other than industrial and social activities.

Combustion of hard coal, lignites and brown coal in electric power plants and in industrial, commercial and residential burners is the major source of airborne Hg, Mo and Se and a very significant source for As, Cr, Mn, Sb and Tl. Combustion of oil for the same purpose is the most important source of V and Ni and is an important contributor of Sn. The non-ferrous metal industry accounts for the largest fraction of Pb (in addition to gasoline combustion), As, Cd, Cu and Zn emitted. Chromium and Mn are derived primarily from the iron and steel industry (Nriagu and Pacyna, 1988). Sources of atmospheric particulates and their elemental markers were tabulated by Ölmez et al., 1997 and it is given in Table 1.1. The elements like Zr, Mo, In, Zn, Cl, As, Au, Cd, Hg, Br, Sb and Se are mostly volatile and are found in the atmosphere at elevated concentration levels due to anthropogenic activities.

Major and minor elemental composition of particles are used as a tracer to determine sources of particles in ambient aerosols (Hopke et al., 1976; Thurston and Spengler, 1985). The impact area ranges from regional to global. Depending upon the type and the characteristics of their emission sources, the atmospheric residence time of most of the gases and some of the elements may be order of several years. Particulate forms of these elements have much shorter atmospheric residence times, but are useful as conservative markers for various industrial processes as listed in Table 1.1.

Throughout the earth's geological history chemicals have been atmospherically transported from continent to continent and from continent to ocean; this long range atmospheric transport is recognized as the most important mode of global transport for a variety of trace substances and elements. The anthropogenic trace substances found in remote locations attest to rapidly the extent of such transport. Trace elements emitted from anthropogenic sources are of interest because when they are emitted they are usually concentrated in much finer aerosol particles than crustal elements. Thus many anomalously enriched trace elements are transported to remote areas on submicrometer aerosols (particles with diameters ranging between 0.01 – 0.1 μm). Once such trace element enriched aerosols are mixed into the free troposphere and stratosphere, the probability of their removal decreases and they can be transported over considerable distances.

Table 1.1. Marker elements and their possible sources (Ölmez et al., 1997).

Source	Elements
Crustal material	Al, Sc, Mn, Fe, REE, Th, U
Marine aerosols	Na, Cl
Coal combustion	As, Se, Hg
Oil combustion	V, Ni, La, La/Sm
Refineries	REE
Motor vehicles	Pb, Br, Zn, Sb
Wood burning	K
Incinerators	Na, K, Cl, In, Hg
Chlor-alkali plants	Cl, Hg
Precious and other metal works	Co, Zn, Au
Aluminum plant	Al, Mg
Industrial urban areas	V, Zn, As, Se, Br, Sb
Iron/steel works	Fe, Mn, Cr, Zn, Se, Mo, Sb
Regional transport	Fine mass, As, Se, Hg
Zn, Cd, Pb smelters	In, Zn, Cd, Sb, Pb
Ni, Cu smelters	Ni, Cu, Hg, As, As/S

REE: rare earth elements like La, Ce, Sm etc.

1.3. Global View of Sampling Region

The Aegean Region of Turkey has a cosmopolitan structure with respect to both population and industrialization. That's why this is very suitable region to study air pollution in various subregions which have different pollutant characteristics and types. In order to study air pollution in the region in detail, the region was divided into five subregions by evaluating the concentration ranges of elements. The subregions are shown in Figure 1.1. The first region is named as the urban light industry region because this region is highly urbanized especially around the city of İzmir and also it involves many industries. These industries are populated along the corridor between the city center and Kemalpaşa, the east of the city center. Also there are Menemen and Çiğli organized industrial areas in the city of İzmir.

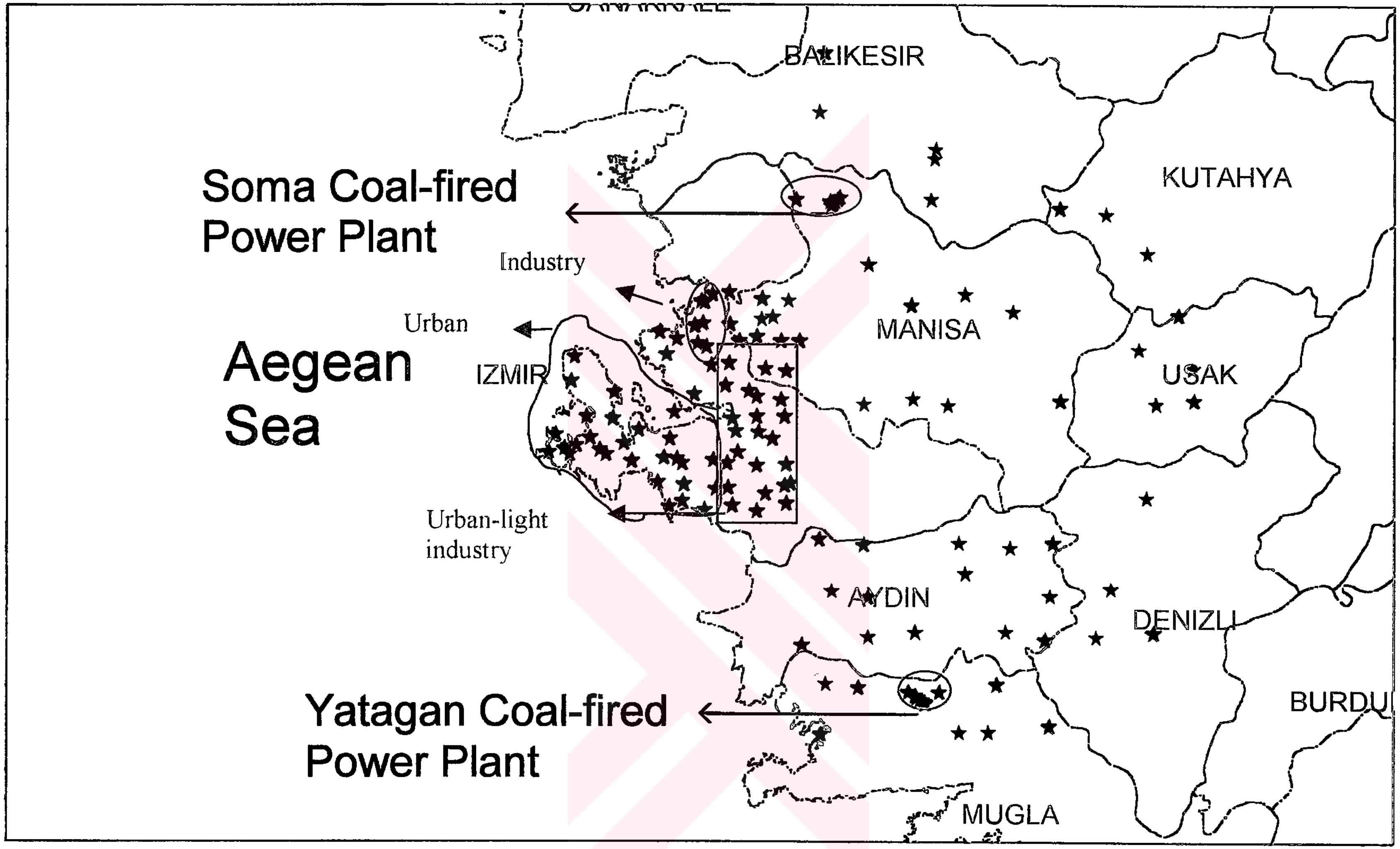


Figure 1.1. The division of sampling region into subregions according pollution loadings

The city center and Manisa organized industry area are also included in this region at the north-east of the city center of İzmir.

The second region is urban region. This region was originally not very populated. By the time population has increased with the increasing number of summer resorts. It is now considered as an urban region.

The third area is completely industrialized and that's why it is called an industrial area, which covers many industies (İzmir İron-Steel, Akdemir Iron-Steel, Çukurova Steel, Ege Metal and Iron-Steel, Ege Fertilizer and other small industries) in Bozköy and one refinery (Aliağa refinery) in Aliağa. This area has small square measure including 5 grids (500 km^2) and so it is called an area rather than a region.

The fourth region is the power plants region, which comprises two distinct power plants. One of them is situated in Soma (Manisa) and other one is situated in Yatağan (Muğla). They are both coal-fired power plants and thus the composition of their emissions is very similar. That's why they will be evaluated together.

The rest of the region is called as semiurban region. Since this region is less densely populated and it can not be called an urban area. We can not call as a rural area because it includes cities and small industries. There are textile industries in Manisa and Uşak; metal, food plants and household appliances in Manisa; ceramic industries in Kütahya.

The topographical view of the whole region is shown in Figure 1.2. The coastal areas are very flat. The high altitudes start going from coastal side to inside of the region. The pollutants may be well dispersed in the coastal sides. However the air currents can not directly go to the interior part of the region because of high altitudes. With the long years mean wind direction data obtained from Turkish General Directorate of State Meteorological Organization (DMİ) for İzmir, Seferihisar, Karaburun, Dikili, Akhisar and Yatağan, wind roses are formed as shown in Figure 1.3. In Aegean Region the dominating winds generally come from the northern directions except for Dikili where southern directions dominate. These

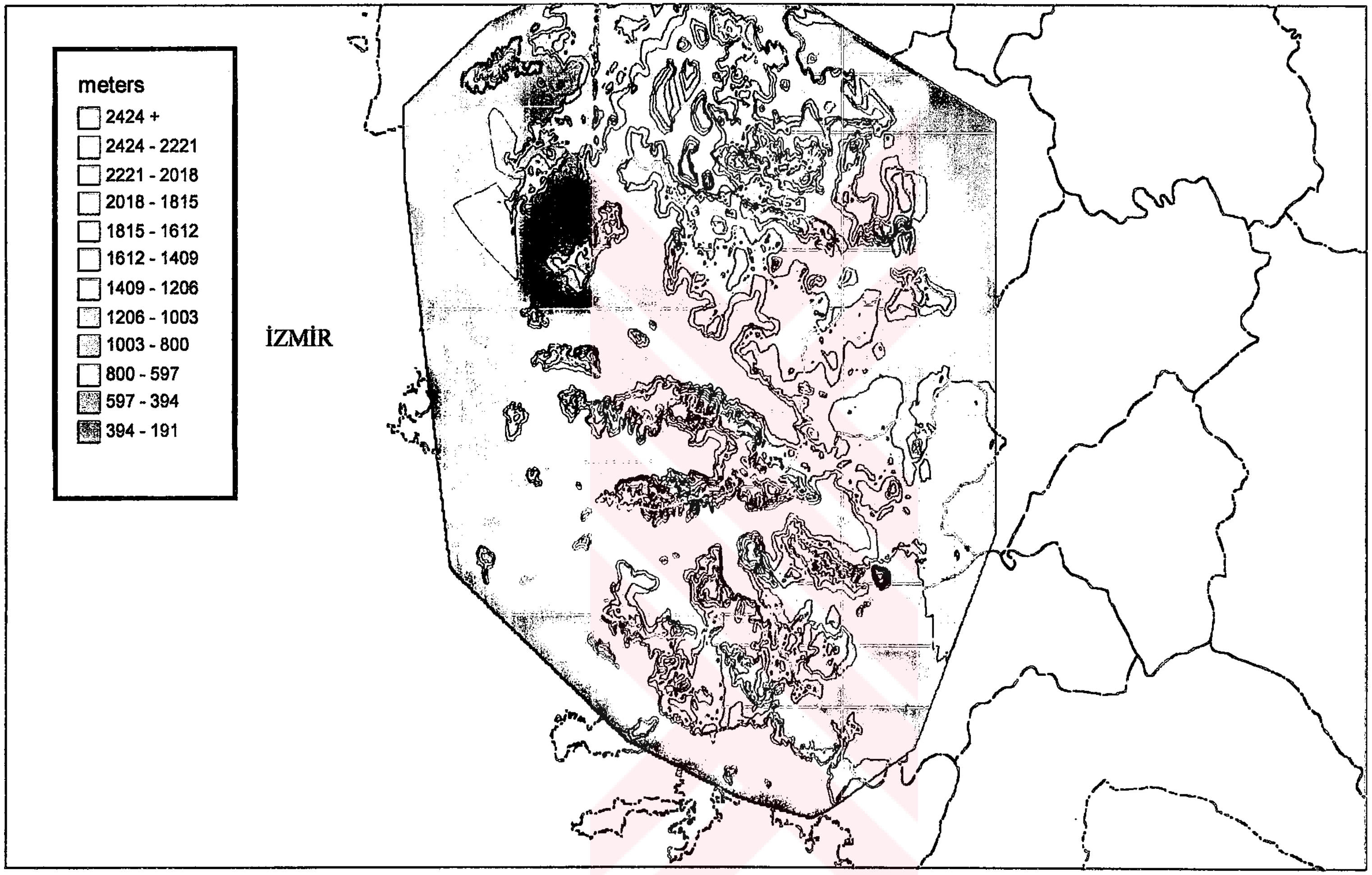


Figure 1.2. The topographical features of the sampling region

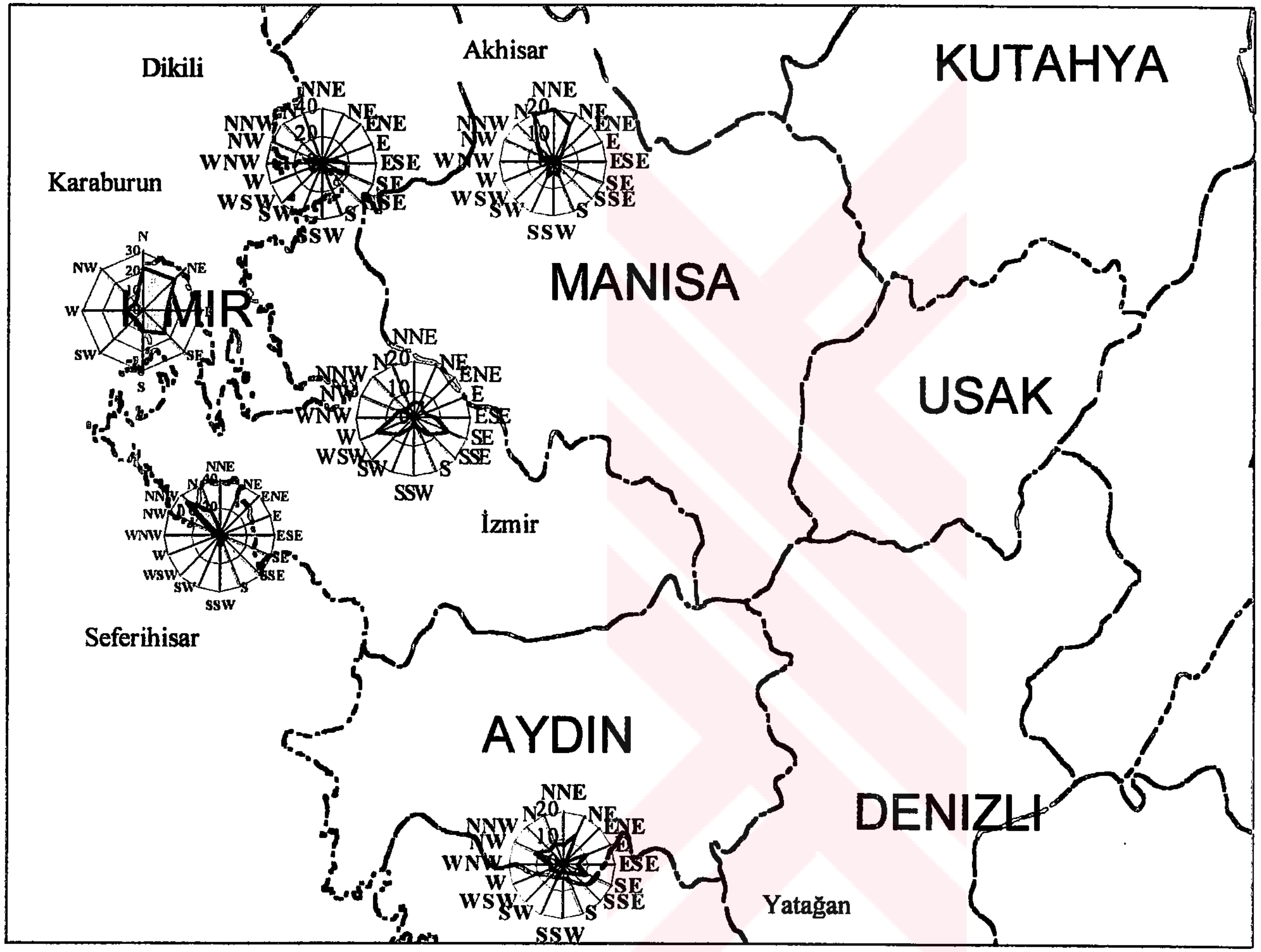


Figure 1.3. The wind roses of the whole region

dominating winds carry the pollutants of city of İzmir and industries to Dikili and Karaburun. Especially Karaburun was found to be polluted place even though it is away from the urban and industrial sources. Seferihisar area, however, is not polluted as Karaburun. Because the winds carry the pollutants of summer resort areas to the city of İzmir. In both power plant regions, dominating winds come from the north. In these areas local pollution from power plants is a possible source.

1.4. Biomonitoring Systems

Higher plants such as trees and lower plants such as lichens, mosses and fungi are frequently used as accumulative bioindicators of elements. Which group and which species has to be chosen depend on the monitoring purposes and on the ecosystem under investigation (monitoring of ecosystem fluxes, of effects on the ecosystem, with particular respect to human health, with emphasis on a particular emission source, as a general screening etc.).

1.4.1. Lichens

1.4.1.1. The Morphology-Structure and Reproduction of Lichens

Lichen is Greek for tree-moss (http://teaching.safs.bangor.ac.uk/, 1999). Lichens are symbiotic organisms composed of fungi (mycobiont) and green algae or cyanobacteria (photobiont). The fungal partner of the lichen mostly unable to develop without an algal partner. As a contrast, the alga mostly belongs to genera or species which occur in a free-living state as well (Tyler, 1989). The alga synthesizes and excretes a specific carbonhydrate that is taken up and utilized as food by the fungus. The cyanobacteria can take nitrogen gas from the air and turn it into biologically usable compounds, so lichens with cyanobacteria can make major contributions to soil fertility (http://www.lichen.com/, 1999). The fungus, in return, protects the alga from adverse conditions, particularly from drought. The algal partner is usually is the dominant partner, controlling the morphology and fruiting of the lichen (Bidwell, 1974).

The names of the lichen species are given in two words. The first word starts with capital letter and identifies the genus; the second word starts with small letter and identifies subspecies.

The body of a lichen consists of fungal filaments (hyphae) surrounding cells of green algae and/or blue-green cyanobacteria. The vegetative body of a lichen is called a thallus.

Lichen communities may be classified conveniently according to their substrate: tree bark, wood, rock, soil, humus etc. The gross appearance of these communities is similar throughout great areas of the world although species composition varies from region to region (Hale, 1967).

Their mode of growth may be crustose (crust-forming), foliose (leaf-like) or fructose (shrub-like, stalked or hair-like) including various intermediates such as squamulose (pebble-like) (Tyler, 1989) as shown in Figure 1.4. As with bryophytes they may be epigeic (growing on soil), epilithic (growing on rocks) or epiphytic (growing on higher plants, usually trees). Lichens are classified according to the type of fungal component.

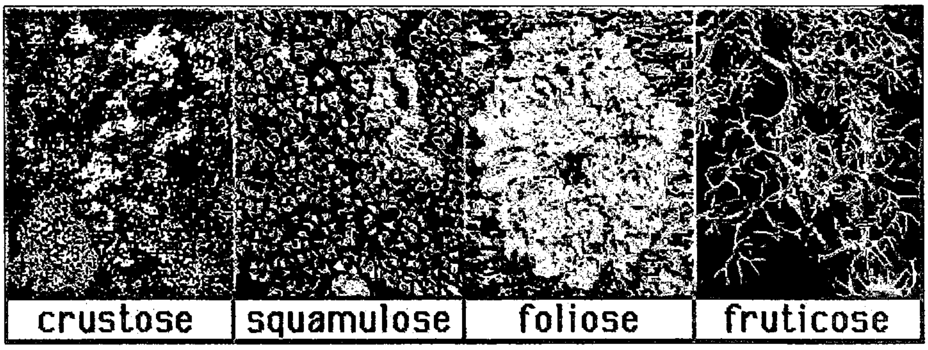


Figure 1.4. Lichens according to their mode of growth
(http://www.ucmp.berkeley.edu/,1999)

Despite the wide diversity of the basic growth forms, all lichens have a similar internal morphology. The body of the lichens is formed from filaments of the fungal partner and the relative density of these filaments defines the layers within the lichen as depicted in Figure 1.5. (1) As its outer surface, where it comes in contact with the environment, the filaments are packed tightly together to form the cortex. The dense cortex serves to keep out other organisms and helps to reduce the intensity of light which may damage the alga cells; (2) the algal partner cells are distributed just below the cortex in a layer where the fungal filaments are not so dense. This is very similar to the arrangement in a plant leaf, where the photosynthetic cells are loosely packed to allow air circulation; (3) below the algal layer is the medulla, a loosely woven layer of fungal filaments; (4) in foliose lichens, there is a second cortex below the medulla and (5) rootlike structures (rhizines), but in crustose and squamulose lichens, the medulla is in direct contact with the underlying substrate, to which the lichen is attached. In fruticose lichens there is another algal layer after medulla and then lower cortex comes and there is no rhizines. This layered structure makes sure that lichens have a long lifetime (http://bionet.informatik.uni-oldenburg.de/,1999; http://www.ucmp.berkeley.edu/, 1999).

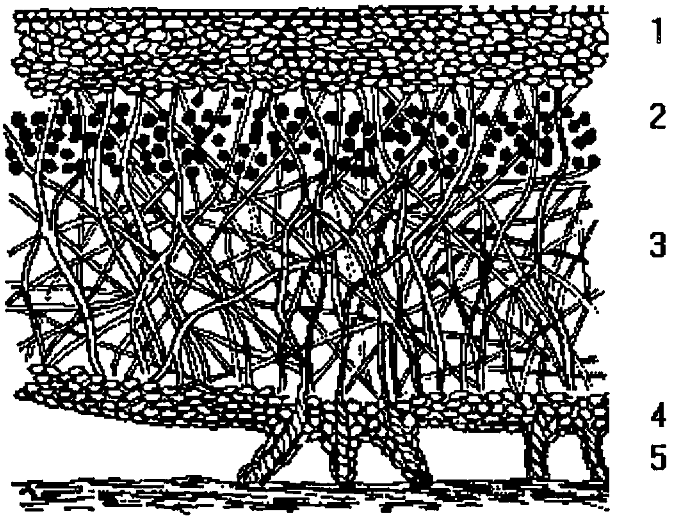


Figure 1.5. The structure of lichens (http://bionet.informatik.uni-oldenburg.de/, 2000)

Reproduction of lichens occurs in different ways. Some reproduce by breaking off and forming new colonies. Others release a soredium (powderlike areas usually on the last segments edges) which consist of a few algal cells and a few hyphae bound together. For example, this type of reproduction is seen in Parmelia species. In other way of reproduction, the fungus releases spores from the cup shaped or dishlike fruiting bodies (apothecia). These might germinate and find a free living algal cell and form new lichen. A difference between mosses and lichens is that lichens are able to make dishlike fruitbodies apothecia, just like fungi (http://bionet.informatik.uni-oldenburg.de/,1999; http://teaching.safs.bangor.ac.uk/, 1999). Especially, this type of reproduction is seen in Xanthoria species.

1.4.1.2. Lichen Chemistry and Metabolism

Lichen chemistry belongs to the earliest fields of organic compounds after its foundation and it is still a flowering branch of natural product chemistry (Huneck, 1991). Lichen chemistry is attractive because it comprises many different types of organic compounds (acetogenins, mevalonate groups, amino acid derivatives and carbonhydrates). Lichens acids are effective chelating compounds (Ahmadjian, 1966).

Lichens produce and excrete many secondary compounds (compounds not involved in primary metabolism such as respiration and photosynthesis). Many of the compounds are unique in the biological world e.g. phenolics (orcinol), organic acids (oxalic acid). Toxins and antibiotic compounds (e.g. phenolics) stop other microbes living inside the thallus, grazing by large animals and inhibit moss growth (who would quickly take over the space on the substrate). Hydrophobic compounds prevent water loss and stops waterlogging (maintain air spaces). Metal chelating compounds (e.g.organic compounds) dissolve the rock away to get nutrients. Coloured pigments act as a light protection. Dark pigments increase heat absorption (http://teaching.safs.bangor.ac.uk/, 1999).

1.4.1.3. Ecology, Environmental Adaptation of Lichens

Lichens are important constituents of the vegetation of many ecosystems of the world. These plants include about 13 500 species. Lichens can survive periods of extreme cold. Specimens frozen in liquid oxygen (-183 °C) for 18 hours still respired after thawing. Lichens also withstand extreme heat and prolonged drying. The temperature limits reached 101 ^{0}C. Resistance limits of lichens, when moist, dropped by 40 ^{0}C- 50 ^{0}C. It is not suprising that dried lichens can withstand extreme heat in light of the information that on hot summer days, exposed lichen thalli reach temperatures of 50 ^{0}C- 70 ^{0}C. The most resistant forms survived air-dried conditions for over 1 year without detectable signs of injury (Ahmadjian, 1966).

1.4.1.4. Growth Rates and Longevity

In spite of reports on their persistence and agelessness, lichens surely have a maximum thallus size and finite life spans. Life spans seem to average at least 30 to 50 years but for some species as high as 80 years and even range from 1000 to 3000 years in alpine-arctic areas. The overall growth rate as measured by distance for fruticose lichens is estimated to be 4.1 mm per year. This may be between 2-11 mm depending on species and the place where they live. Some typical values for average annual radial rate is 1 mm for crustose and 2 mm for foliose lichens. This radial growth rate may be between 0.01-27. The order of rates of growth increaseas from crustose to fruticose in general. This rate is 2.5 mm for Xanthoria parietina (Hale, 1967). Total rainfall per month was the most important climatic variable positively correlated with monthly growth (Armstrong, 1993). In addition the results support the hypothesis in that periods of maximum growth can occur in any season and depend on distribution of periods of high total rainfall and whether or not these period coincide with the periods of maximum sunlight.

1.4.1.5. Lichens and Air Pollution

Many scientists analyze lichens for their S content as a bioindicator of pollution. It disrupts photosynthesis. A combination of low pH, high SO_2 and moisture are the killers for lichens. Pine bark is naturally acid so a small amount of SO_2 will tip the balance and kill the lichen. Elm bark is naturally alkaline and it can buffer the acidity more. Thus lichens living on elm trees can survive longer under acid rain (http://teaching.safs.bangor.ac.uk/, 1999).

The ways in which they are used as bioindicators is now being re-examined because the distribution of lichen species has, and is, being altered by changing pollution climates throughout the industrialized world (Richardson, 1993). In the latter half of the last and first half of this century, high sulphur dioxide and smoke levels affected relatively limited areas around the larger and more industrialized cities. Following the reductions in SO_2 emissions in the United Kingdom (and other areas of Europe) in recent years, several lichen species are migrating back into areas from which they had previously disappeared (Rose and Hawsksworth, 1981).

By examining the lichen flora around such cities, and relating the distribution of particular species to measured winter mean SO_2 levels, there is clearly defined negative relationship between species diversity and SO_2 when SO_2 is more-or-less stable or increasing in concentration with anthropogenic factors clearly overriding such factors as climate and topography (Seaward, 1976). The Hawskworth and Rose's (1970) biological scale has been used in order to evaluate the atmospheric concentration of SO_2 in different areas. As shown in Table 1.2, this scale identifies 7 zones by relating the presence of some species of epiphytic lichens to well defined concentration ranges of this pollutant in the atmosphere.

Table 1.2. Hawskworth and Rose's biological scale

Concentration SO_2 $\mu g\ m^{-3}$	Index Species
>170	Desmococcuc sp.(subspecies)
100-170	Physcia adscendens, Lepraria incana
70-100	Xanthoria parietina, Hypogymnia physodes
50-70	Physcia stellaris, Evernia pruinastri
40-50	Flavoparmelia caperata, Pseudevernia furfuracea
30-40	Ramalina fraxinea, usnea sp.
<30	Lobaria puilmonaria, Anaptychia ciliaris (with apothecia)

A rich flora indicates good air quality. The absence of lichens is an indication of poor air quality. This situation is merely qualitative. However, by comparing more than two sampling sites along a pollution gradient it is found that lichens are not either present or missing, but there is a distinct increase in lichens parallel to the increase in air quality. The same can be done with a single species of lichen or even by measuring chlorophyll content, fertility or growing rates of distinct species. That is why we can say that no matter whether we are on the sociological level (total lichen community), the population level (frequency of a single species), the physiological level (growing rate) or the biochemical level (chlorophyll contents), a certain quantification is possible.

The high stack emission polices have lead to transboundary pollution and increasing awareness of acid rain. The very pollution sensitive of ancient woodlands, especially those containing cyanobacteria as photobionts, appear to be damaged by acid rain. After two years of acidification there was no significant effect on the growth of C. stellaris, but thallus discoloration was evident below pH 3.5. (Lechowicz, 1987). The deleterious effects of acidification may be partially offset by nitrogen enrichment when precipitation is relatively rich in nitrate compared to sulfate ions. Other laboratory and field experiments supported the observations related with SO_2 and acid rain mentioned above (Türk and Wirth, 1975; Hutchinson et al., 1986; Gilbert, 1986; Lechowicz, 1987; Balaguer and Manrique, 1991).

The ability of lichens and bryophytes to accumulate metals to levels far above their expected physiological needs and neither lichens nor bryophytes have a well developed root structure and depend, therefore, on airborne mineral nutrients deposited on their surface for their nutrition. Because of their biological properties, lichens have been used, in general, as a biomonitor organism especially to provide information for different heavy metals absorbed in lichen thallus. Much less information was yielded on the localization of such metals in the lichen thallus or the influence of different heavy metals on physiological processes in lichens exposed to contaminated air under field conditions. Lichens lack cuticles, stomata and functional roots. In consequence they have evolved both highly efficient nutrient uptake systems and ability to absorb and lose water rapidly; being metabolically active when moist. Where the absorbed water contains dissolved pollutants, the more sensitive species of lichens may be poisoned and this leads to a change in the community of lichen species growing on a particular substratum such as soil, rocks or tree trunks. This feature enables lichens to be used as bioindicators not only for air pollution but also for monitoring the dissolved metal in natural waters (Beck and Ramelow, 1990). If the occurrence and abundance of particular species is recorded, it is then possible to calculate, indices of atmospheric purity, number of lichens (Oksanen et al., 1990; Oksanen et al., 1991; Wolseley and Aguirre-Hudson, 1991; Galloway, 1992; Pirintsos et al., 1993; Brakenhielm and Qinghong, 1995; Loppi, 1996) or distribution of each species in the study area (Seaward, 1987; Showman, 1988; Türe, 1990). Where the lichens are not actually killed, enhanced levels of atmospheric pollutants are found when samples are analyzed. By analyzing samples collected at different distances, lichens provide valuable bioindicators of a wide range of atmospheric pollutants including metals, non-metals, radionuclides and organic substances chlorinated hydrocarbons. The detailed literature survey will be given in section 2.1.

1.4.1.6. Economic Uses and Applications

Lichens have not been utilized as a food source by man to any great extent. The thalli, though edible, are often tasteless and may have certain bitter irritating acids, especially fumarprotocetraric acid, that must first be leached out by boiling in soda. Their food value, however, compares favourably with that of cereal crops. In times of famine, peoples in boreal or subarctic regions have resorted to lichens as a supplemental source of carbonhydrates, mixing them with flour or boiling to extract gelatins. In Japan the foliose rock tripes (Umbilicaria), called Iwatake, are eaten in salads or fried in deep fat; they are considered as a delicacy (Hale, 1967). Lichens are important as food for animals in the arctic regions. Sheep in the Libyan deserts are reported to graze on the subfoliose lichen which also appear to be a common source of food for land snails and slugs.

The use of lichens in folk medicine has persisted into modern times. In 1944 the extracts from 52 different species in eastern North America were discovered which inhibited growth of several kinds of bacteria. Until 1954 practically all available lichen species and substances were tested. The most promising lichen substance is the yellow pigment usnic acid, a broad spectrum antibiotic. This medication, now widely available in Europe, is more effective than penicillin salves in treating external burns and superficial wounds. Lichen substances are also being investigated experimentally as antibiotics in plant pathology. Sodium usnate, for example, has been found effective against the tomato canker. Indeed our own bright orange Xanthoria parietina was also used in medieval times as a remedy for jaundice (http://www.open.ac.uk/, 1999).

Before the discovery of coal-tar dyes, lichens had considerable economic importance as dyestuffs. They were mentioned by the ancient Greeks and apparently used widely in the Mediterranean region, especially as the source of valuable purple dye. The amphoteric dye litmus, a familiar acid-base indicator in chemistry laboratories, is derived from depside-containing lichens. Various essential oils and derivatives of depsides are extracted from species of Evernia, Parmelia and Ramalina. Some have agreeable odours and are in demand for scenting soaps an for an essence in better perfumes. Lichens have found some practical use as indicators in geological exploration. The occurrence of bright lemon-yellow Cetratis, especially C. tilesii, is highly correlated with marble and limestone deposits. Spectrographic analysis of saxicolous lichens in Colorado have shown that the thalli contain high concentrations of rare mineral elements which could lead to the discovery of ore bodies rich in these elements. Fruticose Cladonias are frequently used as facsmile trees and shrubbery for architectural models and model trains.

Lichens are even used to as geochemical indicators when mapping rocks with similar textures and mineralogies which would otherwise be difficult or impossible by more traditional geological methods (Boyle et al., 1987).

1.4.1.7. Harmful effects

Although mentioned above usnic acid is yellow pigment of lichens and used as a broad spectrum antibiotic to treat external burns and superficial wounds it can cause a skin rush and it may be a cause of respiratory allergy. Arctic lichens are having a much more deleterious effect on Eskimos and Laplanders. Reindeer lichens at high latitudes have accumulated large quantities of radioactive cesium and strontium from the fall-out of atomic bomb tests. The animals eat these lichens and soon build up a high body burden of radioactivity. Since the arctic peoples live on caribou and reindeer, the radioactivity is passed along to them in the food chain. Eskimos in Alaska have body burdens as high as one-third of the maximum permissible safe level and Laplanders have accumulated comparably high levels. Although no symptoms of radiation illness have been seen and bomb testing has fortunately ceased, public health authorities are deeply concerned about possible after-effects.

Lichens are often in such intimate contact with their substrates that it might be supposed that they could have harmful effects. It is common practice in some orchards in Europe and southern United States to destroy corticolous lichen growths on fruit trees with fungicides in the belief that lichen-free trees are more robust. Even if direct damage by rhizines is of no consequence, a dense cover of lichens can harbour and provide shelter for many harmful insects and arachnid pests. Saxicolous lichens are suspected to have a comparable role in the breakdown of rocks, although their ability to form soil is probably exaggerated. Crustose lichen thalli are often interspersed with microscopic rock fragments, which have been loosened, by mechanical contraction and expansion when the thallus is alternately moistened and dried. Chelation could be an important mechanism in mineral breakdown (Hale, 1967).

1.4.2. Other Biomonitoring Systems

1.4.2.1. Mosses

Mosses belong to a group of green plants known as bryophytes (from the Greek words bron, “moss” and phyton, “plant”. Bryophytes, which include mosses, liverworts and hornworts, do not produce flowers, fruits or seeds. They are reproduced by spores but also they can be reproduced from new plants from small fragments of stems and leaves that are broken off. Bryophytes have structures that resemble roots, stems and leaves but they lack true water and food conducting tissues. Commonly they are found growing on rocks, soil, rotting logs, trees and even shingles, bryophytes favor cool moist habitats like woodlands, stream banks and swamps. Mosses can withstand harsh environmental conditions as well and can be found in the Arctic, Antarctic and deserts. Mosses along with lichens, are sometimes the first organism to colonize in newly exposed soil (http://www.mpm.edu/, 1999).

Since 1968 mosses have been used in many countries of the northern hemisphere to estimate atmospheric deposition of metals on a regional scale (Markert, 1993). As regards their suitability as biomonitors, mosses and lichens are often discussed together and calibration factors between some moss and lichen species have been calculated. Indeed, there is great similarity in many characteristics: wide geographical range, no seasonal variation in availability and morphology, SO_2 sensibility. However great differences also have to be emphasized, which make some mosses in many cases better suited for accumulative heavy metal monitoring than lichens. In contrast to the longevity of the total lichen thallus, the living parts of mosses (except Sphagna) are generally not more than three years old (often only one or two years). Knowing the morphological characteristics of mosses it is even possible to differentiate between these two or three years. Hence the green parts of mosses reflect the actual deposition rate, while it is often impossible to relate the heavy metal content of lichens to a certain time span. Another great advantage of mosses is the high accumulation rate. Finally, some mosses species even occur in the so-called lichen desert of city centers and industrial areas, where they have been successfully used for passive biomonitoring of heavy metals. The particular demands on a biomonitor are almost completely fulfilled by mosses except for they require the moist weather generally. Because of their comparatively unproblematic cultivation, their physiology is better known than that of lichens, although some questions still exist.

1.4.2.2 Fungi

The restriction to heavy metals in soils is a clear consequence of the life history. The composition, structure, physiological capabilities and genetic potential of fungi are directly affected by the conditions of their growth in soil. The real plant, the mycelia, lives in the substrate (e.g. soil, humus, litter). Only the fruiting bodies exist above ground. As they grow rapidly, there is no doubt that the heavy metal content of young fruiting bodies is soilborne. They accumulate only low amounts of heavy metals directly from the wet or dry deposits. Soilborne in this case does not mean exclusively originating from parent material. Moreover it is very likely that heavy metal input to soil via deposition and litter fall is the main source of the heavy metal concentrations found in fungi. Fungi are better predisposed to absorption of heavy metals present in soil than the majority of other soil organisms are (Markert, 1993).

1.4.2.3. Higher Plants

In contrast to lichens, mosses and fungi, higher plants generally show a clear division into roots, shoots and leaves. As higher plants are in general much larger than the members of the other groups mentioned, there is no difficulty in separating the different plant organs for analysis. The name higher plants refer to the high evolutionary state. Especially the conducting system is very well developed. This leads to the consequence that translocation of all mobile metal species takes place (Markert, 1993). Nevertheless it has been shown in many studies that in polluted areas leaves can be regarded as accumulative monitors of many metal elements and other pollutants, because a great proportion of the elements deposited or intercepted is not imported into the leaf tissues but remains on the surface or in the wax cuticular (Cape et al., 1995; Rodrigo et al., 1999; Monaci et al., 2000).

Physiology, ecology, morphology of the higher plants are better known than in lower plants. Higher plants, particularly trees, are the most important interceptors in forest ecosystems. Hence the use of tree leaves as accumulative monitors is of great importance.

1.4.2.4. Bark

Bark can be defined as all tissues of the tree, outside the cambium layer. In older trees it is divided into inner (living) and outer (dead) bark (Barghigiani et al., 1988; Markert, 1993). While tree trunk continues to grow and increases its diameter, the outermost parts of the bark are shed. Each tree has its typical bark, as each of its finger print. Similar kinds of bark exist, but there are no identical ones. Bark of many tree species is exposed to the atmosphere for a considerable period time, its duration depending of the species. The basic assumption in using bark for biomonitoring purposes is that levels of pollutants in bark should reflect the levels of environmental pollution. The bulk of substances is assumed to accumulate on the surface and in the outermost dead bark cells. In this tissue no substantial active or passive translocation of investigated elements into the wood should take place. If passive translocation of investigated elements into the wood should take place. If such processes occur, they should be quantified and accounted for in a careful interpretation of analytical results. Besides radial movements also an axial transport of substances from roots or assimilation organs into the bark may influence its composition. The extent of this shift may vary for each investigated element, depending on its mobility. The cross section of the bark appears thus, stratified. Analysis of such layers may give information about the extent of pollution in a specified period, respectively certain years. It is frequently used in the analysis of heavy metal deposition (Kuik and Wolterbeek, 1994), sulphur and acid pollutants. The study of the acidity of tree bark is a method that has been used by several researchers to evaluate the impact of air pollution on extensive areas (Santamaria and Martin, 1997). There was a significant correlation between the levels of SO_2 in the atmosphere and the pH of tree bark.

1.4.2.5. Others

There are many other biomonitoring organisms used for many purposes for centuries. Animals represent necessary objects of biomonitoring studies. For example, during the industrial revolution, miners took caged canaries with them as they ventured deep into the shafts. If the bird got sick or died, the miners knew it was time to get back to the surface (http://twri.tamu.edu/, 2000). Bird feathers were used as a biomonitoring tool and Hg levels in feathers of several species of birds from tropical ecosystems were examined (Burger, 1997). In general, moving toward tropical ecosystems increases species diversity. It is apparent that the mercury level in feathers of some tropical birds are as high as those from temperature regions, exceeding levels associated with adverse effects in laboratory studies. However, the birds are present in large numbers only in summer, since a majority of them leave in winter. The large mammals are rare and the number of the small ones fluctuate markedly. In connection with this, soil fauna is of great interest representing 90-99% of the total biomass and 95% of the number of species composing the terrestrial zoocenoses. Rabbits, pheasants, bees, mouse-form rodents, earth worms, fishes and soil microorganisms are generally used as biomonitor organisms (Salanki, 1985).

In the very early of studies of environmental pollution it was observed that some aquatic organism (seaweeds) (Carvalho et al., 1997), both plants and animals are valuable indicators of the extent of pollution in aquatic systems. However, changes in communities of macro organisms are often observed too late to reserve e.g fish mortality. In comparison, microorganisms possess morphological, physiological and genetic characteristics making them a very good early warning system for pollution since they will signal changes when changes may still be reserved. As unicellular microorganisms, bacteria respond directly to environmental changes. Growth conditions will influence the expression of cellular functions including enzymes, affecting the levels and extent of activity. In fluctuating conditions as will occur in estuaries, the capabilities of microorganisms can respond very rapidly to such changes (Salanki, 1985).

Needles and foliage are used to as a bioindicator of S and heavy metal pollution on many occasions (Wyttenbach et al., 1997; Manninen et al., 1991). Prolonged effects of high concentrations of various pollutants have resulted in large-scale dying not only of conifers but also deciduous trees. The pollutants accumulated in the waxy surface of the needles are identified and quantified.

Tree rings have been used to construct records of heavy metal pollution and study the relation between growth and air pollution. The presence and distribution of trace elements in the stem of tree have been attributed to two general factors, nutrition physiology and environmental pollution (Oliveira et al., 1997). Nutrient accumulation in a stem depends on the age of the plant, chemical properties of soil and tree genetic data. These parameters are very important to evaluate if the absorption of a specific element was due to a pollution factor, fertilization or to the own plant demand.

The use of litter and humus (Ayras et al., 1997) is often neglected when talking about biomonitoring. Perhaps intermediate position of these materials between biology and soil science is responsible for this. Ecosystem analyses show that litter and humus are the largest sinks of heavy metals in most ecosystems.

Particularly lead and copper are retained but other trace metals can also be found in large amounts (Markert, 1993).

One of the prospective biomonitors is honey and honeybees (Jones, 1987). Honeybees would appear to have potential in this respect, since by foraging they effectively sample their surroundings for the constituents in or on the forage plants and hence in the soil and the atmosphere of the area. They readily inhabit a variety of environments and are manageable, generating an ample quantity of material each season for sampling and analysis.

1.5. Why Lichens? (Advantages and Drawbacks)

Although the sensitivity of lichens to air pollution has been acknowledged since the observations in south Lancashire in 1859, the lack of recording gauges effectively delayed all critical study in this field prior to 1958 (Ferry et al., 1973). Even comparatively unpolluted small towns in medieval times would have had a marked effect on the lichen flora. The trees, which grew in back gardens and sometimes formed small areas of woodland within the city walls, would have had nitrophilous (confined to habitats rich in nitrogenous matter) lichens upon their boles, such as species of Buellia, Physcia and Xanthoria. By contrast, in woodland outside the towns nitrophobous lichens would have predominated, as they do today (Ferry et al., 1973). The development of the Xanthorion community resolting from the dispersal of artificial fertilizers can be considered as indicative of a particular type air pollution (Ferry et al., 1973).

Various monitor materials have been applied in trace-element air monitoring programs, such as lichens, mosses, tree bark, tree rings and pine needles (Sloof, 1993; Sloof and Wolterbeek, 1991b; Seward, 1995). Evaluation of the criteria mentioned above for the various biomonitor materials, leads to lichens and mosses as the best suitable monitors. For all biomonitors used, the mechanisms of trace element uptake and retention are still not sufficiently known. For grass, tree rings and ferns, substantial element contributions from other sources than atmospheric, such as the soil or the tree bole have to be taken into account. Material trapped by pine-needles has the same composition as soil and washing the waxy needles before analysis can remove over 80% of the trapped trace elements. Rough barks accumulated trace element more than smooth barks. Where comparisons have been made, lichens and mosses show consistently higher metal levels than higher plants. This characteristics allows for a more precise definition of deposition zones, easier trace element analysis and early reflection of enhanced pollution levels. Their high sensitivity to various air pollutants in comparison with higher plants can be ascribed to both morphological and physiology differences which namely include:

- in the absence of a cuticle, pollutants find an easier way into the thallus;
- corticolous (growing on trees) lichens absorb both water and nutrients directly from the air;
- lichens accumulate various materials without selection;
- the material once absorbed will accumulate since there is no excretion;
- the morphology of lichens and mosses does not vary with seasons, thus accumulation can occur throughout the year;
- usually have considerable longevity, which leads to their use as long-term integrators of atmospheric deposition.

Lichens, especially epiphytic ones, are widely known to be good indicators of air quality in regions with high levels of SO_2. Possible responses to air pollution stress include chlorophyll degradation (Zambrano and Nash, 2000; Cañas et al., 1997), change in photosynthesis and respiration (Arb et al., 1990), alterations in nitrogen fixation (Gunther, 1988), membrane leakage (Pearson, 1985; Alebic-Juretic and Arko-Pijevac, 1989; Nash III and Gries, 1995), accumulation of toxic elements and possible changes in spectral reflectance (Garty et al., 1997) lichen cover and/or morphology (Perkins and Millar, 1987a; Perkins and Millar, 1987b; Perkins, 1992), community structure and reproduction (http://www.colostate.edu/, 1999).

About seventy lichen species have been reported as suitable indicators of elemental pollution (Kucera, 1994). Of these, Hypogymnia physodes (L.) Nyl. and Parmelia sulcata are the most frequently used species for biomonitoring in Europe. The former species is widespread in Northern Europe and in mountain regions, it is one of the most tolerant lichen species, it can withstand long periods with fairly low levels of humidity, this lichen has no rhizinae and this perhaps accounts for the insignificant amounts of metals it absorbs from the substrate, it has a large surface to weight ratio. On the other hand, this species grows on acidic bark substrates which are less suitable for monitoring purposes due to possible leaching of metals from the lichen and it is less frequent in sub-Mediterranean areas. In these areas, as well as the European plains, Parmelia species are more frequent and investigated. Lichens may also show interfering element uptake from the substrate (Prussia and Killingbeck, 1991), but are more widespread than mosses especially in densely populated or industrialized areas. Furthermore, substrate/soil interferences can be recognized by the application of factor analysis techniques. Removing adhering sand and/or soil from the lichens is also a debated issue. Another problem of utilizing lichens for monitoring air pollution may be due to stem flow, which may bring to lichens additional nutrients and /or pollutants not necessarily associated with air pollution. This problem can be avoided in small scale studies by employing lichens in the form of transplanted colonies (growing on their natural substrate placed on an exposure plate). In addition the biomonitoring with the transplanted lichens may be used in areas where lichens do not occur. Parmelia (hypogymnia) physodes is most frequently used for this purpose, but the following species are also suitable for transplantation: Parmelia sulcata, P. caperata, P. cortea, P. furfuracea, Xanthoria parietina, Evernia prunastri. The transplanted lichens indicate the level of pollution within a short time (4-15 weeks).

Especially in industrialized and populated areas in Turkey, tolerant lichen species growing on trees (epiphytic) are more widely spread than mosses. Substantial substrate influence on the element content in the biomonitor is less likely to occur in epiphytic lichens than in epigeic (growing on soil) and in epilithic (growing on rocks) lichens.

For this thesis Xanthoria parietina was chosen since this was the only foliose lichen that was found commonly in the Aegean Region. Hopefully this was an easily recognized species with a yellow color as depicted in Figure 1.6. Parietinic acid, which is an anthraquinone produced excusively by Xanthoria parietina and responsible for its yellow color, possesses several functional groups that can bind metals. It was noted that this lichen changes from yellow to green color following its exposure to metallic pollutions, which could be interpreted by the formation of a metal-parietinic acid complex (Sarret et al.,1998). This lichen species was among the lichens to be the closest to the most polluted zone of Eskişehir in Turkey (Türe, 1990). Xanthoria parietina is found sea level to 1250 m. This gives also the sufficient range for this study (Davies and Notcutt, 1988). One disadvantage of it is difficulty in separating from the bark substrate.

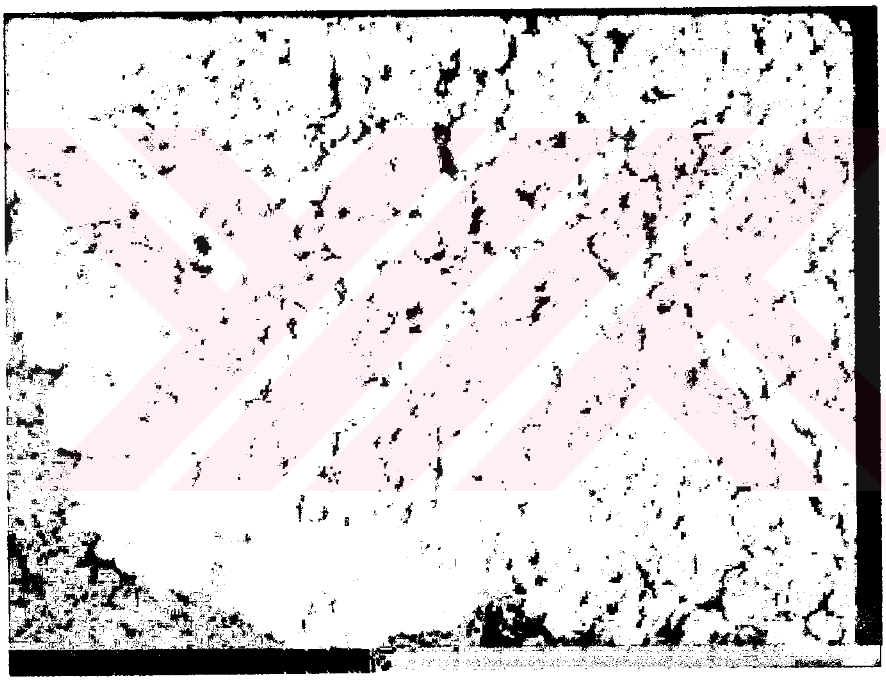


Figure 1.6. The picture of Xanthoria parietina (http://www.lichen.com/, 2000)

1.6. Factors and Mechanism Controlling Bioavalibility and Uptake

1.6.1 Mechanism of Metal Uptake and Retention

Three different mechanisms of metal immobilization are supposed to exist in air and soil polluted lichens 1) entrapment of metal-rich particulates originating from atmospheric aerosols, the metal being in mineral form, 2) intracellular uptake with likely complexation to S-containing peptites called metallothioneins as demonstrated for several higher plants and fungi and 3) extracellular complexation within fungal cell walls, the metal being complexed to hydroxyl, carboxyl, phosphate, amine or sulfhydryl functional groups.

The lichen thallus is characterized by cation exchange properties, just as in bryophytes and the uptake of alkali and alkaline metal ions is mainly or partly a process of passive ion exchange. Also heavy metal cations are absorbed by exchange mechanism (Tyler, 1989). Metals absorbed from solution are in a completely exchangeable form initially. However, the exchangeable fraction decreases if the thalli are air-dried. Sarret et al. (1998) revealed that two lichens absorbed heavy metals by complexation but strategies differ: in D. muscorum, Pb and Zn are accumulated through an enhanced synthesis of oxalate, which precipitates toxic elements as insoluble salt, whereas in X. parietina, Pb is complexed to carboxylic groups of the fungal cell walls. They concluded that hyperaccumulation of metals results from a reactive mechanism of organic acid production, whereas metallo-tolerance is achieved by a passive complexation to existing functional groups.

Garty et al. (1985) found that there is a correlation between chlorophyll degredation and the amount of Br, Pb, Fe and Ti in the lichen Ramanila Duriaei.

Heavy metals were found to affect membrane integrity in lichens. Increasing concentrations of Pb, Cu, Ni e.g. produced in lichen a gradual K loss from the thallus, interpreted as an increased cell permeability, as most K is located intracellularly in a freely diffusible form normally contained by the permeability barriers of the cell (Markert, 1993; Tyler, 1989; Tarhanen et al., 1996; Branquinho et al., 1999). Lead and copper whether taken up naturally or artificially was bound to insoluble anionic sites in an exchangeable form. Competitive uptake studies revealed the selectivity sequence Fe (III)>>Pb>Cu>>>Ni, Zn>Co, similar to the one demonstrated for moss. The sequence is in accord with a cation uptake mechanism involving ion exchange modified by metal-complex formation. The Zn binding was dependent on pH, explainable as competitive inhibition of Zn-binding by H^+. The mass balance of the exchange of Ni for Sr, Sr for Tl and Sr for H^+ was consistent with a cation exchange mechanism of metal-ion uptake in Umbilicaria muhlenbergii. Both the kinetics and the thermodynamics of Ni absorption are governed by physicochemical processes. Metabolic inhibitors caused no significant decrease in Ni-uptake and dead thalli accumulated Ni to a slightly extent than did live thalli. However, the major anions are likely accumulated against an electrochemical potential gradient and actively sorbed.

The nature of the binding sites in lichens is still insufficiently known. As about 90% of the biomass usually is made up by the mycobiont, most of the cation exchange capacity is propably localized to the fungal cell walls, but consistent data to document this seems to be lacking. The percentages of 66 and 34% of the Ni^{2+} taken up by the thallus was associated with fungal and algal zones, respectively. Potassium may be particularly abundant in the alga zones.

Lichen compounds (acids) seem not to be responsible for detectable cation binding. It was concluded that carboxylic and hydrocarboxylic groups were probably involved in the cation exchange but considered the phenolic (-OH), carboxylic acid and other functional groups (e.g., -CH=O) of the lichen compounds appropriate for metal-complex formation.

1.6.2. Sources and Localization of Mineral Nutrients and Heavy Metals

Precipitation and throughfall is a main or major source of mineral nutrition and heavy metals in lichens. The occurrence of extracellular heavy-metal containing particles in the medullar region of the thallus, entangled amongst the mycobiont hyphae, was demonstrated. Distinction has to be made between real uptake and accumulation as all chemical species are certainly not instantaneously available to the lichen. In a longer perspective, however, elements contained in particulate matter may become soluble and incorporated in the ecosystem circulation (Tyler, 1989).

Epiphytic lichens may obtain Ca, Mn, Zn and Cd from the bark substrate, whereas bark was probably not a significant source for several other metal elements (e.g., V, Fe, Co and As) (Bruin and Hackenitz, 1986).

1.6.3. Intracellular Uptake

Soluble metals in lichens may be located extracellularly or intracellularly (Branquinho et al., 1999). The extracellular metals reflected environmental sources whereas those located within the cell are more related to the effects on the physiological processes. K is located intracellularly in a freely diffusible form normally contained by the permeability barriers of the cell (Buck and Brown 1979; Markert, 1993; Tyler, 1989; Tarhanen et al., 1996; Branquinho et al., 1999). Heavy metals immobilized in cell wall constituents or otherwise extracellularly located are usually considered non-toxic to the plant. The knowledge of intracellular uptake of heavy metals in lichens is scanty.

Heavy metal ions with lower affinity values for cell wall ligands than e.g., Pb may to some extent penetrate the cytoplasm like Zn and Cd. In metals with a high affinity for the cell wall ligands (e.g., Pb) only very small amounts are supposed to be present intracellularly (Garty and Theiss, 1990). Copper and Ni, though practically no experimental evidence exists, must be postulated to take an intermediate position (Tyler, 1989). It must be concluded that the uptake of heavy metal ions is primarily a passive extracellular process of ion exchange and complex formation. Ligands are present in the cell walls of symbionts (alga, fungus), those of the mycobiont being quantitatively most important.

1.6.4. Toxicity and Tolerance

As is with bryophytes the tolerance of lichens to elevated tissue concentrations of heavy metals varies greatly between species, populations and elements. Extreme tolerance to high tissue concentrations has been reported in several cases. Few studies have been carried out where several metals have been considered simultaneously, which makes comparisons between elements difficult. Generally, however, Hg, Ag and Cu seem to be toxic than Pb, Zn and Ni. Lichens containing cyanobacterial phycobionts seem to be more sensitive to heavy metals (Zn, Cd, Cu and Pb) than those containing green algae (Tyler, 1989).

Peltigera membranacea was shown to be tolerant to Zn-induced inhibition of photosynthesis, displayed a reduced rate of Cd intracellular uptake, suggesting that metal exclusion was a tolerance mechanism. However, a severe metal stress was required before metal tolerance by exclusion occurred. Inherent cytoplasmatic tolerance, cytoplasmatic immobilization of ions and transport of ions to regions external to the plasma membrane on the cell wall were the mechanisms of heavy metal tolerance in lichens. However, the high affinity of Pb for cell wall ligands makes it unnecessary to postulate any cytoplasmatically located tolerance mechanism for Pb in lichens.

A special from of detoxification seems to be accomplished by the rhizinae of certain lichen species (foliose and crustose). The capability of rhizinae to accumulate and regulate metals may prevent toxic amounts from reaching the sensitive parts of the thallus.

Morphological changes of lichen thalli related to high levels of heavy metals have occasionally been reported. The morphology of lichens was changed in a metal polluted environment: the rhizinae became shorter, the thallus smaller with profusely branched veins, and hypertrophy of the medulla occurred. Otherwise, toxic effects on lichens under field conditions have been recorded as a sudden or gradual decrease in species abundance or species numbers/diversity along a known gradient of heavy metal exposure.

Limited information is available from the field concerning threshold concentrations of metals in lichen thalli. Quantitatively important woodland species may endure ca. 300 mg kg^{-1} Cu and 500 to 1300 mg kg^{-1} Zn without visible damage. However, only slightly higher tissue concentrations may be lethal. There is evidence that the most sensitive lichens are affected already at a concentration of ca. 80 mg kg^{-1} (Cu), i.e. 5 to 10 times the current regional base-line level of south Sweden. In combination with SO_2 or strong acidity the critical metal concentrations would be lower, though it is usually not apparent which factor is limiting the distribution under such conditions.

1.7. Materials and Methods

1.7.1. Analytical Techniques Used in the Content of the Thesis

A variety of instruments have been used in this study. For choosing the analytical technique, the factors like sensitivity, accuracy and precision obtainable with the analytical technique and availability of the instrument were taken into account. Based on the above criteria instrumental neutron activation analysis (INAA), inductively coupled plasma atomic emission spectrometry (ICP-AES), graphite furnace atomic absorption spectrometry (GFAAS) techniques were used for trace element measurements in lichen and total deposition samples, ion chromatography (IC) was used for determination of major anions in transplant lichen and total deposition samples. The technical and experimental details of the analytical techniques are given in experimental section of this thesis.

1.7.2. Mapping

In this study, MAPInfo 4.1 mapping program was used to prepare the distribution maps of elements. Interpolation is the procedure used to predict the unknown values with the help of known values at neighboring points, which are regularly or irregularly spaced. Many mathematical tools are used for interpolation. Some of them are the average of the neighboring values or a weighed average where the weights are inversely proportional to the distance. In this study, triangulation with smoothing method was used. On the maps, contour lines are used to portray surface relief as a set of lines that connect points having the same value.

In order to prepare topographic feature of three dimensional plots of power plant regions, SURFER 6.04 mapping program was used. Kriging method was applied. It is special regression method for interpolation of spatially and temporally correlated data with minimization of variance. Applying the kriging point estimation, isolines can be computed both from regular distributed sampling points and from irregular distributed points (Einax et al., 1997).

1.7.3. Receptor Modeling

Receptor oriented models have been employed to identify possible sources of pollution to resolve the elemental composition of the sources and to determine the contribution of each source to the total pollution level. In lichen studies enrichment factors (Wiersma et al., 1992; Calvelo et al., 1997; Varrica et al., 2000), interelement correlations (Fuchs and Garty, 1983; Loppi and Bargagli, 1996), multivariate statistical approaches such as factor analysis (Schaug et al., 1990; Sloof and Th. Wolterbeek, 1991b; Kuik and Th. Wolterbeek, 1994; Sloof, 1995b; Jeran et al., 1996; Freitas et al., 1997; Bennett and Wetmore, 1999) most commonly applied to arrays of pollution variables to derive information about pollution sources influencing the data. Enrichment factor calculations and interelement correlations are preliminary step giving an insight about the characteristic of the trace element data set. Factor analysis is the most appropriate choice to obtain the desired information about possible pollution sources in cases where no priori information about the number and the composition of the sources is available. In an earlier publication, Sloof and Wolterbeek (1991b) have reported on the application of target transformation factor analysis in the analyses of large data sets of elemental concentrations measured in samples of Parmelia sulcata. Trace element concentrations in lichens are generally assumed to reflect the concentrations of those elements in wet and dry deposition. Therefore, the common statistical methods applied in air pollution studies can also be applied to lichen samples (Kuik et al., 1993).

1.7.3.1. Enrichment Factors

Enrichment factors (EF) provide qualitative information on the natural and anthropogenic components in the lichens. To better understand the complex data sets, EFs were calculated for all of the elements according to the following equation (Puckett and Finegan, 1980). Enrichment factor of an element is the ratio of the concentrations of the test element to the reference element in the sample divided by the same ratio in reference material (e.g. rock, soil, sea water).

$$EF= (C_x/C_R)_{lichen}/C_x/C_R)_{reference}$$

Where, C_x is the concentration of the element of interest in the sample and in the reference and reference materials and C_R is the concentration of the reference element in the sample and reference materials.

Aluminum and sodium are frequently used as reference elements for calculating crustal and seawater enrichment factors, respectively. The reference element in crustal enrichment factor calculations should be a typical non-volatile lithophile element like Al, Fe that has abundance in crustal material. It should not have any source other than crustal material and should be accurately measured with available analytical techniques. Although Al satisfies all of these criteria, other elements such as Ti, Fe and Sc are also used in crustal enrichment factor calculations. The crustal concentration for both the element and aluminum are obtained from standard geochemical reference tables (Taylor, 1972).

If the only source of an element is crustal material, the EF for that element should be unity. However, due to natural variations in the compositions of Earth's crust, the enrichment factors should exceed 10 to indicate the influence of an additional source. Elements whose EF values are between 10 and 100 are called moderately enriched elements. These elements do have noncrustal sources, but a significant fraction of their observed concentrations still have an origin from soil. The elements having EF values higher than 100 are considered to be highly (anamolously) enriched elements and have the contributing sources to the atmosphere different than the earth crust.

1.7.3.2. Factor Analysis

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

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

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

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

Where $\bar{x}_j$ and σ_j are the mean and standard deviation of element j, respectively.

Concentrations of all elements in each sample are normalized. This normalization gives each element equal weight in the factor analysis regardless of its average concentration. This normalized concentration, z_{ji} has a mean value of 0 and a variance of 1.

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

$$z_{ji} = (\sum_{k=1}^{m} a_{jk} f_{ki}) + d_j u_{ji}$$

The coefficients a_{jk}, forming an n x m matrix A, are often referred to as the loadings of the factors. They represent the correlation of element j with factor k, and thus they are indicative for the relative elemental composition (source profile) of the factor k. The components f_{ki}, forming an m x N matrix F, symbolize the contribution of factor k to sample i. The product $d_j u_{ji}$ represents the residual error for element j in sample i, which is not accounted for by the m common factors. The total variance of each element j can be split into a fraction, which is accounted for by the factor model, and unexplained fraction given by the uniqueness d^2_j. This unexplained variance is reflected in observed variations on a local scale (i.e. multiple measurements within a single sampling site). Hence the uniqueness is also referred to as local variance. The coefficients u_{ji} indicate how sample i contribute to the uniqueness of element j.(Kuik et al., 1993).

In factor analysis the number of factors m is decided by the eigenvalue cutoff. As the cutoff value decreases m is increases. One of the serious drawback in factor analysis is the selection of this cutoff value which in turn governs the value of m. On the selection of the cutoff value, there is no universally applicable method for establishing m and it is necessary to discard a number of small eigenvalues. Generally, eigenvectors with eigenvalues greater than 1 are more signal than noise and should be kept in the model. Those eigenvectors with eigenvalues less than 0.5 have more than twice and as much noise as signal and should be eliminated from the model. For eigenvalues between 0.5 and 1, the associated eigenvectors are more noise than signal, but they may be important enough to kept in the model. The total variance explained by the factors is also important in the reduction of the number of factors. At least a minimum of 70% of the total variance is tried to be explained by the factors. The unrotated components of the factor analysis are often not readily interpretable since they attempt to explain all data set. Physical interpretation of components is easiest if a few elements have large loadings and the loadings of the remaining elements are near zero. Factor analysis seldom has this form and several transformations of FA's are in use to improve their ease of interpretation. The most widely used of these transformations is the Varimax (maximization of variation) rotation (Schaug et al., 1990). The short expression of these ideal structure criteria is the minimization of medium factor loadings to the benefit of near zero and high factor loadings. After rotation the descending order of eigenvalues of factors may be revoked (Einax et al., 1997). The communality is introduced as a mathematical measure of common element variance. The communality is the part of the variance of one element, which is described by the common factor solution in FA. High communalities mean that this element variance is highly explained by the factor solution. Low communalities for one element detect either a specific variance or high random error. The sum of the squared factor loadings of one element in every factor is equal to the communality of this element. The sum of the communalities of all elements is equal to sum of the eigenvalues of factors, which contribute to the common factor solution. The sum of squared factor loadings of one factor is equal to its eigenvalue.

The factor scores are correlated with their respective pollution sources having an impact on the site (higher factor score implies a higher pollution impact by the pollution source in the study area). Each factor has its percent variance and it shows the strength of that factor. The sum of the percent variance of each factor gives total variance explained by the number of factors chosen.

By definition, multivariate analysis requires several observations, the more the better. If there are too few samples, the results of a multivariate model are not likely to be reliable. Experience has shown that this number should be at least 30 and preferably 60 (Güllü, 1996) or some scientists claim that this number should be 100 or more (Henry et al., 1984) to obtain reliable results.

1.7.3.2.1. Factor Analysis-Absolute Factor Score (FA-AFS) Method

Factor Analysis-Absolute Factor Score (FA-AFS) is a method, which allows the estimation of source particle characteristics for an unconventional source category. This approach first developed by Thurston and Spengler (1985). In their work, Principal Component Analysis (PCA) was applied to fine and coarse elemental concentration data collected in Watertown, Massachusetts over a two-year period. Based upon these PCA results, fine and coarse particle pollution sources affecting the monitoring site were identified. The particle mass contribution of each identified source was the estimated using PCA-Absolute Principal Component Scores (APCS) technique: the technique was based on the computation of APCS's for each sample, followed by the regression of sample particle mass concentrations on these APCS's to derive each identified sources's estimated mass contribution. By using Factor Analysis instead of PCA was then used by Tuncel et al., (1985). Errors in analytical process and feature-specific variances can be separated from the common reduced solution by means of estimation of the communalities. This shows the advantage of the application of FA rather than PCA for such data structures. Because the total variance of the data sets has been investigated by PCA, it is difficult to separate specific factors from common factors (Einax et al., 1997). By performing a multiple linear regression of the concentration of each element vs. the absolute scores of the factors, Tuncel et al., (1985) determined the regional sulfate component at Shenandoah Valley.

In this method, after the Varimax rotated Factor Analysis has been applied to the data set, the factor scores (f_{ki}) were calculated.

The absolute zero factor score (FS) has been estimated for each factor score by separately scoring an extra sampling site wherein all elemental concentrations are zero. This accomplished by deriving the z-score for absolute zero concentrations.

$$(z_0)_i = \frac{0-\bar{x}_j}{\sigma_i} = -\frac{\bar{x}_j}{\sigma_i}$$

and then calculating the rotated absolute zero FS scores, F_o, for each of m components,

$$F_{om} = \sum_{i=1}^{n} A_{mi} (z_o)_i$$

These estimates of the FS scores for each component at absolute zero are then used to estimate Absolute Factor Scores (AFS) for each component on each sampling site as follows

$$[AFS]_{mxj} = [F]_{mxj} - [F_o]_{mxj}$$

where the j columns of $[F_o]$ are all identical equal to the values calculated in above equation for extra sampling site. It can be proved that the calculation of [AFS] gives the exact score, which would be achieved if the original scoring had been executed using unnormalized data.

Then the concentration of each element is regressed on these AFS values obtained for each factor in each sampling site. The result of analysis gives estimates of the coefficients, which convert the AFS into pollutant source contributions (in mg kg^{-1}) of each element for each sampling site as follows

$$M_{ik} = \zeta_{io} + \sum_{j=1}^{m} \zeta_{ij} AFS_{ijk}$$

where M_{ik} is the concentration of element i at the sampling site k; AFS_{ijk} is AFS value of element i for factor j for sample k; ζ_{ij} is the coefficient obtained for element i and factor j and ζ_{io} is the contribution made by sources unaccounted for in the FA. The value of $\zeta_{ij} AFS_{ijk}$ gives the contribution of factor j to the concentration of an element i in sample k.

1.7.4 Power Plants

The most important energy sources in Turkey are lignite and hydrology. Hence, most of the large-scale coal-fired power plants (13 out of 18) use local lignites with low calorific value and high ash content (approximately 35 %) (Hamzaoğlu, 1998). The use of coal for electricity generation has resulted in important environmental problems since SO_x, NO_x and suspended particulate matter (SPM) emissions from low stacks result in high levels of pollutants close to plants, local air pollution problems and hazardous high SO_2 levels. Later power plants were built outside urban areas. Stack height increased up to 600 m in order to prevent regional acid pollution problems.

The use of lignite with high ash content (typical for coal burned in Turkish power plants) has potential impacts on environment. For instance, stack emissions may cause acidification of the receiving bodies (i.e. soil, surface waters, vegetation). On the other hand, ash deposited in dump areas may leach heavy metals including Se, As, Pb, Zn and Ni which can be toxic for soils as well as surface ground water resources. In the study of Hamzaoğlu (1998), from the distribution concentrations of elements Cd, Zn, Pb, Cr and Ni, it was concluded that the region within the vicinity of the plant and ash disposal site was impacted up to 5-6 km away from the sources. As a result of separate runs of stacks and ash disposal site carried out by Industrial Short Complex Short Term (ISCST) model, stacks have more contributions in both ground level concentrations and deposition values of SPM. Biomonitoring studies concerning power plants were well documented in section 2.1.2.

1.7.4.1. Dispersion Modeling

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

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

Even if the results obtained from dispersion models were accurate, the source emission inventories upon which they rely are not (Gordon, 1988). The deposition of dust particles predicted by the models is not reliable since the size distribution is the major factor in deposition and it can only be known by sampling.

The reliability of the results obtained from models is dependent on the accuracy of input data. For instance, it is generally not possible to find a meteorological station within the study area and the meteorological data are taken from 20-30 km away whose data representation for the study area is doubtful. Although the real values of most parameters are not known, they are used in the model (Hamzaoğlu, 1998). Within this intention, the results of the dispersion models can be compared with the concentration of elements in lichens at the sampling site quantitatively. The dispersion model used in this study was Industrial Source Complex-Short Term (ISCST) computer model is developed by the USEPA and frequently used for the air quality studies. The basic concept of the ISCST model is similar to that of the steady state, straight-line Gaussian plume equation. The model combines various dispersion model algorithms for pollutant sources such as stack and fugitive emissions. The details of the model formulations are given in the ISCST Manual (EPA, 1992a).

The four input sets used by the model are:

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

1. Meteorological data: This data set consists of hourly wind speed and direction, ambient air temperature, Pasquill stability class, mixing height, wind profile exponent and potential vertical temperature gradient (optional) values (EPA, 1992b). Basic meteorological parameters are usually obtained from meteorological stations preferably at the study area and secondary parameters, such as stability classes, mixing heights are calculated by pre-processors.
2. Source data: Deposition and concentration can be evaluated for more than 200 pollution sources. Variety of pollutants including sulfur dioxide (SO_2), nitrogen oxides (NO_x), suspended particulate matter (SPM) and carbon

multiple sources, which are categorized as point, volume and area sources. These different source types are explained below:

Releases from stack and isolated vents are referred as point sources. The input data for the point source algorithms include point emission rate, release height above ground, stack gas exit velocity, stack gas exit temperature and stack inside diameter.

Releases from a variety of industrial sources, like building roof monitors, multiple vents and conveyor bents are categorized as volume sources and the input data needed for this algorithm are volume sources and the input data needed for this algorithm are volume emission rate, release height (from the center of the volume) above ground and initial horizontal and vertical dispersion parameters (σ_y and σ_z values).

Releases from storage piles, ash dumping area, lagoons as well as toxic air release sites are area sources. The input data for this category are area emission rate, release height above ground and side length of the square source area. The ISCST accepts only square areas whose sides are oriented north-south and east-west. In order to model irregularly shaped area, the area must be subdivided into smaller square areas (EPA, 1992b)

3. Receptor data: The ISCST model calculates ground level concentration and deposition values at the corner points of a user defined grid system. The coordinates and elevation of the grid corners within the study area are the receptor points.
4. Control data: Program control parameters can be selected by the user among 30 different alternatives. Prediction of either GLC or deposition rates, definition of discrete points other than receptor locations and calculation of concentration values concerning different time intervals are some of the control parameters.

1.7.4.1.1. Topography and Meteorology of the Power Plant Regions

The study area selected for ISCST was defined as a square having the power plant at its center with sides having approximately 10 km distance to the center in all directions. The 3-digitized topographical map of the Yatağan power plant (YPP) is shown in Figure 1.7. The topography of the region is generally steep but there are some flatter places. There are very high altitudes at western side right after the YPP and at eastern side of YPP. In the figure, the solid lines show the roads. The samples were taken from in between YPP and Turgut town.

The 3-digitized topographical map of the Soma power plant (SPP) is shown in Figure 1.8. Compared with Yatağan region it is flatter. However there are high elevations on the south-west and north-east of the SPP. There is one highest point on close proximity of SPP on south-east direction. The solid lines in the figure show the roads and the samples were picked up in between SPP and Evciler town.

Dispersion of the pollutants emitted from a given source is influenced by meteorological conditions. Thus, reliability of meteorological data has a great importance for modeling studies. There is one nearest meteorological station in the Yatağan region; namely, Yatağan meteorological station. This station is approximately 19 km south-southeast of the power plant. This meteorological station can be accepted to be representative of the regional meteorology even though there are some topographical obstacles in between the meteorology station and the power plant. However they have very close altitudes; YPP is at 337 m altitude and meteorology station is at 365 m altitude. For SPP the nearest meteorology station is located in Akhisar, which is approximately 35 km on the south-east of the SPP. The altitude of SPP is 150 m and that of the Akhisar meteorology station is 93 m. They have close altitudes.

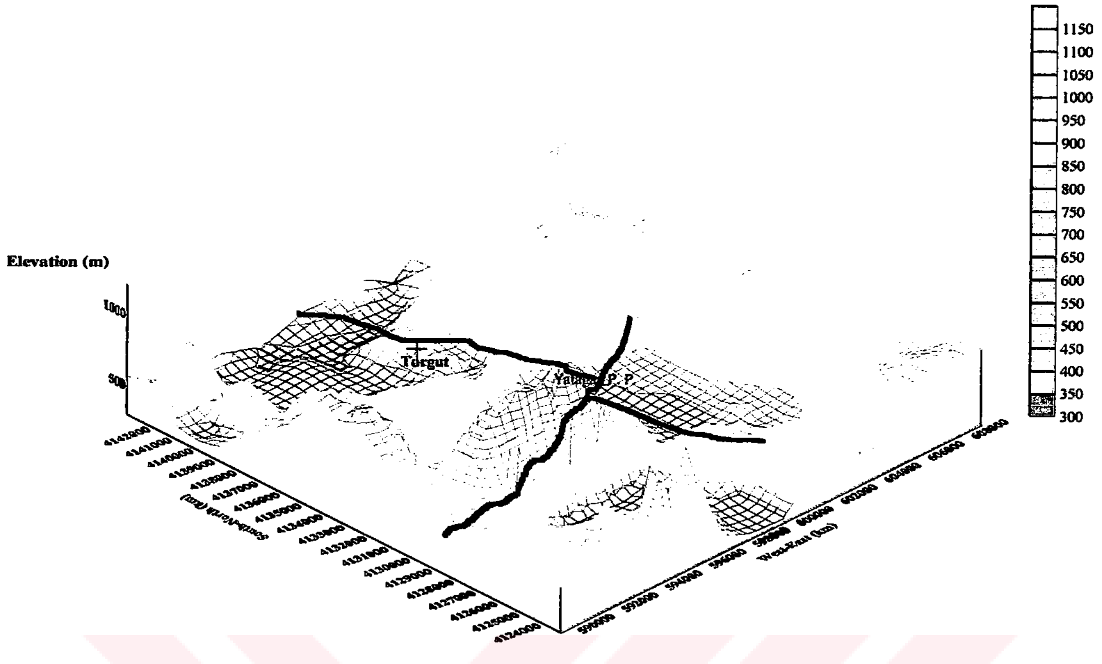


Figure 1.7. 3-D Digitized topography of the Yatağan power plant region

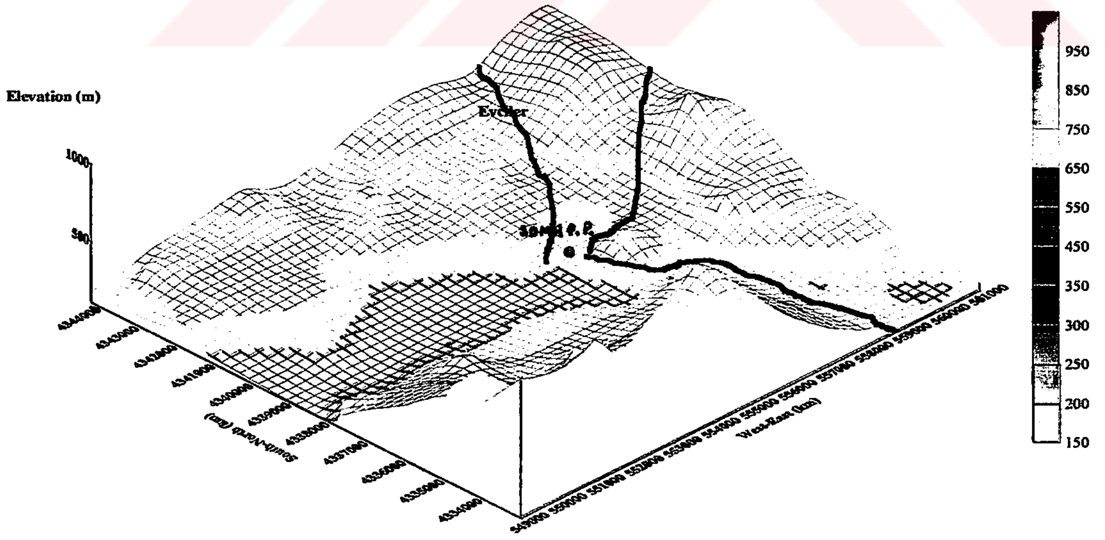


Figure 1.8. 3-D Digitized topography of the Soma power plant region

Hourly data recorded in 1998 were used in order to obtain wind roses. The wind rose for Yatağan meteorological station is represented in Figure 1.9. The wind rose of this station based on long term average data (between 1950-1990) is also given in Figure 1.10. As can be seen from the figures, when compared with the long-term averages of the same station, 1998 data were found to be typical for the region with dominating northern directions over southern directions. Within the 23 years of observation, the maximum and minimum recorded temperatures were recorded as 42 ^{0}C and –8.6 ^{0}C. Average annual wind speed observed in the region is 1.8 m s^{-1} for both long term records and 1998 data of Yatağan meteorological station. According to the 1998 data, calm conditions are observed 43% of the time in the region. This implies that pollutants may not be well dispersed in the region.

The hourly 1998 wind rose and the long term (1929-1990) wind rose of Akhisar meteorological station are given in Figure 1.11 and Figure 1.12, respectively. The same conclusion can be drawn for this station. The 1998 data constitute typical set for the station. The long term data also dominating in northerly directions is given in Figure 1.12. Within 54 years of observation, the maximum and minimum recorded temperatures were recorded as 44.6 ^{0}C and –13.6 ^{0}C. Average annual wind speed observed in the region is 2.3 m s^{-1} for long term records and 2.2 m s^{-1} for 1998 data of Akhisar meteorological station. The 1998 data, calm conditions are observed 42% of the time in the region. This implies that pollutants may not be well dispersed in the region.

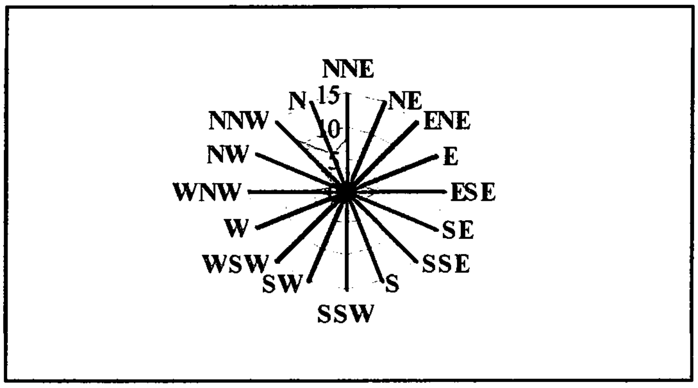


Figure 1.9. Wind rose of YPP in 1998

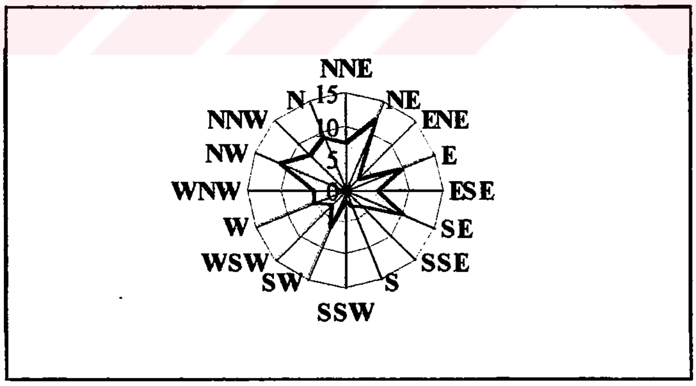


Figure 1.10. Wind rose of YPP between years 1950-1990

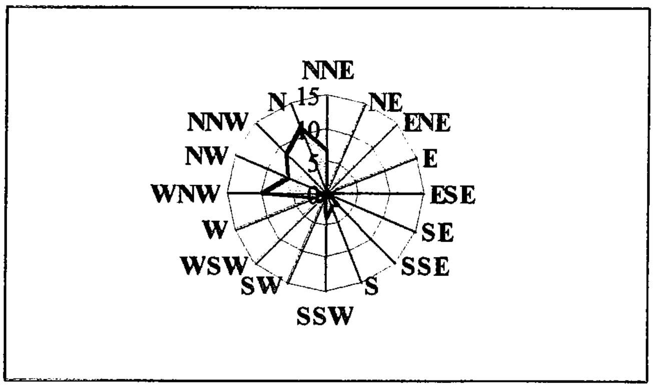


Figure 1.11. Wind rose of SPP in 1998

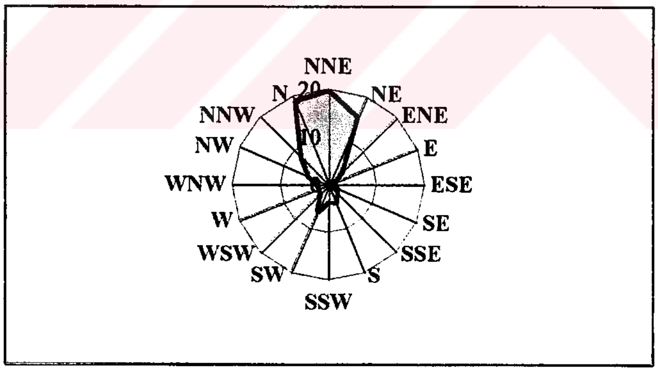


Figure 1.12. Wind rose of SPP between years 1929-1990

1.7.4.1.2. Preparation of the Model Input Files

Meteorological data: First input files are prepared from meteorological data, which were obtained from Turkish General Directorate of State Meteorological Organization (DMİ) for meteorological station at Yatağan. However for Soma Power plant the Akhisar meteorological station was the nearest one. The coordinates and altitudes of the meteorological stations are also needed. This basic meteorological data set consists of hourly wind speed and direction, ambient air temperature, pressure, cloudiness and snow cover of year 1998. These files were converted into suitable forms using special programs in order to use these files in the ISCST program. The hourly mixing height variations and the Pasquill stability classes were calculated by means of the REG-308 meteorological pre-processor.

Source data: The source parameters required by ISCST2 include location, elevation, diameter and pollutant emission rate of source, exit velocity, exit temperature of exhaust gas and stack height for each stack separately. The general characteristics of the sources at the exit of each stack for Yatağan power plant and Soma power plant are given in Table 1.3 and Table 1.4, respectively. Note that there exists one or more electrostatic precipitator (ESP) for each unit with an efficiency of about 99.2% (TEAŞ (Turkish Electricity Production Corporation), 1999).

Receptor data: Topography of the region was determined in a square with dimensions of 20 x 20 km taking power plant as its center point. The altitude of region with 1 km distances were entered to the computer which read from 1/25000 scaled maps which were obtained from Turkish General Directorate of Cartography. The altitude data entered with coordinates. The coordinates and elevation of the grid corners within the study area are the receptor points. In order form grid data Surfer program was used. In this step, the coordinates are divided into maximum 9 chosen spans. According to these spans, the receptor points are constructed.

Table 1.3. General characteristics of the stacks of Yatağan power plant*

Parameter	Unit 1	Unit 2	Unit 3
Capacity (MW)	210	210	210
Start of operation	1982	1983	1984
Coal Utilization (t day^{-1})	6000	6000	6000
Stack exit SPM emission (g s^{-1})	244	244	244
Stack exit temperature (^{o}C)	160	160	160
Stack exit velocity (m s^{-1})	16	16	16
Stack inside diameter (m)	6.4	6.4	6.4
Stack height (m)	130	130	130
Efficiency (%)	64.6	64.6	64.6

* (TEAŞ, 1999); (Yatağan Thermal Central Managing Directorate (YTSİ), 2000)

Table 1.4. General characteristics of the stacks of Soma power plant*

Parameter	Soma (1-2)	Soma(3-4)	Soma (5-6)	Soma (7-8)
Capacity (MW)	165 x 2	165 x 2	165 x 2	22.5 x 2
Start of operation	1981	1985	1993	1953
Coal Utilization (t day^{-1})	6000	6000	6000	6000
Stack exit SPM (g s^{-1})	1263	370	23.2	266
Stack exit temperature (^{o}C)	178	150	133	148
Stack exit velocity (m s^{-1})	16.6	16.4	17.2	23
Stack inside diameter (m)	6.15	6.15	7.10	3.60
Stack height (m)	150	150	275	52
Efficiency (%)	71.6	71.6	71.6	110.3

* (TEAŞ, 1999); (Soma Electricity Generation and Trade Co General Management (SEAŞ), 2000); (Muezzinoğlu, 1999).

The size distribution is a crucial component, because settling velocity and surface reflection depends on the size of particles. In order to obtain the correct size distribution, sieve analysis should be applied to ash samples taken from the area. This data were gathered from the analysis of fly ash emitted from Yatağan power plant, which was studied by Tokyay and Erdoğdu (1998) in the structure of TÇMB (The Union of Turkish Cement Members). The mass fraction between certain ranges of particle diameters was obtained which was determined by using laser particle dispersion technique. Then the mass-mean diameter can be calculated using the below equation.

$$d=[0.25 \times (d_l^3 + d_l^2 \times d_2 + d_l \times d_2^2 + d_2^3)]^{1/3}$$

where

d_l: lower bound of the particle-size category

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

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

$$V_s = \frac{2\rho g r^2}{9\mu}$$

where;

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

ρ : particle density (g cm^{-3})

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

r : particle radius (cm) or mass mean diameter

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

According to the calculated velocities, reflection coefficients were found from the user's guide (EPA, 1992a). The reflection coefficient is a function of settling velocity and roughness of the ground surface. A reflection coefficient 0.0 means that the plume material for that settling category is completely removed when it reaches the ground surface and a reflection coefficient 1.0 means that all of the plume material is reflected from the surface without any deposition (EPA, 1992b). The calculated values for Yatağan Power plant and Soma (1-4) units, Soma (5-6) units and Soma (7-8) units are given in Table 1.5.

Table 1.5. Characteristics of particles used in deposition modeling

Particle size (μm)	Mass mean diameter (μm)	Mass fraction	Settling velocity (m s^{-1})	Reflection coefficient
		Yatağan		
0-30	18.9	0.35	0.0085	0.81
30-60	46.6	0.20	0.0517	0.61
60-80	70.5	0.10	0.118	0.45
80-120	101.3	0.35	0.244	0.15
		Soma (1-4)		
0-10	6.3	0.50	0.00094	0.90
10-30	21.5	0.28	0.011	0.78
30-60	46.6	0.12	0.0517	0.61
60-110	87.4	0.10	0.182	0.28
		Soma (5-6)		
0-10	6.3	0.34	0.00094	0.90
10-30	21.5	0.29	0.011	0.78
30-60	46.6	0.17	0.0517	0.61
60-110	87.4	0.20	0.182	0.28
		Soma (7-8)		
0-10	6.3	0.40	0.00094	0.90
10-30	21.5	0.27	0.011	0.78
30-60	46.6	0.11	0.0517	0.61
60-110	87.4	0.22	0.182	0.28

1.8. Aims of This Research

The goals of the study can be summarized as follows:

1. to set up the first biomonitoring network in western part (mostly Aegean Region) of Turkey by sampling lichens. The many European countries have started to set up the biomonitoring networks since 1970's either by using mosses or lichens. This region was selected because of having opportunity to study the effects of various pollution sources. The lichens were found to be suitable biomonitor organisms for this study. Because they are more commonly found in the region compared to mosses. Xanthoria parietina was decided to be best lichen species for this study and future study considering common occurrence, altitude, meteorological conditions and tolerance limits.

2. to compare the accumulation capacities of two lichen species in order to investigate the interchangeability of two different lichen species for future use. Another most common lichen species Parmelia tiliacea were collected in some of the same grids together with Xanthoria parietina. They are evaluated by using scatter plots, ANOVA or paired t-test.

3. to compare the results of lichens with the results of bulk deposition samples in order to obtain a quantitative knowledge from the lichens. Three lichen species (Xanthoria parietina, Parmelia tiliacea, Evernia prunastri) and tree bark are also compared according to their accumulation capacities of total deposition for elements and ions.

4. to study local variation.

5. to indicate the location of the important pollution sources and their impact areas. For this purpose distribution maps of the concentrations of all elements are prepared. These maps are very useful in order to see the location of pollution sources and their impact areas in the region.

6. qualitative and quantitative identification of major source categories affecting the region. For this purpose several statistics are applied to data set such as enrichment factor, factor analysis and absolute factor score-multiple linear regression.

7. to compare the results of lichen with the results of models. Dispersion model will be applied to Yatağan and Soma power plant regions. The deposition results will be compared with the concentrations of elements that are known tracers of coal fired power plants quantitatively.

CHAPTER 2

LITERATURE SURVEY (LICHEN AND MOSS)

2.1. Local Scale Pollution

Many kind of studies focusing on pollution from urban sites, rural sites, power plants, smelters, geothermal and/or volcanic areas are compiled under several headings in order to clarify what has been done in the literature concerning with especially lichens and then mosses.

2.1.1. Pollution Around Urban/Industrial Areas

There are many investigations using lichens and mosses in order to monitor air quality that have been carried out around known pollution sources such as coal-fired power plants, steel works or other industrial and urban centers.

The fruticose lichen Ramalina duriaei (De Not.) Jatta was used in order to estimate the air quality in areas of both urban and rural of Israel (Fuchs and Garty, 1983). Large quantities of sulfur were found in R. Duriaei transplanted to sites around Hadera, after 1 year of exposure. Chlorine and bromine were found in significant amounts in the sites along the seashore. Chlorine seemed to originate from the marine aerosol, while the origin of the high amounts of bromine was probably related to the brominated gasoline used by the cars on the highways, which are parallel to the seacoast. A statistical cluster analysis was performed on the amounts of Ca, P, K, Br, Cl, S, Ti, Li and Sr and on the concentration of six additional elements: Zn, Ni, Cu, Cr, Pb and Cd, which were previously determined from the same biological material. They obtained clusters of locations with similar overall levels of the elements. This clustering was based on the data collected prior to the operation of the power station and can be later used as a baseline for determining the effects of the pollutants emitted from the power station.

As part of an epidemiology project dealing with air pollution, the metal pollution emanating from the town's steel factory were monitored by using mosses in central Scotland (Yule and Lloyd, 1984). As in other surveys, Hypnum proved to be most useful in collecting at least 9 metals from the atmosphere. Some values, such as Fe, were significantly lower in Armadale, than those levels found in a similar survey sited around the steelworks in Consett, England. However other metals such as Cu were present in much higher concentrations. All metals measured (apart from Pb values, which showed the influence of traffic routes) revealed an increasing concentration from the periphery of the town towards the vicinity of Armadale's steel foundry. Other study conducted in this area aimed to ascertain the appropriate length of exposure for the transplanted moss bags, lichen Hypogymnia physodes and an exposure of 2 months was selected for the main monitoring survey (Gailey and Lloyd, 1986a).

The two lichen species were transplanted to 12 stations in the vicinity of the steelworks in Denmark (Pilegaard, 1979). The transplants were exposed for 7 months. Bulk precipitation was collected simultaneously. The concentrations of the metals Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn were analyzed. The amounts of accumulated metals in the transplants were linearly correlated with fallout from the atmosphere. The metal concentrations in the transplants, as well as the bulk precipitation, followed decreasing power curve when the distance to the steelworks was increased. The old oil-fired open-hearth furnaces at the steelworks had been shut down and steel was produced entirely by electric-arc furnaces. For that reason it was decided to repeat the pollution monitoring surveys in 1982 in exactly the same way as in 1977 in order to see whether the pollution had increased or decreased (Vestergaard et al., 1986). Theoretically, the new electric-arc furnace emits larger amounts of suspended particles with a different elemental composition but, on the other hand, pollution was abated by means of bagfilters. Previously, no filters were used. The results showed that heavy metal pollution from the steelworks was severe and that it followed a decreasing power curve when the distance to the steelworks was increased. However, a reduction in the deposition of heavy metals close to the steelworks has been observed, pointing to the conclusion that the change in situation has lead to changes in the emission. At the sampling stations with the highest deposition levels measured in bulk precipitation the corresponding concentrations in the lichens were relatively lower indicating a change in particle size distribution. Within each station there was a direct proportionality of metal concentrations in lichens and atmospheric fallout measured in bulk precipitation.

The effect of atmospheric Pb pollution on moss nematofauna was studied in an industrial area in the Po river plain (Northern Italy). Moss samples, affected by Pb pollution were taken monthly for a year from eight stations. It was shown that the nematode community proved to be sensitive to Pb pollution (Zullini and Peretti, 1986).

In the study of Thompson et al. (1987) and Mueller et al. (1987) in Louisiana there was a decrease in metal concentrations with distance from the industrial/urban corridor. In the former it was found out that the highest concentrations of elements (Th, Cs, Se, Hg, Cr, Ir, Ce, Sc, Rb, Fe, Zn, Co, Ta, Eu, K and Sb) in lichens were observed within a 10.8-km radius of the industrial/urban zone. In the latter, metals V, Mn and Al concentrations were found to decrease exponentially with distance outward from the industrial corridor. The major industries included were an Al plant, two refineries and five chemical plants mostly related to plastics production.

Total S concentrations in Scots pine needles and the lichen Hypogymnia physodes collected from the vicinity of an oil refinery in southern Finland and steel works in northern Finland were used (Manninen et al., 1991). Total S concentration in both needles and lichens were higher in the vicinity of the oil refinery due to the greater influence of long range transport S deposition in southern Finland. The two industrial plants had approximately equal SO_2 emissions in 1985.

Effects of emissions from a new aluminum works, on previously unpolluted assemblages of corticolous lichens, were described in the study of Perkins and Millar (1987a) in Great Britain. Injury symptoms included chlorosis, red colorations, necrosis and weakening of attachment of thalli to the bark substratum, resulting in reductions in % cover. Before emissions commenced in 1970, lichens contained <19 μg F^- g^{-1} dry weight. Where concentrations in annually monitored samples of Ramalina reached > 100 μg F^- g^{-1} dry weight, within 4 km downwind of the works, severe injury occurred with >75 % losses of cover of some species. At increasing distances injury and F^- concentrations decreased.

Concentrations of S, N and seven metals were reported for the lichen from three monitoring stations in Maryland and Virginia in USA (Lawrey, 1993). Concentrations of Cd, Cr, Ni, Zn and Pb were consistently highest at Plummers Island (Maryland) and lowest at Stony Man Mountains (Virginia); concentrations of the other four elements (N, S, Al and Cu) were also consistently higher at both places. Recent collections, in 1988 and 1992, revealed marked reductions in the concentration of all nine elements except Al at all three stations, providing limited, but encouraging, signs of improved air quality in the region.

The results of long term study performed (data of 1978 and 1993) in central Italy using epiphytic lichens both as indicators and monitors were presented (Loppi and Dominicis, 1996). The results of the survey indicated that air quality in the study area has remained relatively unchanged in the 15-year period of the study. However, Montieri is located in an area without any substantial local source of air pollution and is not a recipient of contaminants arriving by long range atmospheric transport. The only negative point regarded Cs-137, which doubled after the Chernobyl accident to levels that are nevertheless low.

Samples of Evernia prunastri collected in a mountainous zone, were exposed in urban and highly industrialized areas in order to monitor the atmospheric pollution in Italy (Caniglia et al., 1994). Amounts of Cr, Mn, Fe, Ni, Cu, Zn and Pb were determined by EDXRF. An increase in metal concentrations was noted on all sites with time exposition increased, but the highest final amounts were observed on those thalli mounted near steel works.

2.1.2. Pollution Around Power Plants

Lichens or transplanted lichens were also widely used to monitor the pollution caused by coal-fired power stations. In one of the earliest publications, the samples of two different species of lichens were analyzed to determine the concentrations of trace elements near a coal-fired power plant in Washington, D. C. in USA (Ölmez et al., 1985). The relation between atmospheric concentrations of elements borne by particles and composition patterns in lichens were examined by calculating enrichment factors. Lichens collected preferentially larger particles, which were probably deposited by impaction and/or dry deposition, but not rain or filtration. No significant differences in concentrations were observed among lichens collected at various distances ranging from 1.6 to 20 km from the plant, suggesting that the effects of plume touchdown were small compared with normal ambient concentrations of particles.

The lichen Ramalina duriaei was transplanted to 22 biomonitoring sites for 1 year (1981-1982) in Israel (Garty, 1987). The amounts of Ni, Cr, Cu, Zn, Pb, Mn and Fe were measured at the end of the transplantation period. The increase in amounts of some of the metals in the 1981-1982 period. Lead, Ni and Cr reflected the increase in the total number of motor vehicles between the two periods within the study area. The decrease of Zn in the lichen after the second period reflected a decrease in the use of Zn as a constituent of foliar nutrients in agriculture used for crop spraying. The increase of Cr and Ni in the transplanted lichen after the 1981-1982 period probably also reflected, apart from vehicle pollution, a certain emission from the 250 m high stacks of a new coal-fired electricity generating power station. The second research which was conducted in the same area, the elements Ni, Cr, Cu and Zn were again determined in the lichen exposed to environmental influences for a period of 1 year (Garty and Fuchs, 1982). The concentrations of metals were compared with concentrations of the same metals measured in transplanted lichen to the study area prior to the operation of the power plant. The results showed that after the 1983-1984 period, the regional concentrations of Cr in the transplanted lichen thalli were found to be higher than in the lichen thalli transplanted to the same sites during the period February 1979-March 1980, prior to the operation of the coal-fired power plant. It was probably connected with the operation of the coal-fired power plant.

The epiphytic lichen was collected in the neighborhood of a Portuguese coal-fired power station as monitor for heavy metal air pollution (Freitas, 1994). A study of the metal contents variability along 1991 and 1992 was performed. The heavy metals Ag, As, Br, Co, Cr, Fe, Hg, Sb, Se, and Zn were determined. The concentrations of found in 1991 and 1992 showed an accumulating process of Co and Fe (~5%/mo) and of Cr and Sb (~7%/mo). Low accumulation was observed for Ag, Se and Zn (~2%/mo) and no concentration variation was observed for As, Br and Hg. It was concluded that the metal accumulation observed was the result of the nearby ash and coal deposits.

Vanadium contamination was monitored in the vicinity of three oil-fired power plants in eastern Canada (Juichang et al., 1995). Vanadium is the most prominent metal in most crude oils. During crude oil refining, virtually all vanadium remains in the heavier oil fractions, which are marketed as residual fuel oils. These residual oils are used primarily for industrial purposes, especially in oil-fired power plants, but also for the production of industrial steam, for the central production of space heating and as ship fuel. The vanadium concentrations in lichens and tree foliage decreased exponentially with increasing distance from the power plants. Substantially larger concentrations of vanadium occurred in lichen tissues than in tree foliage. Lichens clearly are more suitable for biomonitoring environmental contamination with vanadium near oil-fired power plants.

Levels of 12 trace elements were measured in samples of the moss Hypnum cupressiforme Hedw. and in soil collected in the surroundings of oil-fired power plant in Northern Italy (Genoni et al., 2000). Metal bioaccumulation in moss was estimated after soil correction in order to obtain deposition patterns and individuate potentially toxic metals emitted from the plant. Vanadium and Ni, occurring together in fuel oil, showed highest bioaccumulation values near the stacks. Mean contamination of the study area for these elements is 5.5 (V) and 3.3 (Ni) times the background levels of the reference site. Other elements showed only limited alterations of bioaccumulation values, in relation to agricultural and industrial activity in the study area.

2.1.3. Pollution in Volcanic and Geothermal Areas

Volcanic emissions have now been well established as important source of environmental Hg (Barghigiani et al., 1988; Bargagli et al., 1989). These studies confirmed and extended previously reported unique features of lichen-soil source distribution patterns for Hg relative to those from other metals. On Mt. Amiata lichens accumulated Hg from degassing nearby soils whereas Zn was probably wind-carried from remote sources. The Fe/Al and Fe/Mn ratios reflected the accumulation of soil particles within the thallus; the other metals appeared to be mainly from atmospheric depositions. Evidence was presented, however, for other distinctive source relationships as, for example, those expressed in element atomic ratios (e.g. Fe/Al). It is also demonstrated that widely separated populations (Mt. Amiata vs. Mt. Etna) of the same lichen can display biogeochemical differences best explained on an eco-physiological basis including selectivity both in accumulation and for Hg reemission.

Two common and abundant species of epiphytic lichens were collected at six localities in Yellowstone National Park, USA in 1998 and analyzed for 22 chemical elements (Bennett and Wetmore, 1999). They studied in a geothermal area without power plants to determine the natural levels of mercury and other elements. Levels of most elements were comparable with those in other national parks and wilderness areas in the region, except Hg, which was unusually high. The most likely sources of this element were the geothermal features, which are known emitters of Hg. Multivariate analyses revealed strong positive associations of Hg with S, and negative associations with soil elements, providing strong evidence that the Hg in the lichens was the result of soil degassing of elemental Hg rather that particulate Hg directly from soils.

Fluorides may be emitted from a volcano either as particulate matter, in the form of microscopic salt particles compounds adsorbed on to tephra (volcanic ash), or as a gas phase (Davies and Notcutt, 1988). Measurement of gaseous fluorides is difficult. Samples of lichens were collected from the slopes of Etna Volcano in 1985 and 1987 in order to monitor these gases. Subsequent analysis for fluoride showed levels ranging from 2 to 141 $\mu g\ g^{-1}$, compared with control values of <2 $\mu g\ g^{-1}$. The fluoride accumulation pattern clearly showed that there was a major input from the volcano's plume, with the highest levels on the downwind side; these were attributed to the prevailing winds and to the local topographic influences.

Volcanoes are also trace element emitters. Major and trace element concentrations were determined in two lichen species from the island of Vulcano and all around Mt. Etna (Varrica et al., 2000). In both areas, the average concentrations of Al, Ca, Mg, Fe, Na, K, P and Ti were substantially greater than those of other elements. Several elements (Br, Pb, Sb, Au, Zn and Cu) resulted enriched with respect to the local substrates. The Br and Pb enrichment factors turned out to be the highest among those calculated in both areas. Data indicated that mixing between volcanic and automotive produced particles clearly explained the range of Pb/Br shown by lichen samples. Antimony was also enriched, revealing a geogenic origin at Vulcano and a prevailing anthropic origin at Mt. Etna. Distribution maps of the enrichment factors showed a generalized enrichment of Au and Zn near Mt. Etna, whereas Cu appeared to be enriched prevalently in the NE-SE area. The highest levels of Au and Cu at Vulcano occurred E-SE from the craters, following the prevailing wind direction.

Although geothermal energy was regarded as a clean resource until the 1960's, it is by no means free from causing environmental impact (Loppi and Bargagli, 1996). The environmental hazard due to geothermal emissions has mainly been investigated in terms of mercury, however airborne pollutants such as hydrogen sulfide, ammonia, radon, boron and arsenic are also associated with geothermal exploitation. The epiphytic lichen Parmelia caperata was used systematically to biomonitor trace elements in the geothermal field in Italy. The results showed a very low occurrence of potentially toxic heavy metals such as Cd, Hg and Pb and relatively high values for As, B, Mo and elements associated with soil dust (Al, Co, Cr, Fe, Mn and Ni). Boron was the principal elements of geothermal origin. Arsenic seemed to originate both from power plants and adjacent thermal springs. It was concluded that trace element pollution in the area was low. In another work of Loppi (1996) it was seen that the levels of boron and mercury concentrations in air, soil, mosses, lichens and leaves around Italian geothermal power plants have been shown to decline within about 500 m from emission sources also observed damage to leaves of vascular plants only within the 500 m zone. Thus, the lichen distribution results presented agreed with those other workers. They concluded that there are four zones around geothermal power plants as indicated by lichens, mosses, soil and vascular plants: zone A-high pollution; zone B-moderate pollution; zone C-low pollution; and zone D-negligible pollution.

2.2. Regional Scale Pollution (Geographical Distribution of Elements)

Lichen and mosses have been started to monitor mostly local deposition around point and area emission sources, but their use has been also extended to describe regional deposition in many places of the world.

Lichen transplants of Hypogymnia physodes were used in a high density network of sites for collecting airborne metals from the atmosphere in Armadale a small industrial town in central Scotland (Gailey et al, 1985). The mapping of the concentrations of various metals revealed a gradient of metal values, which decreased outwards from the town's steel foundry. One zone at the northern periphery of Armadale often had metal values, which were greater than those in the second-outermost zone. The finding is of interest because a small cluster of lung disease was also found in that part of the town. While such high levels of metallic pollution had not been expected in that peripheral zone because of its distance from the steel foundry, a wind tunnel experiment had indicated that the topography of Armadale caused the pollution from the foundry to be into that area.

Comparing the different areas of Canada S and Pb were the only elements which showed consistently higher values in lichens from eastern Canada when compared to the Northwest Territories (Zakshek et al., 1986). A sampling grid was 127 x 127 km . The spatial distribution of S and Pb in the lichen from eastern

Canada was described. A regional gradient in lichen S concentrations was evident with the highest concentrations being found in central and north-central Ontario and the lowest in Newfoundland. A regional gradient for Pb was apparent but was not as well defined as that for S. The regional distribution of S illustrated by the lichen agreed with another indirect measurement of S deposition. Lichen S concentrations correlated with measured wet sulfate deposition.

Data from a national survey of trace element atmospheric deposition in Norway comprising 26 elements in 512 moss samples were examined using principal component analysis with a varimax rotation (Schaug et al., 1990). Ten factors explaining 78.4% of the total variance were identified. The three dominant principal components represent long-range atmospheric transport of polluted aerosol to southern Norway (Pb, Sb, As, V, Cd, Se, Zn, Cr, Mo, Ag and Th), soil particles (Sc, Al, Na, Fe and Sm) and contribution from trace element enriched marine aerosols (I, Br, and Se). Furthermore components representing local and regional air pollution phenomena, specific geological components in the soil particle fraction, and factors related to specific uptake mechanisms in the moss are identified and shown as distribution maps.

Lichen samples were collected from 30 stations in the greater area of Baton Rouge, Louisiana and analyzed for Al, Cu, Fe, Zn and Pb content in USA (Walther et al., 1990a). A univariate analysis of the data showed a significant difference between metal concentrations and sampling stations. When the stations were separated into two groups representing those in the industrial and urban zones, a discriminant analysis was over 90% successful in correctly assigning stations based solely on metal concentrations. No significant differences in metal concentration with species could be observed. Average metal concentrations for the two lichen species were used to construct contours and three-dimensional plots of metal distribution across the study area which clearly demonstrated the effects of the industrial zone on airborne metal levels.

Two species of lichen native to southwest Lousiana had been investigated as air pollution monitors (Walther et al., 1990b). The metal concentration data were used to construct contours and three-dimensional plots. These plots showed dramatic changes in airborne metal levels that have taken place recently through both reduced metal concentrations and also through changes in distribution patterns. As the effects of industrial zone decreased and the three dimensional plots of metal levels over geographical area flatten out, other sources of lesser metal emissions might have become apparent. Such a situation was observed for Zn; when the industrial emissions decreased, the distribution of a municipal incinerator to airborne Zn levels became apparent.

Epiphytic lichens were sampled in a Dutch national monitoring survey based on a grid of 10 x 10 km, which was carried out twice within 5 years (Sloof and Wolterbeek, 1991a; Sloof and Wolterbeek, 1991b). The samples were analyzed by INAA. The lichen data sets were presented in plots of geographical concentration patterns. These gave insight possible location of pollution sources. The geographical comparison of the lichen data sets showed changes in the (geographical) concentration patterns with time. For all elements the areas with enhanced concentration classes increased from 1982-1983 to 1986-1987. The most striking change in concentration pattern was found for Cd. The application of factor analysis techniques in interpreting the concentration data yielded the composition of the various pollution components, which may facilitate identification of the associated sources.

In 1992, a monitoring survey has been started on the national scale in Slovenia using the epiphytic lichen Hypogymnia physodes. The primary aim has been to analyze lichens using INAA method to obtain information about the levels of elements in the atmosphere and to identify significant pollution sources (Jeran et al., 1996). Lichen samples were collected 16 x 16 km grids. It has been found that concentrations patterns in lichen yielded 9 factors. The geographical patterns of the contributions of all factors were also shown in the form of the contour maps.

Data for 26 elements from a nationwide survey in Norway using the moss Hylocomium splendens as a biomonitor were used to illustrate the feasibility of this technique for multi-element studies (Steinnes et al., 1992). The samples were collected within an area of 50 x 50 km. Some elements might occur in the moss biomonitor for more than one reason. The feasibility of the moss for monitoring the deposition of a particular element might therefore depend of the pollutant level. This was in particular the case for Zn, which is inevitably present in moss wherever it grows intermixed with higher plants, which is most often the case. For other elements the suitability as an air pollution biomonitor may depend quite critically on the extent of soil contamination of the moss. In such case a typical crustal element such as Al or Sc may provide useful information. The results of distribution maps and statistical analysis indicated that the following source categories to be significant: Long range atmospheric transport of pollutants from other parts of Europe. Local point sources of air pollution within or closely outside Norwegian borders. Natural cycling processes, mainly atmospheric transport from the marine environment. Root uptake in vascular plants from soil and subsequent transfer to mosses by leaching from living or dead plant tissues. Mineral particles mainly windblown dust from local soils. Eight years after the mentioned study, the second study was done in Norway in order to compare the data of different years (Steinnes et al., 1994). The atmospheric deposition of sixteen trace elements, as inferred by their concentration in moss samples collected in 1985 from 500 sites in Norway, was compared with data from a similar survey in 1977. The deposition patterns from the maps of V, Zn, As, Se, Cd, Sb and Pb were also substantially influenced by long range transport from other parts of Europe, but a general decline was evident from 1977 to 1985, most strongly for Pb. For Cr, Fe, Co, Ni and Cu the deposition patterns were largely determined by contribution from point sources within Norway and on the Kola peninsula close to Russian/Norwegian border. The moss data for Br, I and partly Se reflected airborne supply from the marine environment, whereas Al and Sc served as indicators of contributions from soil dust.

In Germany first attempt to determine pollution with metals throughout in country by analyzing moss samples was realized by Markert et al. (1996). Samples were collected at 593 sites and analyzed by ICP-AES and AAS for the elements As, Cd, Cr, Cu, Fe, Ni, Pb, V and Zn. In many cases it was possible to trace the areas affected by known sources of heavy metal emissions in addition to isolated local increases in values and shown as contour maps. The moss monitoring program showed up the highly industrialized and urban locations such as the Ruhr, parts of

Saarland and Baden-Württemberg and large areas of eastern Germany. Lower levels of many elements were found in wide stretches of Lower Saxony and Bavaria. The results largely reflect the pollution patterns found in these areas. On the other hand, expected correlations between the effects of traffic (e.g. Pb) and concentrations in moss could not be demonstrated with certainty.

During the months of July and August 1993 a lichen (Parmelia sulcata Taylor) collection campaign was held in Portugal where samples were obtained from olive tree bark at 228 sites, following a grid of 10 x 10 km along the Atlantic coast and 50 x 50 km in the interior of the country (Freitas et al., 1999). The sample were analyzed by INAA and PIXE techniques. Concentration data patterns for the pollutants As, Cr, Hg, Ni, Pb, S, Sb, Se and V were observed for the whole country surface by making use of an extinction rule of $1/r^3$ when preparing the pollution maps preventing any cut-off distance from being artificially introduced. Some pollution sources were identified: 1) oil-powered plants of the Lisboa-Setubal axis (V, Ni), 2) coal- powered plants in Porto and Sines (S, Se), 3) traffic in the northern area and the Lisbon-Setubal axis (Pb), 4) a chemical industry south of Porto (Hg, As) and 5) soil influence (Cr, Sb). Arsenic and chromium results largely exceed, in a few areas, the concentrations acceptable to plants and in a few spots also Hg, Ni and Pb data.

In Italy the biomonitoring of air in Livorno Province (Tuscany) using lichen (Xanthoria parietina) for both quantitative monitoring of airborne metals and air quality assessment were studied (Scerbo et al., 1999). On the basis of possible sources of metal pollution in the study area, the following elements were analyzed: As, Cd, Cr, Ni, Pb, V, Zn and Hg. The small number of lichen species, the often stunted appearance of the specimens and metal analysis revealed widespread atmospheric pollution in the study area. The results indicated extensive anthropic impact. The highest levels of contamination were recorded for Hg, Cd, Pb and V concentrations. Good agreement was found between bioindication and metal concentrations in lichens. The impact of anthropic activities was particularly due to steelworks and chemical plants, combustion processes related to energy production and vehicle emissions. In addition to air pollution, some natural factors, such as climate, rocky shores or ozone, were assumed to affect lichen occurrence. Comparison with the lake Orta area in northern Italy showed Livorno Province was more contaminated by trace elements. Similar contamination levels were found in another area of Tuscany, probably due to the geological characteristics of that region.

A survey of heavy metal deposition in the mountainous territories of Northern Italy was carried out in 1995-1996 (Gerdol et al., 2000). Moss samples were collected in a dense network of sites (about 3.2 sites/1000 km^2) and the data of metal concentrations in moss tissues were statistically correlated with environmental and climatic factors, as well as with bulk depositions of elements and elemental concentrations in the soil. Three main geographic patterns of metal concentration mosses could be defined: 1) Fe, Ni and Cr, all derived both by soil particulates and anthropogenic emissions connected with ferrous metal manufacturing, were mostly concentrated in Northwestern Italy; 2) Cu and Zn, as typical multi-source elements, showed rather high concentrations with little ranges of variation over the whole area and small peaks reflecting local source points; 3) Cd and Pb reflected long-distance transport and showed highest concentrations in the regions with highest precipitation, especially in the Eastern Alps.

The concentrations of 13 elements in peripheral parts of the epiphytic lichen Xanthoria parietina were measured at 200 stations of Veneto (NE Italy) (Nimis et al., 2000). For each element, two maps are presented, showing, respectively, geographic patterns and deviations from background levels. The results were summarized by a map, showing the joint distribution of elements with concentrations close to Italian backgrounds, and of those deviating from background levels. The results allowed selection of high-risk areas for instrumental monitoring.

2.3. Miscellaneous Studies

2.3.1. Obtaining Baseline Lichen Data (National Parks)

As part of an effort to establish quality baseline data and to monitor trends overtime, there are some works done in national parks. The concentrations of heavy metals (Cd, Co, Cr, Ni, Cu, Pb, Zn, Mn and Fe) and other elements (Mg, Na, K and Ca) were determined in the samples of two mosses from 12 Polish national parks. The significant differences in the concentrations of all heavy metals between particular parks were found. The lowest concentrations of these metals were recorded in the mosses from the national parks in northern Poland, the highest in southern Poland. Significant differences in the heavy metals contents of the mosses between central and peripheral park areas, between green and brown parts of mosses, as well as between moss species were also found (Grodzinska, 1978).

Ten years after the mentioned work above similar study was conducted in 1986 in Poland (Grodzinska et al., 1990). Significant differences were found between particular parks in the concentration of heavy metals and nutrients, the lowest concentration being recorded in the mosses from the parks in northern and eastern Poland, the higher ones in the southern parks. Significant differences in the content of elements were also observed between the green and brown parts of mosses, between moss species and between years of sampling.

Element concentrations baselines were given for Parmelia sulcata and associated soils, Parmelia chlorochroa was found sporadically in Theodore Roosevelt National Park, North Dokota in USA and therefore only representative concentration ranges were reported for this species (Gough et al., 1988a). Element data include (1) for lichens: Al, As, Ba, B, Ca, Cr, Cu, Fe, Hg, Mn, Ni, P, Sr, S, Ti, V, Y and Zn and (2) for soils: Al, Ba, Be, Ca, Cs, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Nb, P, Pb, Sr, S, Ti, V, Y and Zn. Very little (usually<10%) of the variability in the element data for lichen material occurred regionally (>7.2 km); thus, P. sulcata was, in general, chemically similar throughout the park. This same uniformity was found for soil geochemistry. Numerous samples collected at close intervals would be required, therefore, to produce detailed element-concentration maps for P. sulcata and soils. No instances of elemental phytotoxic conditions were found; however, P. sulcata apparently possessed large concentrations of Ba, Cu, Fe, Pb, S, V and possibly Zn.

Hypogymnia enteromorpha and Usnea spp. were collected in the Little Bald Hills of Redwood National Park, California in USA, to establish element-concentration norms (Gough et al., 1988b). Baselines were presented for Ba, Ca, Cu, Mn, Ni, P, Sr, V and Zn for both lichen species; for Li, Mg and K for H. enteromorpha; and for Al, Ce, Cr, Co, Fe, Na and Ti for Usnea. Element concentrations of future collections of this same material can be used to monitor possible air quality changes anticipated from mining activities planned nearby. The variability in the element concentrations was partitioned between geographical distance increments and sample preparation and analysis procedures. In general, most of this variability was found in samples less than a few hundreds of meters apart rather than those at about 1 km apart. Therefore, except for Ba and Co, no large geographical element-concentration trends were observed.

The heavy metal concentrations in lichen in Mt Rainier and Olympic National Parks in USA were found to be far below toxic levels for plants (Frenzel et al., 1990). Mt. Rainier National Park have been exposed to greater levels of As, Zn, Cu and Cd than sites in Olympic National Park. The most important source of these elements has probably been the copper smelter at Tacoma (58 km away). Strong inverse relationships were found between the distances of sample sites from the smelter and concentrations of Cd, Cu and Zn in lichens. With increasing industrialization and human development of the area, the potential will exist for serious contamination of the parks by airborne heavy metals.

The results of elemental composition of lichens from a remote forest site in southern Chile (Wiersma et al., 1992) gave the following conclusions: Most elements (Ca, Mg and K) and metals (Pb, Zn and Cd) met quality assurance limits established for monitoring and exhibited low levels of spatial variability indicating their utility for baseline monitoring within an ecosystem context. Trace element concentrations for elements that have potential anthropogenic sources, particularly

Pb were among the lowest reported in the literature and similar to other species of lichens collected in remote locations in the northern hemisphere. No enrichment was exhibited for Pb and Cu in any of the samples collected from Chile and this was matched by similar results from a remote Alaskan site. The results from lichens were supported by similar results for moss collected simultaneously at the same location.

Five species of epiphytic lichens were sampled from urban and periurban areas of Bariloche, a non industrial city located on the East side of the Nahuel Huapi National Park, North-western Patagonia, Argentina (Guevara et al., 1995). The results of the analysis showed high concentrations of lithophile elements with very good correlations among them. The relative concentration of these elements in all lichen species is in good agreement with the elemental composition of sediments collected in the park.

2.3.2. Deposition of Radionuclides

Lichens are efficient accumulators of radionuclides that are released into the atmosphere because of natural and human activities. For example: Transplanted lichens to the environment of the former uranium mine at Zirovski, Slovenia were used to determine the levels of the long-lived radionuclides, U-238, Ra-226 and Pb-210 (Jeran et al., 1995). They were also compared with the nuclide levels found in air particulates at the regular site monitoring stations. The results showed that each of the radionuclides had its own distribution pattern in this environment which were in agreement with instrumental air monitoring. The highest Ra-226 levels were found in lichens in the near vicinity of the dry-tailings pile, while U concentrations were high close to the former yellow-cake production plant and then decreased downstream. Pb-210 was the most uniformly distributed radionuclide and exhibited the highest level.

In another comprehensive paper an environmental radiocontamination assessment carried out in different world areas by using different species of lichen and mosses as radionuclide biological detectors were reported (Triulzi et al., 1996). Concentrations of Sr-90, Cs-134, Cs-137 and Pu-239, 240 were detected in some species of lichens and mosses collected in Italy, Scandinavia, Nepal and Antartica during the period 1986-1993. Major differences were observed between areas strongly influenced by the Chernobyl accident and other ones coming from extreme environments (Antarctica and Nepal). The usefulness of these sensitive species in radioecological studies has been demonstrated through the determination of anthropogenic radionuclides in areas long considered as unpolluted sites. In particular, a good correlation between Cs-137 and altitude was also determined in the 1993 Italian samples.

In Turkey there are few studies concerning with radionuclides after the Chernobyl accident. Long-lived fission radionuclides spread out after the Chernobyl accident have been measured in samples collected from the Black Sea and the Aegean coasts of Turkey between June 15 and September 15, 1987. The activity remaining after 16 months after the event was found to be enhanced in coniferous needles as well as in lichens, while foodstuff did not show any appreciable contamination. The relatively high Ru-106/Cs-134 and Ce-144/Cd-134 ratios compared to those found in analogous samples from Southern Europe, might result from a fractionation between refractory and volatile elements (Akçay and Ardisson, 1988). The radioactive amounts (Ru-106/Cs-134, Cs-134/Cs-137, Sb-125/Cs-134 and Ce-144/Cs-134) indicated some important clues about the radioactive falling seen in West Anatolia (Akçay and Kesercioğlu, 1990).

Because of the great detectability and variable lifespans of radionuclides, the Chernobyl accident illustrated well the way vaporized elements disperse in the atmosphere to affect very distant ecosystems. For instance Quebec, which is located near the northeast of North America received Chernobyl debris from the northeast (Scandinavia-Greenland route) and from the west (Siberia-Bering Sea route) (Crete et al., 1992). Cadmium and lead were the most closely related pollutants in lichens, while there was a little relationships between Cs-137 and the three trace metals. The distribution of the elements over the territory was not uniform and the altitude influenced three of them. The concentrations of cadmium, lead and mercury were higher in the northwest quarter of the study area than elsewhere, while cesium contamination was highest in the southeast quarter. It seems preferable that caribou should be harvested at low elevation when they are taken in winter in order to minimize the risk associated with cesium consumption by humans.

2.3.3. Determining Organic Pollutants in Lichens

There are really few studies conducted in order to determine organic compounds in lichens in the literature. Thomas et al (1985) did the most detailed work, which includes both organic, and inorganic substances. Chemical residue analysis of 15 plant (mosses, lichens and leaves) and humus samples from a rural site in southwest Sweden was carried out for polyaromatic hydrocarbons (PAHs), polychlorinatedbiphenyls (PCBs) and heavy metals. It was found out that while most of the higher plants with low surface to biomass ratios are only able to accumulate pollutants in small amounts, some of the lower plant species are effective filter systems for all these pollutants which are transported in the atmosphere bound to particulate matter. This is noticed for PAH and most of the metals investigated. The enrichment of chlorinated hydrocarbons (pesticides and PCB) in plants can only reach high concentrations in those species, which contain fatty material for the dissolution of these pollutants, such as found in coniferous plants. Cluster analysis has been shown to be an effective tool for the multivariate and objective classification of different plant species of an ecosystem by its pollutant accumulation levels.

The second work about the organic pollutant was done by Migaszewski (1999) in Poland. The objectives of that investigation in the Holy Cross Mountain region of Poland were 1) to establish organic-concentration baselines and 2) to determine spatial distribution pattern of polynuclear aromatic hydrocarbons in topsoil. These objectives were accomplished using an analysis of variance (ANOVA). Samples of topsoil, Scots pine needles and lichen thalli were collected for PAHs, PCBs, organochlorine pesticides and phenols. Of these four organic groups, PAHs was detected in topsoil of nearly all investigation sites. The results showed that some concentrations of compounds were elevated probably due to air pollution. Nonetheless, some portions of them, especially phenols, might have been products of metabolic activity. Topsoil, Scots pine and partly lichens of Lysica Mt. revealed the highest concentrations of PAHs, PCBs and organochlorine pesticides. The content of PCBs in lichens of the study region was somewhat higher than in Lapland.

The third study was realized in Canada. Spatial trends and patterns of accumulation of organochlorine (OC) contaminants were determined in lichen samples from 35 locations across Ontario, Canada between 1985 and 1987 (Mulr et al., 1993). Concentrations of total DDT isomers, total chlordane and dieldrin in 1987 were significantly higher in lichen from south-central Ontario locations than samples from northern and northwestern locations, while several of the latter sites had higher levels of hexachlorocyclohexane isomers and pentachloroanisole. Similar levels and relative proportions of these compounds were observed in 1986 samples. Total PCB congener concentrations were elevated at south-central Ontario sites and unexpectedly, at several other locations remote from obvious sources. Principal components analysis indicated that in 1987 northwestern Ontario samples were distinguished from most southern locations by higher proportions of more volatile OCs.

2.3.4. Comparing Accumulation Capacity of Lichen Species

Many authors have determined the metal concentrations in different species. It is quite clear, however, that the metal concentrations can vary sometimes considerably between species in the same site. With no quantitative information on these differences it has not been possible to use alternative species in a survey. This is unfortunate as it is often difficult to find material in each sample site if the survey is restricted to one species.

One of the earliest studies described a method for including nine alternative moss and lichen species in heavy metal air pollution surveys based on concentrations in one of the species (Folkeson, 1979). Iron, Cu, Zn, Pb, Ni and Cd concentrations have been measured in lichens and mosses from 57 sites in coniferous woodland surrounding a brass foundry in Sweden. Concentrations vary decidedly between species. The mosses frequently showed higher concentrations than the lichens. The use of different monitor species in a deposition survey without interspecies calibration was not advised. Calibration factors for concentrations in different species can be calculated from the mean concentrations in each species. With the help of the factors, concentrations in a species not found in a certain site can be estimated than concentrations measured in any of the other species sampled. The applicability of the reported calibration factors to surveys in other regions was discussed. Where these factors were not applicable, local calibration factors for indicator species of interest can be set up using the method presented.

The amounts of Ni, Cr, Zn, Pb, Cu, Fe and Mn in seven lichens growing in Switzerland were determined (Garty and Ammann, 1987). The lichen species were Hypogymnia physodes, Pseudevernia furfuracea, Cladonia rangiferina, Cetraria islandica, Parmelia sulcata, Usnea sp. and Letharia vulpina. By the use of intersite, interelement and interspecies comparisons, it is concluded that some metals within the thalli of Swiss lichens may reach high levels even these plants are growing in rural areas and isolated sites. High amounts of Cr, Ni, Cu and Fe were detected in Pseudevernia furfuracea growing far away from industrial plants and busy motorways. The same phenomena were observed in Parmelia sulcata. In general, Fe, Zn and Pb were found in higher amounts in lichens collected in Switzerland relative to other metals. The amounts of Pb in Swiss lichens were especially high in material collected close to busy roads and at tourist sites. P. sulcata demonstrated large differences in the Pb content of thalli collected at two sites in the same city. A difference existed between the affinity of P. furfuracea and Hypogymnia physodes to accumulate Ni. There also existed a possible difference among P. sulcata, P. furfuracea and H. physodes to accumulate Mn. A coefficient of variation obtained for the measured metal in the studied lichen was suggested for uptake comparisons. This parameter was suggested for elucidation of whether a certain metal incorporated in the lichen thallus occurred in minute well-dispersed particles, as was assumed in the case of Zn, or in big particles. High coefficients of variation obtained for Cr, Ni and Cu in most of the studied lichens were attributable to big metal-containing particles entrapped in the lichen thallus.

The objective of the following study was to compare the short term accumulation capacity of two epiphytic lichens characterized by a different type of thallus (Garty et al., 1996). The lichens Hypogymnia physodes (L.) Nyl. and Usnea hirta (L) Weber em. Mot. were transplanted either to the vicinity of streets of low volume and slow traffic or to the vicinity of a highway in the city of Oulu, N. Finland, for a period of 45 d. Eleven elements were analyzed before and after transplantation. The two lichen species were found to possess a similar accumulating capacity for K and Mn. Hypogymnia physodes manifests a higher accumulating capacity than U. hirta for Na, Fe and Cu , whereas the more sensitive lichen U. hirta exhibits a higher accumulating capacity for Mg, despite a higher primary concentration of these elements in the thallus of H. physodes. Those findings showed a relative high concentration of K, Fe, Mg, Zn, Mn, Pb and Cu in thalli of H. physodes and Mg, Zn, Pb, Cu and Cd in U. hirta in material transplanted to streets of low volume and slow traffic over and above the concentration found in thalli retrieved from the vicinity of the highway. This may be explained by the higher rate of abrasion of car engines running idle near traffic lights and by the lesser ventilation near the close-clustered streets of the inner city.

A suite of 12 saxicolous lichen species were collected from a remote site in the south-central District of Keewatin, Canada (Chiarenzelli et al., 1997) and analyzed As, Cd, Cr, Cu, Ni, Pb, Sb, V and Zn. Concentrations of these metals were comparable to results from elsewhere in the NWT obtained up to 28 years ago, and from remote sites in northern Quebec, Alaska, Greenland and northern Finland. Heavy metal concentrations of the lichens were compared to that of 7 immediate substrates. Substrate is not a significant source of metals to the lichens because: 1) correlation between lichen and substrate chemistry was generally poor; and 2) metal concentrations in lichen species growing on a substrate lacking measurable concentrations of trace metals were analytically indistinguishable from the same species growing on enriched substrates. Interspecies calibration ratios, calculated with respect to C. stellaris, decreased from crustose to foliose to fruiticose varieties, indicating that the crustose types were the most efficient accumulators and/or retainers of heavy metals.

The results of a research aimed to study the environmental quality in the area of the Rieti town (Central Italy) using the macrolichen vegetation as bioindicator were reported (Owczarek et al., 1999). An estimation of SO_2 content in the atmosphere, based on the Hawsworth and Rose's biological scale, had been also given. The analysis of the distribution of the epiphytic lichens in five areas, from the town center to the near mountain area, confirmed the efficiency of fruticose and foliose lichens as bioindicators and the low sensitivity of the crustose ones to the pollutants.

2.3.5. Analysis Techniques

Several analysis techniques were available for the elemental analysis of plants such as used in pollution monitoring studies. One of the papers examined the advantages and disadvantages of X-ray fluorescence spectrometry, for determining the elemental content of lichen (Richardson et al., 1995). The technique can be used for macro nutrients such as K and Ca and for trace metals such as Cu, Pb and Zn as well as for non-metals, especially S. Consideration was given to collection, preparation and analytical procedures for lichens using this analytical method. Data from studies using XRF were presented. Improvements were suggested with regard to sample preparation, and limitations, which prevent the method being more widely adopted, were reviewed. The new generation of computer-assisted spectrometers have significantly lowered detection limits, so that background elemental levels in remote areas as well as enhanced levels near industrial activities could effectively be assayed in lichen or other plant samples.

The results of a research in progress at the University of Milan on natural and determination of anthropogenic elements in mosses as biological indicators were shown (Vecchi et al., 1994). The analytical technique was the energy dispersive X-ray fluorescence (EDXRF) spectrometry. The spectrometer was calibrated for these elements: S, Al, Ca, Ti, Fe, Ni, Cu, Zn, Br and Pb using Community Bureau of Standards (BCR) and National Institute of Standards and Technology (NIST) standards. Detection limits found were of about 1-2 µg /g of dry weight for elements present in low concentrations.

Total reflection X-ray fluorescence spectrometry was applied for the certification of IAEA lichen 336 (Schmeling et al., 1997). The elements Ca, Mn, Fe, Cu, Zn, Rb, Sr and Pb were determined simultaneously. The concentrations ranged from 1.8 mg/kg for Rb to 2360 mg/kg for Ca. The results were compared with those of other methods and laboratories having participated in this certification for the International Atomic Energy Agency (IAEA) (Emission spectrometry, mass spectrometry, atomic absorption spectrometry, X-ray spectrometry, neutron activation analysis and voltammetry). The results determined by TXRF were in good agreement with the overall means of accepted values and differed from the means by 1 to 10%.

Trace elements in epiphytic lichens were determined by ICP-MS after solubilization of the material in a microwave oven (Bettinelli et al., 1996). Three different acid mixtures were tested but only HF acid ensured complete recovery of many elements present at very low concentrations. The accuracy and precision of the method were evaluated by analyzing BCR CRM 482, Trace elements in lichen, and by comparing the results with those obtained for real samples using different analytical techniques. The use of a pneumatic and ultrasonic nebulizer with ICP-MS was evaluated and the results were discussed. The method detection limits for the standard configuration using ICP-MS with the pneumatic nebulizer were generally better than 0.2 µg/g, making the method suitable analytical requirements.

The elemental composition of lichens from remote southern South America regions has been studied with analytical and statistical techniques to determine if the values obtained reflected species, growth forms or habitat characteristics (Calvelo et al., 1997). The enrichment factors were calculated discriminated by species and collection site and compared with data available in the literature. The elemental concentrations were standardized and compared for different species. The information was statistically processed, a cluster analysis was performed using the three first principal axes of the PCA; the three groups formed were presented. Their relationship with the species, collection sites and the lichen growth forms were interpreted.

Instrumental neutron activation analysis has been applied to analyze epiphytic specimens of the lichen Canoparmelia texana in Brazil (Saiki et al., 1997). Samples collected from the barks of the trees were previously cleaned, lyophilized and ground to be irradiated under a thermal neutron flux in the IEA-R1 nuclear reactor. Elements Al, As, Br, Ca, Cd, Cl, Co, Cr, Cs, Fe, Hf, K, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Mg, Mn, Na, Rb, Sc, Se, Th, Ti, U, V and Zn were determined quantitatively by using short and long irradiations. Comparisons were made between the results for washed and unwashed samples as well as those collected in two different years, from individual palm trees and also from different sites of Sao Paulo State. The precision and the accuracy of the method were evaluated by analyzing NIST 1572a Citrus Leaves, IAEA 336 Lichen and USGS W-1 Rock reference materials.

2.3.6. Accumulation of Heavy Metals in Lichens Growing in Arid or Semi-arid Zones and in Arctic and Antarctica

Most of the work on the accumulation of heavy metals by lichens has focused on pollution from smelters, power plants, busy roads, urban sites and rural areas. Furthermore, most of the studies took place in the northern hemisphere and generally in countries with a humid climate. A smaller number of publications exists on the accumulation of airborne heavy metals in lichens growing in arid or semi-arid zones ratios and lead isotopes from epiphytic lichens were useful for distinguishing between sources of airborne PM, and for gauging anthropogenic inputs into desert ecosystems. Abundance patterns of the trace elements La, Nd and Sm in the lichens suggested origination from continental crust, but rare earth elements displayed a pronounced enrichment relative to the major element Fe by a factor of about 5. This enrichment appears related to geologic weathering, aeolian transport and grain-size biases toward trace element rich mineral grains in the arid setting. Using the metal Pb as an indicator of human inputs, epiphytic lichens typically show Pb enrichments by a factor of about 25-60 over typical upper crustal values. Regional scale differences in Pb isotope ratios of these lichens relate to different pollutant sources in southwestern North America.

Two measurement techniques were employed to evaluate the feasibility of using lichens as in situ biomonitors of atmospheric pollution in a semiarid climate-trace element analysis and electrolyte leakage from cells (Rope and Pearson, 1990). Trace element concentrations were generally higher in Lecanora melanophthalma (Ram.). Ram. tissues than previously measured in sagebrush (Artemisia tridentata) and perennial grasses from the same locations, but lower than in soil. Lichens from an urban area (Idaho Falls) in USA had statistically higher concentrations of ten elements, particularly lead and zinc, than those from the Idaho National engineering laboratory (INEL) and Craters of the Moon National Monument. Levels of fluoride, nickel and seven other elements were high at the INEL relative to the other sites. Thalli collected downwind from the Idaho Chemical Processing Plant (ICPP) at the INEL were significantly higher in boron and lead content than those collected at crosswind locations: levels of eleven elements were significantly higher in lichens collected at 5 or 10 km from the ICPP than in those collected at 2 km. Electrolyte leakage was greatest from thalli collected in the nighttime downwind direction from the ICPP, even though daytime winds, which blow in the opposite direction, are more frequent, suggesting that in a semiarid climate, injury from atmospheric SO_2 and NO_x pollution in lichen tissues is greatest when the thalli are moist from morning dew or other sources. These results demonstrate that some lichen species, especially Lecanora melanophthalma, have potential for biomonitoring of atmospheric pollutants in the semiarid regions of the Intermountain West.

As one of the dominant and most widespread groups of arctic plants, lichens have been used frequently in deposition studies, particularly as related to radionuclides and metals (Nash III and Gries, 1995). As receptors of atmospheric deposition, lichens have advantages over vascular plants due to the relative lack of lichens' morphological variability with time, their lack of a cuticle and associated stomates and their lack of roots. Mechanisms by which contaminants are accumulated and tolerated by lichens were briefly reviewed. Data regarding elevated elemental concentrations associated with certain industrial activities in relation to putative background levels were tabulated. The use of enrichment factors and multivariate analyses provided two procedures by which patterns in complex data sets can be discerned where pollution was minimal. Finally, arctic lichens may also be useful in documenting deposition patterns of persistent organic contaminants, particularly in relation to the lichen-caribou-human food chain, as was previously documented for radionuclides.

Trace metal contents were recorded for the epilithic Antarctic lichens Usnea aurantiacoatra and U. Antartica, sampled close to the Argentina scientific station Jubany on 25 de Mayo (King George) Island, in the Southern Shetland Archipelago (Antarctica) (Poblet et al., 1997). The corresponding heavy metal levels had been measured through atomic absorption spectrophotometry, following internationally accepted analytical methods. The results obtained supported the hypothesis that an atmospheric circulation of trace metals existed on the assessed area, and the activities developed at the different scientific stations located on this island would be a potential source of heavy metals to the evaluated environment. The geographical distribution of trace metals atmospherically transported in the area close to Jubany station was studied through the corresponding metal contents of the assessed lichens. Finally, the suitability of both analyzed lichen species, Usnea aurantiacoatra and U. Antartica, as biological indicators for quantitative monitoring of airborne metals for this Antarctic environment was recognized.

2.3.7. Studies About Mercury and Mercury Speciation

There was only one study in the literature reporting the mercury species in lichens (Lupsina et al., 1992). Hypogymnia physodes was chosen in order to determine total mercury and methylmercury in lichens taken from various polluted and unpolluted locations in Slovenia, including a mercury area around Idrija. Additionally, total gaseous mercury in air was also determined at several sampling points. The use of biological indicators is inexpensive and easy and gives accurate information about the distribution pattern of mercury. Mercury and methylmercury levels were in good statistical correlation, although it was clear that the fraction of mercury present as methylmercury fell at sites with heavy inorganic contamination. In addition, further experiments will be performed in order to confirm the possibility of biometylation in lichens.

Mercury content was analyzed in black spruce and needles and in the epiphytic lichens found growing on trees (Zhang et al., 1995). The samples were collected in two distinct boreal forests of northeastern Canada (province of Quebec). The chosen sites were far from direct industrial mercury sources and were located close to man made lakes of different ages. The objective of the study was to determine the role of atmospheric transport in the mercury contamination of trees growing in close proximity to reservoirs, both old and recently flooded. The lichen samples contained the highest mercury concentrations: 400-800 ng/g. They were several times higher than in the bark and one to two orders of magnitude greater than that found in the needles. The mercury concentrations measured in the lichens were significantly different between the two reservoir sites, whereas those of the needles and bark were not. The mercury concentrations in the black spruce bark sampled near the reservoirs were almost twice as high as (~130 ng/g) as those measured in the bark of black spruce trees growing near natural lakes (40-70 ng/g). However no differences were found between the mercury concentrations of young needles sampled close to reservoirs and those sampled near natural lakes, suggesting the existence of a relatively low but stable level of mercury in the local atmosphere.

Mercury deposition was monitored at two mountain sites in Quebec using transplanted lichens and moss (Evans and Hutchinson, 1996). The terricolous lichen species Cladina rangiferina, the epiphytic lichen species Hypogymnia physodes and the feather moss Pleurozium schreberi were transplanted from a northern Ontario boreal site to the bases and summits of Roundtop Mountain and Mt. Tremblant in southern Quebec. After 12 months, transplants of C. rangiferina sited at the base and summit of Roundtop mountain and the summit of Mt. Tremblant showed a significant increase in mercury concentration over controls ($p<0.05$). The largest difference occurred at the summit of Roundtop mountain where mercury concentration was 81.4 ± 10.9 ppb as compared to 45.6 ± 10.6 ppb at the control site. No significant increases in mercury concentration in P. schreberi were seen after 12 months at any site although trends of increase were apparent. After 20 months, further significant increases in Hg content were observed in both the terricolous lichen and the feather moss at both the Roundtop Mountain base and summit sites. A significant increase in Hg content of P. schreberi was also noted at the Mt. Tremblant summit site. Over the length of the study the greatest mercury concentration increases were observed in the feather moss at the Roundtop Mountain summit site (with a 248.3 ± 30.0 ppb mercury concentration as compared to 108.3 ± 30.0 ppb in controls). No significant change in mercury concentration in the epiphyte H. physodes was found during the study. These data indicated that mercury deposition was occurring, especially to higher elevation sites. While mercury inputs at the summits may be increased by the effects of fog, increases in mercury at the base sites cannot be accounted for the same way, but may represent the importance of dry deposition processes.

2.3.8. Comparison of Deposition or Aerosol data with Lichen or Moss Data

The use of lichens and mosses and other biomonitors such as forest litter, spruce and pine needles assumes that the concentration of a substance in the organism can be related to its atmospheric deposition. However, one of the inherent problems with the use of bioindicators is that they do not provide information on the absolute magnitude of deposition, nor the seasonal variations.

Concentrations of trace metals in mosses Hylocomium splendens (Hs) and Pleurozium schreberi (Ps) were compared along with wet deposition at 8 sites in Sweden (Ross, 1990). Cadmium, Mn, Zn and Cr concentrations were similar in both mosses, while Cu, Fe, Pb, Ni and V levels were 14 to 24% higher in Hs than in Ps. The comparison to wet deposition estimates indicated that concentrations in mosses were also influenced by other factors than the adsorption of precipitation. No correlation was observed between the wet deposition of Mn, Cr and Ni and moss concentrations.

At 8 stations spread over The Netherlands transplants of Parmelia sulcata Taylor and impregnated cloth (rag) as non-biological monitor were exposed to the atmosphere for periods of up to 12 months (Sloof, 1995a). At the same stations bulk (wet and dry) deposition was collected on a monthly basis. Quantitative linear relationships between the concentrations in the 12 months exposed lichens and the cumulative bulk deposition during the same period, yielded accumulation factors for cobalt, scandium and zinc. The lichens reflected the bulk deposition. The ratios between the accumulation factors for cobalt, scandium and zinc in lichens and rag of metal uptake by moss was significantly correlated with the metal concentration in atmospheric aerosols. The results indicated that moss bags of S. auriculatum can provide a quantitative estimation of the concentration of different heavy metals in urban atmospheres, when specific calibration by mechanic monitoring, at the same sampling point, is performed during a first stage of biomonitoring. The mean aerosol metal concentrations found in the Oporto atmosphere were similar to those observed in other urban atmospheres in different countries. The relative order of the mean metal concentrations was Fe (1.8 $\mu g/m^3$) > Zn> Pb > Cu > Cr > Mn > Ni (20 ng/m^3). The aerosol Pb levels were monitored at different sampling points over various periods of time between 1991 and 1997. The mean Pb levels were $\leq 0.5\ \mu g/m^3$ and approximately constant at each sample point up to January 1996. After that date it decreased by approx. 50%, in consequence of the reduction of the Pb concentration in leaded gasoline.

Measurement of air particulates is restricted to experienced laboratories with access to expensive sampling equipment (Rossbach et al., 1999). Additionally, the amount of material collected generally is just enough for one determination per sampling and no multidimensional characterization might be possible. Further, fluctuations in air masses have a pronounced effect on the results from air filter sampling. Combining the integrating property of bioindicators with the world wide availability and particular matrix characteristics of air particulate matter as a prerequisite for global monitoring of air pollution was discussed. A new approach for sampling urban dust using large volume filtering devices installed in air conditioners of large hotel buildings in Germany was assessed. A first experiment was initiated to collect air particulates (300-500 g each) from a number of hotels during a period of 3-4 months by successive vacuum cleaning of used inlet filters from high volume air conditioning installations reflecting average concentrations per 3 months in different large cities. This approach is expected to be upgraded and applied for global monitoring. Highly positive correlated elements were found in lichens such as K/S, Zn/P, the rare earth elements (REE) and a significant negative correlation between Hg and Cu was observed in these samples. The ratio of concentrations of elements in dust and Usnea spp. was highest for Cr, Zn and Fe (400-200) and lowest for elements such as Ca, Rb and Sr.

The metal concentrations of V, Cr, Co, Ni, Cu, Zn, Cd, Hg and Pb were analyzed in distilled water extracts of Parmelia caperata and in bulk deposition, throughfall and an experimental in situ washing of leaves at two forests at Montseny (NE Spain) submitted to different exposure to the industrial and traffic activities around Barcelona (Rodrigo et al., 1999) . Lichen concentrations of Zn, Cu, V and Cd were higher at the site of greater exposure to pollutants. Consistently, there was higher dry deposition of these metals at the more exposed site. The order of abundance of trace metals in the lichen was similar to that deposition variables, although Pb and Cu had intermediate concentrations in the lichen but were very low in the deposition measurements. This indicated the higher affinity of Pb and Cu for the exchange sites in the lichen cell wall and the fact that lichens accumulated Pb for the last 12-18 y when emissions were much higher than today. The ability of Parmelia caperata to indicate the deposition of heavy metals, together with its easy sampling and handling, its broad distribution and its easy identification suggest that the lichen extract procedure described could be used to establish gradients of atmospheric deposition of heavy metals at a general geographic level.

CHAPTER 3

EXPERIMENTAL

3.1. Sampling

3.1.1. Sampling Area

Sampling area is Aegean Region of Turkey. The area of total sampling region is 51800 km^2. The sampling area is shown in Figure 3.1.

3.1.2. Sampling Strategies

Before sampling it is crucial to determine the sampling strategies correctly. Sampling strategies are set up considering topography, industry and urbanization. Aegean region is divided into 10 km × 10 km and 40 km×40 km grids by using 1:250 000 scaled maps. The coastal sites of the region is much more developed and industrialized than the interior part of the region. That is why 10 × 10 km grid was chosen around the city of İzmir and 40 × 40 km grid was preferred for the rest of the region. Additionally, around Soma and Yatağan power plants sampling was done by approximately 1 km distances. Sampling points are also shown in Figure 3.1.

The flow diagram in Figure 3.2. summarizes the sampling strategies that were applied for this study.

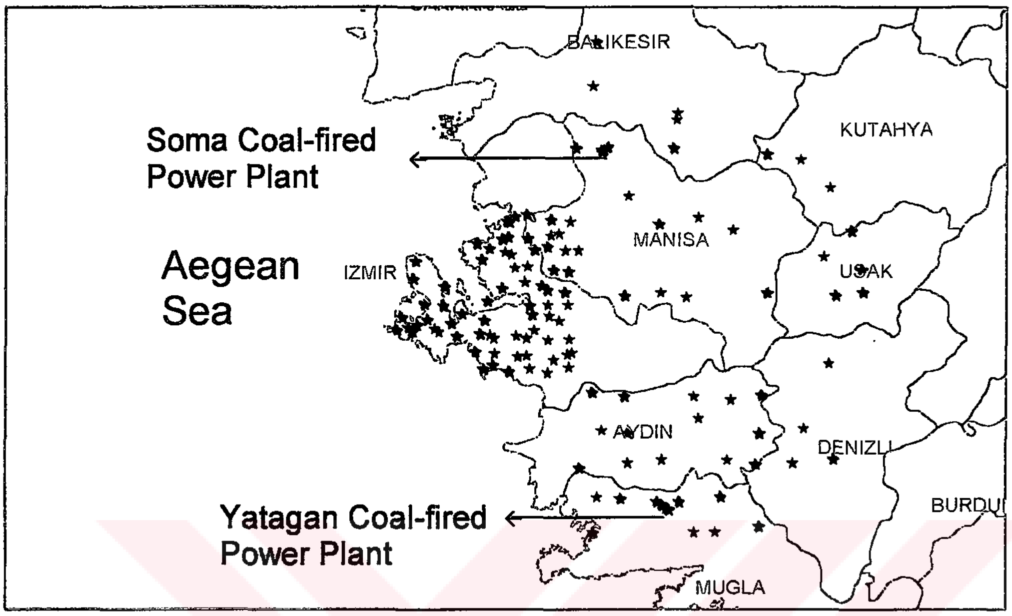


Figure 3.1. The sampling points

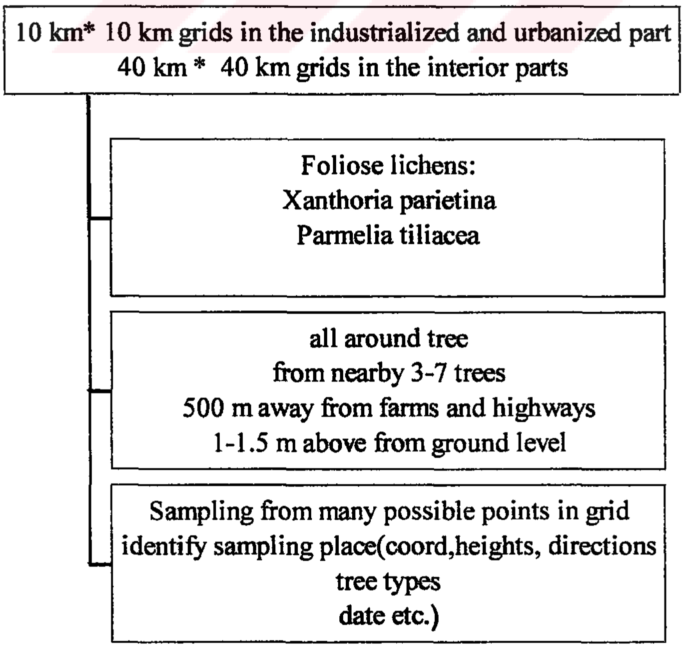


Figure 3.2. The flow diagram of sampling strategies

To select the suitable lichen species was the most important step in the sampling strategies and also for future works, which might be conducted on the other parts of the country. The lichen species should be very common in the region, tolerant to pollution, easy to recognize in the field and easy to separate from the substrate. After consulting the lichenologist (Zeybek,1996) at Ege University and investigation in the field, Xanthoria parietina (L.) Th. Fr. was decided to be best for this study. It fulfils all requirements mentioned above except one disadvantage. Although it is a foliose lichen, in most of the places it has very small leaves (due to pollution) and it was not easy to collect enough samples from the tree bark by using nylon tweezers. That's why we had to sample a lichen thallus with its bark substrate using a steel knife by a great afford not to touch lichen thallus and by just cutting the tree bark. This also brought a trouble in separating the lichen thallus from the tree bark in laboratory. It was not possible to separate lichen from the tree bark without moistening with deionized water. Another lichen species, which was chosen, is Parmelia tiliacea (Hoffm) Ach. It was not found in all grids but in order compare the accumulation capacities of lichen types it was collected wherever it was found because it has advantage of easy separation from the bark being a foliose lichen with big leaves. In some of the grids there was no sample because we could not found even one tree or trees without lichen species. In addition sometimes we could not take samples from the center of grids since we could not reach to these places because of high mountains or no way for vehicles to go.

Two hundred thirty four samples were collected during sampling periods of July 1997 and November 1998-January 1999. Several lichen thalli of different size were collected if possible at 1-2 m from the ground (sometimes it was not possible to find enough lichen samples on the branches or trunks of the trees we had to collect from the bases of the trees) and all around the tree likewise from 3-7 nearby trees to reduce influences from prevailing wind directions and relative source positions and also to obtain enough sample. Sampling in the grid was done from many possible points to make representative sample of the grid. Samples were collected at least 300-500 m away from main roads, farms, villages and industries. They were removed from the body of the tree with their substrates using a steel knife. After the identification of the sample (coordinates, elevation, directions, tree types and date etc.), it was put in polyethylene bags, labelled and sealed with clips. Material from the same tree and from nearby trees in a grid was combined to yield one representative sample of this point. During the sampling, sample handling and preparation polyethylene gloves were worn.

3.1.3. Sample Collection and Preparation

3.1.3.1. Lichens

In all sample preparation and analyses deionized water was used which was produced using Barnstead nanopure ultrapure deionization unit equipped with two ion exchange cartridges to remove ions, a third cartridge to remove the organic and fourth one to remove particulate matter. The produced deionized water finally has a resistance of 18.3 MΩ.

The preparation step of the samples especially for Xanthoria p. for the analyses was tedious work since it was very difficult to separate lichen thallus from the bark substrate without moisturing as mentioned before. In order to separate the lichen thallus from the substrate, the samples were rinsed with deionized water. The lichen thallus together with bark substrate was floated in deionized water in beaker and stirred for about 30 seconds. Debris and soil particles settled down. After rinsing for 30 seconds, they could be separated from the substrate with nylon tweezers. Actually rinsing can be required in order to remove soil particles without leaching out metals as well. They were sorted to remove dead tissue and extraneous material (adhering bark, mosses, other lichen species, soil particles, etc.). After separation, they were put in folded filter papers and air-dried in clean glass box approximately one day at room temperature. Then the dried samples were kept in the labelled polyethylene bags.

3.1.3.2. Transplant Lichens

Transplantation has been used in areas where no suitable monitor organism could be found in the indigenous vegetations and in case where the more comparable substrate and exposition conditions of transplants were considered to be superior to the conditions in the natural vegetation. In the content of this work the transplant lichens were used in order to obtain a quantitative knowledge from the lichens. Because there were no indigenous lichen samples in the campus of Ege University. Indigenous lichen species Xanthoria parietina (foliose lichen with yellow color), Parmelia tiliacea (foliose lichen with grey color) and Evernia prunastri (L.) Ach. (fruticose lichen with grey color) were collected fromYamanlar Mountain which was assumed to be a clean area but later it was seen that this was not the case. Little from each of the three lichen species with their substrates were put in the transplant bags (using big nylon filter with 1mm x 1mm netting) avoiding the overlapping to each other. Nine transplant bags were prepared and hanged on the branches of trees avoiding throughfalls from other branches and 1-2 m above from the ground. Transplant lichens were exposed to air pollution during the period of December 12, 1997-November 11, 1998. The first transplants were taken from the bags on March 18, 1998; the second transplants on June 18, 1998 and the last ones on November 11, 1998.

3.1.3.3. Deposition Samples

In order compare the accumulation capacity of transplant lichens, 200 m away from the transplant lichens, deposition samples were collected weekly. The sampler consisted of a white plastic funnel (17.5 cm dia.) fixed with wood blocks. The funnel was connected to a 1 L polyethylene bottle. The sampler was set up 1 m above the ground at the yard of Biology Building of the Ege University Campus. At the end of the week, deposition sample (rain and dry deposition) in the bottle was taken after washing the deposites on the funnel with approximately 100 mL of deionized water. Field blanks were taken after the sample by washing with approximately 100 mL deionized water in every month. The volume was measured by means of calibrated bottles to reduce contamination and then pH measurements were done at the sampling site. Samples were sent to Ankara at the end of each month. Samples were collected during the period of 12 December 1997-11 November 1998. The number of weekly collected deposition samples was 49.

3.2. Sample Handling

3.2.1. Preparation of Lichen Samples for Instrumental Neutron Activation Analysis (INAA)

Instrumental neutron activation analysis (INAA) of the samples was conducted at Massachusetts Institute of Technology (MIT) reactor laboratory in USA. Samples were reopened in a laminar flow clean hood. Polyethylene bags in which lichen samples were put were washed with dilute nitric acid, rinsed with deionized water and air dried in the clean bench under HEPA filtered air flow. Lichen sample was weighed in a small acid washed polyethylene bag and heat-sealed. Then it was placed in another polyethylene bag and heat sealed again, sample identification number was written over the outer polyethylene bag. After irradiation, outer polyethylene bag was removed and small bag with sample was placed in another radioactive clean bag for counting. Standard reference materials NBS SRM 1633:Coal fly ash, NBS SRM 1571: Orchard leaves, IAEA 336: Trace elements in lichen and NIST 8408: Mercury in sediment were routinely used to check the accuracy of the analysis. NIST 8408: Mercury in sediment for Hg and NBS SRM 1633:Coal fly ash for other elements were used as standard reference materials. Known amount of SRM was weighed to the nearest 0.01 mg. The weighing and sealing processes of SRM's were directly applied like in the case of lichen samples except for mercury standard. Mercury standard was placed into precleaned polyethylene bag to eliminate any loss of mercury from the standard causing a sample contamination problem, the standard encapsulated into a clean quartz tube. After irradiation the quartz tube was broken and the mercury standard was placed into precleaned polyethylene bag. All of the SRM standards were included to each 4 sets of samples irradiated for counting with 4 detectors.

3.2.2. Preparation of Lichen Samples for Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) Analysis

Approximately 200 mg lichen sample was weighed and put in TFM (Tetrafluormethaxil-regulated trademark of Hoechst) digestion vessels with a capacity of 125 mL. TFM exhibits a polytetrafluoroethylene (PTFE) based material, which exhibits many of advantages. It has high density, very compact surface, high insulating power and high working temperature (330 ^{0}C - 350 ^{0}C). Five of these vessels were used for the digestion of lichen samples and one of them was used for acid blanks. Acid mixture of 8 mL of 65 % HNO_3 (Merck extrapure) + 2 mL of 35 % H_2O_2 (Merck extrapure) + 0.5 mL of 38-40 % HF (Merck extrapure) was found to be suitable to digest the lichen samples. Hydrofluoric acid was used because botanical materials may contain various soil and/or mineral fractions and might therefore be difficult to digest. The digestion vessels were placed in the rotor body and the rotor was placed into microwave cavity. Ethos 900 Milestone Microwave Digestion Oven was used for sample digestion. The optimized program on Table 3.1 was used for digestion. It was completed in 25 minutes including 5 minutes ventilation time. Ventilation time was required because high temperature and pressure are reached inside the vessels. It was therefore necessary to cool down the rotor before opening the vessels. After 15 minutes extra cooling under tap water, digestion vessels were open under the hood with tension wrench. Samples were diluted to 50 mL with polyethylene flasks. All digestion vessels and polyethylene flasks were kept in 30 % (v/v) HNO_3 at least one hour before use.

Table 3.1 Operating program for lichen samples using Ethos 900 Milestone Microwave Oven.

Step	Time (min.)	Power (Watts)
1	2	250
2	2	0
3	6	250
4	5	400
5	5	600

(Ventilation time: 5 minutes)

3.2.3. Preparation of Deposition Samples for Analyses

The deposition samples were measured again for pH and volume to determine whether there was any volume loss or pH change during storage and transportation. All sample handling and preparation were done in clean room under five high efficiency particulate (HEPA) filters to remove particles (sizes smaller than 0.1 μm) in Environmental Engineering Department of METU. The measurement of pH in low ionic strength, unbuffered solution of atmospheric depositions has a variety of experimental difficulties, which can compromise the validity of the data collected and takes very long time to measure. For this reason, WTW SenTix 97 T, low ionic strength electrode was used.

Flow diagram of sample preparation steps is shown in Figure 3.3. Samples were filtered using 0.22 μm cellulose acetate filter and polyethylene filtration system. Soluble fraction was divided into two portions. One of them was used for IC analysis and ammonium determination. Another portion was acidified with few drops of concentrated high purity HNO_3 for ICP-AES and Atomic Absorption Spectrometry (AAS) analyses. The samples were kept in the refrigerator at 4°C until analyses. During sample handling processes, all sample manipulations were done using Teflon coated tweezers and polyethylene gloves. Insoluble fraction was kept in petridishes until digestion time at 4°C .

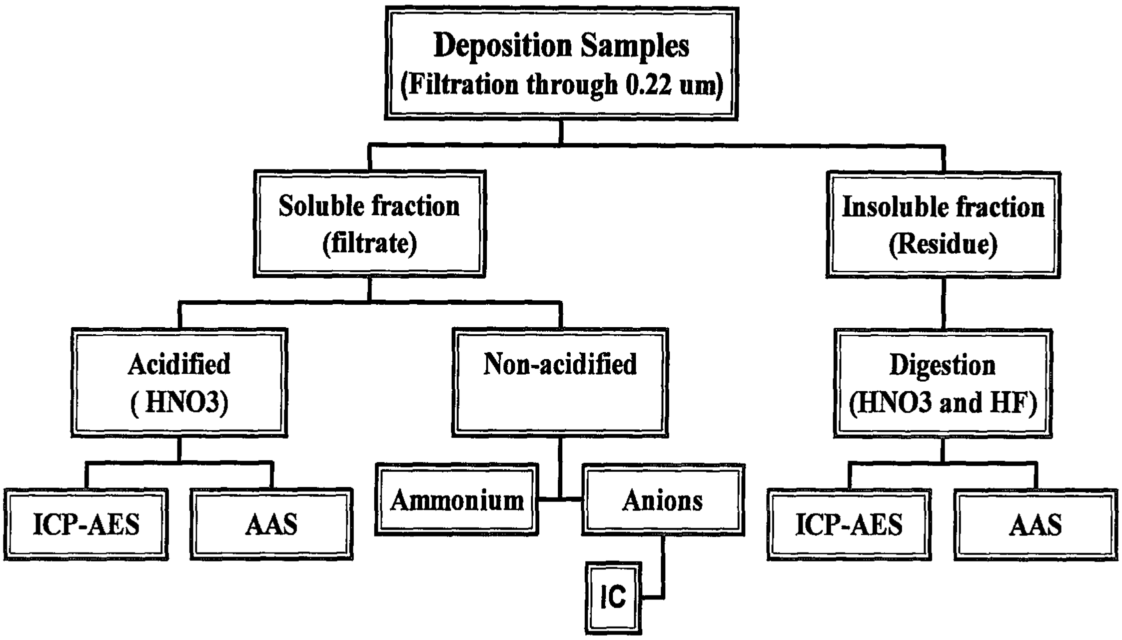


Figure 3.3. The flow diagram of preparation steps of deposition samples

Insoluble fraction (cellulose acetate filter paper) was digested with an acid mixture of 6 mL HNO_3 + 2 mL HF in a program given in the catalogue of the microwave oven in Table 3.2. All solutions were diluted to 25 mL with polyethylene flasks. Six empty filter blanks were also digested together with samples.

Table 3.2 Operating program for filters using Ethos 900 Milestone Microwave Oven

Step	Time (min.)	Power (Watts)
1	5	250
2	5	400
3	5	500
4	5	350

(Ventilation time: 5 minutes)

3.2.4. Preparation of Transplant Lichens for Ion Chromatography (IC) Analysis and Ammonium Determination

The unwashed transplant lichen samples were extracted with deionized water. The very little amount (~20 mg) of samples could be separated from the tree bark without moisturing this was especially valid for Xanthoria p. The small size of total amount of samples of transplants was another restriction. The birds in that area took away the transplant lichens probably for making a nest. For the last period of transplantation there were no Parmelia t. and Evernia p. samples left and very tiny amount of Xanthoria p. Nevertheless 20 mg was found to be enough for obtaining good and accurate results. The ions in samples were extracted in 5 mL of deionized water in 50 mL beakers. The beakers were decided to be shaken in an ultrasonic shaker for 1.5 hours after trying 5 hours and then they were filtrated using 0.22 μm cellulose acetate filter papers. The filtrate was analyzed for anions Cl^-, NO_3^- and SO_4^{2-} by Ion Chromatography (IC) and NH_4^+ ion by colorimetry.

3.3. Analysis of Samples

The criteria for choosing the analytical technique, the factors like sensitivity, accuracy, precision and availability to the instrument should be taken into account. In this respect Instrumental Neutron Activation Analysis (INAA), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Graphite Furnace Atomic Absorption Spectrometry (GFAAS) techniques were found to be suitable for trace element measurements in lichen and total deposition samples and Ion Chromatography (IC) was chosen for determination of major anions in transplant lichens and total deposition samples according to above mentioned criteria. The analytical techniques used for the analyses of all kind of samples are summarized in Table 3.3.

Table 3.3. Analytical techniques used in all kind of samples

Parameter measured	Analytical technique
Na, Mg, Al, Ca, Cl, K, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, As, Se, Br, Mo, Cd, In, Sb, Ba, Cs, Rb, La, Ce, Sm, Eu, Tb, Ta, Sr, Yb, Lu, Hf, Au, Th, U and Hg (in 154 lichen samples)	Instrumental Neutron Activation Analysis
Al, Mg, Fe, Mn, Na, K, Ca, V, Cr, Zn, Cd, Pb, Ni , La and Cu (in 80 lichen samples) Pb, Cu and Ni (in previously INAA analyzed samples)	(Leeman Lab) Direct Reading Dual View Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
Al, Mg, Fe, Zn, Mn, Na, K, and Ca (in deposition samples)	(Leeman Lab) Direct Reading Dual View Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
Cr, Cd and V (in deposition samples)	(Perkin Elmer 1100B) Graphite Furnace Atomic Absorption Spectrometer coupled with HGA 700 atomization unit (GFAAS)
Cl^-, NO_3^- and SO_4^{2-} (for deposition and transplant lichen samples)	Ion Chromatography (Varian 2010 (Vydac column with Jasco 875 UV/VIS detector)
H^+ (for deposition and transplant lichen samples)	WTW SenTix 97 T, low ionic strength electrode with Consort digital pH meter
NH_4^+ (for deposition and transplant lichen samples)	UNICAM 8625 UV-VIS spectrometer (Nessler's Method)

3.3.1. Determination of Elements in Lichen Samples by INAA

Highly sensitive nuclear methods of analysis have been developed for measuring concentrations of up to fifty elements in individual samples of many types of environmental samples. With the introduction of high resolution Ge(Li) γ-ray detector in the mid-sixties the instrumental neutron activation analysis (INAA) became one of the widely used analytical technique for the analysis of environmental samples.

Neutron activation analysis uses the production of radionuclides from the elements present in the sample from the identification and quantitative determination of these elements. The samples to be analyzed are irradiated with thermal neutrons in a nuclear reactor. As a result of nuclear reactions, i.e. (n, γ) reactions, between these neutrons and the stable isotopes of the elements, radionuclides may be produced. The radiation emitted by the decaying radionuclides is measured with γ-ray detector (Güllü, 1996). The number of nuclides generated in an element is directly proportional to the total number of atoms present in a sample. The radiation emitted is characteristics of each isotope and thus be used to identify and quantify individual elements (Markert, 1993).

Decay corrected activity can be calculated by the formula:

$$A_{0.} = \frac{A\lambda e^{-\lambda t_1}}{1 - e^{-\lambda(t_2 - t_1)}}$$

Where, A_0 : decay corrected count rate at the end of the irradiation, A: measured activity, t_1 :time out of the reactor to beginning of counting, t_2: time out of the reactor to end of counting, λ: decay constant of radioisotopes produced ($\lambda = 0.693/t_{1/2}$, $t_{1/2}$ is half life) (Anderson and Aras, 1987).

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 following 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.

There are sufficiently developed softwares for identification of γ-ray peaks and determination of their area. These programs mainly consist of a search for statistically significant γ-ray peaks and the resolutions of pairs of unresolved peaks and the calculation of the net counting rate due to the isotopes present in the complex spectra. The γ-ray spectra obtained at the end are processed by computer packages for each energy line and are compared with that of standards irradiated with the sample.

The INAA technique is widely used in lichen analysis. Because it has multielement capacity, high sensitivity, precision and accuracy, possibility of analyzing microsamples and reproducibility at different ranges. Thus it is reliable analytical tool in analyzing plant samples (Ölmez et al., 1985; Thompson et al., 1987; Bruin, 1990; Sloof and Wolterbeek, 1991a; Steinnes et al; 1992; Steinnes et al, 1994; Freitas, 1994; Sloof, 1995b; Guevara et al., 1995; Juichang et al., 1995; Jeran et al., 1996; Chung et al. 1997; Oliveira et al., 1997; Chiarenzelli et al., 1997; Calvelo et al., 1997; Freitas and Nobre, 1997; Saiki et al, 1997; Freitas et al., 1997; Rossbach et al., 1999; Freitas et al., 1999; Varrica et al., 2000). In order to improve and control the quality of trace element determinations of lichens, The Commission of the European Communities (through BCR programme) has established a program. Many laboratories were participated to this program and INAA was the most used and preferred technique for determining 17 elements in lichen standard reference materials (Quevaulviller et al., 1993).

3.3.1.1. Irradiation and Counting

Samples were irradiated at Massachusetts Institute of Technology (MIT), USA, 4.9 MW MITR-II research reactor at a neutron flux of $8x10^{12}$ $n.cm^{-2}.s^{-1}$ using pneumatic tube system. A pneumatic tube facility shortens the sample transfer time down to 3-4 seconds, which is crucial in INAA. Especially in the analysis of short-lived isotopes, since the irradiation time was only 1 min., the decay time would be significant for very short lived elements such as Al if the transfer time between reactor and counting system were long.

The 30-80 mg subsamples and approximately 10 mg standards (NBS SRM 1633: Coal fly ash, NBS SRM 1571: Orchard leaves, IAEA 336: Trace elements in lichen) and 4-5 mg mercury standard (NIST 8408: Mercury in sediment) were put in the acid-washed polyethylene bags and irradiated in a preacid-washed pneumatic tube sample carrier called rabbit. Before the analysis, the necessary files for the counting and computing the concentrations were prepared by using the software in the computer. INAA procedure developed by Zoller and Gordon (1970) and modified by Ölmez (1989) was used to determine the concentrations of about 40 trace and major elements in the lichen samples. These elements are Na, Mg, Al, Ca, Cl, Dy, K, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, As, Se, Br, Mo, Cd, In, Sb, Ba, Cs, Rb, La, Ce, Sm, Nd, Eu, Tb, Ta, Sr, Yb, Lu, Hf, Au, Th, U and Hg. The gamma ray energies used for the determination of elemental concentrations are given in Table 3.4.

The summary of irradiation, cooling and counting for INAA procedure is given in Table 3.5. For short-lived isotopes, around 10 samples and three standards

Table 3.4. Gamma-ray energies used in the determination of elements with their half-lives and scanning stage.

Element	Half-life	Energy (keV)	Scanning stage	Element	Half-life	Energy (keV)	Scanning stage
Al	2.25 m	1780	Short 1	Br	1.47 d	554.3	Long
Mg	9.45 m	843	Short 1	Rb	0.05 y	1076.6	Long
Ti	5.76 m	320.1	Short 1	Mo	2.75 y	140.5	Long
V	3.76 m	1434	Short 1	Cd	2.23 d	336.3	Long
Ba	1.39 h	165.9	Short 2	Sb	2.70 d	564.1	Long
Sr	0.29 h	388.4	Short 2	Cs	2.07 y	795.8	Long
Dy	2.3 h	94.7	Short 2	Nd	11 d	91.0	Long
In	0.90 h	417	Short 2	La	1.48 d	1596	Long
Na	14.96 h	1368.5	Short 2	Ce	0.09 y	145.4	Long
Cl	0.62 h	1642.3	Short 2	Sm	1.93 d	103.2	Long
K	0.52 d	1524.7	Short 2	Eu	13.5 y	1407.9	Long
Mn	0.58 h	846.6	Short 2	Tb	0.19 y	879.4	Long
Ca	4.54 d	1297	Long	Yb	4.19 d	396.3	Long
Sc	0.23 y	889.3	Long	Lu	0.02 y	208.4	Long
Cr	0.08 y	320	Long	Hf	0.12 y	482.2	Long
Fe	0.12 y	1099.2	Long	Ta	0.31 y	1221.5	Long
Co	5.27 y	1332.5	Long	Au	2.79 d	411.8	Long
Zn	0.67 y	1115.5	Long	Th	0.07 y	311.9	Long
As	1.09 d	559.5	Long	U	2.36 d	106.4	Long
Se	0.33 y	264.5	Long	Hg	2.67 d	77.0	Long

Table 3.5 Summary of the irradiation and counting scheme for instrumental neutron activation analysis

Irradiation Conditions	Cooling period	Counting period	Half-life range	Elements Determined
1 min		7 min	2-9 min	Al, V, Mg, Ti
		20 min	17 min- 15 h	Ba, Sr, In, Dy, Na, Cl, K, Mn
6 hours	3 weeks 3 days	6-10 hours	40 h-13.2 y	Ca, Sc, Cr, Fe, Co, Zn, As, Se, Br, Rb, Mo, Cd, Sb, Cs, La, Ce, Sm, Eu, Tb, Nd Yb, Lu, Hf, Ta, Au, Th, U, Hg

and with same number of samples and standards four rabbits were prepared. They were irradiated for 1 minute. At the end of the irradiation rabbit was transferred back from the reactor to the sample processing area. The rabbit was opened behind a lead shield and irradiation sample containing outer polyethylene bags were replaced with clean one. With no decay and they were immediately counted for 7 minutes (Al, Mg, Ti and V) with half-lives in the range of 2 min. (Al) to 9 min. (Mg) using four high purity germanium detectors with a resolution of < 2.0 keV at the Co-60 peak of 1332 keV coupled to 8192-channel pulse-height analyzers (Canberra, CT). At the end of this Short-1 count, they were recounted for 20 minutes to determine the gamma ray activities of the isotopes with half-lives in the range of 17 min. (Sr) to 15 hours (Na). The typical γ-ray spectra for Short-1 and Short-2 counts are given in Figure 3.4 and Figure 3.5, respectively.

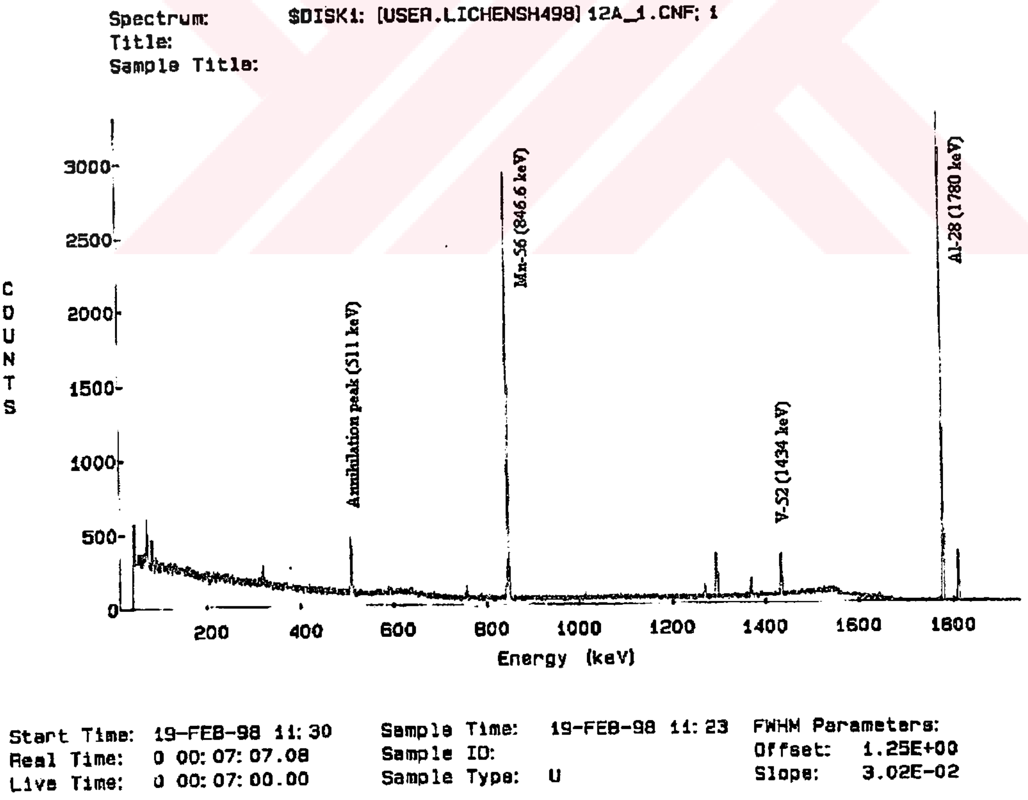
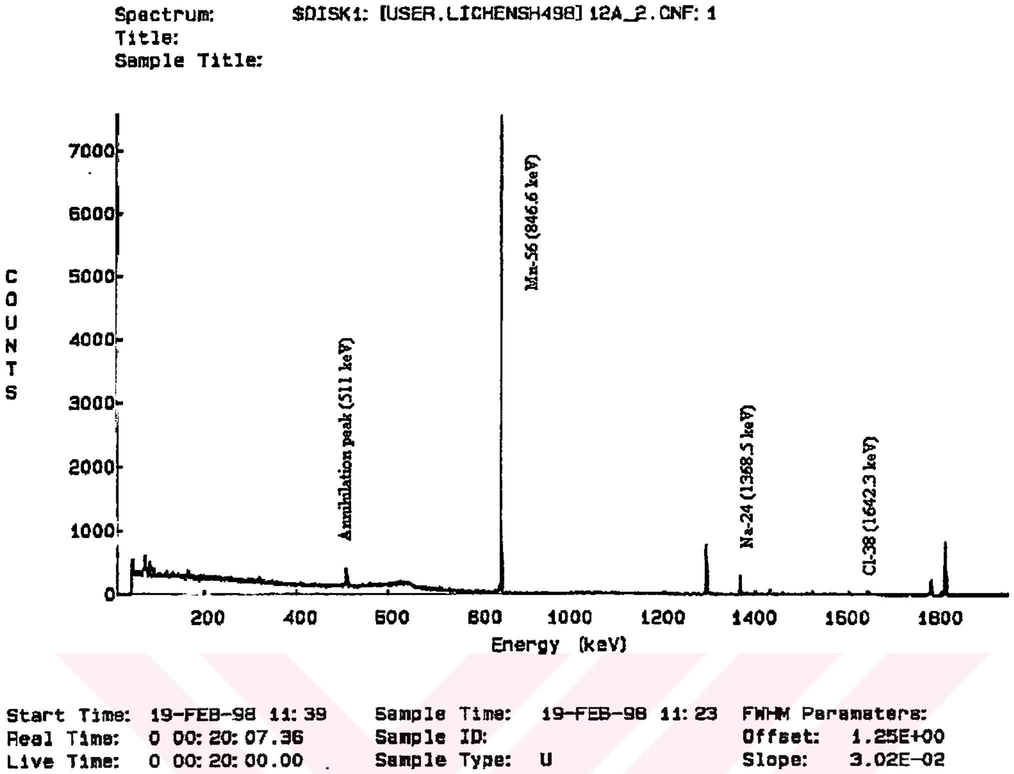


Figure 3.4. A typical gamma-ray spectra for Short-1 counts

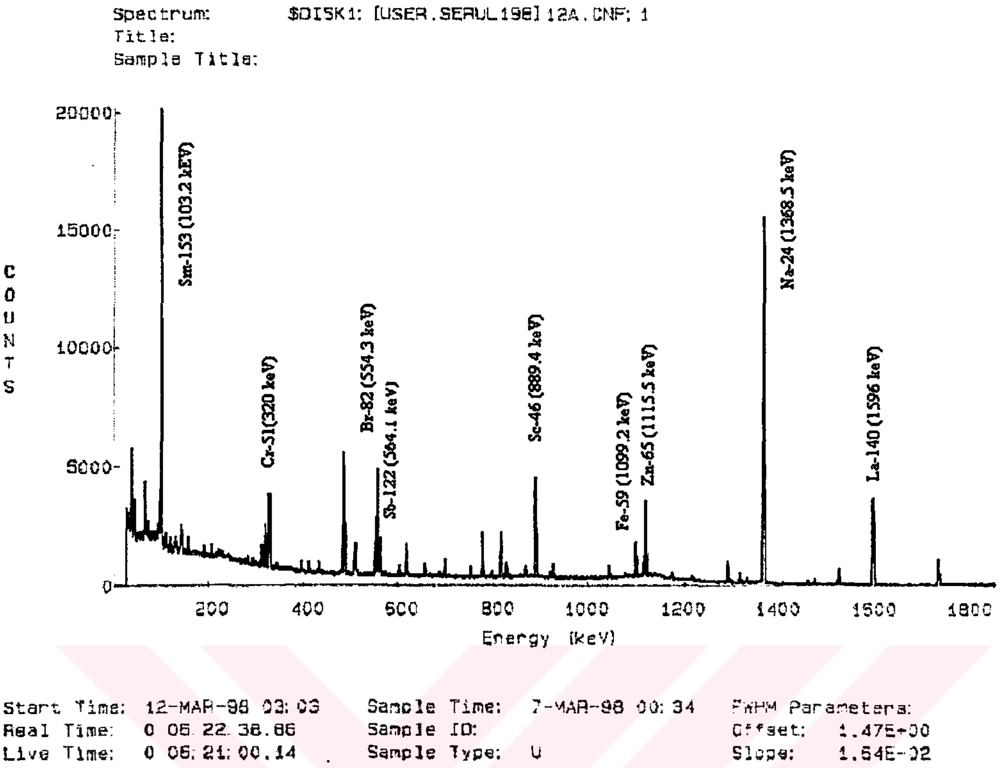


```
Spectrum:      $DISK1: [USER.LICHENSH498] 12A_2.CNF; 1
Title:
Sample Title:
```

```
Start Time:  19-FEB-98 11:39     Sample Time:  19-FEB-98 11:23   FWHM Parameters:
Real Time:   0 00:20:07.36       Sample ID:                      Offset:   1.25E+00
Live Time:   0 00:20:00.00       Sample Type:  U                 Slope:    3.02E-02
```

Figure 3.5. A typical gamma-ray spectra for Short-2 counts

For long irradiation prepared rabbit was transferred to the reactor and re-irradiated at the same neutron flux for 6 hours. After irradiation, rabbits were allowed to decay for 3 days and counted for 6 to 10 hours for the determination of the activities of the long lived isotopes with half-lives in the range of 40 hours (La) to 13.2 years (Eu). A typical γ-ray spectra for long irradiations is illustrated in Figure 3.6. Only Mercury standard is counted for 20 minutes since the concentration of Hg in the standard is very high (107 ppm).



```
Spectrum:          $DISK1: [USER.SERUL198] 12A.CNF; 1
Title:
Sample Title:
```

```
Start Time:  12-MAR-98 03:03    Sample Time:  7-MAR-98 00:34    FWHM Parameters:
Real Time:   0 05:22:38.86      Sample ID:                      Offset:   1.47E+00
Live Time:   0 06:21:00.14      Sample Type:  U                 Slope:    1.54E-02
```

Figure 3.6. A typical gamma-ray spectra for Long counts

3.3.1.2. Analysis of the Gamma-ray Spectra

The spectra obtained at the end of short and long irradiations were analyzed using computer programs, 3100 WAX software run on VMS 200 to search for the γ-peak(s) of each isotope by doing peak fitting.

Before spectra of samples were collected, the detector was calibrated for energy using the isotopes with known γ-peaks. The ^{22}Na (511 and 1274.4 keV), ^{60}Co (1173.2 and 1332.5 keV) and ^{137}Cs (661.6 keV) were used in the energy calibration. All parameters describing the samples (sample ID, irradiation time, counting time, weights etc.) were entered and saved with the spectra.

Computer program uses peak shape parameters, which can be calibrated using actual peaks in samples to improve the accuracy, consistency and speed of fitting. The peak shape function consists of a gaussian centre part and exponential upper and lower tails, which are joined smoothly to the gaussian part. The fitting intervals are automatically and manually done by the program.

The program uses the available library, which includes for each nuclide; its label, proton and neutron number, half-life, number of gamma lines and their energies and branching ratios. Since the library provided by the software includes too many isotopes, separate dedicated libraries were prepared for the analysis of long spectra.

The nuclide identification procedure is started by comparing the energy of each spectrum peak with the energies of gamma lines of the nuclides in the gamma library. If the energies match with a given tolerance for a gamma line nuclide, it is possible that this nuclide is present and its other peaks are checked.

3.3.2. Determination of Elements in Lichen and Deposition Samples by ICP-AES

Atomic emission spectrometry with inductively coupled plasma discharge as an excitation source (ICP-AES) is based on measurement of the optical emission of sample fed into the plasma in a finely dispersed form (aerosols).

The most commonly employed plasma head consists of a system of three coaxial quartz tubes through which streams of argon flow. Surrounding the top of this tube is a water-cooled induction coil that is powered by a radio frequency generator. When RF power (typically 700-1500 watts) is applied to the load coil, an alternating current moves back and forth within the coil or oscillates at a rate corresponding to the frequency of the generator. This RF oscillation of the current in the coil causes RF electric and magnetic fields to be set up in the area at the top of the torch. With argon gas being swirled through the torch, a spark is applied to the gas causing some electrons to be stripped from their argon atoms. These electrons are then caught up in the magnetic field and accelerated by them. Adding energy to the electrons by the use of a coil in this manner is known as inductive coupling. These high energy electrons in turn collide with other argon atoms, stripping off still more electrons. The collisional ionization of the argon gas continues in a chain reaction, breaking down the gas into a plasma consisting of argon atoms, electrons and argon ions forming what is known as an inductively coupled plasma (ICP) discharge. The ICP discharge appears as a very intense, brilliant white, teardrop-shaped discharge. Most samples begin as liquids that are nebulized into an aerosol a very fine mist of sample droplets in order to be introduced into the ICP. The sample aerosol is then carried into the center of the plasma by nebulizer argon flow. The functions of the ICP discharge are several fold. The first function of the high temperature plasma is to remove the solvent from or desolvate the aerosol usually leaving the samples as microscopic salt particles. The next steps involve decomposing the salt particles into a gas of individual molecules (vaporization) that are then dissociated into atoms (atomization). Once the sample aerosol has been desolvate, vaporized and atomized, the plasma has excitation and ionization functions. While the exact mechanisms for excitation and ionization in the ICP are not yet fully understood, it is believed that most of the excitation and ionization in the ICP takes place as a result of collisions of analyte atoms with energetic electrons. The chief analytical advantage of the ICP over other emission sources are derived from the ICP's ability to vaporize, atomize, excite and ionize efficiently and reproducibly a wide range of elements present in many different sample types (Boss and Fredeen,1997).

One of the important reasons for the superiority of the ICP over flames and furnaces for the above is in the high temperature (5000-10000 K) within plasma. The high temperature of the plasma sources is also responsible for the very complex nature of the emission spectra, which contain not only the lines from the atoms but also those of ions. This can be an advantage for the analysis. In the occurrence of a physical interference (line coincidence) at a definite wavelength of one element, often one can find another sensitive line sufficient for an interference free analysis. Due to the high plasma temperatures, ICP-AES is relatively free of matrix influences. Since in comparison to atomic absorption spectroscopy the radiation intensity is directly proportional to the concentration, calibration relations are linear over several orders of magnitude. However the sample preparation is the rate determining step of the total analytical procedures. The detection limits are in ng mL^{-1} range.

Another advantage of the ICP-AES that has enhanced its popularity is its inherent multielement capability. This simplifies the task of method development, since numerous sample types can be analyzed under virtually identical plasma conditions.

The Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) has become the dominant technique for trace metal analysis. The combination of low detection limits for most of the elements, wide dynamic ranges and freedom from chemical interferences has enabled the ICP to be successfully applied to many sample types. While other techniques may have some of these attributes, none possess them all. Due to high level of automation ICP-AES is used today by a large number of laboratories on a routine basis and is thus probably the most appropriate method for a number of elements in lichens (Frenzel et al., 1990; Kauppi and Halonen, 1992; Loppi and Dominicis; 1996; Loppi and Bargagli, 1996; Markert et al., 1996; Bennett and Wetmore, 1997; Monaci et al., 2000). This technique is also used as a complementary to INAA (Oliveira et al., 1997).

Leeman Labs Direct Reading Echelle Spectrometer was used in this thesis, equipped with Hildebrand grid nebulizer and dual-view (radial and axial viewing) torch. Dual-view torch allows versatility in viewing configurations: radial view for the complex matrices and axial view for high sensitivity.

The design of the Leeman Labs DRE is unique in using a fixed echelle grating with a moving detector. This design offers two important benefits. First, the echelle grating allows a high resolution spectrometer to fit on a lab bench. Second, the stationary optics provide maximum stability while direct reading, moving detector eliminates the need for a peak search for each determination, thus saving considerable analysis time.

In echelle grating instead of using high groove densities to achieve high resolution (long focal length), the blaze angle (and the order) was increased to achieve very high resolution. The echelle grating appears quite similar to a normal blazed plane grating except that short side of grooves is used. Echelle gratings are designed to be used at blaze angles greater than 45^0. In this way, a spectrometer using the echelle grating gives high dispersion without a very long focal length and high resolution without extremely fine groove spacings. The orders must be separated from each other. This is accomplished by placing an auxiliary dispersing element, usually prism or low dispersion grating in the spectrometer so that it disperses wavelengths at right angles to the echelle and thus effectively separates the orders (Borman, 1982). The Hildebrand nebulizers operate by running the sample over metal grid. The gas passes through the grid at high velocity, shearing the sample solution into fine droplets. Such nebulizers have greater transport efficiency than pneumatic nebulizers owing to the very fine droplets produced; although they also suffer from salt deposition if solutions containing high dissolved solids are aspirated. The photo multiplier tube (PMT) was used as a detector. For simultaneous analyses it requires many detectors. This is a disadvantage compared to charge coupled device detectors (CCD), which cover the entire spectral range simultaneously (Brenner and Zander, 2000). The array segments detect three or four analytical lines of high analytical sensitivity and large dynamic range and which are free from spectral interference. Compared with PMTs, CCD detector offers an improvement in quantum efficiency and a lower dark current (Ebdon et al., 1998).

3.3.2.1. Optimization of Instrumental Conditions

According to Signal/Blank ratios best line (λ) for an element was chosen. Other instrumental parameters were optimized using the directions given in the M.Sc. Thesis of Aysun Doğangün (2000). She has done similar analyses in her study. These parameters are listed in Table 3.6. According to these parameters and analysis results, the best lines of the determined elements are given in Table 3.7.

The standard deviation of the measurements based on the average of three replicates for each sample was given as default to the instrument. The rinse time is 30 seconds and uptake time is 40 seconds and the uptake time is the time it takes for the sample to move from the sample filter tip, through the pump tubing, through the spray chamber, and into the plasma and equilibrate.

Table 3.6. ICP-AES operating parameters

Parameter	Value
RF power	1.1 kW
Coolant	18 LPM
Auxiliary	0.3 LPM
Nebulizer pressure	45 psi
Pump rate	1.4 mL min^{-1}

Table 3.7. The best lines of elements determined by ICP-AES

Element	Best line (nm)
Al (I)	308.215
Ca (II)	393.366
Mg (II)	279.553
Na (I)	589.592
K (I)	766.490
Fe (I)	259.940
Mn (II)	257.610
Zn (I)	213.856
Cr (II)	205.552
Cu (I)	324.754
Pb (II)	220.353
Ni (II)	216.555
V (II)	292.402
Cd (II)	214.438
La (II)	333.749

I: atomic lines; II: ionic lines

3.3.2.2. ICP-AES Operation

Preparation for ICP-AES operation includes several steps. Since metal contamination is a potential hazard to analysis, all benches were cleaned, all plastic containers and glassware were soaked into 30 % (v/v) HNO_3 and rinsed with deionized water several times. Instrument was heated at least 25-30 minutes, first peak optics was done by Hg lamp. It is specifically designed to check the physical movement of the optics and data acquisition components of the spectrophotometer.

Since the alignment of the prism, gratings and mirrors within the spectrometers are susceptible to any changes in temperature and humidity, which cause the position of dispersed wavelengths of light in the spectrometer to vary. To compensate for these variations, the optics of the DRE are automatically realigned by periodically blocking the light from the ICP source with a mercury (Hg) emission line (296.73 nm) which establishes an optical home position which will vary over time by changing temperature and environmental conditions. All other wavelengths are aligned relative to this Hg line, allowing the spectrometer to maintain the alignments of all wavelengths through periodic realignments of the Hg line. Two versions of peak optics are available: full and quick. A full peak optics moves both the aperture plate and the PMT, and takes about 90 seconds. A quick peak optics only makes minor adjustments to the aperture plate and takes about 40 seconds. Normally a quick peak optics occurs automatically every 20 minutes and full peak optics every 120 minutes. The user can make peak optics at any time during the analysis.

Then peak source was done by choosing one of the elements namely Mn (II) (257.610), Ni (II) (231.604) and Fe (II) (259.940) free from chemical interferences. For general analytical work in aqueous matrices, the Mn1 line is recommended as the peaking line. This line will result in an observation height that will provide excellent results for all elements for any multi-element analysis. Another line that can be used for aqueous matrices is the Ni (II) line. When using an organic solvent such as kerosene, the Fe (II) line is the best choice to peak the source. The concentrations for the source peaking solutions should be approximately 10 mg L^{-1} for the Mn (II) line and 20 mg L^{-1} for the Fe (II) and Ni (II) lines (Leemans Labs manual, 1996). Manganese solution (Leeman Labs) is used to search the plasma for the best area in which to view the analyte emissions. The intensity of 10 mg L^{-1} Mn solution also gives an idea whether it is necessary to prepare a new calibration plot by checking each time when you start up the instrument. After these, if the calibration plot was done before, the accuracy of calibration plot was again checked. If there was not any problem, samples were read. Otherwise new calibration curve was prepared.

One of the important things with working with ICP-AES is to use the scanning mode properly. Scanning of all solutions (matrix, standard addition solutions, standard reference materials, blanks, water) may be very helpful in many respects before passing to read your solutions.

1) In order to select best line with respect to intensity (S/B ratio), interferences, shape of the peak.

2) In order to see the concentration ranges of elements in some randomly selected samples. This gives an idea about the addition of standards for preparing standard addition calibration curves. Also the ranges of the calibration curves can be arranged accordingly for both preparing standard addition and aqueous calibration curves.

3) In order to compare matrices of standard reference material and analyte sample especially if one can not find the SRM which exactly match with your matrix. After the scanning process one can decide whether the SRM requires dilution or not, especially working with aqueous calibration curves in order to insert the intensity of SRM in the dynamic range of the calibration plot and match the backgrounds of SRM with analyte sample

The sequential mode of instrument was used for all analyses. Rather than moving the grating, it is instead possible to move a detector to a desired position in the focal plane of a desired wavelength of light presented from the diffraction grating. Echelle gratings are especially suited for a configuration of this kind, providing a highly-dispersed X-Y image pattern in which light is sorted by order as well as wavelength. Using an exit aperture plate to precisely define wavelength positions from the echelle grating, a detector (PMT) can rapidly and exactly be positioned sequentially to acquire any wavelength desired.

3.3.2.3. Standard Addition Method

For some samples, it is difficult to prepare standards that are sufficiently similar to the sample solution. This may occur when the samples contain very high and variable concentrations of matrix materials, or when the samples contain very high solids. In such instances the standard addition method can be used to correct the nonspectral interferences. It should be noted that the standard addition method could not be used to correct any background attenuation interference. Because of the influence of the matrix upon the emission signal it is essential to ascertain that the analyte additions behave in a similar manner to the analyte already in the sample during atomization.

Standard addition methods were used for all calibrations. The orchard leaves and the lichen standard were tried as the matrix for the preparation of the calibration curves and then the lichen standard was chosen as the best matrix by double checking both with the results with standard reference materials and the results of samples which were analyzed by INAA. Standard reference material was diluted 1:2 with a deionized water and then was used as matrix in order to not change the matrix with high volume of additions of elements. 1000 mg L^{-1} (Aldridge) or 100 mg L^{-1} (Leeman Labs) standard solutions of elements were used for the additions.

Two different calibration curves were prepared for low (Mn, Zn, La, Cr, Ni, Cu, Pb, Cd and V) and high (Al, Fe, Mg, Na, Ca and K) concentration elements according to concentration ranges of elements obtained from INAA data. For all elements except for Ca axial view was used. Axial systems can potentially suffer from easily ionizable elements because the detector is saturated with the photons and gives the same intensity value for the concentrations greater than 10 mg L^{-1} solution of Ca. That's why for Ca, radial view was used because of its very high concentrations which made the dynamic range of calibrations curves smaller and all sample solutions required dilutions in all lines of Ca with axial view.

3.3.3. Analysis of Deposition Samples and Transplant Lichens

3.3.3.1. ICP-AES Analysis

The optimized ICP-AES conditions for lichen samples was also suitable for deposition samples and thus they were used to determine the elements (Al, Ca, Ba, Mg, Na, K, Fe, Zn and Mn) in soluble and insoluble fraction of deposition samples. Aqueous calibration curves were prepared in order to find the concentrations of elements in both fractions. To check the accuracy of the analysis GSP-1 (U. S. Geological Survey), GSP-2 (U. S. Geological Survey, Granodiorite, Silver plume Colorado same location to provide material for GSP-1) and STM-1 (U. S. Geological Survey, Syenite) were used as standard reference materials.

3.3.3.2. Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

Graphite Furnace Atomic Absorption Spectrometry (GFAAS) has long been the preferred analytical method for the routine determination of trace metals in environmental and biological samples owing to its reliability, sensitivity, low detection limits at ng mL^{-1} levels and relatively low cost (Al-Momani et al., 1995; Udas et al. 2000; Bettinelli et al., 2000). For this reason, GFAAS was the choice for determination of these trace elements (Cr, Cd and V). In this work, a Perkin Elmer 1100B Model with HGA 700 electrothermal atomizer unit, graphite furnace atomic absorption spectrometer was used to determine the concentrations of these three trace elements. The concentrations of the elements were not detectable by ICP-AES, since their concentrations were below the detection limits of this technique.

Argon was used as a carrier gas and a deuterium lamp was used to correct the non specific background absorption. The argon gas was passed through the graphite tube during the drying, ashing and cleaning steps with a gas flow rate of 300 mL min^{-1}, while it was reduced to zero during atomization step. Instrumental settings and the temperature programs for each element are listed in Table 3.8, Table 3.9.

Table 3.8. Recommended parameters for GFAAS technique

Element	Cd	Cr	V
Graphite tube type	uncoated	pyrocoated	pyrocoated
λ, nm	228.7	357.8	318.4
Slit Width, nm	0.7	0.7	0.7
Injection volume, μL	30	30	40
Lamp current, mA	3	16	20

Table 3.9. Temperature program used in GFAAS for the trace element determination in deposition samples

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

Some refractory and carbide forming elements like Cr showed a memory effects from the graphite tube after injection the sample. When the concentrations of Cr is high, it is deposited at the colder regions of the graphite tube and appear as a memory effect during next injections. Using additional cleaning step in the temperature program of the instrument for about 6 seconds after the completion of all temperature program steps solved this problem.

3.3.3.3. Ion Chromatography (IC) Analysis

Water soluble anions Cl^-, NO_3^- and SO_4^2 are important major components of deposition samples to be determined by Ion Chromatography (IC). It is a versatile, selective and sensitive method for the determination of a variety of anions and cations at trace and ultra-trace levels in one run in various fields involving ionic analysis such as industrial water matrices, foodstuffs, rain, snow, aerosol (Mosko, 1984; Frankenberger et al., 1990; Pereira, 1992; Karakaş and Tuncel, 1997). The major reason for the rapid growth in popularity of IC is its usefulness in the environmental field.

Soluble fraction of deposition samples and water extract of transplant lichens were analyzed for Cl^-, NO_3^- and SO_4^{2-} by using a Varian model 2010 IC coupled with a VYDAC 302 IC anion exchange column and a JASCO UV/VIS 875 detector. The IC system was connected to a personal computer. A program called PEAK 2 software was used for data acquisition via interface card with the IC detector. The operation conditions of the Ion Chromatography are given in Table 3.10. The column packing material is high purity spherical silica with 20 μm in size with low surface area. Silica-based ion exchange column is preferred because of its better efficiency and overall performance than polymer-based columns. All solutions were filtered with a 0.2 μm size celulose acetate filter paper to remove bacteria. Leaving the column in acetonitrile (30% (v/v)) also prevented the bacterial growth which shortens the column life when the column is not used for 2 days or more.

The mobile phase used was 1.0 mM phthalic acid buffered to pH between 4.93 and 4.95 with the additions of saturated sodium tetraborate solution. To prepare mobile phase 0.3326 g phthalic acid was dissolved in sufficient amount of water and diluted to 2 L. The mobile phase was degassed for approximately 15 minutes to expel the dissolved air, which may de-stabilize the flow of mobile phase. Calibration curves were prepared with 1, 3, 5, 10, 15 mg L^{-1} standard aqueous solutions (multi standard) made from Cl^- (from NaCl), NO_3^- (from $NaNO_3$), and SO_4^{2-} (from K_2SO_4). All chemical were from Merck and extra pure.

For the analysis of major anions a 100 μL of aliquot was injected and pumped through an ion exchange column. The eluent used was phthalic acid, which absorbs in UV range (254 nm). Therefore a decrease in the background concentration was observed during the elution of the individual anion. This method called as indirect UV method. During the analysis, the chromatogram was first observed on the screen of the computer then about ten minutes after the injection, three peaks of Cl^-, NO_3^- and SO_4^{2-} were obtained. Concentrations of the anions were calculated according to the calibration that was loaded to the program after the peak identification.

The concentrations obtained for these anions agreed with the SRM NIST simulated rain water 2694a-I. Also calibration plots were checked with the aqueous standard solutions.

Table 3.10. Operating parameters for ion chromatography

Eluent (mobile phase)	1.0 mM phthalic acid
Anion exchange column	302 IC
Sample injection volume	100 µL
Buffered pH (mobile phase)	4.93-4.95
Mobile phase flow rate	3.0 mL min^{-1}.

3.3.3.4. Ammonium Determination

Soluble fraction of deposition samples and water extracts of transplant lichens were analyzed directly by adding Nessler's reagent to the sample, whenever the concentration exceeds the linear calibration curve, a suitable dilution factor was performed. Ammonium ion in samples was determined using UNICAM 8625 UV-VIS Spectrometer. Direct Nesslerization method was used (ASTM, 1979). All chemical were from Merck (extra pure). In this method, Nessler's reagent which is an alkaline solution of mercuric iodide (K_2HgI_4) combines with NH_3 to form a yellowish-brown colloidal dispersion which the intensity is directly proportional to the concentration of NH_3 originally present. The following reaction takes place in Nesslerization;

$$2HgI_4^{2-} + 2NH_3 \rightarrow NH_2Hg_2I_3 + NH_4^+ + 5I^-$$

One mL Nessler reagent and 0.5 mL of sodium potassium tartrate solution to prevent cloudy tubes were added to 10 mL of sample solution. The absorbance of the colored solution was measured at 425 nm in a 1 cm path length glass cell after waiting 20 minutes. Ammonium standard stock solution was prepared from ammonium sulfate after drying the solid reagent at 100°C for about 1 hour.

3.4. Quality Assurance

3.4.1. Blanks for Lichen Analyses

For ICP-AES analyses, the only blank was laboratory blank. The preparation of these blanks in the laboratory is particularly important to estimate the contribution of each reagent during digestion procedure and laboratory process and to find the sources of contamination if a contamination problem occurs.

to be

The blank used in INAA analyses was the acid washed polyethylene bags. Since lichen samples were irradiated and counted with these bags, the contribution from bags to the concentrations of all elements in samples should be known. The average concentrations of all elements for 5 acid washed polyethylene bags in ppm are given in Table 3.11. Although the blank values of Ca (27 ppm), Al (23 ppm), K (22 ppm), Na (18 ppm) and Fe (12 ppm) seem high, their contributions to the concentrations in samples are not significant when the sample to blank ratios considered as given in Table 3.12. Except for Au sample to blank ratios of all elements are higher than 10. Standard deviations are generally higher than the averages. This is only due to the different ranges of concentrations of elements in samples because approximately 90 % for all data, ratios are above 10 and for the rest of data ratios are not below 2. This means that the elemental contributions from bags to the concentrations of elements in the samples are negligible. However since the weights of SRM's were 10 fold less than the weights of samples the blank contributions were significant to the concentrations of SRM's when calculating the accuracy of the results.

Table 3.11. The average concentrations and standard deviations (STD) of elements determined from the 5 acid washed polyethylene bag blanks by using INAA technique

Element	Avg. Conc. ± STD (ppm)	Element	Avg. Conc. ± STD (ppm)
Al	23 ± 3.2	Se	0.026 ± 0.009
Mg	6.7 ±2.0	Br	0.16 ± 0.11
V	0.16 ± 0.04	Rb	0.27 ± 0.20
Ba	1.6 ± 0.5	Mo	0.016 ± 0.007
Cl	5.3 ± 1.6	Cd	0.010 ± 0.002
In	0.001 ± 0.0009	Sb	0.0047 ± 0.022
Mn	0.095 ± 0.006	Cs	0.053 ± 0.099
K	22 ± 4.2	La	0.0096 ± 0.0036
Na	18 ± 1.9	Ce	0.014 ± 0.005
Ca	27 ± 13	Sm	0.0019 ± 0.0003
Sc	0.0035 ± 0.0003	Eu	0.003 ± 0.002
Cr	0.28 ± 0.16	Tb	0.0012 ± 0.0010
Fe	12 ± 2.8	Lu	0.0002 ± 0.00008
Co	0.036 ± 0.017	Hf	0.0043 ± 0.0029
Zn	3.82 ± 0.97	Ta	0.014 ± 0.011
As	0.0091 ± 0.068	Au	0.00042 ± 0.00020
Hg	0.003 ± 0.002	Th	0.0037 ± 0.0018

Table 3.12. Sample to blank ratios of elements (the numbers in parenthesis are the number of samples)

Element	Ratio ± STD	Element	Ratio ± STD
Al	140 ± 160 (120)	Se	26 ± 21 (100)
Mg	245 ± 110 (120)	Br	55 ± 50 (120)
Ti	97 ± 130 (117)	Yb	120 ± 140 (117)
V	40 ± 50 (120)	Rb	200 ± 190 (115)
Ba	28 ± 38 (108)	Mo	30 ± 60 (102)
Cl	76 ± 60 (120)	Cd	30 ± 60 (56)
In	10 ± 14 (38)	Sb	95 ± 270 (120)
Mn	625 ± 1570 (120)	Cs	170 ± 290 (113)
K	220 ± 80 (120)	La	200 ± 230 (120)
Na	20 ± 30 (120)	Ce	190 ± 220 (120)
Sr	30 ± 34 (44)	U	27 ± 40 (55)
Ca	90 ± 130 (119)	Sm	145 ± 160 (120)
Sc	170 ± 210 (119)	Eu	24 ± 26 (106)
Cr	35 ± 100 (120)	Tb	36 ± 40 (100)
Fe	120 ± 420 (119)	Lu	115 ± 130 (120)
Co	30 ± 30 (106)	Hf	56 ± 72 (115)
Zn	26 ± 110 (119)	Ta	13 ± 16 (62)
As	400 ± 360 (120)	Au	5 ± 8 (120)
Hg	36 ± 70 (120)	Th	320 ± 400 (120)

3.4.2. Clear Room Effect and Homojenity Test for Lichen Samples

Lichen samples were detached from tree bark in a clean room but not under HEPA filters. They were hold in folded filter papers during the separation process and after separation they were dried in the same folded filter papers in a closed glass box approximately one day at room temperature by devoting maximum care to avoid the dust. In order to check whether this separation process is suitable comparing with the separation process under HEPA filters in clean room, two samples were also cleaned under the HEPA filters. The mean ratio of the clean room with HEPA filters to clean room without HEPA filters were listed with their standard deviations in Table 3.13. As can be seen from the table, the results showed that the errors for the mean ratios were within 15% error limit except for the elements Fe, Cs, La, Ce, Lu and Hf due to clean room without HEPA filters but higher values are also acceptable for these elements.

The lichen samples were not powdered in order to reduce any contamination risk. Therefore to check the homogenity of samples, three samples were randomly selected and three subsamples from each sample were prepared and analyzed. The coeffiecient of variations (CV) were calculated for each element in three samples and results are given in Table 3.14. The elements Ti, In, Hg and U have CV values greater than 20 in at least two of the samples, because in one sample high CV can be caused by the uncertainties in the analysis. Other elements are homogeneously distributed in lichen samples. Homogenity of moss samples was also verified for the elements Sc, V, Cr, Co, As, Se, Br and Sb in the study of Steinnes et al., (1994).

Table 3.13. The ratios, mean ratios and standard deviations of concentrations of elements in lichens detached from the tree bark in the clean room with HEPA filters to that in the clean room without HEPA filters in two samples

Element	Ratio for Sample 1	Ratio for Sample 2	Mean Ratio ± STD
Al	1.11	0.55	0.84 ± 0.40
Mg	0.97	0.73	0.85 ± 0.17
Ti	1.09	0.81	0.95 ± 0.19
V	1.08	0.71	0.89 ± 0.26
Ba	1.26	0.73	0.99 ± 0.37
Cl	1.02	1.05	1.03 ± 0.025
Mn	1.05	0.74	0.89 ± 0.22
K	0.97	0.99	0.98 ± 0.012
Na	1.13	0.79	0.96 ± 0.24
Ca	1.09	0.82	0.95 ± 0.19
Sc	1.00	0.69	0.85 ± 0.22
Cr	0.80	1.71	1.25 ± 0.64
Fe	0.91	0.69	0.80 ± 0.15
Co	0.86	1.00	0.94 ± 0.10
Zn	0.84	1.47	1.15 ± 0.44
As	0.93	1.00	0.97 ± 0.047
Se	0.64	1.86	1.25 ± 0.86
Hg	1.00	0.97	0.98 ± 0.022
Br	1.13	1.31	1.22 ± 0.12
Rb	0.94	0.91	0.92 ± 0.018
Cd	1.08		
Ni	1.81		
Cu	0.98		
Pb	2.78		
Sb	1.00	0.87	0.94 ± 0.089
Cs	0.66	0.84	0.74 ± 0.13
La	0.77	0.83	0.80 ± 0.038
Ce	0.72	0.63	0.67 ± 0.067
Nd	1.14	1.44	1.29 ± 0.21
Sm	0.88	0.88	0.88
Yb	1.17	0.60	0.88 ± 0.39
Lu	0.92	0.63	0.78 ± 0.21
Hf	0.53	0.76	0.65 ± 0.16

Table 3.14. Coefficient of variation of elements in three subsamples of three samples

Element	CV of sample 1	CV of sample 2	CV of sample 3
Al	2.4	7.6	13
Mg	3.8	10	3.3
Ti	27	17	24
V	9	11	19
Ba	14	30	6.7
Cl	4.1	4.4	3.1
In	8.5	19	28
Mn	3.2	1.8	5.3
K	1.1	5.2	7.7
Na	2.5	14	4.8
Sc	5.3	11	7.5
Cr	13	27	14
Fe	1.0	0.50	1.9
Co	12	17	21
Zn	14	7.0	4.0
As	8.3	4.0	2.3
Se	11	17	
Hg	29	27	20
Br	2.0	10	8.0
Rb	4.0	6.6	18
Mo	14	24	8.0
Cd	16	14	5.7
Sb	8.0	7.0	16
La	2.4	8.5	12
Ce	12	19	17
Sm	5.0	9.0	12
Yb	1.7	15	1.5
Lu	5.9	26	8.3
Hf	12	22	30
Au	13	3.3	
U	28	27	

3.4.3. Analyses of Standard Reference Materials

For quality assurance, the Lichen and Orchard Leaves standard reference materials were both analysed by INAA. Figure 3.7 and Figure 3.8. show the ratio (INAA/certified value (C.V.) or INAA/information value for IAEA 336 lichen reference standard material) for Orchard Leaves and Lichen standards, respectively.

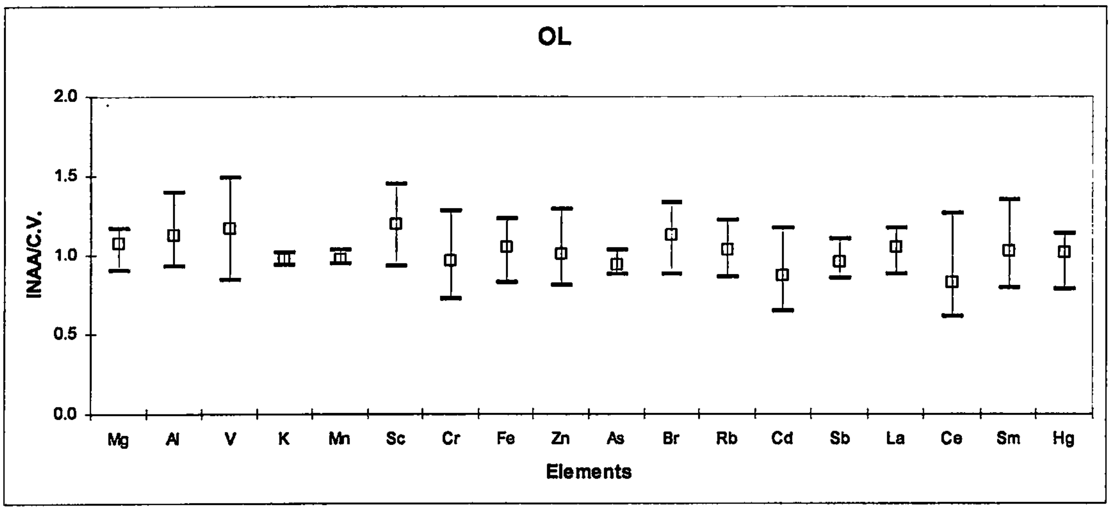


Figure 3.7. Ratio (INAA/certified values) for NIST 1571 Orchard Leaves

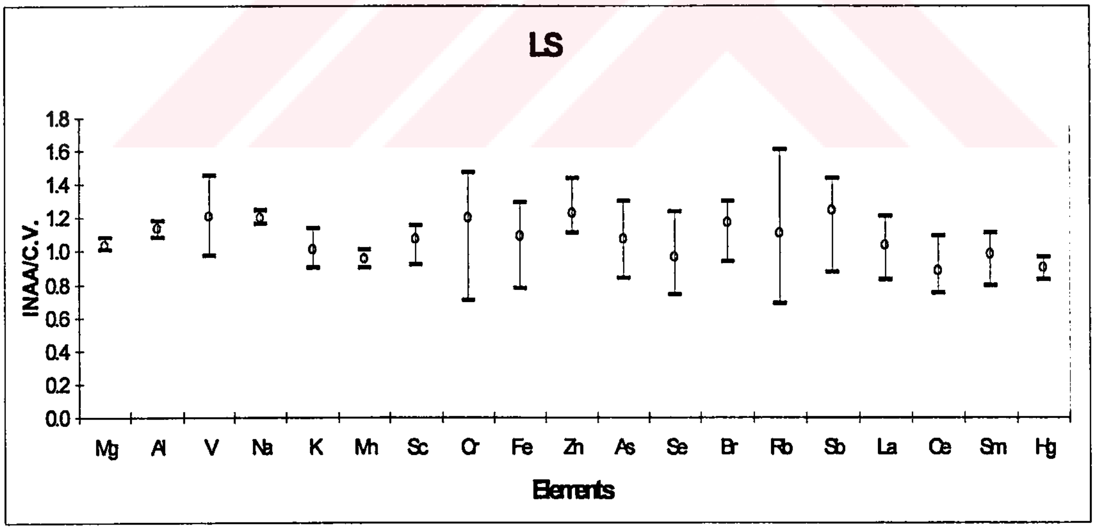


Figure 3.8. Ratio (INAA/certified values) for IAEA 336 Lichen

It is observed that the average INAA/C.V. values are in the interval 0.8 – 1.2 for all of the elements in both standard reference materials. Other than average values we can see the minimum and maximum values from the graphs. They are also reasonable values mostly changing between 0.7 and 1.3. These ranges were obtained from 10 different experiments.

The accuracy check of ICP-AES analyses was done using the same SRM's. Accuracy check was done each time before starting the experiment and repeated approximately every 30 samples by checking the intensities. Standard addition method was used in order to calculate concentrations. The accuracy results of the technique are given in Table 3.15. In general our results were in good agreement with NIST 1571 Orchard leaves (except for Na) other than Lichen 336 standard. Sometimes concentrations of some elements in SRM's may not be enough to detect by ICP-AES. However when you are comparing the results obtained for real samples by independent analytical techniques (e.g. ICP-AES with INAA) then you can obtain very good correlations as will be mentioned in section 3.4.5 because the elemental concentrations of most of the samples are higher than that in SRM's.

Deposition samples were analyzed with ICP-AES. The accuracy results are given in Table 3.16. The analyses of samples were resumed if the results were within ± 10% of the certified values. The aqueous calibration curves were used in order to calculate the concentrations. The standard reference materials (GSP-1 (U. S. Geological Survey), GSP-2 (U. S. Geological Survey, Granodiorite, Silver plume Colorado same location to provide material for GSP-1) and STM-1 (U. S. Geological Survey, Syenite)) were diluted ten times in order to simulate the matrices to aqueous matrix. Standard reference material GSP-1 generally gave better results.

Table 3.15. Concentrations of elements observed in standard reference materials (mg kg^{-1}) analyzed by ICP-AES (number of samples are given in the parenthesis)

Element	Found ± std	IAEA 336 ± std	Found ± std	NIST 1571 ± std
Al	650 ± 60 (13)	680 ± 110	350 ± 70 (10)	320 ± 110
Mg*	780 ± 30 (9)	610	6090 ± 480 (12)	6000 ± 400
Na	265 ± 21 (8)	320 ± 40	140 ± 23 (9)	82 ± 6
K	1410 ± 64 (9)	1840 ± 200	12810 ± 770 (12)	14800 ± 500
Fe	410 ± 50 (9)	430 ± 50	265 ± 28 (10)	280 ± 20
Ca*	2640 ± 34 (3)	2600	15380 ± 245 (2)	20400 ± 700
Cd*	0.159 ± 0.074 (2)	0.117 ± 0.017	0.180 ± 0.072 (10)	0.162 ± 0.029
V*	1.47 ± 0.17 (2)	1.47 ± 0.22	0.590 ± 0.10 (2)	0.510 ± 0.11
Cr*	1.03 ± 0.24 (7)	1.06 ± 0.17	2.7 ± 0.3 (6)	2.6 ± 0.6
Ni	1.52 ± 0.56 (8)		1.1 ± 0.45 (10)	1.5 ± 0.4
Cu	3.1 ± 0.6 (9)	3.6 ± 0.5	11.8 ± 0.2 (14)	11.8 ± 0.6
Pb*	4.9 ± 1.04 (5)	4.9 ± 0.6	43 ± 4.6 (10)	44 ± 2.0
Mn	59 ± 6.1 (7)	63 ± 7.0	86 ± 3.8 (9)	86 ± 3.0
Zn	23.8 ± 2.01 (8)	30.4 ±3 .4	22 ± 7.9 (14)	25 ± 2.0

* Information values of elements in IAEA 336 SRM

Table 3.16. The accuracy results of ICP-AES technique for deposition samples

Element	STM-1		GSP-1		GSP-2	
	Found values	Certified values	Found values	Certified values	Found values	Certified values
Al (%)	10.5	9.74 ± 0.12	8.3	8.2	6.22	7.88 ± 0.11
Ca (%)	0.66	0.77 ± 0.043	1.39	1.46	1.2	1.5 ± 0.04
Fe (%)	3.2	3.6 ± 0.07	3.2	3.01	3.08	3.43 ± 0.11
K (%)	3.2	3.5 ± 0.06	4.58	4.57	3.95	4.48 ± 0.12
Mg (%)	0.059	0.060 ± 0.012	0.660	0.596	0.51	0.58 ± 0.02
Na (%)	5.82	6.63 ± 0.15	1.95	2.08		
Zn (µg g^{-1})	237	235 ± 22	106	103	110	120 ± 10
Mn (µg g^{-1})	1770	1700 ± 120	322	310		

Three elements were analyzed with AAS because detection limits of ICP-AES were not enough to determine these elements. For the accuracy check with AAS for deposition samples, three SRM's were used: NIST 1646 Estuarine Sediment, NIST 2704 Buffalo River and GSP-1 U. S. Geological Survey. The concentrations of elements found were compared with the certified results in Table 3.17. The found results were very close to the certified ones.

Table 3.17. The comparison of average concentrations found in this study with certified average concentrations by using GFAAS

Element	Found values ± std			Certified values		
μg g^{-1}	GSP-1	2704	1646	GSP-1	2704	1646
Cr	13.4±0.85	129±1.5	73±2.3	13.0	135	76
V	50±1.9	97±3.6	98±4.1	53	95	94
Pb		159±0.42	29±1.9		161	28.2

The accuracy check of IC was done using SRM NIST simulated rain water 2694a-I, The accuracy for Cl^-, NO_3^- and SO_4^{2-} were 6.7%, 14% and 4.5%, respectively. The % error in accuracy of nitrate is high most probably because of bacterial growth in SRM during long time usage of this SRM.

3.4.5. Comparison of ICP-AES and INAA Techniques for Some Elements

As mentioned before, the common elements (Al, Ca, Mg, Fe, K, Na, Mn, Zn, Cd, V and Cr) were measured by using INAA and ICP-AES techniques in lichen samples. The results are illustrated as scatter plots. The number of samples, which were compared, and the equations with R^2 values are also shown on the graphs. It can be seen that the concentrations of Al, V, Mn, Na, Fe and Zn obtained in both techniques show very high correlation as shown in Figure 3.9. The R^2 values change in the range of between 0.9111 (for V) and 0.9572 (Fe). The rest of the elements are also fairly good correlated in both techniques as shown in Figure 3.10. The R^2 values change in the range of between 0.6919 (Mg) and 0.891 (Ca) and the R^2 values

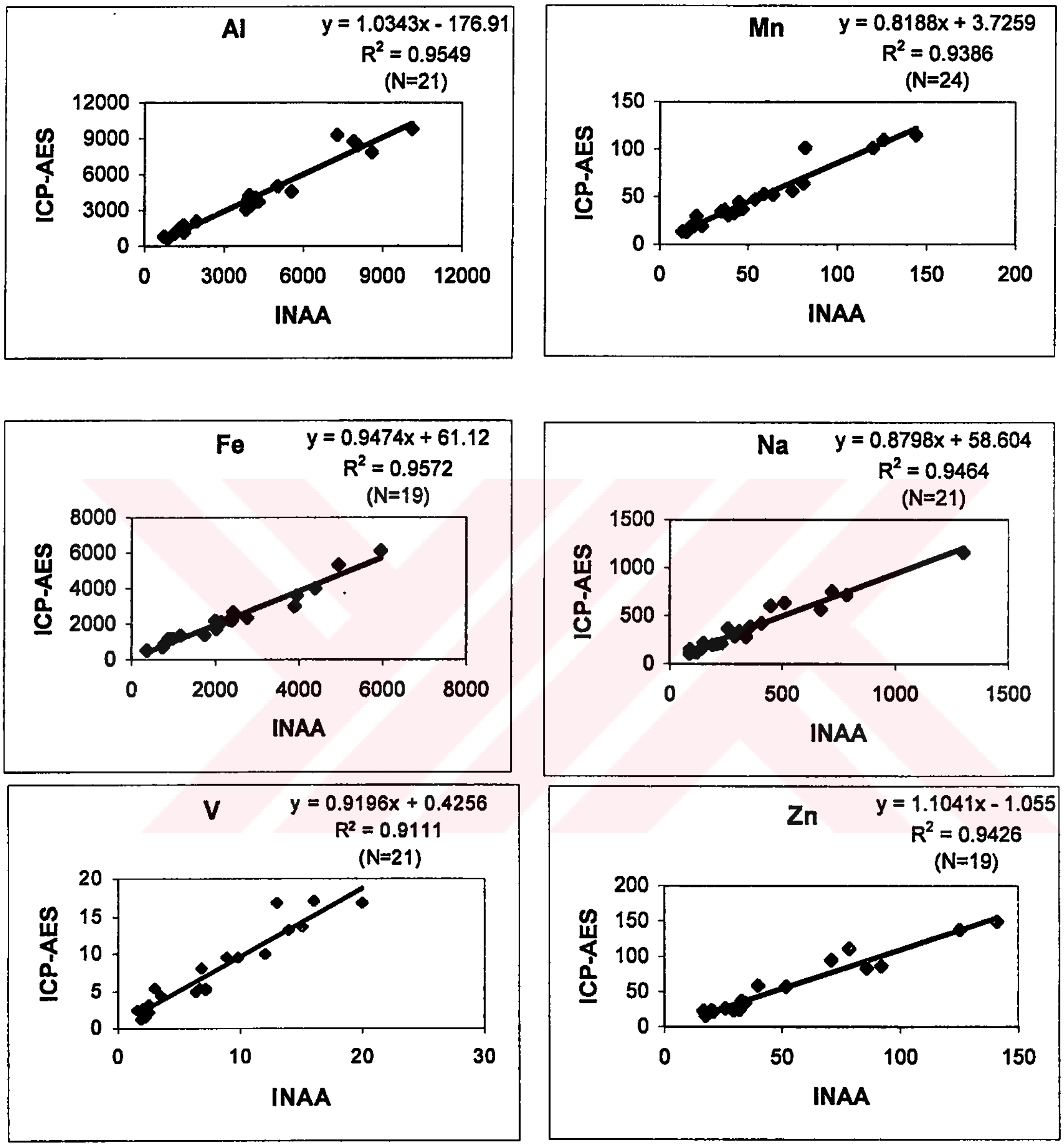


Figure 3.9. The scatter plots of comparison of INAA and ICP-AES techniques for the elements Al, Mn, Fe, Na, V and Zn ($p<0.01$).

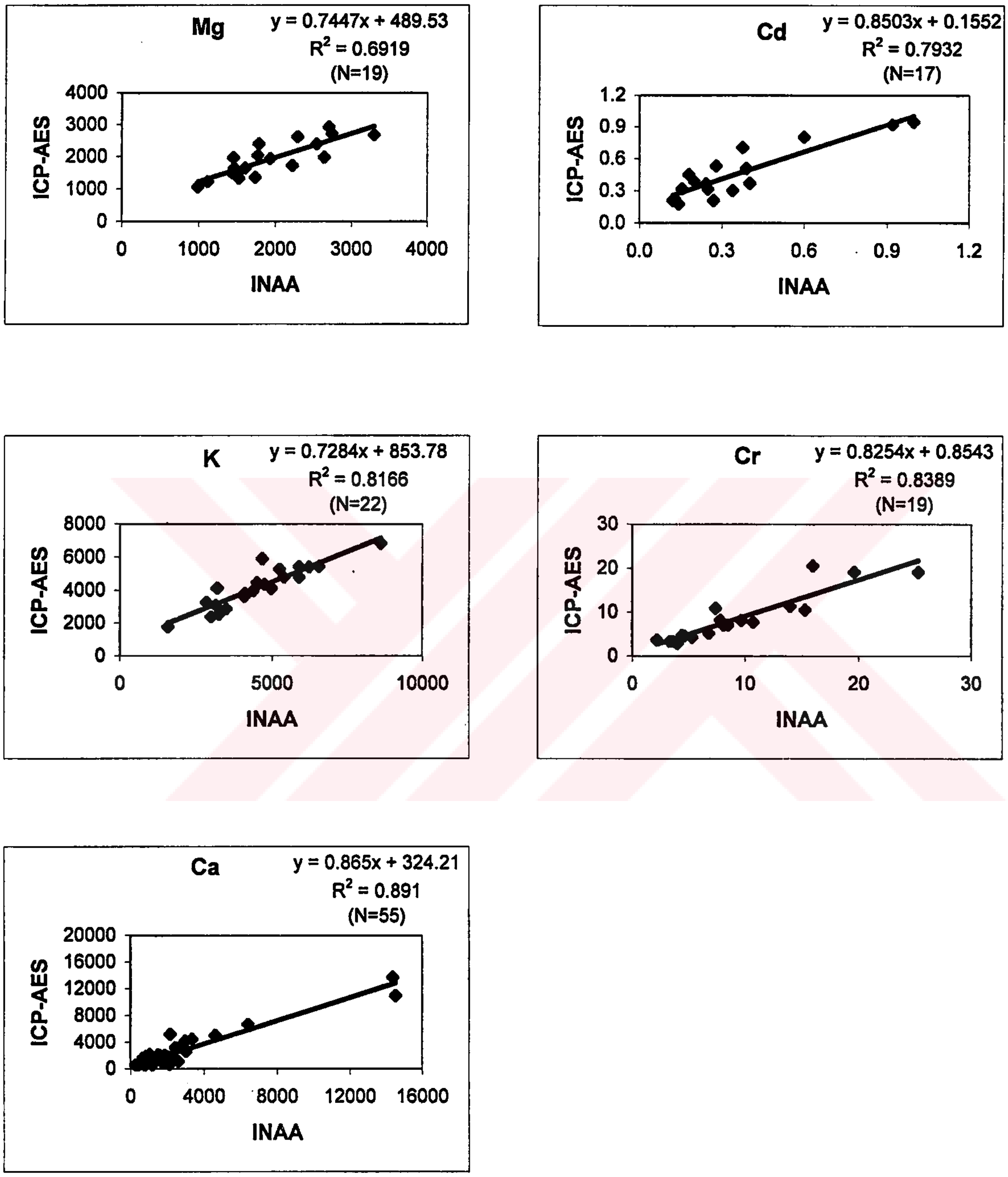


Figure 3.10. The scatter plots of comparison of INAA and ICP-AES techniques for the elements Cr, Cd, K, Ca and Mg ($p<0.01$).

greater than 0.7 are assumed to be acceptable lower limit. The results tell us that both techniques are comparable techniques for analyzing the lichen samples for these elements with good accuracy.

3.5. Detection Limits

In INAA technique, the detection limit is controlled by several factors like intensity of neutron flux, the background in the gamma-ray spectrum, composition and geometry of the sample and experimental parameters. Therefore the detection limit in the INAA is unique to each sample and determined by both the element under consideration and the presence of other elements. If the concentration of an element is too high, it yields a very high background levels (compton peak of that element overlaps with the peak of other element with small concentrations) in the spectra and results in poor signal to noise ratio. In this case the detection limits are higher values than actual value in that sample for other elements. The detection limits for INAA are based on actual measurements from the samples and include matrix effects due to the other elements present in the samples. The calculations of detection limits were done by the equation given by Jaclevic and Walter (1977).

$$C = 3.29\frac{\left(\frac{R_b}{t}\right)^{1/2}}{S}$$

Where

C = detection limit, µg,

R_b = counts/s of background under the photo peak used,

t = counting time of spectrum used for determination of C, seconds,

S = sensitivity, $\frac{(counts/s)}{\mu g}$.

The calculated typical detection limits of all elements determined by INAA technique are given in Table 3.18 together with arithmetic and geometric mean and their standard deviation values of all data set. The detection limits of elements except for Ba, Cd, In, Mo, Se, Sr, Ta and Tb are very low compared with the average values of elements.

In ICP-AES analysis, the detection limits of the measured elements were defined as the concentration of an element which will give a signal three times higher than the standard deviation of 10 replicate analysis of one acid blank.
Detection limit was calculated according to the following formula:

$$C_m = \frac{S_m - \overline{S}_{bl}}{m}$$

where $\overline{S}_{bl}$ is the mean blank signal and S_m is the minimum distinguishable analytical signal which is equal to $S_m = \overline{S}_{bl} + ks_{bl}$ where s_{bl} is the standard deviation of the blank, m is the slope of the calibration plot and k was taken as 3. Table 3.19 gives the detection limits of ICP-AES.

Table 3.18. The typical detection limits and arithmetic mean and geometric means with their standard deviations of the elements determined by INAA technique for lichen samples

Elements	Detection Limit ($\mu g\ g^{-1}$)	Arithmetic Mean (STD) ($\mu g\ g^{-1}$)	Geometric Mean (STD) ($\mu g\ g^{-1}$)
Al	4.6	2650 (3150)	1950 (1.06)
As	0.0098	4.1 (2.2)	3.6 (1.05)
Au	0.17*	1.97 (2.28)*	1.31 (1.10)*
Ba	22	37 (57)	25 (1.09)
Br	0.027	6.5 (4.9)	5.4 (1.07)
Ca	460	1940 (1960)	1450 (1.06)
Cd	0.20	0.30 (0.38)	0.19 (1.08)
Ce	0.17	2.2 (2.2)	1.6 (1.09)
Cl	9.0	300 (260)	240 (1.06)
Co	0.083	0.96 (1.18)	0.71 (1.08)
Cr	0.46	5.1 (5.9)	3.4 (1.08)
Cs	0.10	1.1 (2.05)	0.49 (1.13)
Dy	0.057	0.30 (0.35)	0.19 (1.12)
Eu	0.022	0.067 (0.076)	0.048 (1.10)
Fe	49	1650 (1810)	1250 (1.06)
Hf	0.047	0.24 (0.34)	0.14 (1.12)
Hg	0.019	0.12 (0.23)	0.069 (1.08)
In	0.036	0.015 (0.012)	0.010 (1.18)
K	330	3490 (2320)	2620 (1.07)
La	0.0031	1.71 (1.80)	1.27 (1.06)
Lu	0.0028	0.018 (0.021)	0.013 (1.09)
Mg	86	1610 (710)	1490 (1.03)
Mn	0.13	36 (37)	28 (1.06)
Mo	0.29	0.36 (0.44)	0.25 (1.10)
Na	4.6	285 (435)	200 (1.07)
Nd	0.53	1.5 (1.7)	1.1 (1.09)
Rb	1.9	11.7 (12.7)	9.2 (1.07)
Sb	0.0069	0.30 (0.39)	0.21 (1.07)
Sc	0.0049	0.54 (0.74)	0.39 (1.08)
Se	0.36	0.37 (0.29)	0.27 (1.07)
Sm	0.81*	0.23 (0.28)	0.16 (1.08)
Sr	21	25 (29)	18 (1.10)
Ta	0.12	0.21 (0.27)	0.13 (1.17)
Tb	0.044	0.038 (0.042)	0.027 (1.10)
Th	0.044	1.20 (1.56)	0.73 (1.11)
Ti	21	183 (260)	130 (1.09)
U	0.022	0.16 (0.12)	0.12 (1.11)
V	0.23	4.4 (6.3)	3.0 (1.07)
Yb	0.0083	0.10 (0.12)	0.072 (1.10)
Zn	3.1	37 (43)	26 (1.06)

* $ng\ g^{-1}$

Table 3.19. Detection limit of ICP-AES

Elements	Detection Limit ($ng\ mL^{-1}$)
Al	18
Mg	1.0
Na	30
K	5.0
Mn	0.14
Ca	21
Fe	9.0
Cu	1.4
Zn	0.76
Pb	7.9
Ni	2.3
Cr	1.6
V	0.94
Cd	0.22

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Qualitative and Quantitative Comparison of Biomonitoring Organisms

4.1.1. Interspecies Comparison of Lichens as Biomonitors for Trace Element Air Pollution

The use of lichens as biomonitors for air pollution offers means for achieving preliminary estimates of the extend of such pollution, the location and identification of the pollution sources and also a method for the comprehensive mapping of the pollutant in an area.

Many investigations have been reported on only one monitor species, which conditioned the locations of the sampling sites, by its presence. In biomonitoring studies, the selection of species used is of prime importance; species tolerance levels often restrict the available number of relevant species. The tolerance of lichens to elevated tissue concentrations of elements varies greatly between species and elements. As the information on species-specific accumulation characteristics is only scarcely available, it is in practice not possible to replace one lichen species by another, when the monitor species is not present in a chosen sampling site. Interspecies calibration permits the inclusion of sampling sites that lack the monitor species under study.

As it was mentioned in section 3.1.2, the most commonly observed lichens in Aegean Region were Xanthoria parietina and Parmelia tiliacea. Before the details of produced data are discussed, a comparison of the above mentioned lichen species that were collected at the same sampling points are given considering qualitative accumulation capacities of them. It is known from the literature that Xanthoria parietina is tolerant to pollution as given in Table 2.1 and it is used in many studies as discussed in Chapter 2. As elements very rarely occur as the only pollutants but generally combined with other harmful substances, especially SO_2, the ideal accumulators of elements should be rather toxitolerant, in particular SO_2 tolerant (Markert, 1993). Other lichen, Parmelia tiliacea is one of the species of Parmelia genus, which are used very often in other studies. It is also good accumulator of pollution. The first aim is to evaluate whether the accumulation capacity (tolerance level) of lichen Xanthoria parietina was enough or comparable with other lichen species which is known to be good accumulator also. Then other aims are to investigate the interchangeability of these lichen species and to evaluate the method for the determination of the calibration factors between two species for future works.

4.1.1.1. Comparison of Accumulation Capacities of Two Lichen Species

The comparison of accumulation capacity of two lichens species namely Xanthoria parietina and Parmelia tiliacea is the first step in order to see the differences in uptake efficiency of them for many elements in general. This was performed using ANOVA (Analysis of Variance) statistical analysis by using Statgraphics Plus program package (Statgraphics Manual 3.1, 1997). In order to apply ANOVA analysis, the following requirements are needed (Berenson et al., 1983):

1)Independence

2)Normality

3)Homoscedasticity (i.e. homogeneity of variances)

It must be assumed that the subjects in each of the independent sample groups are randomly and independently drawn so that an observed value in any one group has no effect or influence on any other observed value in that group or any of the other groups. This assumption of independence can not be relaxed. For the second assumption, it is very difficult to make judgment of normality when the sample sizes are very small. If, however, we have good reason to believe this assumption has been violated, a good strategy is to seek appropriate transformations to normalize the data (take square root, log transformation, take reciprocals etc.). Since we know that the data is lognormally distributed as will be discussed in section 4.2.1, the log transformation was preferred and applied for our data (Wiersma et al., 1992). After transformation, the third assumption (homoscedasticity) was also realized. Since some of the variances of two lichen species were not close to each other as given in Table 4.1. By log-transformation they came close to each other.

The number of samples, the results of analysis at a probability level of P=0.05, average values and standard deviations of two species are given in Table 4.1. The F ratio is a ratio of the variance between group estimate (variance between two lichen species) to the within group estimate (variance in individual lichen species). This ratio can be compared with the table values of F test with two-tailed distribution in order to compare the means of two lichen species. Other way of evaluating the ANOVA analysis result is to use P-value that is one of the output of ANOVA analysis. In recent years an approach to hypothesis testing, which has increasingly gained acceptance, deals with the concept of P-value. The P value is often referred to as the observed level of significance- the smallest level at which the hypothesis of two means are equal can be rejected for a given set of data. Uses of P-values do not require the additional use of critical value tables as in traditional testing procedures (Berenson et al., 1983). If P-value of the F-test is greater than or equal to 0.05, there is not a statistically significant difference between the means of the two lichen species at the 95% confidence level and this case is denoted by NS in the table. If P-value of the F-test is smaller than 0.05, there is a statistically significant difference between the means of the two lichen species at the 95% confidence level and this case is denoted by S in the table. Other than ANOVA analysis, paired t-test is suitable statistical tool for this purpose and it was also applied to this data and it gave the same results as ANOVA analysis by using both mean and median values.

Table 4.1. Element concentrations and their standard deviations in lichen Xanthoria parietina and Parmelia tiliacea collected from the same sampling points and ANOVA results at P=0.05.

Element (unit)	Number of samples	F ratio	P value	Significance	Xanthoria parietina Average ± STD	Parmelia tiliacea Average ± STD
Al (µg g^{-1})	17	0.47	0.49	NS	2940 ± 2490	3510 ± 2330
As (µg g^{-1})	13	1.37	0.25	NS	3.8 ± 1.8	4.7 ± 2.0
Au (ng g^{-1})	9	0.08	0.78	NS	1.5 ± 1.0	1.6 ± 0.85
Ba (µg g^{-1})	8	0.02	0.89	NS	52 ± 68	49 ± 32
Br (µg g^{-1})	9	3.20	0.93	NS	6.8 ± 7.9	17 ± 16
Ca (µg g^{-1})	17	13.9	0.00070	S	2420 ± 2570	5420 ± 2095
Cd (µg g^{-1})	15	0.35	0.56	NS	0.22 ± 0.15	0.25 ± 0.14
Ce (µg g^{-1})	9	1.16	0.29	NS	2.2 ± 2.7	3.7 ± 3.4
Cl (µg g^{-1})	9	124	0.00	S	250 ± 120	960 ±150
Co (µg g^{-1})	9	1.29	0.17	NS	0.74 ± 0.60	1.06 ± 0.59
Cr (µg g^{-1})	17	0.06	0.81	NS	4.9 ± 5.8	5.3 ± 4.0
Cs (µg g^{-1})	9	0.01	0.93	NS	0.99 ± 0.95	1.0 ± 0.87
Cu (µg g^{-1})	12	9.68	0.005	S	4.8 ± 1.6	7.1 ± 2.0
Dy (µg g^{-1})	8	2.78	0.12	NS	0.24 ± 0.28	0.53 ± 0.41
Eu (µg g^{-1})	8	0.09	0.76	NS	0.07 ± 0.07	0.08 ± 0.06
Fe (µg g^{-1})	17	0.30	0.58	NS	1800 ± 1540	2060 ± 1270
Hf (µg g^{-1})	9	0.37	0.55	NS	0.21 ± 0.20	0.27 ± 0.25
Hg (µg g^{-1})	13	3.55	0.072	NS	0.20 ± 0.24	0.078 ± 0.049
In (µg g^{-1})	2	4.12	0.18	NS	0.030 ± 0.014	0.056 ± 0.011
K (µg g^{-1})	17	1.94	0.17	NS	2890 ± 1450	3610 ± 1560
La (µg g^{-1})	17	2.18	0.15	NS	2.0 ±1.5	2.7 ±1.4
Lu (µg g^{-1})	9	1.69	0.21	NS	0.018 ± 0.018	0.041 ± 0.505
Mg (µg g^{-1})	17	0.08	0.78	NS	1480 ± 600	1540 ± 550
Mn (µg g^{-1})	17	0.05	0.83	NS	48 ± 80	43 ±32
Mo (µg g^{-1})	7	0.81	0.38	NS	0.43 ± 0.55	0.85 ± 1.10
Na (µg g^{-1})	16	0.02	0.89	NS	360 ± 330	380 ± 310
Nd (µg g^{-1})	9	3.16	0.095	NS	1.2 ± 1.3	2.6 ± 2.1
Ni (µg g^{-1})	12	1.35	0.26	NS	3.2 ± 1.3	4.2 ± 2.7
Pb (µg g^{-1})	12	8.01	0.0097	S	4.4 ± 2.5	10 ± 6.7
Rb (µg g^{-1})	9	0.13	0.72	NS	15 ± 8.6	17 ± 15
Sb (µg g^{-1})	13	0.31	0.58	NS	0.26 ± 020	0.30 ± 0.22
Sc (µg g^{-1})	9	0.41	0.53	NS	0.53 ± 0.64	0.72 ± 0.62
Se (µg g^{-1})	11	1.03	0.32	NS	0.31 ± 0.17	0.41 ± 0.28
Sm (µg g^{-1})	9	2.21	0.16	NS	0.21 ± 0.24	0.42 ± 0.35
Ta (µg g^{-1})	4	0.06	0.81	NS	0.33 ± 0.44	0.41 ± 0.49
Tb (µg g^{-1})	5	0.06	0.82	NS	0.054 ± 0.063	0.065 ± 0.078
Th (µg g^{-1})	9	1.45	0.24	NS	0.67 ± 0.68	1.16 ± 1.02
Ti (µg g^{-1})	8	0.13	0.72	NS	200 ± 220	240 ± 200
V (µg g^{-1})	17	3.22	0.08	NS	4.4 ± 4.6	7.0 ± 3.9
Yb (µg g^{-1})	9	1.55	0.23	NS	0.096 ± 0.12	0.23 ± 0.30
Zn (µg g^{-1})	17	5.50	0.025	S	34 ± 33	63 ± 40

As can be seen from the table the two lichen species were found to possess a different accumulating capacity for the elements Ca, Cl, Cu, Pb and Zn according to ANOVA results. They showed similar accumulating capacity for the rest of the elements. The average concentrations of elements in Parmelia tiliacea are higher than the average concentrations of elements in Xanthoria parietina except for the elements Ba, Hg and Mn. This means that the accumulating capacity of Parmelia tiliacea is higher than Xanthoria parietina possibly related to morphological differences in lichen features (Sloof, 1993) and also chemical properties like exchange capacity and amount of ligands are also important (Folkeson, 1979).

In literature there are some studies comparing the accumulating capacities of two lichen species. In one of them they compared two lichen species namely Parmelia praesorediosa and Ramalina stenospora collected in USA, the ANOVA results showed a significant difference in Th, Sc, Fe and Zn between species (Thompson et al., 1987). The elements Ce, Hg, Cr, Ir, Cs, Rb, Co, Eu, K and Sb did not show differences. In another study they compared the moss species of Scleropodium purum and Hypnum cupressiforme collected in Spain (Fernández and Carballeira, 2000). They found that the differences in the concentration of As, Co, Cu, Hg and Zn in two moss species were not significant. However they found significant differences in the concentrations of Al, Ni, Pb and Fe according to ANOVA test. In the study of Berg and Steinnes (1997), the t-test results indicated that there were no differences in Li, Be, Mg, Ca, Zn, Ge, As, Se, Sr, Y, Zr, Sn, Cs, Ba, La, Ce, Pr, Nd, Sm, Ho, Tb, Hf, Ta and U concentrations in two moss species. The elements Cr, Fe, Co, Ni, Cu, Ga, Nb, Mo, Sb, Eu, Gd, Tb, Dy, Er, Tm, Lu, W, Tl, Pb, Th, V, Mn, Rb and Cd showed significant differences between the moss species.

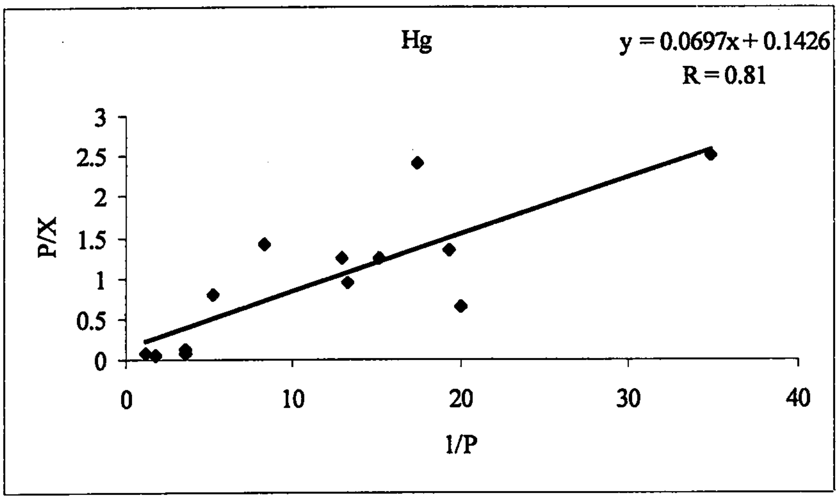
4.1.1.2. Intercalibration of Two Lichen Species

As it was stated above the result of this test can be very useful in the future on the cases that common lichen is not available since we did not encounter with this type situation for this thesis. The way of determining the intercalibration factors is to obtain an equation $y=ax+b$ with high r (correlation coefficient) values. The significance of correlation was tested using ANOVA table. The statistically significant correlation is denoted by S and statistically insignificant correlation is denoted by NS in the Table 4.2. The values of the equation parameters of each element are also given in Table 4.2. From the table it was seen that both species were correlated for Ba, Br, Co, Cr, Cs, Fe, K, Mg, Mn, Mo, Nd, Rb, Sb and Ti.

The equation $y = ax+b$ can be very useful for intercalibration for these elements especially in large-scale surveys (Berg and Steinnes, 1997). However, no significant correlations could be determined for Al, As, Au, Ca, Cd, Ce, Cl, Cu, Dy, Eu, Hf, Hg, La, Lu, Na, Ni, Pb, Sc, Se, Sm, Ta, Tb, Th, V, Yb and Zn. The correlation coefficients are very low due to large variations in the data set and possibly the species are not linearly related in the full range of concentrations due to the saturation effects. If the concentrations in Xanthoria have reached the saturation level, than the concentration ratio of Xanthoria to Parmelia as a function of the inverse concentrations in Parmelia would be a straight line, going through the origin (Sloof, 1993). For example, in the study of Sloof (1993), Parmelia to Lecanora ratio for Br, Cu, Cd, Cr, Fe, La, Sb, Se and W were significantly correlated with inverse of Lecanora and the intercepts were nearly zero. This supported the conclusion that Parmelia has reached saturation levels. In our case, the elements Hg, Ni, Cu and Pb showed the saturation effects, which means that interspecies calibrations are not possible for these elements. For Hg and Cu, Xanthoria parietina showed saturation effects whereas for Ni and Pb, Parmelia tiliacea showed saturation effects as shown in Figure 4.1. and Figure 4.2., respectively. However in each case the other species also showed saturation effects for some points in the data set by giving considerable correlations.

Table 4.2. Correlation coefficients (r) and the parameters (a,b) for the function y=ax+b, with y and x being the elemental content in Xanthoria p. and Parmelia t., respectively

Element	No. of samples	r	a	b	Sign.of corr.	Confidence level	Xanthoria/Parmelia ± STD
Al	17	0.38	0.41	1520	NS	90 % or higher	1.00 ± 0.76
As	13	0.44	0.41	1.9	NS	90 % or higher	0.86 ± 040
Au	9	0.18	0.22	1.1	NS	90 % or higher	1.05 ± 0.58
Ba	8	0.83	1.79	-35	S	90 % or higher	0.98 ± 0.53
Br	9	0.99	0.49	-1.7	S	99%	0.35 ± 0.10
Ca	17	0.15	0.19	1380	NS	90 % or higher	0.47 ± 0.46
Cd	15	0.29	0.30	0.14	NS	90 % or higher	1.02 ± 0.82
Ce	9	0.16	0.13	1.7	NS	90 % or higher	0.70 ± 0.74
Cl	9	0.34	0.27	-7.4	NS	90 % or higher	0.26 ± 0.11
Co	9	0.63	0.63	0.075	S	90%	0.75 ± 0.44
Cr	17	0.70	1.00	-0.47	S	90 % or higher	1.03 ± 0.71
Cs	9	0.65	0.72	0.25	S	90%	1.08 ± 0.65
Cu	12	0.34	0.27	2.9	NS	90 % or higher	0.70 ± 0.23
Dy	8	0.34	0.23	0.12	NS	90 % or higher	0.48 ± 0.53
Eu	8	-0.14	-0.16	0.084	NS	90 % or higher	1.22 ± 1.04
Fe	17	0.51	0.62	520	S	95%	0.99 ± 0.74
Hf	9	0.54	0.44	0.086	NS	90 % or higher	0.95 ± 0.63
Hg	13	-0.33	-1.6	0.33	NS	90 % or higher	5.26 ± 7.88
K	17	0.72	0.67	460	S	90 % or higher	0.85 ± 0.28
La	17	0.25	0.27	1.3	NS	90 % or higher	0.79 ± 0.48
Lu	9	0.19	0.066	0.015	NS	90 % or higher	0.64 ± 0.60
Mg	17	0.70	0.76	310	S	99%	1.01 ± 0.33
Mn	17	0.45	1.14	-1.3	S	90 % or higher	1.02 ± 0.91
Mo	7	0.82	0.40	0.084	S	95%	0.67 ± 0.50
Na	16	0.23	0.25	270	NS	90 % or higher	1.24 ± 083
Nd	9	0.65	0.40	0.12	S	90%	0.48 ± 0.28
Ni	12	-0.026	-0.012	3.3	NS	90 % or higher	1.04 ± 0.58
Pb	12	0.34	0.13	3.1	NS	90 % or higher	0.56 ± 0.38
Rb	9	0.64	0.38	8.7	S	90%	1.00 ± 0.35
Sb	13	0.48	0.44	0.13	S	90%	0.99 ± 0.71
Sc	9	0.44	0.46	0.20	NS	90 % or higher	0.84 ± 0.57
Se	11	0.25	0.16	0.25	NS	90 % or higher	1.04 ± 0.99
Sm	9	0.19	0.13	0.16	NS	90 % or higher	0.60 ± 0.61
Ta	4	-0.20	-0.18	0.4	NS	90 % or higher	1.61 ± 1.58
Tb	5	0.08	-0.065	0.050	NS	90 % or higher	1.16 ± 1.22
Th	9	0.058	0.039	0.63	NS	90 % or higher	0.90 ± 0.80
Ti	8	0.73	0.79	12	S	95%	0.85 ± 0.35
V	17	0.35	0.42	1.4	NS	90 % or higher	0.69 ± 0.55
Yb	9	0.22	0.087	0.076	NS	90 % or higher	0.63 ± 0.68
Zn	17	0.40	0.33	13	NS	90 % or higher	0.56 ± 0.46



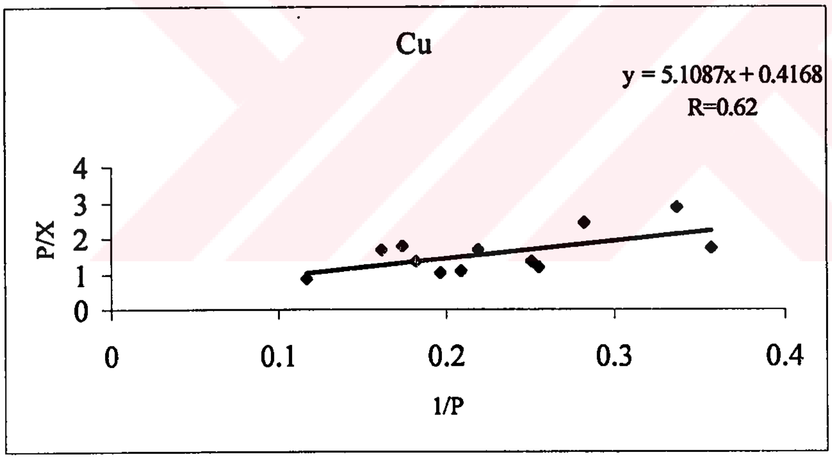
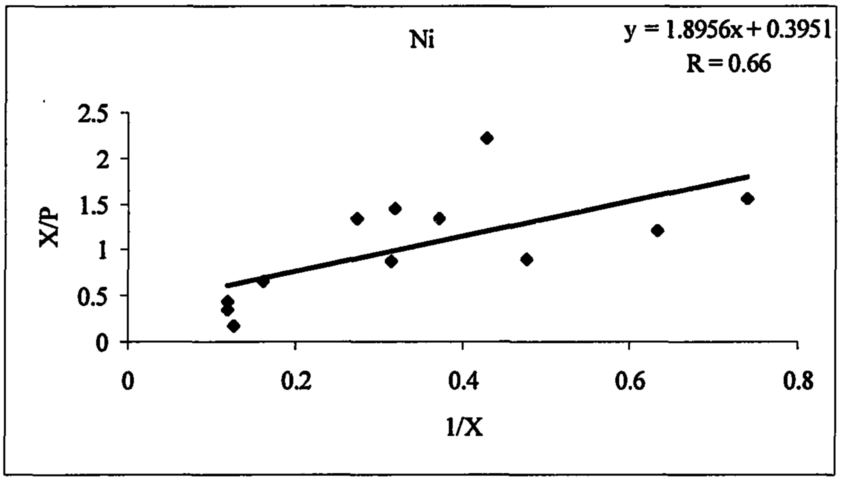


Figure 4.1. Parmelia/Xanthoria Hg and Cu concentration ratios as a function of the inverse Parmelia concentrations (mg kg^{-1})$^{-1}$.



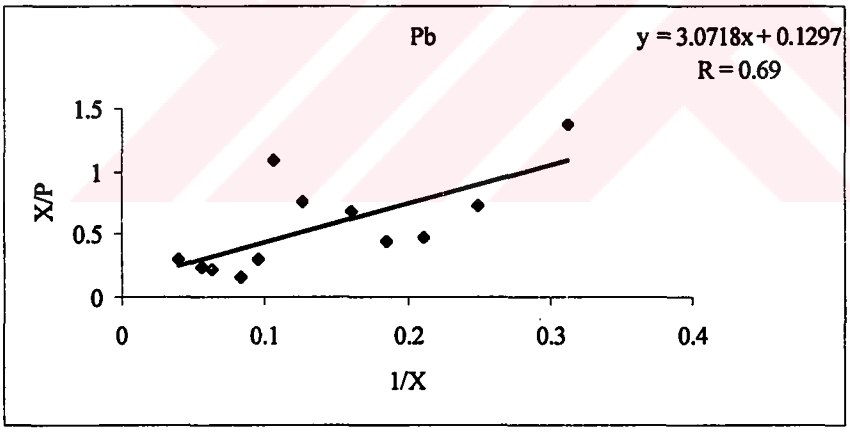


Figure 4.2. Xanthoria/Parmelia Ni and Pb concentration ratios as a function of the inverse Xanthoria concentrations (mg kg^{-1})$^{-1}$.

Intercalibration studies for different moss or lichen species have been reported by Folkeson (1979), Boileau et al., (1982) and Sloof (1993). First two studies did not present level of significance of the interspecies correlations. The calibration factors given were invariably determined as the element concentration ratios between species. Folkeson (1979) reported ratios varying from 0.35 to 3.2 for four moss species and four lichen species against the corresponding Fe, Cu, Zn, Pb, Ni and Cd content in Hylocomium splendens and Pleurozium schreberi. The ratios Boileau et al., (1982) computed for three lichen species and four moss species against the corresponding Fe, Ni, Pb, Ti, and U content of Cladonia rangiferina varied from 0.76 to 3.43. The ratios obtained in the study of Sloof (1993) varied from 0.50 for Sb to 1.41 for Cd including the elements As, Cr, Co, Cu, Fe, La, Se, V, W and Zn. Folkeson reported standard deviations of about 5%. The data were probably obtained from a uniform set of concentrations. Boileau et al. (1982) reported standard deviations of ratios between 5-30%. Sloof (1993) presented the ratios changing from 32 to 80 %. Xanthoria/Parmelia ratios of elements are given in Table 4.2. Our data showed the greatest variation that changed between 33% (Mg, K and Cu) and 150% (Hg). Average ratios of about unit value suggest similar accumulation characteristics and full interchangeability according to Boileau et al. (1982). However our results and Sloof's results (1993) show that analysis of the ratios should indicate whether or not any conclusions on relations between species can be drawn. Since the concentration ratios will change with increasing or decreasing concentrations and therefore averaged or even unit ratios may not be used for intercalibration, unless the actual concentration relationship values (a, b) or trends in ratio values have been examined. To gain knowledge about the differences in element accumulation characteristics between various lichen species, further research should be done with laboratory and field experiments.

It should be noted that Xanthoria and Parmelia might be significantly correlated for these elements (Al, As, Mn, Sb, Sc, Zn, Au, Ca, Cd, Ce, Cl, Cu, Dy, Eu, Hg, La, Lu, Na, Ni, Pb, Se, Sm, Ta, Tb, Th and Yb) in other survey areas showing different element levels. Therefore, separate calibration parameters should be established in different biomonitoring studies. In biomonitoring studies in remote areas, there may be no problems regarding saturation effects.

4.1.2. Lichens and Tree Bark as Quantitative Biomonitors for Atmospheric Element Deposition

In this part quantitative aspects of lichens as biomonitors are discussed. Before we get into details of the elemental interpretation, one need to know whether lichens can be used as quantitative biomonitors or not as well as qualitative biomonitors. For this purpose transplanted lichens were used as explained in section 3.1.3.2. The concentrations of elements in transplant lichens were compared with total deposition samples collected at the same sampling site as the transplant lichens were collected as described in section 3.1.3.3.

So far, only a few quantitative comparisons of biomonitoring methods with the chemical measurements of atmospheric deposition have been published. Pilegaard (1979) showed that the amounts of Cr, Cu, Fe, Pb and Zn accumulated in transplant lichens were linearly related with the concentrations in total deposition in the vicinity of Danish steelworks. However, in a follow-up study from Vestergaard et al., (1986), it was found out the uptake in lichen transplants was not directly proportional to the concentrations in total deposition, using the same species and methodology as Pilegaard (1979). Kansanen and Venetvaara (1991) inferred a log-log linear relationship between the metal content of moss and deposition from snow samples near ferrochrome and steel works in Finland. Berg and Steinnes (1997) presented regression equations for converting moss data to deposition rates for the elements Mg, Se, Sb, V, Mo, Tl, As, Cd and Pb with $r^2>0.50$. Sloof (1993) found the significant relationship between transplant lichens and annual total deposition but not with the annual mean concentrations in air particulate matter indicating that lichens tend to reflect total deposition more than air particulate matter for the elements Co, Sc and Zn.

Elements are deposited to the lichen surface either as dry particulates or as material dissolved and/or suspended in wet precipitation. They may be retained by particulate entrapment, physio-chemical processes such as ion exchange, as well as by passive and active intracellular uptake (Nioboer et al., 1978; Tyler 1989). However there are other factors affecting the accumulation capacity of lichens such as microclimate, pH, rainfall, chemical forms of pollutants, tolerance, metal load, age, growth rate (Sloof, 1993). Therefore, it is very difficult if not impossible to define these characteristics in the field.

In order to investigate whether simple quantitative relationships exist between element concentrations in lichens and those in the atmospheric deposition under varying field conditions, the total deposition samples were collected together with transplant lichens and discussed in the following sections .

4.1.2.1. Choice of Elements

As quantitative biomonitors, lichens were interpreted for ten elements namely Al, Mg, K, Na, Fe, Mn, Zn, Cr, V and Cd. Choice of elements were restricted by the analysis techniques and the amount of sample obtained. As a matter of fact, the amount of transplant lichens is the most important drawback of this part of study. Although the last exposed period was the most crucial one, we could not get any sample of Parmelia tiliciae and Evernia prunastri and we obtained so tiny amount of Xanthoria parietina that it can only be analyzed by INAA. The last sample limited the number of elements that can be determined by INAA (not including Cu, Pb and Ni). In addition, the deposition samples were analyzed by ICP-AES and AAS. This also limited the determination of important pollution derived elements such as As, Sb, Se and Hg due to higher detection limits of ICP-AES with respect to INAA.

4.1.2.2. Comparison of Washed and Unwashed Lichen Concentrations

The way of sample handling must be carefully determined when doing the study of quantitative comparison of lichens with atmospheric deposition of elements. For example, there is a debate in the literature whether the lichen should be washed or not before the analyses. This may change according to the purpose of the study. However, we should know how much decrease will occur if they are washed. In this study lichen samples were washed (rinsed) because of the following reasons:

1. In order to detach lichens from the tree bark. Unless washing it will be very very difficult to separate lichens from tree bark.
2. At some sampling sites, lichens also had to be taken from the bases of the trees because of shortage of lichens on the upper parts. Therefore, soil contribution was dominated and should be avoided.

Washing should be long enough to remove soil particles without leaching out metals from the lichen surface (Yule and Lloyd, 1984; Gough et al., 1988a).

In order to see how much of elements lost by washing process, the ratios of unwashed to washed concentrations in three different lichen species are given in Table 4.3. The concentration ratios of Mn, Zn, Cr, V and Cd are very close to 1 which means they are not affected from washing process. Mostly soil related elements were affected from the washing procedure.

Similar results were obtained in other works. In the study conducted by Rope and Pearson (1990) lichens were washed for 20 minutes and only nickel was significantly less in washed samples, while Ca difference was seen between the concentrations of washed and unwashed lichens. For others (Al, Ba, Ca, Cr, Fe, K, Mn, Sr Ti and V) they did not observe significant difference. Saiki et al., (1997) saw that only Al, K, Na, Se and Ti over 32 elements were affected from the washing procedure. In another work it was said that Ca and K concentrations were generally decreased by washing process (Richardson et al., 1995). Elements, which are tightly bound to cell components such as lead and sulfur, were generally little changed by washing (Richardson et al., 1995; Hale and Lawrey, 1985).

Washing procedure have little effect on Evernia p. for soil derived elements than others in our study. Previous studies have shown that washing procedure may induce losses on Xanthoria p. whereas it has less effect on the concentrations of elements in Evernia p. (Caniglia et al., 1994).

Table 4.3. Ratios of unwashed to washed concentrations in three lichens

Element	Unwashed/washed (Xanthoria parietina) number of samples=3	Unwashed/washed (Parmelia tiliacea) number of samples=3	Unwashed/washed (Evernia prunastri) number of samples=2
Al	8.0 ± 4.9	11 ± 7.5	4.9 ± 0.31
Mg	8.6 ± 3.6	5.3 ± 1.8	4.9 ± 0.30
K	9.2 ± 2.6	4.4 ± 2.4	4.2 ± 0.79
Na	7.3 ± 5.5	14 ± 15	3.6 ± 0.66
Fe	7.4 ± 4.3	6.7 ± 4.3	4.2 ± 0.45
Mn	1.0 ± 0.64	1.9 ± 2.0	0.76 ± 0.13
Zn	1.0 ± 0.31	0.96 ± 0.35	0.86 ± 0.07
Cr	0.95 ± 0.60	0.91 ± 0.60	0.64 ± 0.26
V	1.0 ± 0.12	0.97 ± 0.48	0.77 ± 0.18
Cd	1.2 ± 0.65	1.3 ± 1.7	

4.1.2.3. Xanthoria parietina

The concentration of lichen transplants combined from each of 9 transplant bags which were hanged on the branches of trees (not getting throughfalls from other branches) away from 200 m from the deposition sampler. The results of analyses of transplant lichen samples and cumulative total deposition are given in Table 4.4. The deposition concentration of an element was found by multiplying the concentration of the element in the total deposition sample by the volume of the total deposition of that sample divided by the area of the funnel.

For washed Xanthoria parietina lichen samples, the scatter plots of total deposition versus lichen concentrations are given in Figure 4.3. As we saw, high starting concentrations in the lichen make the interpretation difficult, which is experienced by other scientists (Sloof, 1993; Sloof, 1995a). The concentrations in the 11-month exposed lichens were correlated with the cumulative total deposition.

Table 4.4. The concentrations of washed transplant lichen Xanthoria p. and the cumulative total deposition

Element	Exposure time							
	0 month		3 months		6 months		11 months	
	Lichen	Dep.	Lichen	Dep.	Lichen	Dep.	Lichen	Dep.
Al	5230	0	3420	2320	3970	5920	26330	11520
Mg	2030	0	1030	340	2700	1740	3320	2430
K	1980	0	2930	920	4910	2380	6910	4230
Na	2030	0	1030	450	2700	1720	3320	2740
Fe	3550	0	2490	1320	2550	3270	14630	5780
Mn	56	0	58	46	54	110	452	200
Zn	82	0	73	16	56	39	410	64
Cr	9600	0	10000	2520	9600	5320	54000	12290
Cd	870	0	890	100	460	175	1400	320
V	870	0	520	350	770	810	4780	1105

For Cr, Cd and V the unit of deposition concentration : $\mu g\ m^{-2}$ and the unit of lichen concentration : $\mu g\ kg^{-1}$ for others $mg\ m^{-2}$ and $mg\ kg^{-1}$, respectively.

The quantitative relationships can be described by the following equation.

$$L_x = b + mD_x$$

Where, L_x is the concentration of element x in lichen ($mg\ kg^{-1}$ or $\mu g\ kg^{-1}$); b is the intercept (~ starting concentration); m is the slope of equation (accumulation factor, $m^2\ kg^{-1}$); D_x is cumulative total deposition of the element x ($mg\ m^{-2}$ or $\mu g\ m^{-2}$). The correlations between lichen concentrations and deposition concentrations for all elements except for K and Cr are not statistically significant at 90% or higher confidence level. This is expected since the number of samples is few and the dots are generally not on the regression line. However, the R^2 values of the equations show strong or moderate positive relationship between lichen concentrations with the deposition values except for Cd in spite of high starting concentrations as can be seen also from Table 4.4. The highest accumulation factor was obtained for Zn followed by Cr and V. The lowest ones were obtained for Mg and Na.

The quantitative relationships will be mostly valid for the elements that are not affected from the washing since the lichen samples were washed but the total deposition samples included soil contribution.

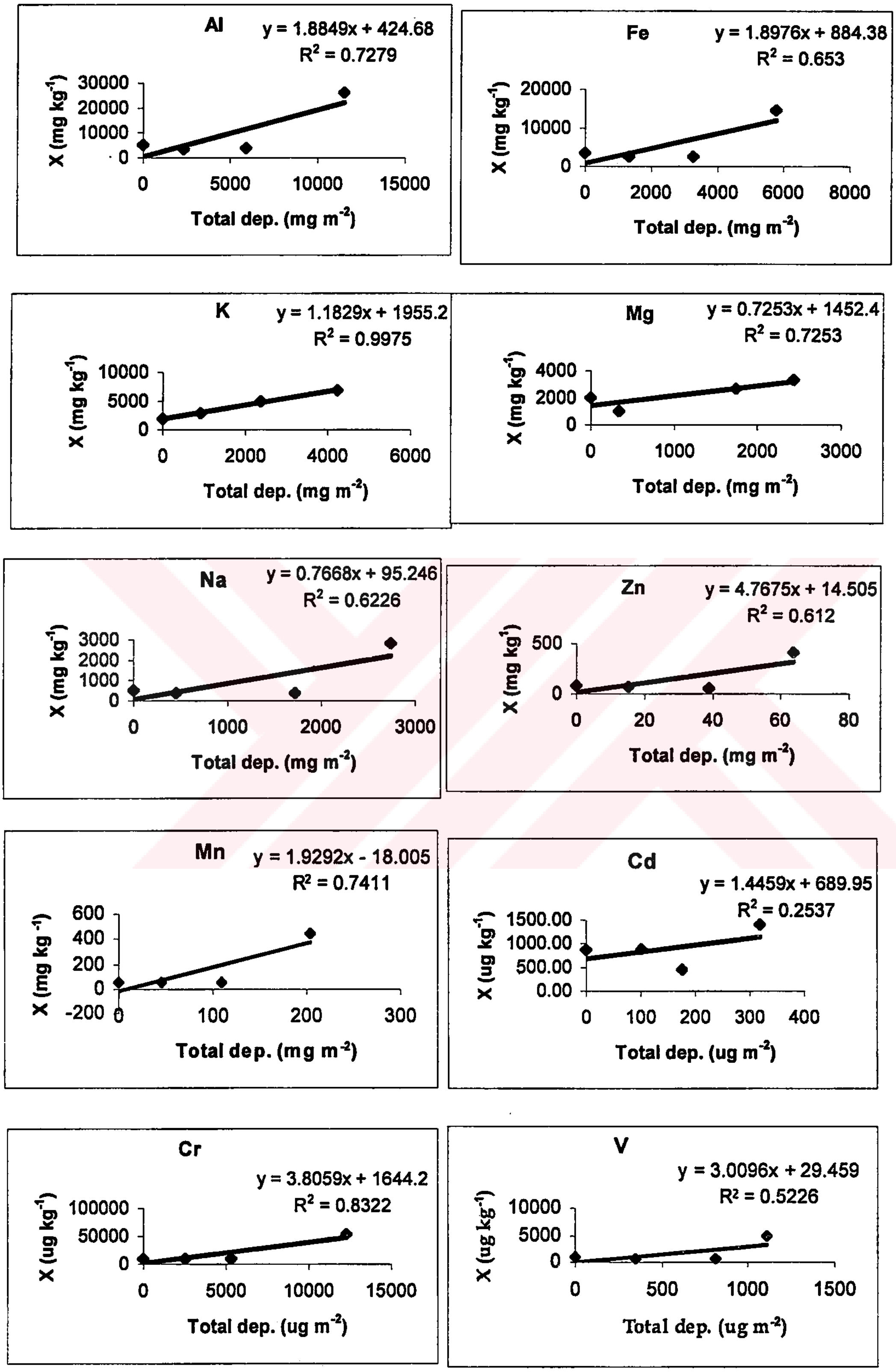


Figure 4.3. The relation between the concentrations in washed lichen Xanthoria parietina and the cumulative total deposition

Except for K, all element concentrations for 3 months exposure time are lower than the starting concentrations as shown in Figure 4.3. This may be due to 1) Short accumulation time. Accumulation time shows differences according to the pollution load of the place. For example, in the study of Pilegaard (1979), the exposure time of at least 7 months was suggested in the vicinity of steelworks in order to achieve equilibrium between the fall out of metals from atmosphere and metal content in lichens. Sloof (1993) and Garty (1987) showed that at least one year of exposure time is required to distinguish the concentration of the exposed lichen from the starting concentration of the lichen. The exposure time of 2 months in industrial town was considered to be the most appropriate for the moss transplants (Gailey and Lloyd, 1986a; Gailey and Lloyd, 1986b).

2) Heavy rainfall season following the starting time (December) of the experiment. The heavy rainfalls during 21-22 January, 2, 5-6 February, 10-11 March 1998 with a total of 220.6 mm probably leached the metals from the lichen thallus. Leaching of the elements K, P, Ca and Mg (macro-nutrients) were also observed by Wiersma et al., (1992) and other elements (Boonpgrob and Nash III, 1990). Macro nutrient elements are originally transferred to lichens by also leaching from living or dead plants (Berg et al., 1995). Potassium being the most important with P of these does not show this trend probably since almost all K is located intracellularly in a freely diffusible form normally contained by the permeability barriers of the cell (Buck and Brown 1979; Markert, 1993; Tyler, 1989; Tarhanen et al., 1996; Branquinho et al., 1999). Some part of Mg and Ca are also located intracellularly in the cytoplasm (Boonpragob and Nash III,1990; Branquinho et al., 1999). Generally it is very difficult to lack the intracellularly located elements. Calcium is known to stabilize cell membranes of plant and animal cells (Nieboer et al., 1979). If extracellular Ca^{2+} is substantially deplete, K^+ loss reflecting some reduction in membrane integrity and stability may be expected (Boileau et al., 1985).

Generally, 6-month lichen sample is either decreased or little increased for all elements except for K and Mg. This type of behavior was observed in other study (Sloof et al., 1993). In this period again heavy rainfalls were seen with peak values on 17, 19 May 1998 with a total of 179.4 mm.

In the third period dry days are dominated and the lichen accumulation for all elements are favoured (rain amount is 119.7 mm). Dry periods may also be one of the reasons of the higher starting concentrations of the transplant lichens. These lichens were picked from the mountainous site (Yamanlar) and expected to be less polluted, however this site of Yamanlar Mountain is open to the pollution coming from the city of İzmir and the second factor may be the collection time of these lichens which possesses a higher accumulation dry summer time (July 1997). During the last period uptake of all elements increased considerably. This is due to long exposure time and also dry deposition is dominant during summer months and this situation reflect the uptake of mostly from dry deposition as found in the study of Boonpragob et al., (1989).

The change in concentrations of the elements Al, Fe, Na and Zn, V, Cr in Xanthoria parietina and in total cumulative deposition samples during exposure periods is given separately in Figure 4.4 and Figure 4.5, respectively. The accumulation of these elements in lichens and in cumulative total deposition samples can be best inferred from the slopes of the equations. Then the ratio of lichen accumulation versus months (the slope of the curve) to the slope of the curve of cumulative total deposition versus months of an element gives the same accumulation factor value for that element as obtained from the above mentioned equation. For example, the ratio obtained for Al by dividing 1953.9 by 1067 gives 1.83 from the Figure 4.4. This value is very close to one shown in Figure 4.3. which is 1.88. This is another way of representation of the accumulation capacity of lichens.

4.1.2.4. Parmelia tiliacea

Although the last exposed transplant of Parmelia tiliciae sample was missing, there were enough sample size of other transplants to analyze the transplant Parmelia tiliciae samples as unwashed and washed. In order to compare the unwashed and washed data with respect to total deposition, the scatter graphs are given in Figure 4.6 and Figure 4.7. Comparing both graphs, it can be seen that soil contribution from

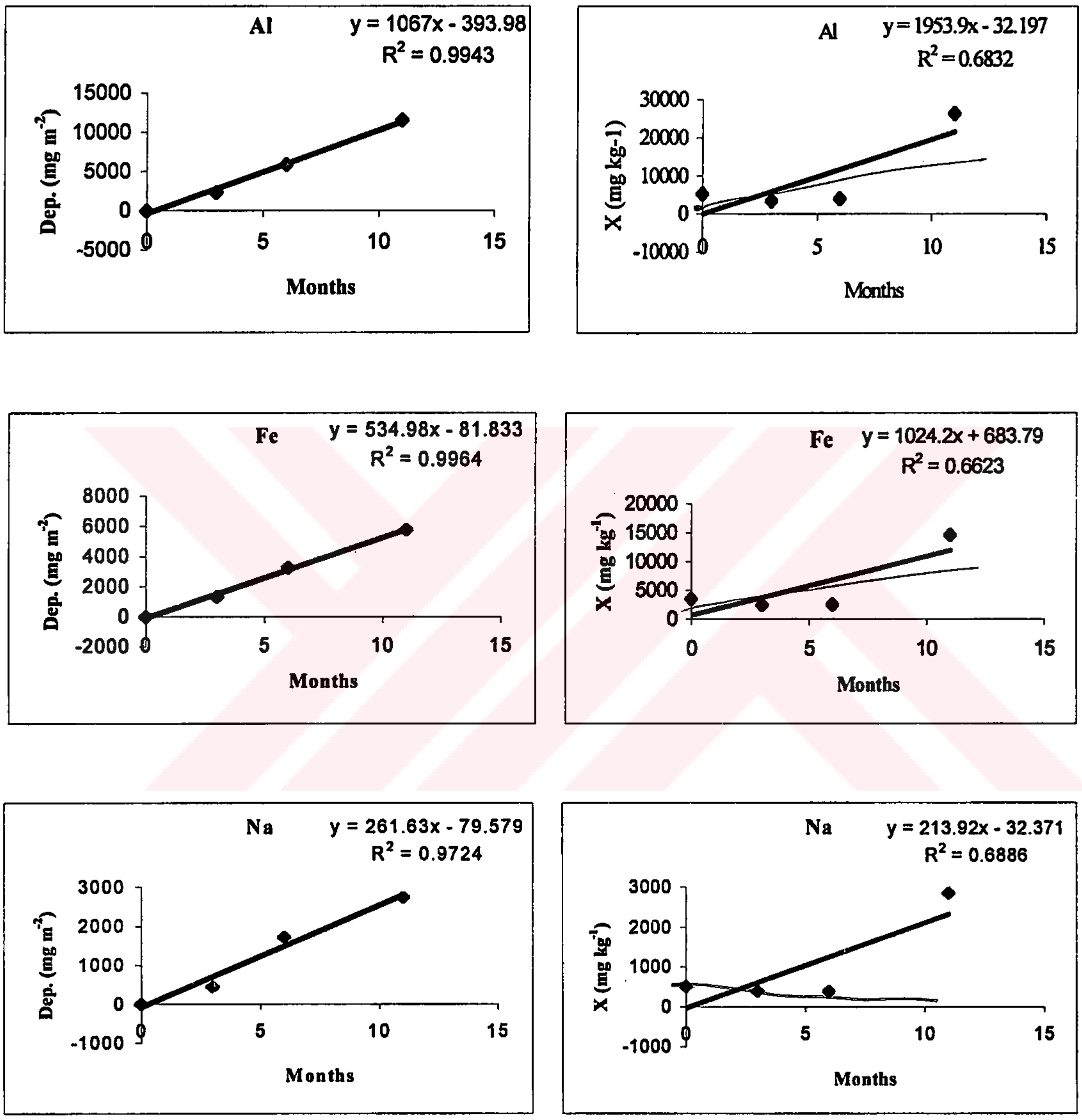


Figure 4.4. The change in concentrations of Al, Fe and Na in washed lichen Xanthoria parietina and in cumulative total deposition during exposure months.

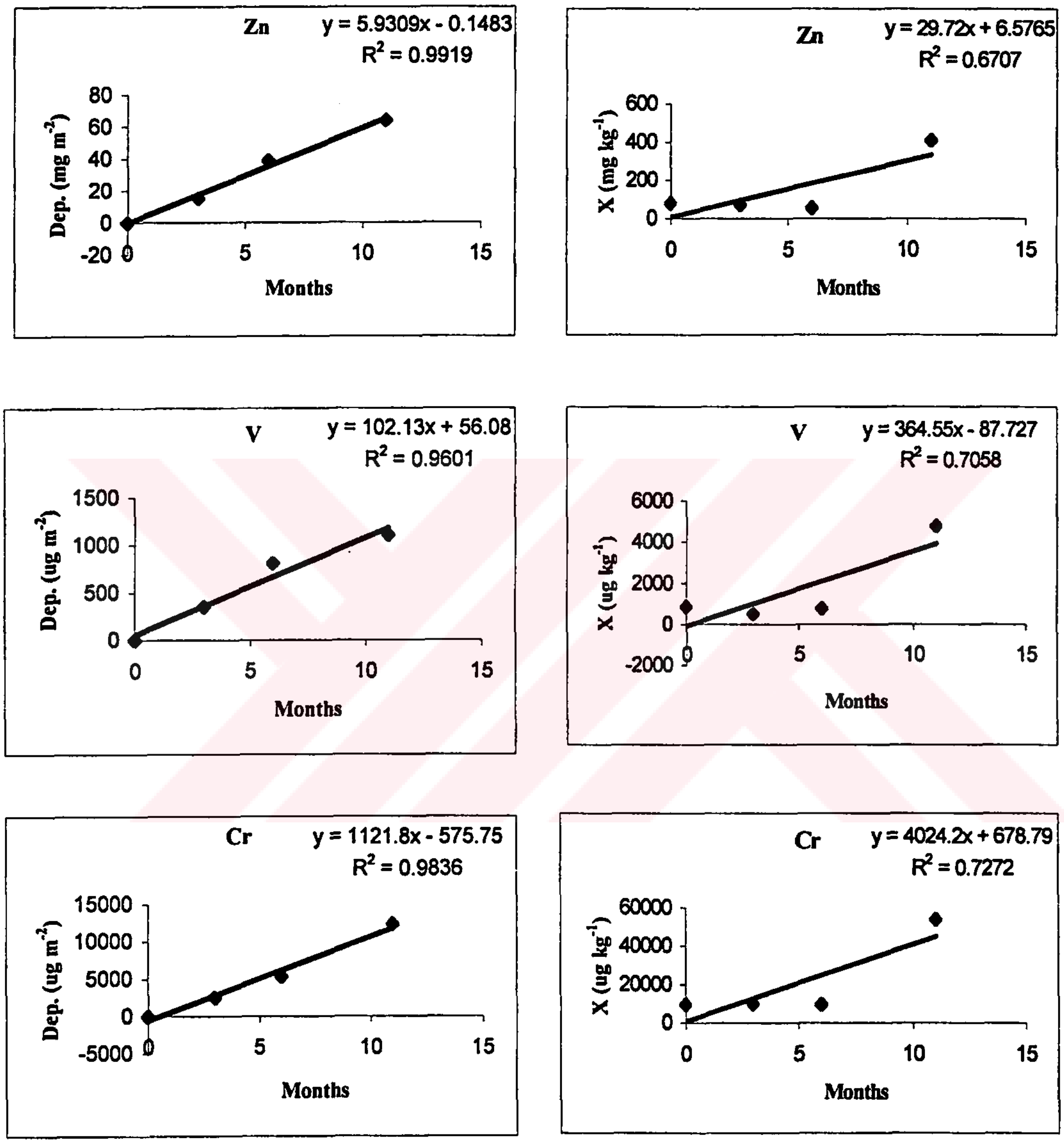


Figure 4.5. The change in concentrations of Zn, V and Cr washed lichen in Xanthoria parietina and in cumulative total deposition during exposure months.

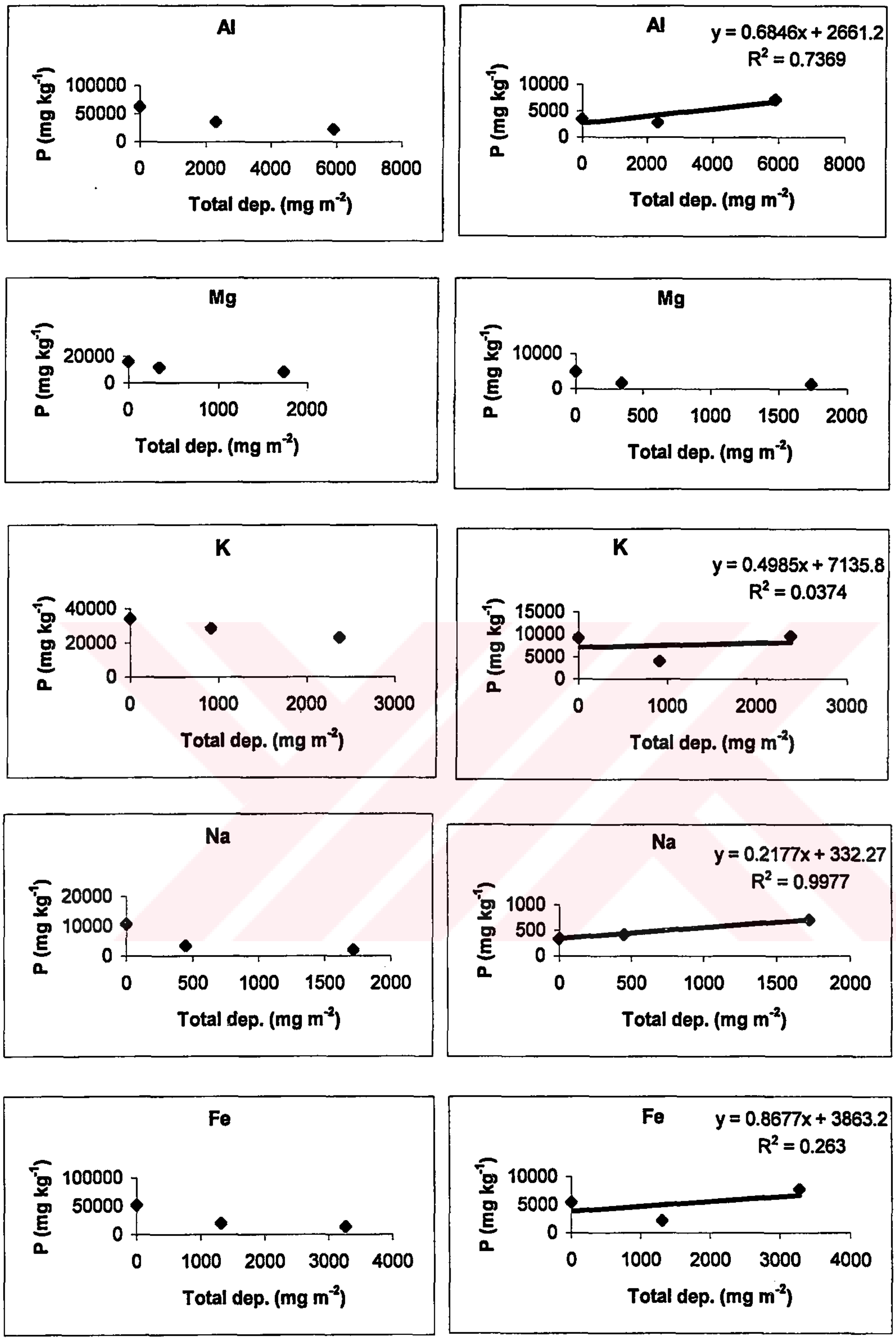


Figure 4.6. Comparison of total deposition of unwashed (left-hand side) and

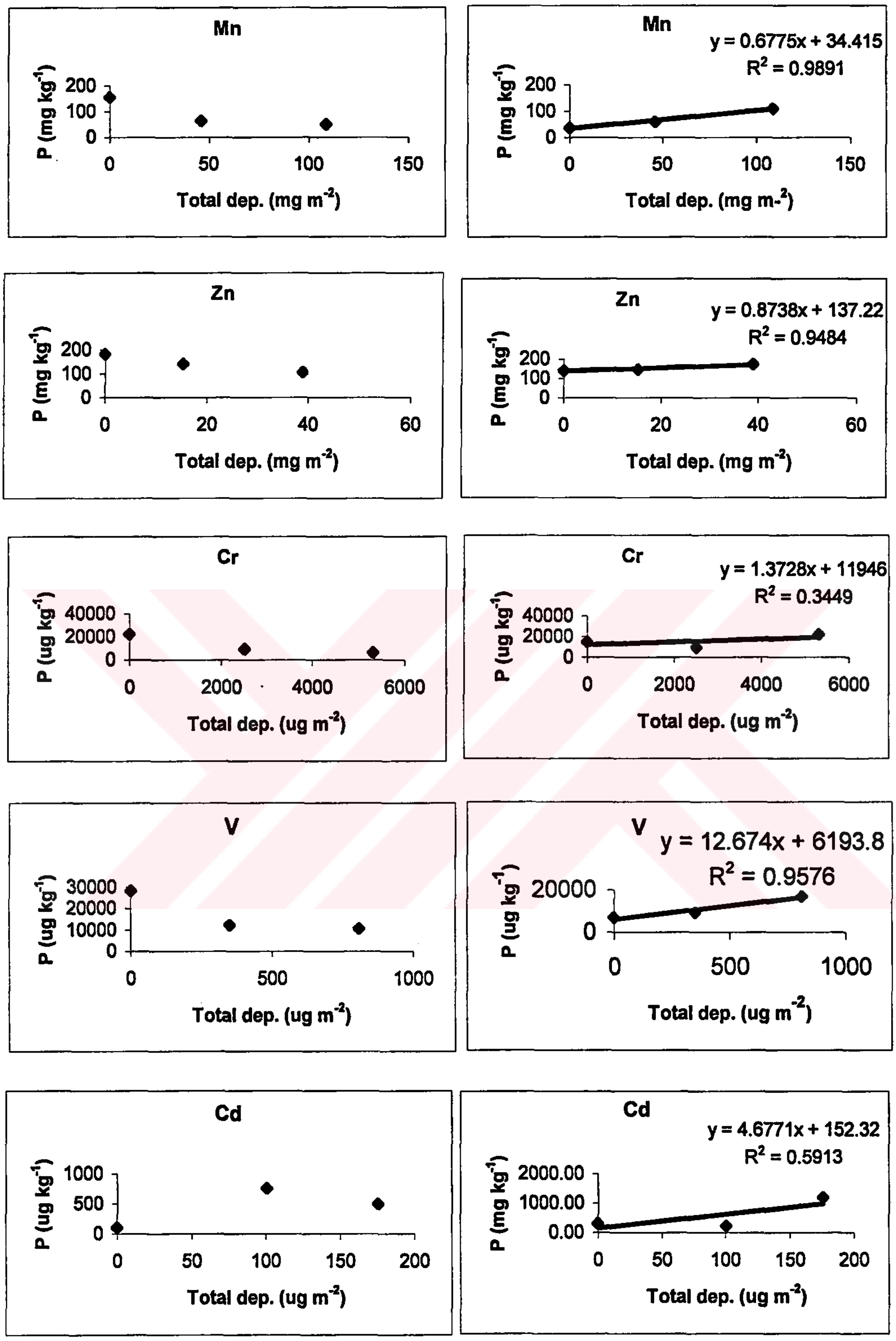


Figure 4.7. Comparison of total deposition of unwashed (left-hand side) and washed (right- hand side) Parmelia tiliacea for the elements Mn, Zn, Cr, V and Cd.

unwashed lichens obscured the variations in concentrations for 6-month exposed samples, which means that the washed lichen samples showed an increase in concentrations for the last sample except for K and Mg.

4.1.2.5. Comparison of Accumulation Capacity of Parmelia tiliacea and Evernia prunastri

It was suitable to compare only the accumulation capacities of Parmelia t. and Evernia p. Since they had the lack of the last exposed sample and if you compared the first three samples of transplanted Xanthoria p. with the trends in transplanted Parmelia t. and Evernia p. samples, you would see no good trends for all elements in first three exposed samples of Xanthoria p. versus total deposition graphs except for K and Mg as shown in Figure 4.3.

When comparing the accumulation capacity of both lichens, as mentioned above the last exposure time was missing and the washed transplanted lichens were used. The parameters of the above mentioned equation are given in Table 4.5. Intercept gives the starting concentration obtained from the equation and m represent the slope of the equation that is an accumulation capacity of lichen species. The correlations are not statistically significant as expected for all elements except for Mn, V and Na in Parmelia t. and for all elements except for Mn in Evernia p. at 90% or higher confidence level. The R^2 values are high or moderate except for K in both species and Na and Cd in Evernia p. The equations can be used for quantitative purposes in the ranges of the concentrations of lichens and total depositions for the elements Mn, Zn, Cr, V and Cd in Parmelia t., Mn, Cr and V in Evernia p.

We can compare the both lichen species with respect to their accumulation capacity of total deposition. The lichen species of Parmelia t. gives higher accumulation capacities for all elements. The accumulation capacity of V is the highest and that of Na is the lowest for both lichen species. The accumulation capacities of V and Cd of Parmelia t. are even higher than that of Xanthoria p. in this short period of exposure. The accumulation capacity of Parmelia t. was also found to be higher than that of Xanthoria p. for most of the elements as discussed in section 4.1.1.1.

Table 4.5. The comparison of accumulation capacity of Parmelia tiliciae and Evernia prunastri

Element	Parmelia tiliacea				Evernia prunastri			
	R^2	m	b	Starting Conc. (lichen)	R^2	m	b	Starting conc. (lichen)
Al	0.74	0.68	2661	3510	0.93	0.11	130	1590
Mg					0.62	0.56	1100	1460
K	0.037	0.49	7136	9270	0.078	0.15	2545	2970
Na	0.99	0.22	332	340	0.0061	0.0023	278	300
Fe	0.26	0.87	3863	5500	0.89	0.72	1080	1370
Mn	0.99	0.68	34.4	37	0.98	0.093	35.5	36
Zn	0.94	0.87	137	140				
Cr	0.34	1.37	11950	15000	0.74	0.54	5620	6140
V	0.96	12.7	6194	6900	0.81	2.3	5110	5400
Cd	0.59	4.6	152	320	0.22	1.5	250	370

For Cr, Cd and V, the unit of lichen concentration : $\mu g\ kg^{-1}$ for others $mg\ kg^{-1}$

In a study conducted by Caniglia et al., (1994), it was confirmed that Evernia p. exhibited a useful capability in monitoring atmospheric pollution, since it gave a sensitive response on both short and long periods of exposure, maintaining a good living status and without reaching a saturated condition. Actually this is an exceptional species since it was known that fruticose lichens are the least tolerant species to air pollution. However Evernia p. has some disadvantages like it can only be found only at high altitudes (>600 m) and less polluted sites. Some of the variation in concentrations between species can be explained by differences in environmental exposure. The great inherent differences in the growth rate and morphology between species seem to be still more important. Chemical properties like exchange capacity and amount of ligands are also important (Folkeson, 1979) as said before. The accumulation capacity of lichen Parmelia t. may be also affected from the morphology because it is foliose (like leaf) lichen whereas Evernia p. is fruticose (like shrub) lichen. This was also supported by other workers (Calvelo et al., 1997).

4.1.2.6. Tree Bark

The outer part of bare tree bark (wild pear) which was the substrate for transplanted Xanthoria parietina after the same exposure periods as other transplanted lichens and analyzed in order to see the accumulation capacity of different biomonitor organism other than lichens. The results of barks at the exposure times and deposition values are given in Table 4.6. As in the case of lichens the starting concentrations are very high.

Table 4.6. The concentrations of tree bark and the cumulative total deposition

Element	Exposure time							
	0 month		3 months		6 months		11 months	
	Bark	Dep.	Bark	Dep.	Bark	Dep.	Bark	Dep.
Al	5180	0	5285	2320	4110	5920	5520	11520
Mg	7770	0	3030	340	2750	1740	3990	2430
K	2290	0	745	920	2700	2380	2250	4230
Na	660	0	460	450	530	1720	620	2740
Fe	2950	0	3650	1320	2580	3270	5860	5780
Mn	100	0	96	46	127	110	170	200
Zn	100	0	82	16	70	39	160	64
Cr	9300	0	7500	2520	10000	5320	16700	12290
V	12000	0	10400	350	10700	810	13200	1105

For Cr and V the unit of deposition concentration: µg m^{-2} and the unit of lichen concentration: µg kg^{-1} for others mg m^{-2} and mg kg^{-1}, respectively.

The scatter diagrams that give the relation between the tree bark and total deposition are depicted in Figure 4.8. The correlations are not statistically significant for the elements Al, Mg, K, Na, Fe, Zn and V at 90% or higher confidence level. The R^2 values are also low for Al, K, Na, V and Mg. The accumulation factors are generally lower than that for other lichen species although tree barks are exposed for long periods when compared with Parmelia t. and Evernia p. The highest accumulation factor is obtained for V and the lowest one for Na and the negative relation was seen with Mg and total deposition as in the case of Parmelia t. The intercepts of the curves are very close to the starting concentrations. These equations can be used for

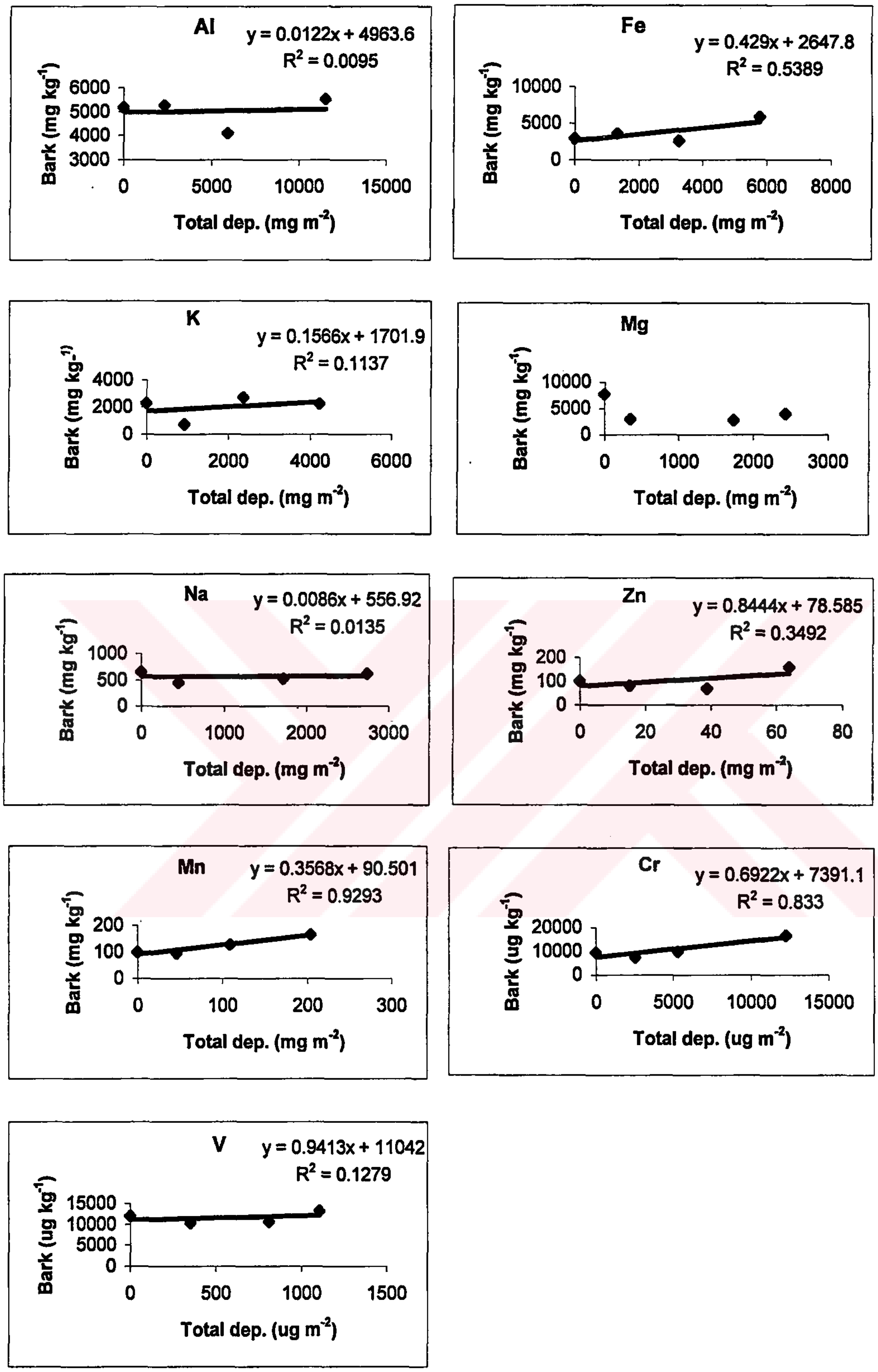


Figure 4.8. The relation between the concentrations in tree bark and the cumulative total deposition

quantitative purposes for the elements Fe, Zn, Mn and Cr since tree barks were not washed.

4.1.2.7. Comparison of Accumulation Capacity of Three Species for Ions

The studies concerning biomonitoring were mainly based on the element deposition. With the exception of fluoride, atmospheric deposition of anions and ammonium ion are rarely studied and consequently little information relevant to acidic deposition is available from lichenological investigations (Boonpragob et al., 1989). Anions like NO_3^- and SO_4^{2-} are the major ions that result from the oxidation of the common air pollutants SO_2 and NO_x, respectively as well as the Cl^- ion for investigation. Studying accumulation of leachable anions provides important information on the ability of lichens to uptake anions from total deposition in the lichenological literature. Only one study was available in the literature in which the ability of a lichen species (Ramalina menziesii) was studied during dry drought periods in California by Boonpragob et al., (1989). In contrast to cations, an anion uptake is an active energy dependent one (Richardson et al., 1984). Additionally, in contrast to cation uptake, anion uptake is much slower and saturation after hours occurs at lower concentrations than most cations (Boileau et al., 1985).

It is important to remove all extracellularly bound ions with enough washing of lichens. In the study of Boonpragob et al., (1989) in southern site of California. 200 mg samples were rinsed by placing each sample in 20 mL deionized water and stirred with a sterile pipette for 30 seconds. This procedure removed a surface deposited ions or ions held internally between cells but not major fraction of ions held exchange sites on cell walls. Our rinsing time of 1.5 hours with shaking in ultrasonic bath may be more satisfactory to obtain major fraction of ions held cell walls. Since we tried 5 hours there was no significant increase in concentrations of anions by increasing the time of shaking from 1.5 hours to 5 hours.

The concentrations of ions Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ in lichen Xanthoria parietina during the transplantation periods were plotted versus total cumulative total

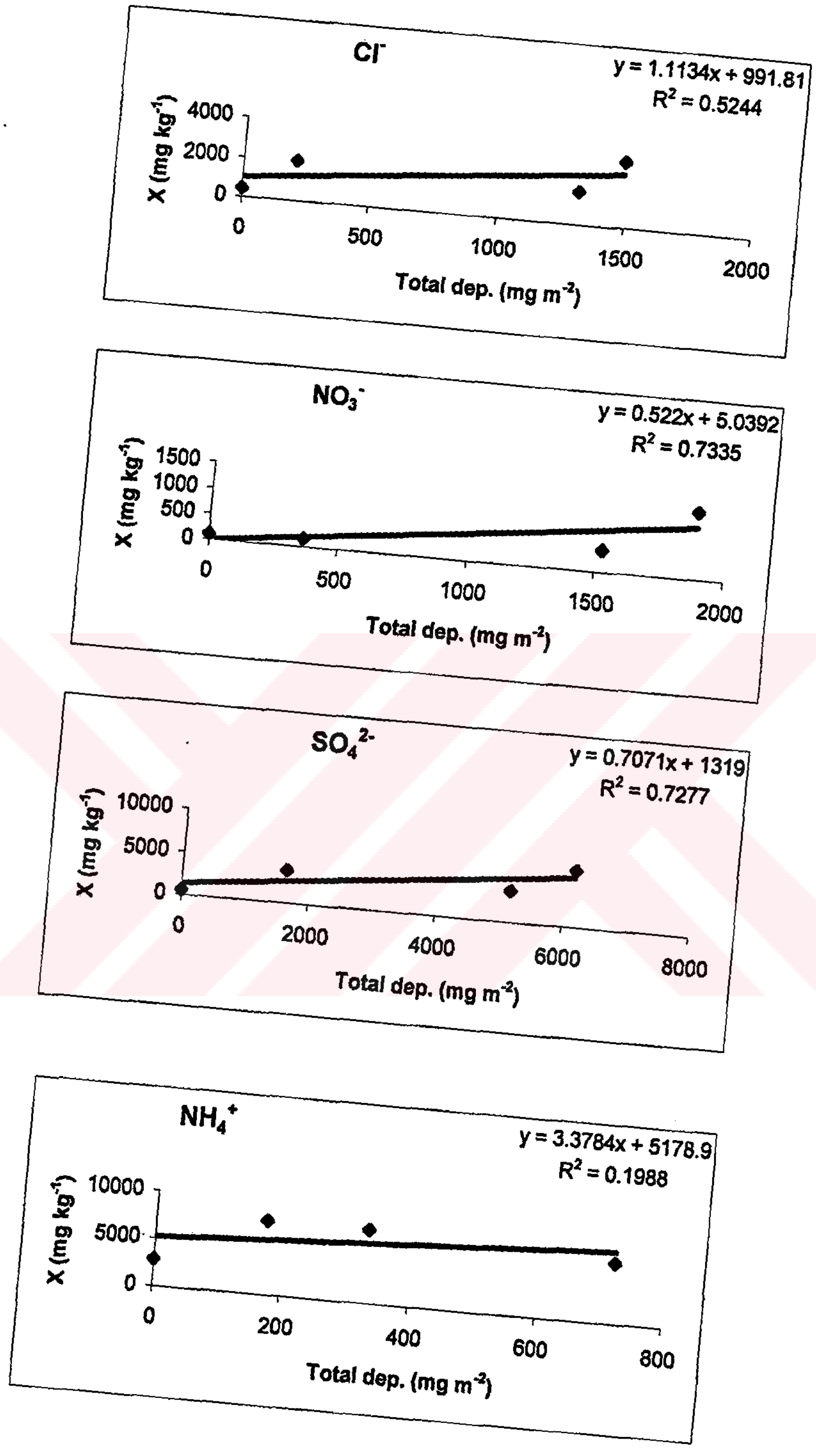


Figure 4.9. The relation between the concentrations of ions in lichen Xanthoria parietina and cumulative total deposition.

deposition like in the case of elements as shown in Figure 4.9 and the results of analyses of transplant lichen samples and cumulative total deposition are also given in Table 4.7. Although the correlations are not statistically significant at 90% or higher confidence level, the starting concentrations are not high as in the case of elemental deposition in lichens. The R^2 values of equations are fairly good for Cl^-, NO_3^- andSO_4^{2-} ions but not for NH_4^+. The intercepts of the equations are not close to starting concentrations as in the case of element deposition in Xanthoria parietina. The highest accumulation factor is obtained for NH_4^+ and then Cl^-, SO_4^{2-} and NO_3^-. Although total deposition of Cl^-, NO_3^- and SO_4^{2-} during the second transplantation period (18 March-17 June 1998) is higher than other periods, uptake of ions by lichen is little. This is probably again because of heavy rainfalls during this period (Boonpragob et al., 1989). In contrast to this, during the last period the total deposition is lower than the second one, lichen uptake is very high. This observation was seen for the elements V, Na and Mg. Dry deposition is dominant during summer months and this situation reflect the uptake mostly from dry deposition as found in the study of Boonpragob et al., (1989). Major sources of the accumulated ions include aerosols from combustion and industrial processes, but also marine aerosols, soil particulates and the lichen itself.

Table 4.7. The concentrations of ions in lichen Xanthoria parietina and the cumulative total deposition

Element	Exposure time							
	0 month		3 months		6 months		11 months	
	Lichen	Dep.	Lichen	Dep.	Lichen	Dep.	Lichen	Dep.
Cl^-	445	0	1980	213	1630	1320	3285	1500
NO_3^-	110	0	160	370	430	1525	1300	1900
SO_4^{2-}	615	0	3760	1650	3580	5180	6525	6190
NH_4^+	2840	0	7815	170	7760	330	6455	720

Unit of deposition concentration: mg m^{-2} and the unit of lichen concentration: mg kg^{-1}

When we examined the chemical form of ions we observed that in lichens sulfate and nitrate ions are not in the acid form. They are either neutralized or they are related with sea salt particles. Since the average pH of the leachates of lichens was 7.46 but the natural lichen pH is around 4.6 (Richardson. 1984). And also the deposition samples had an average pH of 7.23 due to a probable neutralization by $CaCO_3$ from soil. This observation is also verified by looking at correlations in between Ca and SO_4^{2-} in deposition samples. The correlations in between SO_4^{2-} and Ca (r=0.38, n=48, p<0.01), NO_3^- and Ca (r=0.46, n=45, p<0.01) are given in Table 4.8. Relatively good correlation coefficients indicate that SO_4^{2-} and NO_3^- are mostly in the form of Ca compounds or they are originated from sea. However Ca is highly related with other soil elements Na, Mg and K; Na-Ca (r=0.51, n=49, p<0.01), Mg-Ca (r=0.79, n=49, p<0.01), K-Ca (r=0.55, n=49, p<0.01). There are no good correlations of NH_4^+ ion with any of the ions analyzed in soluble fraction of total deposition samples. These acidic anions show also good correlations with Cl which also suggest that they also come from sea [Cl-NO_3^- (r=0.43, n=44, p<0.01); Cl-SO_4^{2-} (r=0.63, n=63, p<0.01)]. Sodium, Cl and Mg come also from sea salt aerosols. Since the correlation coefficients between the species of Cl-seasalt Na (r= 0.86, n=28, p<0.01), Cl-Mg (r=0.32, n=47, p<0.01) are high. Sea salt concentrations of Na were calculated by using Ca as a reference element for soil, although Ca also comes partially from sea salt particles because it gives a correlation with Cl (r=0.23, n=47, p<0.01).

Table 4.8. Binary correlation coefficients between ions and elements of soluble fraction of total deposition samples

	Ca	Mg	Na	ssNa	K	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	H^+
Ca	1									
Mg	0.79	1								
Na	0.51	0.70	1							
SsNa	0.33	0.34	0.15	1						
K	0.55	0.77	0.98	0.081	1					
Cl	0.23	0.32	-0.013	0.86	-0.014	1				
NO_3^-	0.46	0.34	0.19	0.54	0.21	0.43	1			
SO_4^{2-}	0.38	0.26	0.044	0.65	0.063	0.63	0.43	1		
NH_4^+	0.016	-0.027	-0.007	-0.21	0.0031	-0.13	0.046	-0.014	1	
H^+	-0.056	0.29	0.032	0.058	0.10	0.35	0.14	0.094	-0.10	1

The concentrations of ions Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ in lichens Parmelia tiliacea and Evernia prunastri during the transplantation periods except for the last period were plotted versus cumulative total deposition as shown in Figure 4.10 in order to compare the accumulation capacity of both lichens. The parameters of the

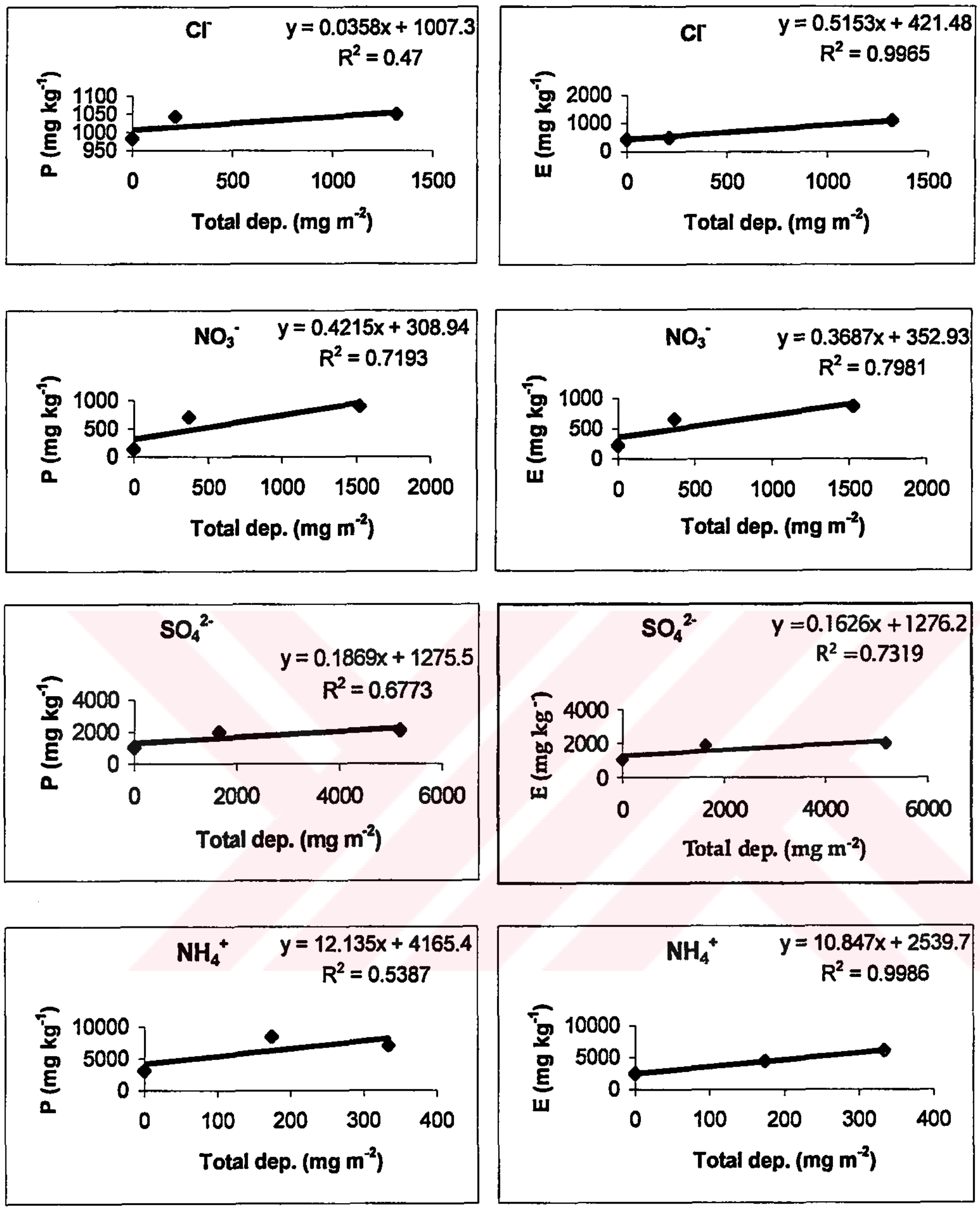


Figure 4.10. The relation between the concentrations of ions in lichen Parmelia t. and Evernia p. and cumulative total deposition.

above mentioned equation are given in Table 4.9. Intercept gives the starting concentration obtained from the equation and m represent the slope of the equation that is an accumulation capacity of lichen species. The starting concentrations are not high as in the case of elemental deposition in lichens. However the correlations are not statistically significant for all ions in Parmelia t. and for NO_3^- and SO_4^{2-} in Evernia p. at 90% or higher confidence level. The R^2 values of equations are fairly good for Cl^-, NO_3^-, SO_4^{2-} ions and also for NH_4^+ ions as opposed to Xanthoria parietina. However probably it would be better to compare the equations obtained by excluding the last period data also from Xanthoria parietina.

Table 4.9. The comparison of accumulation capacity of Parmelia tiliciae and Evernia prunastri for ions

Element	Parmelia tiliacea				Evernia prunastri			
	R^2	m	b	Starting Conc. (lichen)	R^2	m	b	Starting conc. (lichen)
Cl^-	0.47	0.036	1007	983	0.99	0.51	421	441
NO_3^-	0.72	0.42	309	133	0.80	0.37	352	229
SO_4^{2-}	0.68	0.19	1276	1013	0.73	0.16	1276	1076
NH_4^+	0.54	12	4165	3133	0.99	11	2540	2503

Unit of deposition concentration: mg m^{-2} and the unit of lichen concentration: mg kg^{-1}

That's why new table formed for Xanthoria parietina in order to compare the accumulation capacities of three lichen species qualitatively and given in Table 4.10. From this table it is seen that the highest accumulation factor is again obtained for NH_4^+ and then Cl^-, SO_4^{2-} and NO_3^- but R^2 values and accumulation factors for Cl^- ion decreased and that of for NH_4^+ increased substantially in lichen Xanthoria parietina as compared to Figure 4.9. The accumulation factors of NH_4^+ and SO_4^{2-} ions in lichen Xanthoria parietina are higher than other lichen species but that of NO_3^- ion is less than others. The accumulation factors for Cl^- ion are comparable for Xanthoria parietina and Evernia prunastri whereas Parmelia tiliacea has the lowest accumulation factor value for that ion. Comparing the accumulation capacity of Evernia prunastri and Parmelia tiliacea, the former has little lower accumulation capacities for NO_3^-, SO_4^{2-} and NH_4^+ but substantially higher value for Cl^- ion. From the table it is seen that the highest accumulation factors for Evernia prunastri is again obtained for NH_4^+ and then Cl^-, NO_3^- and SO_4^{2-}. For Parmelia tiliacae, the highest accumulation factor is also obtained for NH_4^+ but then NO_3^-, SO_4^{2-} and Cl^- follow.

As a result, the accumulation capacity of Xanthoria parietina for ions except for NH_4^+ among other species is the highest. For quantitative purposes, the equations obtained for Cl^-, NO_3^- and SO_4^{2-} in Xanthoria parietina can be used. For NH_4^+ the equation in Table 4.10 and for other species the equations in Table 4.9 can be used in the given concentrations ranges of both lichens and total deposition samples.

Table 4.10. The accumulation results of Xanthoria parietina by excluding last period data for ions (unit of deposition concentration: mg m^{-2} and the unit of lichen concentration: mg kg^{-1})

Element	Xanthoria parietina			
	R^2	m	b	Starting conc. (lichen)
Cl^-	0.19	0.50	1096	445
NO_3^-	0.99	0.22	95	110
SO_4^{2-}	0.51	0.47	1571	615
NH_4^+	0.76	15	3608	2840

4.2. Overview of the Data

4.2.1. Summary Statistics of Data

The concentrations of elements in 234 lichen samples collected from Aegean region of Turkey were analyzed. However the concentrations of 145 Xanthoria parietina lichen samples are presented in this part of thesis in order to interpret the data obtained from using only one common species. The data were also given in the literature using only one species as sometimes the concentrations of elements may differ in different lichen species as discussed in the previous sections. Other part of data was used for different purposes in the scope of this thesis. Eighty of samples were analyzed by INAA technique and 65 of them were analyzed by ICP-AES technique.

Statistical summary of elemental concentration obtained from all lichen data set (Xanthoria parietina) is given in Table 4.11 that includes number of samples, arithmetic and geometric means with associated standard deviations, range and median.

The highest arithmetic and geometric mean values belong to K in lichen samples. Important portion of K comes from the lichen metabolism as potassium is an important nutrient element for lichens together with P (Wiersma et al., 1992; Bennett and Wetmore, 1997; Rahn and Huang, 1999). Aluminum comes the second considering again both arithmetic and geometric means. The decreasing arithmetic mean order of first 5 high concentration elements as follows: K>Al>Ca>Fe>Mg. The increasing arithmetic mean order of first 5 low concentration elements as follows: In <Lu<Tb<Eu<Yb.

Table 4.11. Summary statistics of all lichen data set (Xanthoria parietina)

Element (unit)	Number of samples	Arithmetic Mean (STD)	Geometric Mean (STD)	Range	Median
Al (μg g^{-1})	145	2650 (3150)	1950 (1.06)	390-330000	1830
As (μg g^{-1})	120	4.1 (2.2)	3.6 (1.05)	0.5-10.4	3.4
Au (ng g^{-1})	80	1.97 (2.28)	1.31 (1.10)	0.25-15	1.13
Ba (μg g^{-1})	75	37 (57)	25 (1.09)	6-430	22
Br (μg g^{-1})	80	6.5 (4.9)	5.4 (1.07)	1.7-33	5.7
Ca (μg g^{-1})	144	1940 (1960)	1450 (1.06)	400-13720	1260
Cd (μg g^{-1})	125	0.30 (0.38)	0.19 (1.08)	0.018-2.3	0.19
Ce (μg g^{-1})	80	2.2 (2.2)	1.6 (1.09)	0.4-16	1.4
Cl (μg g^{-1})	80	300 (260)	240 (1.06)	44-1920	230
Co (μg g^{-1})	80	0.96 (1.18)	0.71 (1.08)	0.17-9.4	0.68
Cr (μg g^{-1})	145	5.1 (5.9)	3.4 (1.08)	0.52-50	3.6
Cs (μg g^{-1})	77	1.1 (2.05)	0.49 (1.13)	0.079-16	0.46
Cu (μg g^{-1})	121	5.9 (4.3)	5.07 (1.05)	1.2-30	5.08
Dy (μg g^{-1})	66	0.30 (0.35)	0.19 (1.12)	0.03-2.1	0.18
Eu (μg g^{-1})	72	0.067 (0.076)	0.048 (1.10)	0.008-0.58	0.052
Fe (μg g^{-1})	145	1650 (1810)	1250 (1.06)	270-18930	1170
Hf (μg g^{-1})	78	0.24 (0.34)	0.14 (1.12)	0.007-2.6	0.13
Hg (μg g^{-1})	117	0.12 (0.23)	0.069 (1.08)	0.0035-1.81	0.066
In (μg g^{-1})	39	0.015 (0.012)	0.010 (1.18)	0.001-0.045	0.011
K (μg g^{-1})	145	3490 (2320)	2620 (1.07)	220-13930	3490
La (μg g^{-1})	140	1.71 (1.80)	1.27 (1.06)	0.19-18	1.21
Lu (μg g^{-1})	80	0.018 (0.021)	0.013 (1.09)	0.002-0.15	0.011
Mg (μg g^{-1})	145	1610 (710)	1490 (1.03)	440-6330	1520
Mn (μg g^{-1})	145	36 (37)	28 (1.06)	8.8-350	25
Mo (μg g^{-1})	72	0.36 (0.44)	0.25 (1.10)	0.039-3.4	0.25
Na (μg g^{-1})	139	285 (435)	200 (1.07)	25-4790	180
Nd (μg g^{-1})	77	1.5 (1.7)	1.1 (1.09)	0.15-14	1.2
Ni (μg g^{-1})	121	3.9 (4.6)	2.8 (1.08)	0.12-37	3.0
Pb (μg g^{-1})	120	8.8 (20)	4.3 (1.10)	0.28-170	4.2
Rb (μg g^{-1})	80	11.7 (12.7)	9.2 (1.07)	2.3-110	9.2
Sb (μg g^{-1})	121	0.30 (0.39)	0.21 (1.07)	0.031-3.5	0.18
Sc (μg g^{-1})	80	0.54 (0.74)	0.39 (1.08)	0.09-6.3	0.34
Se (μg g^{-1})	112	0.37 (0.29)	0.27 (1.07)	0.04-1.4	0.28
Sm (μg g^{-1})	80	0.23 (0.28)	0.16 (1.08)	0.032-2.1	0.14
Sr (μg g^{-1})	32	25 (29)	18 (1.10)	4.4-170	16
Ta (μg g^{-1})	44	0.21 (0.27)	0.13 (1.17)	0.006-1.4	0.13
Tb (μg g^{-1})	70	0.038 (0.042)	0.027 (1.10)	0.004-0.25	0.025
Th (μg g^{-1})	80	1.20 (1.56)	0.73 (1.11)	0.08-8.8	0.65
Ti (μg g^{-1})	79	183 (260)	130 (1.09)	29-2140	114
U (μg g^{-1})	44	0.16 (0.12)	0.12 (1.11)	0.031-0.52	0.13
V (μg g^{-1})	145	4.4 (6.3)	3.0 (1.07)	0.28-67	2.8
Yb (μg g^{-1})	79	0.10 (0.12)	0.072 (1.10)	0.011-0.91	0.063
Zn (μg/g)	145	37 (43)	26 (1.06)	6.4-423	26

Standard deviations are high for most of the elements as expected. Since the study area covers clusters of locations with different air shed compositions like urban, industrial, power plant areas and semiurban areas. Additionally, there are large variations in geographical and meteorological patterns in the region. Characteristics of lichen data in the literature are generally described by arithmetic mean and standard deviations, which assume normally distributed data. However, in data set which is affected by many parameters (different sources, source strengths, meteorological conditions and geographical differences) tend to be lognormally distributed. Lognormally distributed data set can be better described by geometric mean and standard deviation. Although geometric means and standard deviations are presented in Table 4.11, arithmetic means and standard deviations are also included to facilitate the comparison of data with literature where arithmetic means are more frequently reported.

The geometric mean is defined as:

$$\bar{x}_g = \exp\left[\frac{\sum_{i=1}^{N} \ln x_i}{N}\right]$$

Where x_i is the concentration of element and N is the number of samples.

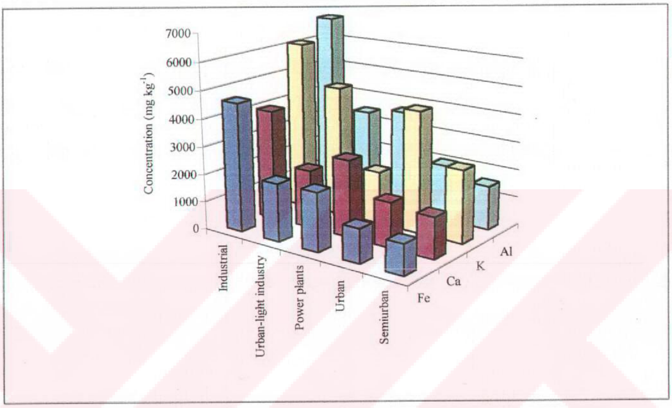
The dimensionless geometric standard deviation (σ_g) for each element represents the spread in the data around the geometric mean. The geometric standard deviations reflect the different levels of stochastic processes that influence the chemical components. The geometric standard deviation, which represents the slope of the log probability plot, is calculated using the following formula (Güllü, 1996).

$$\sigma_g = \exp\left[\frac{\sum_{i=1}^{N} (\ln x_i - \ln \bar{x}_g)^2}{N-1}\right]^{1/2}$$

where $\bar{x}_g$ and σ_g are geometric mean and standard deviation, respectively, and N is the number of samples. If arithmetic mean, geometric mean and median values are close to each other then the data is normally distributed. If arithmetic mean is different from geometric mean then the data is generally lognormally distributed. In this case geometric mean and median values are close to each other. As can be seen in the table, there are differences between arithmetic and geometric mean concentrations. Geometric mean and median values of elements, however, are fairly similar except for K which behaves differently than other pollution derived elements as mentioned above K is one of the two major nutrient elements in lichens.

To investigate the data in more detail and more meaningful way we should divide the sampling region into several subregions as shown in Figure 1.1, since the pollution sources and loads of elements showed very different patterns.

The region was divided into five subregions as discussed in section 1.3: 1) Industrial region covers the industries of iron-steel factories, Aliağa refinery and other industries 2) Urban light industry region covers the city center of İzmir and many small scale industries 3) Power plants regions cover two important coal-fired power plants of the region namely Soma and Yatağan power plants because they showed similar pollution loadings 4) Urban region covers mostly coastal areas of İzmir 5) Semiurban areas covers the rest of the region which has generally the least pollution loadings for most of the elements. The difference in average concentrations of common elements in five different regions is shown in Figure 4.11, Figure 4.12 and Figure 4.13. Summary statistics of the urbanlight industry region is given in Table 4.12 in the similar way as all data set. From Figure 4.13 it is seen that the highest average concentration of Se is in this area. The average concentration of As is also very high and it is not very much different from industrial and power plant region. This is due to domestic heating with coal in this heavily urbanized region. The highest arithmetic and geometric mean values again belong to K in lichens. The decreasing arithmetic mean order of first 5 high concentration element is as follows: K>Al>Fe>Ca>Mg. The increasing arithmetic mean order of first 5 low concentration elements is as follow: In<Lu<Tb<Eu<Hg. This trend is not very much different than that of all data set.



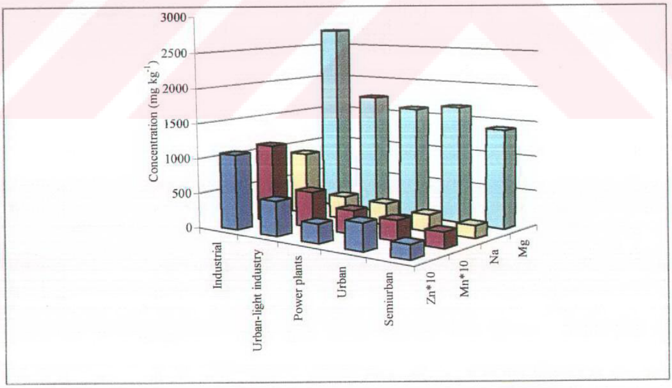
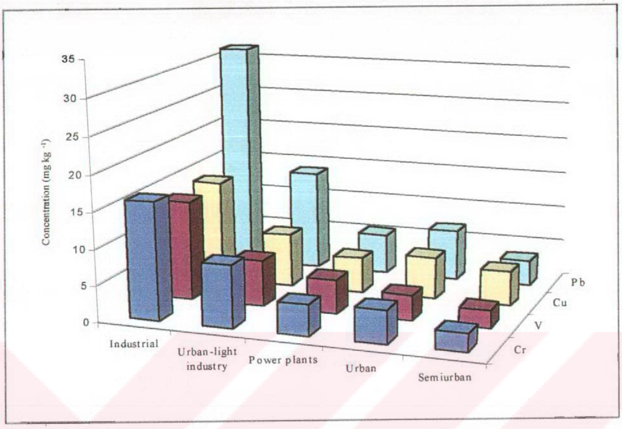


Figure 4.11. The average concentrations of the elements Al, Ca, K, Fe, Mg, Na, Mn and Zn in five subregions



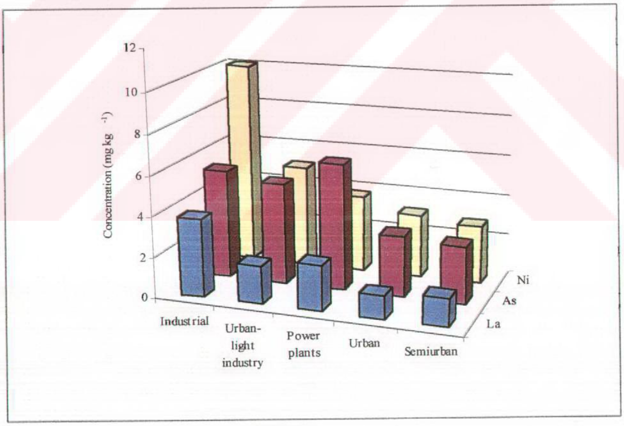


Figure 4.12. The average concentrations of the elements Cr, V, Cu, Pb, La, As and Ni in five subregions

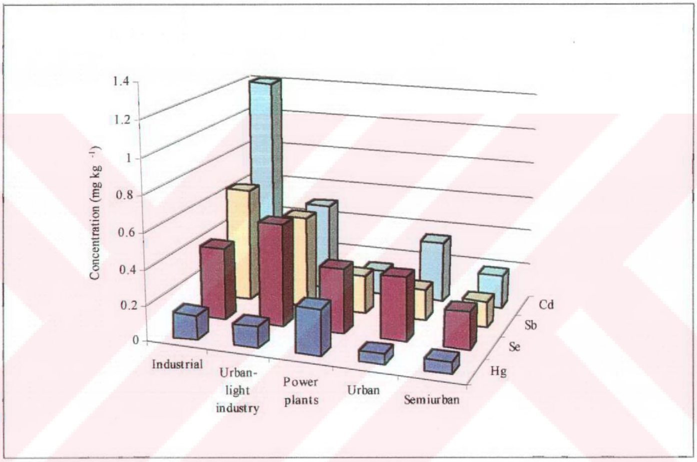


Figure 4.13. The average concentrations of the elements Hg, Se, Sb and Cd in five subregions

Table 4.12. Summary statistics of urban light industry region lichen subset data

Element (unit)	Number of samples	Arithmetic Mean (STD)	Geometric Mean (STD)	Range	Median
Al (μg g^{-1})	33	3440 (2420)	2730 (1.13)	630-8060	2420
As (μg g^{-1})	33	5.1 (2.4)	4.6 (1.09)	1.5-10.4	4.4
Au (ng g^{-1})	32	2.9 (2.9)	2.0 (1.16)	0.57-15	1.7
Ba (μg g^{-1})	31	40 (33)	30 (1.16)	8.2-150	34
Br (μg g^{-1})	32	5.4 (2.9)	4.7 (1.10)	1.7-13	4.9
Ca (μg g^{-1})	32	2060 (2040)	1450 (1.16)	400-10680	1210
Cd (μg g^{-1})	22	0.49 (0.55)	0.35 (1.17)	0.12-2.3	0.33
Ce (μg g^{-1})	32	2.5 (1.7)	1.98 (1.13)	0.5-8.7	2.1
Cl (μg g^{-1})	32	350 (385)	240 (1.15)	44-1920	235
Co (μg g^{-1})	32	1.29 (1.57)	0.95 (1.14)	0.22-9.4	0.88
Cr (μg g^{-1})	33	8.4 (6.1)	6.5 (1.14)	1.07-28	6.8
Cs (μg g^{-1})	31	1.14 (1.48)	0.62 (1.22)	0.12-7.1	0.52
Cu (μg g^{-1})	22	7.46 (3.70)	6.77 (1.10)	3.1-17	6.45
Dy (μg g^{-1})	29	0.39 (0.33)	0.27 (1.18)	0.05-1.2	0.29
Eu (μg g^{-1})	29	0.063 (0.037)	0.050 (1.15)	0.008-0.14	0.06
Fe (μg g^{-1})	33	2070 (1300)	1700 (1.12)	400-4950	1780
Hf (μg g^{-1})	32	0.31 (0.27)	0.21 (1.18)	0.032-1.22	0.24
Hg (μg g^{-1})	33	0.12 (0.22)	0.076 (1.13)	0.028-1.35	0.075
In (μg g^{-1})	14	0.018 (0.014)	0.010 (1.18)	0.001-0.045	0.018
K (μg g^{-1})	33	4600 (2720)	3890 (1.11)	680-13930	3490
La (μg g^{-1})	33	1.89 (1.32)	1.49 (1.13)	0.45-5.3	1.3
Lu (μg g^{-1})	32	0.023 (0.016)	0.018 (1.14)	0.004-0.067	0.017
Mg (μg g^{-1})	33	1720 (587.4)	1620 (1.06)	930-2930	1540
Mn (μg g^{-1})	33	50 (35)	40 (1.13)	13.0-157	41
Mo (μg g^{-1})	30	0.45 (0.63)	0.30 (1.17)	0.059-3.4	0.26
Na (μg g^{-1})	33	327 (204)	270 (1.12)	78-785	271
Nd (μg g^{-1})	30	1.34 (1.01)	1.00 (1.16)	0.27-3.9	1.0
Ni (μg g^{-1})	22	4.9 (5.9)	2.95 (1.27)	0.12-24	3.2
Pb (μg g^{-1})	21	21.5 (41.0)	8.8 (1.3)	1.6-172	7.6
Rb (μg g^{-1})	32	10.8 (6.7)	9.1 (1.1)	3.3-33.4	8.3
Sb (μg g^{-1})	33	0.54 (0.62)	0.37 (1.16)	0.086-3.5	0.4
Sc (μg g^{-1})	32	0.60 (0.40)	0.48 (1.13)	0.12-1.7	0.42
Se (μg g^{-1})	27	0.57 (0.36)	0.46 (1.15)	0.12-1.4	0.44
Sm (μg g^{-1})	32	0.28 (0.20)	0.21 (1.15)	0.056-0.93	0.19
Sr (μg g^{-1})	10	28.2 (15.3)	24.7 (1.20)	11.0-56.0	24
Ta (μg g^{-1})	21	0.23 (0.21)	0.16 (1.20)	0.034-0.98	0.20
Tb (μg g^{-1})	26	0.041 (0.038)	0.032 (1.14)	0.012-0.21	0.036
Th (μg g^{-1})	32	0.89 (0.59)	0.70 (1.15)	0.13-2.4	0.66
Ti (μg g^{-1})	31	219 (159)	175 (1.13)	52-700	160
U (μg g^{-1})	18	0.18 (0.13)	0.15 (1.16)	0.052-0.51	0.12
V (μg g^{-1})	33	6.3 (4.6)	4.7 (1.2)	0.55-16	4.8
Yb (μg g^{-1})	31	0.13 (0.09)	0.099 (1.16)	0.016-0.35	0.091
Zn (μg g^{-1})	33	50 (28)	44 (1.09)	19-148	42

The standard deviations are generally not higher than average values except for the elements Cd, Cl, Co, Cs, Hg, Pb and Sb. This may show the influence of more sources to the concentrations of these elements. The average values are different from geometric means as expected. The geometric mean and median values of elements are fairly similar. This is typical behavior observed in the lognormally distributed data set.

The summary statistics of the urban region is given in Table 4.13 and as can be seen from Figure 4.12, Pb shows higher average concentration than power plants region this may be because of heavy traffic to coastal areas in summer times. The decreasing arithmetic mean did not change very much as follows: K>Al>Mg>Ca>Fe. The increasing arithmetic mean order of first 5 low concentration elements are also same with urban light industry region as follow: In<Lu<Tb<Eu<Hg.

The standard deviations are not higher than average values. The arithmetic mean, geometric mean and median values of the most of elements are fairly similar. This result is expected since the region is not affected by very different sources.

The summary statistics of semiurban region is given in Table 4.14. Concentrations are generally the lowest ones as can be seen from the Figures 4.11, 4.12. and 4.13. The decreasing arithmetic mean order of first 5 high concentration element as follows: K>Al>Ca>Mg>Fe. The increasing arithmetic mean order of first low concentration elements as follow: Hg<Sb<Cd<Se<V. This trend is also not very much different than that of above mentioned data sets without considering non-analyzed elements in this region.

The standard deviations are also not higher than average values there is not much difference between arithmetic means and geometric means although this region has the largest area among the other five. The area seems to be not under the strong influence of high pollution loadings.

Table 4.13. Summary statistics of urban lichen subset data

Element (unit)	Number of samples	Arithmetic Mean (STD)	Geometric Mean (STD)	Range	Median
Al (μg g^{-1})	25	2035 (1050)	1830 (1.09)	880-4880	1550
As (μg g^{-1})	25	3.0 (0.94)	2.85 (1.07)	1.5-5.0	3.1
Au (ng g^{-1})	25	0.95 (0.69)	0.80 (1.11)	0.31-3.6	0.72
Ba (μg g^{-1})	22	19 (12)	16 (1.13)	6.0-61	17
Br (μg g^{-1})	25	8.1 (3.1)	7.6 (1.08)	2.8-15	7.3
Ca (μg g^{-1})	25	1620 (1280)	1300 (1.14)	575-5630	1130
Cd (μg g^{-1})	20	0.35 (0.28)	0.24 (1.24)	0.026-1.2	0.32
Ce (μg g^{-1})	25	1.6 (1.04)	1.39 (1.12)	0.67-4.3	1.17
Cl (μg g^{-1})	25	280 (146)	240 (1.12)	50-590	225
Co (μg g^{-1})	25	0.65 (0.27)	0.58 (1.09)	0.47-0.71	0.58
Cr (μg g^{-1})	25	4.6 (2.1)	4.2 (1.09)	2.2-9.8	4.0
Cs (μg g^{-1})	23	0.40 (0.38)	0.30 (1.17)	0.08-1.8	0.28
Cu (μg g^{-1})	15	5.9 (1.6)	5.7 (1.08)	3.5-8.6	5.7
Dy (μg g^{-1})	17	0.17 (0.12)	0.14 (1.17)	0.05-0.53	0.14
Eu (μg g^{-1})	20	0.045 (0.033)	0.038 (1.14)	0.015-0.16	0.04
Fe (μg g^{-1})	25	1220 (565)	1125(1.08)	550-2900	985
Hf (μg g^{-1})	24	0.13 (0.085)	0.10 (1.16)	0.022-0.31	0.11
Hg (μg g^{-1})	25	0.058 (0.022)	0.054 (1.08)	0.028-0.1	0.054
In (μg g^{-1})	11	0.0089 (0.0057)	0.0066 (1.35)	0.0013-0.018	0.0084
K (μg g^{-1})	25	4390 (960)	4300 (1.04)	3000-6500	4370
La (μg g^{-1})	25	1.12 (0.57)	1.01 (1.09)	0.59-2.77	0.90
Lu (μg g^{-1})	25	0.012 (0.0063)	0.011 (1.09)	0.0057-0.026	0.010
Mg (μg g^{-1})	25	1680 (500)	1610 (1.06)	900-2740	1580
Mn (μg g^{-1})	25	29 (11)	27 (1.08)	13-51	25
Mo (μg g^{-1})	20	0.32 (0.26)	0.25 (1.17)	0.072-1.2	0.30
Na (μg g^{-1})	25	240 (130)	210 (1.11)	90-670	190
Nd (μg g^{-1})	25	1.70 (1.01)	1.42 (1.13)	0.37-3.9	1.5
Ni (μg g^{-1})	15	3.1 (1.8)	2.53 (1.22)	0.39-6.3	3.2
Pb (μg g^{-1})	15	7.0 (4.4)	5.6 (1.22)	1.7-15	7.6
Rb (μg g^{-1})	25	8.1 (4.9)	6.9 (1.13)	2.3-24	8.1
Sb (μg g^{-1})	25	0.18 (0.075)	0.17 (1.09)	0.073-0.37	0.17
Sc (μg g^{-1})	25	0.38 (0.18)	0.34 (1.09)	0.19-0.87	0.29
Se (μg g^{-1})	25	0.36 (0.17)	0.33 (1.10)	0.12-0.87	0.35
Sm (μg g^{-1})	25	0.16 (0.084)	0.14 (1.10)	0.077-0.40	0.11
Sr (μg g^{-1})	10	16 (8.7)	14 (1.20)	6.2-30	12
Ta (μg g^{-1})	12	0.27 (0.40)	0.13 (1.43)	0.026-1.4	0.10
Tb (μg g^{-1})	22	0.028 (0.023)	0.021 (1.17)	0.006-0.11	0.022
Th (μg g^{-1})	25	1.31 (1.80)	0.72 (1.23)	0.18-7.0	0.61
Ti (μg g^{-1})	25	110 (57)	97 (1.10)	44-250	90
U (μg g^{-1})	14	0.13 (0.063)	0.11 (1.19)	0.032-0.25	0.14
V (μg g^{-1})	25	3.5 (2.1)	3.1 (1.11)	1.2-9.5	2.7
Yb (μg g^{-1})	25	0.070 (0.040)	0.062 (1.11)	0.023-0.17	0.056
Zn (μg g^{-1})	25	38 (21)	34 (1.11)	15-110	33

Table 4.14. Summary statistics of semiurban region subset data

Element (unit)	Number of samples	Arithmetic Mean (STD)	Geometric Mean (STD)	Range	Median
Al (µg g^{-1})	61	1600 (1010)	1340 (1.03)	390-5410	1390
As (µg g^{-1})	37	2.82 (1.52)	2.47 (1.02)	0.53-8.3	2.5
Ca (µg g^{-1})	61	1480 (1090)	1250 (1.03)	470-5730	1100
Cd (µg g^{-1})	57	0.19 (0.16)	0.14 (1.04)	0.018-0.68	0.15
Cr (µg g^{-1})	61	2.6 (2.2)	1.96 (1.04)	0.52-14	1.8
Cu (µg g^{-1})	58	4.8 (3.7)	4.1 (1.03)	1.2-29	4.0
Fe (µg g^{-1})	61	1100 (770)	900 (1.03)	270-3700	900
Hg (µg g^{-1})	37	0.066 (0.048)	0.051 (1.04)	0.0035-0.28	0.051
K (µg g^{-1})	61	2630 (1950)	1800 (1.05)	220-9130	2500
La (µg g^{-1})	57	1.39 (0.98)	1.09 (1.04)	0.19-4.93	1.15
Mg (µg g^{-1})	61	1410 (580)	1300 (1.02)	435-3070	1350
Mn (µg g^{-1})	61	23 (12)	20 (1.02)	8.8-67	19
Na (µg g^{-1})	55	180 (170)	130 (1.04)	25-1030	130
Ni (µg g^{-1})	58	2.8 (1.8)	2.3 (1.04)	0.30-8.2	2.5
Pb (µg g^{-1})	58	3.5 (2.5)	2.6 (1.04)	0.28-11	2.8
Sb (µg g^{-1})	38	0.14 (0.08)	0.12 (1.02)	0.03-0.4	0.13
Se (µg g^{-1})	35	0.21 (0.19)	0.16 (1.03)	0.04-0.91	0.14
V (µg g^{-1})	61	2.5 (1.6)	2.0 (1.04)	0.28-7.1	2.2
Zn (µg g^{-1})	61	20 (14)	16 (1.03)	6.4-62	14

The summary statistics of industrial region is given in Table 4.15. The number of samples is not statistically significant to give all statistics. The geometric mean, standard deviation and mean values are included just to give the same format as other tables. Concentrations are generally the highest ones except for Se and Hg as can be seen from the Figures 4.11, 4.12 and 4.13. The decreasing arithmetic mean order of first 5 high concentration element as follows: Al>K>Fe>Ca>Mg. The arithmetic mean of Al is the highest one because the effect of iron-steel factories is very much to pollution loadings of the area. The increasing arithmetic mean order of first low concentration elements as follow: In<Lu<Tb<Hg<Eu. This trend is also not different than that of above mentioned data sets.

The standard deviations are generally higher than average values. One sample nearest to the iron-steel factories generally increases the averages. It also increases the standard deviations very much for the elements Al, Ca, Cs, Fe, Hf, La, Na, Nd, Rb, Sc, Th, Ti and V since the concentrations of the elements are three or four fold higher than the concentrations in the sample taken from nearest to Aliağa refinery which has also very high concentrations for all elements.

The summary statistics of the last subregion is power plant areas and is given in Table 4.16. The order of elements with 5 highest concentrations changes as Al<Ca<Fe<K<Mg. The basic nutrient element K and Cd have their lowest values in this area. Another important observation is the highest concentration of Hg in the power plant area. Given that Hg is thought to be one of the most toxic chemical elements to lichens (Tyler, 1989) and that in addition there should be elevated levels of S and other metals in these lichens. Lowest K concentrations appear mirror to those of toxic elements since potassium is known to leak from cells under gaseous air pollution exposure and from some metals, particularly Pb, Cu, Ag and Hg (Puckett 1976; Nieboer et al., 1978; Nieboer et al., 1979). This behaviour of lichens was also proven by Bennett and Wetmore (1997). The reason for decrease in concentrations of Cd can also be Hg which replace Cd at exchange sites of fungal cell wall of lichens.

4.2.2. Distribution Characteristics of Data

Frequency distributions of pollutants are useful to search for similarities and differences among the components and sampling places, which may lead to insights regarding the sources and stochastic processes that influence the concentrations in lichens. To search these characteristics of data two extreme regions were selected with respect to pollution loadings; the highest and the lowest loading. These tests can not applied to industrial region data because of the limited number of samples from this area. The urban light industry region and semiurban region were investigated in order to see what the distribution of data could tell about the sources of pollution.

For a symmetric gaussian distribution, the values of the arithmetic mean and median are identical. However, this is not valid for the elements determined in urban light industry region. All of the elements are lognormally distributed according to a test of

Table 4.15. Summary statistics of industrial lichen subset data

Element (unit)	Number of samples	Arithmetic Mean (STD)	Geometric Mean (STD)	Range	Median
Al ($\mu g\ g^{-1}$)	9	6840 (10300)	3385 (1.61)	1180-33000	1830
As ($\mu g\ g^{-1}$)	9	5.44 (2.87)	4.80 (1.24)	2.7-9.6	4.2
Au ($ng\ g^{-1}$)	9	2.50 (3.53)	1.47 (1.31)	0.36-11.7	1.22
Ba ($\mu g\ g^{-1}$)	9	92 (140)	43 (1.66)	18-430	27
Br ($\mu g\ g^{-1}$)	9	11 (11)	8.0 (1.43)	3.5-33	6.4
Ca ($\mu g\ g^{-1}$)	9	3985 (4820)	2380 (1.55)	860-13720	1807
Cd ($\mu g\ g^{-1}$)	8	1.21 (0.88)	0.88 (1.52)	0.24-2.31	1.19
Ce ($\mu g\ g^{-1}$)	9	4.4 (5.1)	2.8 (1.51)	1.1-16	1.6
Cl ($\mu g\ g^{-1}$)	9	310 (130)	285 (1.14)	110-530	305
Co ($\mu g\ g^{-1}$)	9	1.52 (1.82)	1.10 (1.48)	0.42-5.55	1.10
Cr ($\mu g\ g^{-1}$)	9	16 (15)	11 (1.53)	3.6-50	15
Cs ($\mu g\ g^{-1}$)	9	2.42 (5.10)	0.85 (1.84)	0.17-16	0.78
Cu ($\mu g\ g^{-1}$)	8	14 (9.1)	12 (1.36)	6.2-30	12
Dy ($\mu g\ g^{-1}$)	6	0.70 (0.74)	0.44 (1.76)	0.097-2.1	0.46
Eu ($\mu g\ g^{-1}$)	9	0.14 (0.17)	0.085 (1.54)	0.019-0.58	0.068
Fe ($\mu g\ g^{-1}$)	9	4630 (5610)	3050 (1.52)	1230-18930	2880
Hf ($\mu g\ g^{-1}$)	9	0.53 (0.80)	0.27 (1.67)	0.069-2.59	0.14
Hg ($\mu g\ g^{-1}$)	9	0.14 (0.087)	0.12 (1.24)	0.058-0.33	0.12
In ($\mu g\ g^{-1}$)	7	0.022 (0.016)	0.015 (1.67)	0.0016-0.04	0.018
K ($\mu g\ g^{-1}$)	9	6130 (2810)	5700 (1.17)	3600-12900	5540
La ($\mu g\ g^{-1}$)	9	3.87 (5.59)	1.99 (1.60)	0.67-18	1.22
Lu ($\mu g\ g^{-1}$)	9	0.037 (0.048)	0.020 (1.58)	0.007-0.16	0.014
Mg ($\mu g\ g^{-1}$)	9	2740 (1580)	2420 (1.25)	1380-6330	2170
Mn ($\mu g\ g^{-1}$)	9	110 (100)	83 (1.44)	34-350	78
Mo ($\mu g\ g^{-1}$)	8	0.36 (0.22)	0.31 (1.33)	0.15-0.83	0.31
Na ($\mu g\ g^{-1}$)	9	900 (1500)	410 (1.62)	144-4790	230
Nd ($\mu g\ g^{-1}$)	9	2.91 (4.34)	1.36 (1.60)	0.17-14	1.69
Ni ($\mu g\ g^{-1}$)	8	10 (12)	6.1 (1.67)	2.2-37	3.9
Pb ($\mu g\ g^{-1}$)	8	32 (28)	20 (1.54)	5.3-79	25
Rb ($\mu g\ g^{-1}$)	9	27 (32)	19 (1.39)	10.6-110	17
Sb ($\mu g\ g^{-1}$)	9	0.65 (0.46)	0.50 (1.40)	0.15-1.56	0.71
Sc ($\mu g\ g^{-1}$)	9	1.33 (1.96)	0.66 (1.59)	0.20-6.26	0.43
Se ($\mu g\ g^{-1}$)	9	0.41 (0.35)	0.32 (1.37)	0.16-1.18	0.24
Sm ($\mu g\ g^{-1}$)	9	0.49 (0.66)	0.26 (1.58)	0.089-2.13	0.15
Sr ($\mu g\ g^{-1}$)	5	51 (68)	27 (2.18)	6.5-170	24
Ta ($\mu g\ g^{-1}$)	5	0.20 (0.20)	0.14 (1.66)	0.049-0.55	0.14
Tb ($\mu g\ g^{-1}$)	9	0.076 (0.081)	0.050 (1.47)	0.021-0.25	0.04
Th ($\mu g\ g^{-1}$)	9	2.04 (2.68)	1.09 (1.52)	0.24-8.80	1.20
Ti ($\mu g\ g^{-1}$)	8	450 (720)	180 (1.79)	31-2140	130
U ($\mu g\ g^{-1}$)	6	0.20 (0.19)	0.14 (1.85)	0.049-0.52	0.11
V ($\mu g\ g^{-1}$)	9	14 (21)	7.4 (1.61)	2.1-67	4.7
Yb ($\mu g\ g^{-1}$)	9	0.22 (0.29)	0.11 (1.63)	0.034-0.91	0.07
Zn ($\mu g\ g^{-1}$)	9	170 (150)	125 (1.24)	34-425	110

Table 4.16. Summary statistics of powerplant area lichen data set

Element (unit)	Number of samples	Arithmetic Mean (STD)	Geometric Mean (STD)	Range	Median
Al ($\mu g\ g^{-1}$)	18	3720 (1900)	3240 (1.48)	1040-8270	3750
As ($\mu g\ g^{-1}$)	16	6.5 (1.3)	5.9 (1.05)	4.84-9.8	6.2
Ca ($\mu g\ g^{-1}$)	18	2785 (1790)	2380 (1.14)	1025-7920	2260
Cd ($\mu g\ g^{-1}$)	18	0.14 (0.12)	0.11 (1.18)	0.032-0.58	0.12
Cr ($\mu g\ g^{-1}$)	18	4.3 (2.2)	3.6 (1.16)	0.89-9.6	4.1
Cu ($\mu g\ g^{-1}$)	18	4.9 (1.7)	4.6 (1.11)	1.3-7.6	4.8
Fe ($\mu g\ g^{-1}$)	18	2110 (1000)	1865 (1.14)	510-4400	2340
Hg ($\mu g\ g^{-1}$)	13	0.26 (0.29)	0.12 (1.56)	0.0063-0.81	0.17
K ($\mu g\ g^{-1}$)	18	1920 (1100)	1630 (1.16)	630-4100	1620
La ($\mu g\ g^{-1}$)	17	2.25 (1.26)	1.79 (1.22)	0.24-4.88	2.25
Mg ($\mu g\ g^{-1}$)	18	1610 (500)	1545 (1.07)	900-2960	1610
Mn ($\mu g\ g^{-1}$)	18	33 (17)	29 (1.13)	13-80	31
Na ($\mu g\ g^{-1}$)	18	310 (220)	250 (1.16)	99-855	220
Ni ($\mu g\ g^{-1}$)	18	3.8 (2.0)	3.7 (1.12)	1.5-7.4	4.04
Pb ($\mu g\ g^{-1}$)	18	5.6 (5.6)	4.3 (1.17)	1.53-26	4.2
Sb ($\mu g\ g^{-1}$)	17	0.22 (0.10)	0.20 (1.13)	0.08-0.43	0.24
Se ($\mu g\ g^{-1}$)	17	0.37 (0.29)	0.29 (1.20)	0.12-1.1	0.24
V ($\mu g\ g^{-1}$)	18	4.7 (2.9)	3.85 (1.19)	0.54-12	4.2
Zn ($\mu g\ g^{-1}$)	18	27 (24)	22 (1.15)	10-110	22

normality (including standard skewness and standard kurtosis) obtained from statgraph software as given in Table 4.17. In this test, the concentrations of elements are tested whether they are normally distributed or not. Skewness is a measure of the symmetry or shape of the data. When the standard skewness values are outside the range –2.0 to +2.0, the data may depart significantly from a normal distribution. A skewness of zero indicates that the data are symmetrically distributed. Positive values of skewness tell you that the upper tail of the curve is longer than the lower tail as seen in this study; negative values tell you that the lower tail is longer. Kurtosis is a measurement of how flat or steep the distribution of the data is with respect to a gaussian or normal distribution. When standard kurtosis values are outside the range –2.0 to +2.0, the data may depart significantly from a normal distribution. For a normal distribution, z score for kurtosis is zero. When the z is less than zero, the curve is flat with short tails. When the z score is greater than zero, the

Table 4.17. Distribution fitting results of urban light industry region data

Element (unit)	Std. Skewness	Std. Kurtosis	K-S DN	Distribution type
Al (μg g^{-1})	1.78	-0.70	0.12	Lognormal
As (μg g^{-1})	1.04	-1.03	0.11	Lognormal
Au (ng g^{-1})	6.3	11	0.13	Lognormal
Ba (μg g^{-1})	3.9	3.6	0.09	Lognormal
Br (μg g^{-1})	2.7	1.0	0.11	Lognormal
Ca (μg g^{-1})	6.2	11	0.12	Lognormal
Cd (μg g^{-1})	5.1	6.3	0.20	Lognormal
Ce (μg g^{-1})	3.9	5.2	0.13	Lognormal
Cl (μg g^{-1})	6.9	11	0.09	Lognormal
Co (μg g^{-1})	10.9	28.6	0.13	Lognormal
Cr (μg g^{-1})	3.1	2.2	0.07	Lognormal
Cs (μg g^{-1})	5.8	9	0.13	Lognormal
Cu (μg g^{-1})	3.1	2.1	0.12	Lognormal
Dy (μg g^{-1})	2.5	0.7	0.10	Lognormal
Eu (μg g^{-1})	0.98	-0.78	0.15	Lognormal
Fe (μg g^{-1})	2.0	-0.40	0.071	Lognormal
Hf (μg g^{-1})	3.3	2.9	0.10	Lognormal
Hg (μg g^{-1})	13	36.4	0.21	Lognormal
In (μg g^{-1})	0.69	-0.50	0.20	Lognormal
K (μg g^{-1})	3.6	4.2	0.12	Lognormal
La (μg g^{-1})	2.2	-0.22	0.10	Lognormal
Lu (μg g^{-1})	2.1	-0.11	0.13	Lognormal
Mg (μg g^{-1})	1.2	-1.03	0.12	Lognormal
Mn (μg g^{-1})	2.8	1.4	0.14	Lognormal
Mo (μg g^{-1})	8.9	20	0.12	Lognormal
Na (μg g^{-1})	2.1	-0.20	0.10	Lognormal
Nd (μg g^{-1})	2.03	-0.14	0.14	Lognormal
Ni (μg g^{-1})	4.7	5.6	0.15	Lognormal
Pb (μg g^{-1})	5.8	9.2	0.20	Lognormal
Rb (μg g^{-1})	3.4	3.2	0.095	Lognormal
Sb (μg g^{-1})	8.4	19	0.091	Lognormal
Sc (μg g^{-1})	2.2	0.11	0.11	Lognormal
Se (μg g^{-1})	1.6	-0.20	0.12	Lognormal
Sm (μg g^{-1})	2.9	1.9	0.10	Lognormal
Sr (μg g^{-1})	1.1	-0.14	0.12	Lognormal
Ta (μg g^{-1})	4.6	6.9	0.11	Lognormal
Tb (μg g^{-1})	7.4	16	0.11	Lognormal
Th (μg g^{-1})	2.0	0.20	0.11	Lognormal
Ti (μg g^{-1})	3.5	2.4	0.10	Lognormal
U (μg g^{-1})	3.1	2.2	0.14	Lognormal
V (μg g^{-1})	1.9	-0.60	0.12	Lognormal
Yb (μg g^{-1})	1.6	-0.71	0.11	Lognormal
Zn (μg g^{-1})	4.0	3.8	0.13	Lognormal

curve is either very steep at the center or has relatively long tail (Statgraphics for windows 3.1 manual, 1997).

Kolmogorov-Smirnov (K-S DN) statistics is used to test the goodness-of-fit of the data to lognormal distribution. The K-S test involves the entire distribution of the examined variable, not just its central value and compares the empirical cumulative distribution function to that of the hypothesized distribution. In case of the lognormal distribution, the maximum absolute distance between the data and the hypothesized distribution is calculated to test the conformance of the two cumulative distribution functions. The observed significance level for the Kolmogorov-Smirmov DN statistic is also given in Table 4.17. The DN values are calculated from statgraphs software as the distribution function of lognormal distribution is chosen. It changes from 0 to 1 and it is the largest absolute difference between the hypothesized and real distribution. The K-S DN value was compared with the critical value from the standard critical value table at 95% confidence level (htpp://phoenix.som.clarkson.edu, 2000). All calculated DN values are lower than the critical values so all elements show lognormal distribution. The examples of these distributions of crustal elements Al, Ca and Fe are shown in Figure 4.14. When comparing the results of std. skewness and std. kurtosis values with frequency histograms they match very well. Aluminium has std. skewness value smaller than 2. It means that it has not significant departure from normal distribution but it is not normally distributed also from the distribution fitting results. According to std. kurtosis value it has negative value this means that curve is flat with short tails. This can be better understandable when compared with the distribution of Ca. The frequency histogram of Fe is similar to that of Al. Calcium shows different histogram than other elements probably because it is a macronutrient for lichen (Wiersma et al., 1992; Bennett and Wetmore, 1997).

The frequency histograms of anthropogenic elements Cd, Hg and Zn are shown in Figure 4.15. The distribution of Hg is different from Cd and Zn, which is supported by std. skewness and kurtosis values in which both elements have short tails. These results could be interpreted as higher number of sources contributing Hg concentrations than Cd and Zn.

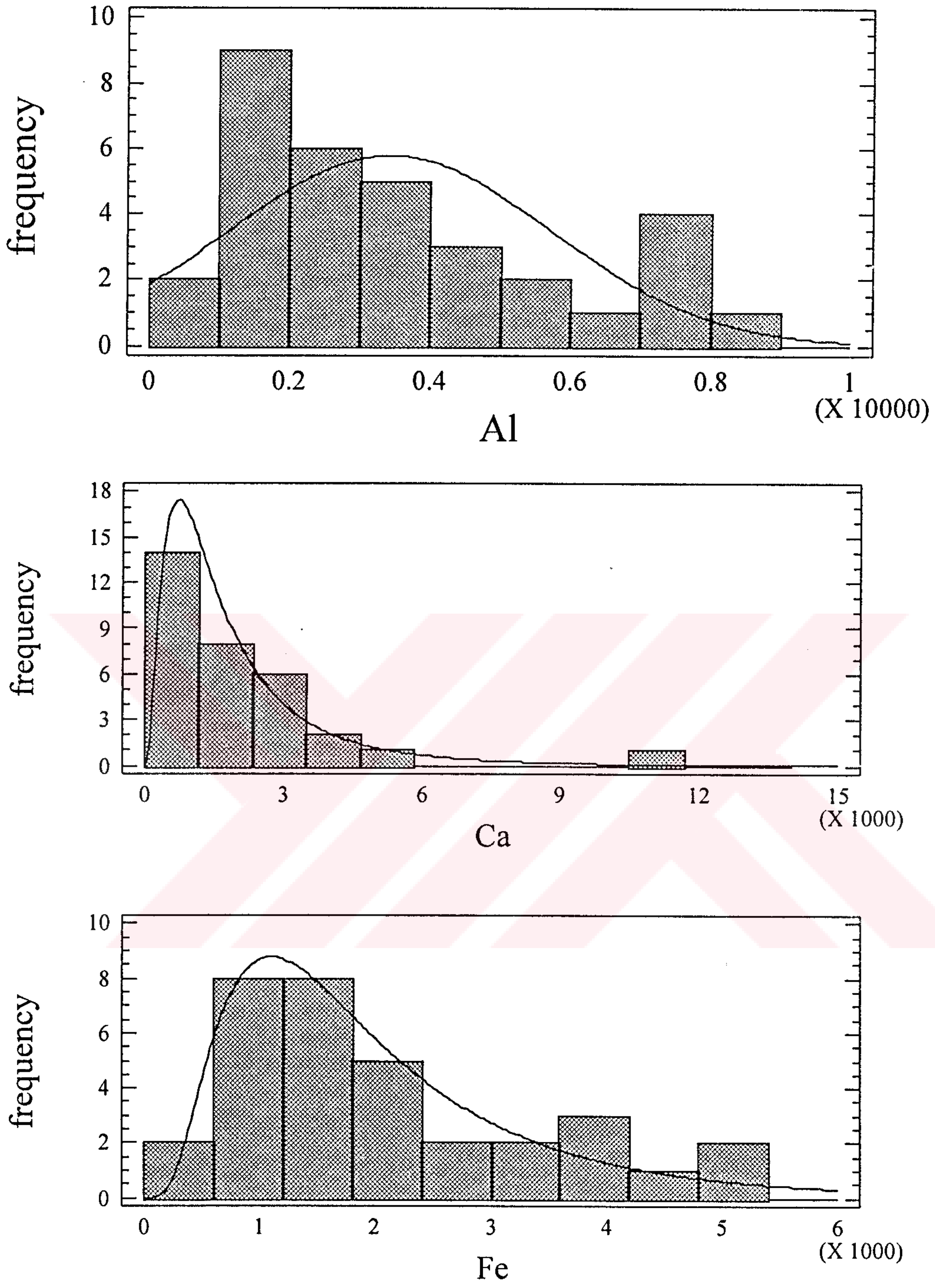


Figure 4.14. Frequency histograms and distribution curves for crustal elements Al, Ca and Fe for urban light industry region.

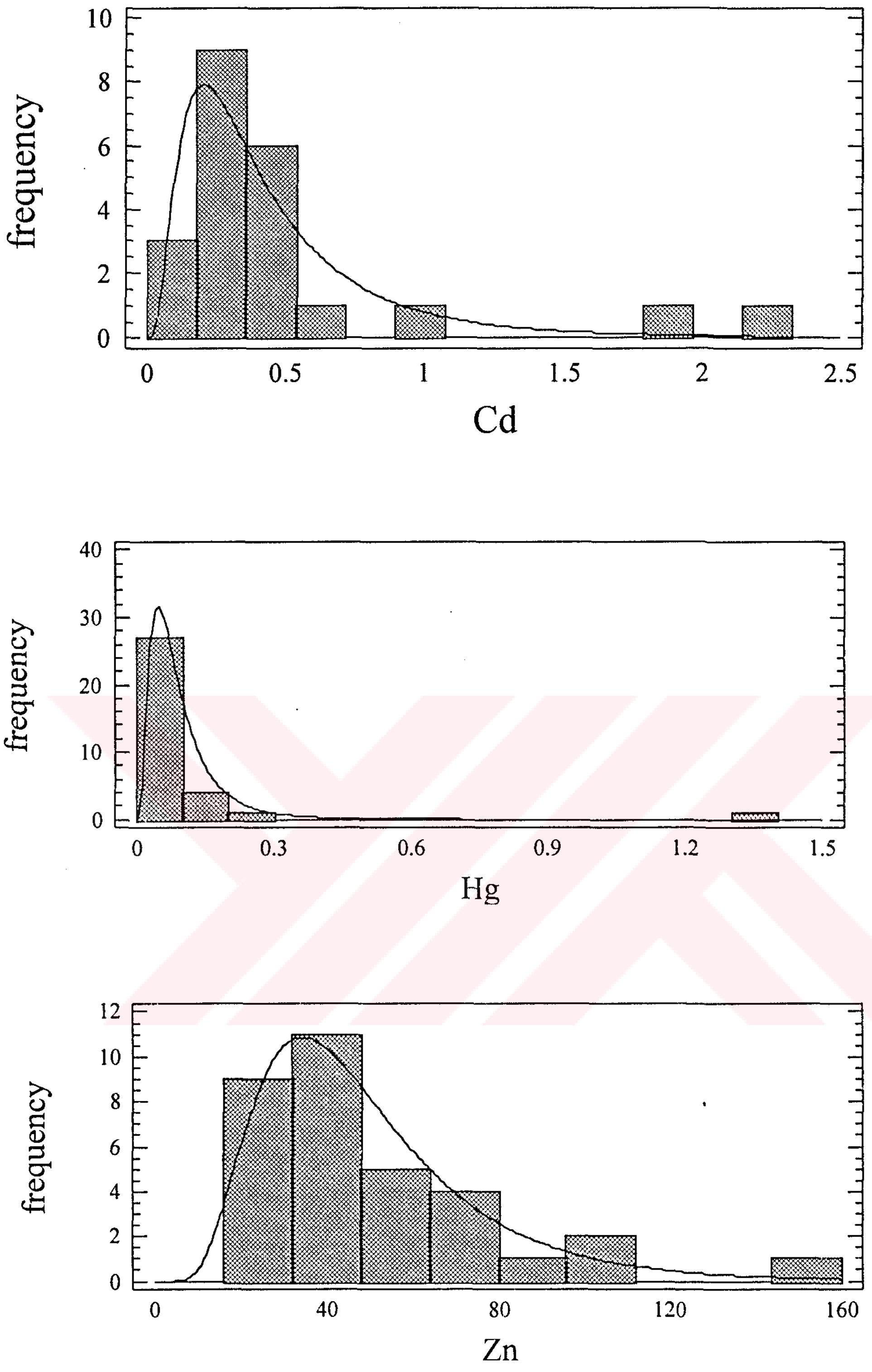


Figure 4.15. Frequency histograms and distribution curves for anthropogenic elements Cd, Hg and Zn for urban light industry region

The summary statistics for semi-urban region data is given in Table 4.18. An extra column is added to this table for alpha value. If the number of samples exceeds 40, the significance level of an observed value of DN is represented by alpha value (as a disproof of null hypothesis that the distribution is lognormal). It is given approximately by:

$$Alpha = \left[\sqrt{N} + 0.12 + \frac{0.11}{\sqrt{N}}\right].DN$$

Thus critical value of alpha should be 1.36 at a 95% confidence level. The results are given in Table 4.18. According to Table 4.18 the elements K do not show lognormal distribution after K-S DN distribution fitting test. Alpha value for K is greater than 1.36, indicating that data do not fit to the hypothesized distribution (i.e. lognormal distribution). There are large family of distribution functions that are likely to fit this element. When the goodness of fit test was applied using other distribution functions, only weibull distribution is fitted to K visually. As explained above K is a nutrient element for lichens and its concentrations are not changing much from one place to another. The frequency histogram and distribution curve of K is shown in Figure 4.16. The distribution of crustal elements Al, Ca and Fe are shown in Figure 4.17. Calcium shows longer tail than others again. The distribution fitting of anthropogenic elements Cd, Pb and Zn are shown in Figure 4.18.

Table 4.18. Distribution fitting results of semiurban region

Element (unit)	Std. Skewness	Std. Kurtosis	K-S DN	Alpha	Distribution type
Al ($\mu g\ g^{-1}$)	5.0	4.80	0.07	0.58	Lognormal
As ($\mu g\ g^{-1}$)	4.1	4.9	0.10		Lognormal
Ca ($\mu g\ g^{-1}$)	7.8	9.6	0.14	1.11	Lognormal
Cd ($\mu g\ g^{-1}$)	4.4	2.4	0.07	0.52	Lognormal
Cr ($\mu g\ g^{-1}$)	8.9	18	0.07	0.58	Lognormal
Cu ($\mu g\ g^{-1}$)	15	49	0.06	0.46	Lognormal
Fe ($\mu g\ g^{-1}$)	4.8	3.1	0.09	0.71	Lognormal
Hg ($\mu g\ g^{-1}$)	6.5	13	0.22		Lognormal
K ($\mu g\ g^{-1}$)	2.1	0.51	0.18	1.44	Weibull
La ($\mu g\ g^{-1}$)	5.0	5.2	0.10	0.78	Lognormal
Mg ($\mu g\ g^{-1}$)	1.8	-0.07	0.10	0.84	Lognormal
Mn ($\mu g\ g^{-1}$)	5.3	4.5	0.09	0.72	Lognormal
Na ($\mu g\ g^{-1}$)	9.1	18	0.07	0.55	Lognormal
Ni ($\mu g\ g^{-1}$)	3.4	1.3	0.07	0.53	Lognormal
Pb ($\mu g\ g^{-1}$)	3.5	1.4	0.08	0.62	Lognormal
Sb ($\mu g\ g^{-1}$)	2.6	1.4	0.09		Lognormal
Se ($\mu g\ g^{-1}$)	5.1	6.2	0.12		Lognormal
V ($\mu g\ g^{-1}$)	3.8	1.7	0.09	0.74	Lognormal
Zn ($\mu g\ g^{-1}$)	4.8	2.2	0.15	1.23	Lognormal

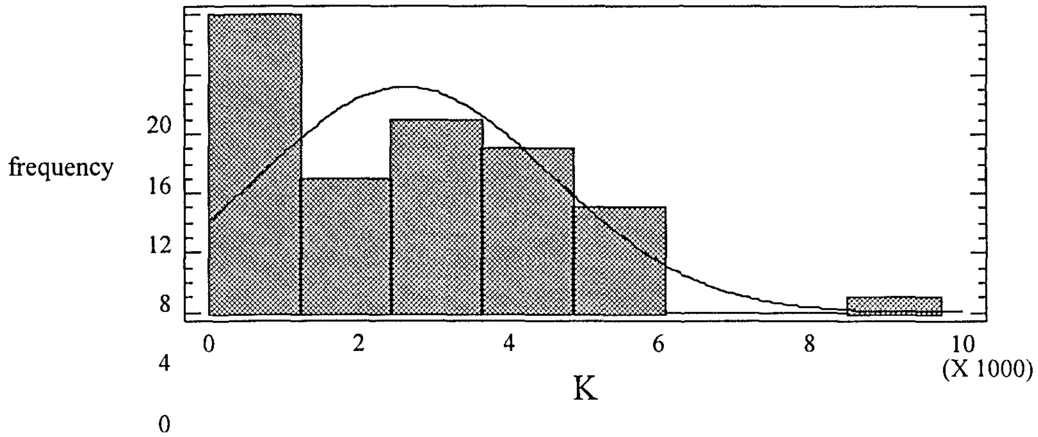


Figure 4.16. The frequency histogram and distribution curve of K for semiurban region

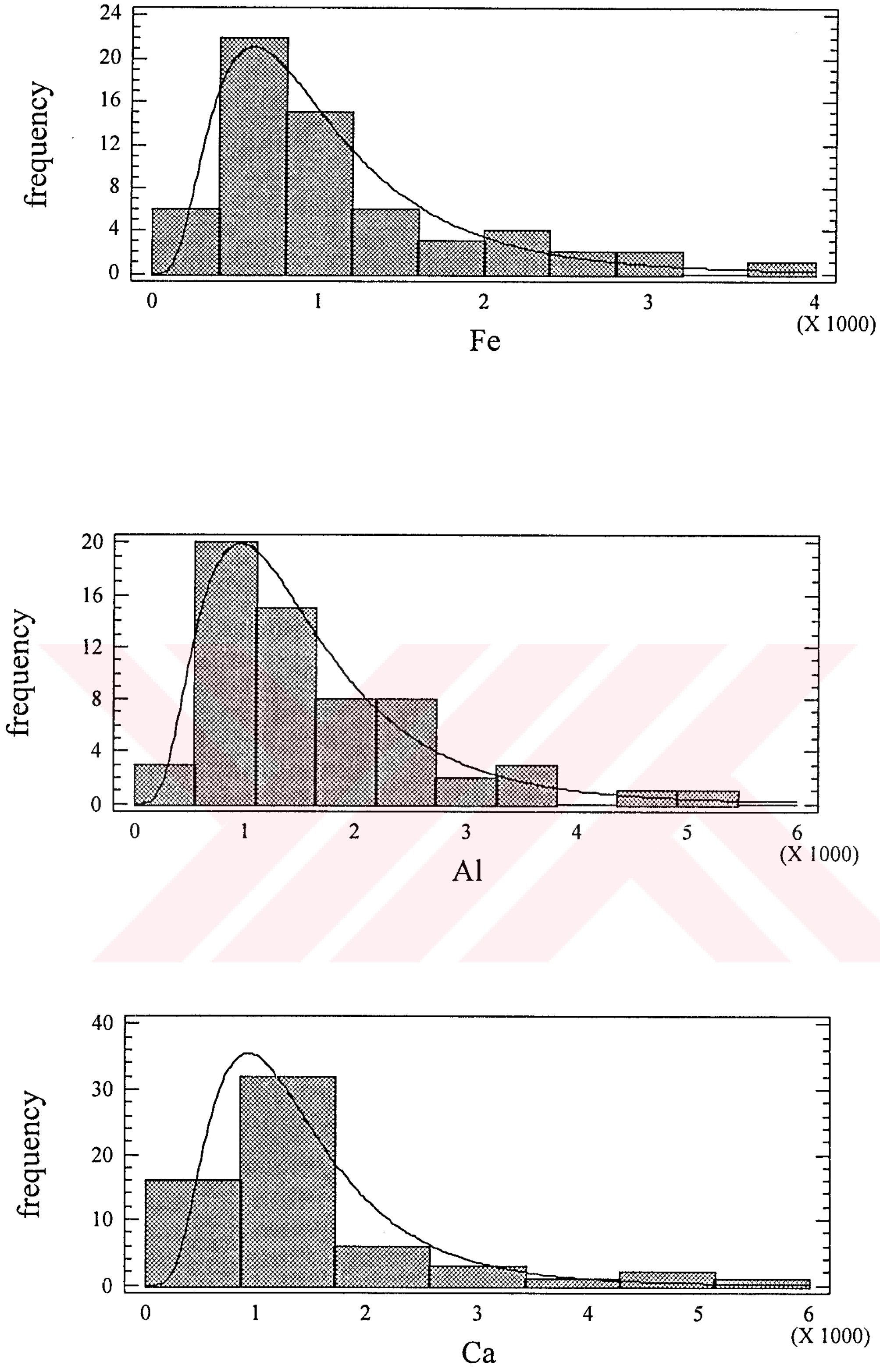
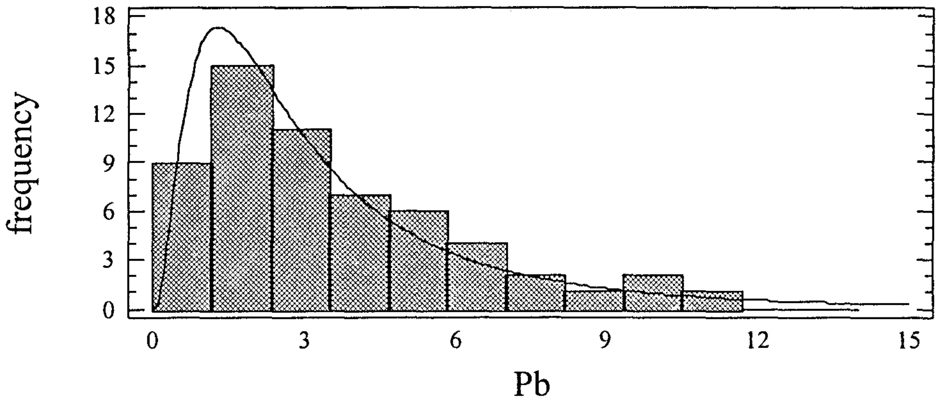
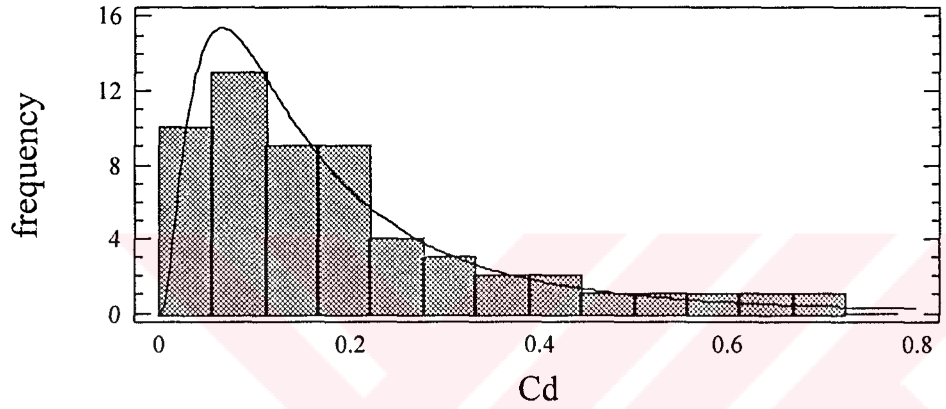


Figure 4.17. Frequency histogram and distribution curves for crustal elements Fe, Al and Ca





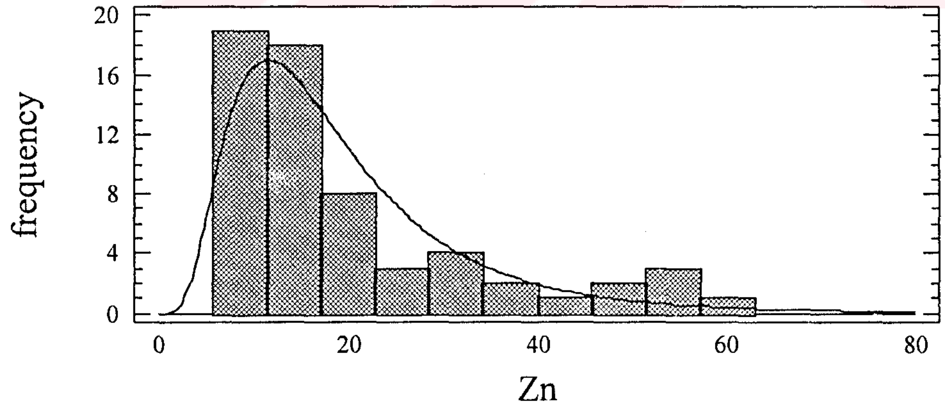


Figure 4.18. Frequency histograms and distribution curves Pb, Cd and Zn for semiurban region

4.2.3. Comparison with Other Data

Comparison of the produced lichen data with the literature values is one of the ways of the screening used in environmental research. Areas under study constitute rural areas and mixed areas (rural + urban + industrial). The urban and industrial areas are the ones, which are under the direct influence of the local anthropogenic emissions, while rural areas are reasonably far away from any local sources. Therefore in order to have pre- knowledge about the extent of pollution in the study region, the results are compared with literature data. The data obtained from the air sheds which are affected by similar pollution sources or pollution levels in the regional scale give approximately same average concentrations even if different lichen species are used.

Observed concentrations of elements are compared and listed in Table 4.19 with those found by rural areas in order to see roughly how the levels of pollution deviate from the baseline concentrations. In the literature of lichen studies the concentrations observed at rural areas or national parks are called as baseline concentrations. Lichen studies involve different species, habitats (which will influence moisture levels and exposure to air currents, canopy throughfall, and other environmental factors), growth forms (on tree, rock or soil, methods of sample preparation (washed or unwashed; whole thallus analysis or not), analysis and sample size. That's why the results should also be interpreted accordingly. While we are comparing our data with the literature values, some of these parameters are kept constant like growth forms (on trees), sample preparation (washed and whole thallus) and sample size. Unfortunately due to different techniques used in the analyses of samples, data are not available for all elements in all studies. Comparison of concentrations of elements measured in Aegean Region of Turkey with those measured in rural sites show that, the concentrations of Al, As, Ce, Fe, La, Sc and Ti are higher than the baseline concentrations in rural areas in the table. Except for As, all elements are crustal origin. Arsenic may come from heavy coal burning in the region. The concentrations of these elements reach up to an order of magnitude higher than the baseline concentrations. However, the concentrations of Cr and Cu are generally higher than the baseline concentrations. It is suprising that

Table 4.19. Comparison of lichen data set with baseline concentrations in the literature ($\mu g\ g^{-1}$)

Elements	Geom. Mean [1] (STD)	Geom. Mean[1*]	Arith. Mean [2]	Arith. Mean[2*]	Arith. Mean[3]	Arith. Mean[4]	Range[5]	This Study Arith. Mean (STD)	This Study Geom. Mean (STD)
Al	1100 (1.18)	260 (1.49)	143	267	480		150-2200	2650 (3150)	1950 (1.06)
As			0.49	0.69			0.20-3.55	4.1 (2.2)	3.6 (1.05)
Ba	24 (1.67)	16 (1.61)					7.9-59.7	37 (57)	25 (1.09)
Ca	3800 (1.65)	3300 (1.38)	1585	3730	3340	4600		1940 (1960)	1450 (1.06)
Cd			0.23	0.36	0.70	0.7	0.05-0.70	0.30 (0.38)	0.19 (1.08)
Ce	0.55 (1.42)	0.22 (1.43)						2.2 (2.2)	1.6 (1.09)
Cr	4.9 (1.50)	1.0 (1.72)	0.59		2.1		1.25-6.26	5.1 (5.9)	3.4 (1.08)
Cu	3.7 (1.59)	2.6 (1.75)	2.09	1.74	7.3	4.5	3.75-12.3	5.9 (4.3)	5.4 (1.05)
Fe	850 (1.42)	170 (1.52)	168	230	540		492-1037	1650 (1810)	1250 (1.06)
Hg			0.14	0.11			0.05-0.55	0.12 (0.23)	0.069 (1.08)
K	1800 (1.39)		3180	2860	2750	9500		3490 (2320)	2620 (1.07)
La	0.37 (1.50)	0.11 (1.78)						1.71 (1.80)	1.27 (1.06)
Mg	1300 (1.44)	1600 (1.21)	440	690	400	1400		1610 (710)	1490 (1.03)
Mn	89 (1.63)	97 (1.72)	51	93	131		10.9-87.4	36 (37)	28 (1.06)
Mo							0.21-0.89	0.36 (0.44)	0.25 (1.10)
Na	320 (1.40)	300 (1.29)	36	31				285 (435)	200 (1.07)

Table 4.9 Continued

Elements	Geom. Mean[1] (STD)	Geom. Mean[1*]	Arith. Mean[2]	Arith. Mean[2*]	Arith. Mean[3]	Arith. Mean[4]	Range[5]	This Study Arith. Mean (STD)	This Study Geom. Mean (STD)
Ni	11 (1.51)	6.0 (1.40)	0.94	1.00	2.6			3.9 (4.6)	2.8 (1.08)
Pb		7.5 (1.25)	2.7	3.1	18	0.25	2.1-52.6	8.8 (20)	4.3 (1.10)
Sb							0.05-0.70	0.30 (0.39)	0.21 (1.07)
Sc		0.26 (1.37)						0.54 (0.74)	0.39 (1.08)
Sr	28 (1.50)	18 (1.53)					12.3-57.4	25 (26)	19 (1.1)
Ti	16 (1.20)	51 (1.47)	12	16.5	25.9		29.7-117.8	183 (260)	130 (1.09)
V	4.4 (1.48)	2.5 (1.45)	0.29	0.44			0.74-5.76	4.4 (6.3)	3.0 (1.07)
Zn	95 (1.58)	25 (1.43)	24	27	86	50	22.2-55.4	37 (43)	26 (1.06)

[1] Gough et al., 1988b (Redwood National Park, California (Hypogymnia enteromorpha))

[1*] Gough et al., 1988b (Redwood National Park, California (Usnea spp.))

[2] Bennett and Wetmore, 1999 (Yellowstone National Park, Wyoming (Bryoria fremontii))

[2*] Bennett and Wetmore, 1999 (Yellowstone National Park, Wyoming (Letharia vulpina))

[3] Kubin 1990 (Rural areas of Finland (Hypogymnia physodes))

[4] Wiersma et al., 1992 (Torres del Paine National Park, Southern Chile (Nephroma antarcticum)

[5] Bargagli et al., 1987; Nimis et al., 1993; Loppi et al., 1994; Loppi and Bargagli, 1996 (unpolluted areas in Italy (Parmelia caperata)

the concentrations of Mn are lower than the baseline concentrations. The concentrations of other elements including anthropogenic elements like Cd, Hg, Ni, Pb and Zn were comparable with the baseline concentrations. However, arithmetic mean values of V and Ni excluding the work of Gough et al., (1988b) in California are higher than other studies. The background areas of California may be high especially for considering the concentrations of V. Similar results were obtained by Ölmez et al., (1985) in Washington D. C. on state due to heavy combustion of oil. From this comparison it may seem that the region is not polluted very much considering these anthropogenic elements.

When we compare our data with the literature data as a national base (regional scale) survey in Table 4.20, the concentrations of reference 3, Dutch National Survey, are considerably higher than the other studies as well as our study. This is due to the high pollution loadings (the element concentrations patterns showed high concentration classes for As, Cd, Cr, Cs, Fe, Ni, Pb, Sb, Se, V and Zn along the Belgian and west German border and probable Dutch local pollutions sources of Br, Cs, La, N, Se and V were found in the northern region of the country (Sloof, 1993)). In addition to this instead of giving the mean values it would be better to give the geometric mean data because it is said that the number of extreme values are much higher in that study. That is why when we are discussing the literature values it will be suitable to compare studies without including the Dutch study with our study in the following pages. Same conclusion is drawn from the study in Portugal. In that study it is said that in the Netherlands the elemental contents in the lichen are much larger than in the moss while in Portugal the elemental contents in the lichen are similar to the elemental contents in the moss. Also when they compared their values with the Netherlands they found that their country is relatively clean especially the interior parts of the country (Freitas et al., 1999).

The mean values of Al, As, Cl, Cs, Th and U in our study are relatively larger than the other literature values. The high concentrations of As, Th and U are closely related with the lignites, which are extensively used as an energy source or domestic heating in Turkey (Eğilli, 1999).

Table 4.20. Comparison of lichen data set with the concentrations in the literature ($\mu g\ g^{-1}$)

Element	Arith. Mean[1] (STD)	Arith. Mean [2]	Arith. Mean[3]	Arith. Mean[4] (STD)	This Study Arith. Mean (STD)
Al				945 (802)	2650 (3150)
As	1.24 (0.50)	2.19	5.7	0.52 (0.55)	4.1 (2.2)
Ba	28.3 (26.7)				37 (57)
Br	14.5 (5.52)		56	6.5 (4.6)	6.5 (4.9)
Cd	1.05 (0.65)		2.8	0.30 (0.29)	0.30 (0.38)
Ce	2.57 (1.28)				2.6 (2.7)
Cl				188 (118)	300 (260)
Cr	5.78 (3.84)	5.77	26	2.8 (6.5)	5.1 (5.9)
Cs			0.8	0.19 (0.21)	1.1 (2.0)
Cu				7.5 (7.9)	5.9 (4.3)
Fe	1253 (665)		5800	687 (649)	1650 (1810)
Hf	0.17 (0.10)				0.24 (0.34)
Hg	0.11 (0.15)	0.32	0.5		0.12 (0.23)
K	4094 (1208)				3490 (2320)
La	1.16 (0.57)		6.2	0.72 (1.15)	1.71 (1.80)
Mn				310 (321)	36 (37)
Mo	0.72 (1.01)				0.36 (0.44)
Na	181 (99.3)			346 (377)	285 (435)
Ni		3.92	16	2.6 (5.7)	3.9 (4.6)
Pb		18.4	147	26 (29)	8.8 (20)
Rb	14.4 (9.38)			11.3 (7.8)	11.7 (12.7)
Sb	0.35 (0.38)	0.36	3.3	0.30 (0.32)	0.30 (0.39)
Se	0.27 (0.12)	0.43	1.8	0.47 (0.36)	0.37 (0.29)
Sc	0.37 (0.21)			0.18 (0.17)	0.54 (0.39)
Sm	0.19 (0.09)			0.098 (0.111)	0.23 (0.28)
Sr	22.2 (14.5)				25 (29)
Tb	0.027 (0.014)				0.038 (0.042)
Th	0.29 (0.15)			0.12 (0.19)	1.20 (1.56)
U	0.12 (0.06)				0.22 (0.29)
V		14.5	32	3.61 (3.91)	4.4 (6.3)
Zn	90.2 (24.4)		210	41 (26)	37 (43)

[1] Jeran et al., 1996 (National monitoring survey, Slovenia (Hypogymnia physodes))

[2] Freitas et al., 1999 (National monitoring survey, Portugal (Parmelia sulcata)

[3] Sloof and Wolterbeek, 1991a (National monitoring survey, the Netherlands (Parmelia sulcata))

[4] Steinnes et al., 1992 (National monitoring survey, Norway (moss Hylocomium splendens))

However, the mean values of Pb and Mn are relatively lower in our study than the mean values in other studies.

In the study conducted in Slovenia, Br (a factor of approximately 2), Cd (a factor of 3.5), Mo (a factor of 2) and Zn (a factor of approximately 2) are larger than ours. In Slovenian data Br represents the marine component. Cadmium and Zn come from metal producing or steel factories. Whereas the mean values of As (a factor of approximately 3.5), Na (a factor of approximately 1.5), U (a factor of 2) and Th (a factor of 4) are lower than ours.

In the study of Portuguese workers, the mean values of V (a factor of 3), Pb (a factor of 2) and Hg (a factor of about 3) are higher than ours but the mean value of As is lower than ours by a factor of approximately 2. In the paper it is said that the ratio V/Ni is about 4, being larger than the expected ratio of 3 for the oil combustion emission estimates (Freitas et al., 1999). It might be assumed that either the V uptake of lichens is slightly favoured relatively to Ni uptake or else the oil typically burnt in two oil electrical plants is V enriched. Arsenic may also originate from coal source in only one region of the Portugal but in general As appears especially accumulated in the lichens collected in the northeast of the country which should be due to the influence of the parent rocks of the soil. Our V/Ni ratio is 1.5 as oil burning is not common in the region.

The last study in Table 4.20 was done in Norway, we compared the moss national survey since on the average for most of the elements there was no significant difference between lichen and moss samples (Freitas et al., 1999). Mean values of Al, As, Cl, Cr, Cs, Fe, La, Ni, Sc, Sm, Tb, and Th are lower than ours with factors varying from 1.5 to 9. However, mean values of Mn (a factor of 9) and Pb (a factor of approximately 3) are larger than ours. In Norway, main classifications of sources are the followings (elements in parentheses represent a secondary association with the group in question): Contribution from long range transport: V, (Co), (Cu), (Zn), As, Se, Ag, Cd, Sb, Pb.

Contribution from local sources: Cr, Ni, Cu

Contribution from the marine environment: (Na), Cl, Se, Br, I

Associated with local soil dust: As, Al, Sc, (V), (Cr), Fe, Co, La, Sm, Th.

Transfer from soil via higher plants: Mn, Zn, Rb, Cs.

In the literature, we could have not found enough data to compare all subregions. Although there are many studies related with these subregions, they do not provide data in table format with their mean and deviations. That's why we can only compare three subregions.

First one of these is urban light industry region. The comparison of data is given in Table 4.21. Other study is conducted with two different lichen species namely Hypogynmia physodes and Usnea hirta in the city of Oulu in Finland by Garty et al., (1996). In our study the average concentrations of Fe and Mg are higher than the other site whereas the concentrations of Na, Zn, Ni and Cd are lower than the study of Garty et al. (1996). Standard deviations are higher in our study since our sampling area is very large. However in other study, they collected the samples just from one site but from several points.

The second region to be compared is industrial region. The comparison values are listed in Table 4.22. First study was done in Baton Rouge with high industry such as metal processing and petrochemical and high urban traffic using the lichen species of Ramalina stenospora (Walther et al., 1990). The average value of Fe in our study is higher. However, the average values of Pb and Cu in the study of Walther et al. are higher than that of our study. Iron is emitted in high amounts from iron-steel plants as expected. Lead (leaded gasoline), Zn (lubricating oil and automobile tires) and Cu (lubricating oil) concentrations increased with a heavy traffic in Baton Rouge besides the metal processing. The highest concentrations in industrial corridor at one station were given 10105 μg g^{-1}, 421 μg g^{-1}, 342 μg g^{-1} and 53 for the elements Fe, Zn, Pb and Cu, respectively. Our highest values were 18930 μg g^{-1}, 163 μg g^{-1}, 53 μg g^{-1} and 30 μg g^{-1} for the elements Fe, Zn, Pb and Cu, respectively. As can be understood from these values, Fe has also higher concentration in our study regarding the nearest points to the industrial sources.

The second study was done in Armadale in Scotland with a lichen species of Hypogymnia physodes around steel foundry (Gailey et al., 1985). The average concentrations of all elements other than Pb and Cu are considerably higher in our study although they did not wash the lichen samples since in Armadale there was

Table 4.21. The comparison of urban light industry region data with literature values (µg g^{-1})

Element	Average ± STD (N)*1	Average± STD (N)*2	This study Average ± STD (N)
K	4115 ± 180 (12)	3790 ± 150 (7)	4600 ± 2720 (33)
Ca	2170 ± 580 (11)	1320 ± 350 (7)	2060 ± 2040 (32)
Fe	1890 ±260 (11)	490 ± 50 (7)	2070 ± 1300 (33)
Mg	815 ± 80 (12)	610 ± 70 (7)	1720 ± 590 (33)
Na	780 ± 310 (12)	600 ± 250 (7)	330 ± 200 (33)
Zn	150 ± 70 (10)	105 ± 50 (6)	50 ± 28 (33)
Mn	80 ± 8 (11)	55 ± 5 (7)	50 ± 35 (33)
Pb	21 ± 2.7 (10)	27 ± 10 (3)	22 ± 41 (21)
Cu	14 ± 1.8 (11)	8.4 ± 1.1 (7)	7.5 ± 3.7 (22)
Ni	9.8 ± 3.9 (9)	12 ± 3.6 (5)	4.9 ± 5.9 (22)
Cd	1.8 ± 0.9 (11)	5.2 ± 2.9 (5)	0.49 ± 0.55 (22)

N shows the number of samples

* Garty et al., 1996 (The city of Oulu in Finland with heating plant, a sulfate pulp mill and a chemical factory)

*1: Hypogynmia physodes

*2: Usnea hirta

Table 4.22. The comparison of industrial region data with literature values (µg g^{-1})

Element	Average ± STD [1]	Average (N)[2]	Average ± STD[3] (N)	This study Average ± STD (N)
Fe	1971 ±2330	975 (47)	4450 ± 350 (5)	4630 ± 5610 (9)
Zn	164 ± 87	80 (47)	1230 ± 70 (5)	170 ± 150 (9)
Mn		58 (47)	340 ± 30 (5)	110 ± 100 (9)
Pb	99 ± 105	29 (47)	480 ± 80 (5)	32 ± 28 (8)
Cu	24 ± 13	13 (47)	40 ± 3.2 (5)	14 ± 9.1 (8)
Ni		5.1 (47)	11 ± 1.3 (5)	10 ± 12 (8)
Cr		10.8(47)	41 ± 6.9 (5)	16 ±15 (9)

N shows the number of samples

[1] Walther et al., 1990 (Baton Rouge with high industry such as metal processing and petrochemical and urban traffic), Ramalina stenospora.

[2] Gailey et al., 1985 (Armadale in Scotland with steel foundry), Hypogymnia physodes

[3] Caniglia et al., 1994 (Padua in Italy with steel works), Evernia prunastri

only one steel foundry but in our study area there were two important iron-steel plants, metal works and one refinery.

The third study was conducted by Caniglia et al. (1994) in Italy around steel works with a lichen species of Evernia prunastri. Average concentrations of all elements except for Fe and Ni are higher than our study. Samples were collected in front of works (0.3 km). We collected the nearest samples approximately 0.5 km away from the factories but these are the lichen species of Parmelia tiliacea on pine trees (acidic bark) on which Xanthoria parietina species can not live (Brooks and Hawes, 1995). The concentrations of Fe (28880 $\mu g\ g^{-1}$), Zn (2770 $\mu g\ g^{-1}$), Mn (940 $\mu g\ g^{-1}$) and Cr (181 $\mu g\ g^{-1}$) in Parmelia t. are 6.5 times for Fe, 2.2 times for Zn, 2.8 times for Mn and 4.4 times for Cr than that of the other study (Caniglia et al., 1994). The nearest Xanthoria parietina samples were collected after going down approximately 100 m from the hill that avoids the most of the plume of the factories to reach that area. The average concentrations of two Xanthoria parietina samples at that point in our sampling site are 2945 $\mu g\ g^{-1}$for Fe, 422.5 $\mu g\ g^{-1}$ Zn, 118 $\mu g\ g^{-1}$ for Mn, 65.3 $\mu g\ g^{-1}$ for Pb, 18.8 $\mu g\ g^{-1}$ for Cu, 4.8 $\mu g\ g^{-1}$ for Ni and 16 $\mu g\ g^{-1}$ for Cr. If we compare these nearest concentrations to the plants in Xanthoria p. in our study to Caniglia's study, the average concentration of Fe is 1.5 times, that of Pb is 7 times and the average concentrations of other elements Zn, Mn, Pb, Cu, Ni and Cr are 2-3 times higher than our concentrations.

Power plants area is the third subregion that will be compared with available studies in the literature. The first study was conducted by Ölmez et al., (1985) around the Dickerson coal power plant near Washington, D. C. with two species lichens Parmelia caperata and Parmelia rudecta. Samples were collected in 20 km distance from the plant. The average concentrations of both lichen species are given in Table 4.23. The average concentrations of Al, Fe and Na are observed to be higher in our study. However the average concentrations of Ca, Cd, K, Mn, Se, V and Zn are found to be lower in our study. The average values of elements As, Cr, La and Sb are comparable in both studies. The As/Se ratio was calculated for each sample was

Table 4.23. The comparison of power plant area data with literature values (μg g^{-1})

Element	Average ± std *[1](N)	Average ± std *[2](N)	Average ± std [3] (N)	This study Average ± std (N)
Al	1630 ± 910 (5)	2100 ± 1150 (6)		3720 ± 1900 (18)
As	3.9 ± 1.0 (5)	5.0 ± 2.0 (6)		6.2 ± 1.7 (17)
Ca	32000 ± 21000 (5)	17000 ± 12000 (6)		2785 ± 1790 (18)
Cd	1.2 ± 0.2 (5)			0.14 ± 0.12 (18)
Cr	3.8 ± 1.2(5)	4.6 ± 1.5 (6)	9.4 ± 6.5 (125)	4.3 ± 2.2 (18)
Cu			13.4 ± 7.1 (125)	4.9 ± 1.7 (18)
Fe	1400 ± 600 (5)	1620 ± 780 (6)		2110 ± 1000 (18)
K	4020 ± 980 (5)	3300 ± 500 (6)		1920 ± 1100 (18)
La	2.4 ± 0.8 (5)	2.8 ± 1.7 (6)		2.25 ± 1.26 (17)
Mn	240 ± 100 (5)	230 ± 100 (6)		33 ± 17 (18)
Na	130 ± 60 (5)	145 ± 30 (6)		310 ± 220 (18)
Ni			36 ± 21 (125)	3.8 ± 2.0 (18)
Pb			120 ± 73 (125)	5.6 ± 5.6 (18)
Sb	0.35 ± 0.14 (5)	0.38 ± 0.12 (6)		0.22 ± 0.10 (17)
Se	1.1 ± 0.8 (5)	1.1 ± 0.5 (6)		0.37 ± 0.29 (17)
V	8.5 ± 2.6 (5)	6.8 ± 2.1 (6)		4.7 ± 2.9 (18)
Zn	64 ± 8 (5)	68 ± 24 (6)	57 ± 30 (125)	27 ± 24 (18)

N shows the number of samples

[*] Ölmez et al., 1985 (A coal-fired powerplant, Washington D. C.)

*[1]: Parmelia caperata

*[2]: Parmelia rudecta

[3] Garty, 1987 (A coal-fired power plant, Israel), Ramalina duriaei

almost constant and equal to about 4.0 for the Dickerson power plant. For the Soma power plant average ratio is equal to 48 ± 12 and for the Yatağan power plant it is equal to 13 ± 7.1. The difference between two power plants in our study comes from low Se content since As is not changing very much. For the Yatağan power plant Se content is about 5 times higher on the average than that for the Soma power plant. Nevertheless the ratio found in our power plants is very higher than that were found for the Dickerson power plant. Since As content in Turkish lignites is higher (Eğilli, 1999). They said that V was enriched in the Dickerson background samples as it is throughout the Eastern U. S. because of combustion of residual oil, which has substantial concentrations of V.

The second study was performed in Israel around Maor David coal-fired power plant with a lichen species of Ramalina duriaei within a distance about 25 km from the plant. The average concentrations of all elements Cr, Cu, Ni, Pb and Zn are higher in the study of Garty (1987). He said that the coal that was used in the power plant imported from South Africa. This coal contains high amounts of Cr. The mean Pb/Zn ratio in lichen samples obtained in Garty's study (1987) is 2.11. However in our study it is calculated as 0.25 and even in the closest sample to Soma power plant the ratio was 1.15. As can be seen from this comparison, without considering As, power plants areas are not as polluted as in the areas in other studies discussed here.

4.3. Geographical Concentration Patterns of Elements in Lichens

The primary aim of this thesis is to study epiphytic (growing on trees) lichens as biomonitors of levels, geographical gradients of air pollution. The pollution maps were prepared using the concentration of elements in order to indicate the location of the important pollution sources and their impact areas. Before the main study commenced, a methodological investigation was carried out to document the degree of consistency of the element concentrations collected by this lichen. In the section 4.1, we discussed different lichen species and tree bark considering their accumulation capacities. We decided that lichen Xanthoria parietina is suitable lichen species also with respect to accumulation capacity of elements. During sampling we tried to collect nearly same size of lichens from all sides of 3 or 7 nearby trees. During the sample preparation, Xanthoria parietina were separated from the tree bark with both its apothecia and leafy parts. Before we comment about the geographical distribution of the concentration we must be sure that size or morphology differences did not cause large changes in concentrations. Without such a test, deriving conclusions from concentration data would not be very meaningful. Then we should also be sure that the local variation of element concentrations is not large enough to disturb the concentration pattern on a regional scale. For this purpose the variation of the element concentrations in Xanthoria parietina within the same sampling site was determined. These variations are named as local variation.

4.3.1. Local Variations in Element Concentrations

4.3.1.1. Examining of the Concentration Differences within Xanthoria parietina Thalli

In order to determine the degree of consistency in element concentrations within and among lichen thalli, we can investigate whether there is a difference in accumulation capacities of elements in morphologically different parts of lichen thallus and different size ranges of lichen thalli.

Xanthoria parietina has an apparent morphological structure. In some of the lichen thallus, the leafy part of the lichen thallus is dominant, in some of the lichen thallus, the apothecia part which are the cup shaped (or dishlike) fruiting bodies cell in which fungus releases spores to find a free living algal cell and form a new lichen is dominant. In some of the lichen thalli both are equally distributed. Whether there is an accumulation difference in these morphologically different (probably the chemical structures are also different) parts of the lichen thallus was tested using the ANOVA (Analysis of Variance) statistical analysis by using Statgraphics Plus program package (Statgraphics Manual 3.1, 1997). The results of the analysis at a probability level of P=0.05 are given in Table 4.24. The F ratio is a ratio of the between group estimate (variance between two different parts of lichen thallus) to the within group estimate (variance in individual parts of lichen thallus). This ratio can be compared with the table values of F test with two-tailed distribution in order to compare the means of two parts of the lichen thallus. Other way of evaluating the ANOVA analysis result is to use P-value that is one of the output of ANOVA analysis. If P-value of the F-test is greater than or equal to 0.05, there is not a statistically significant difference between the means of the two lichen parts at the 95% confidence level and this case is denoted by NS in the table. If P-value of the F-test is smaller than 0.05, there is a statistically significant difference between the means of the two lichen parts at the 95% confidence level but in our case it was seen that there is no statistically significant difference for all elements at 95% confidence level.

Table 4.24. The ANOVA table showing the difference between apothecia and leafy part of the lichen Xanthoria parietina and thallus size (<2.5 cm and >2.5 cm) collected from the same sampling points at P=0.05.

	Apothecia versus leafy part				Thallus size			
Element	Number of samples	F ratio	P value	Sign.	Number of samples	F ratio	P value	Sign.
Al	5	0.01	0.93	NS	7	1.17	0.30	NS
As	5	2.46	0.15	NS	7	0.29	0.59	NS
Au	4	0.53	0.48	NS	7	0.02	0.89	NS
Ba	4	0.00003	0.99	NS	5	1.42	0.26	NS
Br	5	0.34	0.57	NS	7	2.86	0.12	NS
Cd	3	0.05	0.83	NS	4	0.61	0.46	NS
Ce	5	0.69	0.43	NS	7	0.13	0.73	NS
Cl	4	0.79	0.40	NS	7	0.83	0.38	NS
Co	5	0.46	0.51	NS	7	0.0029	0.95	NS
Cr	4	0.42	0.53	NS	7	0.02	0.89	NS
Cs	4	1.09	0.33	NS	7	0.46	0.51	NS
Eu					7	0.19	0.67	NS
Fe	4	0.06	0.82	NS	7	0.73	0.41	NS
Hf	5	0.19	0.67	NS	7	0.01	0.91	NS
Hg	5	1.60	0.24	NS	6	0.79	0.39	NS
K	5	0.75	0.41	NS	7	0.15	0.70	NS
La	5	0.07	0.79	NS	7	0.28	0.60	NS
Lu	5	0.47	0.51	NS	7	0.08	0.77	NS
Mg	5	1.40	0.27	NS	7	0.09	0.77	NS
Mn	5	1.84	0.21	NS	7	0.16	0.69	NS
Na	5	0.34	0.57	NS	7	0.43	0.52	NS
Nd	5	0.20	0.67	NS	7	3.77	0.076	NS
Rb	4	0.73	0.42	NS	7	0.06	0.81	NS
Sb	5	1.26	0.29	NS	7	0.01	0.94	NS
Sc	4	0.06	0.82	NS	7	0.74	0.40	NS
Se	5	0.05	0.82	NS	7	0.69	0.43	NS
Sm	4	0.01	0.91	NS	7	0.43	0.52	NS
Th	5	1.46	0.26	NS	7	0.53	0.48	NS
Ti	4	0.003	0.95	NS	7	0.01	0.94	NS
V	5	0.47	0.51	NS	7	0.70	0.42	NS
Yb	5	0.12	0.74	NS	7	0.13	0.73	NS
Zn	4	0.10	0.76	NS	7	0.07	0.80	NS

Our other investigation topic is about the size and consequently the age of the lichen thallus (Armstrong, 1974). The lichen species, which are collected as whole thallus without breaking into pieces, were chosen for this purpose. After investigating of them it was seen that they can be grouped into two parts considering the diameters of the whole thallus. The whole thallus diameter smaller than 2.5 cm

(1 cm-2.5 cm) and whole thallus diameter greater than 2.5 cm (2.5 cm-4 cm) were analyzed separately. The most of the collected samples enter the group of the thalli with diameters greater than 2.5 cm. The results of ANOVA analysis are also given in Table 4.24. From the table it can be seen that there is no statistically significant difference between the collection capacities of two sizes of the lichens collected at the same sampling points. One similar study was conducted by Armstrong (1997). In that study the relationship between ion levels (Mn, Cu, Zn, Mg and Ca) and thallus size was studied in lichen Xanthoparmelia conspersa and Parmelia glabratula ssp. fuliginosa growing on rock surface. Five replicate samples were collected from five size classes of thalli: less than 1 cm, 1.1-2 cm, 2.1-3 cm, 3.1-4 cm and greater than 4 cm in diameter. The levels of Ca, Cu and Zn were similar in thalli from under 1 to over 4 cm in diameter. However, the level of Mg increased with thallus size in X. conspersa while the level Mn decreased with thallus size in both species. Ion levels were similar in the marginal segments and centers of large diameter (over 4 cm) and small diameter (under 2 cm) X. conspersa thalli.

In another study (Gailey and Lloyd, 1986b), fruticose lichen Hypogymnia physodes was tested in the thallus size ranges between 0.2 to 1.4 cm diameter in order to find whether there is an accumulation differences of metals Fe, Mn, Zn, Pb, Cu and Cr in these size ranges. Generally, the mean concentrations for each size of thallus increased with length of thallus, the trend being continuous for all metals except Fe, Mn and, to a lesser extent, Cr. The lowest coefficient of variation (CV) was in thalli between 0.8 cm and 1.2 cm. The highest coefficients for Pb, Mn, Zn and Cr were in the smallest size of thallus, the second smallest size having the highest coefficient for Fe and the second highest for Mn, Zn and Pb. Above a thallus size of 1.2 cm, the coefficients for all metals increased. As a result the thallus size range of 0.8-1.2 cm was chosen as the best consistent size range to conduct the studies with this lichen species.

4.3.1.2. Calculation of Local Variation

The local variation was considered to comprise the variation in substrate, age, size and morphology of lichen samples, and the individual variation in lichen specimens (Sloof, 1993). The local variation of element concentrations in Xanthoria parietina was determined considering the different morphology of Xanthoria parietina, size of the lichen thallus and the variation in substrate (olive tree) by calculating the coefficient of variation (CV).

In order to investigate the local variation, mean coefficient of variations (CV) of apothecia part and leafy part and ranges of CV are given in Table 4.25. In general mean CV ranged from 0.4 to 40. A few high values were observed for Cr (49) and Hf (50). The smallest variation range was found for Zn (7.6-15) and the highest variation range was found for Hf (2.8-50). The mean local CV over all elements considered was 15.

Mean CV and the range of size separated lichen thalli (<2.5 cm and >2.5 cm in diameter) are given in Table 4.25. In general mean CV ranged from 0.0 to 40. High values were obtained for Eu (44) and Se (45) and these values may include instrumental uncertainties. The smallest variation range was observed for Ba (11-16). The highest variation range was obtained for Se (1.5-45). The mean local CV over all elements considered was 12.

The most common tree species on which lichens were collected was olive as olive production is very common in Aegean Region. The lichen samples in the same sampling point from different olive trees were analyzed separately in order to investigate the substrate effect. Mean CV and the range of CV of olive trees are also given in Table 4.25. Mean CV ranged from 0.0 to 40. High values were observed for Eu (46), Hf (42), Hg (57) and Nd (42). The smallest variation range was observed for Ti (8.4-13). The highest variation ranges were obtained for Hg (11-57) and Eu (0.0-46). The mean local CV over all elements considered was 15.

Table 4.25. The local variation of element concentrations in Xanthoria parietina with respect to morphology, size of the lichen thallus is expressed as mean coefficient of variation (CV) and range of CV and with respect to tree species are expressed as mean CV and range of CV; the regional variation of element concentrations is expressed as CV. Numbers in parenthesis show the number of samples

	Morphology		Size		Tree species		Regional
Element	Mean CV	Range	Mean CV	Range	Mean CV	Range	CV
Al	13 (5)	1.5-32	12 (7)	7.6-16	11 (4)	0.9-20	118 (145)
As	11 (5)	3.2-14	6.1 (7)	0.9-15	4.9 (4)	0.0-7.7	54 (120)
Au	23 (5)	12-33	13 (7)	1.3-29	13 (3)	3.0-19	115 (80)
Ba	23 (4)	15-41	13 (5)	11-16	14 (4)	10-22	150 (75)
Br	14 (5)	3.0-35	11 (7)	1.0-23	14 (4)	0.0-40	75 (80)
Cd	15 (3)	0.9-36	13 (4)	5.4-25	6.4 (2)	1.9-11	128 (125)
Ca	1.4 (1)		8.9 (7)	2.5-21	24 (3)	22-28	100 (144)
Ce	13 (5)	2.7-37	8.6 (7)	1.2-20	20 (3)	0.0-35	103 (80)
Cl	10 (4)	0.0-18	10 (7)	1.2-17	10 (3)	2.4-17	87 (80)
Co	17 (5)	2.4-40	13 (7)	1.4-40	29 (4)	9.4-38	123 (80)
Cr	22 (4)	6.7-49	8.1 (7)	1.3-15	9.4 (4)	5.8-16	115 (145)
Cs	17 (4)	0.0-27	16 (7)	4.7-24	24 (4)	8.0-32	204 (77)
Eu			21 (7)	8.7-44	20 (2)	0.0-46	114 (72)
Fe	12 (4)	1.7-31	9.5 (7)	2.2-18	11 (4)	2.7-24	109 (145)
Hf	27 (5)	2.8-50	13 (7)	2.1-21	21 (4)	5.2-42	144 (78)
Hg	11 (5)	3.3-16	15 (6)	2.5-28	32 (4)	11-57	158 (116)
K	8.3 (5)	2.4-18	4.3 (7)	0.5-12	13 (4)	3.6-35	66 (145)
La	10 (5)	0.4-31	11 (7)	3.1-17	16 (4)	2.9-34	105 (140)
Lu	17 (4)	5.5-30	13 (7)	4.7-23	14 (3)	0.0-34	113 (80)
Mg	12 (5)	2.9-26	7.2 (7)	1.1-15	14 (3)	7.0-28	44 (145)
Mn	13 (5)	3.5-30	7.2 (7)	0.0-13	7.9 (4)	2.4-11	104 (145)
Na	12 (5)	3.3-34	9.1 (7)	1.3-17	7.3 (4)	0.7-13	152 (139)
Nd	9.9 (5)	0.7-20	15 (7)	5.9-33	23 (3)	7.4-42	113 (77)
Rb	7.1 (4)	0.8-22	6.5 (7)	0.0-13	14 (3)	2.5-32	108 (80)
Sb	8.0 (5)	3.5-11	7.2 (7)	0.9-14	9.7 (3)	0.0-21	131(121)
Sc	13 (4)	1.2-30	10 (7)	5.2-16	14 (4)	0.8-28	136 (80)
Se	18 (5)	7.2-24	18 (7)	1.5-45			79 (112)
Sm	15 (4)	4.8-34	11 (7)	4.0-18	12 (4)	1.8-33	119 (80)
Th	28 (5)	1.1-41	19 (7)	3.7-36	26 (3)	24-27	130 (80)
Ti	17 (4)	6.5-32	12 (7)	0.0-26	11 (3)	8.3-13	141 (79)
V	15 (5)	4.2-29	8.7 (7)	0.6-14	14 (4)	4.1-24	141 (145)
Yb	15 (5)	3.1-32	13 (7)	2.4-23	19 (4)	15-29	115 (79)
Zn	11 (4)	7.6-15	9.3 (7)	2.5-18	5.0 (4)	0.8-15	116 (145)
Pb					1.6 (1)		223 (120)
Ni					2.1 (1)		118 (121)
Cu					2.5 (1)		73 (121)

For some elements Br, K, Se and Mg, the variation on a local scale is of the same order of magnitude as on a regional scale as given in Table 4.25. To determine whether the local variation in element concentrations is acceptable if compared to the variation on a regional scale, information is needed on the ranges of concentrations. For this purpose the largest range (spread) of data on a local scale is compared to spread of data on a regional scale in Table 4.26. The local variation of element concentrations is not large enough to disturb the concentration patterns on a regional scale, since the spread of the element concentrations on a local scale is at least 4 times (As, K, Mg and Se) and most of the cases an order of magnitude lower than the element concentrations on a regional scale.

These local variation samples were collected from the sampling sites, which have different pollution loadings such as urban light industry region, industrial region, urban region and semiurban region. In order to investigate whether there is an effect of pollution level of the sampling site, the local variation, CV, in each sampling region are given with respect to morphology, size of the lichen thallus and tree species in Table 4.27. From the table it is seen that local variation (either range of CV or only CV value) in different regions has similar ranges or values.

It can be concluded that the local variation is not important related to morphology, size of the lichen thallus and tree species, nor to air pollution level of the element at the sampling site. This conclusion was also reached in the Sloof's work (1993) considering only tree species. The mean local variation over all elements considered was 15%. This value was found to be 25% in Sloof's work. In the study of Jeran et al. (1996), the mean relative standard error in % was within the acceptable variability of 30-35% (Gailey et al., 1985).

Table 4.26. The spread of local scale of element concentrations versus the spread of a regional scale of element concentrations

	Morphology	Size	Tree species	Regional
Element	Spread	Spread	Spread	Spread
Al	995	1400	1350	32610
As	1.9	1.4	0.30	9.9
Au	1.8	1.9	0.31	15
Ba	14	14	18	420
Br	3.2	3.4	2.9	30
Cd	0.11	0.13	0.080	2.30
Ca		710	1230	13320
Ce	1.2	2.3	1.90	16
Cl	160	120	130	1880
Co	0.40	0.8	0.63	9.2
Cr	5.7	3.7	2.1	49
Cs	0.27	0.72	0.80	16
Eu		0.034	0.029	0.57
Fe	630	780	1130	18660
Hf	0.12	0.29	0.22	2.6
Hg	0.051	0.95	0.19	1.8
K	3400	2200	2380	13710
La	0.57	1.1	1.8	18
Lu	0.010	0.0090	0.025	0.15
Mg	1290	700	880	5890
Mn	35	12	6.0	340
Na	140	130	70	4765
Nd	0.26	1.2	2.3	14
Rb	3.8	2.9	14	110
Sb	0.11	0.19	0.26	3.5
Sc	0.18	0.29	0.43	6.2
Se	0.39	0.24		1.4
Sm	0.085	0.20	0.26	2.1
Th	0.83	0.83	1.1	8.7
Ti	150	80	32	2110
V	3.6	2.3	2.9	67
Yb	0.030	0.080	0.12	0.90
Zn	34	55	6.0	417
Pb			0.27	170
Ni			0.10	37
Cu			0.20	29

Table 4.27. The local variation (expressed as CV) relation to pollution level for all elements in Xanthoria parietina with respect to morphology, size of the lichen thallus and tree species

	Morphology			Size			Tree species	
Element	Urban light industry	Urban	Semi urban	Urban light industry	Industry	Urban	Urban light industry	Urban
Al	7.9-32	7.2	1.5	7.6-16	12-13	16	0.9-20	9.0
As	3.2-14	13	10	0.9-9.2	4.3-15	7.3	0.0-7.7	7.0
Au	12-33	15	31	3.1-27	1.3-29	18	3.0-19	
Ba	15-40	20	15	11-16	12-13		10-22	14
Br	6.2-35	3.0	13	1.0-13	9.0-23	16	0.0-40	16
Cd	36	0.9	9.0	5.4-25	9.9		11	1.9
Ca		1.4		3.0-9.5	2.5-13	21	22-23	28
Ce	2.7-37	9.2	6.4	1.2-20	7.9-11	9.0	0.0-35	26
Cl	6.1-17	18	0.0	1.2-17	9.0-14	10	2.4-17	
Co	2.4-19	6.4	40	1.4-24	5.7-8.8	40	9.4-38	34
Cr	6.7-49		6.8	3.3-12	1.3-15	8.4	5.8-16	8.8
Cs	7.9-27	0.0		14-24	13	4.7	8.0-28	32
Eu				9.3-28	8.7-44	26	0.0-14	46
Fe	3.6-31	1.7		4.1-14	2.2-11	18	2.7-24	3.1
Hf	20-50	2.8	16	5.7-21	2.1-20	8.0	12-42	5.2
Hg	3.3-16	12	12	14-28	2.9-27	2.5	11-36	57
K	2.4-18	3.2	10	3.2-4.4	0.5-12	1.4	3.6-6.6	35
La	5.6-31	0.4	6.4	3.1-17	12	13	2.9-34	16
Lu	11-30	5.5		4.7-14	19-23	12	0.0-34	16
Mg	9.1-26	2.9	4.4	1.1-15	3.7-12	4.2	7.0-28	
Mn	3.5-30	8.1	6.8	4.0-13	0.0-6.7	10	7.9-11	2.4
Na	6.9-34	7.3	3.3	3.9-17	1.3-11	10	0.7-13	3.3
Nd	0.7-16	8.6	20	5.9-21	6.5-26	33	7.4-42	
Rb	2.1-22	0.8		0.0-13	3.9-11	8.2	2.5-6.1	32
Sb	10-11	7.1	3.5	2.5-14	0.9-4.7	3.7	0.0-21	3.0
Sc	8.7-30	1.2		5.2-16	9.8-11	14	0.8-28	16
Se	7.2	12	24	1.5-45	14-26			
Sm	8.5-34		4.8	4.0-18	11-13	14	1.8-33	8.2
Th	21-40	1.1	37	3.7-21	12-36	30	26-27	24
Ti	7.1-23	6.5	32	5.9-26	0.0-19	13	8.3-13	
V	12-30	5.1	4.2	0.6-14	7.6-13	14	4.1-24	13
Yb	7.2-32	3.1	8.8	2.4-19	12-23	8.0	15-29	14
Zn	7.6-14	15		2.5-18	5.5-17	3.4	1.3-15	0.8

According to Rasmussen (1978) differences between bark concentrations of elements on different trees are often significant, but in an unpredictable way. Rasmussen and Johnson (1976) found no differences in elemental concentrations in epiphytically growing mosses on two different tree species. In our study, high CV (>40) values for the elements Al, Ba, Ca, Ce, Cl, Cs, Eu, Hf, Hg, La, Lu, Nd, Rb, Sc, Sm, Th, Ti, V and Yb and high mean CV values for the elements Cs, Hf, Nd and Yb were obtained as given in Table 4.28. For crustal elements, one reason for high values may be the washing procedure. Coefficient of variation for some elements like Ba, Eu, Hf, Lu, Nd, Th, Ti and Tb may also include instrumental uncertainties in INAA technique. However on the average, most of elements show no differences considering lichens growing on two different tree species. This was expected result since for most of the trace elements, uptake from the bark into the lichen is not likely to occur, but for cadmium and zinc the possibility of such uptake was claimed by Bruin and Hackenitz (1986). However, in our case, mean CV's for Zn and Cd are among the lowest ones.

Table 4.28. The range and mean CV of elements on different tree species at the same sampling sites (numbers in parentheses show the number of samples)

	Different tree species	
Element	Range of CV	Mean CV
Al	20-54	36 (4)
As	10-34	23 (4)
Au	14-36	25 (4)
Ba	3.4-47	27 (3)
Br	26-40	31(3)
Cd	16-21	19 (2)
Ca	14-76	40 (4)
Ce	4.2-44	23 (4)
Cl	0.0-47	24 (4)
Co	26-42	32 (4)
Cr	19-35	23 (4)
Cs	2.2-78	42 (3)
Eu	13-51	38 (3)
Fe	24-44	31 (4)
Hf	4.0-85	52 (3)
Hg	1.8-47	28 (4)
K	0.2-25	16 (4)
La	16-48	32 (4)
Lu	26-53	39 (4)
Mg	6.7-20	15 (4)
Mn	9.4-28	23 (4)
Na	24-40	33 (4)
Nd	4.2-73	45 (4)
Rb	8.0-50	25 (4)
Sb	1.3-34	21 (4)
Sc	18-49	32 (4)
Sm	21-45	32 (4)
Th	10-43	23 (3)
Ti	6.1-88	47 (4)
V	10-68	37 (4)
Yb	24-60	40 (4)
Zn	0.0-26	15 (4)
Pb	30	30 (1)
Ni	8.3	8.3 (1)
Cu	2.6-12	7.1 (2)

4.3.2 Enrichment Factors

The details of this calculation is described in section 1.7.3.2. Enrichment factors are used as to get an idea about man-made sources. Enrichment factor value more than 10 can be considered as the influence of man-made sources. If EF value is 1 that means earth crust is only contributor to the given element.

The crustal enrichment factors (EF) values in this work are based on the data given for the mean abundance's of the elements in the Earth's crust by Taylor (Taylor, 1972). Calculated crustal enrichment factors of elements with their ranges and median values in lichen samples for all data set are illustrated in Figure 4.19. Elements in this figure are arranged according to increasing median enrichment factors, which indicate the increasing anthropogenic content. As it is shown in the figure, elements like Na, Sc, Ti, Fe, Yb, V, Ce, Lu, Sm, Tb, Co, Mn, Nd, Ca, Eu, Cr, Ni, La, Ta, Sr, Hf, Ba, U, Th, Dy, Mg, Rb, Cu, In, Cs, K and Mo for which the main source in the atmosphere is the Earth's crust are not enriched in Aegean Region. Their crustal enrichment factors are less than 10. The EF values of Na, Sc and Ti show depletion with respect to Al, which is probably due to composition difference between the sampled crustal material and Taylor's (1972) crustal abundance table. Depletion of these elements in lichen samples was observed in the study of Varrica et al., (2000) and the depletion of Na was observed in the study of Ölmez et al (1985). The depletion of Sc was frequently observed in aerosol samples collected in the eastern Mediterranean atmosphere (Güllü, 1996) and in the western Black Sea atmosphere (Karakaş, 1999). Although Na, V, Ca, Co, Cr, Ni, Mg, Cu, In, K and Mo have other sources such as marine for Na, marine and lichen metabolism for Ca, Mg and K, anthropogenic for others, they appear in the non enriched group of elements. For example V is known to be emitted from residual oil burning. However, since this element has relatively high abundance in the Earth's crust and the contribution of soil contribution is highly seen in lichens, the enrichment factor for V is less than 10. The soil contribution is also high for other anthropogenic elements Cr, Ni Cu, In and Mo. The most of nonenriched elements have very wide EF ranges. The wide range of EF values show that there are additional sources along with the crustal material contributing to its ambient concentrations. The wide ranges of the elements

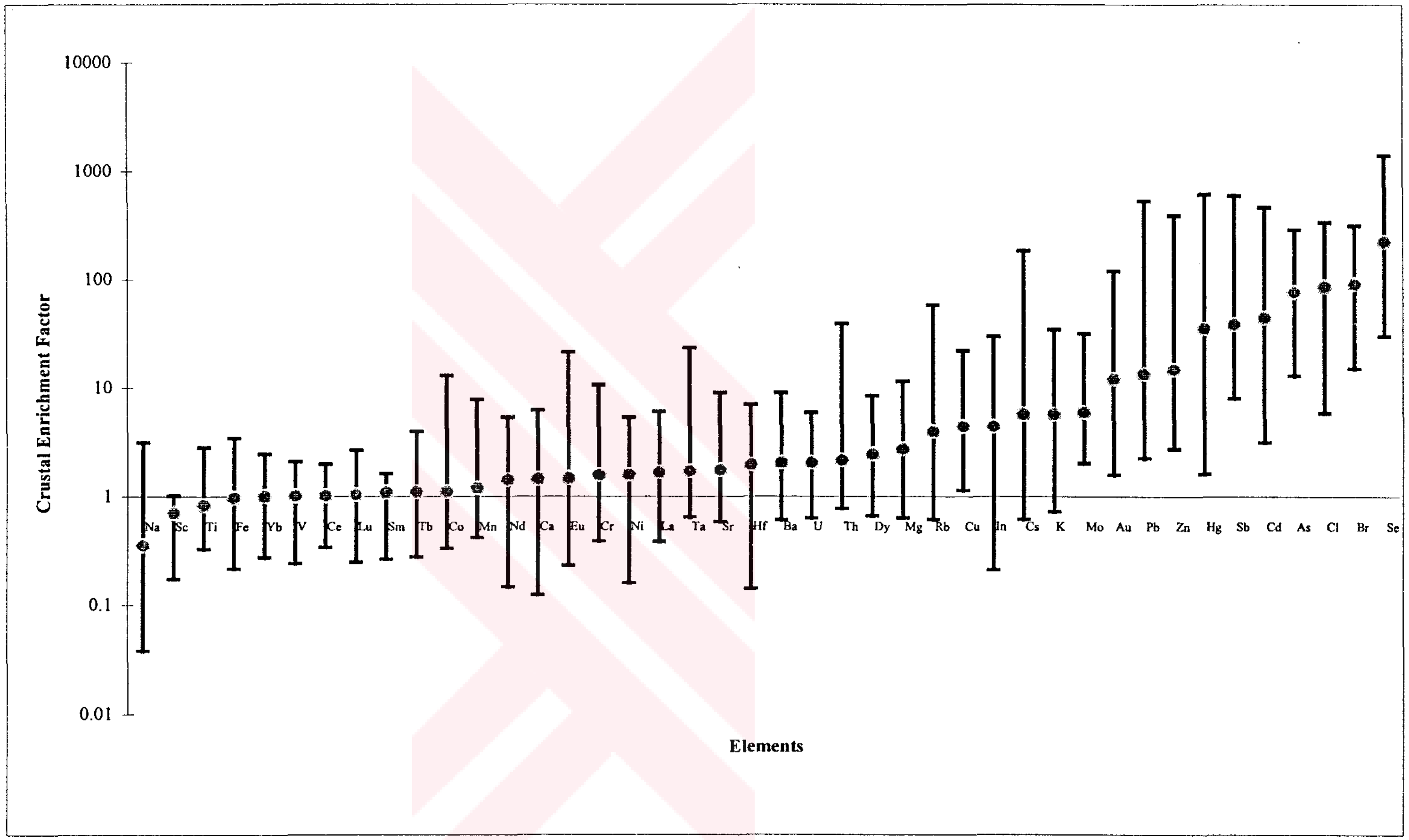


Figure 4.19. The crustal enrichment factor of the elements for all data set

such as Ta and In can be caused by the uncertainties in the analysis, however the other elements are mainly contributed by multiple sources. In order to distinguish the natural and other sources of the nonenriched elements (EF<10), enrichment factor diagrams which are log-log plots of the crustal EF's of the elements versus Al concentrations were prepared. The crustal EF of purely crustal elements does not change with the changes in the Al concentration (which was used as the normalizing element in the EF calculations) resulting in a horizontal line in the EF diagram. Since concentrations of both the crustal element and Al change in similar manner with increasing or decreasing loading of crustal particles in the atmosphere as a result the crustal enrichment factor stays the same. The EF diagrams of two purely crustal elements Sc and Sm together with V and Na are shown in Figure 4.20. The element V which known to be anthropogenic origin and Na which is a reference element of sea come completely from the crust. The elements of Sr, Fe, Yb, Ce, Lu, Ti, Cr, Mo, Ni, Cs, U, Ba, Th, Ta, Hf, La, Dy, Tb and Co show also the same trend in the EF diagrams.

Enrichment factors of noncrustal elements on the other hand are independent of the Al concentration in the lichen samples. The EF_c values of such type of elements decrease with increasing Al concentration and results in a negatively correlating line in the EF diagram. That means these elements behave like noncrustal elements at low Al concentrations, but behave like purely crustal elements at high Al concentrations (Güllü, 1996). As can be seen from Figure 4.21 EF_c diagrams for Mg, K, In and Cu show different pattern from that of the above mentioned elements. Therefore, it is clear that they have additional sources other than the crust in some sampling sites. Consequently, slight enrichments of these elements in some samples are due to the presence of noncrustal sources. The EF_c of the elements Nd, Eu, Mn, Rb and Ca show similar negative trend with increasing Al concentrations. The more detailed investigation of data will be done by calculating EF values for 5 subregions.

There are seven elements belonging to the second group called moderately enriched which are Au, Pb, Zn, Hg, Sb, Cd and As. They have wide ranges indicating additional sources or analytical uncertainties.

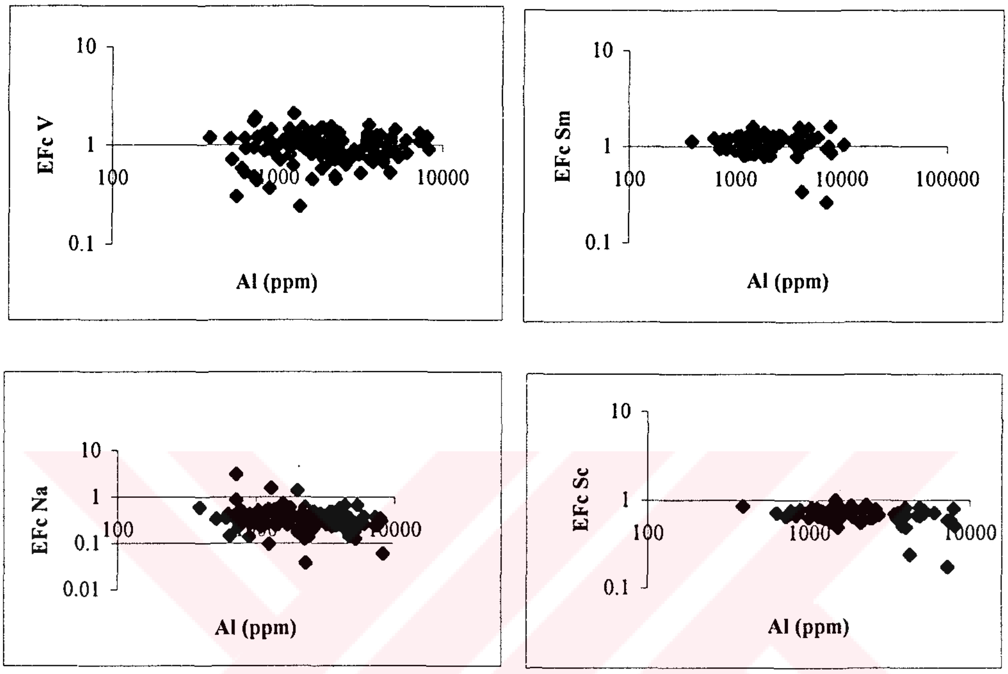


Figure 4.20. EF_c diagrams of V, Sm, Na and Sc for all data set

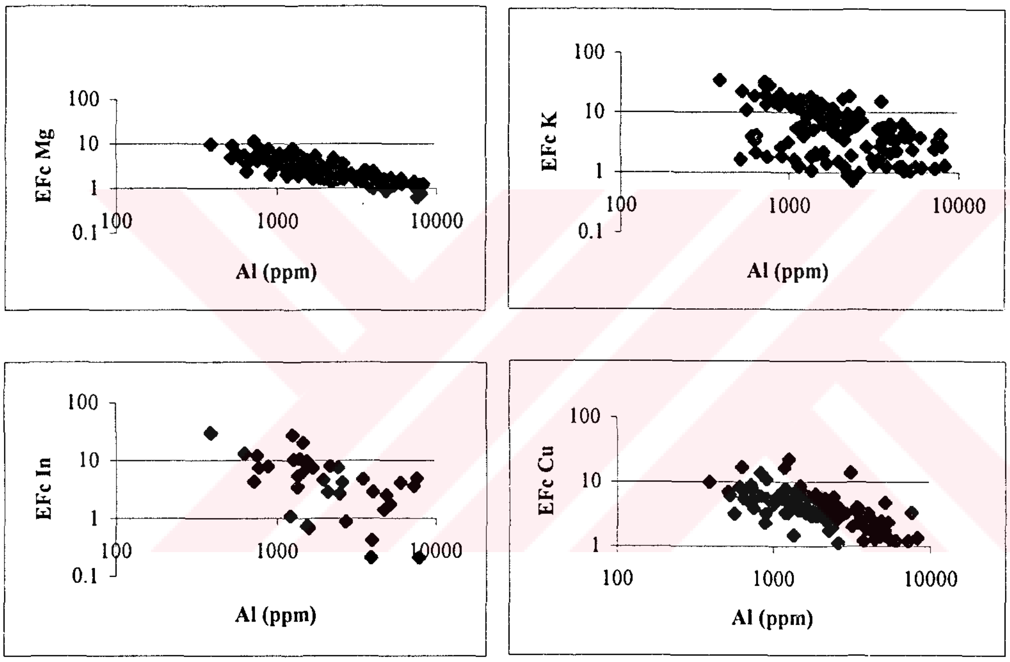


Figure 4.21. EF_c diagrams of Mg, K, In and Cu for all data set

The anthropogenic source of Au is generally precious metal works. The rest of the elements will be attributed to different industrial processes as will be discussed in Section 4.4.

Elements, which are highly enriched, are Cl, Br and Se. They are volatile elements and are found in the atmosphere at elevated concentration levels due to the anthropogenic activities. Their impact areas range from regional to global. Selenium is the most enriched element followed by Br and Cl, both have very close median values. This trend for Se is rather common and is even observed in very remote areas such as the South Pole (Meanhaut et al., 1979; Tuncel et al., 1989). These highly enriched elements are released to atmosphere as fine particles or gases. The gaseous ones have atmospheric residence time of several months to years depending on the reactivity in the atmosphere. Particulate forms of highly enriched elements have much shorter atmospheric residence times than the gaseous ones and are useful as the conservative markers for various industrial processes. Known sources of Se are fossil fuel burning and industrial activities. The selenium in the air generally associates with aged particles and represents long range transport. Traditionally, the major source for Br in the atmosphere is considered to be motor vehicles burning leaded gasoline. However, as leaded gasoline has started to being phased out, this source became less significant (Ölmez et al., 1997). Huang et al., (1994) reported Br emissions from vehicles probably due to the use of bromobenzene as an additive to motor oils, although emission rates are not as significant as when it was used in anti-knocking compounds in the form of ethylene bromide. There are numerous industrial uses of Br and Cl. They are used in organic synthesis and are a constituent of oxidizing and bleaching agents and solvents. In addition they both have another source, which contributes Cl concentration in the atmosphere more than that of Br is the sea. However since the EF values of Na show that Na comes from the crust, the possibility of sea contribution to Cl and Br decreases. Chloride may come from incinerators.

For urban light industry data set, the enrichment factor median values with their range values are presented in Figure 4.22. The nonenriched elements did not change but only their ordering changed. Among the nonenriched elements, the

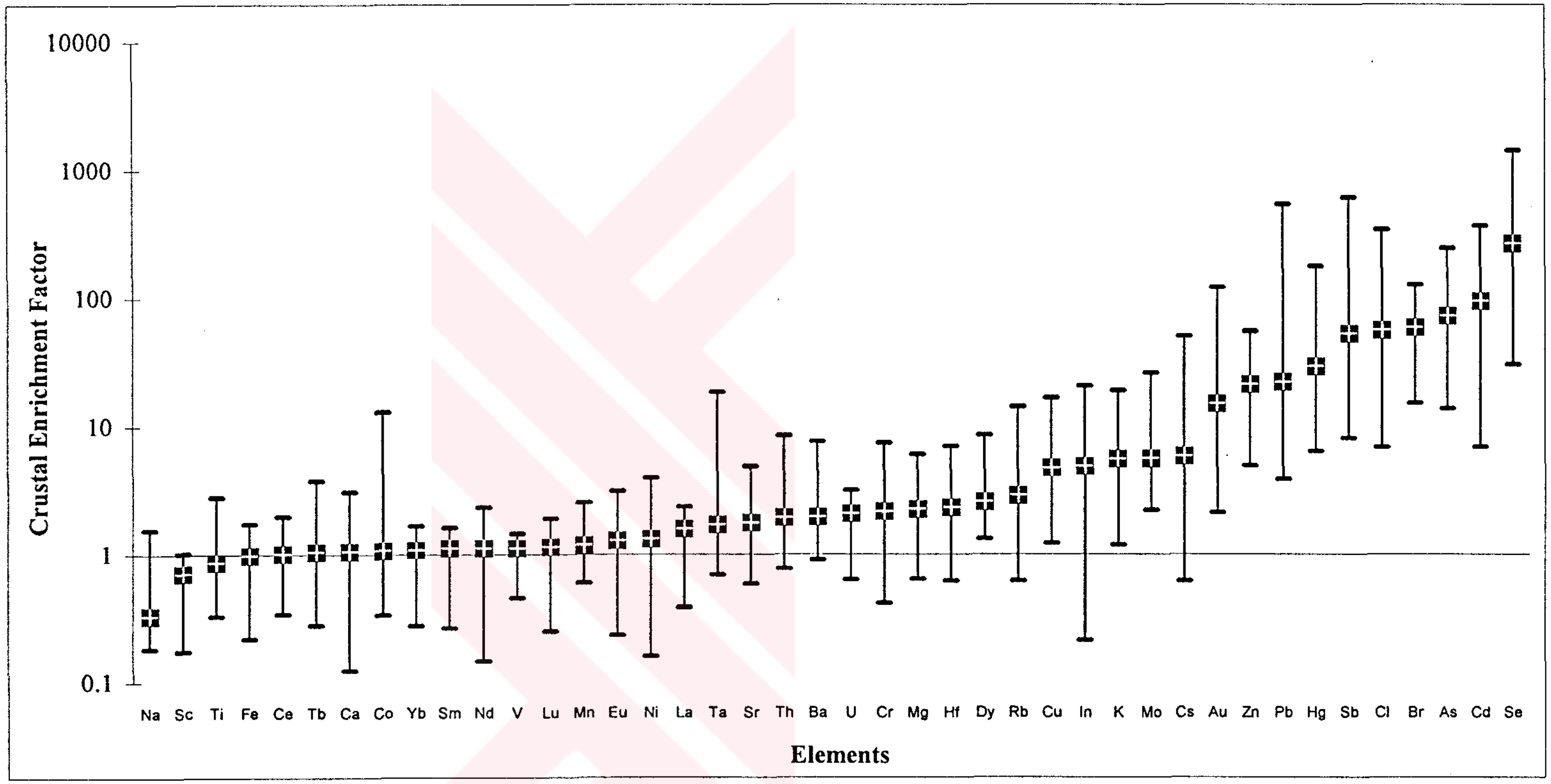


Figure 4.22. The crustal enrichment factor of the elements for urban light industry data set

elements Mg, Mn, Mo, In, Eu, Th, K, Ca, Cs, Cu, Cr, Co, Ni and Rb have other sources inferred from EF diagrams. The elements Au, Zn, Pb and Hg are moderately enriched. The elements Sb, Cl, Br, As, Cd and Se are highly enriched. Enrichments of these elements are always seen in the data sets generated from urban, industrial and rural regions. They are referred to as anamolously enriched elements.

The enrichment factor median values with their range values are shown in Figure 4.23 for the urban data set. The element Au went to nonenriched group. Hovever EF diagram showed that it was not coming only from the crust. The other elements, which have the sources other than the crust, are Mg, In, Mn, K, Ca, Cr, Co, Rb, Mo, Ni and Cu. Enriched elements behaved like the elements in all data set. This region is not very much polluted as urban light industry region.

The enrichment factor values of another data set which belongs to semiurban region are shown in Figure 4.24. The EF values of elements show similar trends with the EF values of the elements in all data set. The EF log-log correlation plots showed that the elements Mg, In, Mn, K, Rb, Mo, Cu and Cs have sources other than the crust.

The enrichment factor plot of the data set of industrial region is shown in Figure 4.25. The element Au went to the nonenriched group. However the EF diagrams showed clearly that Fe, Mn, Mg, K, Rb, Cu, Au, Th and Cr have another sources other than crust even though the sample size is very limited (7). The elements Fe, Mn, Cu, Au and Cr are known tracers of metal works and iron steel works. The two Parmelia tiliacea samples were taken from approximately 500 m away from İzmir iron steel works and in the direction of wind that carries the plume of the plants where there were no Xanthoria parietina lichen species as explained before. Especially the elements Fe (about 5 times), Mn (about 6 times), Cr (about 9 times), Mo (about 4 times), Zn (about 16 times), Cd (about 4 times), Sb (about 9 times) and Hg (about 5 times) are more enriched in these two samples than in the X. parietina samples. The Scanning electron microscope (SEM) (Topcon ABT150 model) picture of P. tiliacea sample was shown in Figure 4.26. On the right side of picture, the single sphere was chosen to get the EDX (Energy Dispersive X-rays) spectrum. Since it is 1 μm diameter and spherical it is emitted from an anthropogenic source. This spectrum is shown in Figure 4.27. In order to compare

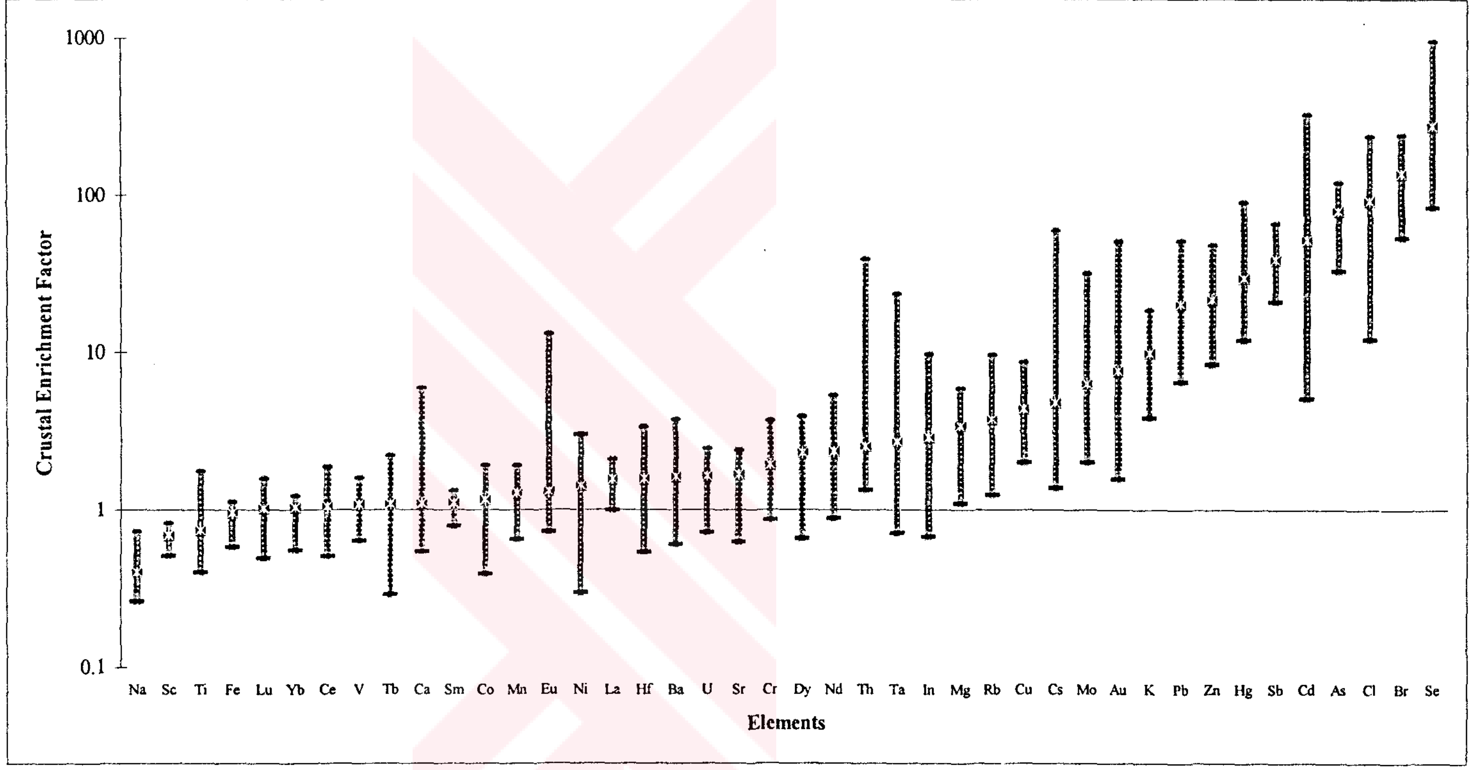


Figure 4.23. The crustal enrichment factor of the elements for urban data set

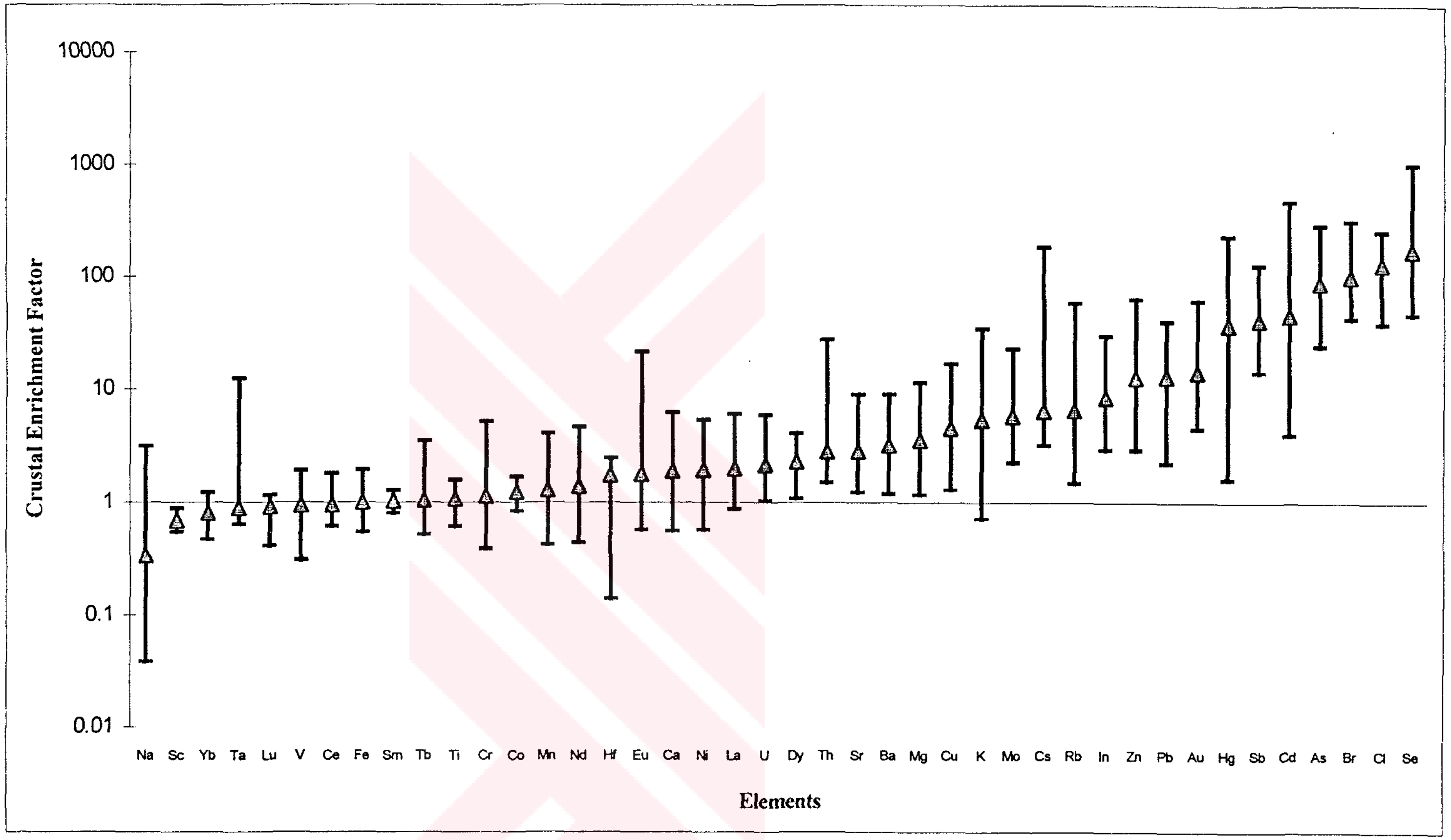


Figure 4. 24. The crustal enrichment factor of the elements for semiurban data set

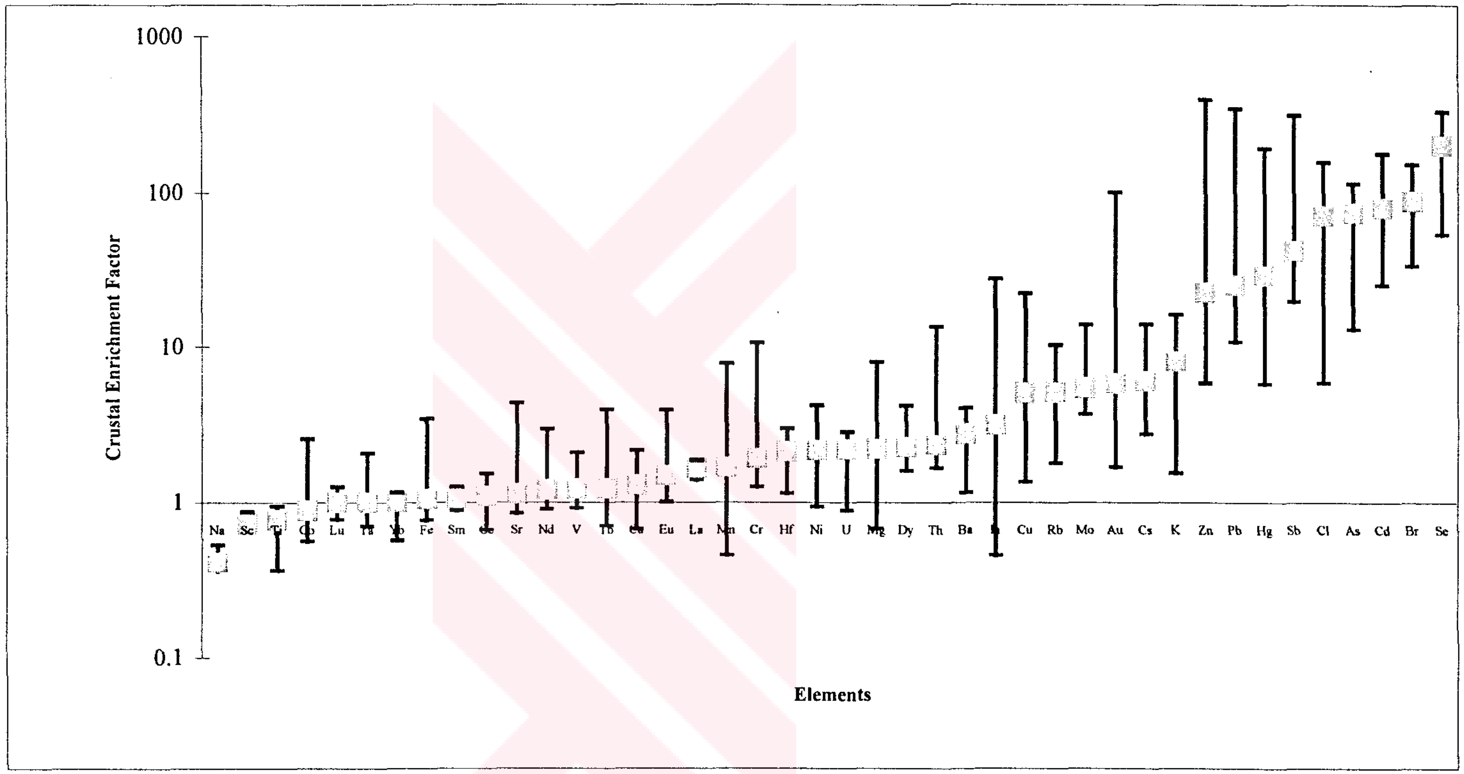


Figure 4. 25. The crustal enrichment factor of the elements for industrial data set

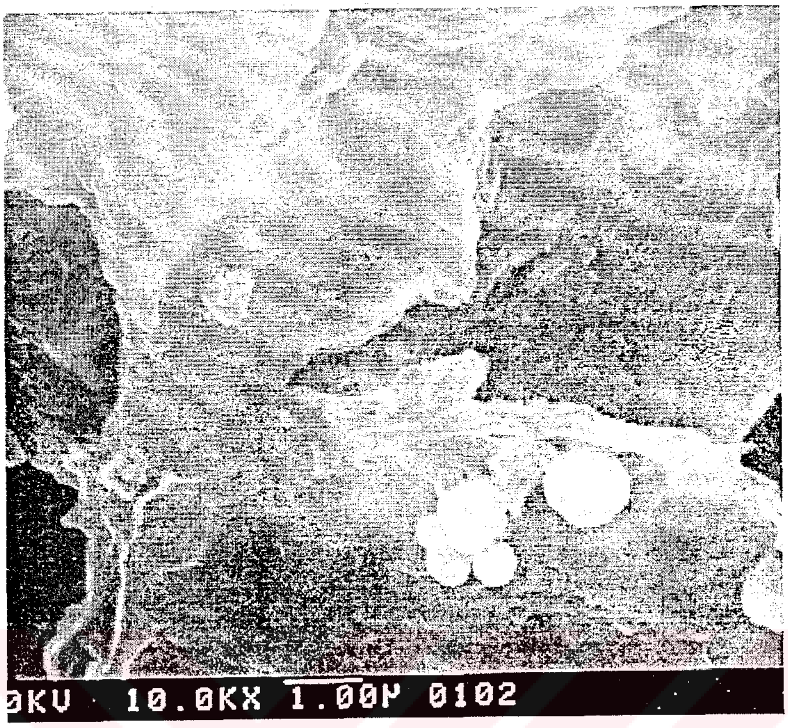


Figure 4.26. The SEM picture of Parmelia tiliacea

the composition of an anthropogenic particle with the crustal particle, the spectrum of nonspherical and big particle (crustal) is shown in Figure 4.28. As can be seen from the figures the composition of an anthropogenic particle is very different from the crustal one. The concentrations of crustal element like Al, Si, Ca, K and Ti in crustal particle are very higher than that of anthropogenic particle. Whereas the concentrations of anthropogenic elements like Mn, Zn, Cu, Cr and especially Fe are higher than that of crustal particle. The very high concentrations of Fe proved that this particle was emitted from iron-steel plants beside the other elements like Mn, Zn, Cu and Cr, which are emitted highly from these plants. However, the EF values of Mn and Fe have around unity probably due to the high contribution of the crust. The moderately enriched group includes the elements Hg, Zn, Pb, Cl, Cd, As and Br. The only anamolously enriched element is Se.

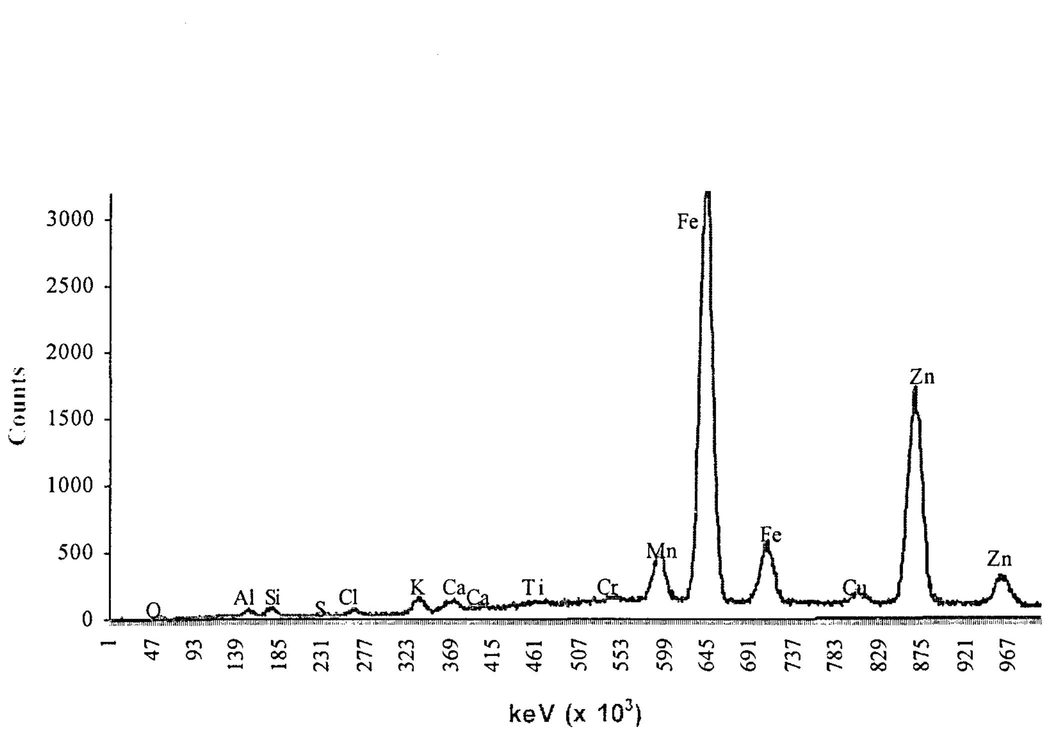


Figure 4.27. SEM-EDX spectrum of Parmelia tiliacea sample for spherical particle

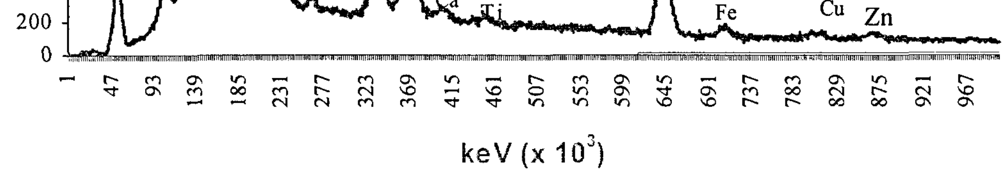


Figure 4.28. SEM-EDX spectrum of Parmelia tiliacea sample for nonspherical particle

The last region for which the enrichment factors of the elements was calculated is the power plants region. The enrichment factor plots are illustrated in Figure 4.29 with the median values and ranges. The elements Na, Mn, V, Fe, Cr, Ni, Ca, Mg, La, K, Cu, Pb, Zn are nonenriched. However the EF diagrams showed that there are other sources for the elements Mg, Mn, K, Ca, Na, Zn, Ni and Cu. For Pb it seems that it comes mostly from the crust, it was surprising since lead is highly emitted from the coal-fired power plants. However the EF value for the nearest sample, approximately 1 km to Soma power plant is 36. EF values of 4. and 5. km samples are greater than 10. For Yatağan power plants EF values of the 1., 8. and 10 km samples are greater that 10.

The median EF values of enriched elements in all data set and subregions are shown in Figure 4.30 in order compare EF values site wise. The EF values for Au are not changing very much from region to region. The EF values of Pb, Zn, Sb and Cd are the lowest in power plants region. For Pb and Zn, the second lowest EF values are for semiurban region and both elements show close values for other regions. Median EF value of Hg is the lowest in industrial area and other EF values are not changing very much from region to region. Antimony and Cd have their highest mean EF values in urban light industry region. For Cd the second highest value is for industrial area. These two elements have comparable values for other regions. Arsenic has very close EF values for all regions with highest value for semiurban region. Chloride has its highest EF value for semiurban region and secondly urban region comes. Other two regions have the same EF values for Cl. Bromide has its highest value in urban region then semiurban region, industrial area and urban light industry region. Selenium follows in the order of urban region, urban light industry region, semiurban region, power plants region and industrial area in decreasing EF values.

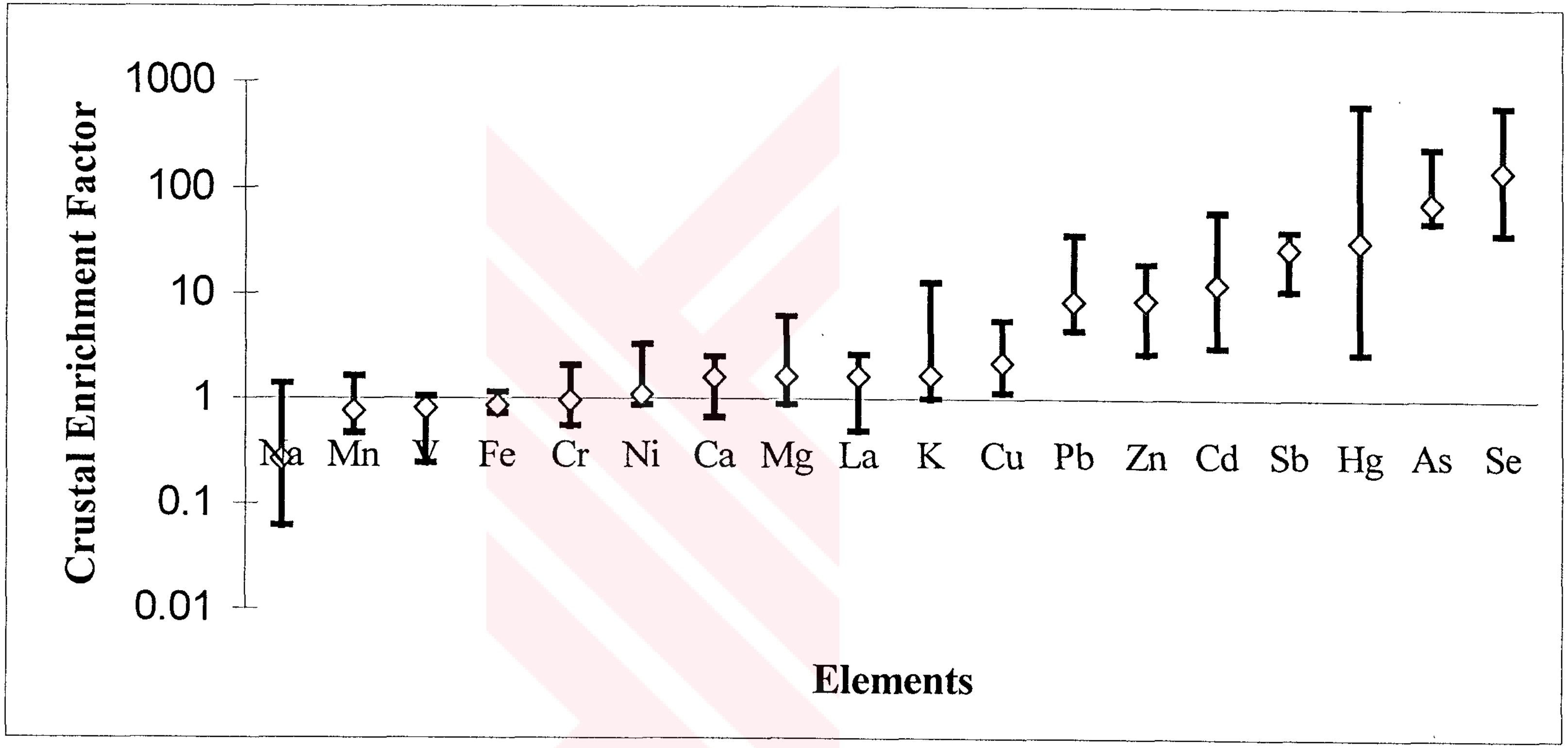


Figure 4.29. The crustal enrichment factor of the elements for power plants data set

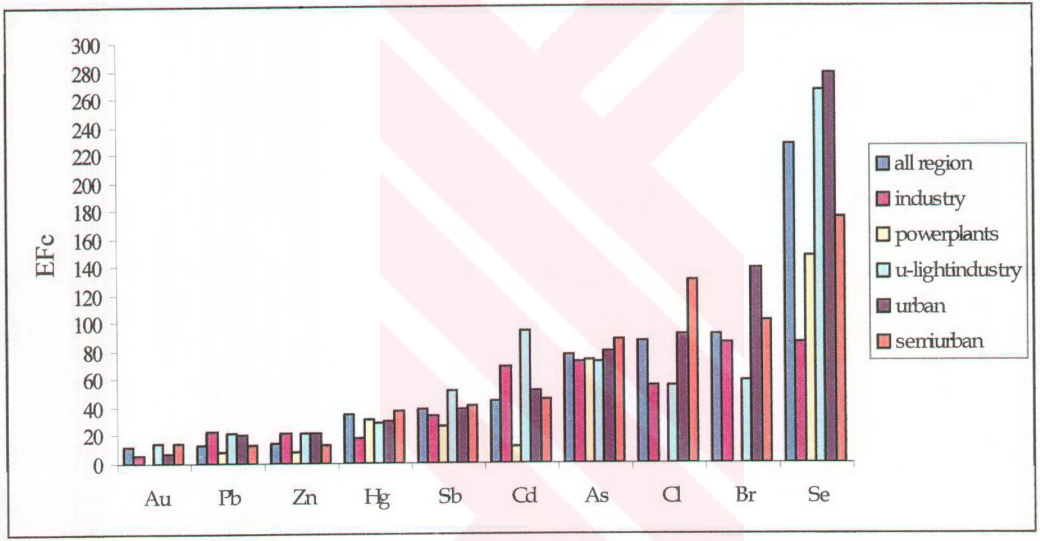


Figure 4.30. Median EF values for enriched elements for all region and subregions.

4.3.3. Distribution Maps of Elements

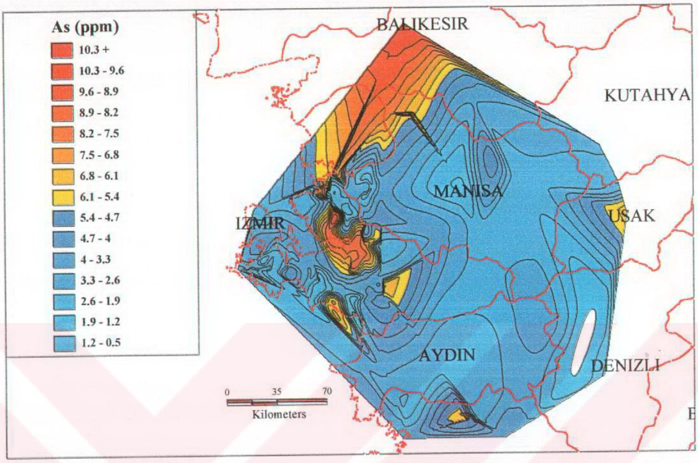
In this section data for selected elements are presented as contour maps of concentrations and enrichment factors. As it was explained before soil contributes to most of the elemental concentrations. That's why just looking at concentrations could be misleading about man-made sources. Because of this concentration and enrichment factors contour maps are given together. If a region has higher levels in concentration and EF values that means in addition to soil there are also man-made sources. If only concentration levels are high that means the element under question only comes from the soil. The elements presented in this section are As, Se, Hg, Cd, Zn, Pb, Sb, Cu, Al, Fe, Cr, Ni, Mn, V, La, Ca, Na, K and Mg. The counties of İzmir city is shown in Figure 4.31 in order to easily follow the interpretations in the text.

Figure 4.32: Concentration and EF distribution maps for As

It is well known that the largest contribution of atmospheric As comes from coal burning, but paints and electronic components industries are also important. Furthermore it is added to lead and copper for the production of non-ferrous alloys. Copper arsenide, $Cu(AsO_2)_2$ is effective as insecticide and fungicide (Markert, 1992).

The highest levels of As are found around the city center of İzmir, Menemen, Çiğli (in Karşıyaka), Kemalpaşa, Torbalı, Aliağa area, around Balıkesir, Soma and Yatağan coal-fired power plant areas and Uşak. The concentrations of As are high in places with high population and/or industrialization. High concentrations of As is mostly agreement with enrichments in the same localities. There are many different industries in the city center of İzmir, Kemalpaşa and Torbalı. The organized industry areas are located in Menemen and Çiğli. Aliağa is a well known pollution source with its heavy industry namely iron-steel plants, metal works and refinery. As we know As is a tracer element for especially Turkish coals as we discussed in the

Figure 4.31. The counties of İzmir city



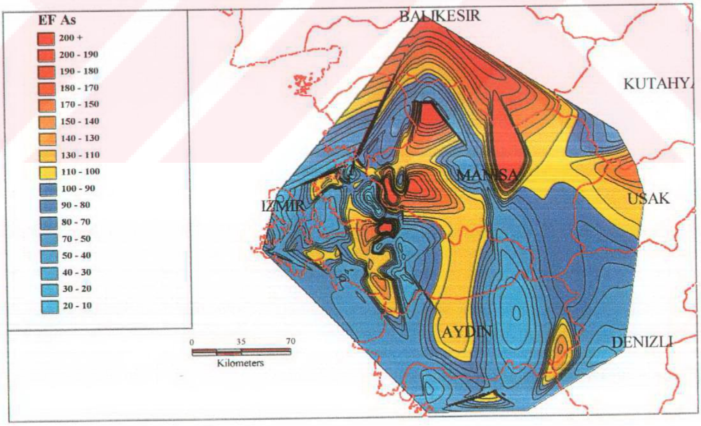


Figure 4.32. Concentration and EF distribution plots of As

previous sections. The coal consumed only for domestic heating at city centers are as follows: Aydın: 6000 tons/year; Denizli: 50000 tons/year; İzmir: 480000 tons/year; Manisa: 60000 tons/year; Muğla: 20000 tons/year; Uşak: 45000 tons/year (Müezzinoğlu et al., 2000). Since Balıkesir is not in Aegean Region, there is no related datum. As we see coal consumed at the city center of İzmir is at least 8 times higher than that at others. High As concentrations are also found in Menderes but there are no pollution sources in that area. In Manisa there are metal and food plants, household appliances factories. In Uşak, there are a big textile industry, organized industry area and other small industries. In the sampled part of Muğla other than Yatağan power plant, there are no other pollution source. In Denizli there are many textile and textile related dye industries. In Aydın there are mine grinding factories, fabric dyeing, chicken farm, many oil production and olive oil factories and ceramic raw material production.

There are some areas that although the concentrations are not very high, there are considerable enrichments (around 200-300) like in Aydın, Denizli, Uşak and Manisa. In Aydın the highest concentration is around 1.2 ppm which a factor of 10 less than the highest observed concentration. But still the enrichment is around 130. The same observation applies for Denizli. In the following sections there is going to be similar results for other elements. This usually because of the different soil composition and presence of some point sources which are not very strong but cause considerable enrichments. For example in Denizli, Manisa and Aydın, there are may industries which are not as strong sources as like power plants and other heavy industries around İzmir and city center of Manisa.

Figure 4.33: Concentration and EF distribution maps for Se

The largest contribution of atmospheric Se comes from coal burning. Glass industry and semiconductor industry also release Se (Markert, 1992).

Elevated levels of Se are found in İzmir, industrial areas of Manisa and power plants areas. Concentration distribution pattern shows similarities with As

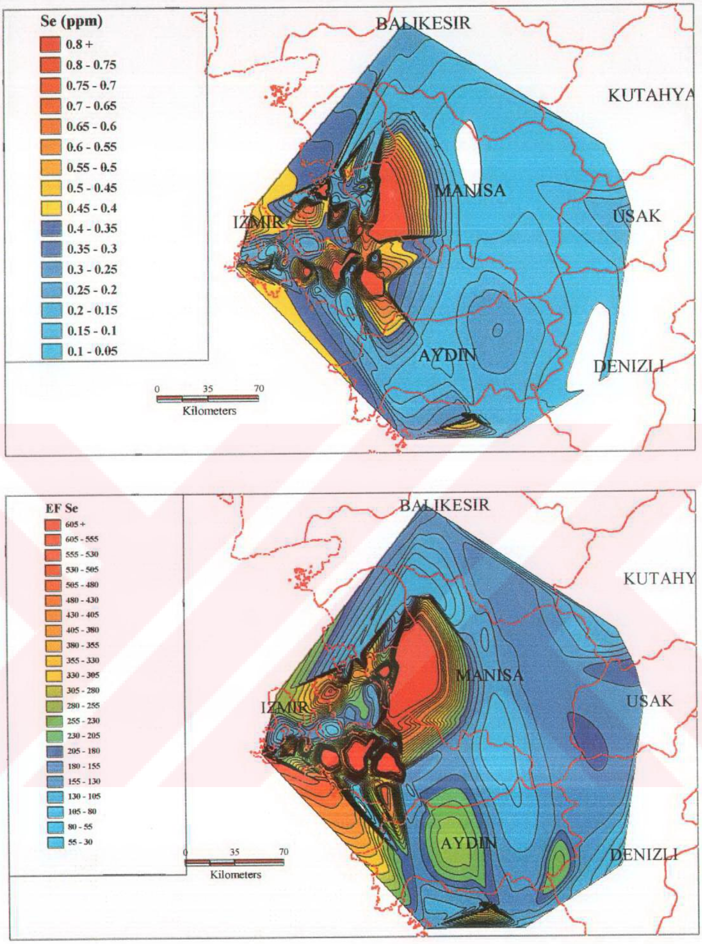


Figure 4.33. Concentration and EF distribution plots of Se

especially in Uşak, Denizli, Aydın, power plants areas and most of the places in İzmir as Se comes from mostly coal and other industries (glass industry in İzmir). Se is anamolously enriched (EF>100) in many places in the region. The EF distribution pattern is very similar to concentration distribution pattern. This means that all sources are also important contributors for Se.

Figure 4.34: Concentration and EF distribution maps for Hg

Mercury is one of the less abundant elements on earth. Coal is a source of Hg but it is also widely used in numerous sectors: the chemical industry, chlor-alkali plants, steel making, paints, paper mills, the production of electronic components and fungicides (Scerbo et al., 1999).

The highest concentrations of Hg are seen around Yatağan power plant due to coal and in Aydın due to fabric dyeing. There are no heavy industries in Aydın, fabric dyeing is one point source which emits pollutants in considerable amounts (Müezzinoğlu et al., 2000). Elevated concentrations are also seen in the city center of İzmir due to chemical industry, dye industry which emits large amounts of particulate and gaseous pollutants (Müezzinoğlu et al., 2000), Aliağa area and Soma power plant.

Mercury shows enrichment in every part of the region and EF distribution is the same as with concentration patterns for the areas stated above but Soma power plant and city center of İzmir do not appear as hot spots that means they are not important contributors of Hg. Additionally although concentrations are not very high there is an enrichment in organized industry part and middle of Manisa, Denizli and Uşak. There are chemical and paper industries in Manisa organized industry area. In middle part of Manisa where As give also higher EF values, it comes from coal burning. In Denizli and Uşak, its high EF values are related with textile and textile related dye plants.

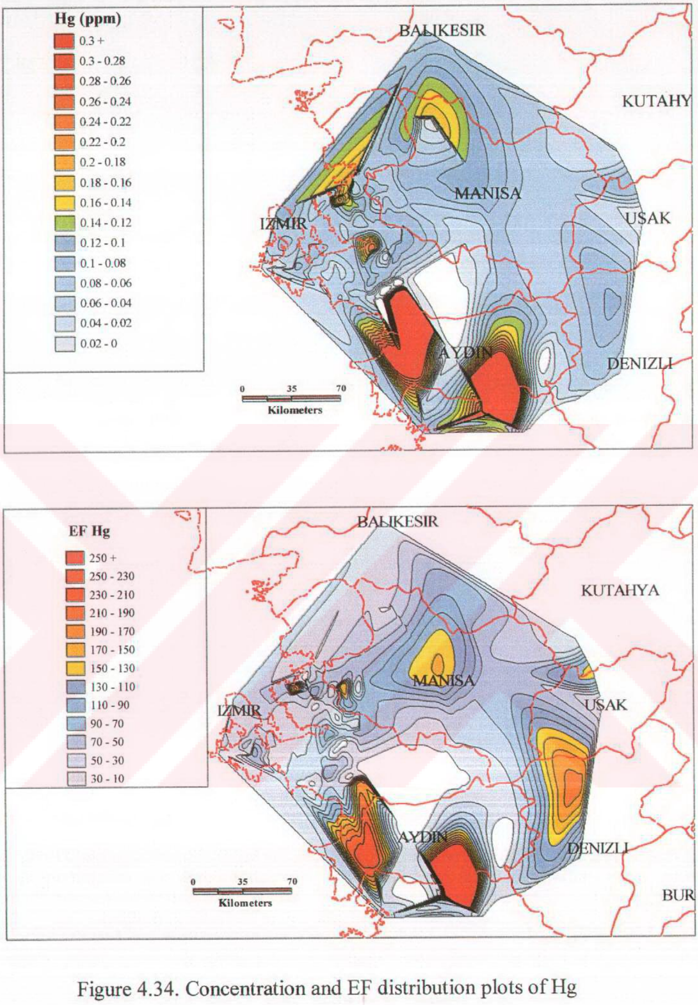


Figure 4.34. Concentration and EF distribution plots of Hg

Figure 4.35: Concentration and EF distribution maps for Pb

For many years vehicle emissions are known to be major sources of Pb but because increased use of unleaded gasoline, the contribution of gasoline to atmospheric Pb is decreasing, while combustion of coal and petrol remain the principal sources of this toxic element in the environment. This trend in the world may not be applied in our country, because of the many old cars still in the traffic.

When the concentration and EF distribution maps are observed, high levels are accumulated close to city center of İzmir, in Menderes, in Aliağa area in Karaburun and in Balıkesir. Other than Aliağa area, higher concentrations in other places are due to traffic. There are other enriched areas where the concentrations are low. These areas are located in Seferihisar, Urla, Menderes between Balıkesir and Manisa, between Aydın and İzmir, between Uşak and Manisa, in Uşak and in Denizli. The main roads and secondary roads in the region are shown in Figure 4.36. Lead is enriched in some places which are close these roads such as roads between Aydın and İzmir, Manisa and Uşak, Manisa and Balıkesir. In Denizli its enrichments are related with industry.

High EF Pb values in Seferihisar, Urla and Menderes are due to mainly traffic. The towns in İzmir, between İzmir and Aydın are the most popular summer resorts. Population of region increases 100 fold during the summer. Therefore it is not unusual to get Pb enrichments.

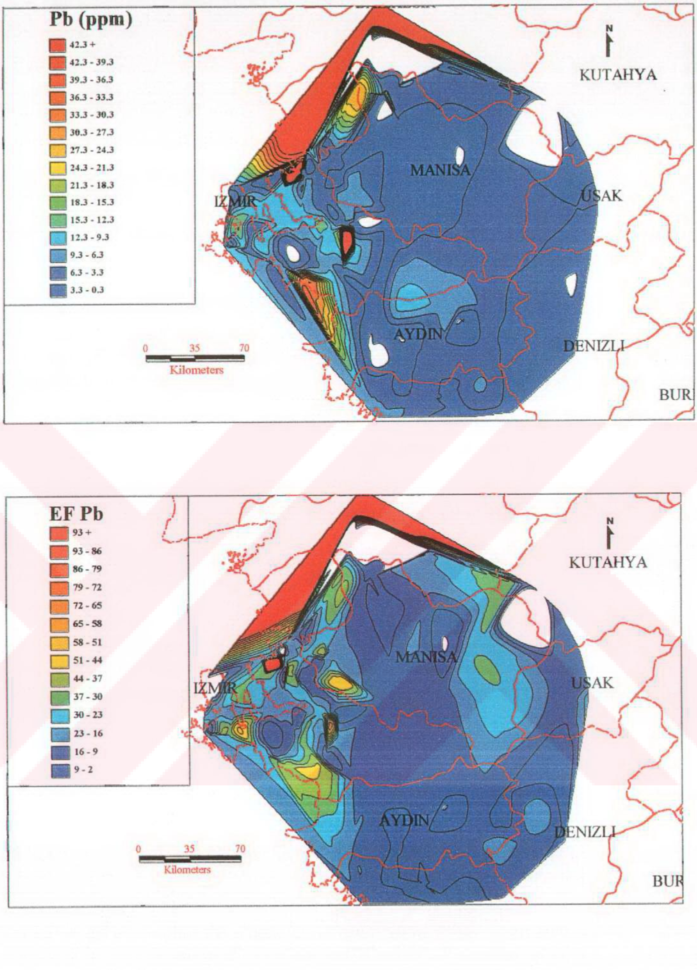


Figure 4.35. Concentration and EF distribution plots of Pb

Figure 4.36. The roads in Aegean Region (black roads are main roads, red ones are secondary roads)

Figure 4.37: Concentration and EF distribution maps for Sb

Antimony is used in semiconductor industry, in rubber additives, in pigments and paints. It can be emitted from the coal combustion (Markert, 1992).

Antimony has its highest concentrations and higher EF values in the city center of İzmir, Kemalpaşa, Torbalı, Menemen, Balıkesir and Aliağa area. In addition high levels are seen in power plant areas, Menderes and Karaburun. Therefore, it is found in both the most urbanized and industrialized areas as expected. It shows similar distribution pattern with Pb in Menderes and Urla and that's why it comes from traffic emissions. The highest enrichments factor values are found the places where Sb has low concentrations. These areas are located in Manisa and Uşak as in the case of As due to coal burning. In Denizli, enriched areas in Sb show the same pattern with As and Se. This shows that Sb emissions are again related with coal burning. There is a big area between Manisa and Uşak which moderately enriched and it is also seen in the distribution EF plot of Pb. This can be related to automobile emissions. High enrichment of Sb is also seen around Yatağan power plant due to coal combustion.

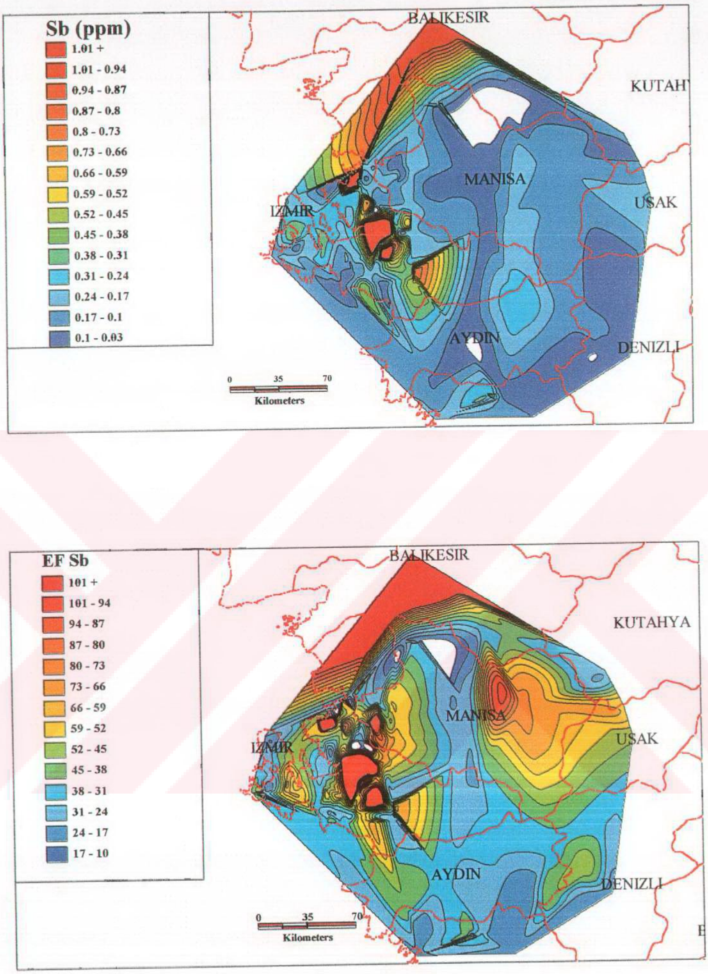


Figure 4.37. Concentration and EF distribution plots of Sb

Figure 4.38: Concentration and EF distribution maps for Cd

Cadmium is a by-product of the Zn and Pb industries and is aslo derived from fertilizers, coal burning and urban wastes (Scerbo et al., 1999). It is also used as a plastic stabilizer (Markert, 1992).

Elevated cadmium levels were found close to city center of İzmir which is both industrialized and urbanized part (coal burning, urban wastes), in Balıkesir (urban) and in Aliağa area (many industries). However, in EF map there are no hot spots for the place which is close to city center that means it is not effective source for Cd. High cadmium concentrations are also found in Menderes where there is no known source as discussed above. Although low levels of Cd are observed in Menemen, Menderes, Aydın, Denizli, between Manisa and Uşak, high enrichments are seen in these places. There are industries in Menemen, Manisa, Aydın, Denizli and Uşak. These results show that Cd is not very much related with coal burning but rather it is related with industry. Between Uşak and Manisa and in Balıkesir, it shows similar pattern with Pb due to vehicle emissions. Cadmium is released by tyre wear and fuel combustion (Monaci et al., 2000).

Figure 4.39: Concentration and EF distribution maps for Zn

Zinc is ubiquitous in nature and its most relevant anthropogenic emission sources are incinerators, traffic, pesticides and fertilizers, the rubber industry, iron and steel production as corrosion protection and coal burning (Scerbo et al., 1999).

Elevated levels of Zn are found in Aliağa area, in the city center of İzmir, Menemen organized industry area, Balıkesir and Urla. For Balıkesir and Urla traffic may be source associated with also Pb concentration distribution. Zinc shows higher enrichments where concentrations are also higher. Although the concentrations are low in Torbalı, Menderes and Seferihisar, city center of Manisa, Manisa organized

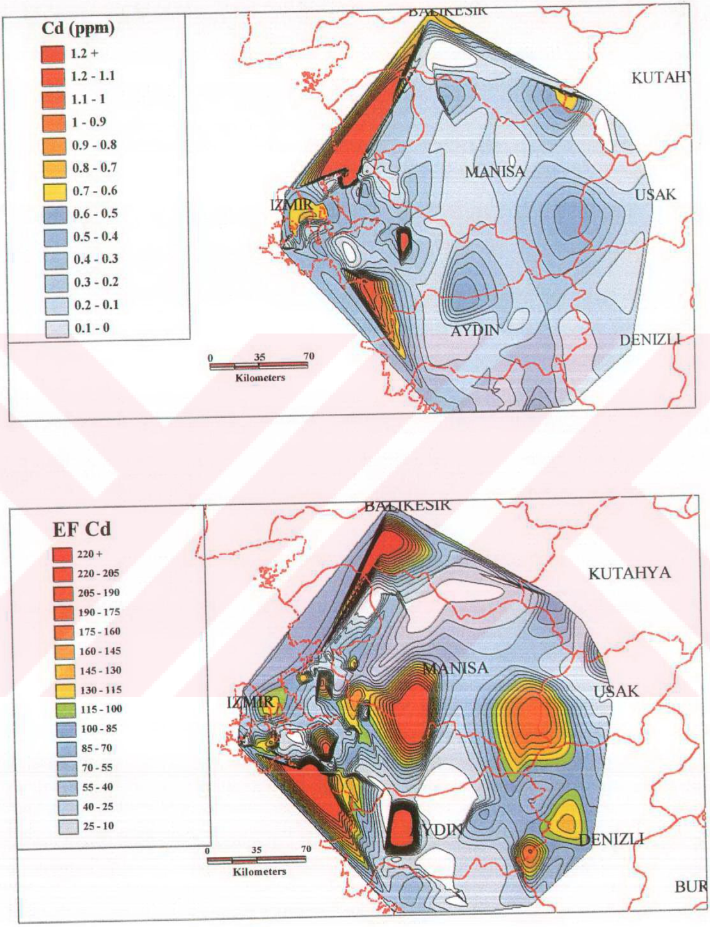


Figure 4.38. Concentration and EF distribution plots of Cd

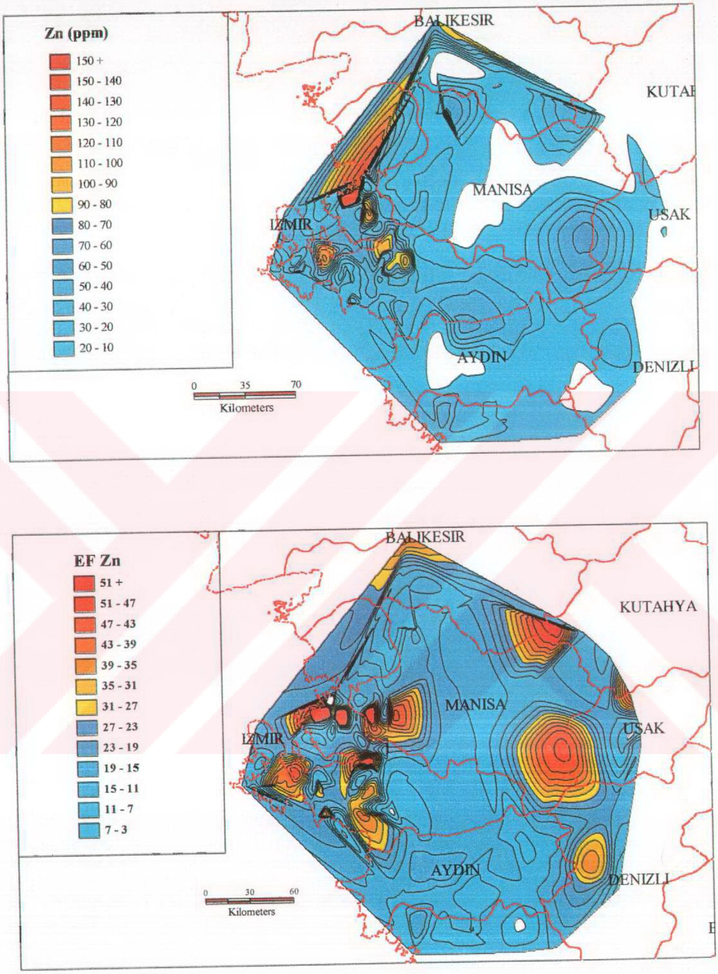


Figure 4.39. Concentration and EF distribution plots of Zn

industry area, Uşak, Denizli, areas between Manisa and Uşak, Kütahya and Balıkesir, Uşak and Kütahya, Zn has high EF values. In these areas traffic can be a source for Zn other than industries. In Torbalı, Manisa, Uşak and Denizli, its high values are related with industry. In other areas it may be related with vehicle emissions because Pb shows similar patterns.

Figure 4.40: Concentration and EF distribution maps for Cu

Copper is used mostly in electrical engineering. Also it is used for alloy, water mains, roofing, household goods and coins. It is used as fungicide, bactericide, algicide and molluscicide (Markert, 1992).

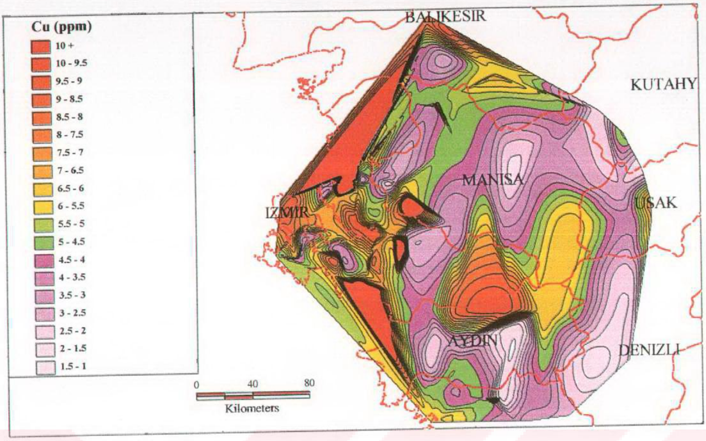
The highest concentrations are found in the city center and all main industrial areas of İzmir (electrical industries) and Manisa (electrical and household goods). Also in Karaburun, Urla, Seferihisar and Menderes there are very high concentrations of Cu. The cities Balıkesir, Uşak, Aydın and power plant areas also have high concentrations of Cu.

Copper shows the enrichments only in Kemalpaşa and Manisa organized industry area, Aliağa region, Uşak and Balıkesir. This implies that the contributions of these areas are important for Cu. Other than Balıkesir area, Cu is associated with industry in the stated areas. Copper and As show similarities in Balıkesir area probably due to usage of them as insecticide and fungicide in agricultural area.

Figure 4.41: Concentration distribution maps for Al

Aluminium is not used very much in industry. It is only applied in producing sheet metal, wires and alloys. Aluminium salts are used in sewage plants to precipitate (Markert, 1992).

The regional distribution of Al in lichens shows that Al concentrations are higher in industrial areas of İzmir especially in Aliağa area and power plant areas. This means that Al concentrations differ not only due to lithological differences in soil but also pollution.



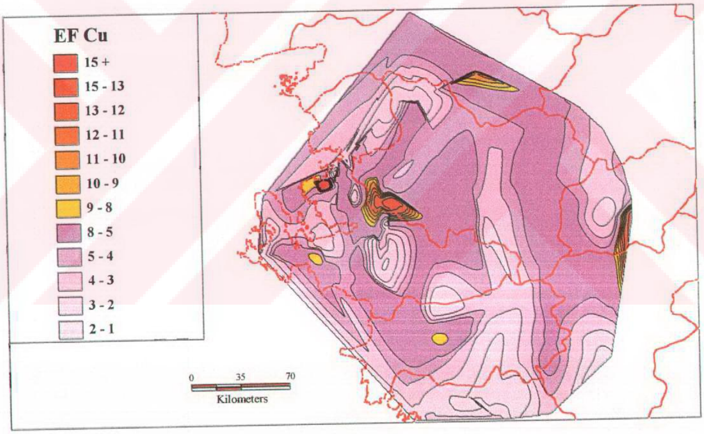


Figure 4.40. Concentration and EF distribution plots of Cu

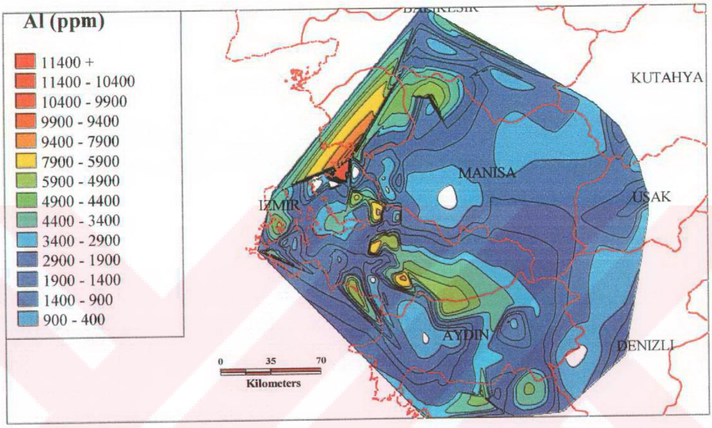


Figure 4.41. Concentration distribution plot of Al

Figure 4.42: Concentration and EF distribution maps for Mn

Manganese is used in steel production and also in alloys and batteries (Markert, 1992).

The highest levels of Mn is found in Aliğa region due to iron-steel factories as expected. Manganese concentrations are higher in the city center of İzmir, Manisa organized industry area and Torbalı. These high concentrations are associated with high enrichments indicating anthropogenic contribution. But there are the areas that concentration contours are moderate but enrichments are high with respect to other areas since EF values show that Mn is not enriched with respect to crust in all region.

Manganese is relatively enriched close to city centers of İzmir and Manisa, in Aliağa, in Manisa organized industry area and in Menemen. There are higher EF values of Mn between cities in large areas such as between Manisa and Uşak, Kütahya and Balıkesir, Uşak and Kütahya and in Balıkesir showing the same distribution pattern with Zn and between Uşak and Manisa and in Balıkesir showing the same trend as Cd. In these areas Pb shows moderate EF values except for Balıkesir. In these areas the contribution of vehicle emissions are likely to occur. Manganese is released by brakes (Monaci et al., 2000).

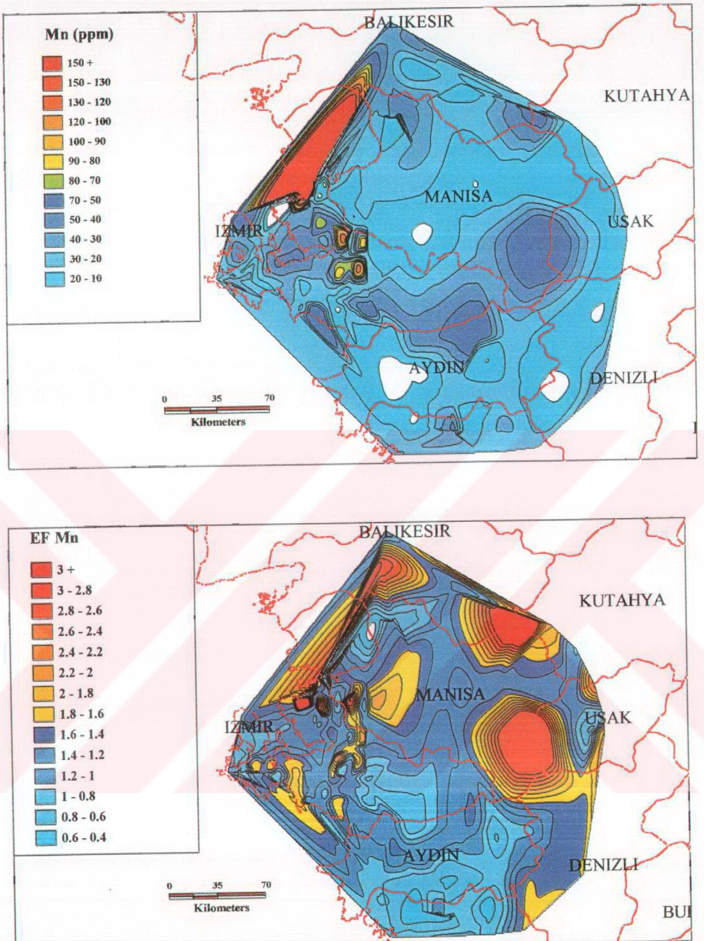


Figure 4.42. Concentration and EF distribution plots of Mn

Figure 4.43: Concentration and EF distribution maps for Fe

Iron is applied as a construction material. It is also emitted from iron related plants and also during combustion of fossil fuels such as coal (Fernandez et al., 2000).

It is thought that this element is from soil since its concentration distribution pattern matches very well with the distribution pattern of Al. However, the Çukurova iron-steel plant is responsible from 83.6% of SPM emissions in Aliağa area and 66% in İzmir city according to emission factor calculations (Müezzinoğlu, 2000). Therefore in Aliağa area it comes from iron-steel plants. Distribution map of EF supports this interpretation as Aliağa is the major region that Fe shows relatively more enrichments with respect to crust. Other enriched areas are in Manisa organized industry area and in the city center of İzmir due to mainly coal combustion and industrial activities. These three areas are important contributors for Fe.

Figure 4.44: Concentration and EF distribution maps for V

Vanadium is often associated with lead in nature as a component of gas oil and coal. This element is mainly used in the chemical and ceramic industries and in nickel-vanadium steel production (Markert, 1992).

The distribution pattern of this element suggests a negligible level of contamination all over the region as it shows the same concentration distribution pattern with Al. Vanadium is not enriched all over the region. However it is relatively higher EF values in Aliağa area, other industrial areas in İzmir and Manisa due to oil or coal combustion, at the eastern part of Manisa and Uşak due to mainly different soil composition.

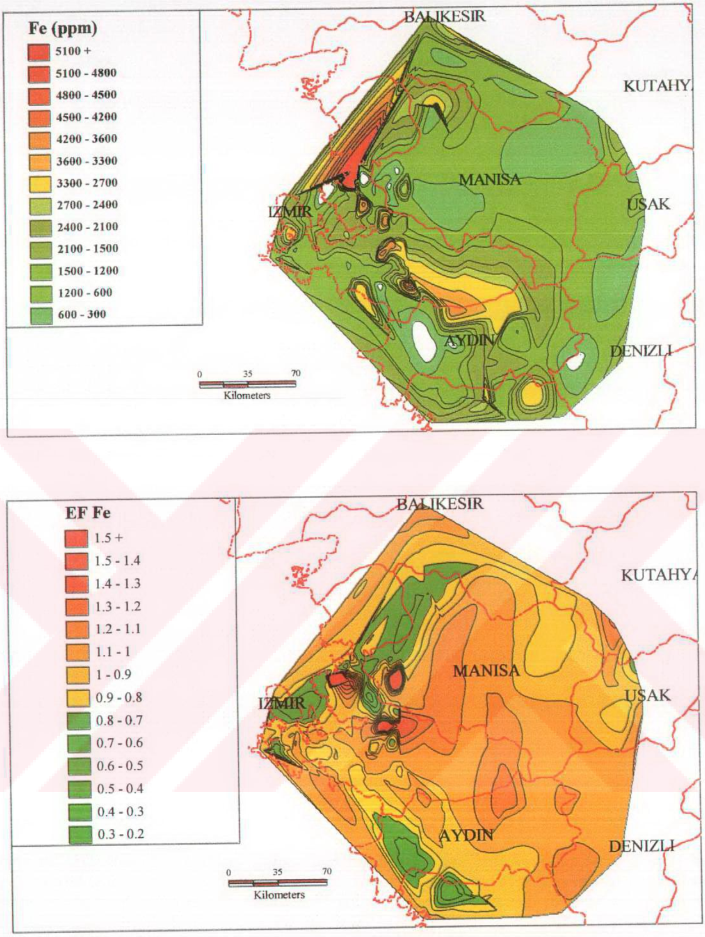


Figure 4.43. Concentration and EF distribution plots of Fe

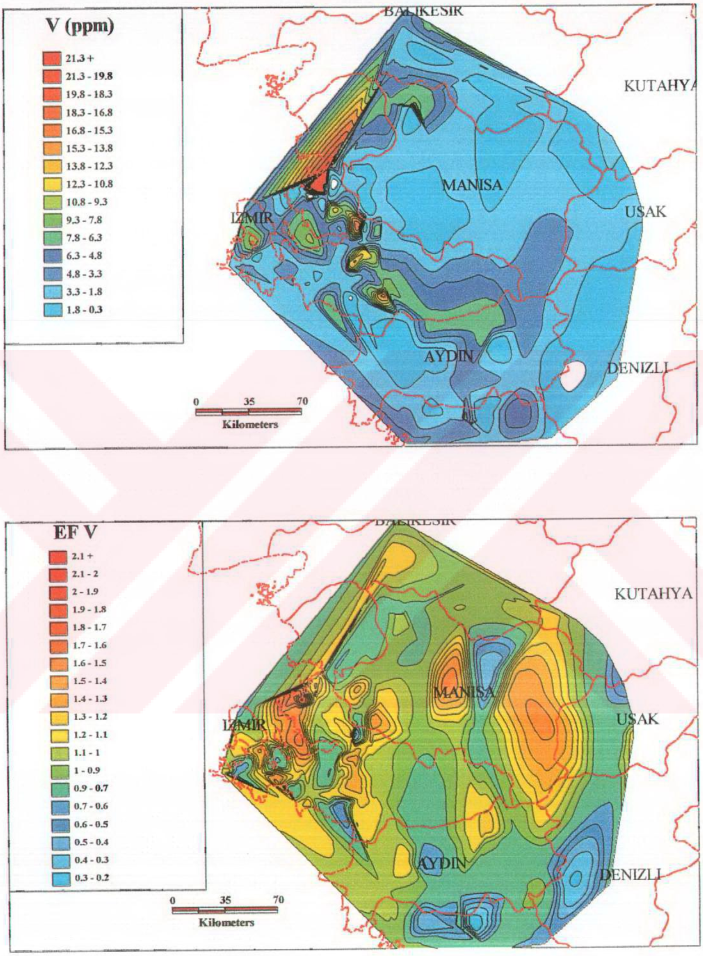


Figure 4.44. Concentration and EF distribution plots of V

Figure 4.45: Concentration and EF distribution maps for Cr

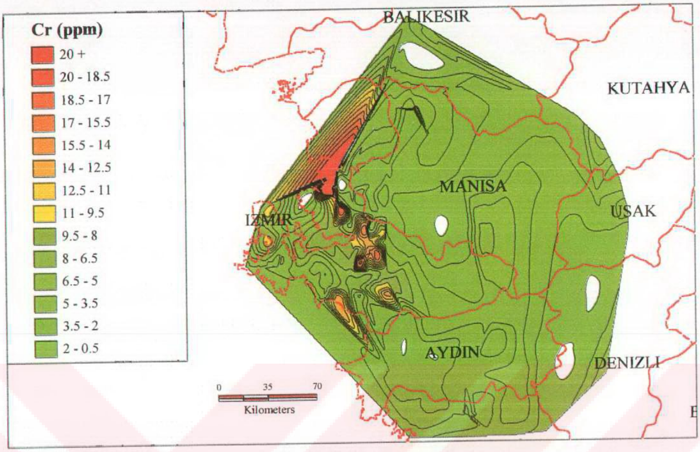
Chromium is extensively used in chrome plating, in steel and paper mills, paints and dyeing plants (Scerbo et al., 1999).

Aliağa area has the highest levels of Cr as expected since Cr is one of tracer elements for steel plants. It has also high concentrations in the city center of İzmir, Menemen, Kemalpaşa, Torbalı and Menderes. Chromium is only enriched in Aliağa area and close to city of İzmir implying that these are important sources contributing to concentrations of Cr. The levels of concentrations and EF values suggest that Cr is prevalently of terrigenous origin, derived from the deposition on lichen thalli of solid particles up by the wind.

Figure 4.46: Concentration and EF distribution maps for Ni

Nickel is ubiquitous in nature, but its level in the atmosphere is enhanced by coal, oil, and gas combustion and incinerator emissions (Scerbo et al., 1999).

The distribution of concentrations of Ni shows similarities as Cr except for Cr has also high concentrations in Menemen and Kemalpaşa. Nickel is not enriched all around the region with respect to crust. Correlation patterns with V in individual regions indicate contribution from local usage of fuel oil such as in Aliağa area and from soil component. The most important source that contributes to Ni is Aliağa area.



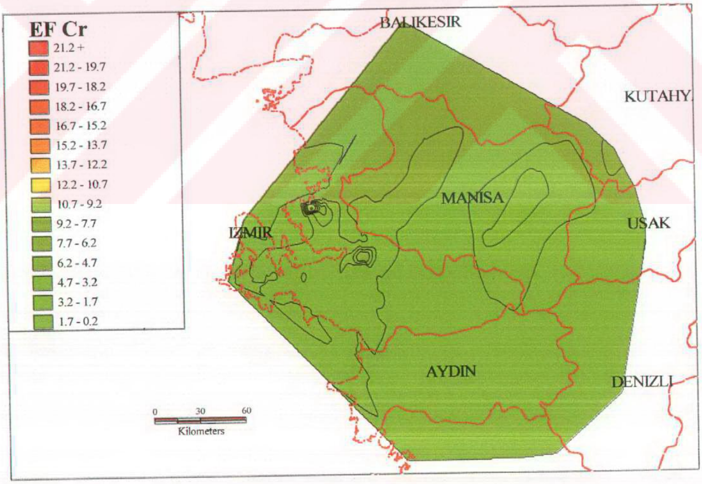


Figure 4.45. Concentration and EF distribution plots of Cr

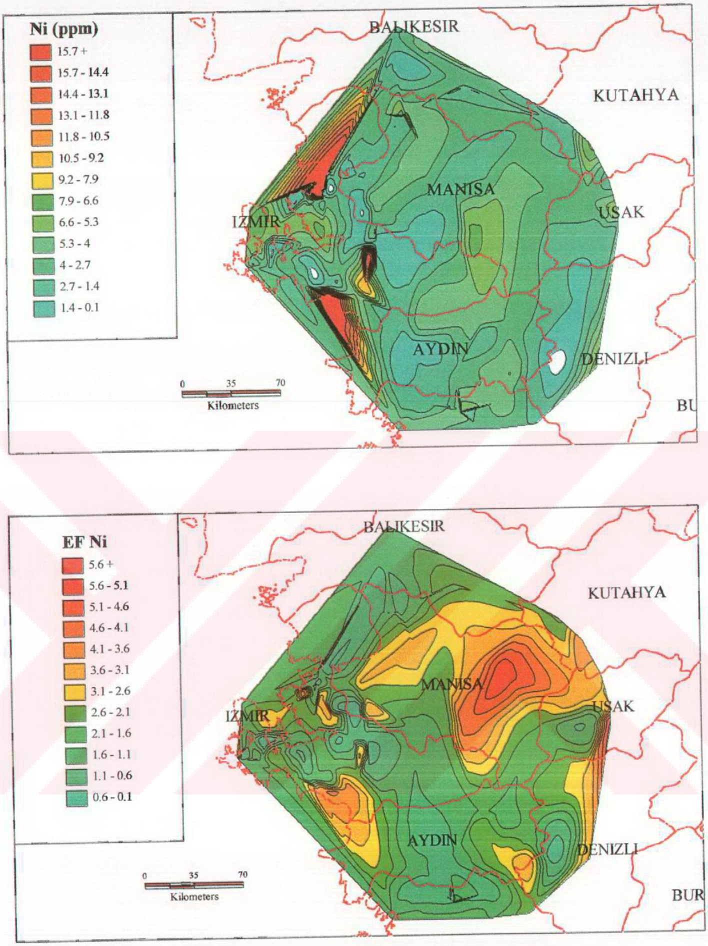


Figure 4.46. Concentration and EF distribution plots of Ni

Figure 4.47: Concentration and EF distribution maps for La

The lanthanides are used in industry as catalysts, for mineral oil cracking, as luminescent material for colour TV sets and additives for Hg and fluorescent lamps (Markert, 1992)

Concentration distribution map shows similarities to that of V, Fe, Ni and Al. Since it is also typical representative of the crustal components. It is not enriched element as expected. The EF distribution pattern is again similar to V, Ni and Fe except there are no hot spots in İzmir and Aliağa area in EF plot of La. There are contributions from these areas only to V, Ni, and Fe concentrations as discussed before not to concentrations of La.

Figure 4.48: Concentration and EF distribution maps for Ca

Calcium comes from concrete material and cement factories. Calcium show similar distribution pattern as Al in general except for Urla and Denizli. It is not enriched with respect to crust in all region and EF distribution pattern is similar to EF of La EF distribution pattern except for the areas in Manisa organized industry area and Urla. In Manisa organized industry area, there are cement-concrete and ceramic factories. For Urla there is no explanation for high EF values of Ca.

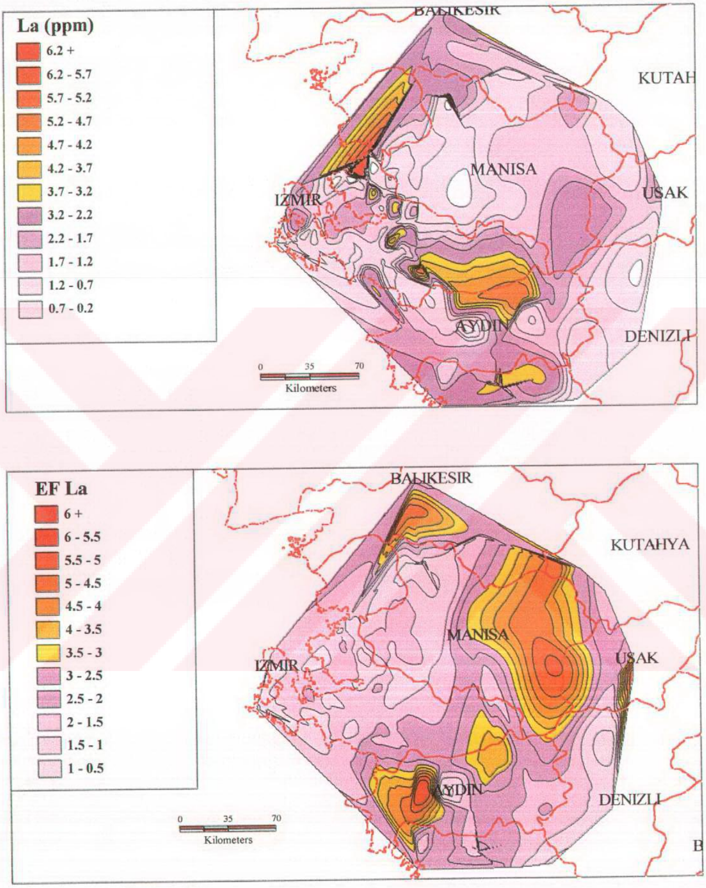


Figure 4.47. Concentration and EF distribution plots of La

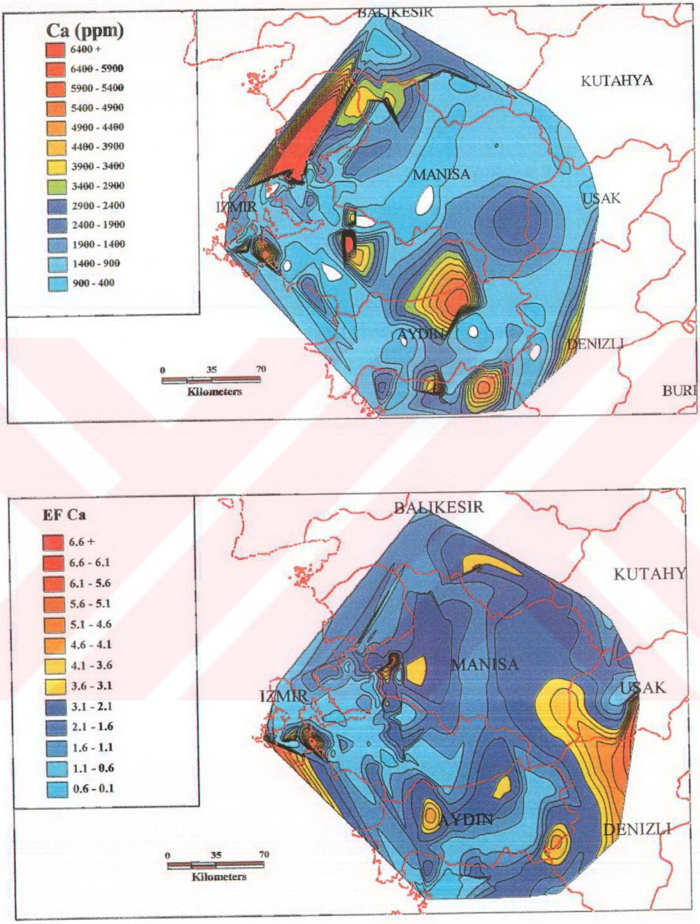


Figure 4.48. Concentration and EF distribution plots of Ca

Figure 4.49: Concentration and EF distribution maps for Na

Sodium is expected to be sea origin however it shows similar concentration patterns as Al except for Uşak. Sea effect is seen little around the coastal sites with moderate concentrations of Na namely in Karaburun and Çeşme. The EF distribution map of Na shows again no effect of sea. It has little higher EF values in Aliağa and Çiğli. Although concentration pattern is similar to Al, EF distribution pattern differs from crustal elements.

Figure 4.50: Concentration and EF distribution maps for K

The source of K in lichens is lichen metabolism itself. Since it is nutrient element for lichens. It also takes K from leachate obtained from other dead foliar (Steinnes et al., 1992) not only from the atmosphere. The behaviour of distribution of concentration is different from other crustal elements as we see in section 4.2.2 except for industrial areas like Aliağa area, Kemalpaşa, the city center of İzmir and Torbalı. Along the coastal sites moderate levels of K are seen. The EF distribution pattern of K is not very different from the concentration pattern since it is enriched in places where concentrations are also higher.

Figure 4.51: Concentration and EF distribution maps for Mg

The distribution of concentration and EF values of Mg is very similar to that of K. Since it is also important macronutrient for lichens as discussed before. That's why it generally behave in similar way as K.

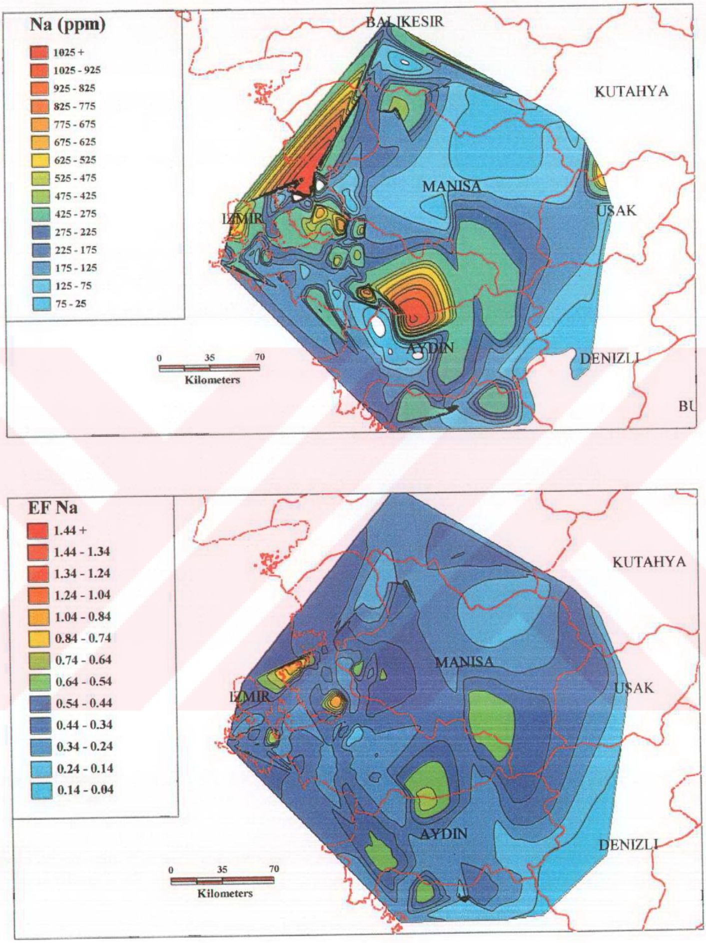


Figure 4.49. Concentration and EF distribution plots of Na

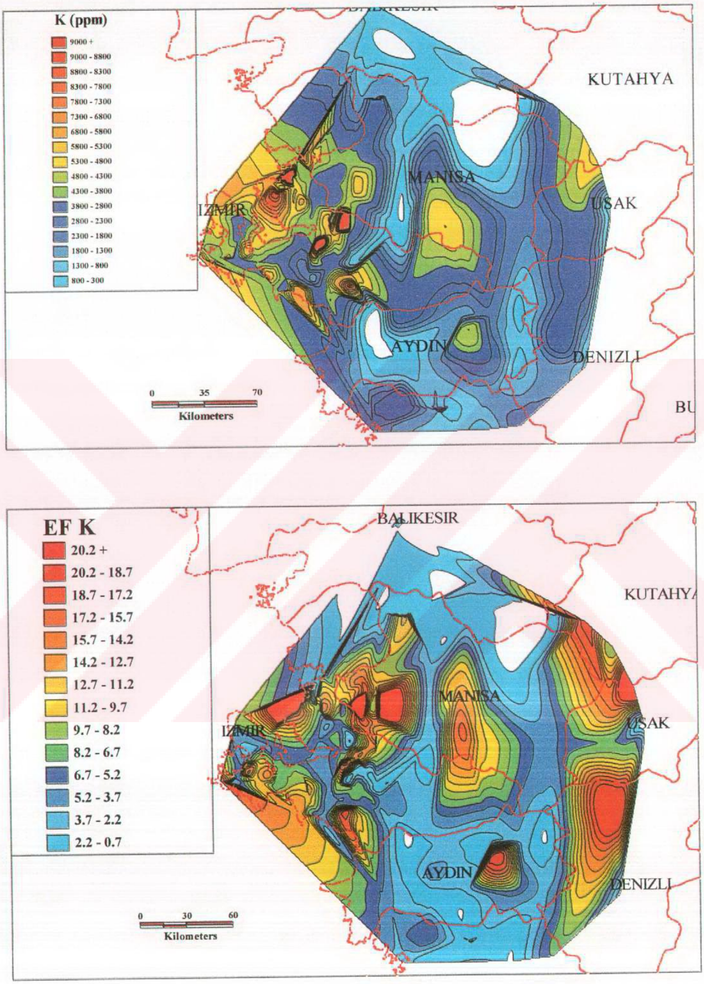
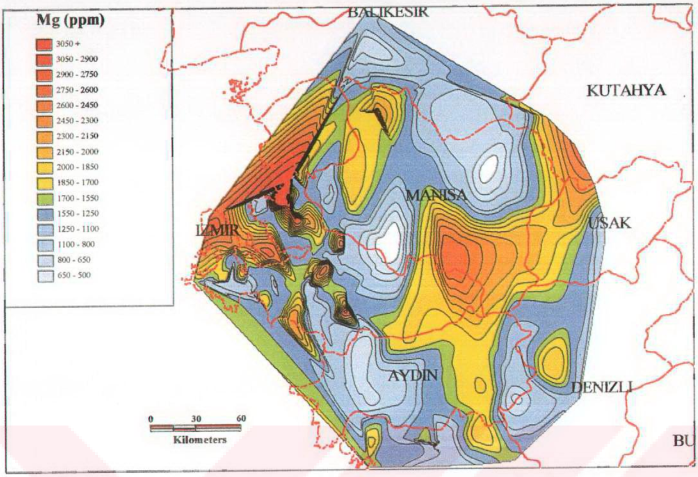


Figure 4.50. Concentration and EF distribution plots of K



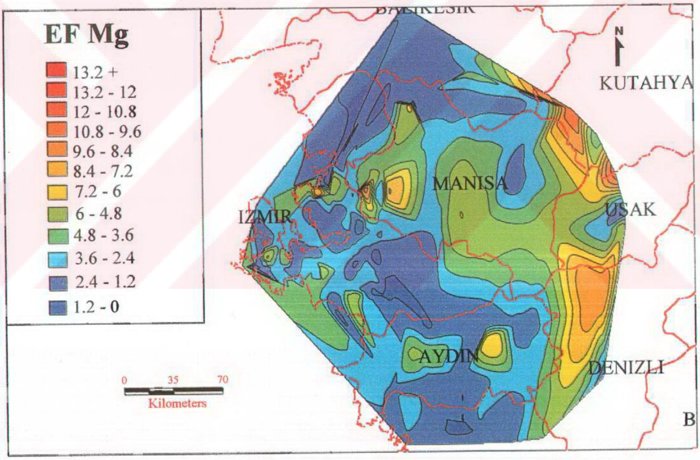


Figure 4.51. Concentration and EF distribution plots of Mg

4.4. Source Apportionment and Quantification

The discussion in the previous section (4.3.3) provided an information about concentration contours and enrichment of elements with respect to soil in different parts of the Aegean Region. But one of the main objectives of this work is to categorize different classes of the sources or source regions and afterwards to calculate their quantitative contribution to an airshed in the region. In this way one can comment about air quality of the region qualitatively and quantitatively.

Various mathematical models have been applied widely to apportion the lichen or other biomonitor organisms measured at a region to its likely sources. Receptor modeling is one of the most commonly used one which means possible sources are identified at a given receptor site. Among the different approaches of receptor modeling are cluster analysis (Calvelo et al., 1997; Nimis et al., 2000) and principal component analysis (PCA) (Schaug et al., 1990; Calvelo et al., 1997) or factor analysis (Sloof and Th. Wolterbeek, 1991b; Kuik and Th. Wolterbeek, 1994; Sloof, 1995b; Jeran et al., 1996; Freitas et al., 1997; Bennett and Wetmore, 1999). Among the multivariate methods, factor analysis (FA) is the most used one to qualitatively apportion the sources.

As discussed in the previous sections, different sources such as power plants, coal combustion, iron-steel plants, automobile emissions, various industries and crustal sources are identified in the Aegean Region. In addition lichen metabolism can be a source for K.

The receptor modeling approach is used at two levels. At the first step, sources contributing to observed levels of elements were qualitatively determined using factor analysis. However other than source identification, FA can also give other important information about the sources such as how much of the whole variation in the data set is explained by the each source and what is the priority of that source. At the second step, further statistics, which is known as absolute factor score-multiple linear regression (AFS-MLR) analysis was performed to the results of the FA to determine quantitative contributions (%) of factors (sources) to the concentrations of elements used in FA.

4.4.1. Factor Analysis

For selecting the elements to be included in FA analysis, a minimum of 70% of the samples need to have measurable levels of the element.

In principle, FA actually groups the elements of which concentrations fluctuate together from one sample to another and separates these elements into so called "factors" (Henry et al., 1984). Factor analysis is used for source apportionment in environmental data with the argument that those of elements fluctuate together means that they have something in common like their sources. Ideally, each extracted factor represents a source affecting the samples. Although there are no well-defined rules on the number of factors to be retained, usually either factors that are meaningful or factors with eigenvalues larger than one are retained. In theory, irrelevant factors have zero eigenvalues and eigenvalues less than one indicate that factor contributes less than a single variable. In this study, factors, which have eigenvalues larger than unity, have been retained.

Difficulty in performing the analysis is due to the fact that concentrations of most elements found in a sample are the result of combined influences of several sources. This is the reason a large set of measurements is necessary for the separation to be successful. There needs to be enough change in the measurements, and enough combinations of change for the differences in the relationships to be observed. A large data set, however, is not always sufficient for separation of sources. Because of the use of FA to identify sources from receptor samples is entirely dependent on the transport of the species, it is very difficult to distinguish between two sources located close to each other even if they have very different types of emissions. Thus sources, which are far from the sampling site, tend to get smeared together, and local wind pattens can greatly affect the results by mixing air from different directions.

4.4.1.1. Treatment of Values Below Detection Limit

In this study, for missing values due to the detection limit problem in the data set, lower quartile values were used. Lower quartile means the value below which 25 percent of the data will fall; the 25th percentile (Statgraphics Manual 3.1, 1997). It was observed that treating missing values with lower quartiles or any other values did not alter the results obtained from the factor analysis when the number of missing values were less than 15% of the whole sample size which was the case in this study. This treatment is being done for not loosing the whole sample just for one missing parameter. As it was stated before the number of samples should be large enough to observe fluctuation in the data set.

4.4.1.2. Extraction of Factors

Factor analysis has been performed using the Statgraphics Plus program package (Statgraphics Manual 3.1, 1997). The initial components were rotated using the VARIMAX method to obtain final eigenvectors with more representative of individual sources of variation. Initially factor analysis was performed by using all data points. The first result is a factor matrix, which relates each of the factors to each of the elements or variables. The numbers in the matrix are referred to as the factor loadings and indicate how much of the variance of the given element can be explained by the given factor. The factors in the matrix are given in order of decreasing ability to describe the variance of the whole system. Usually only the higher order factors are retained for further analysis. The physical meaning of the factors must be interpreted by observing which elements or variables display high (>0.20) loading within the factor. Although many elements may display high loadings, a particular source type is usually identified with a factor by the presence of high loadings of a few marker species, which are characteristics of that source type. It is preferred to start with few factors, usually four or five, and progressively increase the number until meaningless factors begin to appear. One can then go back to the beginning of the analysis until the largest number of reasonable factors is obtained. There is not a set rule for the selection of factor numbers but in the application the selected number of the factors must explain at least 70% of the total variance. Always the ordering of factors are the same as with their ability to explain % system variance. The number of used parameters gives total variance, for each parameter having a unit variance. For example, if there are 15 variables, total variance is 15. Then the success of the FA solution is explained by the % variance explained by all factors. Higher the % explained variance better the FA solution. Then the data were screened for the outliers using factor scores. The magnitude of a factor's (i.e. source's) influence on a specific sample is given by factor score for that sample. The factor score is the number of standard deviations from the mean of that factor as averaged over all the samples in another term it is the value of the factor. An average contribution from the factor gives a score of zero, a greater than average contribution gives a positive score, a less than average contribution gives a negative score. Factor scores greater than one indicate a strong influence of that source or factor on that individual sample. The samples having factor score values greater than 15 are generally discarded just for only FA studies in the first run in order to avoid the screening of samples having less contribution to each factor. In this study, it was seen that a sample with factor score greater than 15 changed the whole system variation significantly especially for crustal factor.

4.4.1.3. Factor Analysis with Two Data Sets

To analyze the lichen samples, two techniques were used namely INAA and ICP-AES. The grid elements of 10 km x 10 km were chosen for the city of İzmir and for some part of Manisa city as shown in Figure 3.1. This means mostly coastal areas, which covers the urban light industry region, industrial area, urban region and small part of semiurban region. The grid elements 40 km x 40 km in the interior part of the region, which comprise larger portion of the semiurban area and power plants region. This region has larger area than the 10 km x 10 km gridded region. By this way the region is divided into two portions both gridwise and analytical techniques used. However ICP-AES technique limited the number of elements that was determined in all data set. That's why another FA was applied to small gridded region in order to use the elements that were determined by INAA. Also, the most important pollution sources are located in that region.

Potassium was discarded from the factor analysis due to its strange behaviour as explained in section 4.2.2, since it is a nutrient element for lichens.

4.4.1.3.1. Coastal Sites of the Region

The results of varimax rotated factor analysis of small gridded (10 km x 10 km) region with a sample number of 60 is given in Table 4.29. The table includes

Table 4.29. Varimax rotated factor loading and corresponding probable source type coastal region

Element	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Al	0.85			0.31	0.84
Ti	0.71				0.59
V	0.72			0.44	0.74
Cl				0.85	0.76
Mn	0.31	0.74		0.36	0.80
Na	0.65			0.47	0.64
Ca	0.27			0.48	0.33
Sc	0.96				0.93
Cr	0.38	0.68	0.34		0.74
Fe	0.71	0.54			0.84
Co			0.84		0.76
Zn		0.95			0.92
As	0.46		0.61		0.61
Se			0.31	0.38	0.25
Br	0.27			0.30	0.21
Rb					0.26
Cd		0.94			0.92
Ni	0.55	0.44			0.59
Cu		0.88			0.80
Pb		0.95			0.91
Sb		0.34	0.85		0.84
Cs			0.56		0.47
La	0.95				0.92
Ce	0.93				0.88
Sm	0.94				0.91
Hg		0.66	0.49		0.70
%variance	34.5	18.7	10.6	6.10	69.9 (Total)
Probable source	Dirty soil	Aliağa Area	Indust. Urban areas	Regional background	

factor loadings after rotation, eigenvalues, the variance explained by each factor and communalities of elements. Factor loadings larger than 0.20 were included in the table, because loadings smaller than this value were considered as insignificant. Four identifiable factors accounted for the 70% of the system variance in the data set. Communality is the fraction of each element's variance explained by the factors.

The first factor is attributed to dirty soil, accounting for 34.5% of the total variance, which is the highest percent variance in the data set. Other than the crustal elements like Al, Ti, V, Mn, Na, Ca, Sc, Cr, Fe, Ni, La, Ce and Sm, the anthropogenic element As has also loading in this factor. Vanadium has relatively high abundance in Earth's crust. Chromium and Ni are seen in this factor due to unusual composition of local soil (Güllü, 1996; Hamzaoğlu, 1998). This factor indicates either a simple mixing of crustal material with anthropogenic emissions in the atmosphere or the reemission of past anthropogenic emissions, which had deposited in the local soil. One has to keep in mind that in Aegean Region, the geochemistry of the soil changes in short distances. For example the distance in between İzmir and Turgutlu is just 40 km but the soil composition is a lot different. The factor score map of this factor shows the relative weight of each factor in each sample as depicted in Figure 4.52. Distributions of factor scores give an idea about the different mineral structures of soil, which is contaminated by different elements at different levels in the region.

The second factor has loadings of elements Mn, Cr, Fe, Zn, Cd, Ni, Cu, Pb and Sb, which are mostly the characteristic elements of iron-steel plants and refinery originated from Aliağa area. That's why we named as Aliağa factor. Factor score map of Aliağa factor is shown in Figure 4.52. From this figure it is very clearly seen that the factor represents Aliağa region. Such a clear discrimination of this factor is an important finding in this study. In the following section, the contribution of this factor at any point was calculated quantitatively. As can be seen from Table 4.29, Hg has also high loading in this factor. This factor accounts for 18.7% of the system variance explained.

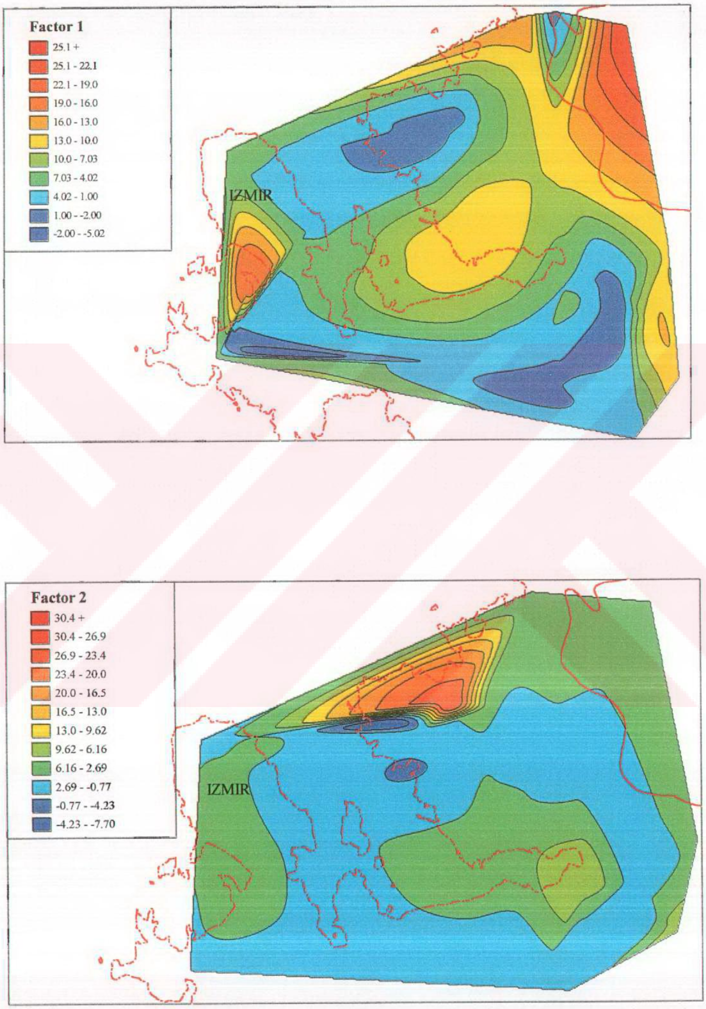


Figure 4.52. The factor score maps of Factor 1 and Factor 2 for coastal region

Factor 3 has high loadings of anthropogenic elements Cr, Co, As, Se, Sb, Cs and Hg. This factor is identified as industrial urban areas factor owing to the presence of As, Se, Sb and Hg, which are typical marker elements for domestic heating with coal and the presence of Sb, Co, Cs and Cr representing industrial activities. Factor score map agrees well with this elemental behaviour as shown in Figure 4.53. As can be seen from the figure factor scores have high values in close to city center of İzmir, which show the location of strong source areas to this factor.

Although this is the coastal part of the Aegean Region, there was not a separate sea contribution. Most probably soil contribution mask Na and Cl concentration coming from the sea. The presence of Al, Mn and Ca also support this interpretation. Also Se and Br come from partly sea (Steinnes, 1995; Berg et al., 1995) and industry and Se from coal burning. It seems that this factor represent a mixture of sea contribution with industry, coal burning and soil. As can be seen from the factor score map in Figure 4.53, this factor covers a large areas of İzmir and Manisa. That's why we called this factor as regional background.

4.4.1.3.2. Whole Region

The results of varimax rotated factor analysis of whole data set with sample number of 96 are given in Table 4.30. In this FA solution there are 17 variables. Four identifiable factors accounted for the 70.7% of the total variance in the data set. Although the number of elements and samples were different from the previous FA, the first three factors did not change much in composition and the value of % variance that they explain. This means that the contribution of these sources to the pollutant levels in the region is very important and these sources affect all Aegean Region not only coastal part.

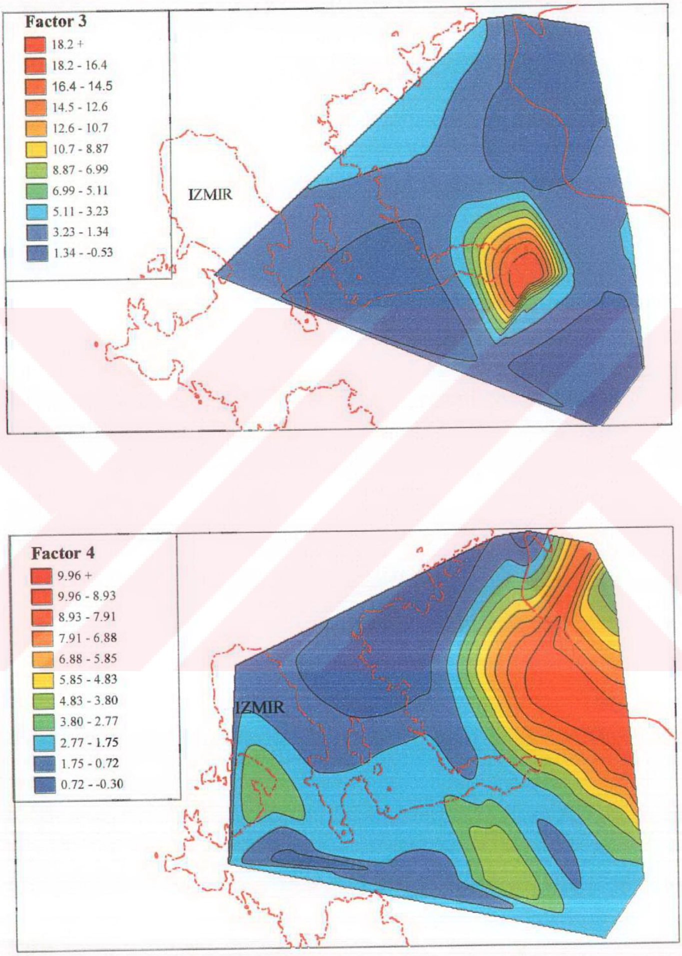


Figure 4.53. The factor score maps of Factor 3 and Factor 4 for coastal region

Table 4.30. Varimax rotated factor loading and corresponding probable source type of whole region

Element	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Al	0.95				0.94
Mg	0.44	0.51			0.47
V	0.81	0.22		0.20	0.76
Mn	0.38	0.74		0.24	0.78
Na	0.49			0.43	0.43
Cr	0.46	0.71		0.20	0.77
Fe	0.86	0.32	0.21		0.89
Zn		0.89	0.20		0.84
As	0.47		0.70		0.73
Se				0.87	0.76
Cd		0.90			0.85
Ni	0.69	0.32			0.62
Cu		0.83	0.21		0.79
Pb		0.47	0.62		0.67
Sb		0.30	0.76		0.68
La	0.87				0.78
Hg			0.36	0.31	0.24
% variance	39.6	16.6	8.1	6.40	70.7 (Total)
Probable source	Dirty soil	Aliağa	Urban industry	Power plants	

The first factor is attributed to dirty soil, accounting for 39.6% of the total variance, which is the highest percent variance in the data set. Since the factor has the loading of the crustal elements like Al, Mg, V, Mn, Na, Cr, Fe, Ni and La as well as the loading of the anthropogenic element As, it is again called as dirty soil. The factor score map is depicted in Figure 4.54 shows the different mineral structures of soil and the effect of especially Soma power plant on the composition of soil as factor score is heavily weighed in this region.

The second factor is named as Aliağa factor as discussed above. The elements Mg, V, Mn, Cr, Fe, Zn, Cd, Ni, Cu, Pb and Sb represent Aliağa region best. This factor explains 16.6% of the explained system variance. Like in the case of FA solution in the coastal region, Aliağa factor heavily weighed in Aliağa as can be seen in factor score map in Figure 4.54.

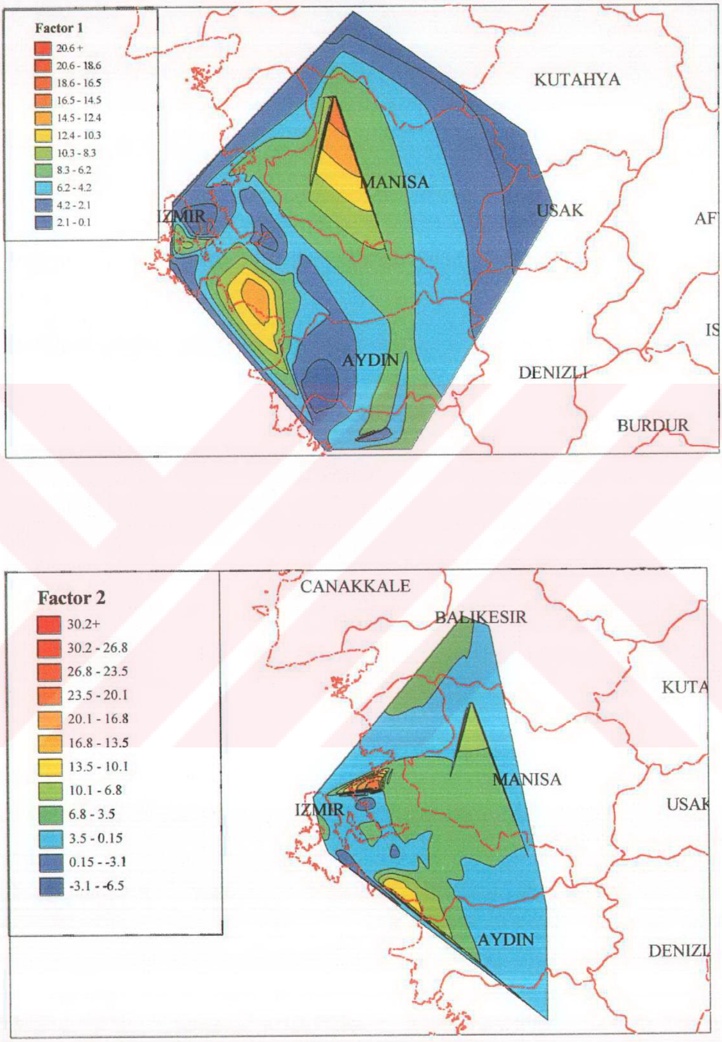


Figure 4.54. The factor score maps of Factor 1 and Factor 2 for all region

The third factor is again urban industrial areas mixed factor. The high loadings of Pb and Sb signal the emissions from motor vehicles. There are also low loadings of Zn and Cu. Antimony and Zn come from motor oil (Huang et al., 1994). Tyre wear is an important source of Zn (Monaci et al., 2000). Antimony is also indication of industry and coal burning. The elements As and Hg are marker elements of domestic coal burning and Cu is an indication of industry. In the factor score map of factor 3 as shown in Figure 4.55, factor scores are heavily loaded in İzmir and Balıkesir.

The fourth factor is characterized by elements Se, Na and Hg. Since the coal burned in Yatağan was enriched in both Se and Hg. It gives separate highly weighed distribution in the factor score map. Soma power plant and industrial areas in İzmir and Manisa give highly weighed big area in the factor score map. Plume of Soma power plant is carried down by major wind patterns and it affected larger region combined with background area as seen in factor score map in Figure 4.55.

4.4.1.4. The Use of Absolute Factor Score-Multiple Linear Regression (AFS-MLR) analysis

As discussed in the previous section, FA exercises have successfully revealed that the region is mostly affected by Aliağa region, urban-industrial areas around city center of İzmir, Balıkesir and power plants. However, the results of FA were qualitative due to the nature of the applied statistics. In other words, although FA has shown the pollution sources affecting the region, it did not provide any information on how much each source contributes to elemental concentrations.

The AFS-MLR is simply an extension of FA where factor scores are used to obtain elemental concentrations at each sample. It is a three step statistical procedure. In the first step absolute zero factor scores are obtained from factor scores of four factors obtained for two FA results. This is realized by inserting an additional hypothetical sample where concentrations of all elements are assigned zero value. The factor scores obtained in FA for this new sample are called "zero factor scores" and subtracted from the factor scores obtained without including the

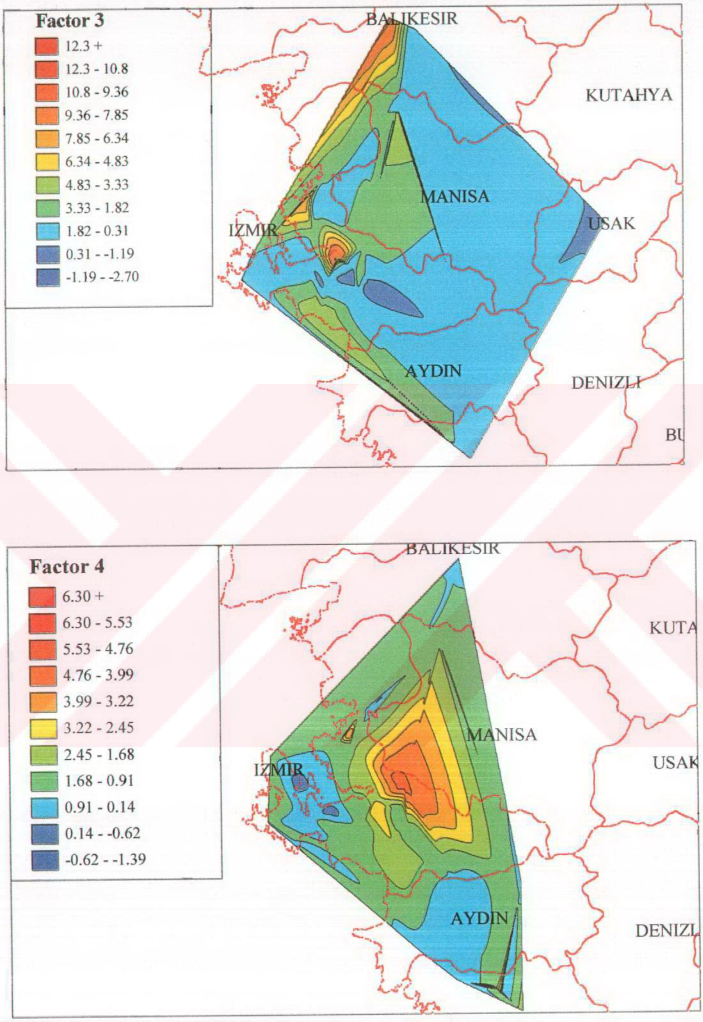


Figure 4.55. The factor score maps of Factor 3 and Factor 4 for all region

hypothetical sample to obtain "absolute factor scores" for each of the four factors. In the second step, concentrations of each element are regressed on these absolute factor scores. In the third step, the obtained equation for the elements (the multiplication of regression coefficients by absolute factor score values) are used to convert factor scores into source contributions and expressed as % contribution. More detailed information on AFS-MLR is given in section 1.7.3.2.1 of this manuscript.

The accuracy of the AFS-MLR exercise can be tested by calculating observed to predicted ratios of elements. Since AFS-MLR gives the contribution of each source on the concentration of each element at each sample, then the sum of these contributions at each sample should be equal to the measured concentration of that element in that particular sample. For a successful AFS-MLR the observed to predicted ratios of elements should be close to unity. The results of these analyses are given in Table 4.31 and Table 4.32 for small gridded data set and whole data set, respectively. The estimated percent mean source contributions for each element in each identified factor, estimated mean to observed mean ratios with their standard deviations and R^2 values are given in these tables. These tables are also represented as figures in Figures 4.56 and Figure 4.57 in order to express the numbers in more understandable way.

In the first table, Table 4.31 only the elements Ca, Se, Br and Rb are poorly explained with absolute factor scores, for other elements R^2 values are quite high and same as communality values of elements in FA. Such lack of correlation implies that significant amount of Ca, Se, Br and Rb were left unapportioned by the regression probably due to some unconsidered source(s). When ratios are compared, all elements except for Ca and Cs were predicted in AFS-MLR with better than 20% average uncertainty. Overprediction of Ca and Cs indicates poor apportionment of these elements. Close to unity observed to predicted concentration ratios for most of the elements suggest that the analysis is successful and calculated source contributions have fairly low errors associated with them. Obviously uncertainties in the calculated source contributions for anthropogenic elements are more important that that for litophilic elements, because they represent the anthropogenic components in lichens and they are the elements that

Table 4.31. Percent mean source contributions to elemental concentrations in lichens with their standard deviations at coastal site in Aegean Region. The mean estimated concentrations to mean measured concentrations of all elements with their standard deviations are also given

Element	Factor 1	Factor 2	Factor 3	Factor 4	Mean estimated/ Mean measured	R^2
Al	85.4 ± 5.54		1.70 ± 0.96	12.9 ± 6.25	1.01 ± 0.21	84
Ti	72.6 ± 4.47		17.8 ± 6.73	9.60 ± 4.40	1.13 ± 0.49	59
V	63.5 ± 24.5	1.00 ± 0.67	2.10 ± 2.64	33.4 ± 27.6	1.04 ± 0.43	74
Cl			22.5 ± 11.4	77.5 ± 11.4	1.17 ± 0.54	76
Mn		57.6 ± 10.7	10.7 ± 6.03	31.7 ± 15.4	1.04 ± 0.36	80
Na	49.9 ± 7.30		6.80 ± 3.29	43.3 ± 9.42	1.09 ± 0.38	64
Ca		12.1 ± 7.02		87.9 ± 7.02	1.23 ± 0.55	33
Sc	100				1.03 ± 0.17	93
Cr	28.4 ± 5.60	53.5 ± 6.30	18.1 ± 5.02		1.11 ± 0.34	74
Fe	69.2 ± 6.97	30.8 ± 6.97			1.06 ± 0.23	84
Co			84.0 ± 7.41	16.0 ± 7.41	1.11 ± 0.73	76
Zn		100			1.05 ± 0.53	92
As	83.8 ± 8.79		16.2 ± 8.79		1.08 ± 0.32	61
Se			49.1 ± 13.2	50.9 ± 13.2	1.16 ± 0.52	25
Br	31.1 ± 5.97	23.8 ± 7.83		45.1 ± 9.87	1.14 ± 0.47	21
Rb	85.5 ± 4.77	2.32 ± 0.90	12.2 ± 4.43		1.16 ± 0.53	26
Cd		100			1.12 ± 0.45	92
Ni	60.7 ± 7.42	39.3 ± 7.42			1.18 ± 0.57	59
Cu		93.4 ± 2.74		6.60 ± 2.74	1.05 ± 0.21	80
Pb		100			1.08 ± 0.46	91
Sb		4.90 ± 1.35	84.4 ± 5.18	10.7 ± 4.72	1.07 ± 0.55	84
Cs	24.3 ± 6.05		75.7 ± 6.05		1.29 ± 0.64	47
La	100				1.00 ± 0.15	92
Ce	100				1.06 ± 0.37	88
Sm	100				1.02 ± 0.17	91
Hg		45.9 ± 6.55	43.2 ± 8.93	10.9 ± 5.20	1.07 ± 0.32	70

are used to assign factors as the primary pollution source in the region.

For coastal region, the first factor explains the whole concentrations of crustal elements like Sc, La, Ce and Sm and the highest percent of other crustal elements Ti, Na, Fe and Rb and anthropogenic elements V, As, Ni and considerable fraction of Cr as can be seen in Figure 4.56. These findings are good agreement with the findings as explained in the previous sections and previous studies. The presence of As in the soil factor can be explained by contamination of surface soil because of heavy coal consumption with high As content in the region.

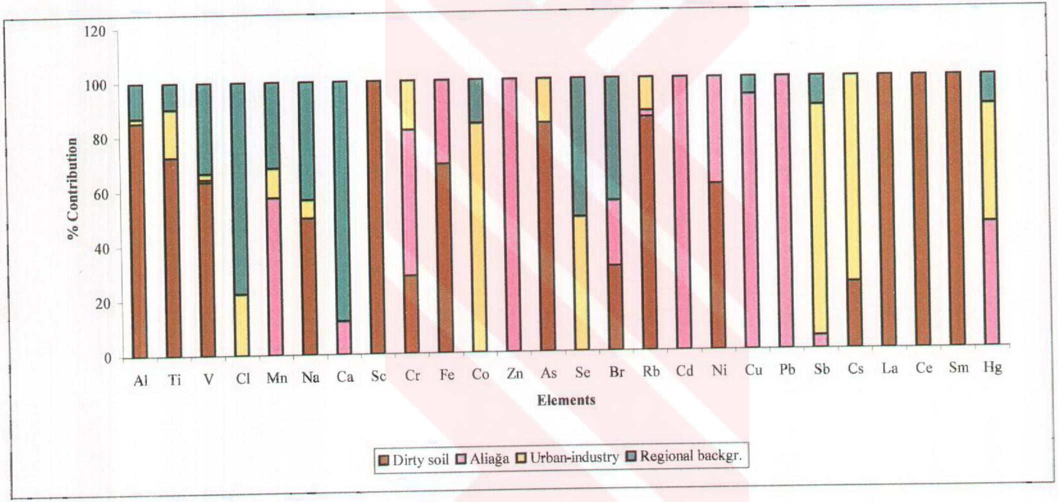


Figure 4.56. Mean percent contributions of sources to element concentrations for coastal region

The second factor is the most important factor, because it explains the whole concentrations of anthropogenic elements Zn, Cd, Pb and the highest percent concentrations of elements Mn, Cr, Cu and Hg, although the third factor contribution is also expected for the elements Pb, Cd and Zn.

The third factor explains the highest percent concentrations of Co, Sb and Cs and considerable portion of Se and Hg as in agreement with FA results. The first group of elements represents industry and the second one represents domestic heating.

The last factor accounts for the most of the measured concentrations of Ca, Na, Cl, Br and Se as seen in FA results. As explained before this factor is not related to marine effect, although it was expected because all elements including Se may come from also sea.

The Table 4.32 belongs to whole data set. Only the elements Mg, Na and Hg are poorly explained with absolute factor scores, for other elements R^2 values are quite high and same as communality values of elements in FA. Such lack of correlation implies that significant amount of Mg, Na and Hg were left unapportioned by the regression probably due to some unconsidered source(s). When ratios are compared, all elements except for Pb and Hg were predicted in AFS-MLR with better than 20% average uncertainty. Overprediction of Pb and Hg indicates poor apportionment of these elements. Ratios close to unity imply that the analysis is successful and calculated source contributions have fairly low errors associated with them.

The factor one contains the same elements Al, V, Fe, Ni and La with the highest percent contributions as coastal region as can be seen in Figure 4.57. The only difference is that this factor contributes less to the concentrations of As but this is again dirty soil factor.

The contribution of second factor is also the highest for the elements Mn, Cr, Zn, Cd and Cu but not for Pb. This is again Aliağa factor.

The contribution of third factor to the elemental concentrations is little changed but more representative for urban-industrial areas. The elements As, Pb, Sb have the highest percent concentrations from this factor and Hg has considerable portion of its concentrations in this factor.

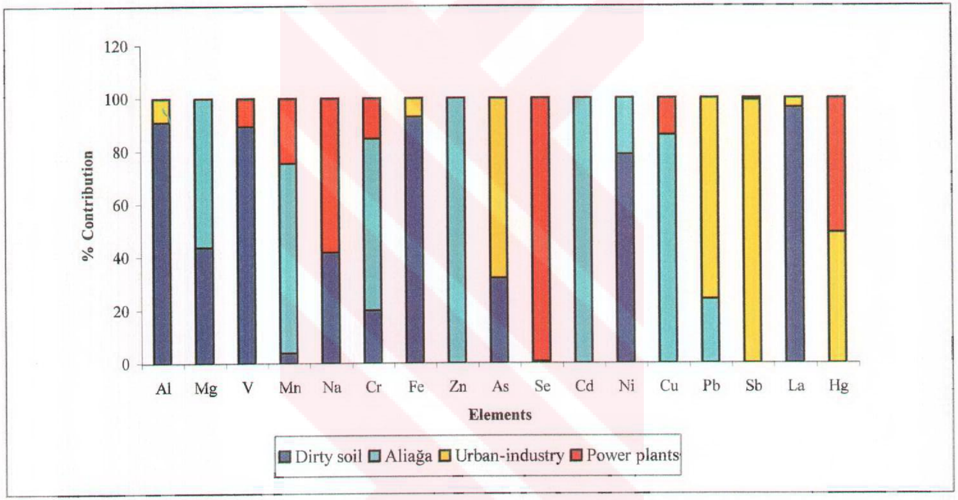


Figure 4.57. Mean percent contributions of sources to element concentrations for all region

Table 4.32. Percent mean source contributions to elemental concentrations in lichens with their standard deviations at whole region. The mean estimated concentrations to mean measured concentrations of all elements with their standard deviations are also given

Element	Factor 1	Factor 2	Factor 3	Factor 4	Mean estimated/ Mean measured	R^2
Al	91.1 ± 2.89		8.90 ± 2.89		1.01 ± 0.15	94
Mg	43.8 ± 6.03	56.2 ± 6.02			1.08 ± 0.31	47
V	89.4 ± 2.77			10.6 ± 2.77	1.06 ± 0.32	76
Mn	3.80 ± 0.79	71.6 ± 5.82		24.6 ± 5.65	1.05 ± 0.26	78
Na	41.8 ± 6.99			58.2 ± 6.99	1.14 ± 0.44	43
Cr	20.0 ± 3.52	64.8 ± 5.40		15.2 ± 3.75	1.06 ± 0.34	77
Fe	93.0 ± 2.35		7.00 ± 2.35		1.03 ± 0.21	89
Zn		100			1.07 ± 0.76	84
As	32.0 ± 5.90		68.0 ± 5.90		1.09 ± 0.33	73
Se		0.70 ± 0.29		99.3 ± 0.29	1.17 ± 0.54	76
Cd		100			1.20 ± 0.58	85
Ni	78.7 ± 4.51	21.3 ± 4.51			1.17 ± 0.60	62
Cu		86.1 ± 3.70		13.9 ± 3.70	1.05 ± 0.24	79
Pb		24.2 ± 4.56	75.8 ± 4.56		1.41 ± 0.85	67
Sb			99.2 ± 0.22	0.80 ± 0.22	1.10 ± 0.58	68
La	96.4 ± 1.31		3.60 ± 1.31		1.06 ± 0.27	78
Hg			49.3 ± 7.82	50.7 ± 7.82	1.23 ± 0.98	24

The last factor contributes mostly to the elements Se, Na and Hg. This mostly represents coal-fired power plants.

Figures 4.56 and 4.57 show average contributions when all regions is considered. Obviously these contributions show variations from one locality to another. That's why calculations are repeated for some major cities and towns for the elements Cr, Mn, V, Se, Pb and Hg. In the coastal region like in İzmir, in Çeşme, in Karaburun, in Menderes and in urbanized and industrialized parts of Manisa, the % mean contributions obtained from coastal region AFS-MLR results were used. Since this is the more representative of this region. Calculating % mean contributions in other cities, all region AFS-MLR results were used. The results were represented as bar graphs on the maps. In general the % concentration of sources of elements is close to each other in the same region. However they differ between two regions. For Manisa two bar graphs are given because Manisa has two distinct parts considering pollution levels. One is close to İzmir and it contains Manisa organized industry and the city center of Manisa, other part is not very populated and polluted, it is in the interior part of Manisa. Percent contributions of each source in these selected cities and counties are given in Figure 4.58 for V. The coastal region, all sources contributes to V but in the interior part soil and power plants contribute to V. Contributions of power plants in the interior part are more than that of coastal region. In the coastal region soil contribution is dominant. Also there are contributions of Aliağa (around 1%) and urban industrial areas (around 2%) to V in the coastal areas. Contributions of these sources are seen in Karaburun, Çeşme and Menderes in close percentages that were found for Manisa and İzmir eventhough Karaburun, Çeşme and Menderes are away from source areas. The effect of Aliağa and urban industrial areas are not seen in the cities in the interior part.

The percent contributions of sources to the selected places for Cr are given in Figure 4.59. The contribution of Aliağa to Cr in coastal region is comparable to that of interior part (Manisa and Aydın). The reason of this situation is that there are other dominant sources in the coastal region. One of them is soil and other one is urban industrial areas. Urban industrial source is not seen in the interior part. Instead of it power plants come. Chromium is known to be emitted from a lot in iron-steel plants as discussed before.

The percent contributions of sources to Mn in the region are given in Figure 4.60. The contributions of Aliağa are dominating source for Mn in two regions. The contribution of Aliağa is comparable to the interior part (Manisa and Aydın) as in the case of Cr. Same explanation is also valid for this situation that is there is no other dominant source for Mn in the interior part. Manganese is also emitted from iron-steel plants in huge amounts. Power plants contributions are higher in both regions. Effect of power plants are seen in higher amounts in industrialized and urbanized part of Manisa and Muğla which are close to these power plants. Urban industrial area contribution disappears in the interior part. The small percent (around 5) contribution of soil is seen in the interior part.

The percent contributions of sources to Hg can be seen in Figure 4.61. The effect of Aliağa in the coastal region is dominant together with urban industrial source. There is also power plant effect in this region around 10%. In the interior part, the effects of power plants and urban industrial areas are almost equal. Urban

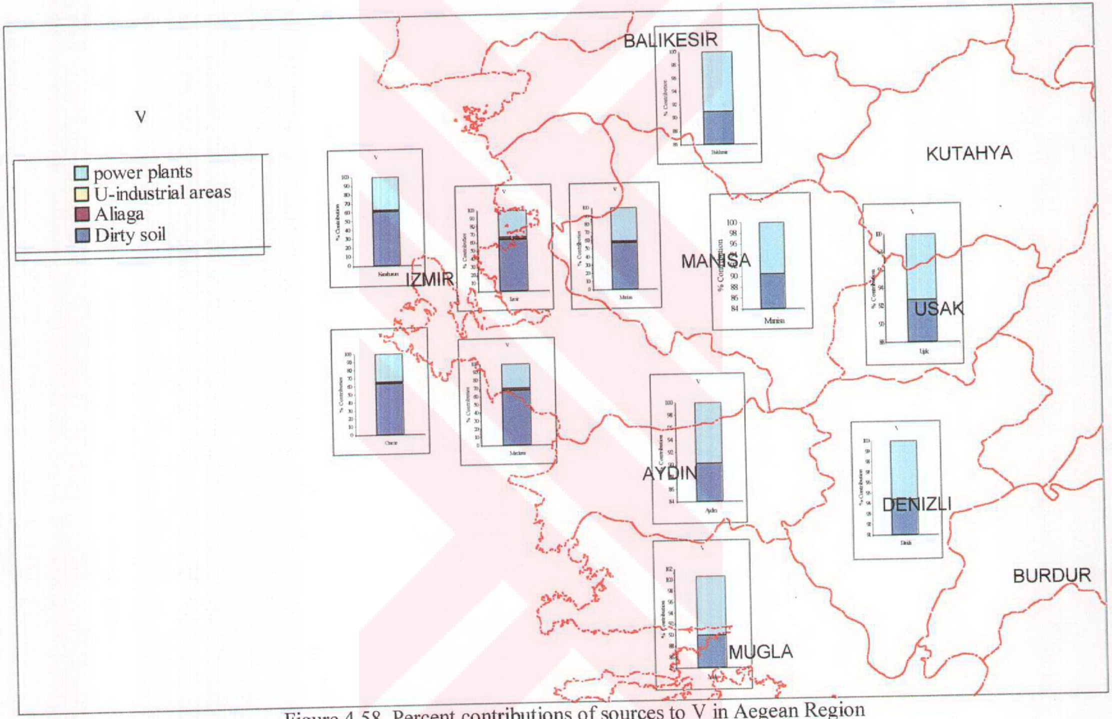


Figure 4.58. Percent contributions of sources to V in Aegean Region

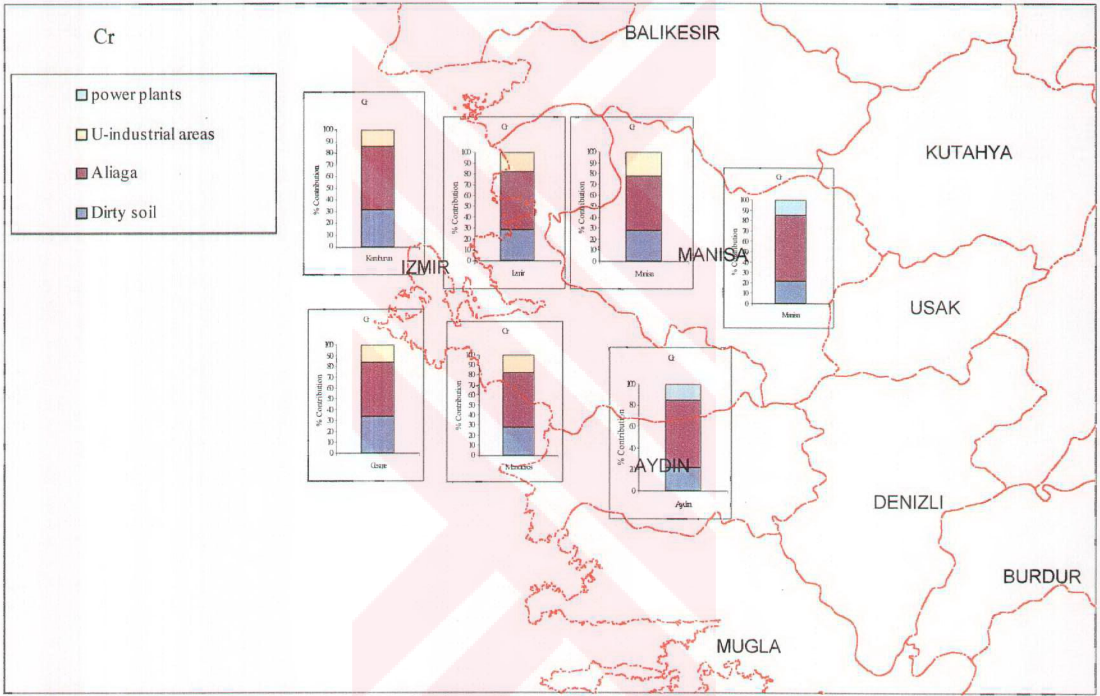


Figure 4.59. Percent contributions of sources to Cr in Aegean Region

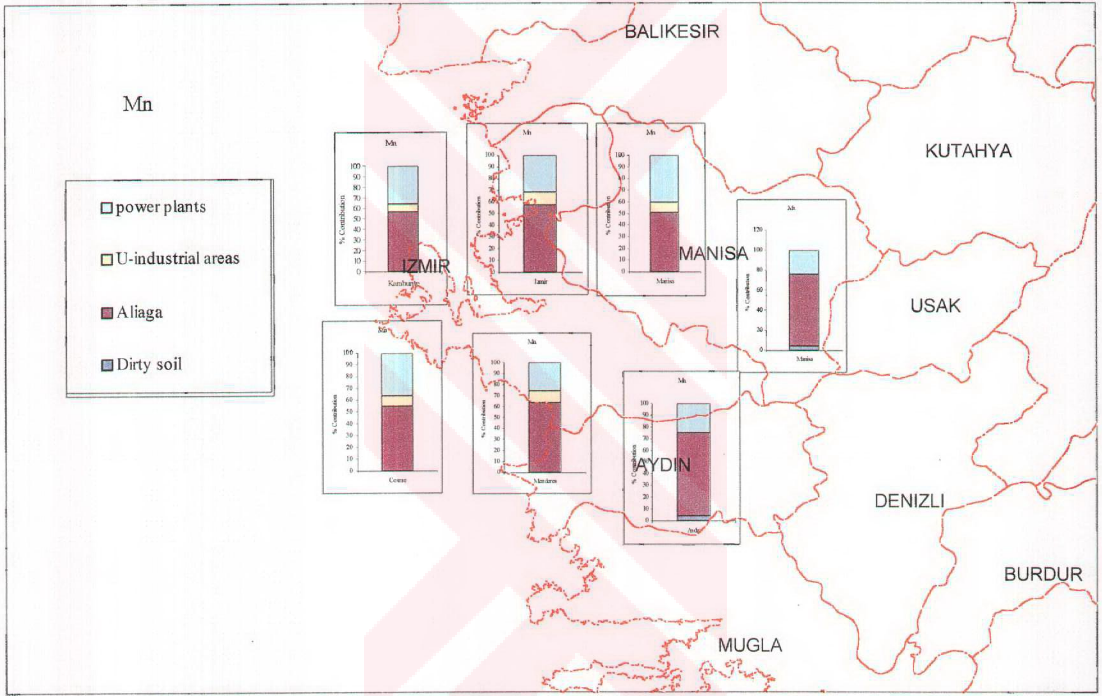


Figure 4.60. Percent contributions of sources to Mn in Aegean Region

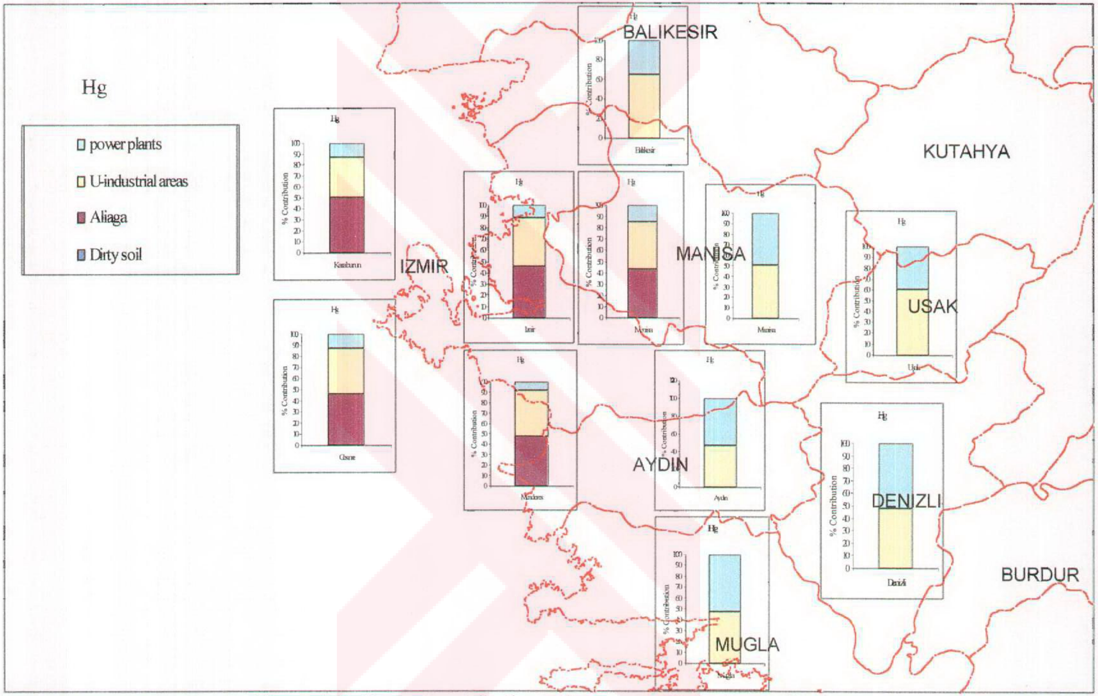


Figure 4.61. Percent contributions of sources to Hg in Aegean Region

industrial area effect is seen less in the coastal region than in the interior region. Since Aliağa area is dominant source that masks the other contributions even in areas like Karaburun, Menderes and Çeşme.

Selenium is emitted highly from power plants as shown in Figure 4.62. Almost all Se in the interior part comes from power plants. There is little (around 1%) contribution of urban industrial areas. In the coastal region, almost equal contributions are made from power plants and industrial urban areas. The contribution of power plants decreases due to increased effect of urban industrial areas which is also very important source in the coastal region.

All lead in the coastal part comes from Aliağa area as shown in Figure 4.63. Since Aliağa is so dominant contributor that the effect of urban industrial areas can not be seen at all eventhough it is expected. The contribution of Aliağa decreases in the interior part which is away from Aliağa area and urban industries source become dominant in the interior part (around 80%) due to mainly traffic.

Above discussion clearly shows that FA-AFS-MLR is a powerful tool for quantitative determination of source contributions to a given spot. But our sampling region is very complex as far as pollutant sources and varieties concerned. That is why factor analysis solution with different number of samples and parameters is under investigation.

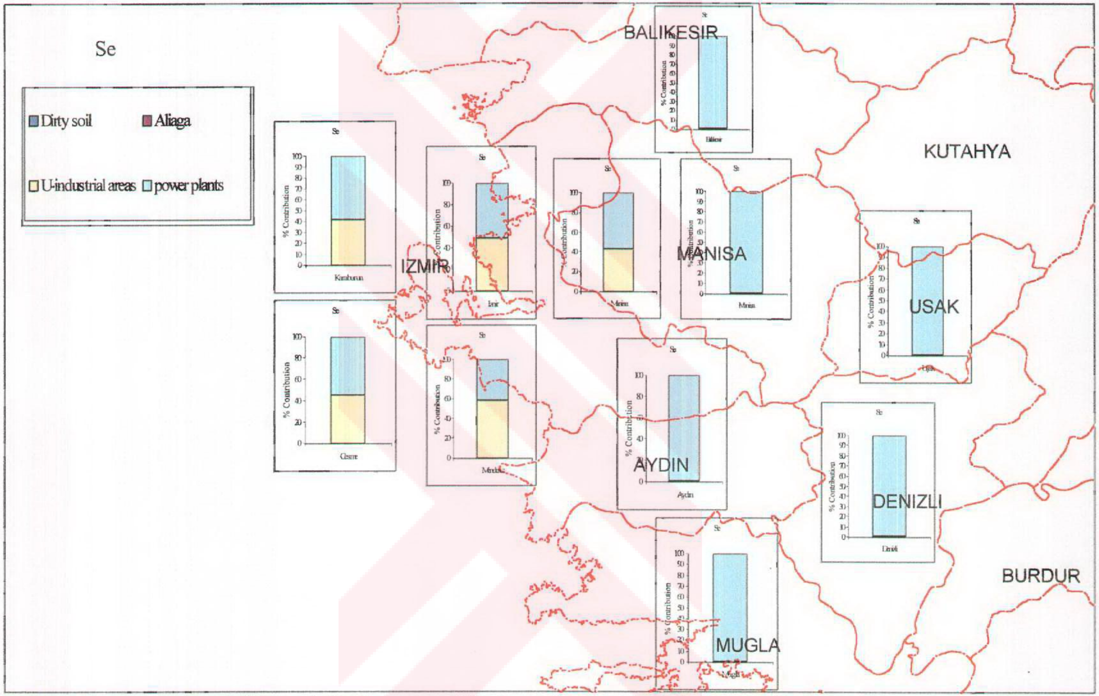


Figure 4.62. Percent contributions of sources to Se in Aegean Region

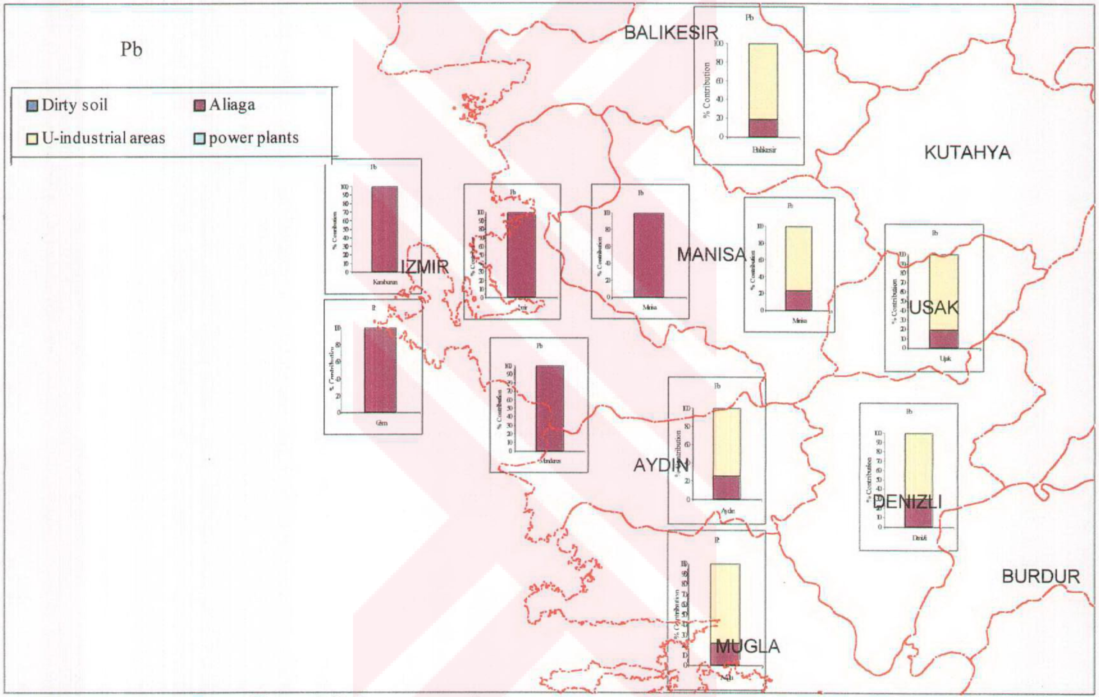


Figure 4.63. Percent contributions of sources to Pb in Aegean Region

4.7. Dispersion Modeling Works

Dispersion models are one of the tools used to apportion the sources of pollution. The reason they are frequently used is their easy application. The predictions obtained from these models, however, are not so accurate because of assumptions involved in computations as explained in section 1.7.4.1. However, we can compare the results of the lichens with the results of model quantitatively since lichens give also qualitative information. Dispersion model used in this study was Industrial Short Complex Short Term (ISCST) computer model developed by the USEPA. This model was applied to find out the deposition amounts around two important coal fired power plants in the region.

4.7.1 Yatağan Power Plant

4.7.1.1. Concentration Results

The results of concentrations of elements are represented as line graphs in order to see the trends of elements at all sampling points. The total number of samples collected from this area was 12 but only the coordinates of 6 were known and three of the rest 6 were Parmelia tiliacea. It is known that tracer element for Turkish coals is As. Therefore, the elements which give high correlations with As can be thought to come from the power plant emissions. The elements like Cr (r=0.67), Fe (r=0.51), Sb (r=0.63), Al (r=0.60) and Ni (r=0.45) gave considerable correlations with As at the $P<0.01$ as shown in Figure 4.64. The concentrations of these elements are also higher in Turkish coals since the concentration ratio of As, Cr, Fe and Sb in Turkish coals to U.S coals is 33, 3, 1.8 and 1 respectively (Eğilli, 1999). Other elements which gave relatively less correlations with As are Hg (r=0.42), Se (r=0.32), Mn (r=0.28), V (r=0.24) and Mg (r=0.30) at $P<0.01$.

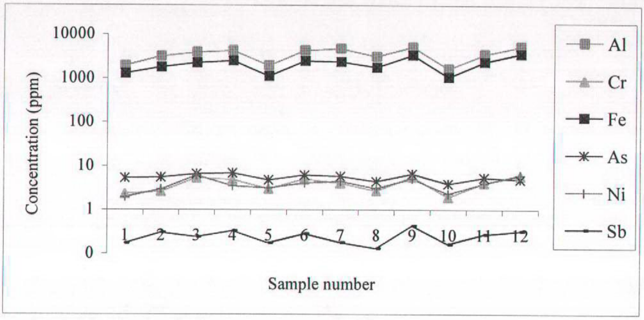


Figure 4.64. The concentration trends of Al, Cr, Fe, As, Ni and Sb in samples collected around Yatağan power plant.

4.7.1.2. Comparison of the Model Results with the Lichen Results

The model results of Yatağan power plant are represented as contour map in Figure 4.65. Deposition results are consistent with the SO_2 concentration results using the same program for Yatağan power plant by TEK (Turkish Electricity Authority) in 1993. High deposition amounts were concentrated on the eastern and partly western part of the power plant and the northern and southern directions got the lowest deposition amounts. This may be related to both wind directions and the topography of the area. Winds mostly blow from the northern directions and they carry the plume of the power plant to the south of the power plant and there are no obstacles at the south of the plants. Pollutants emitted from the plant can be carried to long distances from the plant from north to south direction. The frequency of the winds from the eastern (ESE) and western (WNW) directions is relatively less compared with northern directions as shown in Figure 1.9. However they carry the plume of the power plant to the eastern and western part of the power plant. There are high altitude hills at the eastern and western part of the power plant and the

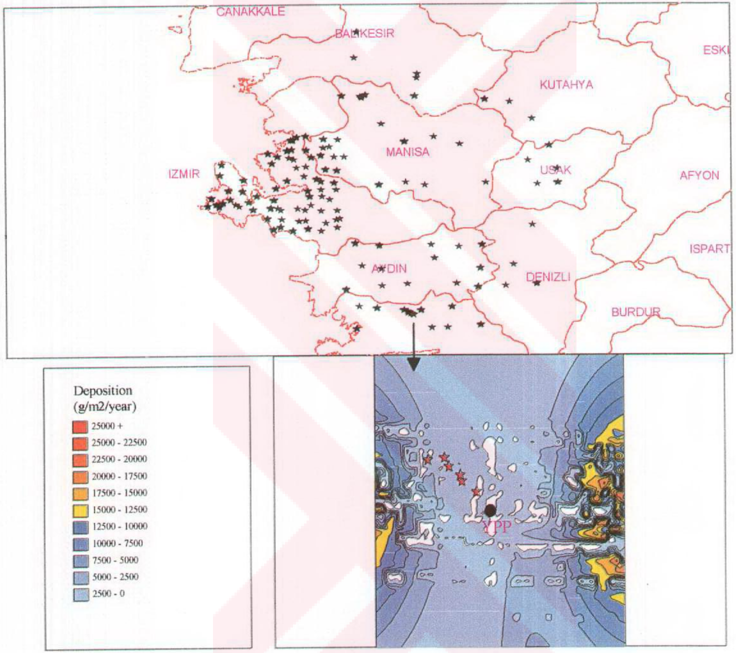


Figure 4.65. The dispersion modeling results of Yatağan Power Plant (Stars show the sampling points)

plume of power plant can hit to these hills and deposits particles there as shown in Figure 4.65.

In order to compare the model results with lichen results, the concentration distribution maps of the elements As, Hg, Se, Fe, Cr, Mn, V, Ni and Sb at same area were examined. When comparing the concentration pattern with deposition patterns, one should concentrate on the places on deposition maps where there are also lichen samples. Since concentration maps are drawn only according to concentrations of these lichen samples. The samples were collected from the least polluted sites according to the model results. The last sample was collected from Turgut town approximately 7 km away from the plant along northwest direction. Among the elements stated above only As, Hg and Cr give the most similar pattern with the deposition of suspended particulate matter (SPM) map as shown in Figure 4.66. The concentration values do not change very much from sample to sample. Deposition values in the sampling area are also not fluctuating.

4.7.2. Soma Power Plant

4.7.2.1. Concentration Results

The results of concentrations of elements are represented as line graphs in order to see the trends of elements at all sampling points. The elements like Ni (r=0.86), Cr (r=0.82), La (r=0.78), Al (r=0.76), Fe (r=0.74), V (r=0.74), Sb (r=0.71), Cu (r=0.67) and Mn (r=0.64) gave considerable higher correlations with As at $P<0.01$ as shown in Figure 4.67. Other elements which gave relatively less correlations with As are Pb (r=0.44), Se (r=0.34), Zn (r=0.36) and Mg (r=0.56) at $P<0.01$. The element Hg which is known to be tracer of the coal combustion did not give significant correlation (r=0.11) with As at $P<0.01$.

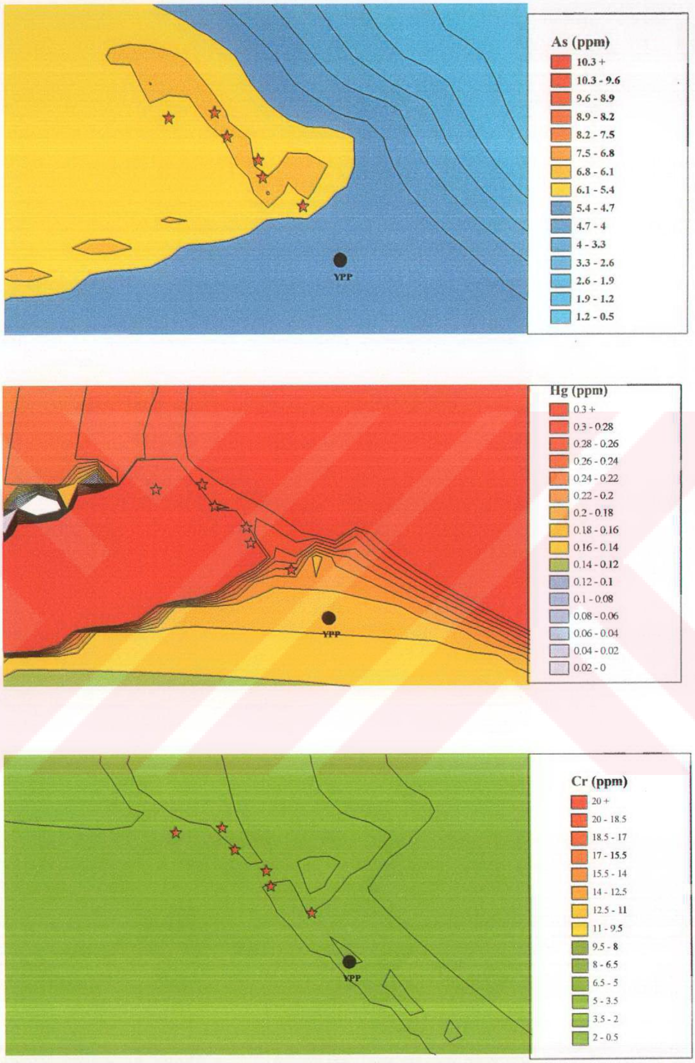


Figure 4.66. Distribution of As, Hg and Cr concentrations around Yatağan Power Plant

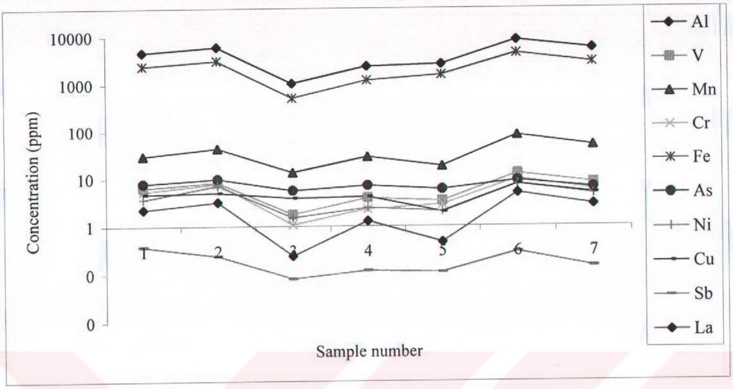


Figure 4.67. The concentration trends of Al, V, Mn, Cr, Fe, As, Ni, Cu, La and Sb in samples collected around Soma power plant.

4.7.2.2. Comparison of the Model Results with Lichen Results

The model results of Soma power plant are represented as contour map in Figure 4.68. High deposition amounts were concentrated on the eastern part of the power plant. This may be again related to both wind directions and the topography of the area. Winds mostly blow from the northern directions and they carry the plume of the power plant to the south of the power plant and there are both hills and flatter places at the south of the plants. Pollutants emitted from the plant can be carried to long distances passing through flatter places. The little part of SPM were deposited to these hills at the south direction as shown in Figure 4.68. Frequency of the winds from the western (WNW) directions is also dominant as shown in Figure 1.11. These winds carry the plume of the power plant to the eastern part of the power plant. There are high altitude hills at the east and north eastern part of the power plant and the plume of power plant can hit to these hills and deposits particles there as shown in Figure 4.68.

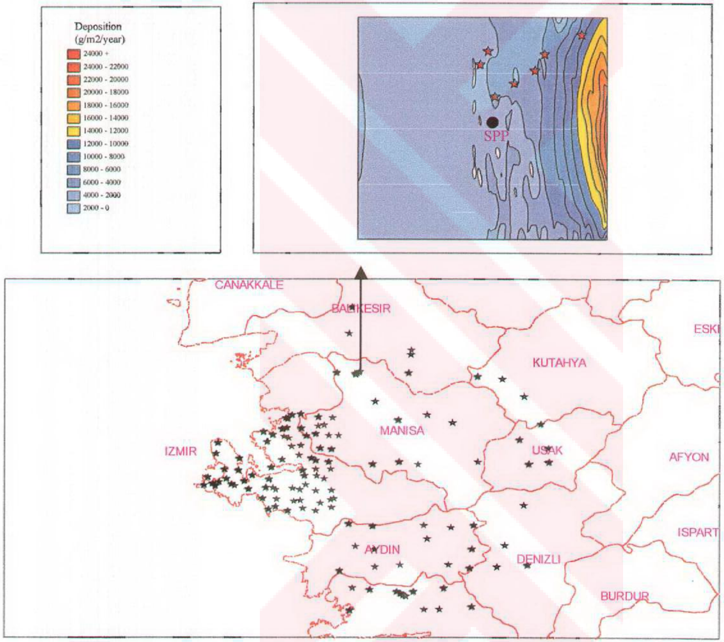


Figure 4.68. The dispersion modeling results of Soma Power Plant (Stars show the sampling points)

In order to compare the model results with lichen results, the concentration distribution maps of the elements As, Se, Hg, Fe, Cr, Mn, V, Ni, Cu, Pb and Sb were examined. The samples were collected from the polluted sites according to the model results. The last sample was collected from Evciler town approximately 7 km away from the plant along north and northeast direction. Generally all elements showed similarities with model results regarding with first four samples. Since the concentrations in these 4 samples showed increasing trend from 1 to 4. This is in accordance with deposition modeling results as values of deposition results also showed increasing trend in the sampled area along sample 1 to 4. Among the above elements, the concentrations of As, Mn and Fe are shown in Figure 4.69. The concentration range of As in the sampling area is in upper part of the rank in the legend as the samples were collected from the polluted sites as can be seen from the distribution map of the model results in Figure 4.68 as opposed to Yatağan power plant.

Considering the limitations of deposition model due to the meteorological data as the data gathered away from the station as discussed in section 1.7.4.1 and limitations in our sample number, the similarities in the concentration trends are fairly good. If there were samples taken all around the power plants, the results would be more harmonious with each other.

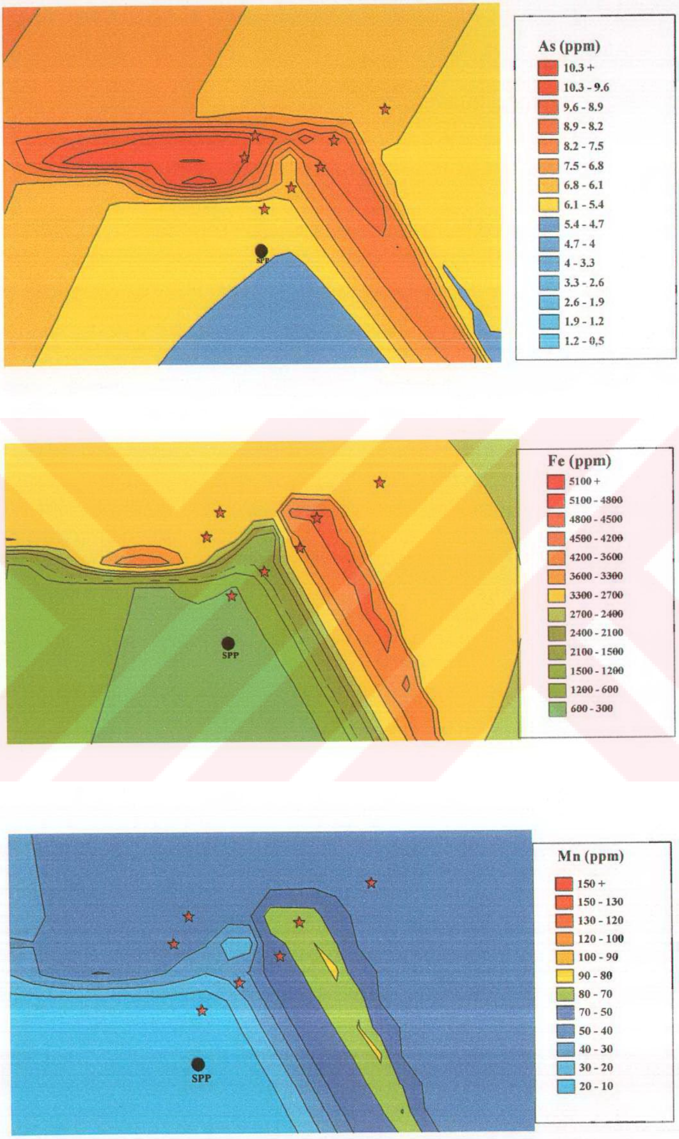


Figure 4.69. Distribution of As, Fe and Mn concentrations around Soma Power Plant

CHAPTER 5

CONCLUSIONS

Concentrations of elements in 234 lichen samples collected in Aegean Region of Turkey were determined by INAA and ICP-AES techniques. For deposition samples and transplant lichen samples ICP-AES and AAS techniques were used to determine element concentrations and IC was used to determine ion concentrations.

The lichen species, Xanthoria parietina was the most common species in the region. Parmelia tiliacea was also collected together with Xanthoria parietina in the some of the same sampling points. The accumulation capacity of Xanthoria parietina was compared with Parmelia tiliacea. It was seen that the accumulation capacities of two species differed only for the elements Ca, Cl, Cu and Pb. Average concentrations of all elements except for Ba, Mn and Hg were higher in Parmelia tiliacea. Interchangeable use of two lichen species was also tested in case if the chosen lichen species is absent in some of the grids for the future works. It was found that only for the elements Ba, Br, Co, Cr, Cs, Fe, K, Mg, Mn, Mo, Nd, Rb, Sb and Ti the equation $y=ax + b$ could be used to make interchangeability possible between two species. The elements Hg and Cu in Xanthoria parietina, Ni and Pb in Parmelia tiliacea showed saturation effects.

Lichens are used only for qualitative purposes since the duration of accumulation of elements in lichens is not known. In order to have an information whether we can use the lichens species in this study quantitatively, the transplant lichens were prepared. Then the concentrations in transplant lichens were compared with total deposition samples for the elements Al, Fe, Mg, K, Na, Cr, Mn, Cd, Zn and V and ions SO_4^{2-}, NO_3^-, Cl^- and NH_4^+. The accumulation capacities of lichen species and tree bark were also compared with respect to each other. It was concluded that Xanthoria parietina, Parmelia tiliace and Evernia prunastri could be used quantitatively for the elements Cr, Mn, Cd, Zn and V when the lichens species were washed. Parmelia tiliacea gave the highest accumulation capacities for all elements compared with Evernia p. It had also the highest accumulation capacities for the elements V and Cd when compared with Xanthoria parietina eventhough Parmelia t. was not analyzed for the last transplant period which included summer-dry deposition periods. These findings implied that the accumulation capacities of Parmelia tiliacea have higher for most of the elements than other lichen species. The same work was done for tree bark. Results showed that tree bark could be used for the elements Fe, Zn, Mn and Cr to obtain quantitative knowledge. However, tree bark was not sensitive to air pollution as lichens. Quantitative results from lichen species were also obtained for ions. The Xanthoria parietina had the highest accumulations for SO_4^{2-} and NH_4^+. The accumulation capacities of NO_3^-, SO_4^{2-} and NH_4^+ were comparable in lichens Parmelia t. and Evernia p. and the accumulation capacity of Evernia p. for Cl^- was 14 times higher than the accumulation capacity of Parmelia t. and it is comparable with Xanthoria p.

Summary statistic of data showed that the highest concentrations belonged to K. Other soil derived elements came next. All of the elements showed lognormal distribution considering urban light industry region and also they showed lognormal distribution considering semiurban region except for K.

To be able to have general idea about pollution levels in Aegean Region, produced data were compared with literature values. Firstly they were compared with baseline concentrations. The mean concentrations of elements As, Al, Ce, Fe, La, Sc and Ti were higher than baseline concentrations in rural areas. The mean concentrations of Cr and Cu were higher in most of the other studies and the mean concentration of Mn was lower than the baseline concentrations. Secondly we compared our data with the literature data. The mean values of Al, As, Cl, Cs, Th and U were relatively higher than the other literature values. High concentrations of As, Th and U were closely related with coal burning especially for domestic heating in the region. However the mean values of Pb and Mn were relatively lower in our study than the mean values in other studies.

The local variation was investigated in some sampling points in order to be sure that local variation of element concentrations was not large enough to disturb the concentration pattern on a regional scale. Local variation was considered to be the variation in substrate, age, size and morphology of lichen samples. The mean local CV was found to be 15, which is less than the literature of 25. It was concluded that the local variation did not affect the concentration of elements in the sampling point.

According to crustal Enrichment Factor calculations, Na, Sc and Ti showed depletion with respect to Al for all data set. The elements Fe, Tb, V, Ce, Lu, Sm, Tb, Co, Mn, Nd, Ca, Eu, Cr, Ni, La, Ta, Sr, Hf, Ba, U, Th, Dy, Mg, Rb, Cu, In, Cs, K and Mo were not enriched. However, log-log plots of nonenriched elements like Mg, K, In, Cu, Nd, Eu, Mn, Rb and Ca versus Al concentrations revealed that they had additional sources other than crust. The elements Au, Pb, Zn, Hg, Sb, Cd and As were moderately enriched related with several industries and coal combustion. The elements Cl, Br and Se were highly enriched again related with mostly industrial processes and coal burning. For subregions nonenriched groups did not change, only the placement of moderately enriched and highly enriched groups differed.

Geographical distribution maps of concentrations and EF values gave the detailed information about the source areas of elements in the region. Important source areas are located in the city center of İzmir and Manisa, Menemen, Çiğli, Kemalpaşa, Torbalı, Aliağa and Soma and Yatağan coal-fired power plant areas. The secondary important pollution areas are located in Balıkesir, Uşak, Denizli and Aydın.

The concentration and EF distribution maps generally showed the same patterns and thus the additional sources or the most important contributors were mentioned in the following text for EF distribution maps. The concentrations of As and Se were high in places with high population and/or industrialization. They were highly enriched also in power plants areas. Mercury concentrations and EF values signalled the most important source areas as Yatağan power plant and Aydın. Cadmium and Zn mostly came from the Aliağa region and industrial areas according to both concentrations and EF values. Lead was seen in high concentrations at populated cities, close to main roads, summer resort areas at coastal sites and Aliağa region. Antimony had its highest concentrations in industrial areas and power plant areas. It is related with vehicle emissions at coastal sites like Pb. Copper had its highest concentrations in main industrial areas. Manganese, Fe, Cr, V and Ni had the highest levels of concentrations in Aliağa and also they came from soil. Lanthanum showed similar concentration patterns with V, Al and Fe as it is crustal element. The concentration map of Ca had also showed same pattern as Al. Sodium did not signal the sea contribution but soil contribution. All soil related elements were enriched in different localities depending on geochemical composition of soil and local point sources. The concentration and EF distribution of K was different from other crustal elements as being a nutrient element. Magnesium had similar pattern with K considering both concentration and EF values since it is also important macronutrient for lichens.

Source categories affecting the region were determined using Factor Analysis. The coastal region data set gave 4 major factors, which explained the 70% of the total variance in the data set. These factors were named as dirty soil, Aliağa area, industrial urban areas and regional background. Beside crustal elements like Al, Ti, Mn, Na, Ca, Sc, Cr, Fe, Ni, La, Ce and Sm, the anthropogenic element As had also loading in the first factor. The second factor had the loadings of elements Mn, Cr, Fe, Zn, Cd, Ni, Cu, Pb and Sb which are mostly the characteristic elements of iron-steel plants originated from Aliağa area. Factor 3 had the loadings of anthropogenic elements Cr, Co, As, Se, Sb, Cs and Hg. This factor was identified as industrial urban areas factor owing to the presence of As, Se, Sb and Hg which are typical marker elements in coal for domestic heating and the presence of Sb, Co, Cs and Cr representing industrial activities. Factor 4 was referred as regional background. The elements Al, V, Cl, Mn, Na, Ca, Se and Br had high loadings in this factor. This factor represented as a mixture of sea contribution (Na, Cl, Br and Se), soil (Na, V, Al, Mn and Ca) and industry and coal burning (Se, Br and Cl). The factor score maps of these factors showed the locations of these identified sources exactly.

The factor analysis of all data set gave also 4 factors accounting the 70.7% of total variance in the data set. The first three factors of coastal region and all region did not change much in composition and value of % variance that they explained. This meant that the contribution of these sources to the pollutant levels in the region was very important and affected all Aegean Region not only the coastal part. The first factor attributed to dirty soil again with high factor loadings of Al, Mg, V, Mn, Na, Cr, Fe, Ni and La as well as the loading of anthropogenic element As. The second factor was named again Aliağa with high loadings of Mg, V, Mn, Cr, Fe, Zn, Cd, Ni, Cu, Pb and Sb. The third factor is again urban industrial areas mixed factor with high loadings of Pb, Sb, As and Hg. The fourth factor was loaded with Hg, Se and Na. This factor was named as power plant factor. Factor score maps were again in accordance with the factors identified.

Quantitative impact of each source to elemental concentrations at Aegean Region was estimated using absolute factor scores. Most part of the region is under the influence of Aliağa source region. The concentrations of Fe, Mn, Sb, Cr, Cu, Pb and Zn were coming mostly from Aliağa region especially from iron steel plants. The concentrations of elements As, Hg, Sb and Pb were very high around İzmir reflecting the effect of both urban and industry. The concentrations of Se and Hg are higher in the power plant region and in industrial areas in İzmir, Kemalpaşa and Manisa. This clearly showed that the FA with AFS-MLR is a powerful tool for quantitative and qualitative determination of source contribution to a given spot.

Fairly good agreement was obtained from the comparison of dispersion model results with concentration distribution of elements in lichens around power plants in this study.

CHAPTER 6

RECOMMENDATIONS FOR FUTURE STUDIES

With increase of the environmental problems originated from the development of population, industry and energy production, biomonitoring organisms have been analyzed in order get maps of geographical distributions of the pollutant concentrations since 1970's in Europe and in North America due to its very low cost.

Deposition patterns of concentrations and EF values resulting from element biomonitoring may help regional authorities to locate analyzers or collectors for direct chemical analyses in order to conduct further ecological and/or epidemiological surveys. That's why in future biomonitoring studies, first thing is to extend these studies to larger regions in Turkey. Additionally these studies give also very valuable information about the pollution sources qualitatively and quantitatively.

Concerning with lichen species of Xanthoria parietina, first thing is to investigate its accumulation characteristics of elements with more detailed works and find the saturation levels of elements with laboratory and field studies. Afterwards, these results will help for more quantitative works. In these works, sampling duration should be at least one year but in several stations in one sampling point and in different points with different pollution levels. The results of them are compared whether the obtained equations are applicable to different levels of pollution or separate calibration equations should be derived. Deposition samples and lichen samples are collected from at least 2.5 m above the ground in order avoid soil contribution as much as possible providing no need for washing the lichens to obtain more correct equations especially for soil derived elements.

Studies about the tree bark and lichen interactions should have to be done in order to bring definite solution to these doubts whether there is an intake from tree bark for the elements Ca, Zn and Cd.

Xanthoria parietina species is found widely on rocks. Studies about the interchangeability of this species on trees and rocks must be done. Then if in one place there is no Xanthoria parietina on trees or no trees, Xanthoria parietina on rocks can be used instead of Xanthoria parietina on trees.

Lichens may be analyzed with ICP-MS including many elements in one run. Thus statistical analyses will become more comprehensive and more explanatory by including more elements. And also we can obtain P concentrations from ICP-MS analyses. It is very important nutrient for lichens. The results of P and K are compared in order to obtain a most representative element for lichen metabolism for different species. We can compile a background lichen composition table and a table for only Xanthoria parietina for all elements. As a result enrichments with respect to lichens can be calculated.

Organic pollutants in lichens have been studied in few works in literature. There is lack of data in this field and organic pollutants in lichens should be in the list of research topics in the future. Since organic pollutants are very important for determining air quality of an environment. Contributing source resolution can be done using organic parameters. Also source quantification can be obtained starting from AFS-MLR.

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