SIZE DISTRIBUTION OF TRACE ELEMENTS AND MAJOR IONS IN THE EASTERN MEDITERRANEAN ATMOSPHERE

ESRA KULOGLU and GURDAL TUNCEL*
Middle East Technical University, Department of Environmental Engineering, 06531 Ankara, Turkey
*(*author for correspondence, e-mail: tuncel@metu.edu.tr, Tel.: +90 (312) 210-5871,*
Fax: +90 (312) 210-1260)

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Abstract. Size distribution of trace elements is measured at the Mediterranean coast of Turkey, by analyzing hi-vol impactor samples collected between August 1993 and May 1994. Mass median diameters of marine elements are between 4.6 and 5.3 μm, and those of crustal elements are between 3.0 and 3.5 μm. Mass median diameters of crustal elements are 30% smaller in samples impacted by Saharan Dust. Pollution derived elements, As, Cd, Mo, Pb, Se, and Zn have MMD's between 1.25 and 1.01 μm. Although 70–90% of the masses of these elements were associated with particles smaller than 2.1 μm, 10–30% of their mass was associated with coarse particles. Coarse component in concentrations of Cd, Pb, Sb and particulate Hg are due to adsorption of fine anthropogenic particles on coarse crustal aerosol, whereas coarse fraction Zn, As, Se, In, Mo and Au are crustal at Al concentrations >100 ng m^{-3}. Bromine, Cr, Ni, and V have bimodal distributions. The fine component, which account for approximately 30–40% of their masses are due to anthropogenic sources, whereas the coarse component, which accounts for 30–50% of their masses are due to sea salt for Br, and crustal particles for Cr, Ni, and V.

Keywords: atmospheric aerosol, eastern mediterranean, impactor, size distribution, trace element

1. Introduction

Wet and dry depositions of chemical species at the earth surface provide a natural sink for atmospheric trace substances and a source of nutrients for the biological systems. Identification of space and time evolution of these depositions will help to assess the relative importance of various sources in air-surface exchange of pollutants.

Although acidic precipitation was the main issue which attracted attentions to atmospheric transport of pollutants on a regional scale in 70's and 80's, potential impact of atmospheric fluxes of pollutants on the pollution of regional seas have shifted the focus of studies in this field in 90's. Transport of pollutants via rivers and streams was believed to be the main source of pollution in the enclosed seas. However, studies in last 10 years in the Atlantic Ocean (Buart-Ménard and Duce, 1986; Church and Scudlark, 1992), the western Mediterranean (Guieu *et al.*, 1994; Migon *et al.*, 1997; Ottley and Harrison, 1993), the North Sea (Cambray *et al.*, 1979; Rojas *et al.*, 1993) and the Great Lakes (Strachan and Eisenreich, 1988)

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clearly demonstrated that transfer of pollutants from atmosphere to the sea is a significant source of pollution even in enclosed or semi-enclosed water bodies (GESAMP, 1985). Recent studies in the Mediterranean have clearly demonstrated the importance of atmospheric fluxes of elements as an important component in the water-sediment system, and should be taken into account when mass balances are performed in the water body (Martin *et al.*, 1989; Guieu *et al.*, 1994; Migon *et al.*, 1997; Hacisalihoglu *et al.*, 1992; Guerzoni *et al.*, 1999).

The Mediterranean Sea is influenced from both strong anthropogenic emissions in the North and strong natural emissions of crustal material in the south (Chester *et al.*, 1993). In addition to these well documented sources, composition of the Mediterranean aerosol is also influenced from biogenic emissions from the Mediterranean Sea itself (Amouroux and Donard, 1996; Ganor *et al.*, 2000; Kouvarakis and Mihalopoulos, 2002; Kouvarakis *et al.*, 2002; Kubilay *et al.*, 2002), sea salt generated over the sea and local sources specific for each study site (Gullu *et al.*, 1998). When such diversity in particle sources is coupled with large spatial and seasonal variations in the meteorology, particularly precipitation patterns in the basin, results in strong temporal and spatial variability in the composition of Mediterranean Aerosol (Dulac *et al.*, 1987; Bergametti *et al.*, 1989; Remuadaki *et al.*, 1991; Chester *et al.*, 1993; Gullu *et al.*, 1998). Understanding the mechanisms responsible for observed variability in complex mixture of particles in the Mediterranean atmosphere is difficult, but essential to assess the role of atmosphere on the pollution of the Mediterranean Sea and to understand biogeochemiclal cycles of elements.

There had been substantial improvements in the database for composition of atmospheric particles and precipitation, both in the western and eastern Mediterranean basins, but there are only few studies for size distributions of atmospheric particles and pollutants associated with them (Dulac *et al.*, 1989, 1992; Sellegri *et al.*, 2001; Masmoudi *et al.*, 2002, 2003; Bardouki *et al.*, 2003; Smolik *et al.* 2003), which is essential for dry deposition calculations for particles.

In this study, size distributions of approximately 40 inorganic elements and ions measured in cascade impactors samples collected continuously for one year on the Mediterranean coast of Turkey are reported. The discussion is focused on the size distributions of elements and contribution of different source types to aerosol in different size fractions.

2. Experimental

The sampling station is located on the Mediterranean coast of Turkey at approximately 20 km to the west of the city of Antalya (30°54′ E, 36°81′ N). Since details of station, sampling and analytical protocols are given elsewhere (Gullu *et al.*, 1996, 1998, 2000; Al Momani *et al.*, 1998; Karakas *et al.*, 2002, 2004), only a brief description of methodology will be presented here.

Impactor sampling was implemented in August 1993 and continued until May 1994. Thirty-three weekly impactor sample sets containing 6 substrates from stages and a back-up filter were collected, using a Sierra Instruments High Volume Cascade Impactor Series 230 attached to General Metal Works Model GMWL 2000 High Volume Air Sampler, in this period. Operating flow-rate was kept constant at 25 SCFM (0.84 m^3 min^{-1}), and the total volume of sampled air was measured with a high-volume dry-gasmeter. Particles were separated into seven size groups with 50% aerodynamic cut-points of >10.2 μm, 4.2 μm, 2.1 μm, 1.4 μm, 0.73 μm, 0.41 μm, and <0.41 μm. Indicated cut-off diameters were obtained by the calibration of the instrument by manufacturer and the impactor was not calibrated in our laboratory. Whatman-41 cellulose substrates placed on each stage were used as collecting media. Particles smaller than the cut-off diameter of the last stage (0.41 μm) were collected on a Whatman-41 cellulose back-up filter.

One-quarter of substrates were digested with HNO_3 – HF mixture using the procedure given by Gullu (1996) and digested samples were analyzed for Al, K, Na, Mg, Fe, Zn and Ca by flame and Pb, Cd, Ni, V, Cr by graphite furnace atomic absorption spectrometry, using a Perkin Elmer 1100B spectrometer coupled to a Perkin Elmer HGA 700 electrothermal atomization system. The method of standard additions was used in all analysis by atomic absorption spectrometry (AAS).

A Varian 2010 model High Performance Liquid Chromatography (HPLC) coupled to a VYDAC 3021C anion exchange column and a JASCO model UV-VIS 875 detector was used to determine concentrations of Cl^-, NO_3^-, and SO_4^{2-}. Ammonium was determined by direct Nesslerization method using a Unicam 8625 UV-VIS Spectrometer (Gullu, 1996).

Seven set of impactor samples, four sets corresponding to dust and three sets corresponding to non-dust periods were also analyzed for approximately 40 elements by instrumental neutron activation analysis (INAA). For INAA, parts of the substrates were irradiated in the MIT research reactor at thermal neutron flux of 1×10^{13} n cm^{-2} sec^{-1}, and counted using a procedure developed by Ölmez (1989).

Possibility of sample contamination was kept at a minimum by routine analysis of field and laboratory blanks. Average sample-blank ratios (STBR) for elements at each stage varied between 2 and 35. Elements that are associated with coarse particles had higher STBR's in the first three stages of impactor, whereas anthropogenic elements, which are known to be associated with fine particles in the atmosphere, have higher STBR's in stages 3–6 and backup filter.

Standards used in both INAA and AAS analysis were checked by analyzing NIST standard reference materials SRM 1571 (orchard leaves) and SRM-2704, SRM-1646 (sediments). In AAS analysis SRM's were analyzed every analysis day and in INAA one SRM was analyzed along with each set of samples that were irradiated. The accuracy of ion chromatography (IC) measurements were checked by using simulated rain water standard SRM 2694.

3. Results and Discussion

3.1. SIZE DISTRIBUTIONS OF CRUSTAL AND MARINE ELEMENTS

Since discussion of behaviors of 41 elements and ions measured in this study, one by one, is not practical, and since spatial and temporal behaviors of elements in atmosphere is known to be related to their sources (together with upper atmospheric meteorology), elements measured in this study are separated into four groups based on their expected sources at the eastern Mediterranean atmosphere and their behavior in collected samples are discussed for these four groups throughout the manuscript.

The first group consisted of Al, Ba, Ca, Ce, Co, Cs, Dy, Eu, Fe, K, Gd, Hf, La, Lu, Nd, Rb, Sc, Sm, Sr, Ta, Tb, Th, Ti and Yb. These are litophilic elements and their only source in rural atmosphere is shown to be crustal material in numerous studies (for example, Braga *et al.*, 2004; Bilos *et al.*, 2001; Marcazzan *et al.*, 2001; Natsagdorj *et al.*, 2003). Calculation of crustal enrichment factors at our staion, using whole filter and precipitation samples, demonstrated that $\mathrm{EF_c}$s of these elements are close to unity (Gullu, 1996; Al Momani, 1995). Origin of the Na, Cl and Mg in all stations close to the sea is the sea salt produced by bubble bursting at the sea surface (Spiel and Leeuw, 1996; Beavington *et al.*, 2004; Querol *et al.*, 2004). Earlier studies at our station have demonstrated that approximately 11% of Na and 29% of Mg originates from atmospheric soil particles, on an annual basis. Crustal contribution on concentrations of Na and Mg decreases during winter, when concentration of crustal material in the atmosphere is low and during sea salt episodes which occurs during periods with high winds in the proximity of the station (Gullu *et al.*, 1998).

The third group includes As, Se, Cd, Mo, $\mathrm{NH_4^+}$, $\mathrm{NO_3^-}$, Pb, Sb, $\mathrm{SO_4^{2-}}$, Zn. These are the elements and ions with well known anthropogenic sources (for example, Gao *et al.*, 2002; Graham *et al.*, 2004; Querol *et al.*, 2004; Han *et al.*, 2005). Crustal enrichment factors of these elements were found to vary between 100 for Zn and $>$10 000 for Cd, in previous studies performed at our station (Gullu, 1996; Al Momani, 1995).

The fourth group includes Br, Cr, Mn, Ni, V. These elements are expected to have mixed sources in the eastern Mediterranean atmosphere. Concentrations of Cr, Mn, Ni and V are fairly high in crustal material (Mason, 1966), indicating that atmospheric soil particles can have a significant contribution to their observed concentrations. However, these elements also have anthropogenic sources (Gordon, 1980; Gao *et al.*, 2002; Pfeifer *et al.*, 1999; Guieu *et al.*, 1994). Relative contributions of crustal and anthropogenic sources on observed Cr, Mn, Ni and V depends on distance between the sampling point and the anthropogenic sources that emit these elements. Earlier studies at our station have revealed that anthropogenic contribution on Cr, Ni, Mn, and V is detectable only in samples with low concentrations of crustal material (when Al concentration is $<100\ \mu\mathrm{g\ m^{-3}}$) (Gullu *et al.*, 1998). Since the eastern Mediterranean basin is an arid region, Al concentration is $>100\ \mu\mathrm{g\ m^{-3}}$ in most of the samples showing that crustal material is dominating source of Cr, Mn, V and Ni, except in approximately 20% of the samples with the lowest Al concentrations. Because of this, in some of the discussions in this manuscript, these four elements are included in crustal group. Bromine, on the other hand, has sources from se salt and traffic emissions (Jernigan *et al.*, 1971; Lammel *et al.*, 2002; Garcia and Munoz, 2002).

Geometric mean concentrations of elements in each impactor stage is given in Table I, together with their mass median diameters (MMD), which are calculated using the procedure given in Dulac *et al.* (1989), and Arimoto *et al.* (1985). Mass median diameters of elements shown in Table I are the average of MMD's obtained from each impactor set.

Approximately 30 to 40% of the masses of crustal elements (Al, Ca, Ce, Dy, Eu, Fe, Gd, Hf, La, Lu, Mn, Nd, Rb, Sc, Sm, Ta, Tb, Th, Ti and Yb) occur in the second impactor stage (with 4.2 μm cut-off diameter). The first three stages, which cover particle diameters larger than 2.1 μm include approximately 70% of the masses of soil related elements. Although, most of the crustal mass was found on coarse fraction, as expected, approximately 10–15% of the masses of crustal elements in each impactor set were found to be on the back-up filter.

Crustal mass on backup filter can be due to either particle bounce off, which brings particles from upper stages or actual presence of fine fraction crustal material. The source of crustal particles on the last stages of the impactor must be known, because if these particles are there because of particle bounce-off, dry deposition calculations based on this data set can underestimate the fluxes of crustal elements. Element-to-Al ratios of elements with crustal origin in first three and in backup filter and last impactor stage are given in Figure 1. If the source of crustal particles on backup filter and last impactor stage is the particle bounce off, then the ratio of concentrations of soil elements to Al in these stages are expected to be completely identical with the corresponding ratios in the first three stages of impactor. Element-to-Al concentration ratios for Ba, Ta, Co, Th, Fe, Tb, Sr, Dy, Eu, La, Ti, Nd, Lu are approximately the same in coarse and fine fractions. However, the ratios are higher in fine fraction for Cs, K, Cr, Ni, Sc, Sm, and Rb and higher in coarse fraction for Gd, Ca, Yb, Zr, and Ce.

Statistical significance of observed differences in means and medians of element-to-Al ratios are compared using t-test and Mann–Whitney W test, respectively. Conclusions derived from comparison of means were identical with the conclusions obtained from comparison of medians. These tests revealed that differences between the means and medians of the element-to-Al ratios of Ca ($p = 0.001$), Cr ($p = 1 \times 10^{-5}$), Cs ($p = 0.003$), Gd ($p = 0.01$), K (0.001), Ni ($p = 0.01$), Rb (0.02), Sc ($p = 0.004$) and Sm (0.02) between coarse and fine fractions are statistically significant at 95% confidence level. These differences point out that particles observed on last impactor stages and back-up filter are fine crustal particles and not an artifact due to particle bounce off.

Mass median diameters of crustal elements change between 2.5 and 3.5 μm, indicating that they are associated with coarse particles, as observed in many other

TABLE I

Geometric mean concentrations and percent mass of elements and ions in each impactor stage[a,b]

	MMD (μm)	Stage 1 (>10.2 μm)	Stage 2 (4.2 μm)	Stage 3 (2.1 μm)	Stage 4 (1.4 μm)	Stage 5 (0.7 μm)	Stage 6 (0.4 μm)	Backup (<0.4 μm)
Al[d]	3.45	64 (13)	133 (27)	84 (17)	77 (15)	49 (10)	29 (6)	64 (13)
As[c]	1.01	0.053 (5)	0.134 (12)	0.083 (8)	0.089 (8)	0.164 (15)	0.310 (28)	0.261 (24)
Br[c]	1.92	2.1 (16)	4.3 (32)	1.4 (10)	0.8 (6)	0.9 (7)	1.5 (11)	2.4 (18)
Ca[d]	3.50	257 (20)	492 (38)	239 (18)	124 (10)	12 (1)	38 (3)	135 (10)
Cd[d]	1.25	0.013 (9)	0.018 (11)	0.017 (11)	0.017 (11)	0.031 (20)	0.029 (18)	0.030 (19)
Ce[c]	3.01	0.12 (13)	0.31 (33)	0.18 (19)	0.11 (12)	0.07 (8)	0.04 (4)	0.10 (11)
Cl[d]	5.32	680 (31)	911 (42)	277 (13)	128 (6)	45 (2)	33 (2)	88 (4)
Cr[d]	1.98	0.29 (12)	0.53 (22)	0.31 (13)	0.25 (11)	0.32 (13)	0.30 (12)	0.40 (17)
Cs[c]	2.19	0.014 (13)	0.030 (26)	0.017 (15)	0.011 (9)	0.012 (11)	0.011 (10)	0.019 (16)
Dy[c]	2.52	0.008 (12)	0.023 (32)	0.013 (18)	0.011 (16)	0.004 (5)	0.003 (4)	0.009 (13)
Eu[c]	2.78	0.002 (12)	0.007 (39)	0.003 (17)	0.002 (9)	0.001 (7)	0.001 (6)	0.002 (9)
Fe[d]	3.52	38 (13)	85 (28)	55 (18)	43 (14)	29 (10)	18 (6)	37 (12)
Gd[c]	3.49	0.007 (14)	0.020 (41)	0.009 (19)	0.005 (11)	0.002 (5)	0.001 (2)	0.004 (8)
Hf[c]	2.44	0.006 (14)	0.016 (39)	0.006 (16)	0.004 (11)	0.003 (6)	0.001 (3)	0.004 (11)
K[d]	3.57	26 (14)	56 (30)	23 (12)	13 (7)	12 (7)	23 (12)	32 (17)
La[c]	3.06	0.070 (14)	0.17 (35)	0.09 (18)	0.06 (11)	0.04 (7)	0.02 (4)	0.05 (10)
Lu[c]	3.11	0.0007 (15)	0.001 (31)	0.001 (16)	0.001 (12)	0.001 (12)	0.000 (3)	0.001 (11)
Mg[d]	3.99	87 (22)	141 (36)	63 (16)	36 (9)	21 (5)	14 (4)	29 (7)
Mn[d]	2.82	1.4 (12)	3.8 (33)	2.0 (17)	1.2 (10)	0.9 (8)	0.7 (6)	1.4 (12)
Mo[c]	1.46	0.005 (2)	0.035 (15)	0.037 (15)	0.029 (12)	0.058 (24)	0.029 (12)	0.044 (19)
Na[d]	4.66	279 (24)	486 (42)	187 (16)	88 (8)	38 (3)	37 (3)	42 (4)
Nd[c]	2.14	0.16 (15)	0.34 (33)	0.14 (13)	0.09 (9)	0.07 (7)	0.08 (8)	0.15 (14)
NH_4^{+}[d]	0.45	17 (2)	21 (3)	24 (3)	31 (4)	92 (13)	223 (32)	298 (42)
Ni[d]	1.84	0.12 (12)	0.21 (21)	0.16 (16)	0.11 (11)	0.10 (10)	0.11 (11)	0.20 (20)
NO_3^{-}[d]	2.53	84 (8)	288 (28)	256 (25)	146 (14)	60 (6)	64 (6)	125 (12)
Pb[d]	0.77	0.34 (2)	1.5 (9)	1.4 (9)	2.1 (13)	2.5 (16)	3.3 (21)	4.6 (29)
Rb[c]	2.32	0.14 (10)	0.51 (37)	0.25 (18)	0.11 (8)	0.11 (8)	0.10 (7)	0.16 (12)
Sb[c]	1.17	0.007 (3)	0.033 (12)	0.034 (13)	0.035 (13)	0.048 (18)	0.061 (23)	0.048 (18)
Sc[c]	3.06	0.020 (14)	0.051 (37)	0.024 (18)	0.015 (11)	0.009 (7)	0.005 (3)	0.015 (11)
Se[c]	1.15	0.008 (4)	0.018 (10)	0.020 (11)	0.020 (11)	0.032 (17)	0.058 (31)	0.033 (17)
Sm[c]	3.12	0.009 (14)	0.023 (36)	0.012 (18)	0.007 (11)	0.005 (7)	0.002 (3)	0.007 (10)
SO_4^{2-}[d]	0.63	132 (6)	196 (8)	114 (5)	128 (5)	299 (12)	763 (32)	767 (32)
Ta[c]	2.84	0.002 (10)	0.007 (38)	0.003 (17)	0.002 (9)	0.001 (5)	0.001 (8)	0.002 (13)
Tb[c]	2.87	0.001 (15)	0.004 (43)	0.001 (15)	0.001 (6)	0.001 (6)	0.001 (10)	0.001 (6)
Th[c]	3.06	0.019 (14)	0.047 (35)	0.022 (17)	0.014 (11)	0.012 (9)	0.006 (4)	0.015 (11)
Ti[c]	2.89	6.0 (14)	15 (35)	8.8 (20)	4.4 (10)	3.7 (8)	1.2 (3)	4.5 (10)
V[d]	1.21	0.15 (8)	0.36 (19)	0.22 (12)	0.18 (9)	0.22 (11)	0.36 (19)	0.44 (23)
Yb[c]	2.75	0.003 (11)	0.011 (39)	0.004 (14)	0.002 (8)	0.002 (6)	0.001 (5)	0.005 (17)
Zn[d]	1.24	1.2 (8)	1.5 (10)	1.7 (11)	1.9 (12)	3.4 (22)	3.0 (20)	2.6 (17)

[a] Concentrations are in ng m^{-3}.

[b] Numbers in parenthesis are the percent mass of each element on impactor stages.

[c] Measured in all 33 impactor sets.

[d] Measured in 7 impactor sets.

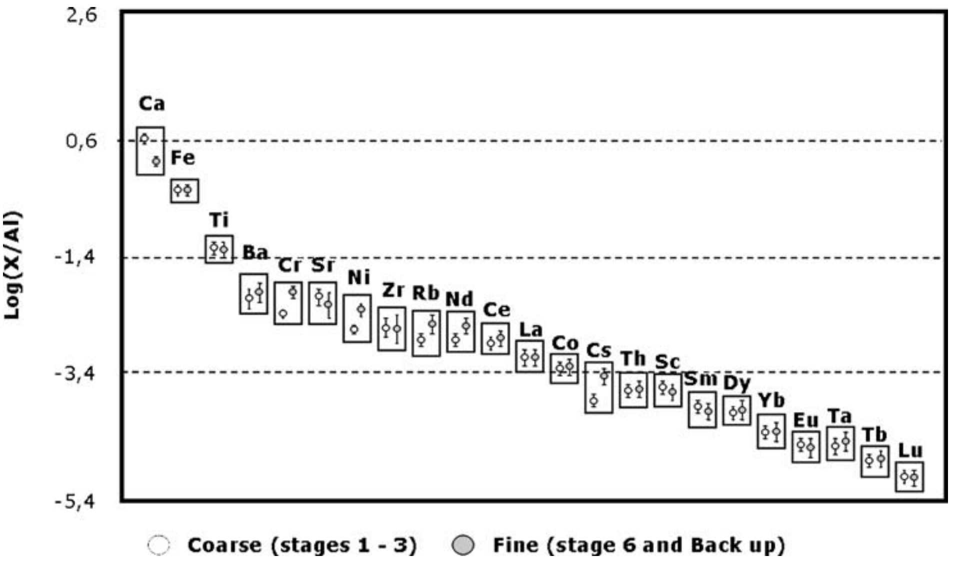


Figure 1. X-to-Al ratios of elements with crustal origin in coarse and fine fractions. Error bars indicate the range in which the average is located with 95% confidence.

studies (Chester *et al.*, 1977; Despiau *et al.*, 1996; Dulac *et al.*, 1992; Guerzoni *et al.*, 1996; Havranek *et al.*, 1996; Smolik *et al.*, 2003).

Local soil particles and dust transported from North Africa are the two main sources of crustal elements in the eastern Mediterranean atmosphere. Since Saharan dust is transported over long distances before it is intercepted at our station, size distributions of crustal elements are expected to be shifted toward smaller sizes when Saharan Dust is sampled. Dust from North Africa was sampled in six of the impactor samples collected in this study. These samples are identified by factors of 5–10 higher Al concentrations relative to measured average Al concentration and backtrajectories pointing to North Africa in at least one of the seven days of sampling. The average mass median diameters of Al and Fe in these 6 samples are 2.8 ± 0.5, and 2.3 ± 0.8 μm, respectively. The average MMD's of the same elements in the remaining samples are both 3.7 ± 0.7 μm. Observed differences are statistically significant at 95% confidence level ($p < 0.05$), demonstrating that Saharan Dust particles arriving to the Eastern Mediterranean are approximately 30% smaller than the crustal particles generated locally. However, it should be pointed that even after such long-range transport MMD's of Saharan Dust particles are still close to 2.5 μm (a tentative boundary between coarse and fine particles). This later observation agrees with the studies performed in the Western Mediterranean atmosphere where coarse particles are observed during Saharan dust episodes (Dulac *et al.*, 1992). Mass median diameters of non-crustal elements did not show a significant difference in Saharan dust impacted samples.

Most of the marine mass (approximately 86% of the Na) also occurs in the first three impactor stages. However, elements that are associated with sea salt have larger MMD's compared to crustal elements (MMDs for Na and Cl are 5.3 and 4.7 μm, respectively). Elements associated with sea salt are produced by bubble bursting over the Mediterranean Sea, which is a process that generates coarse particles (Blanchard, 1985). Association of marine elements, such as Na and Cl with coarse aerosol is well documented (example Dulac *et al.*, 1992; Smolik *et al.*, 2003).

3.2. SIZE DISTRIBUTIONS OF POLLUTION-DERIVED ELEMENTS

Size distributions of anthropogenic elements measured in this study are given in Figure 2. Approximately 60–70% of the masses of pollution-derived elements As, Cd, Mo, Pb, Sb, Se, and Zn occurred in the last two stages and on the backup filter (sizes smaller than 0.41 μm). Mass median diameters of this group of elements cover fairly narrow range between 1.25 μm (Cd) and 1.01 μm (As). These values are not significantly different from the MMD of anthropogenic elements reported for North Pacific and Western Mediterranean (Arimoto *et al.*, 1985; Dulac *et al.*, 1989).

Although majority of the masses of pollution-derived elements and ions is in the submicron range, approximately 10–30% of the masses of As, Cd, Mo, Pb, Sb, Se, and Zn are found to be in the first three impactor stages (larger than 2.1 μm). Understanding the nature of the coarse fraction component of these anthropogenic elements is important, because small fractional masses in the coarse mode have significant impact on their dry deposition fluxes (Kuloglu, 1997; Dulac *et al.*, 1989). Sources of coarse-fraction components of As, Cd, Mo, Pb, Sb, Se and Zn will be discussed in the next section.

Bromine, Cr, Ni, and V have 27–48% of their masses in the first two stages of the impactor, and 29–42% of their masses on the last impactor stage and on the back-up filter. The MMD's of Br, Cr, Ni, and V change between 1.8 and 2.0, which are higher than the MMD's of other anthropogenic elements due to their bimodal distributions. These elements have both anthropogenic and natural components in the atmosphere. Coarse fraction Br is known to have a marine source (Pakkanen *et al.*, 1996; Berg *et al.*, 1983; Duce *et al.*, 1983), whereas Cr, V and Ni are highly enriched in local soil (Kubilay and Saydam, 1995; Gullu *et al.*, 1998). Consequently, coarse particle mode for Br, Cr, Ni and V are due to presence of sea salt particles for Br and crustal particles for Cr, Ni and V. Fine particle modes of the same elements, on the other hand, are due to presence of anthropogenic particles in our samples (Gordon, 1980).

Distribution of SO_4^{2-} among impactor stages is given in Figure 3. Sulfate, and NH_4^+ ions are associated with the smallest sized particles in the eastern Mediterranean region. Approximately 40% of their mass occurs on the backup filter and 80–90% of their mass occurs in the submicron size range. Mass median diameters of SO_4^{2-}, and NH_4^+ are 0.63 and 0.45 μm, respectively which is approximately a

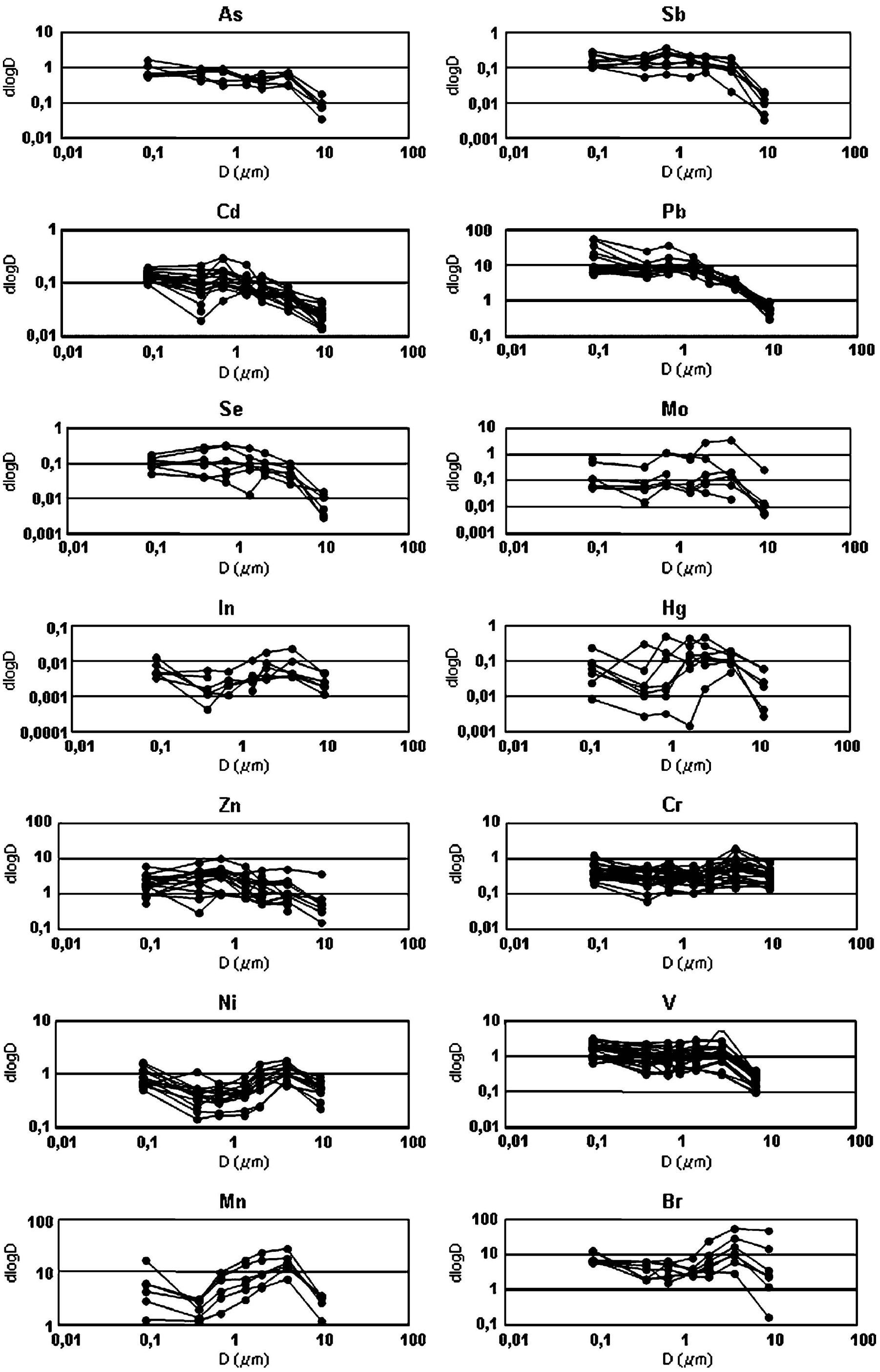
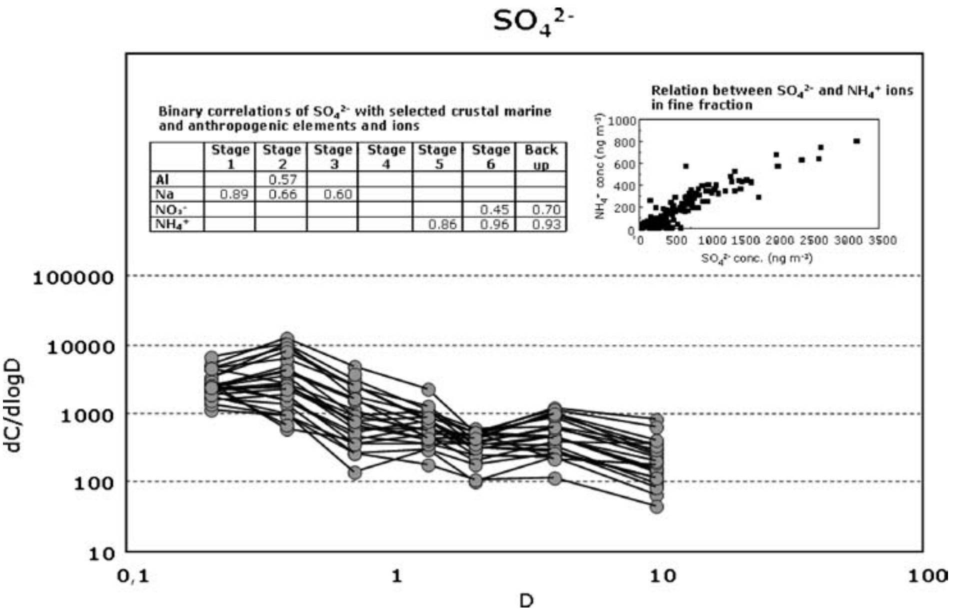


Figure 2. Size distributions of pollution-derived elements and elements which are expected to have mixed sources.



Binary correlations of SO_4^{2-} with selected crustal marine and anthropogenic elements and ions

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Back up
Al		0.57					
Na	0.89	0.66	0.60				
NO_3^-						0.45	0.70
NH_4^+					0.86	0.96	0.93

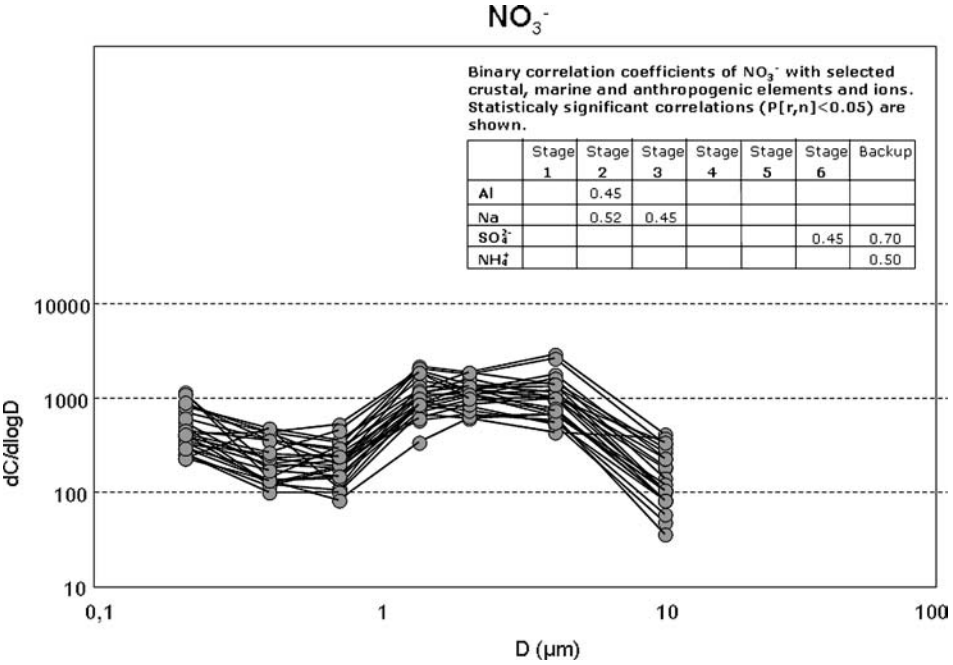
Figure 3. Distribution of SO_4^{2-} among impactor stages and correlations of SO_4^{2-} ion with elements from different source groups.

factor of two smaller than MMD's of other anthropogenic elements, owing to their formation from gas phase precursors.

Distribution of NO_3^- among stages is given in Figure 4. Approximately 75% of the NO_3^- mass occurs on the first 4 stages of the impactor (representing particles larger than 1.4 μm). The MMD of NO_3^- is 2.5 μm, which is higher than MMD's of anthropogenic elements and ions, and comparable with the MMD of crustal elements. Coarse fraction NO_3^- is frequently reported in the literature and attributed to the reaction of precursor gases on marine and crustal particles (Jickells, 1998; Zhuang *et al.*, 1999; Spokes *et al.*, 2000; Yeatman *et al.*, 2001; Bardouki *et al.*, 2003).

3.3. SEASONAL VARIATIONS IN SIZE DISTRIBUTIONS OF ELEMENTS

Summer and winter ratios of MMD's of elements are depicted in Figure 5. The summer season used in the calculations is between April and October, a period that includes 20% of the annual precipitation in the eastern Mediterranean, and winter covered the remainder of the year corresponding to 80% of the annual precipitation. Summer and winter seasons were based on rainfall, because previous studies at our site and at other locations in the Mediterranean region have demonstrated that frequency of precipitation is the most important parameter that governs seasonal variations in the concentrations of elements (Al-Momani *et al.*, 1998; Gullu *et al.*, 1998; Smolik *et al.*, 2003).



Binary correlation coefficients of NO_3^- with selected crustal, marine and anthropogenic elements and ions. Statisticaly significant correlations ($P[r,n]<0.05$) are shown.

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Backup
Al		0.45					
Na		0.52	0.45				
SO_4^{2-}						0.45	0.70
NH_4^+							0.50

Figure 4. Distribution of NO_3^- among stages and correlations of SO_4^{2-} ion with elements from different source groups.

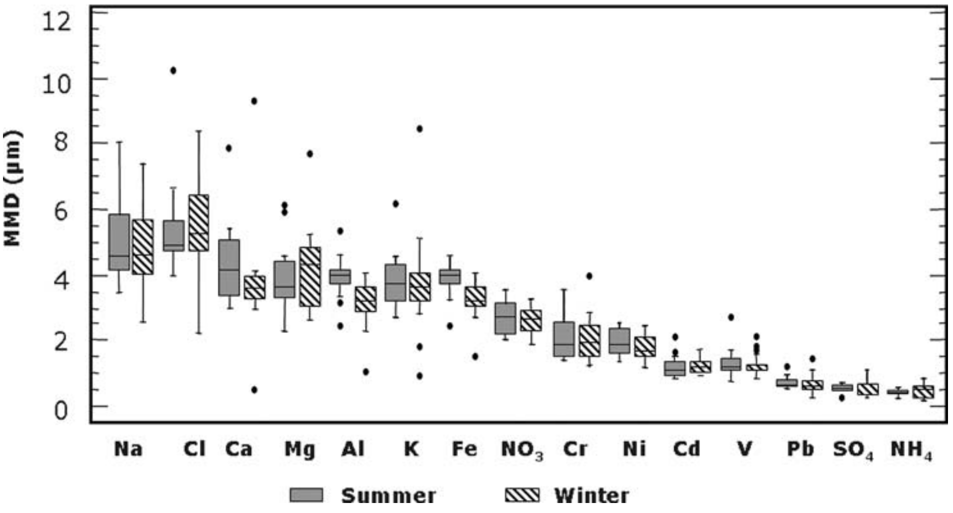


Figure 5. Summer and winter ratios of MMD's. The box includes central 50% of the data. Horizontal line within the box indicates the mean value. Lower whisker extends from lower quartile to the smallest point within 1.5 interquartile ranges from the lower quartile. The upper whisker extends from upper quartile to the largest data point within 1.5 interquartile ranges from upper quartile. Data points lying outside these ranges are indicated as individual points.

Applied t-test demonstrated that with 95% confidence, mass median diameters of elements with marine and anthropogenic origins are approximately the same in summer and winter seasons. Sea salt elements are generated by the bubble bursting process in the vicinity of the station (Gullu *et al.*, 1998). Although surface wind speed determines the amount of sea salt particles generated, it does not effect the size distribution of generated sea salt particles (Blanchard, 1985). Consequently sea salt particles are generated in different quantities, but with approximately the same size distribution in the summer and winter seasons.

Pollution-derived elements are transported to the region from distant sources (Gullu, 1996). Since only small particles bearing these elements can survive wet and dry scavenging during their long-range transport to the eastern Mediterranean region, these particles are also not expected to show significant differences in their MMD's between summer and winter seasons.

The t-test also indicated that, unlike anthropogenic and marine elements, there are significant differences in the MMD's of crustal elements between summer and winter seasons. Mass median diameters of these elements are approximately 40% larger during summer season. The reason for such behavior of soil related elements is not clear.

3.4. CORRELATIONS BETWEEN ELEMENTS AND CRUSTAL ENRICHMENT FACTORS IN DIFFERENT SIZE FRACTIONS

Binary correlations between elements and ions in different impactor stages can be a useful to explain observed size distributions of elements. In the discussions presented in this section elements are considered to be correlated with each other if probability of chance correlation ($P[r,n]) < 0.05$.

Crustal elements Al, K, Mg, Ca, Fe, Sc, Co, Ti, La, Ce and Sm are correlated with each other in both coarse ($d > 2.1$ μm, stages 1–3) and fine fraction particles ($d < 2.1$ μm, stages 4–6 and backup filter), as expected.

Marine elements Na and Cl are also correlated with each other at every impactor stage. These elements are also correlated with Mg and K in the coarse fraction, due to contribution of sea salt on observed Mg and K concentrations. However, K and Mg are not correlated with sea salt elements in the fine fraction, because contribution of sea salt on fine particle mass is small.

In the previous section it was pointed that approximately 10–30% of the masses of anthropogenic elements As, Cd, Mo, Pb, Sb, Se, In, Au, Hg and Zn occurs in the coarse fraction and this small component can have significant impact on dry deposition fluxes of these elements.

All of these anthropogenic elements are correlated with crustal elements in the coarse fraction (stages 1–3), but do not correlate with marine elements Na and Cl, implying that they are associated with crustal rather than sea salt particles.

Association of pollution derived and crustal elements were also reported in literature and attributed to coagulation of fine anthropogenic particles onto coarse crustal aerosol (Rojas *et al.*, 1993; Dulac *et al.*, 1989; Holsen *et al.*, 1993). Although this explanation can be true for some of these elements, it should also be noted that occurrence of these elements in crustal material can also be the reason for at least some of the observed correlations. Crustal enrichment factors (EF_c) and EF_c-Al diagrams were used to differentiate between these two potential sources of correlations between anthropogenic and crustal elements.

Crustal enrichment factors were calculated using the following well-known relation

$$(EF_c)_x = (C_x/C_{Al})_{sample}/(C_x/C_{Al})_{soil}$$

Where $(EF_c)_x$ is the crustal enrichment factor of test element x, $(C_x/C_{Al})_{sample}$ is the ratio of the concentration of test element x to that of Al (element selected as crustal reference) in sample and $(C_x/C_{Al})_{soil}$ is the corresponding ratio in soil. Chemical composition of local soil, which was obtained by analyzing approximately 100 surface soil samples by AAS and INAA, at a 20 km × 20 km area around the station (Guvenc, 1998) was used in EF_c calculations.

Average crustal enrichment factors of the pollution-derived elements in first three impactor stages ($d > 2.1$ μm) were 4.8 for Zn, 28 for Cd, 54 for Pb, 6.7 for As, 3.4 for Se, 2.1 for Mo, 13 for Sb, 1.6 for In, 180 for Hg and 2.9 for Au.

Cadmium, Pb, Sb and particulate Hg are highly enriched in the coarse aerosols relative to local soil, suggesting that coarse fraction component in their concentrations can not be explained by their occurrence in the soil matrix. On the average, contribution of crustal aerosol on coarse fraction concentrations of Cd, Pb, Sb, and Hg, which are calculated using local soil composition and assuming crustal material is the only source of Al are 3.1%, 1.3%, 7.6% and 0.6%, respectively. Sticking of fine anthropogenic particles containing Pb, Hg and Cd on coarse crustal particles can be main reason for their coarse components. For particulate Hg other mechanisms, such as adsorption of gaseous Hg on crustal particles, can also be responsible for coarse fraction Hg. Values of enrichment factors of Zn, As, Se, Mo, In and Au were fairly close to unity. Contribution of crustal aerosol on their observed coarse fraction concentrations vary between 18% for As and 56% for In. With such high crustal contribution, coarse component in concentrations of Zn, As, Se, Mo, In and Au cannot be attributed entirely to sticking of fine anthropogenic particles on crustal aerosol.

Enrichment factor-Al diagrams for Cd, Pb, Zn, As, Se and In are depicted in Figure 6. These diagrams are useful to differentiate between crustal and non-crustal (anthropogenic in our case) sources of elements at different Al concentrations. Since EF_c's of crustal elements will not change with variations in Al concentration (because their concentrations co-vary with Al), EF_c-Al diagrams of purely crustal elements are characterized by a horizontal line at $EF_c = 1.0$. Enrichment factors of anthropogenic elements, on the other hand decrease with increasing Al concentration in the sample.

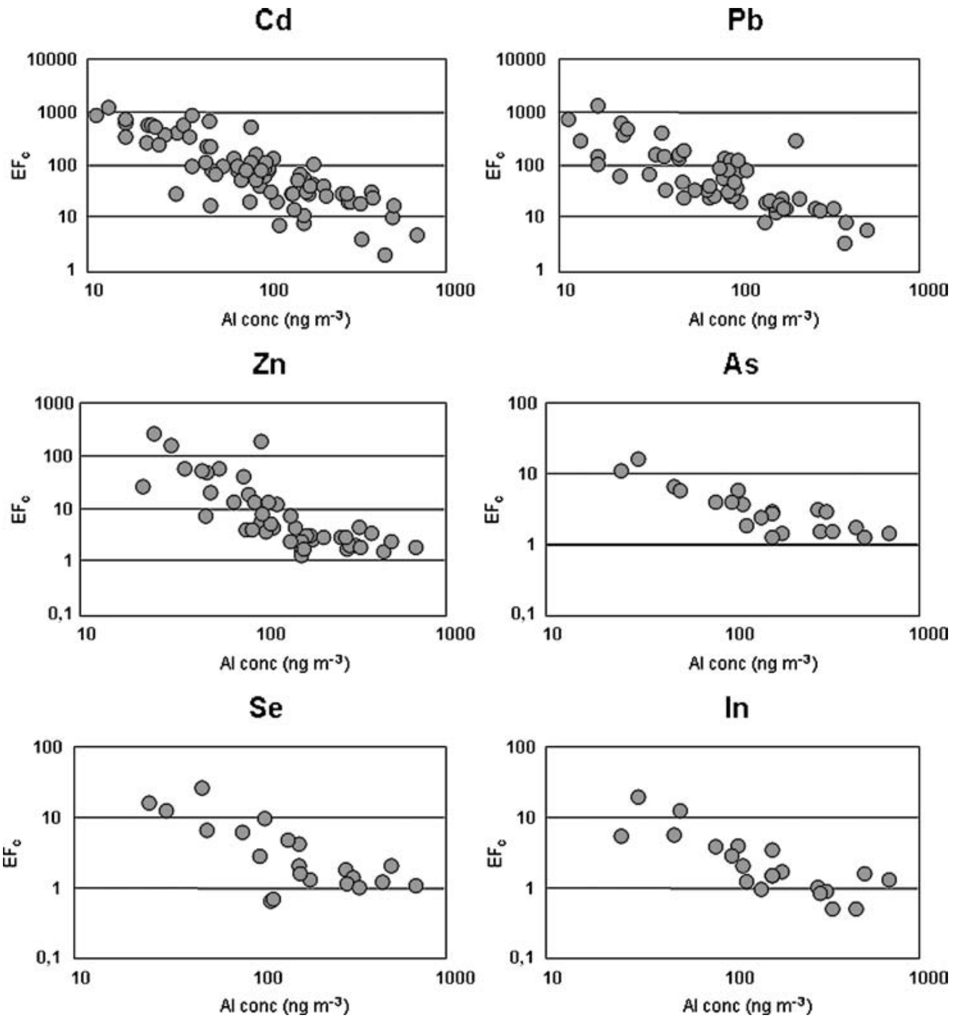


Figure 6. Enrichment factor-Al diagrams for Cd, Pb, Zn, As, Se and In in the coarse fraction ($d > 2.1$ μm).

The EF$_c$-Al diagrams for Cd and Pb display anthropogenic behavior at all Al concentrations. This behavior confirms that Cd and Pb (also Sb and Hg, which displays similar EF$_c$-Al pattern) are anthropogenic at coarse fraction.

Zinc, As, Se and In (also Mo and Au, which are not shown in the figure), on the other hand, have distinctly different EF$_c$-Al patterns. Their EF$_c$'s decrease with increasing Al concentrations at Al concentrations less than 100 ng m^{-3}, but level off at around unity at higher Al concentrations. Such behavior indicates that these elements are from anthropogenic sources at low concentrations of crustal aerosol, but they are from soil (their anthropogenic component is masked by soil) when

Al concentration exceeds 100 ng m^{-3}. Since average Al concentration at this site is 540 ng m^{-3} and Al concentration is >100 ng m^{-3} in 82% of the samples, it is safe to conclude that the source of Zn, As, Se, In, Mo and Au, in particles with aerodynamic diameters >2.1 μm is the crustal material.

In the fine aerosol fraction ($d < 2.1$ μm) pollution-derived elements are not correlated with Al (and other crustal elements), their EF_c's are higher than 50 and their EF_c's decrease with Al concentration at all Al concentrations, indicating that crustal material do not have detectable contribution on concentrations of anthropogenic elements in the fine fraction.

Correlation between Br and Na in the first impactor stage where most of the sea salt occurs and similar Br-to-Na ratio with seawater [the Br/Na ratios are 0.0058, and 0.0062 in the first impactor stage, and in sea water (Goldberg, 1963), respectively] confirms the marine source of the coarse-fraction Br. Bromine is highly enriched relative to both seawater and crustal material in the fine fraction. Bromine-to-Pb ratios in the last impactor stage and in the back-up filter are 0.45, and 0.43, respectively. These ratios are reasonably close to the Br-to-Pb ratio in motor vehicle emissions, which is 0.39 (Ondov *et al.*, 1982), suggesting that the motor vehicle emissions is probably the main source of fine fraction Br.

Vanadium, Cr, and Ni are correlated with Al in the coarse fraction signifying crustal source for the coarse mode of these elements, which is also reported in literature (Kasahara *et al.*, 1996; Gordon, 1980). Crustal enrichment factors of V, Cr and Ni in the coarse fraction (relative to local soil) are 0.8, 1.4 and 1.5, respectively confirming strong contribution of soil aerosol on their coarse fraction concentrations. These elements are moderately enriched relative to local soil in fine fraction (EF_c's are 5.6 for V, 7.3 for Cr and 6.8 for Ni) due to contribution of anthropogenic sources (Mateu *et al.*, 1996; Dulac *et al.*, 1987).

Correlations of SO_4^{2-} with Na, Al, NO_3^- and NH_4^+ are depicted in Figure 3. Sulfate correlates with Na (and Cl, which is not shown in the figure) in the coarse fraction due to sea salt contribution on observed SO_4^{2-} concentrations. Approximately 79 ± 32%, 70 ± 35%, 53 ± 30% of measured SO_4^{2-} concentration in the first, second and third stages originate from sea salt, respectively (calculated by assuming all measured Na is from sea salt particles, and S-to-Na ratio in sea salt particles is similar to that in bulk sea water).

Sulfate also correlates with Al, (and other crustal elements) in the second impactor stage, suggesting that a small fraction of measured coarse fraction SO_4^{2-} can be associated with crustal particles. Crustal and Sea salt particles coated with SO_4^{2-} are reported in aerosol studies in the Mediterranean atmosphere (Levin *et al.*, 1990, 1996) and elsewhere (Dentener *et al.*, 1996).

Sulfate correlates with NH_4^+ in the fine fraction owing to neutralization of atmospheric H_2SO_4 with NH_3 resulting in the formation of $(NH_4)_2SO_4$ and NH_4HSO_4, as reported frequently in the literature (Clarke *et al.*, 1987; Covert, 1988; Silvente and Legrand, 1993; Bardouki *et al.*, 2003). Sulfate-to NH_4^+ mass ratios are 2.7 and 5.3 in $(NH_4)_2SO_4$ and NH_4HSO_4, respectively. The median values of measured

SO_4^{2}-to-NH_4^+ mass ratio are 3.0 in stages-5 and 6 and 2.5 in the back-up filter. Observed SO_4^{2}-to-NH_4^+ ratios are close to mass ratio in $(NH_4)_2SO_4$ and suggest that most of the neutralized sulfate is in the form of $(NH_4)_2SO_4$, as there is not enough SO_4^{2-} to form NH_4HSO_4.

Sulfate also correlates with NO_3, in stage 6 and back-up filter, because they both form from gaseous precursors through photochemical reactions, and meteorological conditions, such as solar flux, which favors formation of SO_4^{2-} also enhances formation of NO_3^-.

Correlations between NO_3^- and Al, Na, SO_4^{2-} and NH_4^+ are given in Figure 4. In the coarse fraction NO_3^- correlates with both crustal and marine elements, confirming that the coarse mode observed in NO_3^- size distribution is due to its association with sea salt and crustal particles in the atmosphere. Based on this argument it can be concluded that approximately 75% of the NO_3^- in the eastern Mediterranean atmosphere is bound to sea salt and crustal particles.

In the fine fraction, NO_3^- correlates with NH_4^+ and SO_4^{2-}. Its correlation with NH_4^+ is due to formation of NH_4NO_3, and correlation with SO_4^{2-} is due to their similar formation mechanisms, as pointed before.

4. Conclusions

Size distributions of trace elements and ions in the eastern Mediterranean are determined by analyzing cascade impactor samples collected at a rural station on the Mediterranean coast of Turkey, for a one year period in 1993–1994.

Most of the crustal and marine masses occur in first three impactor stages as expected. The mass median diameters of crustal elements vary between 3.0 and 3.5 and those of marine elements change between 4.6 and 5.3. Mass median diameters of crustal elements in 6 impactor sets which are effected by the Saharan Dust transported to the sampling site are approximately 30% smaller than the mass median diameters of the same elements measured in samples which are not effected by the dust transport.

Mass median diameters of anthropogenic elements As, Cd, Mo, Pb, Sb, Se, In, particulate Hg and Au vary between 1.01 and 1.25 μm, whereas those of SO_4^{2-} and NH_4^+ are significantly smaller than other pollution-derived elements. Although most of the masses of pollution-derived elements are in the last stages of the impactor and on the backup filter, approximately 10–30% of their masses are found on the first three impactor stages ($d > 2.1$ μm). Coarse component in concentrations of Zn, As, Se, In, Mo and Au are explained by their occurrence in aluminasilicate structure of soil, at least at Al concentrations >100 ng m^{-3}. Coarse fraction Cd, Pb, Sb and Hg are attributed to sticking of fine anthropogenic particles on coarse soil aerosol.

Elements Br, Cr, Ni, and V show bimodal distributions. Coarse component in their concentrations is due to soil and sea salt particles in the atmosphere, whereas fine component consist of anthropogenic particles.

Approximately 80% of the SO_4^{2-} mass occurs in the fine fraction ($>2.1\ \mu$m), and 40% on the backup filter. The fine fraction SO_4^{2-} is produced by gas to particle conversion in the atmosphere and it is mostly in the form of $(NH_4)_2SO_4$. The coarse fraction SO_4^{2-} is partly accounted for by the sea salt. Remainder of the coarse SO_4^{2-} is associated with crustal particles.

Size distribution of NO_3^- is significantly different from distributions of SO_4^{2-}, and NH_4^+. Approximately 75% of the NO_3^- mass is associated with coarse particles due to its formation on sea salt and soil particles in the atmosphere.

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