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Chemical composition of the fine and coarse fraction of aerosols in the northeastern Mediterranean

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Abstract

Two-stage aerosol samples (PM_{10-2.5} and PM_{2.5}) were collected at a coastal rural site located in the northeastern Mediterranean, between April 2001 and 2002. A total of 562 aerosol samples were analyzed for trace elements (Fe, Ti, Mn, Ca, V, Ni, Zn, Cr) and water-soluble ions (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, Br⁻, NO₃⁻, SO₄²⁻, C₂O₄²⁻ and MS⁻:methane sulfonate). PM₁₀, crustal elements, sea salt aerosols and NO₃⁻ were mainly associated with the coarse mode whereas non-sea salt (nss)SO₄²⁻, C₂O₄²⁻; MS⁻, NH₄⁺, Cr and Ni were found predominantly in the fine fraction. Concentrations of aerosol species exhibited orders of magnitude change from day to day and the aerosol chemical composition is heavily affected by dust events under the influence of airflow from North Africa. During the sampling period, 11 specific mineral dust events of duration varying from 1 day to a week have been identified and their influence on the chemical composition of aerosols has been studied in detail. Ionic balance analysis performed in the coarse and fine aerosol fractions indicated anion and cation deficiency due to CO_3^{2-} and H⁺, respectively. A relationship between nssSO₄²⁻ and NH₄⁴⁺ denoted that sulfate particles were partially neutralized (70%) by ammonium. Excess-K/BC presented two distinct ratios for winter and summer, indicating two different sources: fossil fuel burning in winter and biomass burning in summer.

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1. Introduction

Aerosols physically affect the heat balance of the Earth, both directly by reflecting and absorbing solar radiation, and by absorbing and emitting some terrestrial infrared radiation and indirectly by influencing the properties and cloud processes and, possibly, by changing the heterogeneous chemistry of reactive greenhouse gases (e.g., O₃; IPCC, 2001 and references therein). The global radiative forcing due to aerosols is roughly $1.6 \pm 1.3 \text{ W m}^{-2}$, which nearly compensates for the mean global radiative forcing of $2.4 \pm 0.3 \text{ W m}^{-2}$ due to greenhouse gases warming (IPCC, 2001). Recently, Vrekoussis et al. (2005) investigated aerosol optical properties in the eastern Mediterranean and estimated radiative forcing at the top of the atmosphere ranging from

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-12.6 to -2.3 W m² for summer and winter. respectively. Their estimated radiative forcing values are up to five times higher than that induced by greenhouse gases but opposite in sign. The large range of uncertainty associated with aerosol forcing estimates reflects the poor state of knowledge regarding the sources, distributions and properties of atmospheric aerosols. The need for an increased effort in characterizing tropospheric aerosols in order to reduce the uncertainty in the aerosol forcing estimate has been stressed (Schwartz and Andreae, 1996; Ramanathan et al., 2001; Kaufman et al., 2002). Recent model studies reproduced satellite observations and demonstrated the role of three major components of aerosols in surrounding regions of the Mediterranean basin (sulfate, black carbon (BC) and dust), having very high direct radiative forcing for aerosols at the top of the atmosphere (Jacobsen, 2001; Sciare et al., 2003). Knowledge of the spatial and temporal variability of aerosol concentrations, their physical, chemical and radiative properties are very important since they can directly and indirectly influence planetary albedo (climate).

Adverse effects of particulate matter (PM) on human health have been shown by a great deal of studies (Englert, 2004 and references therein). For example, PM_{10} has important health implications through the inhalation of PM, which can be deposited in the lung and high concentrations of trace metals associated with these inhalable particles such as Pb, Cd, V, Fe, Zn, Cr, Ni, Mn and Cu are potentially toxic to human (Singh et al., 2002 and references therein).

Several studies have been conducted in the western Mediterranean (Querol et al., 2001; Rodriguez et al., 2002), considering temporal and spatial variability of the concentration of PM₁₀, aerosol trace elements and water-soluble ions. Nevertheless, studies for the eastern Mediterranean are limited. To our knowledge the only study reporting the temporal variability of trace elements in coarse and fine particles was performed at the arid site, Negev Desert of the Israel (Andreae et al., 2002). This paper addresses the temporal variability of the concentration of PM₁₀, aerosol trace metals and water-soluble ions influencing the Levantine Basin of the eastern Mediterranean, in two-size fractionated aerosol populations (over 1-year period) from the Erdemli site.

A size-fractionated sampling strategy will allow the identification of the (i) size distribution of chemical species, (ii) chemical components and contribution of each component to the coarse and fine PM levels, (iii) meteorological processes (by using local rainfall and back trajectories) on the observed concentration levels, (iv) mineral dust events, (v) evolution of organic (oxalate) and inorganic anions on dust particles.

2. Material and methods

A Gent-type PM_{10} stacked filter unit (SFU) sampler was used in order to collect atmospheric particles in two size ranges, namely, coarse and fine at a rural site located on the coast of the eastern Mediterranean, Erdemli (36° 33' 54"N and 34° 15' 18"E), Turkey (for more details see Kubilay and Saydam, 1995; Kubilay et al., 2002; Koçak et al., 2004a, b). Typical to Mediterranean, the sampling site is mostly wet in winter and dry in summer. Pulp and paper industry exist 45 km to the west and a petroleum refinery, soda, chromium, fertilizer industry, a thermic power plant and the city of Mersin (~1 million inhabitants) are located 45 km to the east of the sampling site. Sampling commenced in April 2001 and ended in April 2002. During this period a total of 562 aerosol filter samples were collected with a temporal resolution of 24 h. After collection of aerosol filters, PM_{10-2.5} and PM_{2.5} concentrations were determined gravimetrically. Water-soluble ions were measured by ion chromatography (IC) at Environmental Chemical Processes Laboratory (ECPL), University of Crete, following the method described in details by Bardouki et al. (2003). Concentrations of the elements (Fe, Ti, Ca, Mn, K, Cr, V, Zn, Cl, S) were obtained using 2 cm^2 of the filter sample applying proton-induced X-ray emission (PIXE) at ATOMKI (Institute of Nuclear Research of the Hungarian Academy of Sciences, Debrecen, Hungary). During the experiments, the aerosol samples were irradiated by a 2 MeV proton beam, which was supplied by the 5 MV Van de Graaff Accelerator of ATOMKI (for more details see Borbely-Kiss et al., 1999). For the evaluation of PIXE spectra, the PIXEKLM software was applied (Szabo and Borbely-Kiss, 1993).

BC content in 46 fine aerosol filter samples collected during winter and summer was determined using a smoke stain reflectometer (SSR, Borbely-Kiss et al., 1999). For this purpose, obtained reflectance was converted into $\mu g m^{-3}$ calibrating instrument using EC. More details about sampling and analysis can be found at Koçak et al. (2007).

Three-dimensional (3-D), 3-day backward trajectories (European Center for Medium Range Forecasts) of air masses arriving at the sampling site on 12:00 UT at a pressure level of 850 hPa representing the top of boundary layer (Katsoulis, 1999) were calculated from April 2001 and 2002. Cluster analysis in the categorization of air masses back trajectories is widely used (Dorling et al., 1992; Cape et al., 2000) since it allows large quantities of data to be processed automatically. The categorization was based on the trajectory coordinates with no inclusion of the information such as whether the trajectory had over land or sea or regions with the potential for emitting crustal materials and/or pollutants into the air mass. In order to use cluster analysis in the categorization of back trajectories, Statistica Package program and the method described by Cape et al. (2000) were applied.

3. Results and discussion

3.1. General characteristics of the data

The average concentrations of PM, trace elements and water-soluble ions in the fine ($d < 2.5 \,\mu$ m, PM_{2.5}) and coarse ($10 \,\mu$ m > $d > 2.5 \,\mu$ m, PM_{10-2.5}) atmospheric particles along with standard deviations are presented in Table 1. The annual average sulfate and nitrate mass concentrations were 4953 and 1857 ng m⁻³, respectively. Ca, Fe, Ti and Mg (mainly originating from crust) mass concentrations were found to be 1550, 351, 27.1 and 7.6 ng m⁻³, respectively. Ammonium and potassium had mean values of at 850 and 203 ng m⁻³, respectively. Sea salt particles consist mainly of sodium chlorite and sulfate (primarily Na₂SO₄, MgSO₄ or K₂SO₄) and non-sea salt fractions of ions was calculated from

Table 1

Statistical descriptions of the elemental and ionic concentrations measured in the coarse and fine fractions of particles collected at Erdemli over the period of April 2001 and 2002

Species	This study		PM ₁₀ eastern Medit	PM ₁₀ western Mediterranean			
	PM _{10-2.5}	PM _{2.5}	This study ^a rural	Sde boker ^b arid	Monagrega ^c rural		
РМ	26.7 ± 26.4	9.7 ± 5.9	36.4	60.4	22		
Fe	298 ± 444	53.3 ± 82	351.3	1293	222		
Ti	23 ± 41.7	4.1 ± 7.6	27.1	125.9	20		
Mn	5.8 ± 7.5	1.8 ± 1.7	7.6	24.9	5		
Ca	1730 ± 1567	158 ± 208	1888	6744	930		
V	4.2 ± 3.1	4.5 ± 3.7	8.7	9.8	2		
Ni	2.1 ± 1.8	1.6 ± 1.3	3.7	5.7	5		
Zn	4.8 ± 2.8	4.9 ± 3.7	9.7	30.6	30		
Cr	3.9 ± 5.3	1.8 ± 3.5	5.7	-	-		
S	515 ± 319	1122 ± 869	1637	2646	-		
K	244 ± 258	116 ± 112	360	599	203		
Na ⁺	3095 ± 4195	339 ± 242	3434	1216	294		
Cl	5384 ± 7772	108 ± 182	5492	1199	349		
Mg^{2+}	435 ± 540	54 ± 39	489	958	117		
nssMg ²⁺	90 ± 128	25 ± 20	115	-	-		
Br ⁻	10.9 ± 21.4	-	10.9	29.2	-		
K^+	95 ± 114	108 ± 127	203	-	-		
nssK ⁺	40 ± 52	99 ± 125	139	-	-		
NH ₄ ⁺	-	850 ± 830	850	-	1284		
NO_3^-	1589 ± 983	268 ± 295	1857	-	2177		
SO_4^{2-}	1541 ± 1352	3412 ± 3093	4953	-	3877		
$nssSO_4^{2-}$	810 ± 834	3336 ± 3072	4146	-	3803		
$C_2O_4^{2-}$	158 ± 94	234 ± 160	392	-	-		
MS ⁻	_	24.1 ± 25.6	24.1	-	-		
Ca ²⁺	1398 ± 1405	162 ± 162	1560	-	_		
nssCa ²⁺	1285 ± 1346	$150\!\pm\!161$	1435	-	-		

Concentrations are expressed in $ng m^{-3}$, except for PM, for which concentrations are in $\mu g m^{-3}$.

^aThis study.

^bAndreae et al. (2002).

^cRodriguez et al. (2002).

measured concentrations of ion interested, Na⁺ and a standard sea water composition (Turekian, 1976). Sea salt-originated water-soluble ions were also found in high concentrations, as expected for a coastal sampling site. Trace metals V, Ni and Zn have anthropogenic origins such as residual oil and smelters and show concentrations of 8.7, 3.7 and $9.7 \,\mathrm{ng}\,\mathrm{m}^{-3}$, respectively. The annual arithmetic mean PM₁₀ mass concentration was $36.4 \,\mu\mathrm{g}\,\mathrm{m}^{-3}$.

Ca concentrations obtained from PIXE analyses are higher than those obtained from IC measurements; the results indicate (Table 1) that on average, water-soluble Ca^{2+} concentrations (IC) are about 20% lower than the total Ca (PIXE). The insoluble fraction (amounting to 20%) might be attributed to the existence of insoluble compounds of Ca such as calcium oxide and feldspar. Water-soluble sulfate has mean values about three times of the elemental S concentration (PIXE). This ratio is identical to the mass ratio of SO_4^{2-}/S and implies that almost all of the observed elemental S is in the form of sulfate.

Size distributions of trace metals and watersoluble ions in coarse and fine fractions are presented in Fig. 1. The largest portion of the atmospheric particle mass is associated with coarse particles and contributes 73.4% to the observed particle mass. Crust-originated trace metals (Fe, Ti and Mn), water-soluble ions Na⁺, Cl⁻, Mg²⁺, Ca²⁺, Br⁻ and NO₃⁻ are associated mainly with coarse particles (>75%). The mass concentration of oxalate ($C_2O_4^{2-}$) and non-sea salt sulfate (nssSO_4^{2-}) was mainly found in the fine mode (60% and 80%, respectively). On the other hand, ammonium (NH₄⁺) and methane sulfonate (MS⁻) mass concentrations were exclusively found in the fine size fraction. Trace metals V and Zn displayed almost half of their mass concentrations in the fine fraction while about 60% and 70% of the mass concentrations of Ni and Cr were found in the fine the fraction, respectively.

3.2. Daily variations of chemical composition

The daily variations in the concentrations of PM, aerosol trace elements and water-soluble ions with daily precipitation between April 2001 and 2002 are presented in Fig. 2.

Aerosol species originating from sea salt (Na⁺ and Cl⁻) exhibit their highest mass concentrations and larger variations during the winter season due to unsettled weather, which enhances the concentrations of the aforementioned aerosol elements throughout periods of severe sea spray generation.

Crustal aerosol species (Fe and Ti, see Fig. 2) indicates strong daily variability in their concentrations. The concentrations of crust-originated species showed lower values frequently during the winter season (due to rain). As is well documented in the



Fig. 1. Relative contributions of PM₁₀ and aerosol species in the fine and coarse fraction.



Fig. 2. Daily variations of sea salt, crustal, anthropogenic and biogenic aerosols throughout the period between April 2001 and 2002 along with daily rain events.

literature (Alpert and Ziv, 1989; Kubilay and Saydam, 1995; Moulin et al., 1998; Kubilay et al., 2000; Koçak et al., 2004a), despite efficient scavenging by wet precipitation, crustally originated aerosol species showed higher concentrations and larger variations during the transitional (spring and autumn) period when the air mass trajectories originated predominantly from North Africa but rarely from the Middle East, and are often associated with intense sporadic peaks of mineral dust. However, during the summer period, crustally originated trace metals exhibited less variability in their concentrations since the soil is dry in this season and the lack of wet precipitation leads to greater re-suspension of local soil particles.

Fig. 2 presents the daily variations of the watersoluble ions $nssSO_4^{2-}$, MS^- , NH_4^+ , $C_2O_4^{2-}$ and NO_3^- . They show larger variabilities and peak values in summer due to the absence of precipitation and changes in air masses origin. For example, the highest MS^- concentration was found on the 3rd of June 2001 under the influence of maritime airflow originating from the Mediterranean Sea. Sharp decreases in the concentrations of MS^- from the summer towards winter may be attributed to variations in several different processes: chemical, biological (primary productivity) and meteorological (Kubilay et al., 2002).

3.3. Influence of dust events on aerosol chemical composition

The Mediterranean region is affected by large quantities of mineral dust associated with air mass transport mainly from sources in North Africa and occasionally from sources in the Middle East. Recently, dust storm source areas have been determined by the total ozone-mapping spectrometer (TOMS) and results indicated that the Saharan desert is the predominant source and the Middle East is one of the key sources (Washington et al., 2003). Mineral dust transport from North Africa can be observed at any time of the year in the eastern Mediterranean; however, the frequency of the events is much greater in March, April, May and October when air masses are associated with cyclonic activity (Alpert and Ziv, 1989; Moulin et al., 1998; Kubilay et al., 2000, 2005).

Fig. 3 presents the daily variations (from winter to transitional seasons) of the aerosol trace metals Fe, Ti, Mn and Ca concentrations between April 2001 and 2002, along with identified dust events and daily rainfall. Aerosol Fe concentrations higher than 500 ngm^{-3} as threshold values, and corresponding air mass back trajectories, satellite images obtained from TOMS were utilized in order to



Fig. 3. Daily variations of trace metals associated with a crustal component from the winter to transitional seasons between 2001 and 2002.

refine mineral dust events at Erdemli in the winter and transitional seasons. During these periods, 34 dust days were identified by an abrupt increase in the concentrations of Fe, Ti, Mn and Ca. These dust days were characterized by 11 specific mineral dust events of duration varying from 1 day to 7 days, but most commonly for 2–3 days (Fig. 3). During dust events, Fe concentrations were found to range from 500 to 7000 ng m⁻³, indicating a large variability of the dust events with time.

Figs. 4a and b show air mass back trajectories along with TOMS satellite images for 13 May when the highest Fe concentration (6666 ng m^{-3}) in the dataset was observed. On 13 May, trajectories showed that at 850, 700 and 500 hPa levels, air masses arrived at Erdemli from the northeastern Saharan region. In addition, TOMS satellite image showed particularly high Aerosol Index values over Libya, Egypt and the Middle East and very intense dust transport in the eastern Mediterranean region.

Table 2 (derived from Fig. 3) shows arithmetic mean concentrations of aerosol species for dust and non-dust events at Erdemli. As can be seen, aerosols definitely show different chemical compositions between dust events and non-dust events. For example, the crustally derived aerosol species (Fe, Ti, Mn and Ca²⁺) for dust events had arithmetic mean concentrations at least three times higher than those observed for non-dust events. Anthropogenically derived aerosol elements (Zn, V, Ni and Cr) also showed enhancements during dust events with values ranging from 1.3 to 1.5. In addition, watersoluble ions $nssSO_4^{2-}$, $C_2O_4^{2-}$ and NO_3^{-} also indicated enhancements during dust events with values ranging from 1.6 to 2.0. Field and laboratory studies indicated that mineral dust particles can serve as reaction surfaces for different species, including those of man-made origin (Mamane and Gottlieb, 1992; Underwood et al., 2001; Aymoz, et al., 2004; Putaud et al., 2004; Alastuey et al., 2005). Gaseous species such as SO₂, N₂O₅, HNO₃ and O₃ can react with mineral dust particles (Mamane and Gottlieb, 1992; Dentener et al., 1996) and result in the modification of optical properties, size distributions and chemical composition of the aerosols (Usher et al., 2003). Aymoz et al. (2004 and references therein) emphasized the limitations of the current knowledge about interactions between mineral dust and organic compounds. Recently, Putaud et al. (2004) have indicated that

Table 2

Arithmetic mean concentrations of aerosol species for dust events and non-dust events at Erdemli

Species	Dust events	Non-dust events
Fe	1200	176
Ti	100.3	10.7
Mn	21.0	4.2
Ca ²⁺	3500	1033
Ant–Zn	9.4	7.5
Ant–V	10.2	7.7
Ant–Ni	4.3	3.3
Ant-Cr	6.9	4.5
$nssSO_4^{2-}$	3960	2563
$C_2 O_4^{2-1}$	412	244
NO ₃	2560	1273

Ant refers to the anthropogenic fraction and is calculated using the formula presented as $(X_{Ant} = X_{total} - [(C_R)_{aerosol} \times (C_X/C_R)_{Reference}]$.



Fig. 4. Air mass back trajectories for the 13th of May 2001 (a) Horizontal component (b) TOMS Aerosol Index. The back trajectory pathway every 12 h is indicated by triangles for 1000 hPa, stars for 850 hPa, circles for 700 hPa and squares for 500 hPa.

there was no significant SO_2 oxidation onto mineral dust particles while NO_3^- shifted to the super-µm fraction due to the adsorption of HNO_3 onto dust particles during Saharan dust plumes. However, very low increases of sulfate and nitrate onto mineral dust particles were found by Aymoz et al. (2004). Furthermore, these authors detected various organic acid (including oxalic acid) levels and have suggested low reactions of primary volatile organics on dust particles, but some uptake of acidic gases such as formic acid during transport. In contrast, Falkovich et al. (2004) clearly showed interaction of semi-volatile compounds with mineral dust particles.

In order to identify the enrichment of sulfate and oxalate onto mineral dust particles, the transitional period was considered since most of the dust episodes take place during this period. Fig. 5 presents the concentrations of $nssSO_4^{2-}$ and $C_2O_4^{2-}$ during the transitional period together with

nssCa²⁺ concentrations in the coarse particle size range. As can be seen, clear enrichment of $nssSO_4^{2-}$ and $C_2O_4^{2-}$ were found to occur during the intense mineral dust events ($nssCa^{2+} > 5000 \text{ ng m}^{-3}$).

As mentioned before, the highest mineral dust outbreak was observed on 13 May 2001 and characterized by an extremely high nssCa²⁺ concentration (around 19000 ng m⁻³; case-3). The corresponding nssSO₄²⁻/nssCa²⁺ ratio is 0.26 in the coarse size range. During the second event, the nssSO₄²⁻/nssCa²⁺ ratio is identical to the ratio observed for case-3 (0.26). During cases 1 and 4, nssCa²⁺ concentrations remained higher than 6500 ng m⁻³. The nssSO₄²⁻/nssCa²⁺ ratios for cases 1 and 4 were 0.74 and 0.67, respectively. Putaud et al. (2004) applying nssSO₄²⁻/nssCa²⁺ ratios (0.4±0.1) in the super-µm aerosol size range during highest mineral dust episodes in their study, suggested that this event showed super-µm nssSO₄²⁻, which was probably of pure Saharan origin. The



Fig. 5. Daily variability of $C_2O_4^{2-}$, nssSO₄²⁻ and nssCa²⁺ in coarse size range during the transitional period.

calculated ratios for cases 2 and 3 are close to the ratio (0.4 ± 0.1) observed by Putaud et al. (2004) and implies there was no enrichment of sulfate onto dust particles. On the other hand, cases 1 and 4 show about three times enhancements of $nssSO_4^{2-}$ compared to cases 2 and 3. For that reason, this enhancement might be attributed to significant SO_2 oxidation onto mineral dust particles or to a significant H_2SO_4 reaction with mineral dust particles.

As can be clearly seen from Fig. 5, oxalate shows highest concentrations in the coarse size range during the mineral dust episodes. Oxalate concentrations showed abrupt increases during the mineral dust outbreaks and indicated 2-4 times enhancement compared to the concentrations observed for the previous day. As a result, this enhancement might be attributed to significant oxidation of adsorbed gaseous precursors onto dust particles or coagulation between fine particles of oxalate and mineral dust particles. Although nitrate concentration for dust events is about two times higher than those for non-dust events, oxidation of gaseous precursors of nitrate onto dust particles or coagulation between fine particles of nitrate and mineral dust particles were not observed. This might be attributed to the accumulation of pollutant nitrate with the dust event following the mechanism suggested by Guo et al. (2004).

3.4. Influence of airflow on aerosol chemical composition

The result of cluster analysis for the whole dataset from April 2001 to 2002 is shown in Fig. 6. The diagram shows the means of clustered trajectories and calculated frequencies for each cluster, respectively. Beginning from the north-west, there are two clusters (1 and 2). First cluster shows trajectories with high wind speeds (long fetch) from the Atlantic Ocean, then passing through Europe and accounting for 5.3% of the airflow during the study period (hereafter EL). The second cluster also denotes north-westerly air flows but they are relatively slower than trajectories of the first cluster, and elucidating 8.2% of the trajectories, (ES) third and fourth clusters show short trajectories originating from north-west (Cluster 3; NWT) and north Turkey (Cluster 4; NT) and they represent 42.8% and 19.8% of the airflow, respectively. Air masses originating from the Middle East/Arabian Peninsula (Cluster 5; SE) and Eastern Saharan (Cluster 6: SAH) represent 9.6% and 7.8% of the trajectories. The last cluster shows trajectories traveling at high speeds, being maritime air masses from the western Mediterranean Sea, representing 6.6% of the airflow (hereafter MS).

In order to assess the influence of air mass movement on observed constituent concentrations,





clusters of trajectories were applied. The Kruskal– Wallis (K–W) test was applied to test for the presence of significant differences in water-soluble and trace metal concentrations categorized by trajectory clusters. Mean concentrations of watersoluble ions and trace metals in eastern Mediterranean aerosol representative of trajectory clusters are presented in Table 3.

3.4.1. PM₁₀

Application of the K–W test would indicate that there was a significant difference in concentrations of PM_{10} (p < 0.01). PM_{10} concentrations in Clusters 5 and 6 were found to be statistically higher than those calculated for the remaining clusters. These two categories are heavily affected by sea spray and crustal aerosol populations, which are the main agents of the eastern Mediterranean aerosol. Therefore, PM_{10} concentrations in the eastern Mediterranean are predominantly controlled by sea spray and crustal-derived aerosols.

3.4.2. Marine components (Na and Cl, Mg, Br; p < 0.006)

As can be seen from Table 3, sea salt aerosols had the highest concentrations under the influence of air mass originating from the south-east since trajectories swept over the Mediterranean Sea before arriving at the sampling site and hence enhances sea salt generation. For this category, calculated concentrations (Cluster 5: SE) are approximately 2.0–3.3 times higher than those calculated for other categories (as the site is more exposed to SE than W or wind speed for SE \gg than W sector).

3.4.3. Crustal components (Fe, Ti and Mn)

As expected, these trace metal aerosol exhibited their highest concentrations when the air masses originated from North Africa (Cluster 6, S), which are often associated with intense sporadic peaks of mineral dust. Crust-originated trace metals Fe, Ti and Mn concentrations in this category (Cluster 6) were found to be about 2–4 times higher than those observed for the remaining categories.

3.4.4. Primary anthropogenic components (V, Ni, Zn; p < 0.05)

V and Ni had statistically significant higher concentrations in trajectory Cluster 1 (NWL) and Cluster 2 (NW). Zn statistically showed lowest concentration under the influence of western Mediterranean airflow. According to the first report (2001) of European Pollutant Emission Register (EPER, which focuses on the prevention and control of pollutants; http://eper.cec.eu.int/eper/) the emission of nickel and its compounds are particularly affected by European countries Spain, Italy, Portugal, Germany, Belgium, United Kingdom and Netherlands (all have contributions higher than 4%). Consequently, it is more likely that airflow from the European continent makes significant contributions of V and Ni to aerosol collected at Erdemli (since air masses can pick up such compounds on both routes; NWL and NW).

Table 3

Mean concentrations of water-soluble ions and trace metals (in PM_{10}) as a function of the cluster corresponding to the 3-day air mass back trajectory arriving at Erdemli

Species	Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5	Cluster 6	Cluster 7
	EL	ES	NWT	NT	SE	SAH	MS
Na ⁺	2645	3667	3189	2450	8040	4050	3232
NO_3^-	1202	1526	1964	2220	1163	1815	1900
$nssSO_4^{2-}$	3467	3331	4064	5816	2982	4064	3503
$C_2 O_4^{2-}$	316	335	376	552	312	379	330
NH_4^+	807	596	844	1301	431	775	652
MS ⁻	13.9	20.4	24.5	36.9	8.7	22.9	22.7
Fe	246	352	313	322	363	763	318
Ti	15.3	25.5	23.8	23.6	27.8	67.5	26.2
Mn	5.9	9.6	6.6	7.1	7.0	14.7	6.4
nssCa ²⁺	1548	1862	1292	1195	1548	2315	1105
V	12.9	10.1	8.6	7.8	7.3	8.1	7.6
Ni	5.9	4.3	3.6	3.2	3.7	3.3	3.1
Cr	5.7	7.3	5.3	6.7	4.3	5.2	6
Zn	11.8	11.7	9.1	10.4	9.1	11.1	6.9
PM_{10}	33.52	40.0	34.3	31.5	56.1	51.4	29.7

3.4.5. $nssSO_4^{2-}$, NO_3^{-} , NH_4^+ , $C_2O_4^{2-}$ and MS^{-}

These water-soluble anions showed statistically significant higher concentrations in Cluster 4, under the influence of airflow from north Turkey. Kubilay et al. (2002) showed that $nssSO_4^{2-}$ and MS^{-} concentrations at Erdemli are affected by air mass flow from the Black Sea, which supplies the aforementioned ions due to DMS-producing species (such as coccolithophorids, flagellates, etc.). Hence, higher concentrations of $nssSO_4^{2-}$ and MS^- ($C_2O_4^{2-}$ as well) might be attributed to high biogenic activities taking place in the Black Sea. It is worth mentioning that the concentrations of $nssSO_4^{2-}$, NO_3^- , NH_4^+ , $C_2O_4^{2-}$ water-soluble ions are also likely to originate from pollution emissions. Urban agglomerations (such as Ankara, Konya) are attractive centers for gathering population (for example increased traffic) and industrial activities; therefore, such air masses can be loaded with these water-soluble ions since trajectories swept over large cities and industrialized parts of Turkey.

3.5. Aerosol ionic balance

An ionic balance (as mole equivalents) can be a useful tool to determine any possible missing ionic species. A plot of total cation equivalents against total anion equivalents for each size class is presented in Figs. 7a and b, respectively. The slope of the regression line for coarse particles indicates a value higher than unity (slope = 1.14, r = 0.97), which may be due to the existence of CO_3^{2-} in this size fraction, which has not been measured using IC. In contrast, the slope of the regression line for the regress

fine fraction is lower than unity (slope = 0.70, r = 0.97), which may be attributed to the presence of H⁺ (not measured) in the aerosol samples. If this is the case, CO_3^{2-} is expected to associate with Ca^{2+} and H⁺ is expected to react with SO_4^{2-} in the coarse and fine fractions, respectively (Figs. 8a and b). A statistically significant correlation was found when Ca^{2+} concentrations were plotted against the anion deficit, defined as an excess of positive charge, indicating that CO_3^{2-} is most probably the missing anion in the coarse aerosol fraction. A significant correlation was also found between SO_4^{2-} and the cationic deficiency in the fine fraction, that the cation deficiency, defined as an excess of negative charge, is possibly due to H⁺ associated with SO_4^{2-} .

Figs. 9a and b highlight the monthly variation of the sum of anions and cations as a function of the coarse and fine particles. It is apparent from Figs. 9a and b in the coarse fraction that the concentrations of anions and cations decrease from the winter towards the summer whereas in the fine fraction concentrations of anions and cations increase from winter towards summer. In the coarse fraction, anion deficiency is observed throughout the year (due to missing CO_3^{2-}). In the fine fraction with the exception of June-August the sum of anions matches the sum of cations, indicating almost complete neutralization of the aerosols. This is highlighted by a plot of total cation equivalent against total anions equivalent for winter and summer (Fig. 10a). The slope of the regression line for winter (slope = 0.95) shows value slightly lower than unity. However, the slope of the regression line for summer (slope = 0.66) is substantially lower



Fig. 7. Sum of the anions vs sum of the cations (a) regression analysis in coarse samples (b) regression analysis in fine samples.



Fig. 8. (a) Variation of anion deficit versus the Ca^{2+} concentrations in coarse samples, (b) variation of cation deficit versus the SO_4^{2-} concentrations in fine samples.



Fig. 9. Monthly variations of sum of cations and anions as function of particle size (a) coarse mode, (b) fine mode.

than unity. Furthermore, in winter almost all of the $nssSO_4^{2-}$ is neutralized by NH_4^+ (Fig. 10b). Therefore, $nssSO_4^{2-}$ can be assumed to exist as $(NH_4)_2SO_4$. However, in summer the amount of NH_4^+ is not sufficient to neutralize $nssSO_4^{2-}$ ($NH_4^+/$ $nssSO_4^{2-}$ equivalent ratio 0.65), thus implying the presence of a significant amount of H^+ . Indeed 35% of SO_4^{2-} in summer is associated with H^+ (see Fig. 10c).

3.6. Correlations between aerosol chemical compositions

The correlation coefficients (r) found for watersoluble ions and elements are shown in Table 4a and b for both coarse and fine particles, respectively.

3.6.1. Coarse particles

As expected, sea salt-associated ions (Na⁺, Cl⁻, Mg²⁺ and Br⁻) illustrate strong correlation coefficients (r > 0.90) between one another, denoting they are primarily originate from sea salt. The slope of

the regression line is 1.80 between Na⁺ and Cl⁻, which is identical to that reported for seawater. The slope of the regression line is 0.13 between Na⁺ and Mg²⁺, which is close to that reported for seawater. Sulfate (SO₄²⁻) also has a strong correlation coefficient (r > 0.85) between sea salt-associated ions, indicating significant contributions from sea salt generation to observed concentrations. Nitrate (NO₃⁻) and oxalate (C₂O₄²⁻) have strong correlations (r = 0.73) and may be attributed to heterogeneous processes on alkaline cations (originating from sea salt and mineral dust) surfaces.

As expected, crustal species Ti, Fe, Mn and Ca²⁺ exhibit strong correlations (r > 0.90). K has a strong correlation (r > 0.85) with crustal species and a moderate correlation coefficient with sea salt aerosol (r > 0.55). Therefore, K has a mixed origin; however, crustal material is the predominant source. V and Zn are moderately correlated with crustal species suggesting at least some of the measured concentrations of these elements are associated with crustal material. V and Ni also present strong M. Koçak et al. / Atmospheric Environment 41 (2007) 7351-7368



Fig. 10. (a) Sum of the anions vs. sum of the cations, (b) relationship between $nss SO_4^{2-}$ and NH_4^+ and, (c) variation of cation deficit versus the SO_4^{2-} concentrations for winter and summer.

correlation coefficients (r = 0.78) and imply residual oil combustion as a contributing source. Ca²⁺ (non-sea salt fraction) also has a significant correlation

coefficient (r = 0.70) with nssSO₄²⁻ and a moderate correlation coefficient with (r > 0.25) NO₃⁻, C₂O₄²⁻ and K⁺. Correlations between nssSO₄²⁻, NO₃⁻ and C₂O₄²⁻ suggest heterogeneous reactions between Ca²⁺ and aforementioned anions.

3.6.2. Fine particles

 Na^+ and Mg^{2+} have strong correlations (r = 0.70) and these cations also show a moderate correlation with Cl⁻, the most probable source being sea salts. Similar to coarse particles, crustal elements show strong correlation coefficients (r>0.80) in the fine particle fraction. K shows a moderate correlation coefficient $(r \sim 0.40)$ with crustal and sea salt aerosols. Hence, observed correlation coefficients imply crustal and sea salt contributions to fine K particles. Biomass and fossil fuel burning might be accounted as additional sources to fine K due to strong correlations with BC in summer and winter, respectively (Fig. 11). Likewise for the coarse fraction, V and Ni show strong correlation coefficients (r = 0.88) in the fine fraction, which would point to residual oil combustion as a source. The anion $nssSO_4^{2-}$ is significantly correlated with NH₄⁺ (r = 0.96), C₂O₄²⁻ (r = 0.86), MS^{-} (r = 0.76) and moderately correlated with K (r = 0.48). Same figures exist for oxalate (correlation with MS^- (r = 0.71), NH_4^+ (r = 0.83) and K (r = 0.64) and NH₄⁺ (correlation with MS⁻ (r = 0.67) and K (r = 0.42). In addition non-sea salt sulfate, NH_4^+ and $C_2O_4^{2-}$ have also statistically significant correlation coefficients (r > 0.70) with Zn. Usually Zn is considered an indicator of refuse incineration (Rahn and Huang, 1999). On the other hand, MS⁻ has only a natural source, arising from the precursor DMS (biogenic activity) through gas to particle conversions. Hence the observed correlations for non-sea salt sulfate, NH_4^+ and $C_2O_4^{2-}$ imply a common mixed origin (natural and anthropogenic).

Relationships between BC and other species were also investigated in 46 fine aerosol filter samples. BC presents a strong correlation only with excess potassium. Andreae (1983) suggested that the mass ratio of excess potassium to BC may provide information enabling the distinction between the K that would be produced by biomass burning and combustion sources. As can be inferred from Fig. 11, the excess potassium to BC ratio indicates two distinct ratios. The slope of the regression line in summer was found to be ~0.366 ($R^2 = 0.72$) and close to the values generally measured in aerosols

Table 4 Binary correlation coefficient matrix

	Ti	Fe	Mn	Ca ²⁺	Κ	Zn	V	Ni	Cr	Cl	Mg^{2+}	Na ⁺	Br^{-}	SO_4^{2-}	nssS	O_4^{2-}	$C_2 O_4^{2-}$	NO_3^-
(a) Coarse	particles																	
Ti	1																	
Fe	$0.99^{\rm a}$	1																
Mn	$0.97^{\rm a}$	$0.98^{\rm a}$	1															
Ca^{2+}	$0.91^{\rm a}$	0.93 ^a	$0.93^{\rm a}$	1														
K	$0.90^{\rm a}$	0.91 ^a	$0.87^{\rm a}$	0.91 ^a	1													
Zn	0.59	0.62	0.66	0.66	0.55	1												
V	0.59	0.61	0.64	0.65	0.53	0.65	1											
Ni	0.30	0.33	0.37	0.44	0.33	0.54	0.78	1										
Cr	0.22	0.27	0.28	0.26	0.18	0.22	0.29	0.25	1									
Cl ⁻	0.24	0.25	0.21	0.42	0.58	0.11	0.09	0.17	-0.02	1								
Mg^{2+}	0.34	0.35	0.30	0.50	0.67	0.16	0.14	0.18	0.01	$0.98^{\rm a}$	1							
Na ⁺	0.25	0.27	0.22	0.42	0.60	0.12	0.09	0.15	-0.02	$0.99^{\rm a}$	$0.96^{\rm a}$	1						
Br ⁻	0.25	0.26	0.22	0.43	0.57	0.15	0.11	0.18	-0.03	0.96^{a}	0.96^{a}	0.93 ^a	1					
SO_4^{2-}	0.53	0.54	0.50	0.66	0.78	0.34	0.31	0.25	0.07	0.89^{a}	$0.93^{\rm a}$	$0.89^{\rm a}$	$0.89^{\rm a}$	1				
$nssSO_4^{2-}$	0.70	0.70	0.69	0.70	0.67	0.52	0.50	0.29	0.18	0.30	0.41	0.27	0.36	0.68	1			
$C_2 O_4^{2-}$	0.38	0.39	0.44	0.37	0.33	0.36	0.23	0.12	0.15	-0.01	0.07	0.03	-0.01	0.28	0.53		1	
NO_3^-	0.27	0.28	0.31	0.22	0.15	0.29	0.12	-0.01	0.12	-0.19	-0.13	-0.16	-0.19	0.09	0.44		0.73	1
	SO_4^{2-}	nss	SO_4^{2-}	NH_4^+	$C_2 O_4^{2-}$	MS ⁻	K	Mg^{2+}	Na ⁺	NO_3^-	V	Ni	Zn	Ti	Fe	Mn	Ca ²⁺	Cr
(b) Fine p	oarticles																	
SO_4^{2-}	1																	
$nssSO_4^{2-}$	$0.99^{\rm a}$	1																
NH_4^+	$0.96^{\rm a}$	0.	96 ^a	1														
$C_2 O_4^{2-}$	$0.86^{\rm a}$	0	86 ^a	$0.83^{\rm a}$	1													
MS ⁻	0.76	0	76	0.67	0.71	1												
K	0.46	0	46	0.42	0.64	0.42	1											
Ma^{2+}	0.40	0.	26	0.42	0.34	0.42	0.20	1										
Na ⁺	0.20	0.	24	0.12	0.34	0.35	0.20	0.70	1									
NO ⁻	0.24	0.	09	0.12	0.30	0.20	0.15	0.70	0.09	1								
NO ₃	0.08	0.	20	0.17	0.21	0.02	0.05	0.05	0.00	0.55	1							
V NT	0.39	0.	.39	0.49	0.45	0.24	0.41	-0.13	-0.10	0.55	1							
N1	0.33	0.	.33	0.41	0.41	0.23	0.46	-0.08	-0.10	0.49	0.88	1						
Zn	0.73	0.	/3	0.75	0.75	0.47	0.54	0.16	0.12	0.23	0.53	0.50	1					
Ti	0.01	0.	01	0.03	0.16	0.19	0.49	0.32	0.05	0.07	0.19	0.41	0.24	1				
Fe	0.08	0.	.08	0.01	0.17	0.17	0.49	0.34	0.06	0.11	0.20	0.41	0.25	$0.96^{\rm a}$	1			
Mn	0.12	0.	13	0.07	0.19	0.23	0.49	0.29	-0.01	0.16	0.27	0.47	0.38	0.86^{a}	0.89^{a}	1		
Ca^{2+}	-0.02	-0.	.03	-0.08	0.08	0.06	0.46	0.29	0.06	0.13	0.27	0.42	0.19	0.80^{a}	0.83^{a}	0.79	1	
Cr	0.02	0.	02	0.01	0.04	0.05	0.12	0.04	-0.05	0.07	0.12	0.10	0.05	0.08	0.29	0.21	0.12	1

Italic fonts show moderate correlation coefficient. ^aStrong correlation coefficient.



Fig. 11. Relationship between excess potassium and black carbon in summer and winter.

dominated bv biomass burning (0.21 - 0.46)Andreae, 1983). Therefore, the observed ratio implies that biomass burning makes an important contribution to fine BC in the summer. However, the slope of the regression line in winter was about $(0.062; R^2 = 0.89)$ 5 times lower than that found in summer and is similar to those found in an urban atmosphere dominated by fossil fuel burning (K/BC = 0.025-0.09, Yang et al., 2005). Hence an excess K-BC ratio suggests that fossil fuel burning predominate the source of fine BC particles during winter. In order to support this suggestion, both air mass trajectories and MODIS fire maps for summer and winter were used. Indeed, summer (unlike to winter) trajectories (mostly originated from Black Sea and Mediterranean coastal regions) and MODIS fire maps (shows very active forest fires Black Sea and Mediterranean coastal regions) suggest biomass burning as main source of BC in this period.

3.7. Seasonal variation of the PM_{10} chemical composition

Fig. 12 presents monthly source apportionment analysis for coarse and fine modes, respectively. Chemical composition was defined by four main classes: dust, sea salt, ionic mass and "unidentified", the later accounting mainly for BC and OC.

Dust levels have been calculated using Fe or Ti as an indicator of crustal material. The total amount of mineral dust was estimated using Fe concentrations assuming a relative ratio to the upper crust of



Fig. 12. Monthly source apportionment analysis for PM_{10} .

3.089% (Wedepohl, 1995). The sea salt contribution was calculated from Na⁺ concentrations, assuming that Na⁺ has a pure marine origin. Finally, ionic mass is the sum of $nssSO_4^{2-}$; NO₃⁻, $C_2O_4^{2-}$, NH₄⁺, $nssK^+$ and $nssMg^{2+}$. Non-sea salt levels of the species were calculated using Na⁺ as the tracer and a standard sea water composition (Turekian, 1976).

As expected, the highest sea salt contribution was observed in winter. Sea salt contribution ranged from 35% to 50% in winter (January, February and December). Its contribution gradually decreased from winter to summer. During the summer (June-September), sea salt accounted for 25% of the PM_{10} . The highest dust contribution was observed during the transition period (March-May) and accounted for more than 40% of PM₁₀. This trend is related to the frequent occurrence of Saharan dust transport to the eastern Mediterranean during the transition season (for more details see Section 3.3). Secondary aerosol contribution $(nssSO_4^{2-}, NO_3^{-} and NH_4^{+})$ showed lower contributions in winter and its contribution sharply increased from winter to summer. Secondary aerosol contributions in summer (ranged from 30% to 35%) were three times higher than those for winter (ranged from 8% to 12%). The unidentified mass might be attributed to residual water associated with aerosol and BC/organic carbon, which was not measured for all samples and accounts for about 20% of the PM_{10} mass in agreement with studies carried out by Putaud et al. (2004) and Gerasopoulos et al. (2006).

4. Conclusion

Chemical composition of the fine $(PM_{2.5})$ and coarse $(PM_{10-2.5})$ fraction of aerosol samples was investigated at a coastal rural site in the north-eastern Mediterranean.

 PM_{10} mass is dominated by coarse fraction, which accounts for about 75% of the total PM_{10} concentration. Crust (Fe, Ti, Mn, Ca), sea salt (Na⁺, Cl⁻, Mg²⁺, Br⁻)-originated species and NO₃⁻ are associated mainly with coarse particles (>75%) whilst trace elements Cr and Ni and water-soluble ions nssSO₄²⁻, C₂O₄²⁻, MS⁻ and NH₄⁺ are primarily found in the fine fraction (>60%). V and Zn are found to be equally distributed between coarse and fine particles.

Aerosol species concentrations exhibit an order of magnitude change from day to day and the aerosol chemical composition is heavily influenced by dust transport from North Africa. For the whole sampling period, 11 specific mineral dust events (with duration from one day to a week) were identified with Fe concentrations ranging from 500 to 7000 ng m⁻³, demonstrating a large variability of the dust events with time. Investigation of strong dust events (nssCa²⁺ > 5000 ng m⁻³) shows that for two events nssSO₄²⁻ and oxalate were enriched in the coarse fraction. Such enrichments might be attributed to the significant oxidation of gaseous precursors onto dust particles or to the coagulation between fine and coarse particles.

Anthropogenic trace elements V and Ni present higher concentrations under the influence of European airflow whereas water-soluble ions ($nssSO_4^{2-}$, NO_3^- , NH_4^+ , $C_2O_4^{2-}$ and MS^-) demonstrate higher concentrations under the influence of airflow from North Turkey.

According to an ionic balance, coarse and fine fractions are dominated by cations and anions, respectively. A relationship between Ca^{2+} and anion deficiency implies that CO_3^{2-} is most probably the missing anion in the coarse fraction whereas significant correlation between SO_4^{2-} and cation deficiency in the fine fraction is might be a consequence of H⁺-associated SO_4^{2-} .

Investigation of the relationship between $nssSO_4^{2-}$ and NH_4^+ indicates that sulfate particles are not sufficiently neutralized by basic NH_4^+ . Equivalent ratio ($NH_4^+/nssSO_4^{2-} = 0.68$) exhibits that about 70% of the $nssSO_4^{2-}$ is neutralized by NH_4^+ . Excess-K/BC presents two distinct ratios for winter (0.066) and summer (0.366), indicating two contrasting BC sources in the area. These ratios suggest that in the winter BC mainly originates from fossil fuel burning whilst it is predominantly emitted from biomass burning in the summer.

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