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Ionic composition of lower tropospheric aerosols at a Northeastern Mediterranean site: implications regarding sources and long-range transport

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Abstract

Daily bulk aerosol filter samples were collected at Erdemli (36.6°N, 34.3°E) on the Mediterranean coast of Turkey for a 4-year period between 1996 and 1999. Concentrations of the water-soluble ions (Cl^-, Br^-, NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, MSA^-, Na^+; NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were measured in a total of 610 samples. In addition, three-dimensional (3-D), 3-day back trajectories of air masses arriving daily at Erdemli were calculated to determine potential aerosol source regions. The results indicated that the seasonal variability of atmospheric concentrations for ionic species at Erdemli were related to precipitation events. The atmospheric concentration of measured species (except those of a marine origin) decreased to minimum values during winter, whereas, during dry summer months the lack of precipitation resulted in their accumulation in the atmosphere. During the transition periods, although there was still precipitation, crustal ions (mainly nss-Ca^{2+} and in lesser extent nss-K^+ and nss-Mg^{2+}) exhibited sporadic but intense concentration peaks due to the intrusion of dust from the Sahara and the Arabian Peninsula. The results obtained from factor analysis and inter-species correlation suggested the presence of three main sources influencing concentrations: crustal, marine and anthropogenic sources. Multiple regression analysis indicated that the main non-sea-salt ions were associated with the formation of NH_4HSO_4, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $CaSO_4$ and $CaCO_3$. Formation of NH_4NO_3 and partial neutralization of H_2SO_4 by NH_4^+ and Ca^{2+} was found to occur mainly in summer.

Keywords: Aerosol; Eastern Mediterranean; Water soluble major ions; Seasonal variation; Long-range transport

1. Introduction

The Mediterranean Sea is a semi-enclosed sea, surrounded by the three continents of Europe, Africa and Asia; with a narrow connection to the Atlantic Ocean through the Strait of Gibraltar. It contains some of the most extreme oligotrophic waters in the world with an increase in oligotrophic nature to the east. The Mediterranean is sensitive to hazardous pollutants and/or nutrient ions through either input from rivers or deposition from the atmosphere. Initially, it was assumed that the main source of material to inland seas such as the Mediterranean was through the discharge of waste into coastal waters. However, it is now accepted that the atmospheric path may be quantitatively equal or more important for certain type of species (Turley, 1999).

The atmospheric transport and deposition of aerosols may also affect both the climate and the hydrological cycle of the Mediterranean (Lelieveld et al., 2002). The magnitude of the effects of aerosols on ocean productivity, hydrological cycle, and climate of the

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Mediterranean are currently poorly understood, owing to a limited knowledge of the processes that influence the distributions, as well as the physical, chemical and optical properties of aerosols. Studies performed in the Eastern Mediterranean suggest that the composition of the aerosol burden is significantly affected by both anthropogenic and natural sources. The anthropogenic component mainly consists of sulfate and carbonaceous particles, that have undergone long-range transport from Europe and Asia. Natural aerosol components are dominated by sea salts, mineral dust particles and biogenically produced sulfur aerosols (Mihalopoulos et al., 1997; Kubilay et al., 2000, 2002; Özsoy et al., 2000; Formenti et al., 2001; Andreae et al., 2002; Sobanska et al., 2003).

The current study reports 4-year measurements on the aerosol ionic composition at a rural site in the Eastern Mediterranean. The aim is to define the chemical composition of the aerosols, determine the factors controlling both short- (daily) and long-term (seasonal) variation, and finally assess the relative contribution of natural and anthropogenic sources over the Eastern Mediterranean.

2. Methods

The sampling station (Erdemli, 36.6°N, 34.3°E), occupied throughout the current study, lies midway along the eastern Mediterranean coast of Turkey and is surrounded by densely cultivated orchards and vegetable farms (Fig. 1a). Bulk aerosol samples were collected from a 21 m atmospheric sampling tower located on the harbour jetty of the Institute of Marine Sciences during the sampling periods of January–December 1996, January–May 1997, February–December 1998, and January–December 1999 on Whatman-41 filters using a high-volume sampler. During this period a total of 610 aerosol samples were collected. Sampling was carried out at daily intervals except over weekends and holidays when multi-day samples were taken. For more details on the local conditions of the sampling site and aerosol collection methodologies please refer to Kubilay and Saydam (1995), Kubilay et al. (2000, 2002) and Özsoy et al. (2000).

One-eighth of each sample and blank filter was extracted using 20 ml of nanopure water. The solutions obtained were analyzed at the University of Crete by ion chromatography (IC) for anions (Cl^-, Br^-, NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, MSA^-) and cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}). More details on the analytical technique are given by Kouvarakis et al. (2002a) and Bardouki et al. (2003).

To assess the blank contributions from the filter papers several ($n = 52$) filters were analyzed for the ions of interest. For all cations and anions the contribution from Whatman-41 filter papers was found to be less than 2% and 6%, respectively, throughout the sample collection period at Erdemli. Using the total procedural blank concentrations and the average-sampled volume of 1773 m^3, the calculated detection limits in aerosol samples (in ng m^{-3}) were: Cl^- (15), Br^- (1), NO_3^- (4), SO_4^{2-} (7), $C_2O_4^{2-}$ (3), Na^+ (28), NH_4^+ (20), K^+ (4), Mg^{2+} (10), and Ca^{2+}(51).

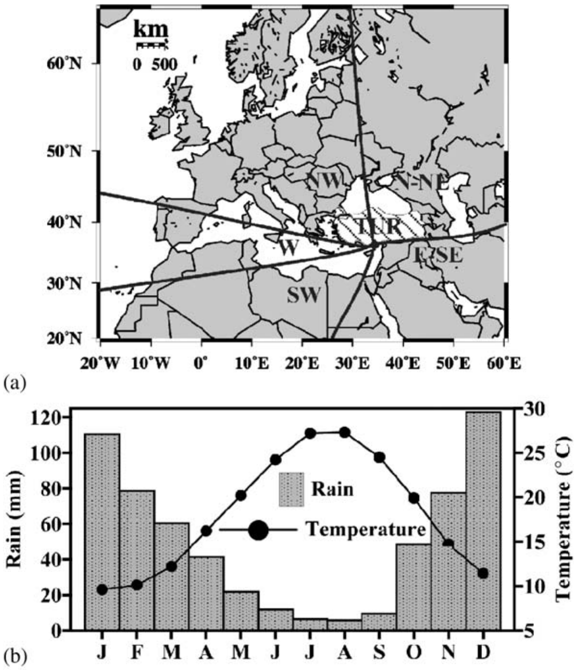


Fig. 1. (a) Classification of 3-day back trajectories ending at Erdemli. Major airflow sectors are also illustrated, (b) monthly average amount of precipitation and temperature (29 years) at the Erdemli station.

Three-dimensional (3-D), 3-day backward trajectories of air masses arriving at the sampling point on 12:00 UT at pressure levels of 900 and 850 hPa within the boundary layer and 700 and 500 hPa within the free troposphere were calculated for each aerosol sampling day. The trajectory model of the European Center for Medium-Range Weather Forecasts (ECMWF) in Reading, England was applied to 3-D analyzed wind fields available from the MARS archive of ECMWF.

3. Results and discussion

3.1. Climatological conditions

Monthly average atmospheric temperatures (°C) and rainfall (mm) for a 29-year period (1971–1999) at the Erdemli station are presented in Fig. 1b. It is clear that the sampling site is mostly wet during the winter period and dry in the summer months. The local ambient temperature (which is affected by solar radiation) starts to increase in April and reaches its maximum in July–August (approx. 27°C) after which it decreases to a minimum of 10°C during January. In the summer months, the removal of aerosol particles by wet deposition is minimal and the possibility for photochemical formation of aerosol particles from their gaseous precursors is at a maximum. During the summer, the whole Mediterranean region becomes dry, and the atmospheric transport of aerosols from distant origins is most efficient. Accordingly, the maximum concentration of measured aerosol components are expected to be relatively higher in the summer months compared to those observed during the winter months.

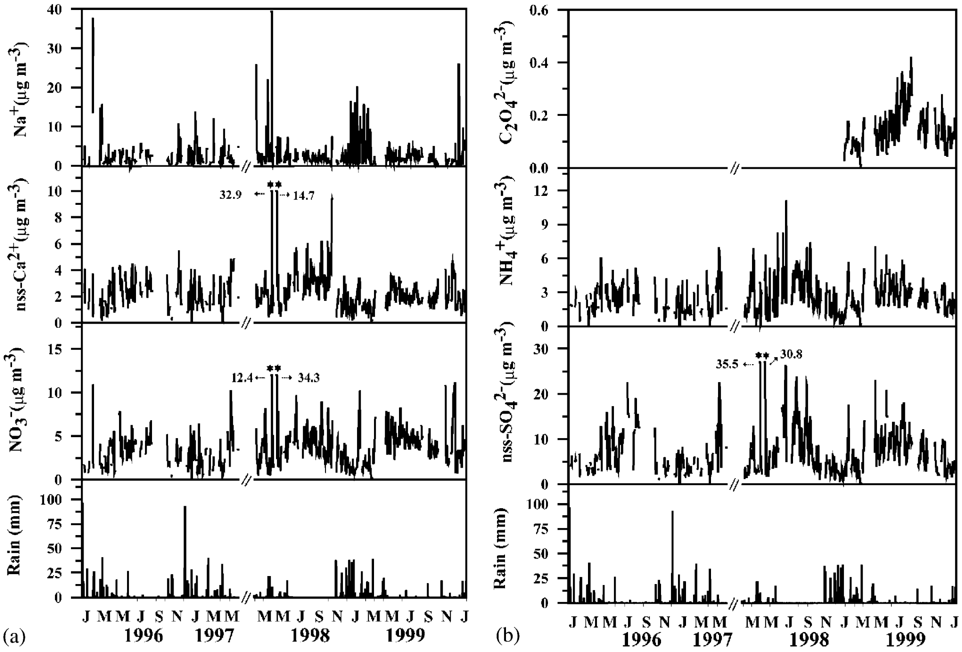
In order to identify the potential importance of different source regions on aerosol composition at the sampling site the air mass trajectories were classified into six airflow sectors according to trajectory direction. They were separated also into long- and short-range flows according to distance of air transport. These categories are as follows (Fig. 1a):

(1) north–northeast (N–NE) sector includes the Former Soviet Union as well as the eastern Black Sea and eastern Anatolia, (2) northwest (NW) sector includes eastern and western Europe as well as the western Black Sea and western Anatolia, (3) southwest (SW) sector includes northwest Africa and short trajectories (SW_s) that have flow from the open Mediterranean, (4) east–southeast (E–SE) sector includes eastern Africa as well as the Arabian Peninsula, (5) western (W) sector includes the long fetch of maritime air masses, and (6) an additional sector (TUR) includes short trajectories that spend most of their time over Turkey.

3.2. Aerosol composition and seasonal cycles

The temporal variations in the concentrations of ions (Na^+, nss-Ca^{2+}, NO_3^-, $C_2O_4^{2-}$, NH_4^+, nss-SO_4^{2-}) characteristic of sources such as sea salt, soil, combustion, agricultural activities, and biogenic activities as well as daily local rainfall between January 1996 and December 1999 are given in Figs. 2a and b. It is apparent, that the concentrations of all species are highly variable on a daily time scale. During rainy days aerosol constituent concentrations demonstrated a drastic decrease, since wet deposition scavenges the particles from the atmosphere very efficiently. Concentrations may change an order of magnitude from day to day. Such high daily variation in the concentrations of trace species has been previously reported over the Mediterranean atmosphere (Bergametti et al., 1989; Kubilay and Saydam, 1995; Güllü et al., 1998; Guerzoni et al., 1999).

Sea-salt components (Na^+, Cl^-, Mg^{2+} and Br^-) demonstrated higher concentrations and stronger variations during the winter season. Daily variability of these components is due to the local meteorological factors.



(a) (b)

Fig. 2. (a,b). Temporal variations in the concentrations of ions (Na^+, nss-Ca^{2+}, NO_3^-, $C_2O_4^{2-}$, NH_4^+, nss-SO_4^{2-}) characteristic of sources like sea-salt, soil, combustion, agricultural activities and biogenic activities with daily local rainfall between January 1996 and December 1999.

Storms are more frequent and more active during the winter period, therefore these weather conditions enhanced the concentration of sea salts throughout the winter time; whereas, during the summer period sea salt generation is at minimum owing to relatively weaker winds and a calmer sea surface.

Short-term changes in the concentrations of soil dust tracers such as nss-Ca^{2+} are also noted in Fig. 2b. Low concentrations are frequently observed during the winter when the soil on both the local and surrounding land masses is damp due to precipitation. During the transitional seasons (spring and autumn) high concentrations of nss-Ca^{2+} and other crustal ions are observed when the air mass trajectories originate from North Africa and occasionally from the Middle East, and are often associated with intense episodic peaks of mineral dust (Koçak, 2001). Between these events the concentrations diminish to comparable magnitudes to those observed during the winter. It was noted that during the summer period concentrations of these ions varied less markedly. Since the soil is dry in summer, this period is favorable for the resuspension of local soil particles.

Concentrations of pollution derived ions such as nss-SO_4^{2-}, NO_3^- also demonstrated a daily variation. During the winter period these ions exhibited lower concentrations compared to those detected during the summer season. This difference may be attributed to the accumulation of particles in the atmosphere during the summer owing to the lower rate of removal via wet deposition. Photochemical formation, which becomes active under summer conditions (high solar radiation and temperatures), also enhances the concentrations of nss-SO_4^{2-} and NO_3^-.

Ammonium, and oxalate, display seasonal cycles with a minimum in winter and a maximum in summer, similar to that observed for nss-SO_4^{2-}, and NO_3^-. Photochemistry, as well as increased traffic owing to greater tourism and the burning of vegetation and forest around the vicinity may be sources of oxalate, leading to its enhanced concentrations. The existence of oxalate in tropospheric aerosols and precipitation has been demonstrated, and a significant correlation of air-borne oxalate with nitrate has been noted, suggesting a pollution source (Norton et al., 1983). It has been further postulated that the mechanism of oxalate production occurs via gas or aerosol-phase photo-oxidation of aromatic hydrocarbons (Kawamura et al., 1996). The observed high oxalate concentrations during the summer period at Erdemli could be also partly attributed to marine biogenic emissions (Kawamura and Sakaguchi, 1999). Additionally during the summer the ambient air temperature is high and the soil is dry favoring enhanced ammonia fluxes to the atmosphere. These conditions may cause profound summer peaks in the ammonium concentration.

Table 1 presents statistics for the aerosol dataset over the 4-year period, including arithmetic and geometric mean concentrations as well as their standard deviations, median, maximum, and minimum concentrations. As can be seen from Table 1, the geometric mean and the median values are very similar which implies that the concentrations of the ions have approximately log-normal frequency distribution. The log-normal distribution of the atmospheric concentrations of the ionic species were verified by a goodness of fit test (Kolmogorov–Smirnov test) using ‘Statistica’ statistical software. The population distribution for the aerosol ionic species was found to be of a log-normal type within the 95% confidence level.

Crustal species exhibited higher concentrations than those detected at other European coastal sampling sites, but were similar to the values reported for other Eastern Mediterranean areas such as Sde Boker, Israel of the Negev desert (Formenti et al., 2001; Andreae et al., 2002) and Finokalia, Crete (Mihalopoulos et al., 1997). These concentrations may be explained by the semi-enclosed Mediterranean region being surrounded by arid and semi-arid regions. Sea-salt aerosol concentrations are also elevated, as one would expect for a coastal sampling station.

For nss-SO_4^{2-} both the concentrations and the seasonal amplitude are consistent with previous studies performed in the Eastern Mediterranean (Luria et al., 1996; Güllü et al., 1998; Kouvarakis et al., 2002a). The sulfate levels at Erdemli confirm the very high sulfate concentrations observed over the Mediterranean by the other studies, levels which are comparably higher than those over continental Europe (EMEP web site; http://www.emep.int).

Table 1
Summary of statistics of the chemical composition of aerosols ($\mu g\,m^{-3}$, σ: standard deviation) at Erdemli during the period January 1996–December 1999 ($n = 610$)

	Arithmetic mean (σ_a)	Geometric mean (σ_g)	Median	Min–Max
Na^+	2.87 (4.05)	1.78 (2.6)	1.86	0.02–39.41
Cl^-	4.63 (7.31)	2.69 (2.7)	2.49	0.01–69.44
Mg^{2+}	0.44 (0.48)	0.32 (2.2)	0.32	0.00–4.84
nss-Mg^{2+}	0.09 (0.12)	0.08 (2.6)	0.09	0.00–1.47
Br^-	0.02 (0.02)	0.01 (2.1)	0.01	0.00–0.24
K^+	0.30 (0.24)	0.25 (2.0)	0.25	0.00–2.78
nss-K^+	0.19 (0.16)	0.15 (2.2)	0.15	0.00–1.32
Ca^{2+}	2.66 (2.16)	2.18 (2.1)	2.42	0.00–34.46
nss-Ca^{2+}	2.55 (2.11)	2.04 (2.2)	2.33	0.00–32.96
NO_3^-	3.34 (2.46)	2.63 (2.3)	3.10	0.00–34.26
$C_2O_4^{2-}$	0.17 (0.14)	0.09 (5.4)	0.16	0.00–1.19
NH_4^+	2.22 (1.40)	1.74 (2.5)	1.89	0.00–9.56
SO_4^{2-}	7.50 (5.29)	6.02 (2.2)	5.78	0.01–45.39
nss-SO_4^{2-}	6.78 (5.17)	5.13 (2.4)	5.10	0.00–35.47
MS^-	0.04 (0.05)	0.02 (3.6)	0.02	0.00–0.38

Levels of NO_3^- and NH_4^+ at Erdemli are higher by a factor of 3–4, compared to those at Finokalia (Kouvarakis et al., 2001) while being comparable to the levels reported by Herut et al. (1999) for Israel. At Israel and Erdemli, aerosols were collected on Whatman-41 filters, whereas at Finokalia aerosols were collected on Teflon filters. Because Whatman 41 filters, are known to collect HNO_3 vapor in addition to NO_3^- with a sampling efficiency higher than 95% (Savoie et al., 1992), we assume our measured NO_3^- concentrations to be those of total inorganic NO_3^-, i.e. particulate NO_3^- plus gaseous HNO_3. Assuming that gaseous HNO_3 levels at Erdemli are comparable to NO_3^-, as in Finokalia (Kouvarakis et al., 2001), a significant part of the difference regarding the NO_3^- levels can be explained. However, local anthropogenic activities at Erdemli such as traffic and fertilizer use, as reported by Özsoy et al. (2000) could also account for the high NO_3^- and NH_4^+ levels (see Section 3.4).

Finally the oxalate levels, especially those reported during summer are in very good agreement with the values reported by Bardouki et al. (2003) for Finokalia during summer. Such levels are amongst the highest reported in the literature for rural areas or even for urban areas (Kawamura and Ikushima, 1993). The high insolation and the high levels of O_3 prevailing during summer above the Mediterranean region (Kouvarakis et al., 2002b) could account for the very high concentrations of oxalate.

3.3. *Factors controlling the levels of ions*

It is clearly seen in Section 3.2 that the two main factors controlling the ionic species in the atmosphere are rainwater frequency and air mass origin. Average ion concentrations for wet winter months (J,F,N,D) and dry summer months (J,J,A,S) and the dry/wet concentration ratios for ions are presented in Table 2. It is apparent from the table that all species, except marine ions (Cl^-, Br^-, Na^+, Mg^{2+}) and K^+, have higher average concentrations during dry months. The corresponding ratios varied between 1.46 and 2.58. The differences in the ratios may be explained by differences in scavenging efficiencies of different sized particles and elemental solubility in rainwater (Buat-Menard and Duce, 1986; Galloway et al., 1993). Galloway et al. (1993) have shown that the scavenging ratios vary significantly from one species to another, with ions associated with the largest-sized aerosol fraction being scavenged most efficiently.

Kubilay and Saydam (1995) stated that crustal ions are dominated by coarse particles having diameters larger than 10 μm; whereas, anthropogenic ions are mainly associated with fine particles (Bardouki et al., 2003). As expected, crustal ions are scavenged from the atmosphere more efficiently by local rain events compared to anthropogenic ions.

Table 2
The ratio of average ion concentrations (μg m^{-3}) in dry summer (J, J, A, S) to wet winter (J, F, N, D) months

	Dry months ($n = 497$)	Wet months ($n = 113$)	Dry/wet ratio
Na^+	2.38 ± 2.57	4.79 ± 7.13	0.50
Cl^-	3.66 ± 3.95	8.47 ± 12.83	0.43
Mg^{2+}	0.39 ± 0.32	0.63 ± 0.85	0.62
Br^-	0.02 ± 0.01	0.03 ± 0.05	0.67
K^+	0.30 ± 0.18	0.30 ± 0.38	1.00
nss-K^+	0.21 ± 0.16	0.12 ± 0.15	1.75
Ca^{2+}	2.98 ± 2.27	1.33 ± 0.85	2.24
nss-Ca^{2+}	2.89 ± 2.20	1.12 ± 0.71	2.58
NO_3^-	3.72 ± 2.50	1.83 ± 1.58	2.03
$C_2O_4^{2-}$	0.19 ± 0.14	0.13 ± 0.12	1.46
NH_4^+	2.46 ± 1.38	1.25 ± 0.96	1.97
SO_4^{2-}	8.15 ± 5.16	4.91 ± 4.99	1.66
nss-SO_4^{2-}	7.55 ± 5.15	3.70 ± 3.94	2.04
MS^-	0.05 ± 0.05	0.02 ± 0.03	2.50

In contrast, the concentration of sea salt components (Cl^-, Br^-, Na^+, Mg^{2+}) are higher (low ratio) during wet months, as rain events in the eastern Mediterranean are generally associated with frontal storms which enhance sea salt generation. The differences between observed ratios of SO_4^{2-}, Ca^{2+}, K^+ and their non-sea salt fraction can be attributed to the sea salt contribution on to the total concentrations of these ions. It is worthwhile to note that the difference between dry/wet concentration ratios for total K^+ and nss-K^+ is more dramatic than those observed for total levels and non-sea salt fractions of Ca^{2+} and SO_4^{2-}. The observed difference of dry/wet concentration ratios for K^+ and nss-K^+ can be attributed to a higher sea salt contribution to total K^+ than Ca^{2+} and SO_4^{2-}. Air mass origin can also influence ionic species levels especially during the intermediate season and during summer due to the absence of precipitation. Table 3 presents the distribution of 4 species (nss-Ca^{2+}, nss-SO_4^{2-}, NO_3^-, NH_4^+) for each sector identified in Fig. 1a. As expected during winter no significant sector predominates since rainwater is the main factor responsible for the variability of ionic species.

During the intermediate season characterized by Saharan dust outbreaks, the NO_3^- levels associated with transport along the SW sector (Sahara desert as denoted by the high nss-Ca^{2+} and other crustal species; Koçak, 2001) were higher by a factor of 1.4–1.8 compared to those associated with the transport along the rest of the sectors including Turkey. Dentener et al. (1996) suggested that mineral dust can significantly take up acidic gases such as HNO_3 and SO_2 from the atmosphere. Additionally, Mori et al. (1998) have suggested

Table 3
Role of air-masses origin on NO_3^-, nss-SO_4^{2-}, NH_4^+ and nss-Ca^{2+} levels

Ion species	Winter				Transition				Summer			
	NO_3^-	nss-SO_4^{2-}	NH_4^+	nss-Ca^{2+}	NO_3^-	nss-SO_4^{2-}	NH_4^+	nss-Ca^{2+}	NO_3^-	nss-SO_4^{2-}	NH_4^+	nss-Ca^{2+}
N–NE	1.51	2.67	1.24	1.55	3.32	4.63	1.81	2.43	4.54	10.03	3.15	2.58
NW	2.15	3.36	1.57	1.32	3.27	5.00	1.59	1.83	3.99	7.77	2.47	2.41
E–SE	2.47	3.60	1.37	1.94	5.74	6.47	1.84	5.46	—	—	—	—
SW	2.32	3.40	1.43	1.27	5.66	6.91	1.64	2.96	—	—	—	—
SWs	—	—	—	—	3.81	5.43	2.12	2.55	3.50	7.76	2.34	2.26
W	—	—	—	—	3.70	6.63	2.12	1.70	3.38	7.90	2.03	2.44
TUR	2.18	3.39	1.50	1.44	4.02	6.69	3.34	2.50	3.99	10.80	3.12	2.56

Geometric mean concentrations are given in $\mu g\,m^{-3}$.

that the calcite within dust particles reacts with ammonium sulfate in the atmosphere to form koktaite ($(NH_4)_2Ca(SO_4)_2 \cdot H_2O$) and finally gypsum ($CaSO_4$). It is interesting to note that the two highest values in NO_3^- were observed during an intense Sahara dust event (see Section 3.5) suggesting the important role of the interactions between acidic gaseous components of the atmosphere with mineral dust in the area. High values of nss-SO_4^{2-} observed under Saharan dust contributions corroborate the above hypothesis. During the intermediate season the highest levels of NH_4^+ are observed within Turkey, indicating an important role for local agricultural activities. Finally during summer, although no significant sector preference is observed for nss-Ca^{2+} and NH_4^+, for nss-SO_4^{2-} and in lesser extent for NO_3^- the highest values are associated with transport within the N/NE sector and Turkey.

3.4. Ion balance and interspecies correlation

When total equivalents of cations are plotted against total equivalents of anions, the slope of the regression line is slightly lower than unity (slope$=$0.95, $r^2 = 0.88$), which may be attributed to the presence of bicarbonate in the samples, not measured using the IC. However, a closer consideration of the regression between anions and cations identifies two distinct periods: A period with cation deficit occurring during summer (J, J, A, S) months (Case A); and a period with an anion deficit occurring mainly during the transition (M, A, M, O) and winter (J, F, N, D) months (Case B) (Fig. 3).

The significant correlation ($r^2 = 0.72$, $p = 0.001$, slope$=$0.61) found when Ca^{2+} is plotted against the anion deficit indicates that bicarbonate can indeed account for the missing anion during the second period. On the other hand, the cation deficit observed during the first period can be attributed to H^+. A similar conclusion was previously reported by Mihalopoulos et al. (1997) and Bardouki et al. (2003) for another Eastern Mediterranean site on Crete.

Contribution of both Br^- and MSA^- is less than 1% of the total anion composition, whereas, Cl^- (37.3%) and SO_4^{2-} (45.4%) contributed more than 80% of the total anion sum. NO_3^- and $C_2O_4^{2-}$contributed 16.2% and 1.1%, respectively.

Ammonium (29%), calcium (30%) and sodium (30%) contributed approximately 90% to the cation sum. K^+ and Mg^+ were minor contributors, only 8.2% and 1.8%, respectively. The most important acidic and alkaline species were nss-SO_4^{2-}, NO_3^- and Na^+, NH_4^+, nss-Ca^{2+}.

3.4.1. Correlations between aerosol chemical constituent concentrations

In aerosol data sets, a high correlation coefficient between two species indicates (i) similar production and/or removal mechanism and/or (ii) similar transport patterns. The correlation coefficients (r) between the measured ions are depicted in Table 4. As expected, marine ions (Cl^-, Br^-, Na^+ and Mg^{2+}, $p<0.00001$) have strong correlation coefficient between one another, indicating they are mainly derived from sea salt. Potassium (K^+) was not significantly correlated with natural (crustal and marine) species, but with anthropogenic species ($p = 0.001$). Therefore, in addition to natural sources, anthropogenic emissions from biomass burning can be suggested as another contributory source for K^+.

The anthropogenic ion nss-SO_4^{2-} was significantly ($p = 0.001$) correlated with NO_3^- ($r = 0.68$) and MSA ($r = 0.64$). Therefore it can be suggested that the observed concentration of the nss-SO_4^{2-} is associated with both anthropogenic and biogenic sulfur emissions. In addition, nitrate and non-sea salt sulfate were also significantly ($p = 0.01$) correlated with crustal ions, probably due to heterogeneous reactions occurring on aerosol surfaces or some fraction of these ions being derived from soil dust. NH_4^+ was significantly correlated with nss-SO_4^{2-} ($r = 0.71$). The slope of the regression between nss-SO_4^{2-} and NH_4^+ for the whole data set was

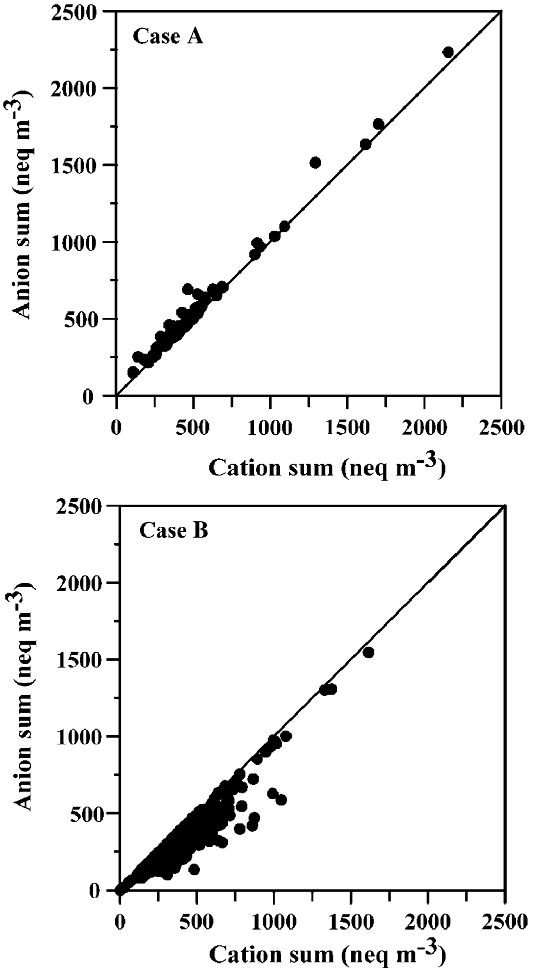


Fig. 3. Sum of anions vs. sum of cations (in nano-equivalent) during the two periods described. Case A, cation deficit—occurring during the summer (J, J, A, S) months. Case B, anion deficit—occurring mainly during the transition (M, A, M, O) and winter (J, F, N, D) months. The 1:1 line is also depicted.

0.53, which indicates partial neutralization of nss-SO_4^{2-} and would suggests that NH_4HSO_4 is mainly formed instead of $(NH_4)_2SO_4$. nss-Ca^{2+}, nss-Mg^{2+} and nss-K^+ can also neutralize nss-SO_4^{2-}. The slope of the regression between nss-SO_4^{2-} and nss-$(Ca^{2+}+Mg^{2+}+K^+)$ was 0.35 and may explain additional neutralization of nss-SO_4^{2-}. Therefore, it would appear that only 12% of the nss-SO_4^{2-} $(1-(0.53+0.35))$ is not neutralized.

3.4.2. Multiple regression analysis

Multiple regression analysis was used to identify the forms in which the most important ions, i.e. nss-Ca^{2+}, nss-SO_4^{2-}, NO_3^-, NH_4^+ exist in the Mediterranean atmosphere. For the multiple regression analysis two periods identified in Section 3.4 were considered: The first (period A) during the dry period when a cation deficit (H^+) existed and the second (period B) during the rest of the year when an anion deficit (bicarbonate) existed. For all scenarios described below the results were statistically significant with $p<0.001$. During case A, nss-SO_4^{2-} was mainly (55%) associated with NH_4^+, whereas nss-Ca^{2+} and H^+ accounted for 26% and 19%, respectively. This is in agreement with the numbers presented above which considered the whole data set. During case B, nss-SO_4^{2-} was again mainly (71%) associated with NH_4^+, whereas nss-Ca^{2+} accounted for the remaining 29%. In the case of nss-Ca^{2+}, during case A, nss-Ca^{2+} was mainly (66%) associated with NO_3^-, with nss-SO_4^{2-} accounting for the remaining 34%. During case B, the situation was quite different with NO_3^-, nss-SO_4^{2-}, and carbonate almost equally participating. The corresponding numbers were 40%, 30% and 30%, respectively.

For NH_4^+ although the majority was associated with nss-SO_4^{2-}, there was a small part (17%) mainly during the dry period present in the form of NH_4NO_3, which could result either from gas-phase reactions of NH_3 with HNO_3 or by volatilization/soil resuspension of NH_4NO_3 from agricultural land, since NH_4NO_3 is a commonly used fertilizer. Gas-phase measurements of NH_3 and HNO_3 as well as size-segregated samples will help us to identify the main source of NH_4NO_3 in the area. Finally NO_3^- was mainly associated with nss-Ca^{2+} and NH_4^+. Especially during the dry period (period A), when 57% of NO_3^- was associated with nss-Ca^{2+} and the remaining part 43% existed in the form of NH_4NO_3. During the period B, NO_3^- was mainly coupled with nss-Ca^{2+} (87%) and only a residual fraction of 13% appeared as NH_4NO_3.

It is worthwhile to note that in rural sites aerosols are imported from long distances. During long-range transport different air masses might be mixed and cause relative dilution or enrichment of ions, and/or heterogeneous chemical reactions between mineral particles and acidic species may occur. Consequently, in rural studies, strong correlation coefficients between measured variables do not necessarily indicate similar sources. Factor analysis offers a more versatile statistical tool to distinguish between possible sources.

3.4.3. Factor analysis

The results of varimax-rotated factor analysis are given in Table 5. Only factor loadings larger than 0.30 were included in the table, smaller loadings (<0.30) were considered to be 'insignificant'. The data can be interpreted on the basis of five common factors accounting for 94.0% of the total variance in the system. The first factor has high loadings of Cl^-, Br^-, Na^+, Mg^{2+} and moderate loadings of Ca^{2+}, K^+. Factor 1 is strongly dependent on the concentrations of Cl^-, Br^-, Na^+ and Mg^{2+} and is attributed to the

Table 4
Binary correlation coefficient matrix of aerosol data at Erdemli

	Na^+	Cl^-	Mg^{2+-}	Br^-	K^+	Ca^{2+}	NO_3^-	$C_2O_4^{2-}$	NH_4^+	SO_4^{2-}	NSSS[a]	MS^-
Na^+	1.00											
Cl^-	0.99	1.00										
Mg^{2+-}	0.97	0.96	1.00									
Br^-	0.94	0.95	0.93	1.00								
K^+	0.76	0.74	0.79	0.80	1.00							
Ca^{2+}	0.50	0.46	0.55	0.57	0.78	1.00						
NO_3^-	0.08	0.03	0.16	0.15	0.44	0.58	1.00					
$C_2O_4^{2-}$	0.06	0.06	0.09	0.06	0.20	0.13	0.41	1.00				
NH_4^+	0.12	0.17	−0.07	0.09	0.17	0.29	0.51	0.25	1.00			
SO_4^{2-}	0.32	0.24	0.39	0.32	0.56	0.66	0.67	0.30	0.65	1.00		
NSSS[a]	0.13	0.05	0.21	0.15	0.42	0.58	0.68	0.31	0.71	0.98	1.00	
MS^-	0.03	0.11	0.01	0.10	0.14	0.22	0.42	0.26	0.44	0.60	0.64	1.00

[a] NSSS symbolizes the non-sea-salt sulfate.

Table 5
Varimax rotated factor matrix and corresponding probable source type for the complete data set

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communalities
Na^+	0.99					0.99
Cl^-	0.99					0.99
Mg^{2+}	0.97					0.95
Br^-	0.96					0.93
K^+	0.78	0.50				0.83
Ca^{2+}	0.48	0.79				0.74
NO_3^-		0.79			0.36	0.63
$C_2O_4^{2-}$					0.96	0.28
NH_4^+			0.94			0.53
nss-SO_4^{2-}		0.53	0.57	0.49		0.80
MS^-				0.95		0.50
Eigenvalue	4.7	1.9	1.4	1.3	1.1	
%Variance	42.5	17.2	12.5	11.6	10.2	94.0
Probable source	Marine	Crustal	Combustion	Biogenic	Photochem.	

sea-salts components in the Erdemli aerosol population. Therefore, this factor is identified as the marine factor and explains 42.5% of the total system variance.

The second factor accounts for 17.2% of the total variance in the system and can be identified as a crustal factor, because it includes high loadings of crustal ions, nss-Ca^{2+} and compounds associated with nss-Ca^{2+} (such as NO_3^- and nss-SO_4^{2-}). Factor 3 is highly loaded in nss-SO_4^{2-} and NH_4^+ and represents the fossil fuel combustion including a possible influence from biomass burning. This factor explains a further 12.5% of the variance. Factor 4 accounts for 11.6% of the total variance and can be identified as a marine biogenic factor since it is highly loaded in MSA^- and moderately loaded with SO_4^2. Factor 5 (10.2% of the total variance) is highly loaded in oxalate, and moderately loaded with NO_3^- and could be attributed to photochemistry. The cumulative variance explained by the marine (Factor-1), crustal (Factor-2) and biogenic (Factor-4) is 71.3%, supporting an earlier conclusion by Özsoy et al. (2000) on the greater influence of natural sources compared to anthropogenic emissions in the region.

3.4.4. *Chlorine deficit*

Na^+ and Cl^- are the major ions in sea salt. Cl^- and Br^- however are generally poor reference ions of seawater. Br^- has an additional anthropogenic source since it originates from motor vehicle emissions. Cl^- is also emitted from biomass burning (Andreae et al., 1998). Cl^- is a non-conservative element since it reacts in aerosols with acidic species (both inorganic and organic acids) [$Cl^- + H^+ \rightarrow HCl\ (g)$], leading to Cl^- depletion. The extent of chloride depletion in the coarse mode decreases with increasing particle size (Zhuang et al., 1999).

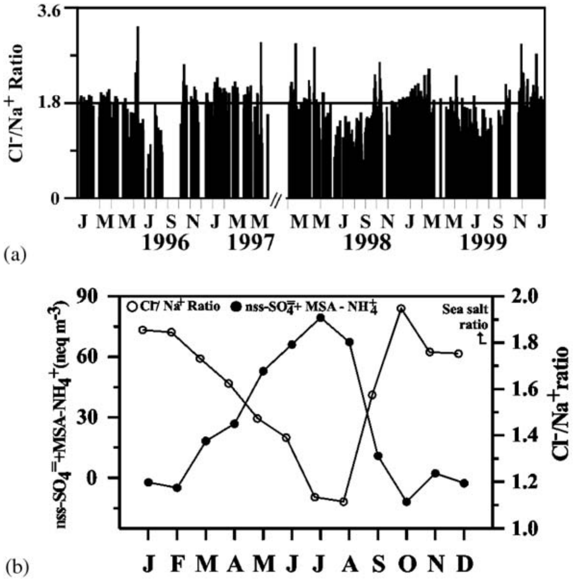


Fig. 4. (a) Seasonal variation of the Cl/Na ratio and (b) variation of the Cl/Na ratio and acidity in excess (defined as the difference between the sum of (nss-SO_4^{2-} + MS^-) and $NH4^+$; see text).

Although chloride is strongly associated with sodium with a slope of the regression identical to that for bulk sea water (1.8), a strong seasonal variation is observed. The seasonal variation of the $[Cl^-]/[Na^+]$ ratio is illustrated in Fig. 4a. Although during winter the $[Cl^-]/[Na^+]$ ratio is identical to that for bulk sea water, during summer time, this ratio decreases to 1.2, i.e. below the seawater ratio $[Cl^-]/[Na^+]$ of 1.8. Mihalopoulos et al. (1997) have also observed Cl^- evaporation in the aerosol composition at Finokalia during summer (coastal station located at the Eastern Mediterranean). This low $[Cl^-]/[Na^+]$ ratio may have been attributed to the reaction between sea salt and the acidic anion nss-SO_4^{2-}, of which 20% is not neutralized by any of the alkaline species during the summer season. To identify the relationship between the $[Cl^-]/[Na^+]$ ratio, Fig. 4b presents the seasonal variability of acidity in excess defined as the difference between the sum of (nss-SO_4^{2-} + MS^-) and NH_4^+. It is clearly seen that free acidity and $[Cl^-]/[Na^+]$ ratio are anticorrelated. Therefore, most of the observed lower ratios may be attributed to Cl^- evaporation from particulate aerosol to form gaseous HCl after reacting with acidic species.

3.5. The role of mineral dust as a potential source of NO_3^- and nss-SO_4^{2-}

Outbreaks of Saharan dust over the eastern Mediterranean region are very frequent in winter and transitional seasons (October–May) and minimal during the summer (Kubilay and Saydam, 1995; Kubilay et al., 2000). To better illustrate the role of Saharan dust as a source of acidic species we focused on the two extreme events presenting the highest NO_3^- and nss-SO_4^{2-} levels during the studied period (marked by stars in Fig. 2). Three-day back trajectories and satellites images were used to identify the distant mineral dust outbreaks from the Sahara during these events. Fig. 5 depicts the 3-day back trajectories showing the transport of air masses to the sampling site during 14 April 1998 and 27 March 1998 (a,c) and regional aerosol absorbing index (mineral dust) distribution on 14 April 1998 and 27 March 1998 (b, d). The back trajectory pathway every 12 h is indicated by triangles for 900 hPa, stars for 850 hPa, circles for 700 hPa and squares for 500 hPa. Two remarks can be made: (i) during these two events the whole atmospheric column up to 500 hPa was influenced by air masses coming from arid areas and (ii) the sampling site was influenced by the Arabian Peninsula in the boundary layer and by the Sahara in the free troposphere. The smaller dilution within the boundary layer since the air masses did not travel above the sea before reaching Erdemli (as in the case of Sahara dust events) was certainly an important contributing factor. It is worthwhile noting that the levels of NO_3^- and nss-SO_4^{2-} observed during these two events were comparable to the values reported for heavily industrialized areas and clearly depicts the important role of dust as an uptake medium for acidic gases like HNO_3 and SO_2 from the atmosphere. An increase in organic and inorganic nitrogen species and sulfate during Saharan dust outbreaks has been previously reported by Mace et al. (2003) and Talbot et al. (1986). However the nature of this association cannot be determined with the data set presented. Furthermore, there is a need to investigate the adsorption of gas phase N and S compounds onto mineral dust. An aerosol size separated study along with gas phase S and N measurements could add insights regarding the findings in this study for elevated sulfate and nitrate concentrations associated with mineral dust.

4. Conclusion

The Eastern Mediterranean aerosol composition shows a broad variability, with the mass concentrations of each individual species varying up to an order of magnitude throughout the sampling campaign. Cl^-, SO_4^{2-}, NH_4^+, Ca^{2+}, and Na^+ contributed 90% to the sum of ions. The lowest values for water-soluble ions were observed during intense rain events, since wet deposition removes particles from the atmosphere efficiently. In general all species, except marine ions, had a higher average concentration in the dry months with dry/wet ratios varying between 1.46 and 2.58. Many species had maximum values during dust

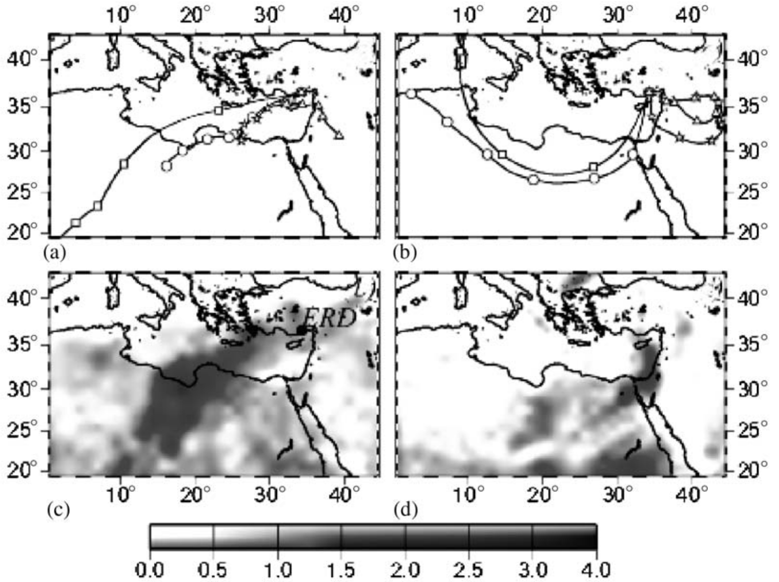


Fig. 5. The 3-day back trajectories showing the transport of air masses to the sampling site during 14 April 1998 and 27 March 1998 (a,c) and regional aerosol absorbing index (mineral dust) distribution on 14 April 1998 and 27 March 1998 (b, d). The back trajectory pathway every 12 h is indicated by triangles for 900 hPa, stars for 850 hPa, circles for 700 hPa and squares for 500 hPa.

intrusions when air masses originated from North Africa and occasionally from the Middle East. Acidic species such as NO_3^- and nss-SO_4^{2-} showed elevated levels during dust events, indicating the significant role of dust to accommodate heterogeneous reactions removing acidic gases like HNO_3 and SO_2 from the atmosphere.

Multiple regression analysis indicated that the main non-sea-salt ions were forming NH_4HSO_4, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $CaSO_4$ and $CaCO_3$. Formation of NH_4NO_3 and partial neutralization of H_2SO_4 by NH_4^+ and Ca^{2+} was found to occur mainly during summer. Factor analysis indicated five factors accounting for 94.0% of the total variance in the system. Crustal, sea salt, and marine biogenic factors were found to account for approximately 70.0% of the total variance in the system. Finally, a clear Cl^- deficit was observed during summer resulting from reactions between sea salt and the acidic anion nss-SO_4^{2-}, of which 20% was not neutralized by any of the alkaline species during the summer season.

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