Investigation of chemical composition of the lower tropospheric aerosols in the Eastern Mediterranean region: implications regarding sources and long-range transport

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Abstract- Daily aerosol filter samples were collected intermittently at Erdemli (36.6°N, 34.3°E) on the Mediterranean coast of Turkey for a 4-year period between 1996 to1999. Concentrations of the water-soluble ions (Cl^-,Br^-,NO_3^-,$SO_4^=$;$C_2O_4^=$, MSA^-,Na^+;NH_4^+,K^+,$Mg^{2+}$and Ca^{2+}) and trace metals (Al,Fe,Mn,Ca,Mg and Zn) measured in a total of 610 samples. Crustally originated elements (i.e. Al, Fe, Mn etc) were present in high concentrations, owing to the arid and semi-arid regions surrounding the semi-enclosed Mediterranean Basin. Sea-salt aerosol concentrations were also elevated as would be expected for a coastal sampling station. Sea salt species exhibited the highest values during the winter season, whereas, the non sea salt chemical species exhibited their maximum values during the transitional or summer periods.

Introduction

Aerosols play important roles in regional scale processes within the Mediterranen atmosphere. They will affect both the climate and the hydrologocial cycle. The magnitude of these effects is 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 would suggest that the composition of the aerosol burden over the Eastern Mediterranean is significantly affected both by anthropogenic and natural sources. The anthropogenic component is mainly consisted of sulphate and carbonaceous particles, which will have undergone long-range transport from Europe and Asia. Natural components are dominated by sea salts, mineral dust particles and biogenically produced sulphur aerosols (Lelieveld *et al.*, 2002; Mihalopoulos *et al.*,1997; Kubilay *et al.*, 2000; 2002; Özsoy *et al.*, 2000; Andreae *et al.*, 2002).

Methods

The sampling station (Erdemli, 36°33'N and 34°15'E), occupied during the current study, is located in a rural area of the southeastern coast of Turkey (Fig. 1b). Rainwater and aerosol samples have been collected from this site over the last

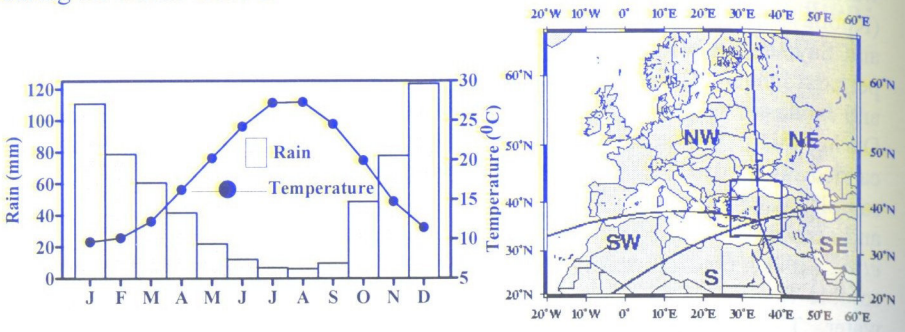
ten years, hence there is an extensive record of the concentrations of elemental and water soluble aerosol associated ions and the chemical character of rainwater (Kubilay and Saydam, 1995; Kubilay *et al.*, 2000; 2002; Özsoy *et al.*, 2000; Özsoy and Saydam, 2000; 2001). Aerosol samples were collected during the sampling periods 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 *et al.* (2000); Özsoy *et al.* (2000). One-quarter of each sample and blank filter was acid digested. The soluble fraction of an 1/8 of each filter was extracted using 20 mL of nanopure water. The solutions obtained from the total acid digestion and partial leaching of filters were analysed by: a) Atomic Absorption Spectrophotometer (AAS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) for the major elements (Al, Fe, Mn, Ca, Mg and Zn), b) Ion Chromatography (IC) for anions (Cl^-, Br^-,NO_3^-,$SO_4^=$, $C_2O_4^=$, MSA^-) and cations (Na^+; NH_4^+,K^+, $Mg^{2+}$and Ca^{2+}). The accuracy and precision of the trace metals measurements was evaluated on the basis of analyses of Community Bureau of Reference (CRM-142, light sandy soil) and National Research Council (BCSS-1). Three-dimensional, 3-day backward trajectories of air masses arriving at the sampling point on 12:00 UT of the sampling day at pressure levels of 900 and 850 hPa within the boundary layer and 700 and 500 hPa within the free troposphere were calculated on a daily base. The trajectory model of the European Center for Medium-Range Weather Forecasts (ECMWF) in Reading, England was applied to three-dimensional analysed wind fields available from the MARS archive of ECMWF. Using a 10-year (1990-1999) trajectory database, we examined the climatological airflow patterns and the differences in transport patterns for four arrival elevations.

Results and Discussion

Climatological Conditions

Monthly average atmospheric temperatures (°C) and rainfall (mm) for a 28-years period (1971-1998) at the Erdemli station are presented in Fig. 1a. 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 minimum and the possibility of photochemical formation of aerosol particles from their gaseous precursors is 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 the measured aerosol components are

expected to be relatively higher in the summer months compared to those observed during the winter months.



(a) (b)

Fig. 1. (a) Monthly average amount of precipitation and temperature (28 years) at the Erdemli station. (b) Classification of 3-day back trajectories ending at Erdemli. Major airflow sectors are illustrated.

Three-day back trajectories were calculated daily at 1200 UT for Erdemli at 900, 850, 700 and 500 hPa and classified into five airflow sectors according to wind direction and speed. The area covered by the rectangle presents the regional (slow) trajectories whereas air masses arriving from outside of the rectangle represents long-range aerosol transport (fast). These categories are as follows (Fig. 1b): (1) North East (NE) sector includes the Former Soviet Union as well as the eastern Black Sea and eastern Anatolia, (2) North West (NW) sector includes eastern and western Europe as well as the western Black Sea and western Anatolia, (3) South West (SW) sector includes north west Africa as well as maritime flow over the Mediterranean, (4) Southern (S) sector includes eastern Africa as well as the Mediterrranean, and finally (5) South East sector includes the Arabian Peninsula as well as the Middle East countries.

Table 1. Contribution (%) of the airflow sectors to the origin of air masses ending at Erdemli

Sectors Month	900 hPa *a*	850 hPa	700 hPa *b*	500 hPa Coefficient
NE	9	(23)	-	-
NW	4 (26)	15	37 (28)	40
SW	11 (34)	13 (33)	17	46
S	-	-	19	15
SE	(16)	(16)	-	-

The percent contribution of each sector (numbers in paranthesis present the regional contribution from the defined sector) is given in Table 1. Up to 850 hpa the regional airflow is dominated by northwesterly and southwesterly air masses. At higher altitudes (700 and 500 hPa) air masses originated either from eastern Europe or from North Africa.

Aerosol Composition and Seasonal Cycles

Table 2 presents the 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. Median and geometric mean values of trace elements and water-soluble ions are a more representative way of presenting the data, as the distributions of the measured species were lognormal (verified by the Kolmogorov-Smirnoff test at the 95% confidence level). However, in the literature atmospheric aerosol data have been usually represented by the arithmetic mean values. Crustally originated elements exhibited higher concentrations than those detected at other European coastal sampling sites. This 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.

Table 2. Summary of statistics of the chemical composition of aerosols (ng m^{-3}) at Erdemli over the period January 1996 to December 1999.

	Arith.Mean (±σ)	Geo.Mean (±σ)	Median	Min-Max
Al	747(592)	530(2.5)	614	7- 4281
Fe	606(455)	449(2.3)	487	7- 3092
Ca	3253(2183)	2651(1.9)	2703	90-15859
Mg	1399(1174)	1022(2.3)	1160	14-12268
Mn	12.4(9.8)	8.6(2.4)	11	0.1-78
Zn	22.4(15.8)	17.0(1.9)	19	1-174
Cl^-	4428(6318)	2692(2.7)	2543	6-69442
Br^-	16.8(19.7)	12.3(2.1)	11.6	0.3-241
NO_3^-	3491(1983)	2805(2.3)	3434	3-11128
$SO_4^=$	7492(4627)	6026(2.2)	6183	8-26916
nss-$SO_4^=$	6803(4636)	5212(2.5)	5476	1-26254
$C_2O_4^=$	190(136)	115(3.9)	168	1-861
Na^+	2741(3402)	1770(2.6)	1842	16-37839
NH_4^+	2131(1240)	1722(2.3)	1891	1-9556
K^+	281(173)	237(1.9)	250	2-1701
nss-K^+	180(130)	143(2.2)	151	1-1259
Mg^{2+}	407(404)	297(1.9)	300	2-4325
nss-Mg^{2+}	88(112)	62(2.5)	74	1-1468
Ca^{2+}	2306(1185)	1959(2.0)	2126	5-9744
nss-Ca^{2+}	2201(1184)	1841(2.1)	2019	4-9453
MSA^-	44(48)	22(3.6)	20	1-383

Highlighted in Fig. 2, are the deviations of the monthly minimum and maximum concentrations of Al, Na^+, NO_3^- and MSA (species characteristic of crustal, sea spray, anthropogenic and marine biological activity, respectively) from the monthly mean concentrations. Fig. also demonstrates the degree of interannual variability. Three seasonal cycles are apparent from these diagrams. The highest concentrations of the sea salt components (Chloride, bromide, sodium and magnesium) occur during the winter and are generally associated with the presence of cyclonic activity and the higher wind speeds which will tend to increase sea salt formation and hence their input into the overlaying air mass. Whereas, during the

summer period sea salt generation is at its minimum owing to low wind speeds and calm sea state.

The crustal elements such as Al, Fe and Ca indicate two peaks in their concentration during the spring and summer seasons. Low concentrations of elements associated with crustally derive material are frequently observed during the winter period (January, February and December) when precipitation scavenging removes particles from atmosphere efficiently. Whereas, during this season high concentrations of crustal elements are observed when the air mass trajectories originate from North Africa and occasionally from the Middle East. During the transitional seasons (spring and autumn) elements associated with crustal material exhibit episodic peaksowing to the intense long-range transport of mineral dust from Northern Africa (Kubilay *et al.*, 2000).

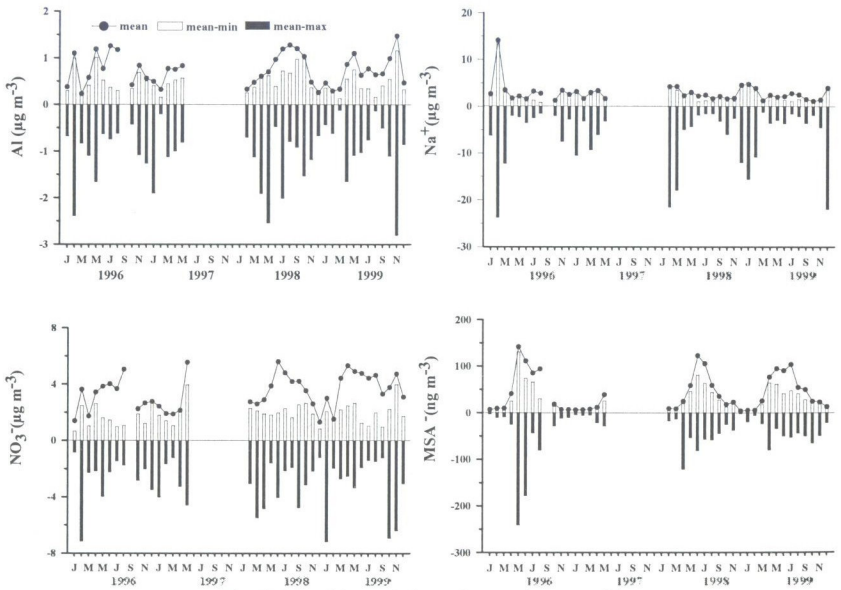


Fig. 2. Monthly variation of aerosol composition.

Nitrate, ammonium, non-sea-salt sulphate and methane sulphonate display seasonal cycles with a minima in winter and a maxima in summer. Photochemical formation, which becomes active under summer conditions (high solar radiation and temperatures), enhances the concentrations of nitrate. Additionally during the summer the ambient air temperature is high and the soil is dry, therefore, these conditions are favourable for enhanced ammonia fluxes to the atmosphere. These conditions may cause profound summer peaks in the ammonium concentration. The observed high non-sea salt sulphate concentrations during the summer period at Erdemli can be attributed to both anthropogenic and biogenic sulphate

emissions. For more details on MSA and nss-$SO_4^=$ at Erdemli please refer to Kubilay *et al.*(2002).

Ion Balance

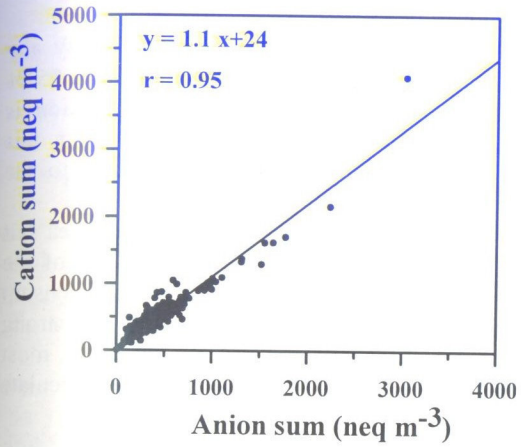


Fig 3. Equivalent of total cations vs anions respectively to the total anion sum

Total equivalents of the cations were plotted against total equivalents of the anions and presented in Fig. 3. The slope of the regression line is slightly higher than unity. In Crete Island (a comparable eastern Mediterranean sampling site) aerosols were dominated by anionic species (Mihalopoulos *et al.*, 1997). However, for the current study the value of the slope would imply an anion deficiency, which may be attributed to the presence of bicarbonate in the samples, which was not measured. Contribution of both Br^- and MSA^- is less than 1‰ to the total anion composition, whereas,Cl^-(37.3%)and $SO_4^=$(45.4%) contribute to more than 80% of the total anion sum. NO_3^- and $C_2O_4^=$contribute 16.2% and 1.1%

Ammonium (29%), calcium (30%) and sodium (30%) contribute almost 90% to the cation sum. K^+ and Mg^+ are minor contributors, amount to only 8.2% and 1.8% , respectively. The most important acidic and alkaline species are nss-$SO_4^=$, NO_3^- and NH_4^+, nss-Ca^{2+}. These species are significantly correlated with each other within the 95% confidence level (n=610). Among these species the highest correlation coefficient was found to be between nss-$SO_4^=$ and NH_4^+ (r=0.74) and the lowest correlation coefficient was found to be between nss-$SO_4^=$ and nss-Ca^{2+}(r=0.51). These results would indicate that the majority of nss-$SO_4^=$ is neutralized by NH_4^+. The slope of the regression between nss-$SO_4^=$ and NH_4^+ for the whole data set was 0.53, which indicates partial neutralization of nss-$SO_4^=$ and would suggests that mainly NH_4HSO_4 is formed instead of $(NH_4)_2SO_4$. Nss-Ca^{2+}, nss-Mg^{2+} and nss-K^+ can also neutralize nss-$SO_4^=$. The slope of the regression between nss-$SO_4^=$ and nss-(Ca^{2+}+Mg^{2+}+K^+) is 0.35 and may explain additional neutralization of nss-$SO_4^=$. Therefore, it would appear that only 12% of the nss-$SO_4^=$ (1-(0.53+0.35)) is not neutralized.

During the winter acidic species nss-$SO_4^=$ and NO_3^- are neutralized by alkaline species. However, during in the summer regression analyses would indicate that

alkaline species partially neutralize nss-$SO_4^=$. Taking into consideration the slopes of regressions between nss-$SO_4^=$ and NH_4^+, nss-Ca^{2+}, nss-K^+ and nss-Mg^{2+}, only 60% (1-(0.40+0.19+0.002+0.03)) of the nss-$SO_4^=$ is neutralized. Therefore, the linear regression analyses clearly indicates that approximately 10% and 40% of nss-$SO_4^=$ are not neutralized by alkaline species for all data set and for summer period, respectively.

Na and Cl are the major elements in the sea salt. In order to identify any relationship between Na and Cl a linear regression was performed within 95 % confidence limits. As expected, the slope (1.85) of the linear regression is indicative of the ratio for sea salt (1.8) during the winter period. However, this ratio decreases to 1.2 during the summer period. It can be attributed to the evaporation of Cl^- or excess Na, which originates from crustal material.

Alternatively the lower ratio may have been due to the reaction between sea salt and the acidic anion nss-$SO_4^=$, of which 40% is not neutralized by any of the alkaline species during the summer season. In order to identify the relationship between Cl^-/Na^+ ratio and nss-$SO_4^=$ linear regression was applied and strong inverse relation (r= -0.74) was found during the summer period. Therefore, most of the observed lower ratios may be attributed to Cl^- evaporation from particulate aerosol to form gaseous HCl.

Mineral Dust Events

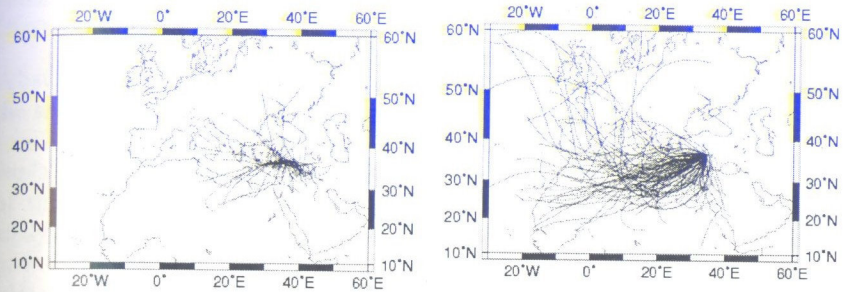
Outbreaks of Saharan dust over the eastern Mediterranean region are very frequent in winter and transitional seasons (October-May) and minimal during the summer [Kubilay and Saydam, 1995; Kubilay *et al.*, 2000]. To identify the distant mineral dust outbreaks from the Sahara during the winter and spring sampling period a threshold of aerosol Al concentrations of 1000 ng m^{-3} was utilized. During the sampling period 40 African dust events were clearly identified by an abrupt increase in the Al, Fe, Ca and also Mn and Zn concentrations in the atmosphere. The average concentrations of the elements for the identified dates were 1468, 1061, 4810, 18, 25 and 4138 ng m^{-3} for Al, Fe, Ca, Mn, Zn and NO_3^-, respectively. The average concentrations of the same elements for the remaining samples (where there was no recorded mineral dust transport) were much lower (310, 283, 2268, 7, 18 and 2502 ng m^{-3} for Al, Fe, Ca, Mn, Zn and NO_3^- respectively).

For 40 events the computed horizontal air mass back trajectories are illustrated in Fig. 4. The origins of the air masses arriving vary with respect to their arriving levels. The shallower trajectories (900 hPa) identified air masses coming from non-Saharan sources, except for the outstanding five cases (Fig. 4a). However, the trajectories arriving at the upper barometric levels (700 or 500 hPa) mostly originated from Africa during all peak events (except six cases), which originated from the Arabian Peninsula (Fig. 4b).

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. The lowest values for the trace elements and water-soluble ions were observed during intense rain events, since wet deposition removes the particles from the atmosphere efficiently. Many species indicate maximum values during dust intrusions when the air masses originate from North Africa and occasionally from the Middle East. Most species show a seasonal cycle with maximum values in the transitional-summer seasons.



a) (b)

Fig 4. Air mass back trajectories arriving at Erdemli. (a) Trajectories arriving at 900 hPa (b) Trajectories arriving at 700 and 500 hPa levels.

Acknowledgements- *This study was funded by Middle East Technical University (AFP-2001-07-01-01) and NATO (through a linkage grant of EST.CLG.977811).*

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