

Chemical composition of eastern Mediterranean aerosol and precipitation: Indications of long-range transport

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Abstract. Daily aerosol and wet-only precipitation samples were collected, between January 1992 and January 1994 at a permanent station established on the Mediterranean coast of Turkey. Collected aerosol and rain samples were analyzed for major ions and a host of trace elements using a combination of analytical techniques, including ion chromatography, atomic absorption spectrometry and instrumental neutron activation analysis. The results have demonstrated that concentrations of parameters studied are higher than corresponding concentrations measured in the western Mediterranean and western parts of the Black Sea due to longer transport distances to source regions of particles and precipitation scavenging from atmosphere. Elemental composition of aerosols and rain differ due to different scavenging efficiencies of elements associated with coarse and fine particles. Temporal behaviour of elements were explained by variations in source strengths and variations in scavenging efficiency.

INTRODUCTION

The Europe is an important source for the observed concentrations of pollutants in the regional seas around the continent, such as the Baltic Sea (1), North Sea (2), Mediterranean Sea (3), and the Black Sea (4). Naturally, the presence of such a strong source have significant impact on the forests and lakes in the regions surrounding Europe.

The studies to understand composition of aerosols and precipitation in the Mediterranean region have began in early 80's with the open sea studies (3,5,6). Substantial information have accumulated on the Western Mediterranean basin since then (7-12). These studies have demonstrated that the chemical composition of aerosols and precipitation in the Western Mediterranean basin is highly variable and consist of marine, crustal and anthropogenic components (3, 11). Experimental and modelling studies also showed that the constituents of aerosols and precipitation are affected from two different source regions. One of these regions is the Europe and the other one is the north Africa (13,14,15). Transport of pollutants from Europe results in relatively acidic rain with high concentrations of ions like SO_4^{2-} , NO_3^- and aerosol mass which is enriched in chalcophilic elements associated with anthropogenic activities. On the other hand, transport of air masses from North Africa is expected to result in relatively clean air with rain pH higher than 5, owing to CaCO_3 which is abundant in Saharan dust and aerosols which is highly enriched with lithophilic elements (14).

Although chemical composition of Western Mediterranean precipitation and aerosols had been fairly well characterized, data is extremely scarce on the chemical composition of the Eastern Mediterranean precipitation and aerosols. In 1992 an atmospheric monitoring station was established in the Mediterranean coast of Turkey to determine atmospheric concentrations and calculate the deposition flux of elements in the eastern Mediterranean as well as to identify their sources and source regions.

METHODS

A 115 daily wet-only rain samples and 700 aerosol samples were collected at a permanent station located approximately 20 km to the west of the town of Antalya, in the Mediterranean coast of Turkey, between December 20, 1991 and January 15, 1994. The area with a diameter of 20 km around the station was free of any point sources and large settlement areas.

Both precipitation and aerosol samplers were installed on a platform which was 20 m above the sea level. The power to instruments was controlled from a container situated 50 m to the north of the platform. The container also acted as a clean area where samples are changed, processed and stored until they were sent to the central laboratory in Ankara. Two wet-only rain samplers; one to collect samples for ion analysis (Andersen, standard "acid rain sampler") and the other for metal analysis (Karlbe) and a PM-10 high volume sampler (Andersen) were used to collect rain and aerosol samples. Collected samples were sent to the central laboratory located in Ankara at the end of every week.

In Ankara, non-acidified precipitation sample bottles were opened and processed in a class-100 clean area. The pH was measured and SO_4^{2-} , NO_3^- , Cl^- were determined by ion chromatography, NH_4^+ by spectrometry, Ca^{++} , K^+ , Mg^{++} and Na^+ by flame atomic absorption spectrometry and trace elements by graphite furnace atomic absorption spectrometry (GFAAS). Details of the sampling and analytical procedures were given elsewhere (16).

One-sixteenth of the aerosol filters were analyzed by instrumental neutron activation analysis (using a procedure developed by Ölmez (17)). The samples were irradiated twice in the 5 MW MITR-II research reactor at a neutron flux of $8 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. Samples were first irradiated for 1 min and counted twice for 5 and 20 min to elements with short half lives. After the samples decayed for several days, they were reirradiated for 12 hours and counted for 6 hours to determine isotopes with longer half lives. The γ -ray spectrum were collected using high-purity Ge detectors coupled to a Canberra, CT multichannel analyzer. The accuracy of the analytical system was checked by periodic analysis of NIST Standard Reference Material #1633. Only the elements which are measured both in aerosols and rain water are presented in this manuscript.

RESULTS

Concentrations of major ions and elements in wet deposition and aerosol samples collected in this study are given in Table 1. Concentrations of elements in the eastern Mediterranean precipitation and aerosols are comparable with the concentrations reported from other rural stations. Concentrations of marine elements are high due to close proximity of the station to the sea. In general aerosol composition observed in the eastern Mediterranean region closely resembles to the aerosol composition reported for the eastern Black Sea (4). Observed concentrations are smaller than corresponding concentrations reported for the western Mediterranean basin. This indicates that pollutants transport longer distance before they reach to the eastern Mediterranean basin. Scavenging processes during transport removes pollutants from the atmosphere and lower concentrations are observed when air masses eventually reach to our receptor site in the eastern Mediterranean basin.

Table 1. Average concentrations of ions and elements in the Eastern Mediterranean aerosol and precipitation

	Precipitation ($\mu\text{g L}^{-1}$)	Aerosol (ng m^{-3})
pH	5.17	
$\text{SO}_4^{=}$	$6,200 \pm 10,900$	
nss- $\text{SO}_4^{=}$	$4,400 \pm 8,900$	
NO_3^-	$4,900 \pm 6,500$	
NH_4^+	$1,300 \pm 1,700$	
Na	$10,000 \pm 19,000$	$1,400 \pm 1,900$
Mg	$1,600 \pm 2,600$	430 ± 360
Al	580 ± 750	520 ± 710
Cl	$18,000 \pm 31,000$	$2,000 \pm 3,300$
K	$710 \pm 1,400$	360 ± 320
V	0.71 ± 0.65	2.2 ± 1.8
Cr	9 ± 12	4.6 ± 3.7
Zn	140 ± 500	11 ± 11
Fe	530 ± 420	370 ± 500
Se	0.26 ± 0.47	0.28 ± 0.18
Br	9 ± 10	18 ± 22
Cd	4.5 ± 6.3	0.11 ± 0.15
Sb	0.18 ± 0.11	0.34 ± 0.19

Crustal enrichment factors of elements in both aerosols and precipitation are given in Table 2. For elements Fe, V, K, Mg, Na and Cl crustal enrichment factors in aerosol and precipitation samples are comparable. For the remaining elements, crustal enrichment factors calculated for aerosols are significantly higher than those for precipitation. Difference in the EF_c values of these two groups of elements indicate that they are scavenged with different efficiencies from the atmosphere. The elements Fe, V, K, Mg, Na and Cl are associated either with either soil or sea salt particles in the atmosphere. Since both sea salt and soil particles are in the coarse mode of the size spectrum, they and elements associated with them are scavenged out fairly efficiently by rain. Anthropogenic elements such as Cd, As, Sb, and Se, on the other hand are associated with sub-micron particles which are not scavenged out as efficiently as coarse particles by the rain. Such difference in the scavenging efficiencies of coarse and fine particles results in the observed difference in the enrichment factors of anthropogenic and lithophilic elements.

Table 2. Crustal enrichment factors of elements in eastern Mediterranean aerosol and precipitation.

	EF _c Aerosol	RF _c rain
Fe	1.7	2.2
V	6.5	4.3
K	10	13
Cr	31	20
Mg	36	33
Zn	97	562
Na	160	190
Cd	1,000	680
Sb	1,700	340
Se	3,500	2,100
Br	15,300	14,700
Cl	56,400	64,400

The annual average rain-water pH is 5.17. However, the acidity in collected precipitation samples was highly variable, ranging between 3.97 and 6.76. Approximately 70% of the samples had pH less than 5.0, and 27% had pH less than 4.5. The air masses intercepted in the station originated from regions with different degrees of industrialization which resulted in a wide range of acidity. When the precipitation was associated with air masses from Europe, low pH and high pollutant concentrations were expected. But, when the precipitation was associated with transport from south or east, high pH and low pollutant concentrations were expected.

The acidity in precipitation depends on the concentrations of acid forming ions as well as concentrations of alkaline species which neutralize the acidity. Consequently, the pH alone can not reveal the overall picture of acid base chemistry in precipitation. Although the pH in the rainwater samples collected in our station were higher than pH values reported for other rural areas, the SO_4^- and NO_3^- concentrations in the eastern Mediterranean precipitation are comparable to or higher than corresponding concentrations reported for regions with known acid rain problem, York, suggesting that the high pH measured in this work was owing to neutralization of acidity, rather than lack of acid forming ions in the rain.

If the acidity of the precipitation originates primarily from H_2SO_4 and HNO_3 , the equivalent ratio of $\text{H}/(\text{nss-SO}_4 + \text{NO}_3)$ should be close to unity. The observed ratio was 0.46, indicating that approximately half of the acid in precipitation has been neutralized.

The most common alkaline species which can neutralize rainwater acidity are NH_3 and CaCO_3 . The main sources of NH_3 in precipitation are fertilizer applications or emissions from barns. Fertilizer application have shown to be an important source for neutralization of rain acidity in productive regions of Turkey (18). However, CaCO_3 is more important potential source for the neutralization of acidity in the eastern Mediterranean precipitation, because (1) the local soil is rich in CaCO_3 , (2) frequent incursions of Saharan dust which transports large quantities of CaCO_3 rich soil to the eastern Mediterranean basin. Such transport of saharan dust have been shown to be main reason for the neutralization of acidity in the western Mediterranean precipitation (2).

If the acidity in rain was due to H_2SO_4 and HNO_3 , and these acids were neutralized by NH_3 and CaCO_3 , then the sum of $(\text{SO}_4^{2-} + \text{NO}_3^-)$ is expected to be linearly related with the sum of $(\text{NH}_4^+ + \text{Ca}^{2+} + \text{H}^+)$. The correlation coefficient between these two parameters was 0.91, indicating that the acidity of rain water was neutralized by NH_3 and CaCO_3 , and contribution of any other base to the neutralization processes was not significant.

High pH values were almost always accompanied by high Ca^{2+} concentrations. High Ca^{2+} concentrations were also associated with high SO_4^{2-} and NO_3^- concentrations. However, temporal variation of NH_4^+ were quite different from that of SO_4^{2-} and NO_3^- , and high NH_4^+ concentrations did not match with high pH values. These observations suggest that CaCO_3 is the main neutralization agent and the role of NH_3 in the neutralization process is small.

The CaCO_3 which neutralizes rain-acidity can originate from both local sources and transport from north Africa. The local soil is alkaline in nature and contains CaCO_3 . The soil which becomes airborne by wind action can generate sufficient airborne CaCO_3 to neutralize acidity. Neutralization with CaCO_3 produced by local soil is probably a below cloud process. Dust transported from Sahara is also shown to be alkaline (19). Consequently, saharan dust incursions to the eastern Mediterranean basin can also neutralize acidity in rain water. Since the transport of Saharan dust to the region occurs in the free troposphere, neutralization by CaCO_3 from this source is expected to be an incloud process.

The temporal behaviour of ions and elements in collected aerosol and rain water samples are determined by both the variations in source strengths and variations in scavenging processes during the transport to the receptor site. Concentration of Na and other marine elements are significantly higher during winter, whereas concentrations of Al and other crustal elements, such as Fe are much higher during summer. The main source of Na, Cl and to a certain extent Mg, K and Ca is the bubble-bursting process at the sea. Since bubble bursting is much more pronounced during stormy winter season, these marine elements are generated in large quantities over the neighbouring sea during winter. Relatively calm conditions over the sea during summer, significantly reduces the generation of marine elements during summer. The dominating source of crustal elements, on the other hand is the airborne soil particles around the station. Since the soil is damp during winter months and very dry during most of the summer season atmospheric concentration of soil particles and crustal elements which are associated with these particles is higher during summer.

Although temporal behaviour of marine and crustal elements can be explained by seasonal variations in their generation mechanisms, variations in the source strengths of anthropogenic elements can not explain observed temporal behaviour of these elements. With few exceptions concentrations of anthropogenic elements such as Zn, Se, Sb and Cr are higher during summer season. However, the difference between their summer and winter concentrations are not as dramatic as in the case of crustal elements. Since there is no anthropogenic emission sources in the vicinity of the station, these elements are transported from other parts of Turkey and from Europe. The observed differences in summer and winter concentrations of anthropogenic elements are due to season dependent scavenging of these elements during their long-range transport to the eastern Mediterranean basin. During summer season the frequency of rain events is small in the Europe and Mediterranean regions consequently anthropogenic particles and elements associated with these particles which are emitted from distant sources can reach to the eastern Mediterranean without a substantial wet deposition. However, during rainy winter season, more of these particles are wet deposited on their way to the eastern Mediterranean.

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