The influence of Black Sea and local biogenic activity on the seasonal variation of aerosol sulfur species in the Eastern Mediterranean atmosphere

Nilgün Kubilay[1], Mustafa Koçak[1], Tülay Çokacar[1], Giorgos Kouvarakis[2], Nikos Mihalopoulos[2] and Temel Oguz[1]

kubilay@ims.metu.edu.tr; mihalo@chemistry.uoc.gr
[1] *Institute of Marine Sciences, Middle East Technical University, Erdemli-Turkey*
[2] *Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, Heraklion – Greece*

Abstract- Methanesulfonate (MSA) and non-sea-salt (nss) sulfate concentrations were measured in aerosol samples collected during January 1996-December 1999 at coastal stations along the Turkish and Cretan coastline. The generated data set enabled the origin and variability of biogenically-derived atmospheric sulfate concentrations in the Eastern Mediterranean atmosphere to be defined. Although similar seasonal patterns of MSA and nss-sulfate concentrations for both stations were detected, the mean concentrations at Erdemli (Turkey) over the sampling period (42±52 ng m^{-3} MSA, and 6.8±5.2 μg m^{-3} nss sulfate) were found to be almost twice that of those measured at Finokalia (25.8±14.9 ng m^{-3} and 3.9±1.7 μg m^{-3}). Analysis of the air mass back trajectory and the SeaWIFS mean normalized water leaving radiation data, suggests that the majority of the biogenic contribution at Erdemli is originated from summer coccolithophorid *Emiliania huxleyi* blooms located in the Black Sea, *Emiliania huxleyi* is known to be a strong dimethyl sulfide producer. The data further points to a significant relationship between Saharan dust transport events and local oceanic production of atmospheric sulfate aerosols through occasional fertilization of the Eastern Mediterranean during wet deposition events. This process accounts for episodic, strong weekly changes in the MSA and nss-sulfate concentrations during the spring months. Considering that Erdemli and Finokalia are approximately 1000 km apart from each other geographically, large differences in their MSA and nss-sulfate concentrations indicates a considerable role of regional mesoscale atmospheric transport processes on the spatial structure of biogenically produced atmospheric sulfur aerosols.

Key words- Methanesulfonate, non-sea-salt sulfate, aerosol, Eastern Mediterranean, Black Sea, Emiliania huxleyi, mineral dust transport.

Introduction

Biologically produced gases in the surface ocean have a major impact on the global atmospheric cycling of elements such as sulfur, nitrogen and carbon, and hence may play an important role in the global climate system. Dimethyl sulfide (DMS) is the principal and most abundant biogenic organic sulfur compound entering the atmosphere, where it undergoes photo-chemical oxidation and

transformation to methanesulfonate (MSA). It provides the biogenic contribution to non-sea-salt sulfate (nss-sulfate) in marine aerosols. The importance of nss-sulfate comes from its effect on the Earth's radiation budget by backscattering solar radiation to space (*Charlson et al.,* 1991) and by controlling the formation of cloud condensation nuclei (*Charlson et al.,* 1987).

To our knowledge, the only long term time series data on MSA measurements in the Eastern Mediterranean belong to the site at Finokalia, a coastal rural site located on Crete (*Kouvarakis and Mihalopoulos*, 2002). While this data set represented the conditions of the western part of the Eastern Mediterranean, the marine atmosphere over the eastern part (i.e. the Levantine Sea) has not been monitored systematically. This paper presents research findings which describes the first-reported time series data for MSA measurements over a four-year period (1996-1999) at a station located along the Turkish coast of the Levantine basin at Erdemli. This data set is evaluated together with the complementary data from Finokalia in order to define the large scale regional and seasonal variations of MSA and nss-sulfate over the Eastern Mediterranean. An independent evaluation of the Finokalia data set within the framework of the local sulfur budget analysis has been presented recently by *Kouvarakis and Mihalopoulos* (2002) and *Kouvarakis et al.* (2002).

Material and Methods

Bulk aerosol samples were collected at a rural site on the south-eastern coast of Turkey (Erdemli, 36° 33' N and 34°15' E) using Whatman 41 cellulose fiber filters (20 cm x 25 cm), and at a remote location on the northern coast of Crete (Finokalia, 35°24' N and 25°60' E) on 0.45 μm Gelman Zefluor PTFE filters using hi-vol and low-vol samplers respectively. Sampling has been carried out at daily intervals at Erdemli. It has varied in the range from 3 to 48 h at Finokalia. The major soluble ion species within the atmospheric aerosol extracts were analysed by ion chromatography (IC) using a Dionex AS4A-SC column with an ASRS-I suppressor. The sampling locations are illustrated in Fig. 1. Non-sea-salt sulfate concentrations were calculated using Na^+ as a conservative tracer of sea-salt origin. Air mass back trajectories were provided by the European Centre for Medium Range Weather Forecasts (ECMWF). The trajectories show

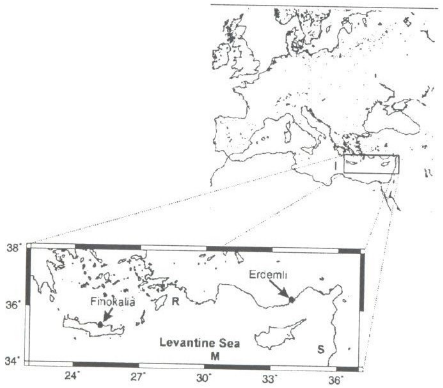

Fig. 1. Location map of the eastern Mediterranean and the sampling site on the island of Crete (Finokalia) and on the southern coast of Turkey (Erdemli).

routes of air masses arriving between the surface and 850 hPa at the sampling sites for the past 72 h.

Results and Discussion

Seasonal variations of MSA and nss-sulfate concentrations

The variations of daily measured MSA and nss-sulfate concentrations during the four years period from January 1996 up to the end of 1999 at Erdemli and Finokalia stations are shown in Fig. 2. Two important features are immediately noticeable from these data sets; (i) both indicate a clear signature of seasonal variations, with high summer to low winter values, (ii) the amplitude of variations at Erdemli are almost twice that of those detected at Finokalia. The mean concentrations of MSA over the measurement periods were 44.6±48.5 at Erdemli and 26.5±20.1 ng m^{-3} at Finokalia. The corresponding nss-sulfate concentrations were 6.97±5.08 and 4.08±2.40 µg m^{-3}. The presence of high standard deviations in the data, comparable to the mean values, indicates significant short-term variability on the order of a few days to a week, especially during the spring and autumn transitions.

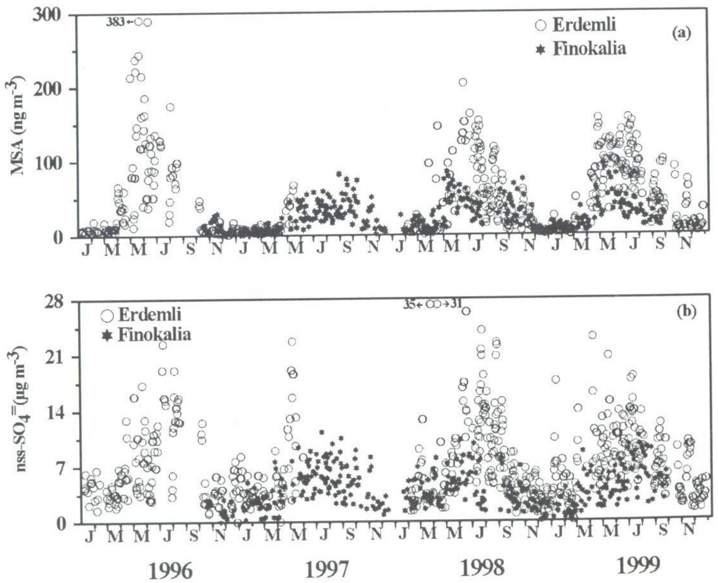

Fig. 2. Distributions of (a) aerosol methanesulfonate (MSA in ng m^{-3}), and (b) non-sea-salt (nss) sulfate concentrations (in µg m^{-3}) in samples collected during January 1996-December 1999 at Erdemli (Turkey) and Finokalia (Crete) shown, respectively, by open circles and solid stars.

Assuming that it can be extrapolated to summer temperatures and coastal marine atmosphere of the Eastern Mediterranean, the empirical relation suggested

by Bates *et al.* [1992] implies that more than 25% of the measured nss-sulfate at Erdemli is estimated to have a biogenic origin during summer (Fig. 3).

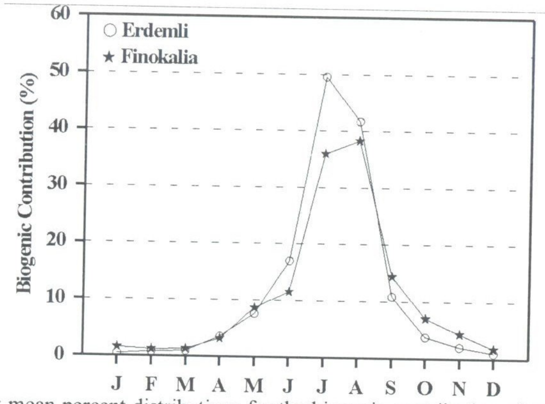

Fig. 3. The monthly mean percent distributions for the biogenic contribution of nss-sulfate estimated by the emprical relation (Bates et al., 1992) at Erdemli (open circles) and Finokalia (solid stars).

Influence of the Black Sea late spring-summer biological production on the aerosol composition of the Eastern Mediterranean atmosphere

The back trajectory analysis of local air masses suggests a clear connection between high biological production in the Black Sea and a considerable increase in the Erdemli and Finokalia MSA concentrations during the summer months (Fig. 4). Here we focus our attention to the June-July periods which matches that of Emiliania huxleyi, strong DMS producer, intense and widespread blooms in the Black Sea (Çokacar et al., 2001)

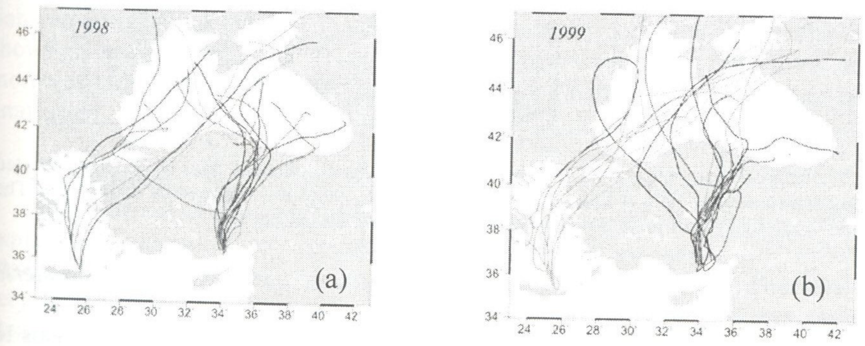

Fig. 4. The 3-day air mass back trajectories showing the transport of air masses to the sampling sites at Erdemli and Finokolia from the Black Sea region at selected times during June-July.(a) 1998; (b) 1999

The back trajectory analysis suggested three distinct periods of atmospheric boundary layer meridional transport from the Black Sea towards Erdemli during June 1998. These periods, as well as others during July and August, are indicated in Fig. 5 by hatched bars superimposed on the temporal variations of MSA concentrations during March-August 1998. The first event persisted approximately for the first 10 days of the month, whereas the second and third ones were shorter and lasted only for three days during 16-18 June and for five days during 26-30 June, respectively. The low level boundary layer transport had a similar monthly structure in July as well. It continued during the first 8 days in July 1998, followed by two more weekly events during 14-21 July and 25-31 July 1998 with some interruptions in between. Thus, the overall duration of transport from the Black Sea amounts to roughly two-thirds of this period. The trajectories from selected days of these events are shown in Fig. 4a. This period was completely dry, without any precipitation, as indicated by the rain data in Fig. 5.

The air mass trajectory analysis for Erdemli and Finokalia therefore points to an unprecended influence of Black Sea biological production on the Eastern Mediterranean sulfur budget. This interaction allows us to provide a more definitive interpretation for the causes of temporal and spatial variabilities observed in the summer MSA measurements of the Eastern Mediterranean. The fact that the Finokalia site is not influenced by air masses from the Black Sea as frequently as the Erdemli site would explain its relatively lower observed concentrations during the summer months.

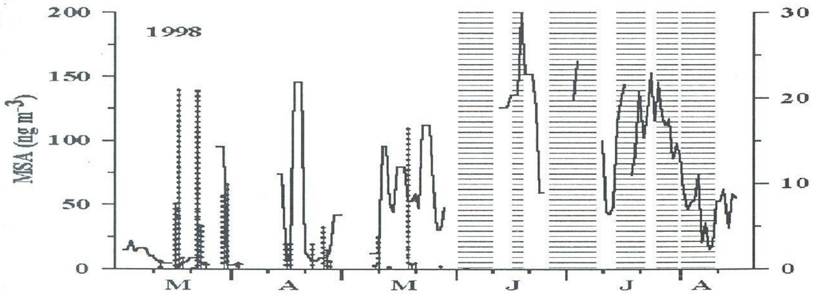

Fig 5. Temporal distribution of aerosol MSA concentrations (continuous line) in samples collected during March-August 1998 at Erdemli (Turkey). Daily rain events are indicated by dotted lines. The periods of northerly transports from the Black Sea are shown by hatched bars.

Contribution of Saharan dust events to oceanic production of atmospheric sulfur

Our analysis of the data during spring months of 1998 and 1999 also seems to suggest contribution of Saharan-based aeolian supply to increase in the MSA concentrations of the Eastern Mediterranean atmosphere. Their link is established by temporal enhancement of DMS production of the Eastern Mediterranean surface layer through its fertilization by wet deposition of phosphate, iron and other nutrients supplied during these dust transports events.

Two sets of three-day back trajectories shown in Fig. 6a indicate that the entire eastern parts of the Eastern Mediterranean Sea are influenced by two simultaneous Saharan dust transport events during the first half of May, 1998. The Saharan dust supply, commenced at the beginning of the month (implied by similar back trajectories as in Fig. 6a), is deposited eventually over the basin as indicated by precipitation monitored at the local meteorological station near the Erdemli site during 9 and 10 May, 1998 (cf. Fig. 5). The precipitation should affect different areas of the basin at different time intervals, and therefore should lead to a longer period of deposition of dust particles with a subsequent increase in phytoplankton production. These sequences of events are seen in an abrupt increase in MSA concentrations from ~10-20 ng m^{-3} measured during the first 10 days of May to 60 ng m^{-3} at Finokalia and 95 ng m^{-3} at Erdemli during 11 May 1998 (cf. Fig. 5). The next event took place a week later. Following the precipitation recorded at Erdemli during 18-20 May, the MSA concentrations increased even further to 72 ng m^{-3} at Finokalia and 111 ng m^{-3} at Erdemli during 22-23 May 1998. The precipitation seemed to have a temporally adverse effect on sulfur aerosols by reducing their concentrations via wet deposition scavenging. For example, the three day mean MSA concentrations of 79 ng m^{-3} during 15-17 May prior to the precipitation event at Erdemli decreased to the mean value of 55 ng m^{-3} at the time of the precipitation event (18-20 May), and then increased to the three day mean value of 111 ng m^{-3} during 22-24 May 1998 (cf. Fig. 5). A similar event was also observed to take place in April 1998 at Erdemli. The MSA concentrations, which had already elevated to 74 ng m^{-3} during 13-14 April, have reduced sharply to the mean value of 10 ng m^{-3} during 15-16 April at the time of precipitation, and then increased to a mean value of 145 ng m^{-3} within the next three days.

Depending on the direction of air masses across the Eastern Mediterranean Sea and patchiness of precipitation associated with local meteorological conditions, the Saharan-derived production will exhibit some variability over the basin. Fig. 6b shows an example for a dust transport and deposition event during April 1999 that increases the MSA concentrations only at Erdemli, while the Cretan side remains unaffected.

Conclusion

In the current study, we highlight a series of processes working concurrently to explain the variations of aerosol sulfate concentrations within the Eastern Mediterranean atmosphere. As the region offers a relatively closed system with a very strong signatures in the ocean-atmosphere sulfate cycling, it may serve as an ideal environment to carry out more detailed interdisciplinary studies to understand the details of the many processes of global importance controlling the functioning of the sulfate cycling from oceanographic, atmospheric and climatic perspectives.

Note-The full article of the presented study has been published in *Global Biogeochemical Cycles*, **16(4)**, 1079, doi:10.1029/2002GB001880, 2002.

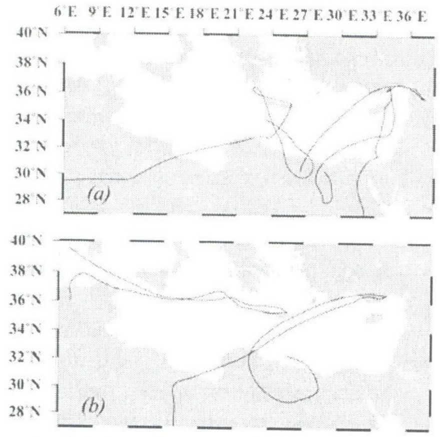

Fig. 6 The three-day air mass back trajectories suggesting Saharan-originated mineral dust transport to the sampling sites at Erdemli and Finokalia with long fetch over the Eastern Mediterranean Sea during (a) 11, 17 May 1998, (b) 18, 27 April 1999.

Acknowledgements-*This study was funded in part by Middle East Technical University (METU) AFP-2001-07-01-01 Project, the Turkish Scientific and Technical Research Council (TUBITAK) project 100Y121, WMO/UNEP through special service agreements (5.115/A/CNS and 18.637/A/CNS).*

References

Bates, T. S., J. A. Calhoun and P. K. Quinn. Variations in the methanesulfonate to sulfate molar ratio in submicrometer marine aerosol particles over the south Pacific ocean, *J. Geophys. Res.*, **97**, 9859-9865, (1992).

Charlson, R. J., J. E. Lovelock, M. O. Andreae. and S. G. Warren. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate: A geophysiological feedback, *Nature*, **326**, 655-661, (1987).

Charlson, R. J., J. Longner, H. Rodhe, C. B. Leavy, and S. G. Warren.. Perturbation of the Northern hemisphere radiative balance by backscattering from anthropogenic sulphate aerosols, *Tellus*, **43AB,** 152-163, (1991).

Çokacar, T., N. Kubilay , T. Oguz. Structure of E. huxleyi blooms in the Black Sea surface waters as detected by SeaWIFS imagery, *Geophys. Res. Lett.*, **28**, 4607-4610, (2001).

Kouvarakis, G., and N. Mihalopoulos. Seasonal variation of gaseous dimethylsulfide and sulfur species in aerosol phase in the Eastern Mediterranean atmosphere, *Atmos. Env.*, **36**, 929-938, (2002).

Kouvarakis, G., H. Bardouki and N. Mihalopoulos. Sulfur budget above the eastern Mediterranean: Relative contribution of anthropogenic and biogenic sources, *Tellus*, **54**, 201-212, (2002).