Influence of Black Sea and local biogenic activity on the seasonal variation of aerosol sulfur species in the eastern Mediterranean atmosphere

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[1] Methanesulfonate (MSA) and non-sea-salt (nss) sulfate concentrations were measured in bulk aerosol samples collected during January 1996 to December 1999 at two stations along the Turkish and Cretan coastline of the eastern Mediterranean. The data set enabled the origin and variability of biogenically derived 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, Crete (25.8 ± 14.9 ng m^{-3} MSA and 3.9 ± 1.7 μg m^{-3} nss sulfate). Analysis of the air mass back trajectory and the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) data suggests that the majority of the biogenic contribution at Erdemli is originated from summer coccolithophorid *Emiliania huxleyi* blooms developed in the Black Sea. The data further points to a significant relationship between Saharan dust transport events and local oceanic production of MSA through occasional fertilization of the eastern Mediterranean during wet deposition events. This process accounts for episodic, strong weekly changes in MSA 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. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 3339 Meteorology and Atmospheric Dynamics: Ocean/atmosphere interactions (0312, 4504); 0933 Exploration Geophysics: Remote sensing; 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; *KEYWORDS:* aerosol, eastern Mediterranean, methane sulfonate, nss-sulfate, Emiliania huxleyi, Black Sea

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1. Introduction

[2] 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 photochemical 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].

[3] As shown in Table 1, concentrations of aerosol MSA and nss-sulfate have illustrated considerable spatial and temporal variabilities within the global atmosphere. When compared to other open ocean locations, the marine atmosphere over the eastern Mediterranean exhibits high levels of nss-sulfate concentrations similar to the values typically observed over the neighboring heavily industrialized landmass of Europe, and of MSA concentrations as in Icelandic-North Atlantic waters and in the North Pacific [*Mihalopoulos et al.*, 1997; *Luria et al.*, 1989; *Ganor et al.*, 2000;

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Table 1. Comparison of the Mean and Range of Aerosol Sulfate and Methanesulfonate Concentrations Reported From Various Locations Around the World

Location	nss-SO_4^{2-}(μg m^{-3})	MSA(ng m^{-3})
Pacific Ocean[a]		
New Zealand (36°S, 174°E)[b]	0.76 (0–1.5)	34.9 (1.9–136)
American Samoa (14°S, 171°W)	0.41 (0.14–0.74)	26 (10–45)
Fanning Island (4°N, 159°W)	0.67 (0.39–0.98)	45 (25–68)
Shemya (52°N, 174°E)	–	97 (10–300)
Atlantic Ocean[c]		
Sal Island (17°N, 23°W)	1.99 (0.25–9.6)	27 (7.8–92)
Miami (26°N, 80°W)	2.17 (1.7–3.6)	39 (25–58)
Mace Head (53°N, 10°W)	1.08 (0.02–22.6)	50 (0.1–552)
Iceland (63°N, 20°W)	0.65 (0.06–23.7)	39 (0.1–408)
Atlantic Ocean (meridional transect from 42°S to54°N)[d]	(0.3–9)	(3–90)
Island Sylt in the North Sea	–	(15–300)
Eastern Mediterranean		
Erdemli (36°N, 34°E)[e]	6.8 (0–35.4)	42 (1–383)
Finokalia (35°N, 25°E)[f]	4.1 (0.1–12.4)	27 (4–99)
Israeli coast[g]	7.4 (2–50)	(21–82)
Continental Europe[h]		
Greece (38°N, 23°E)	3.7(1.1–35.6)	
Hungary (46°N, 19°E)	5.9 (0.06–28.9)	
Italy (45°N, 8°E)	3.3 (0.06–14.1)	
Czech Republic (49°N, 15°E)	4.2 (0.3–14.1)	
Poland (54°N, 17°E)	3.6 (0.3–14.9)	
Lithuania (55°N, 21°E)	3.5 (0.8–15.1)	
Russian Fed. (59°N, 29°E)	2.1 (0.1–18.6)	

[a] *Saltzman et al.* [1986].
[b] *Wylie and de Mora* [1996].
[c] D. Savoie (personal communication, 2002).
[d] *Burgermeister and Georgii* [1991].
[e] Present study.
[f] *Kouvarakis and Mihalopoulos* [2002].
[g] *Ganor et al.* [2000]; *Luria et al.* [1989].
[h] *Hjellbrekke* [2000].

Özsoy et al., 2000; *Kouvarakis and Mihalopoulos*, 2002]. However, recent SeaWIFS time series data has confirmed very poor biological production of the eastern Mediterranean. The data, therefore, indicate inability to support such high levels of MSA concentrations. *Özsoy et al.* [2000] have highlighted a close relationship between high nss-sulfate concentrations measured at Erdemli (Turkey) and a particular *Emiliania huxleyi* bloom event in the Black Sea during July 1992. This relationship, however, has not been supported explicitely by measurements of DMS and/or MSA concentrations as well as the spatial coverage, intensity, and duration of this particular *E. huxleyi* bloom event.

[4] 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 4-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].

[5] The current work primarily aims to provide a more definitive explanation for the presence of appreciably high MSA and nss-sulfate concentrations within the marine atmosphere of the poorly productive Eastern Mediterranean during the summer months. Using in situ MSA and nss-sulfate measurements together with SeaWIFS data, and the air mass back trajectory analyses, the enhanced biological activity in the Black Sea is shown to be the primary explanation for the presence of elevated late-spring, summer sulfate aerosol concentrations in the easternmost part of the eastern Mediterranean. The current work, in addition, explores the role of local production triggered by episodic short-term pulses of Saharan dust on the variability of MSA concentrations during the spring season at times when there is wet deposition onto the surface waters of the eastern Mediterranean Sea [*Kubilay et al.*, 2000].

[6] The paper is structured as follows. Section 2 briefly describes the data collection and analyses techniques, including air mass back trajectory analyses. Section 3 provides an overview for the general ecosystem characteristics of the Black Sea and the eastern Mediterranean from the perspective of atmospheric sulfur aerosol production. This section also includes some new results from our ongoing studies on the characteristics of *E. huxleyi* blooms in the Black Sea-Aegean Sea-eastern Mediterranean system. Following the presentation of seasonal variations of MSA and nss-sulfate concentrations at Erdemli and Finokalia in section 4, we report our findings on the possible connection between the Black Sea summer biological production and the elevated MSA concentrations of the eastern Mediterranean atmosphere in section 5. Section 6 attempts to relate weekly variations of the MSA concentrations during spring to episodic Saharan dust events and their subsequent deposition and fertilization to the eastern Mediterranean surface waters. Finally, a summary of the results and the main conclusions are given in section 7.

2. Material and Methods

[7] 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 × 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 hours at Finokalia. The sampling locations are illustrated in Figure 1. For more details on local conditions of the sampling sites and aerosol collections, please refer to *Kubilay et al.* [2000], *Özsoy et al.* [2000], *Mihalopoulos et al.* [1997] and *Kouvarakis et al.* [2000].

[8] The major soluble ion species within the atmospheric aerosol extracts were analyzed by ion chromatography (IC) using a Dionex AS4A-SC column with an ASRS-I suppres-

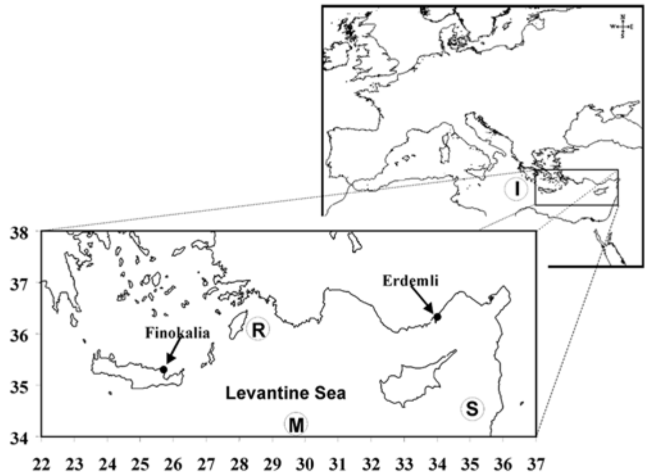

Figure 1. Location map of the eastern Mediterranean and the sampling site on the island of Crete (Finokalia) and on the southern coast of Turkey (Erdemli). R, M, and S refer to approximate locations of Rhodes, Mersa Matruh, and Shikmona gyres of the Levantine Basin, respectively. I in the greater Mediterranean Sea plot represents the region of the Ionian Sea.

sor. SO_4^{-2} (sample volume: 100 μl) was determined with an isocratic elution at 2.0 ml min^{-1} using a $Na_2CO_3/NaHCO_3$ eluent. MSA^- (sample volume: 500 μl) was determined with isocratic elution with a 2.5 mM $Na_2B_4O_7$ eluent and a flow rate of 2.0 ml min^{-1}. For cations a CS12-SC column was used with a CSRS-I suppressor. Separation was achieved under isocratic conditions with a 20 mM MSA eluent and a flow rate of 1.0 ml min^{-1}. The reproducibility of the measurements was better than 2% and the detection limit corresponded to 2 pmol m^{-3} for a mean air volume of 1000 m^3. Non-sea-salt sulfate concentrations were calculated using Na^+ as a conservative tracer of sea-salt origin. More details on the analytical technique are given by *Baboukas et al.* [2000].

[9] Air mass back trajectories were provided by the European Centre for Medium Range Weather Forecasts (ECMWF). The trajectories show routes of air masses arriving between the surface and 850 hPa at the sampling sites for the past 72 hours.

3. General Characteristics of the Black Sea and Eastern Mediterranean Ecosystems in Relation to Oceanic Production of Atmospheric Sulfur

3.1. Black Sea Ecosystem Characteristics

[10] Riverine discharge into the northwestern part of the Black Sea has been altered considerably since the 1970s owing to the diminishing net fresh water inflow (due to the construction of dams). There has also been an enhancement in the nutrient fluxes (due to pollution). This has lead to the development of massive eutrophication events and changes in the nutrient content of surface waters. One outcome has been the dramatic change in the ecosystem of the Black Sea at all trophic levels. Phytoplankton community structure and species succession have been shifted from a diatom-dominated siliceous system to a dinoflagellate and coco-lithophorid-dominated nonsiliceous system [*Humborg et al.*, 1997]. The number of species observed to bloom has doubled, areal coverage of the blooms has expanded tenfold [*Zaitsev and Mamaev*, 1997], and the natural phytoplankton annual cycle with spring and autumn maxima has been replaced by a pattern involving a series of exceptional maxima [*Yılmaz et al.*, 1998]. Quantitative evaluation of the factors controlling these ecosystems changes and their implications on the overall biogeochemical characteristics of the water column have been reviewed by *Oguz et al.* [2001].

[11] The observed SeaWiFS-derived surface chlorophyll concentrations persistently range (every year since 1997) from ∼1.0–1.5 mg m^{-3}. They prevail over the basin throughout the autumn, winter, and early spring, suggesting high biological activity throughout the sea within the second half of the 1990s [see *Oguz et al.*, 2002, Figures 7 and 8]. In addition, the SEAWIFS chlorophyll patterns revealed complex spatial structure around the periphery of the basin where the meandering Rim Current circulation system maintains a continuous supply of nutrients from the northwestern shelf into the basin [see *Oguz et al.*, 2002, Figure 12]. The overall production is especially strong in the heavily polluted waters of the northwestern shelf, as well as of the adjacent Azov Sea on the north and the Marmara Sea to the southwest, which interact with the Black Sea through the Kerch and Bosphorus Straits, respectively. These regions, constituting almost 30% of the Black Sea total surface area, are identified by permanently high surface chlorophyll concentrations greater than 5 mg m^{-3}, irrespective of the seasons.

[12] A major proportion of productivity in the region appears to be composed of strong DMS producers, such as haptophytes (including coccolithophorids and small flagellates) and small dinoflagellates especially during the spring and summer months [*Moncheva et al.*, 1998; *Eker et al.*, 1999; *Çokacar et al.*, 2001]. All the available findings suggest that within the last 2 decades, the Black Sea ecosystem has transformed from a mesotrophic system with a limited plankton productivity into a potential year-round DMS supplier for the atmosphere over the Black Sea-Aegean Sea- eastern Mediterranean Sea system. Unfortunately, the measurements providing quantitative estimates for the annual DMS and MSA production rates and their seasonal variations are not presently available for the Black Sea.

[13] The coccolithoprid *E. huxleyi* has always been one of the predominant species in the Black Sea plankton community. They have been traced by a high carbonate content in sediment cores [*Hay and Honjo*, 1989; *Tekiroglu et al.*, 2001], by in situ measurements [*Sorokin*, 1983; *Benli*, 1987; *Mankovsky et al.*, 1996; *Uysal et al.*, 1998], and from Coastal Zone Color Scanner (CZCS) imagery [*Sur et al.*, 1994] in different parts of the basin, some periods during the late spring-summer and the autumn-early winter. Using the 8-day composite, 9-km resolution, level 3 SeaWiFS water-leaving radiance data (normalized as if it would be measured on the ocean surface with the sun directly overhead) for 1997–2000, the temporal and spatial character-

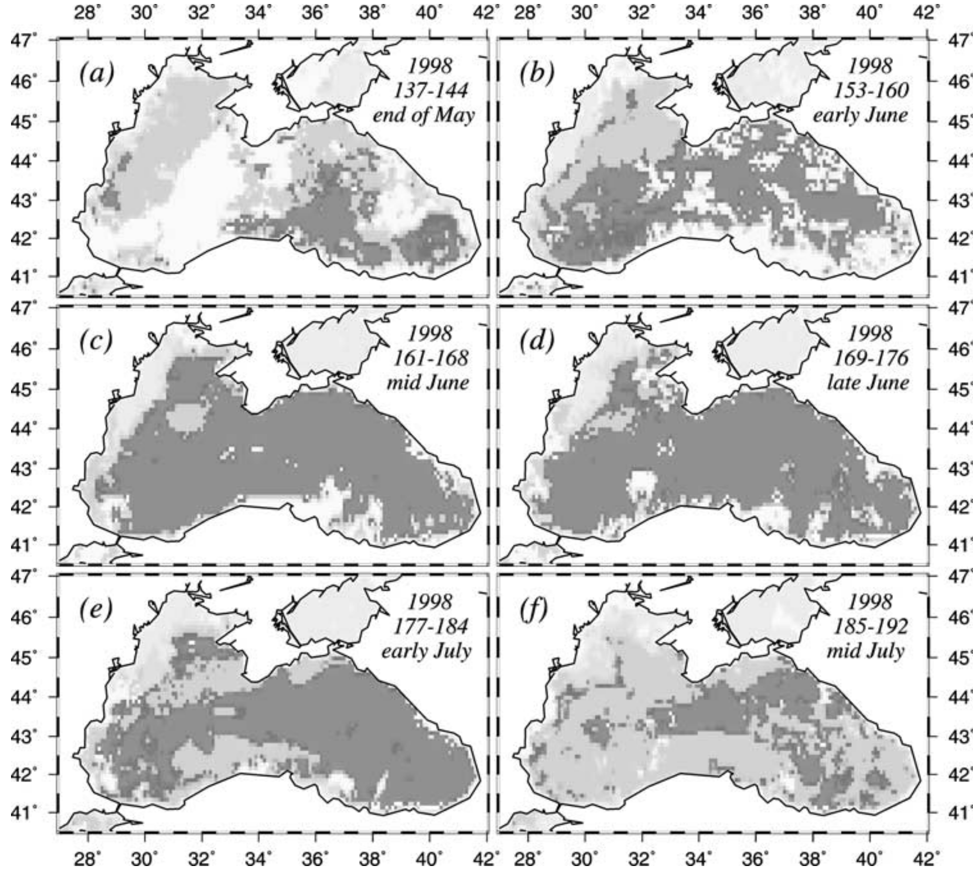

Figure 2. SeaWiFS-derived 8-day-composite coccolith distributions within the Black Sea during May–July 1998 period at Julian days (a) 137–144 (end of May), (b) 153–160 (early June), (c) 161–168 (mid-June), (d) 169–176 (late-June), (e) 177–184 (early July), and (f) 185–192 (mid-July). Black represents the regions covered by coccoliths, shading represents the regions without coccoliths, and white shows no data due to cloud coverage.

istics of the blooms have been identified in the surface waters of the Black Sea according to the distinct spectral signatures of coccolith platelets [*Çokacar et al.*, 2001]. The pixels satisfying the prespecified ranges of five distinct combinations of mean normalized water leaving radiances at 443, 510, and 555 nm have been considered to represent high concentrations of coccoliths.

[14] According to this analysis, the Black Sea experiences high reflectance patches of coccolith platelets throughout the basin each year during the May–July period (Figures 2 and 3). During 1998, the bloom marked in Figure 2 by black areas seemed to originate from the southeastern part of the Black Sea toward the end of May (Figure 2a), and then rapidly spreads throughout the basin within a week (Figure 2b), and persisted on a basinwide coverage for the entire month of June, 1998 (Figures 2c and 2d). The bloom began to diminish by early July (Figure 2e), and finally disappeared toward the end of July (Figure 2f).

[15] During the same period (May–July) of 1999, the bloom structure possessed a more patchy character (Figure 3). It commenced to spread from the northern peripheral waters of the eastern basin during mid-May (Figure 3a), eventually covering the entire eastern basin by the end of May and the early June (Figures 3b and 3c), and then expanded into the western basin toward the end of June (Figures 3d and 3e). By mid-July, some scattered coccolith patches remained noticeable in the eastern basin (Figure 3f).

[16] It should be noted that the Sea of Azov and the western shallow coastal waters are excluded from the interpretation of the data in these figures in order to avoid contamination from high-turbidity shelf waters. Although the current versions of the SeaWiFS algorithms are not reliable enough to infer *E. huxleyi* blooms in turbid waters, these heavily polluted regions, known to be very productive for almost the entire year, are characterized by complex phytoplankton species structure capable of producing DMS.

3.2. Eastern Mediterranean Sea Ecosystem Characteristics

[17] In contrast to the Black Sea, the Mediterranean Sea, particularly the Eastern Basin, is an extremely oligotrophic system [*Dugdale and Wilkerson*, 1988; *Azov*, 1991; *Yacobi et al.*, 1995]. In the eastern Mediterranean Sea, the biological production most actively takes place only along selected coastal and peripheral waters [*Psarra et al.*, 2000], and in the Rhodes cyclonic gyre [*Napolitano et al.*, 2000]. The rest (i.e., the anticyclonic gyres of the Ionian basin and the anticyclonic Mersa-Matruh and Shikmona

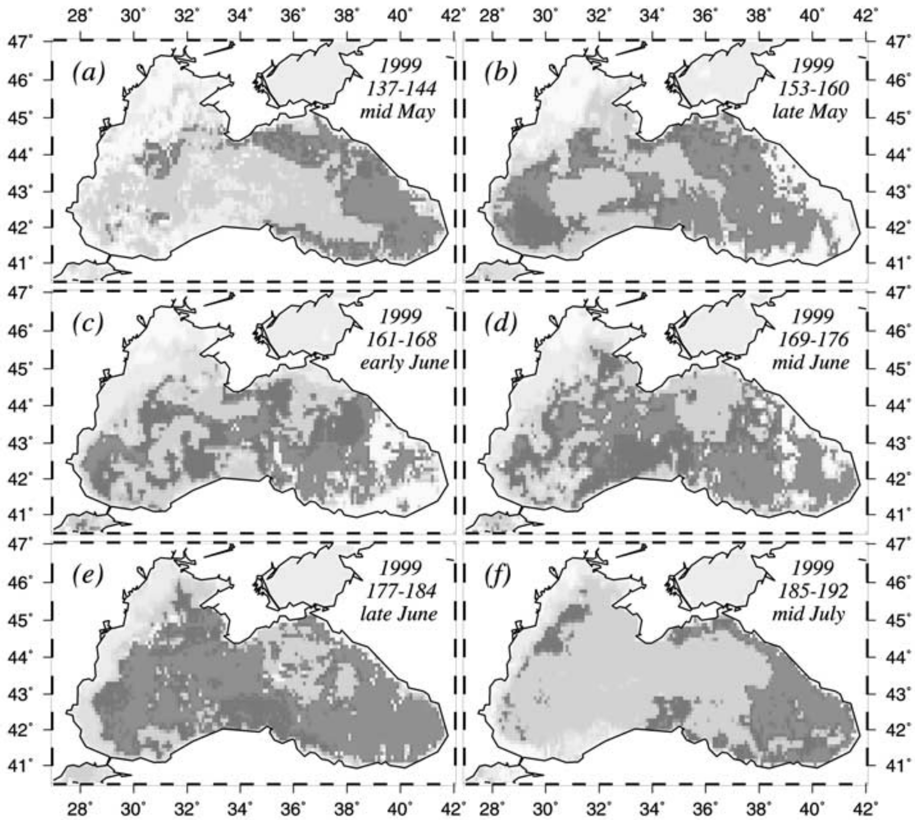

Figure 3. SeaWiFS-derived 8-day-composite coccolith distributions within the Black Sea during the May–July 1999 period at Julian days (a) 129–136 (mid-May), (b) 145–152 (late May), (c) 161–168 (mid-June), (d) 169–176 (late-June), (e) 177–184 (early July), and (f) 185–192 (mid-July). Black represents the regions covered by coccoliths, shading represents the regions without coccoliths, and white shows no data due to cloud coverage.

gyres of the Levantine basin as well as the Cretan Sea) in comparison has a low productivity. The monthly averaged pigment concentrations derived from the CZCS data for the eastern Mediterranean during the period 1979–1985 reveal highest concentrations of $\sim$0.2 mg m^{-3} during the December–March period [see *Ziveri et al.*, 2000, Figure 6]. These concentrations are approximately an order of magnitude smaller than the corresponding values in the Black Sea [see *Nezlin*, 2000, Figure 1].

[18] The sediment trap measurements performed from November 1991 to August 1994 at 3000 and 3500 m depths in the westernmost part of the eastern Mediterranean [*Ziveri et al.*, 2000] indicated that coccolithophores (mainly *E. huxleyi*) are the most dominant and abundant phytoplankton group with the highest fluxes taking place during March–April–May. These findings are also supported by the measurements of *Knappertsbusch* [1993] and *Balopoulos et al.* [1996]. The trap data further suggested that even though coccolithophore production dominated the system, its abundance within traps rarely reached the bloom level. The annual total coccolith flux of 1.0×10^{10} coccoliths m^{-2} yr^{-1} was actually 10–100 times lower than those measured in other oceanographic regions [see *Ziveri et al.*, 2000] and in the Black Sea [*Hay and Honjo*, 1989]. Because of their relatively low abundance, their detection by the SeaWiFS sensors is not as successful as in the Black Sea.

[19] Some correlations between the episodic increases of coccolith fluxes and periods of wet deposition of Saharan dust are evident from the trap data [*Ziveri et al.*, 2000]. This relation has been explained by the fertilization of the sea with inorganic phosphorus, which is known to be the most limiting nutrient [*Zohary and Robarts*, 1998] controlling *E. huxleyi* production in the eastern Mediterranean. The possibility of episodic phytoplankton blooms triggered by atmospheric deposition of nitrogen, phosphorus and iron has also been pointed out by *Guerzoni et al.* [1999]. A similar relationship has been suggested over geological timescales by *Henriksson et al.* [2000]. The laboratory experiments carried out by *Saydam and Senyuva* [2002] have provided an independent confirmation that phosphorus and iron are the two most dominant nutrients within Saharan dust particles. For some cases, when dust depositions leads to sufficiently strong fertilization of the surface waters within a reasonably large area, it is possible to identify enhanced *E. huxleyi* production events by the AVHRR satellite imagery in the form of localized high-reflectance

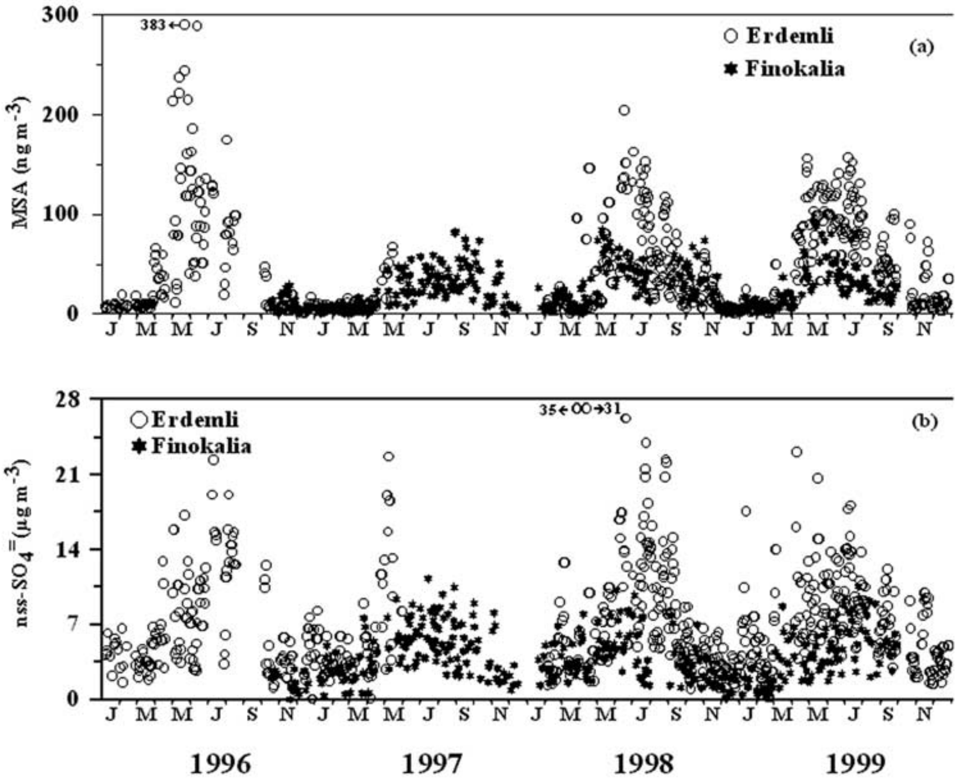

Figure 4. Distributions of (a) aerosol methanesulfonate (MSA in ng m^{-3}) and (b) non-sea-salt (nss) sulfate concentrations (in μg m^{-3}) in samples collected during January 1996 to December 1999 at Erdemli (Turkey) and Finokalia (Crete) shown by open circles and solid stars, respectively.

patches [*Saydam and Polat*, 1999]. In the subsequent sections, we will provide some case studies showing the impacts of such events on the increase of MSA concentrations at Erdemli and Finokalia.

4. Seasonal Variations of MSA and NSS-Sulfate Concentrations

[20] The variations of daily measured MSA and nss-sulfate concentrations during the 4-year period from January 1996 up to the end of 1999 at Erdemli and Finokalia stations are shown in Figure 4. Two important features are immediately noticeable from these data sets: (1) Both indicate a clear signature of seasonal variations, with high summer to low winter values, and (2) 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. The MSA concentrations at Erdemli acquired their peak values of greater than 200 ng m^{-3} in 1996, and around 150–200 ng m^{-3} in 1998 and 1999. High concentrations are consistently observed during late May and early June, and are maintained throughout June and July (Figure 4a). These values are among the highest measured in the world (see Table 1). The peak concentrations during the same months are ∼75–100 ng m^{-3} at Finokalia.

[21] The level of winter-to-summer variations are reduced by 50% when all the data are pooled together to construct a composite, monthly mean annual data set which filters out short term variations. Even in this case, order of magnitude seasonal differences are evident in the data, especially at Erdemli (Figure 5a). The highest Erdemli MSA concentrations of ∼100 ng m^{-3} occur during June and July. They are almost double those observed in April–May and August–September, which signifies the initiation and termination phases of the enhanced *E. huxleyi* activity in the Black Sea, respectively. The December–January–February concentrations below 10 ng m^{-3}, on the other hand, are the lowest of the year. Instead of a Gaussian type distribution at Erdemli, the MSA concentrations at Finokalia maintain more or less a uniform level of around 40 ng m^{-3} during the June–September period with a slightly higher concentration (∼50 ng m^{-3}) in May. October and November are the only two months where the monthly mean MSA concentrations of Finokalia (∼30 ng m^{-3}) exceed those observed at Erdemli (∼20 ng m^{-3}).

[22] The nss-sulfate concentrations follow similar trends (Figures 4b and 5b). The peak values at Erdemli exceed 20 μg m^{-3} every year; even values up to 35 μg m^{-3} are measured during the summer season (Figure 4b). The

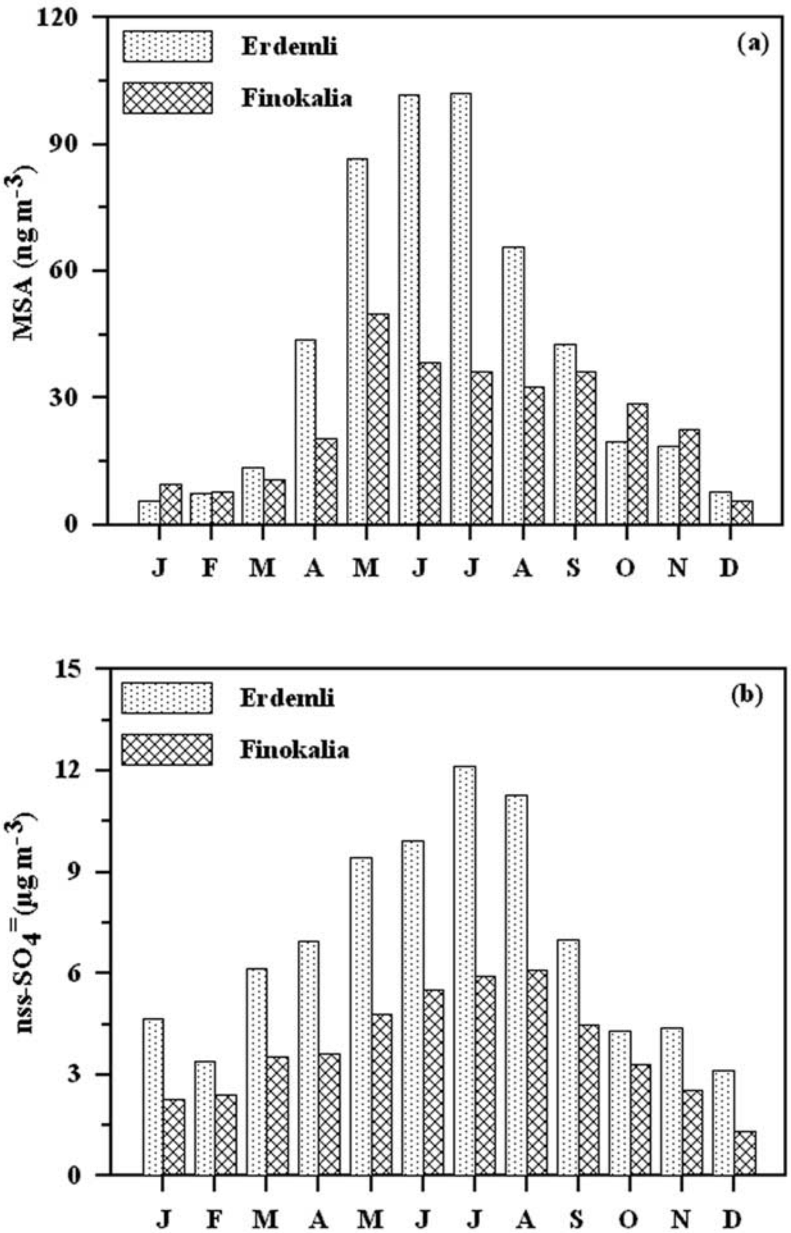

Figure 5. Monthly mean distributions of (a) aerosol methanesulfonate (MSA in ng m^{-3}) and (b) non-sea-salt (nss) sulfate concentrations (in $\mu g\ m^{-3}$) at Erdemli (Turkey) and Finokalia (Crete) shown by dotted and hatched bars, respectively. The monthly means are constructed by forming a composite annual data set.

corresponding maximum concentrations, on the other hand, are around 10 $\mu g\ m^{-3}$ at Finokalia. Once again, the concentrations are approximately halved in the composite, monthly averaged data sets (Figure 5b). From Table 1, it may be noted that the range of values of nss-sulfate concentrations are extremely high when compared with other data sets from different marine regions of the world. The Erdemli mean value of $\sim$7 $\mu g\ m^{-3}$ exceeds the values of the North Atlantic (Iceland) by almost 3 times, and is 20 times the values at some equatorial open Pacific and Antarctic stations. The monthly averaged MSA to nss-sulfate percentage varies between a minimum of 0.2% in winter and a maximum of 1.2% in summer for both Erdemli and Finokalia. Such extremely low values throughout the year would suggest additional contributions of nss-sulfate by means of frequent incursions of pollutant air masses from the three continents surrounding the eastern Mediterranean Sea.

[23] 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-

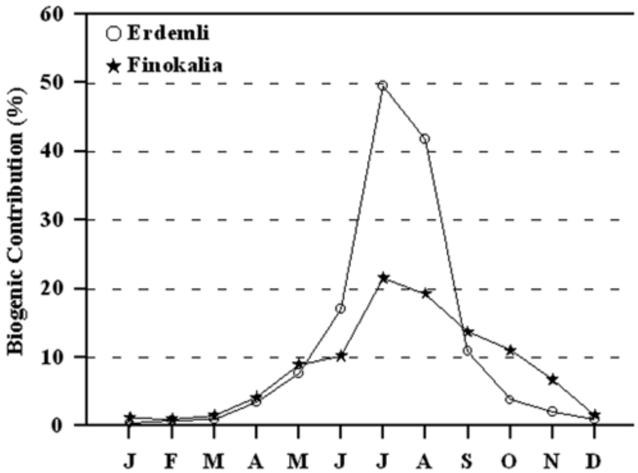

Figure 6. Monthly mean percent distributions for the biogenic contribution of nss-sulfate estimated by the empirical relation [*Bates et al.*, 1992] at Erdemli (open circles) and Finokalia (solid stars).

sulfate at Erdemli is estimated to have a biogenic origin during summer (Figure 6). This contribution may be as high as ~50% during July. The monthly mean biogenically derived nss-sulfate concentrations are about 2.5, 6.0 and 4.0 μg m^{-3}. for June, July, and August, respectively. The corresponding value of the biogenic contribution of nss-sulfate at Finokalia is around 20% in July and is supported independently by the estimate of 26% from the DMS measurements at the same site [*Kouvarakis et al.*, 2002]. This implies that the *Bates et al.* [1992] empirical relationship applies reasonably well for the eastern Mediterranean conditions. We note, however, that this simplistic approach may be questionable and subject to errors if MSA and nss-sulfate are predominantly formed from complex heterogeneous processes [*Davis et al.*, 1999; *Legrand et al.*, 2001].

5. Influence of the Black Sea Late Spring-Summer Biological Production on the Aerosol Composition of the Eastern Mediterranean Atmosphere

[24] 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. Here, we focus our attention to the June–July periods of 1998 and 1999 for which we have a common data set for both the Black Sea *E. huxleyi* bloom activities and sulfur aerosol concentrations at Erdemli and Finokalia. It has already been stated that June–July corresponded to maximum *E. huxleyi* populations in the Black Sea (see Figures 2 and 3).

5.1. Black Sea-Erdemli Teleconnection

5.1.1. Summer 1998

[25] The back-trajectory analysis suggested three distinct periods of atmospheric boundary layer meridional transport from the Black Sea toward Erdemli during June 1998. These periods, as well as others during July and August, are indicated in Figure 7 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 for only 3 days during 16–18 June and for 5 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

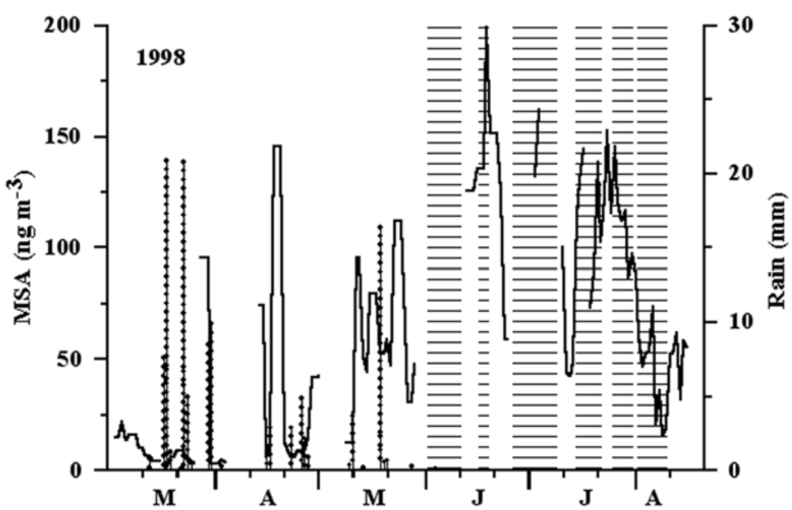

Figure 7. Temporal distribution of aerosol MSA concentrations (solid line) in samples collected during March–August 1998 at Erdemli (Turkey). Daily rain events are indicated by dotted lines. The periods of northerly transports from the Black Sea are shown by hatched bars.

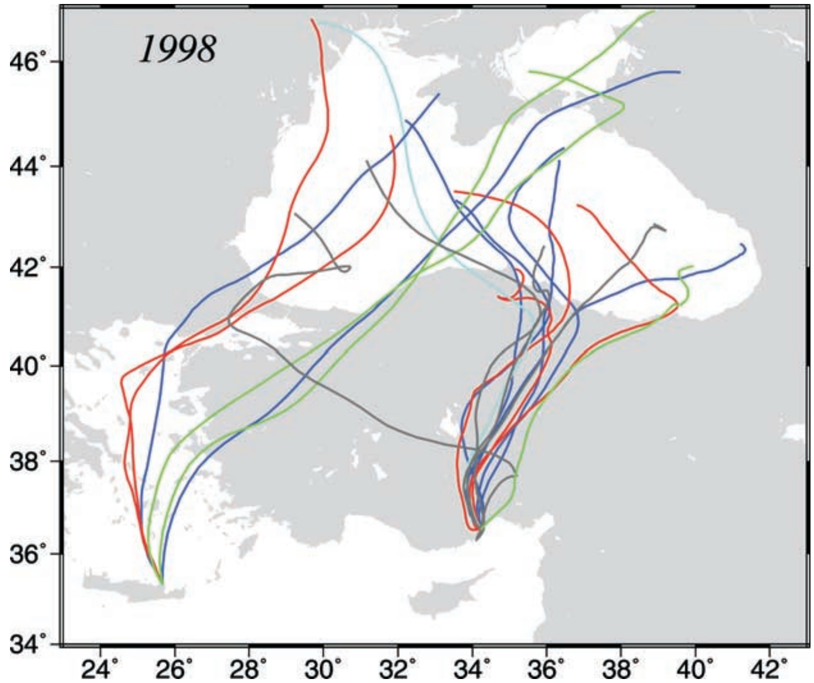

Figure 8. The 3-day air mass back trajectories showing the transport of air masses to the sampling sites at Erdemli and Finokalia from the Black Sea region at selected times during June–July 1998. For Erdemli, blue curves represent the trajectories for 2–6 June, green for 17 June, light blue for 23 June, red for 26–30 June, and black for 1–8 July 1998. For Finokalia, blue curves represent the trajectories for 5–7 June, red for 28–30 June, and green for 22 and 28 July 1998.

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 Figure 8. This period was completely dry, without any precipitation, as indicated by the rain data in Figure 7.

[26] June 1998 MSA and nss-sulfate measurements at Erdemli encompass only the period between 12 and 24 June. In this period, the MSA concentrations tended to increase gradually (cf. Figure 7) from the 3-day mean values of ~125 and ~135 ng m^{-3} to the maximum value of 203 ng m^{-3} during 18 June. The subsequent 3-day mean value of 151 ng m^{-3} was then reduced to ~80 ng m^{-3} during the next 3 days, when the transport from the Black Sea was temporarily interrupted (cf. Figure 7). The 13-day mean value for the whole measurement period corresponds to ~160 ng m^{-3}. The MSA concentrations of 131 and 162 ng m^{-3} measured during 2–3 July 1998 seem to suggest that such high values also persisted during the last week of June.

[27] Figure 9 shows a specific example for such events on 12 June 1998. The high coccolith accumulations in the Black Sea are shown by the turquoise color relative to the dark blue coverage of the eastern Mediterranean representing the absence of any *E. huxleyi* bloom activity during the same period. As shown in Figure 9, the air mass trajectories link the Black Sea DMS production to high level MSA and nss-sulfate concentrations of 136 ng m^{-3} and 12.2 μg m^{-3}, respectively, measured at Erdemli on 16 June 1998. The corresponding values of 47 and 5.1 μg m^{-3} measured at Finokalia do not suggest such an efficient teleconnection mechanism during this particular event. Figure 10 shows the case a week later (24 June 1998) when the low-level transport from the Black Sea to the measurement sites has already shifted toward the northwest over the continental landmass. The MSA and nss-sulfate concentrations then decreased during this period to 59 ng m^{-3} and 5.1 μg m^{-3}, respectively at Erdemli and to 47 ng m^{-3} and 8.4 μg m^{-3} at Finokalia.

[28] It is interesting to note that the reduction in the MSA values to an average value of 47 ng m^{-3} during 8–13 July 1998 matches perfectly with the loss of teleconnection due to the diversion of low-level air transport from northerlies to west-northwesterlies, (i.e., from the Black Sea toward continental Europe), as shown in Figure 7. Once the northerly transport was established again in 14 July, the Black Sea-Erdemli teleconnection brings the MSA concentrations immediately back to their previous level. Their 15-day mean value during the second half of July is ~120 ng m^{-3}. Following a gradual reduction of concentrations at the end of July, they remain more or less at a steady level around 40–60 ng m^{-3} throughout August 1998. As stated in section 3, this period corresponds to the termination phase of the summer *E. huxleyi* bloom episode, even though some flagellate production might continue to take place within deeper parts of the euphotic zone below the seasonal thermocline.

5.1.2. Summer 1999

[29] According to the air mass trajectory analysis (Figure 9), the teleconnection between the Black Sea and Erdemli is established in summer 1999 during the last week of May, following a 3-week-long transport from the south and

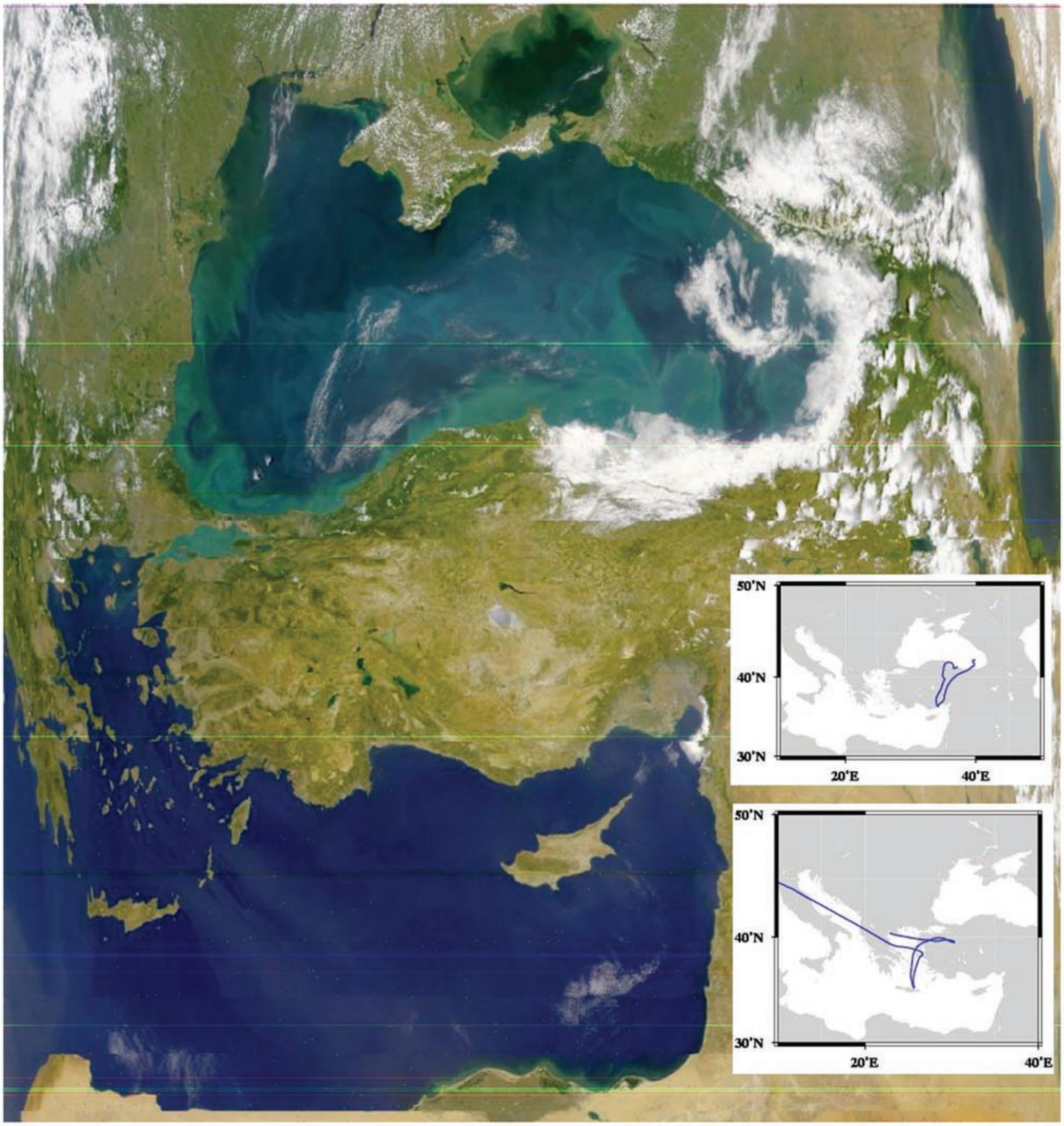

Figure 9. SeaWiFS true color image for 12 June 1998 (Julian day 163) for the Black Sea-Aegean Sea-eastern Mediterranean Sea system. The enhanced *Emiliania huxleyi* bloom activity within the Black Sea is clearly depicted by the turquoise color, in contrast to the rest of the system shown by the dark blue color. Also superimposed on this picture are the 3-day air mass back trajectories for 16–17 June 1998.

southwest over the Sahara and the Mediterranean Sea. A composite of these summer northerly transport events superimposed on temporal variations of MSA concentrations is shown in Figure 12. The northerly transport lasts from 27 May to 9 June. Prior to the northerly transport, the background concentration at Erdemli was around 90 ng m^{-3}. This level of relatively high concentrations should be maintained due to local production, as will be described in more details in section 6. The MSA concentrations attained a mean value of ~110 ng m^{-3} during 27 May to 9 June 1999. Following an interruption period of 9–12 June, it persists during the rest of June and within the first half of July 1999 except two more short-term interruption events (Figure 12). The short-term shift in the air mass

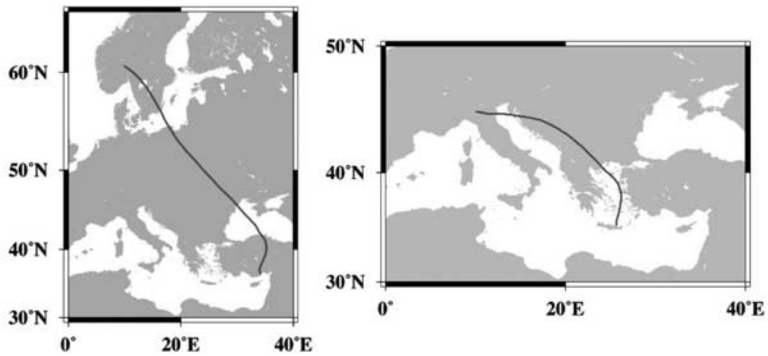

Figure 10. The 3-day air mass back trajectories showing the transport of air masses to the sampling sites at Erdemli (left) and Finokalia (right) from continental Europe on 24 June 1998.

trajectories was immediately seen in the Erdemli MSA concentrations by an almost 50% reduction to 50–60 ng m^{-3} during 9–12 June 1999. A similar reduction was also seen to take place during 18–20 June and 25–27 June as a result of other diversions in the trajectory path from the Black Sea. Otherwise, the MSA concentrations remained around 100–120 ng m^{-3} in June and the first week of July with the highest measured values of ~150 ng m^{-3} on 21 June and 11–12 July 1999. Following a short interruption of the transport from the Black Sea and subsequent decrease in MSA concentrations during 16–19 July, the teleconnection and higher levels of MSA concentrations persist another week within the second half of July. The Erdemli MSA concentrations increases from ~60 to ~110 ng m^{-3} during this event. Thereafter, as in the case of previous year, the concentrations decrease gradually in August.

5.2. Black Sea-Finokalia Teleconnection

[30] The air mass back-trajectory analyses at Finokalia indicated that low level air transport dominated preferentially from the Western Mediterranean during May–July 1998 and 1999. Finokalia was therefore not affected to the same degree by the Black Sea biogenic transport as Erdemli. During 1998, the teleconnection with the Black Sea is established only occasionally during 8–14 May, 4–7 June, 27 June to 2 July, and 19–31 July (Figure 8). Following the relatively lower values of ~30 ng m^{-3} during 1–3 June, the MSA concentrations increased to the mean value of 62 ng m^{-3} during the 4–7 June transport event. Thereafter, they decreased slightly to the mean value of ~45 ng m^{-3} during the rest of June, except with a slight increase to ~55 ng m^{-3} during the week teleconnection event of late June–early July. The rest of July 1998 is characterized by MSA concentrations of less than 30 ng m^{-3}.

[31] The northerly air mass trajectories were also observed occasionally during 7–11, 14–17, and 26–27 June 1999 and 5–9, 12–14, and 17–20 July 1999 (Figure 11). The first two events in June ensured MSA concentrations above 50 ng m^{-3} with a maximum value of 80 ng m^{-3} being measured on 7 July 1999. The MSA concentrations typically varied between 20 and 30 ng m^{-3} during the rest of June and early July with some occasional daily values up to 40 ng m^{-3}. Two peak values of 74 and 81 ng m^{-3} measured during 12 and 20 July coincided with short-term episodic transports from the Black Sea.

[32] The air mass trajectory analysis for Erdemli and Finokalia therefore points to an unprecedented 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.

6. Contribution of Saharan Dust Events to Oceanic Production of Atmospheric Sulfur

[33] The contribution of Saharan-based aeolian supply of nutrients on the generation of the toxic dinoflagellate *Gymnodinium breve* blooms along the west Florida shelf and the eastern Gulf of Mexico has been recently reported by *Walsh and Steidinger* [2001] and *Lenes et al.* [2001]. 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.

[34] Two sets of 3-day back trajectories shown in Figure 13a 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 Figure 13a), 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. Figure 7). 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.

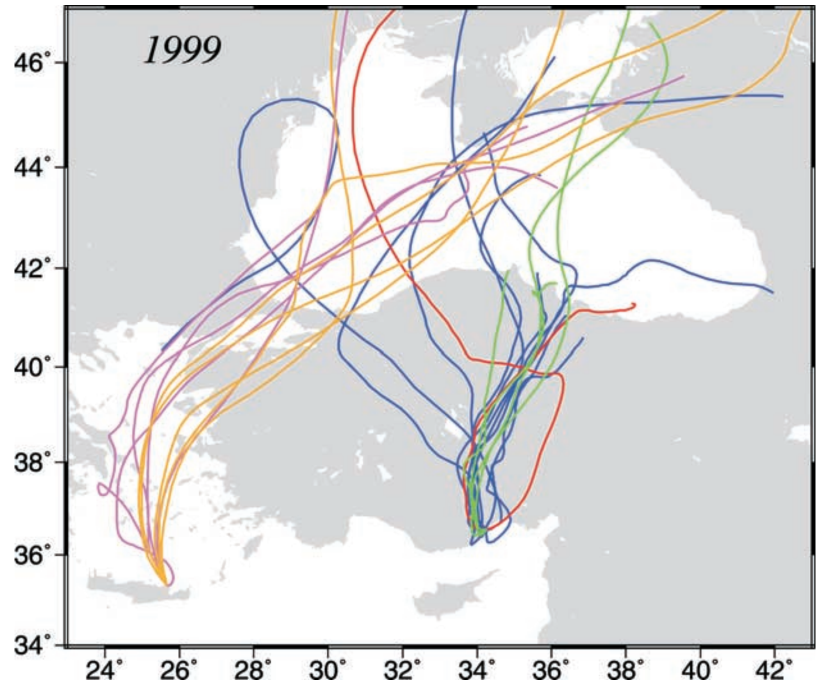

Figure 11. Same as Figure 8 except for June–July 1999. For Erdemli, red curves represent the trajectories for 28–30 May, blue for selected days during 1–29 June, and green for 5–14 July 1999. For Finokalia, violet curves represent the trajectories for 7, 9, 14, 17, and 26 June, and yellow for 6, 9, 14, 17, and 19 July 1999.

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. Figure 7). 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 3-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 3-day mean value of 111 ng m^{-3} during 22–24 May 1998 (cf. Figure 7).

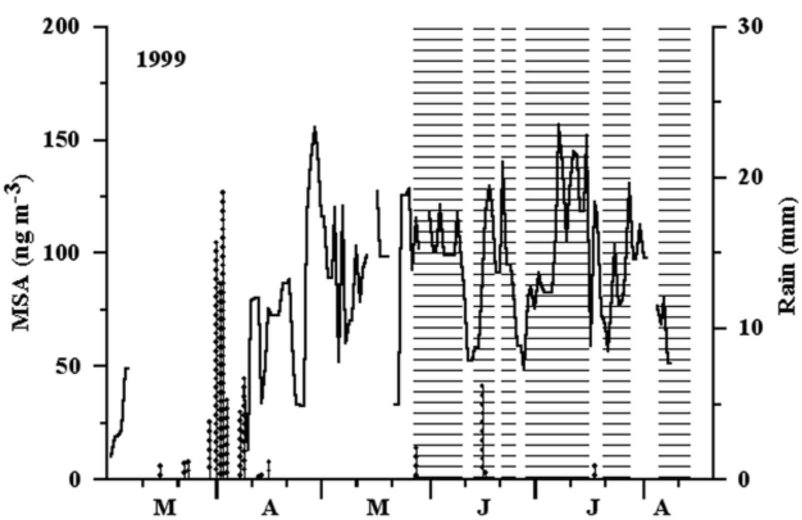

Figure 12. Temporal distribution of aerosol MSA concentrations (continuous line) in samples collected during March–August 1999 at Erdemli (Turkey). Daily rain events are indicated by dotted lines. The periods of northerly transports from the Black Sea are shown by hatched bars.

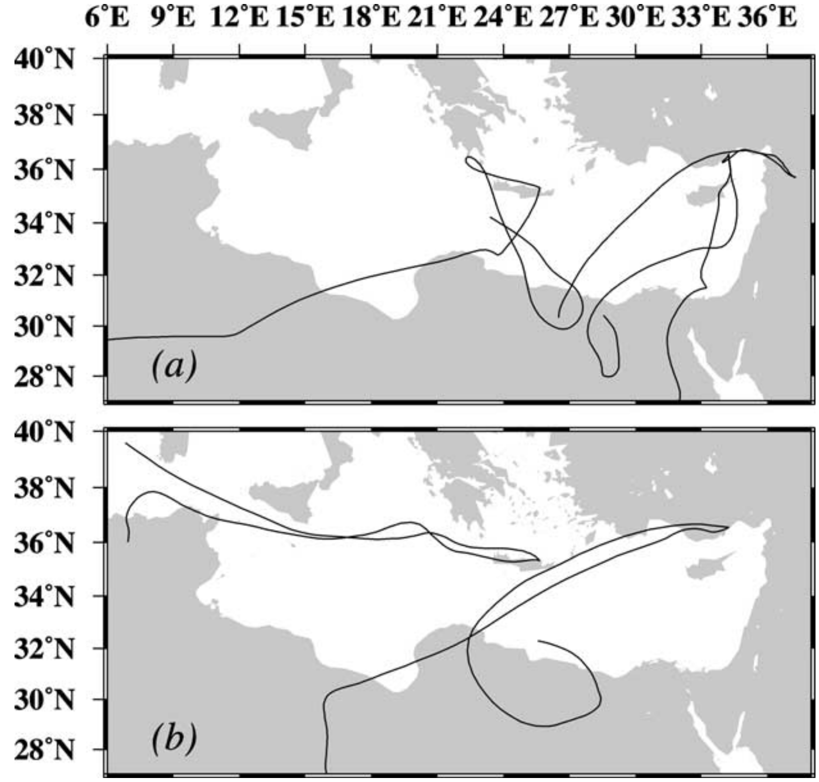

Figure 13. The 3-day air mass back trajectories suggesting Saharan-originated mineral dust transport to the sampling sites at Erdemli and Finokalia with long fetch over the eastern Mediterranean Sea during (a) 11 and 17 May 1998 and (b) 18 and 27 April 1999.

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 3 days.

[35] 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. Figure 13b 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. Following the dust transport during the first week of April 1999 and subsequent wet deposition on 7–8 April, the Erdemli MSA concentrations reduced first to 12 ng m^{-3} then increased up to 79 ng m^{-3} during 9–11 April (cf. Figure 12). As the Saharan-based dust transport continued to affect the Levantine basin, the next rain event reduced the MSA concentrations temporarily to 33 ng m^{-3} during 13–14 April. The concentrations then increased to a mean value of 72 ng m^{-3} during 16–18 April, and 87 ng m^{-3} during the following 3 days (cf. Figure 12). The corresponding MSA concentrations at Finokalia during the same period, on the other hand, were not more than 20 ng m^{-3}. They increased gradually to ~150 ng m^{-3} during 27–29 April at Erdemli, while the Finokalia concentrations did not exceed 30–40 ng m^{-3} during the same time period. In addition to poor local production, the Finokalia site does not receive marine originated sulfur aerosols from the western basin due to its poor biological productivity.

7. Summary and Conclusions

[36] The present work reports for the first time the results from a 4-year-long time series on MSA and nss-sulfate concentrations in the easternmost part of the eastern Mediterranean. The origin of unexpectedly high sulfate aerosol productions over this very poor productive sea is elucidated. Our analyses are based on the measurements at two coastal sites, one located near Erdemli, along the Mediterranean coast of Turkey, representative of the northeastern part of the Levantine basin of the eastern Mediterranean, and the other located on the island of Crete, almost 1000 km west of Erdemli, representative of the western basin of the eastern Mediterranean. These data sets are complemented by Sea-WiFS time series data in order to relate their temporal variations to biological production in the region. Air mass back-trajectory analyses was also used to explain these variations in terms of local versus remote biogenic sources.

[37] The measurements at Erdemli suggest high (>150 ng m^{-3}) MSA concentrations during June–July of each year. Even monthly mean values of ~100 ng m^{-3} obtained from the composite data set exceed many of those measured globally. The corresponding biogenically derived monthly mean nss-sulfate concentrations are ~2.5, 6.0, and 4.0 μg m^{-3} for June, July, and August. Again, high values detected suggest a very efficient ocean-atmosphere coupling of the

sulfur cycling and lateral transport over the region. One of the key factors contributing to such high sulfate aerosol concentrations over the northeastern part of the eastern Mediterranean is the persistence of northerly low-level boundary layer atmospheric transport prevailing over the region during the summer months. The other main factor is the presence of high and almost continuous phytoplankton production over the entire Black Sea as a result of its intense eutrophication that developed within the last 2 decades. DMS-producing species (such as coccolithophorids, flagellates, etc.) constitute a major part of the total phytoplankton community. Therefore the Black Sea serves as a year-round active source for the generation of sulfate aerosols within its atmosphere. It would not, therefore, be surprising to measure higher MSA and nss-sulfate concentrations over the Black Sea when compared to the northeastern Levantine basin. However, no such measurements are yet available.

[38] The summer is not a particularly productive season for the Black Sea. The most abundant phytoplankton species prone to sulfate production in this season are the coccolithophorids *E. huxleyi*. The SeaWiFS mean normalized water leaving radiance data suggests its basinwide blooming within the surface mixed layer during June and July every year. This activity is further complemented by subsurface flagellate production below the seasonal thermocline. The low-level meridional atmospheric transport therefore carries sulfate aerosols, generated as a byproduct of summer biological production, over Anotolia into the marine atmosphere of the northern Levantine Sea. This process occurring approximately from the end of May to the end of September. However, the western basin of the eastern Mediterranean around the island of Crete does not receive sulfate containing aerosol from the remote Black Sea. The peculiar regional atmospheric circulation systems over the Black Sea-Aegean Sea-eastern Mediterranean Sea region can only sustain approximately half of the lateral aerosol flux supplied to the northeastern Levantine basin. In the summer months, the total absence of precipitation ensures that there are no losses through wet depositions. The region is also usually characterized by weak winds. Sulfate aerosol concentrations can therefore be present at high levels during the summer months. More time series measurements at additional sites between Erdemli and Finokalia are needed to more precisely resolve the spatial variability.

[39] The lateral aerosol supply from the Black Sea terminates after September as the direction of low level air transport is shifted preferentially to westerlies during the autumn and winter months. As both the eastern Mediterranean (the local source) and the Western Mediterranean (the remote source) do not possess any appreciable biogenic production during these seasons, the MSA and biogenically derived nss-sulfate concentrations remain at their lowest concentrations both at Erdemli and Finokalia. The estimated biologically derived nss-sulfate concentrations are negligible from October to April, while the presence of more than 3 $\mu g\ m^{-3}$ monthly averaged total nss-sulfate concentrations suggests substantial aerosol supply from anthropogenic sources of continental Europe.

[40] The data reveal considerable short-term variability (weekly) in the MSA and nss-sulfate concentrations during spring months. A closer inspection of the data suggests that these variations in fact correspond to atmospheric and oceanic events triggered by episodic Saharan dust storms over the eastern Mediterranean. Although such storms may occur over the year, only those concurrent with sufficient but short-term rainfalls and dissolution of aeolian nutrients in the water are biogenically important. Short-term rainfall is necessary for wet deposition of dust minerals; longer duration rainfalls, as in the winter months, may lead to a complete washout of sulfate aerosol particles from the atmosphere. April–May is the most favorable periods for such events. When the MSA, air trajectory, and rainfall data are evaluated, it is apparent that Saharan dust particles are first transported over the sea, then undergo wet deposition. The rainy period coincides with an immediate drop in MSA concentrations due to washout. However, as soon as the rain stops, MSA concentrations revert back to their prerainfall concentration, which can only be possible through local biogenic production as a response to fertilization of the surface waters by dust minerals. The Erdemli data suggests two or three such events per month during April–May periods.

[41] 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.

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