# Sulfur budget above the Eastern Mediterranean: relative contribution of anthropogenic and biogenic sources

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### ABSTRACT

To access the relative contribution of anthropogenic and biogenic sulfur sources to the sulfur budget in the Eastern Mediterranean, an area characterized by very high nss-$SO_4^{2-}$ levels, measurements of both wet and dry deposition of sulfur were performed at a remote area on the island of Crete (Finokalia) during a 3-yr period (1996–1999). The estimation of dry deposition is based on both gaseous sulfur dioxide ($SO_2$) and particulate phase non-sea-salt sulfate (nss-$SO_4^{2-}$) and methane sulfonate (MSA) measurements. During the dry period, deposition of $SO_2$ from long-range transport is the main component of anthropogenic sulfur deposition in the area. The results of the wet and dry deposition obtained at Finokalia have been compared with DMS emission from seawater obtained during two yearly surveys (1997–1998) in the Cretan Sea. Our results indicate that the contribution from biogenic sources to the sulfur budget in the Eastern Mediterranean, although negligible during winter, can account for up to 26% during summer.

## 1. Introduction

The study of the sulfur cycle has received much attention during recent decades since, apart from its climatic relevance, sulfur via non-sea-salt sulfate is the main contributor to acidity of both wet and dry deposition at urban as well as at remote areas of the world (Charlson and Rodhe, 1982; Galloway et al., 1982; Rodhe, 1999). According to the model calculations of Charlson et al. (1991), the Eastern Mediterranean area is one of the areas, worldwide, which could be very strongly influenced by the negative radiative forcing induced by the sulfate aerosols. This is due to the fact that the Eastern Mediterranean basin, located at the Southern edge of Europe, receives, at least 70% of the time during the year, air masses influenced by human

activity from Central and Eastern Europe. Indeed, aerosol composition studies conducted in remote or rural areas of the Eastern Mediterranean reported unusually high nss-$SO_4^{2-}$ concentrations comparable to or sometimes even higher than those observed over industrial areas of continental Europe or the United States (Luria et al., 1996; Mihalopoulos et al., 1997; Gullu et al., 1998). Since nss-$SO_4^{2-}$ has both anthropogenic and biogenic sources, it has been suggested that part of the anomalously high nss-$SO_4^{2-}$ levels could be due to biogenic sources (Ganor et al., 1993), i.e. oxidation of dimethyl sulfide (DMS) produced in seawater as a result of the interactions between phytoplankton, zooplankton and bacteria (Groene, 1995). Mihalopoulos et al. (1997), reporting the first methane sulfonate (MSA) measurements in aerosols in the Eastern Mediterranean, evaluated the biogenic sulfur contribution as between 0.6 and 28.3%, with the highest values

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during summer. MSA is a relatively stable compound, with physical and chemical properties similar to that of sulfuric acid, and oxidation of dimethyl sulfide (DMS) seems to be the exclusive source for this compound. Recently Ganor et al. (2000), during a 9 d campaign in August in Israel, measured both gaseous (DMS) and particulate phase (MSA and nss-$SO_4^{2-}$) sulfur compounds. They evaluated the biogenic contribution of sulfur during that period to be equal to 11% (6–22%) of the total nss-$SO_4^{2-}$.

The role of biogenic sources in sulfur budget in the Eastern Mediterranean requires further investigation, since several uncertainties remain, in particular concerning the seasonal variation of DMS in seawater and the existence or not of a seasonal pattern in the biogenic and/or anthropogenic contribution. Up to now the contribution of biogenic sulfur sources has been addressed (Mihalopoulos et al., 1997; Ganor et al., 2000) mainly based on the variability of the MSA/nss-$SO_4^{2-}$ ratio, which is tested only for the remote marine atmosphere (Bates et al., 1992). A complete sulfur budget taking into account all the sulfur components (in gaseous, particulate and liquid forms) is totally missing for the area. To fill this gap measurements of both wet and dry deposition of sulfur have been performed in a remote area on the island of Crete (Finokalia) during a 3-yr period (1996–1999). The estimation of dry deposition is based on both gaseous ($SO_2$) and particulate phase (nss-$SO_4^{2-}$ and MSA) measurements. The results of both wet and dry deposition of sulfur at Finokalia have been compared with concurrent data of DMS emission from seawater obtained in the Cretan Sea from spring 1997 to summer 1998.

## 2. Experimental

### 2.1. Sampling

Atmospheric and seawater data sets were collected in the Crete in the frame of various long-term time series programs. The location of sampling sites is shown in Fig. 1.

*Wet deposition.* Rainwater was collected on an event basis using wet-only collectors installed at two areas on the island of Crete: at the University situated 6 km south of the city of Heraklion

(25°13′E, 35°30′N) and at Finokalia (25°60′E, 35°24′N), a small village on the northern coast of Crete (Fig. 1). Details of Heraklion and Finokalia stations can be found elsewhere (Mihalopoulos et al., 1997; Kouvarakis et al., 2000). After collection of the rain, 100–200 µl of chloroform were added as a biocide, and the sample was stored in the refrigerator until being further analysed within the following month.

*Dry deposition.* Dry deposition of sulfur was estimated in two ways:

(i) Based on the collection of particles on a flat surface covered by glass beads, positioned on a funnel 3 m above the ground. The system was exposed to the atmosphere for a week, after which it was washed with ultra pure water, filtered and then processed as a rainwater sample. The deposition measured using this technique corresponds to the total deposition. However, from April to October almost no rain events occur, thus the measurement during this period corresponds to the dry deposition. More details can be found in Kouvarakis et al. (2001).

(ii) Based on the concentrations of the gaseous $SO_2$ and particulate phase (nss-$SO_4^{2-}$ and MSA) and their deposition velocities obtained from the literature.

Gas-phase $SO_2$ was collected using annular denuder tubes coated with $Na_2CO_3$ (Lawrence and Koutrakis, 1994). Exposure times varied between 3 and 48 h. Following exposure, the tubes were rinsed with 10 ml of Milli-Q water and the extracts were stored in Nalgene opaque polyethylene bottles at 4 °C and analyzed as $SO_4^{2-}$ using ion chromatography.

Aerosol particles were collected on 0.45 mm Gelman Zefluor PTFE filters. The filters were extracted by 20 ml Milli-Q water, for 45 min in an ultrasonic bath. Chloroform (50–100 µl) was then added as a biocide in the sample extracts, which were in turn analyzed within a week using ion chromatography.

### 2.2. Chemical analysis

Analyses of $SO_4^{2-}$ and MSA were performed by ion chromatography using a Dionex AS4A-SC column with ASRS-I suppressor in the autosuppression mode of operation. The reproducibility of the measurements was better than 2%, and the
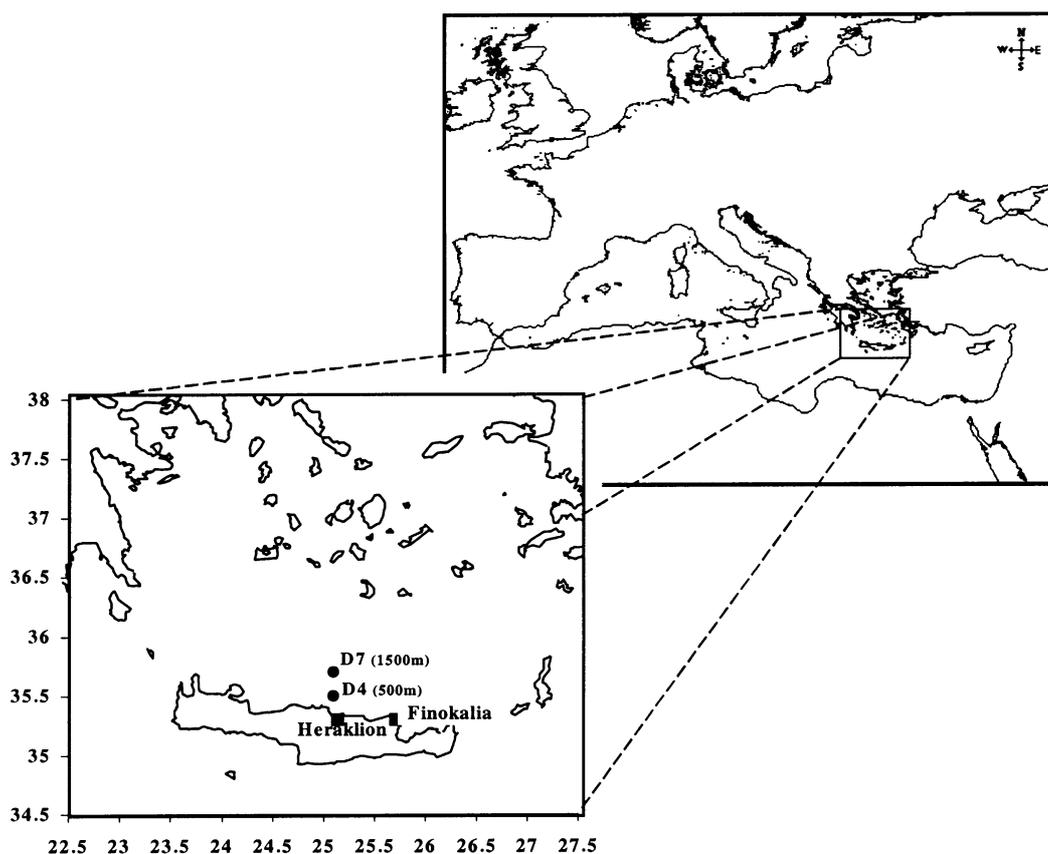
*Fig. 1.* Map indicating the location of the sampling sites referenced in the text.

detection limits corresponded to 40 pmol m$^{-3}$ for a mean air volume of 50 m$^3$ or to 5 ppbv for liquid sample. Filter and denuder blanks were below the detection limits.

### 2.3. DMS in seawater

Seawater was collected in the Cretan Sea by using the vessel's pump situated at 5 m depth. After collection, the samples were immediately filtered on board through Whatman GF/F filter and stored for 3 h maximum at 4 °C until the vessel reached Heraklion, where the samples were immediately extracted and analysed in the laboratory. The extraction was conducted for 10 min under a helium flow of 150 ml min$^{-1}$, and DMS was trapped on a Tenax gas chromatrograph immersed in liquid nitrogen. Further on, DMS was introduced in a packed column (Chromosil 310) by heating the trap with boiling water (90 °C). The analysis was made by using an HP 5890 gas chromatograph equipped with a flame photometric detector. The detection limit was 0.5 ng of DMS. DMS quantification was performed by the mean of a permeation tube maintained at 30 °C, calibrated against liquid standards of DMSP as described by Belviso et al. (1990).

### 3. Results and discussion

To perform a complete sulfur budget in order to estimate the relative contribution of biogenic and anthropogenic sources, the total sulfur depos-

ition (wet and dry) were compared with the sulfur emissions, mainly DMS, from biogenic sources in the area. Table 1 presents the location, type of measurement, sampling period, number of samples as well as a statistical analysis (average, median and range) of all data obtained during this work, which are presented in further detail.

### 3.1. Wet deposition of sulfur

At both sampling sites (Heraklion and Finokalia stations) rainwater has been collected using automatic collectors. Table 1 reports the per event deposition of nss-$SO_4^{2-}$ and MSA at Heraklion during the whole period. Nss-$SO_4^{2-}$ was calculated using $Na^+$ or $Mg^{2+}$ as seawater tracers. Both estimations lead to similar results (within 5%). Wet deposition of nss-$SO_4^{2-}$ ranges from 0.002 to 1.133 mmol m$^{-2}$ event$^{-1}$ (median = 0.10 and 0.15 at Heraklion and Finokalia, respectively). For MSA the corresponding figures are 0.21 and 0.24 μmol m$^{-2}$ event$^{-1}$, respectively. To our knowledge this is the first estimation of wet-deposition of MSA in the Eastern Mediterranean. Figure 2 presents the sum of sulfur wet deposition (nss-$SO_4^{2-}$ and MSA) at both locations. When comparing data of the same sampling period, wet depositions of nss-$SO_4^{2-}$ and MSA at Heraklion were higher than at Finokalia by almost about 27% and 23%, respectively. Since MSA is exclusively of biogenic origin, this result indicates absence of significant local anthropogenic sources
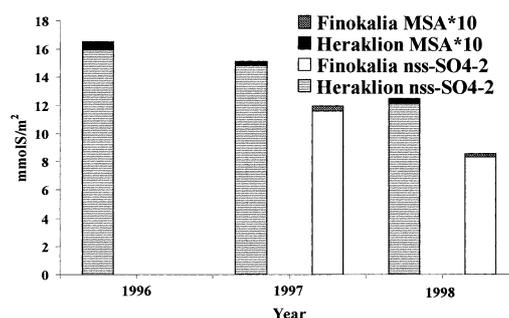


Fig. 2. Variation of annual wet deposition of sulfur at Heraklion and at Finokalia during the period 1996–1998.

at the Heraklion sampling location. The yearly wet deposition of sulfur (mainly of nss-$SO_4^{2-}$) estimated from this work ranges from 13.5 to 17.6 mmol m$^{-2}$ for Heraklion and 10.6 to 12.8 mmol m$^{-2}$ for Finokalia. These figures are low when compared to the value of 32.8 mmol m$^{-2}$ estimated by Herut et al. (2000) for the Israeli coast but are in good agreement with the values reported by Al-Momani et al. (1995;1998) for Antalya, another Eastern Mediterranean coastal area (Table 2). The wet deposition of sulfur reported for Finokalia is in good agreement with that reported by Pio et al. (1991) for a coastal site in Portugal and with the more recent values reported by Avila (1996) for NE Spain. The values reported for Finokalia seem to be representative not only for the Eastern Mediterranean but also

Table 1. *Location, type of measurements, sampling period, number of samples, average, median and range (min, max) of all data obtained during this work*

| Location | Measurement | Period | No | Average | Median | Range | Units |
|----------|-------------|--------|-----|---------|--------|-------|-------|
| Heraklion | wet dep. (nss-$SO_4^{2-}$) | 03/95–05/99 | 349 | 165.40 | 102.80 | 1.6–1132.3 | μmol S (event m$^2$)$^{-1}$ |
| Heraklion | wet dep. ($CH_3SO_3^-$) | 03/95–05/99 | 349 | 0.59 | 0.21 | 0.0–6.1 | μmol S (event m$^2$)$^{-1}$ |
| Finokalia | wet dep. (nss-$SO_4^{2-}$) | 09/96–05/99 | 129 | 186.20 | 151.40 | 9.0–981.3 | μmol S (event m$^2$)$^{-1}$ |
| Finokalia | wet dep. ($CH_3SO_3^-$) | 09/96–05/99 | 129 | 0.53 | 0.24 | 0.0–4.9 | μmol S (event m$^2$)$^{-1}$ |
| Finokalia | nss-$SO_4^{2-}$ | 10/96–09/99 | 496 | 41.02 | 39.44 | 0.6–123.9 | nmol S m$^{-3}$ |
| Finokalia | $CH_3SO_3^-$ | 10/96–09/99 | 496 | 0.27 | 0.31 | 0.0–9.9 | nmol S m$^{-3}$ |
| Finokalia | $SO_2$ | 11/96–09/99 | 285 | 41.71 | 45.18 | 1.1–100.2 | nmol S m$^{-3}$ |
| Cretan Sea | $CH_3SCH_3$ | 03/97–06/98 | 121 | 3.78 | 4.18 | 1.1–8.3 | nM |
| Finokalia | Dry deposition | 10/96–09/99 | 496 | 37.82 | 36.26 | 13.2–86.4 | μmol S (d m$^2$)$^{-1}$ |
| Finokalia | Dry deposition[a] | 10/96–09/99 | 496 | 48.29[a] | 44.34[a] | | μmol S (d m$^2$)$^{-1}$ |
| Finokalia | Dry deposition[b] | 04/97–09/99 | 71 | 33.91[b] | 33.70[b] | 6.9–119 | μmol S (d m$^2$)$^{-1}$ |

[a] For the dry period (1/4–30/9).
[b] Using glass beads, see text.

Table 2. *Comparison between the results obtained during this work and those reported in the literature for Mediterranean, European and remote areas of the world regarding aerosol nss-$SO_4^{2-}$ and MSA, gaseous $SO_2$, seawater DMS and wet deposition of nss-$SO_4^{2-}$ and MSA*

| | Value | Location | Period | Reference |
|---|---|---|---|---|
| Aerosol nss-$SO_4^{2-}$ ($nmol\,m^{-3}$) | $41.0 \pm 17.4$ | Finokalia | 10/96–09/99 | This work |
| | 85.12 | Finokalia | 03/94–04/95 | Mihalopoulos et al., 1997 |
| | 56–128 | Israel (coastal and inland areas) | 1984–1993 | Luria et al., 1996 |
| | $41.8 \pm 16.6$ | Mediterranean coast/Israel | 08/95 | Ganor et al., 2000 |
| | 56.3 | Antalya | 3/92–12/93 | Gullu et al., 1998 |
| | 67.7 | Corsica | 4/1985–4/1986 | Bergametti et al., 1989 |
| | 41.26 | Atlantic coast/Portugal | 11/93–8/94 | Pio et al., 1996 |
| Aerosol $CH_3SO_3^-$ ($nmol\,m^{-3}$) | $0.266 \pm 0.154$ | Finokalia | 10/96–09/99 | This work |
| | 0.470 | Finokalia | 03/94–04/95 | Mihalopoulos et al., 1997 |
| | $0.48 \pm 0.21$ | Mediterranean coast/Israel | 08/95 | Ganor et al., 2000 |
| | 0.621 | Atlantic coast/Portugal | 11/93–08/94 | Pio et al., 1996 |
| | $0.176 \pm 0.027$ | Cape Grim, Tasmania | 08/76–06/84 | Ayers et al., 1986 |
| $SO_2$ ($nmol\,m^{-3}$) | $41.71 \pm 13.79$ | Finokalia | 11/96–09/99 | This work |
| | $38 \pm 47$ | Caesarea, Eastern Med. Coast/Israel | 06/93–11/93 | Luria et al., 1996 |
| | 43.13 | Atlantic coast/Portugal | 11/93–08/94 | Pio et al., 1996 |
| Water $CH_3SCH_3$ (nM) | $3.67 \pm 1.52$ | Cretan Sea/Eastern Mediterranean | 03/97–06/98 | This work |
| | 4.0–8.0 | Eastern Med. and Aegean Sea | 07/93 | Rapsomanikis, 1994 |
| | $2.9 \pm 4.3$ | W. Mediterranean | 06/93–07/94 | Simo et al., 1997 |
| | $2.84 \pm 1.21$ | S. Australia Sea, Tasmania | 05/95–06/95 | Bates et al., 1998 |
| Wet nss-$SO_4^{2-}$ ($mmol\,(m^2\,yr)^{-1}$) | 11.17 | Finokalia | 1/97–12/98 | This work |
| | 15.30 | Heraklion | 1/96–12/98 | This work |
| | 32.79 | Mediterranean coast/Israel | 1981–1990 | Herut et al., 2000 |
| | 5.8–10.4 | Eastern Med coast (Antalya)/Turkey | 1992–1994 | Al-Momani et al., 1995a, 1998 |
| | 18.5 | W. Med coast/N.E Spain | 1989–1994 | Avila, 1996 |
| | 13.30 | Atlantic coast/Portugal | 04/85–10/89 | Pio et al., 1991 |
| Wet $CH_3SO_3^-$ ($mmol\,(m^2\,yr)^{-1}$) | 0.029 | Finokalia | 1/97–12/98 | This work |
| | 0.051 | Heraklion | 1/96–12/98 | This work |
| | 0.190 | Amsterdam, Indian Ocean | 1/89–03/91 | Mihalopoulos et al., 1993 |

for the whole basin. Work is now in progress to better characterize the spatial variability of the wet deposition of nss-$SO_4^{2-}$ in the Mediterranean basin.

### 3.2. Dry deposition of sulfur

*3.2.1. Atmospheric concentration of sulfur compounds.* Dry deposition of sulfur includes deposition in gaseous and particulate phases. To our knowledge the data presented here for long-term simultaneous gaseous $SO_2$ and particulate phase nss-$SO_4^{2-}$ and MSA are the first reported for a remote location in the Mediterranean area. Figure 3a–c presents the variation of the monthly mean concentrations of gaseous and particulate sulfur species during the whole period. In both

phases (gas and particulate) sulfur species present a seasonal pattern with higher levels in summer than in winter.

$SO_2$ levels measured at Finokalia were comparable to the values given by Luria et al. (1996) for Caesarea, Israel, which consist of the only up-to-date reported background levels for the Eastern Mediterranean. Indeed, as mentioned by these authors, their data, which cover the period from June to November 1993, were selectively collected in non-contaminated by local pollution sources air masses.

Aerosol nss-$SO_4^{2-}$ at Finokalia ranges from 10 to 74 nmol m$^{-3}$ (Fig. 3b) and presents a seasonal variation with higher values during summer. The up-to-date annual mean nss-$SO_4^{2-}$ data reported
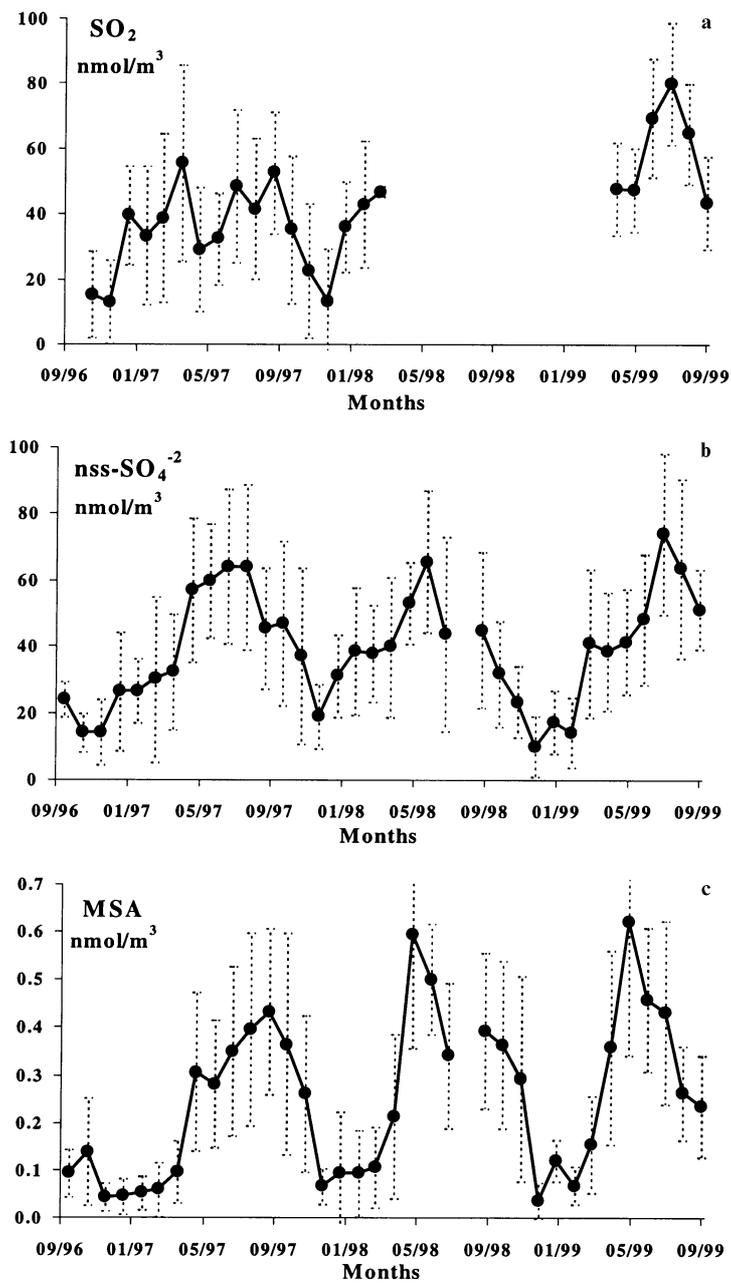
Fig. 3. Temporal variation of monthly averaged particulate gaseous phase $SO_2$ (a), nss-$SO_4^{2-}$ (b) and MSA (c) during the period 1996–1999.

for the Eastern Mediterranean fall in two categories (Table 2): one which comprises values between 40 and 50 nmol m$^{-3}$ and another with values between 80 and 130 nmol m$^{-3}$. Note that this variability exists within the same location (Table 2), for instance Finokalia, the Israeli coast, or even Aliartos (Kouvarakis, Remoundaki and Mihalopoulos, unpublished data, 2001). An important interannual variation in nss-SO$_4^{2-}$ can partially account for this range. Note that since nss-SO$_4^{2-}$ exists mainly in the submicronic fraction, it is not expected to significantly contribute to the dry deposition
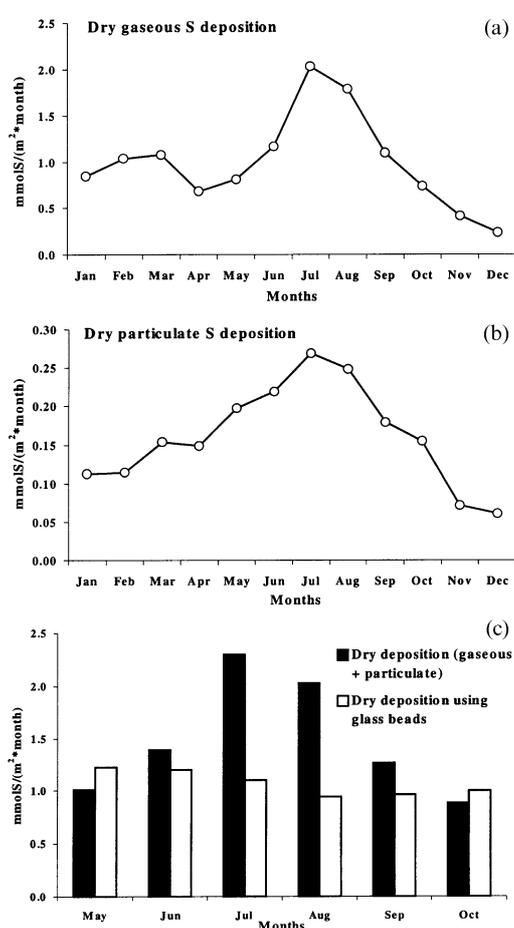


*Fig. 4.* Temporal variation of dry deposition of both gaseous (a) and particulate sulfur (b) and comparison with the dry deposition estimated using glass beads (c).

(Fig. 4b). Thus the possible interannual variability in nss-SO$_4^{2-}$ levels will have little influence on the dry deposition of sulfur.

It is important to note that the levels of MSA in aerosols reported for the Eastern Mediterranean are comparable to or even higher than those reported for remote areas of the world (Table 2), indicating that despite its oligotrophic character, the Eastern Mediterranean could be an active source of DMS to the atmosphere.

*3.2.2. Estimate of dry deposition of sulfur compounds.* As mentioned in Section 2, two approaches are used to estimate dry deposition.

The first estimate is based on the collection of particles on a surface covered by glass beads. Since the reported results cover the dry period from May to October, they represent the dry deposition only. The dry deposition fluxes calculated using this procedure range between 6.9 and 119 µmol m$^{-2}$ d$^{-1}$ and remain quite stable during the whole dry period. From May to October the total dry deposition of sulfur is estimated to be of the order of 6.5 mmol m$^{-2}$, i.e. a factor of 1.8 lower than the annual wet deposition.

The second estimate is based on the concentrations of gaseous SO$_2$, particulate nss-SO$_4^{2-}$ and MSA, their deposition velocities obtained from the literature and the equation $F_d = V_d \times C_d$, where $C_d$, $V_d$ and $F_d$, are the atmospheric concentration, the deposition velocity and the dry deposition, respectively.

The major difficulty in this approach is the estimation of the deposition velocity ($V_d$). For SO$_2$, the model of Hicks and Liss (1976) has been used ($V_d = 0.122U$), suggesting that for readily water-soluble gases such as SO$_2$, the transfer velocity at the air–sea interface is a function of wind speed. Thus using wind speed data obtained at Finokalia deposition velocities of SO$_2$ have been calculated for each month and ranged from 0.5–1.3 cm s$^{-1}$ (mean value of 0.9 cm s$^{-1}$). Among the calculated deposition velocities, the lowest are similar to the values used for modeling studies (0.5–0.7 cm s$^{-1}$), whereas the highest are by up to a factor of 1.9 higher. On yearly basis, the deposition velocity of SO$_2$, is higher compared to the deposition velocities used for modeling studies by a factor of 1.3 to 1.8.

To calculate deposition velocities of aerosol

species, the particle size distribution has to be taken into account, since dry deposition of particles is size dependent. Measurements of particle size distribution of nss-$SO_4^{2-}$ and MSA have been performed using six-stage impactors (Kouvarakis et al., 2001 and Kouvarakis and Mihalopoulos unpublished results). From these measurements 94% of $SO_4^{2-}$ and 93% of the MSA was found to be associated with fine particles (stages 4–6, diameter $< 1.3\ \mu$m) while the remaining part was of coarse particles (stages 1–3). Based on this particle size distribution and assuming deposition velocities of the order of 0.075 cm s$^{-1}$ and 1.25 cm s$^{-1}$ for fine and coarse particles, respectively, deposition velocities of the order of 0.14 and 0.16 cm s$^{-1}$ were calculated for nss-$SO_4^{2-}$ and MSA, respectively (Rendell et al., 1993; Sievering et al., 1989; Seinfeld and Pandis, 1998). As pointed out by several authors (i.e. Rendell et al., 1993 and references therein) the largest errors in dry deposition estimates are likely to arise from the use of theoretically derived values of $V_d$ as a function of size, since experimental validation is extremely difficult. Figures 4a and b depict the seasonal variation of dry deposition estimated for both gaseous and particulate phases. The total dry deposition, of the order of 8.9 mmol m$^{-2}$ during the dry period, can be compared to that estimated using the glass beads (Fig. 4c). The following remarks can be made:

(i) Dry deposition of gaseous $SO_2$ is the main source of dry deposition of sulfur, since it accounts for about 85% of the total dry deposition.

(ii) In absolute values the deposition estimated during the dry period by using the glass beads is lower by a factor of 1.4 (8.9/6.5) compared to that using the $V_d$ of all the individual sulfur species. Such an agreement is quite good given the large uncertainties associated with the estimation of $V_d$, especially that of $SO_2$, which can account for most of the above difference.

(iii) Finally the total annual dry deposition estimated based on both gaseous and particulate sulfur compounds is of the order of 13.8 mmol m$^{-2}$, thus being of at least equal importance to the wet deposition of sulfur, which is in agreement with the results by Al Momani et al. (1995a) for Antalya, an Eastern Mediterranean coastal area.

## 3.3. Seasonal variation of DMS in seawater

The spatio-temporal variation of DMS has been investigated in the Eastern Mediterranean area from spring 1997 to summer 1998. More than 120 DMS data have been collected during eight oceanographic cruises conducted along a transect north of Heraklion ranging from 1500 m depth (staion D7) to 500 m depth (station D4). The above study consists of the first attempt to investigate the seasonal trend of DMS in the Eastern Mediterranean sea.

Seawater DMS concentrations ranged from 1.1 to 8.3 nM, with the lowest values observed during winter (the December, February and early March cruises) and the highest during spring and summer (the April, May, June and September cruises; Fig. 5a). To check for the representativity of our data, at least for the Cretan Sea, two intensive campaigns have been performed during March and October 1997 in the Cretan Sea onboard the RV *Aegaio*. DMS concentrations during the March cruise in the Cretan Sea were 2.3 ± 0.7 nM ($n = 48$). At the same time, along the transect (D7–D4) the DMS concentrations were 2.1 ± 0.6 nM ($n = 12$). The corresponding figures for the October were 4.9 ± 1 nM ($n = 72$) and 5.4 ± 0.7 nM ($n = 19$) for the Cretan Sea and the transect, respectively.

Annual mean seawater DMS concentration was calculated from the results of 120 samples collected through the year in the Cretan Sea and averaged 3.8 nM. Our July value of 5.0 nM falls within the range 4–8 nM reported by Rapsomanikis (1994), for the Eastern Mediterranean and Aegean Sea in July 1993. In addition our spring/summer mean value of 4.8 nM is in good agreement with the value of 5.4 nM reported by Simo et al. (1997) for the Western Mediterranean area during the same period (Table 2). The monthly DMS concentration in seawater significantly correlated with the monthly aerosol concentration of MSA ($r^2 = 0.95$), indicating that DMS oxidation is the exclusive source of MSA in the region (Fig. 5b).

Despite low chlorophyll a levels recorded in the area, mean seawater DMS levels measured in the Eastern Mediterranean sea are among the highest reported in the literature (see for example Andreae, 1986). Our annual DMS value is in very good agreement with the value of 3.9 nM reported by Turner et al. (1996) for the North Sea. The pres-
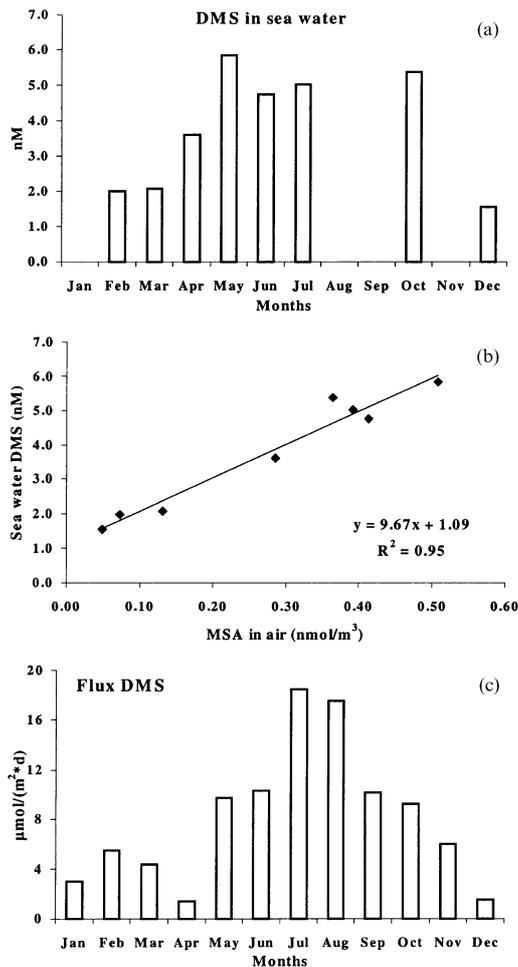
Fig. 5. Seasonal variation of DMS in seawater in the Cretan Sea (a), correlation between MSA and seawater DMS (b) and DMS sea–air flux during 2-yr periods (3/1997–10/1998) (c).

following eq. (Liss and Slater, 1974):

$$F = K_w \times C_w,$$

where $K_w$ is the DMS gas-transfer velocity and $C_w$ the DMS concentration in seawater. The $K_w$ has been calculated using the relationship between $K_w$, wind speed ($u$) and seawater temperature ($T$) proposed by Liss and Merlivat (1986) and modified accordingly for DMS (Sciare et al., 1999).

When no DMS measurements is available, seawater DMS is estimated based on the significant relation between seawater DMS and atmospheric MSA. Our calculated DMS fluxes ranged between 1.4 and 18.5 $\mu$mol m$^{-2}$ d$^{-1}$ ($8.1 \pm 5.6$) and are the first recorded values to date from the Eastern Mediterranean. They are among the highest values reported in the literature and agree very well with the mean value proposed by Andreae (1986) for global coastal and shelf waters. The value obtained during summer (11.3 $\mu$mol m$^{-2}$ d$^{-1}$) is in excellent agreement with the values reported by Simo et al. (1997) and Leck and Rodhe (1991) for the Western Mediterranean shelf waters and North Sea respectively. Note, however, that our sampling, as can be seen in Fig. 1, was not limited to the coastal or shelf waters: an important part extended to the open sea as well. The high wind speed occurring during summer in the Eastern Mediterranean, associated with elevated seawater DMS concentrations, can account for such high DMS fluxes.

### 3.4. Atmospheric deposition versus DMS emissions

By comparing the biogenic sulfur emission to the total sulfur deposition the relative contribution of biogenic versus anthropogenic sources of sulfur can be estimated for the Eastern Mediterranean. Figure 6 depicts the ratio of seawater DMS emission to the total sulfur deposition (sum of the wet and dry deposition) in the area. Our results indicate that the contribution from biogenic sources, although negligible during winter, can account for up to 26% during summer. However, these values should be considered as lower limits since: (i) the calculated dry deposition of SO$_2$, which is the main contributor of the dry deposition of sulfur, could be overestimated by about 30–80%; (ii) dry deposition is estimated, based on long-term aero-

ence of species considered to be high DMS producers, such as dinoflagelates and cocolithophors (Liss et al., 1997), can account for this difference (Bardouki, 2000).

An estimation of the DMS emission from the Eastern Mediterranean sea to the atmosphere can be performed using seawater DMS data together with wind speed and sea temperature data obtained from monthly and long-term meteorological observations. Figure 5c presents the annual variation of DMS fluxes, calculated using the

sol and $SO_2$ measurements and deposition velocities from the literature and not on passive deposition on glass beads, which gives lower figures; and (iii) the estimated total deposition also includes also sulfur from biogenic sources.

## 4. Conclusion

This work consists of the first attempt to estimate the relative contribution of biogenic and anthropogenic sources on the sulfur budget in the Eastern Mediterranean. It is based on a comparison between the total deposition (wet and dry) of sulfur in a remote area on Crete (Finokalia) and DMS emission from the seawater. The estimation of dry deposition is based on both gaseous ($SO_2$) and particulate phase (nss-$SO_4^{2-}$ and MSA) measurements. Dry deposition of gaseous $SO_2$ is the main source of dry deposition of sulfur since it is estimated to account for about 85% of the total dry deposition. The total annual dry deposition estimated based on both gaseous and particulate sulfur compounds is of the order of 13.8 mmol m$^{-2}$, thus being of least equal importance to the wet deposition.

The comparison between the emitted biogenic (as DMS) and total deposited sulfur indicates that the contribution from biogenic sources can account for up to 26% during summer. Therefore DMS oxidation can explain a non-negligible part of the high nss-$SO_4^{2-}$ values observed during
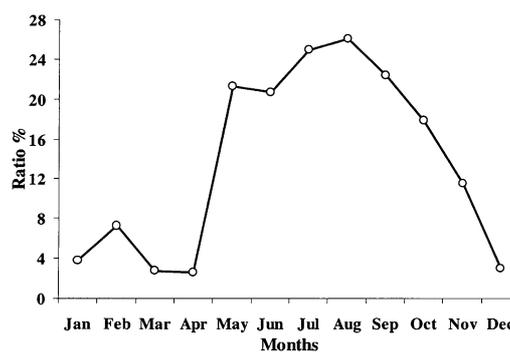


*Fig. 6.* Ratio of biogenic sulfur (DMS emitted from seawater) to the total sulfur deposited (sum of the wet and dry deposition) in the area.

summer in several places in the Eastern Mediterranean area. Work is currently in progress to estimate the relative contribution of biogenic sources of sulfur to the whole Mediterranean basin.

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