



PERGAMON



Atmospheric Environment 36 (2002) 929–938

ATMOSPHERIC  
ENVIRONMENT

www.elsevier.com/locate/atmosenv

# Seasonal variation of dimethylsulfide in the gas phase and of methanesulfonate and non-sea-salt sulfate in the aerosols phase in the Eastern Mediterranean atmosphere

G. Kouvarakis, N. Mihalopoulos\*

*ECPL, Department of Chemistry, University of Crete, PO Box 1470, GR-71409 Heraklion, Greece*

Received 25 July 2001; received in revised form 2 October 2001; accepted 8 October 2001

## Abstract

The seasonal variation of gaseous dimethylsulfide (DMS) and its oxidation products (non-sea-salt sulfate ( $\text{nss-SO}_4^{2-}$ ) and methanesulfonic acid (MSA) have been investigated at a remote coastal location in the Eastern Mediterranean. Daytime atmospheric DMS concentrations were measured in the range  $0.3\text{--}8.9\text{ nmol m}^{-3}$  (with an average of  $2.35 \pm 1.38\text{ nmol m}^{-3}$ ,  $1\sigma$  uncertainty) and present a well distinguished seasonal cycle with higher values in summer. The seasonal variation of atmospheric DMS is in line with that of seawater DMS concurrently measured in the Cretan Sea. Monthly atmospheric DMS concentrations are significantly correlated with sea-surface temperature. By the mean of a 0-D model based on atmospheric DMS observations, the DMS flux calculated for spring and summer is in reasonable agreement with the fluxes deduced from the seawater DMS data and the wind speed. The diurnal variation of atmospheric DMS was investigated during a 4-day intensive campaign in September 1997 and shows a nighttime minimum, which could be explained by the presence of  $\text{NO}_3$  radicals, which are highly reactive towards DMS. Aerosol MSA concentrations varied seasonally from below detection limit (0.04) to 0.99 (average of  $0.27 \pm 0.15\text{ nmol m}^{-3}$ ,  $1\sigma$  uncertainty). Similarly aerosol  $\text{nss-SO}_4^{2-}$  varied from 0.6 to 123.9 (average of  $41.0 \pm 17.4\text{ nmol m}^{-3}$ ,  $1\sigma$  uncertainty). Based on the measured MSA,  $\text{nss-SO}_4^{2-}$  and their ratio, the biogenic contribution to  $\text{nss-SO}_4^{2-}$  was found to exhibit a well-established seasonal pattern ranging from 1% during winter to 17% during summer. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Gaseous DMS; MSA;  $\text{nss-SO}_4^{2-}$ ; Eastern mediterranean atmosphere; Sulfur cycle

## 1. Introduction

Dimethylsulfide (DMS) is the dominant biogenic sulfur gas emitted to the atmosphere from the seawater where it is produced by the biological marine activity (Andreae et al., 1985; Nguyen et al., 1990; Bates et al., 1992a). Dimethylsulfide has been tentatively identified as the major precursor of condensation nuclei (CN) and

eventually cloud condensation nuclei (CCN) in remote marine regions thus influencing the earth's albedo and subsequently climate (Charlson et al., 1987). Once DMS is released to the atmosphere it undergoes a very complex mechanism including gas phase and multiphase processes. In the gas phase, DMS can react with OH, X, and XO radicals during daytime and  $\text{NO}_3$  radicals during nighttime (Barnes et al., 1996; Jensen et al., 1991; Yvon et al., 1996; Sciare et al., 2000a). Via the reaction of DMS with  $\text{NO}_3$  radicals a coupling between the nitrogen and the sulfur cycles can occur in the atmosphere. Indeed  $\text{HNO}_3$ , reported as the main product of this reaction, can be rapidly lost from the gas phase by

\*Corresponding author. Tel.: +30-81-393-662; fax: +30-81-393-601.

E-mail address: mihalo@chemistry.uoc.gr (N. Mihalopoulos).

dry deposition or adsorption onto aerosols or droplets (Jensen et al., 1991). These processes consist of a net sink for gas phase nitrogen oxides in the atmosphere (Platt et al., 1990; Wayne, 1991).

Unusually high levels of  $\text{nss-SO}_4^{2-}$  concentrations have been measured in aerosols in the Eastern Mediterranean and are comparable or sometimes even higher to those observed over industrial areas of continental Europe or United States (Luria et al., 1996; Mihalopoulos et al., 1997; Gullu et al., 1998). Non-sea-salt sulfate has both anthropogenic and biogenic sources whereas methanesulfonic acid (MSA) is produced by DMS oxidation and it is believed to have mainly biogenic origin (e.g. Savoie and Prospero, 1989). Mihalopoulos et al. (1997) while reporting the first methanesulfonate (MSA) measurements in aerosols in the Eastern Mediterranean evaluated the biogenic sulfur contribution between 0.6% and 28.3% with the highest values during summer. Recently, Ganor et al. (2000) measured both gaseous DMS and MSA and  $\text{nss-SO}_4^{2-}$  in aerosol samples in Israel during August (15–23 August) and concluded that during that period the biogenic contribution of sulfur to the total  $\text{nss-SO}_4^{2-}$  was 11% (6–22%). No other data concerning simultaneous measurements of DMS and its oxidation products exist for the whole Mediterranean in general.

This paper presents the results of a long-term study dedicated to the temporal variability of gaseous DMS and its main potential oxidation products MSA and  $\text{nss-SO}_4^{2-}$  in a remote marine site in the Eastern Mediterranean. In addition, during two intensive campaigns performed in September 1997 the diurnal variation of atmospheric DMS has been investigated. To our knowledge this is the first attempt to study on a seasonal basis the variability of gaseous DMS and aerosol  $\text{nss-SO}_4^{2-}$  and MSA in a remote marine site in the Eastern Mediterranean.

## 2. Experimental

### 2.1. Location

Atmospheric DMS and aerosol measurements have been performed at Finokalia (35°24'N, 25°60'E) a remote location in the northern coast of Crete, Greece (Fig. 1). The nearest largest urban center is Heraklion with 150 000 inhabitants at 70 km westward Finokalia. The station is located at the top of an elevation (130 m) facing the sea within the sector of 270–90°. No significant human activity occurs at a distance shorter than 20 km within the above-mentioned sector. Details on the area and the meteorological conditions encountered during the year are given by Mihalopoulos et al. (1997) and Kouvarakis et al. (2000).

### 2.2. Atmospheric DMS

Dimethylsulfide collection and analysis were performed using the technique described in detail by Nguyen et al. (1990) and Putaud et al. (1999); thus, here only a brief outlook is given. Dimethylsulfide was collected into 6-l stainless steel electropolished canisters by compressing air up to 5 bar. Tests performed by simultaneous collection of air in several canisters and analysis carried out every 3–4 days period show that DMS was stable in the canisters for at least 3 weeks after the sample collection. However, in most cases DMS analysis was performed within 24 h following the collection. The sampled air was passed through a magnesium perchlorate cartridge to remove water and subsequently DMS was trapped into a 1/8" Teflon U shaped tube packed with Tenax GC and kept at  $-80^\circ\text{C}$ . By heating the trap to  $90^\circ\text{C}$ , DMS was injected via a six-way valve into a 30 cm long 1/8" packed Chromosil 310 column of a gas chromatograph (HP 5890A) equipped with a flame photometric detector (FPD). The detection limit was typically of the order of 0.2 ng (DMS), which under our sampling conditions corresponds to  $\sim 2$  ppt<sub>v</sub> of atmospheric DMS. The accuracy of the analysis was of the order of 5%. No destruction of DMS by oxidants during the preconcentration step has been detected by performing additions of DMS standard, indicating that the use of canisters prevents possible DMS destruction by the oxidants, which are most probably destroyed in the canister's wall before trapping. The absence of significant difference (within 5%) in the measured DMS levels, when parallel samplings with and without the use of oxidant scrubber (potassium iodide, KI) mounted upstream of the canisters are performed, confirms the above statement. The KI scrubbers have been shown to be very effective in removing oxidants and thus preventing DMS destruction during the cold trapping (Davison and Allen, 1994).

Since DMS concentration presents an important diurnal variation (Andreae et al., 1985; Ayers et al., 1995; Sciare et al., 2000a), to avoid possible bias in the results the sampling was performed at a given time period in the afternoon (between 16–18 h in summer and 15–17 h in winter (local time)). During the 4-day intensive experiment conducted at the beginning of September 1997 to investigate the diurnal variation of DMS, the sampling interval was on average 30 min. Regular DMS calibrations, using the same permeation tube (VICI Metronics, Santa Clara) through the whole sampling period did not show any detectable variation in the sensitivity of the detector.

In total 256 atmospheric DMS determinations have been performed during the long-term (May 1997–October 1999) and intensive periods (from 1 September 1997 at 18:00 to 3 September 1997 at 2:00 and from 5 September 1997 at 7:00 to 6 September 1997 at 18:00).

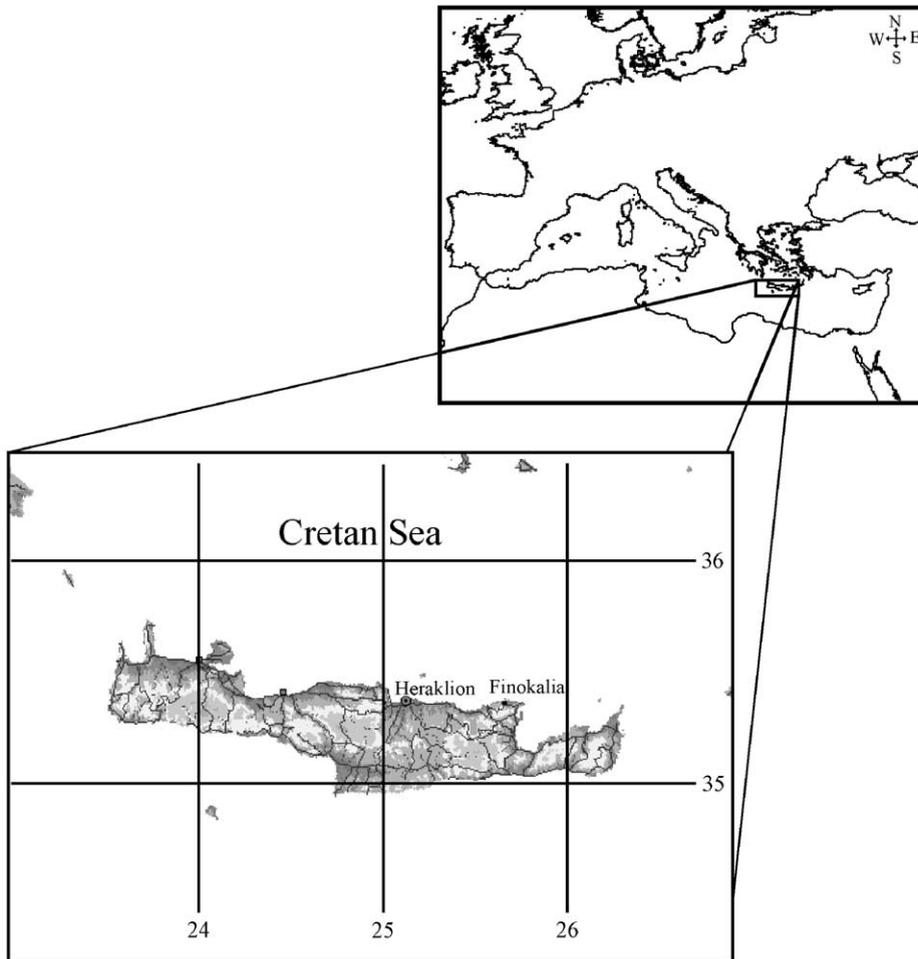


Fig. 1. Map indicating the location of Finokalia and Crete Island in the Eastern Mediterranean.

### 2.3. MSA and $nss\text{-SO}_4^{2-}$ in aerosols

Bulk aerosols were collected on open face  $0.45\ \mu\text{m}$  Gelman Zeffuor PTFE filters placed on the same mast with the inlets of DMS from October 1996 to September 1999. Using a flow rate of  $1.45\ \text{m}^3\ \text{h}^{-1}$ , the mean sampling interval varied between 3 and 48 h. Filter analysis was conducted in the laboratory using ion chromatography. A Dionex AS4A-SC column with ASRS-I suppressor in auto suppression mode of operation was used for the analysis of  $\text{SO}_4^{2-}$  and MSA.  $\text{SO}_4^{2-}$  (sample volume:  $100\ \mu\text{l}$ ) was determined with isocratic elution at  $2.0\ \text{ml}\ \text{min}^{-1}$  of  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  eluent. Methanesulfonic acid (sample volume:  $500\ \mu\text{l}$ ) was determined with isocratic elution with  $2.5\ \text{mM}$   $\text{Na}_2\text{B}_4\text{O}_7$  eluent and flow rate of  $2.0\ \text{ml}\ \text{min}^{-1}$ . For cations a CS12-SC column was used with a CSRS-I suppressor. Separation was achieved under isocratic conditions with  $20\ \text{mM}$  MSA eluent and flow rate of  $1.0\ \text{ml}\ \text{min}^{-1}$ . The reproducibility of the measurements

was better than 2% and the detection limit corresponded to  $40\ \text{pmol}\ \text{m}^{-3}$  for a mean air volume of  $50\ \text{m}^3$ . Filter blanks were below the detection limits. More details are given by Baboukas et al. (2000) and Kouvarakis et al. (2001a).

### 2.4. Ancillary measurements

During the intensive experiment  $\text{O}_3$  was measured by a Thermo Environment model 49 analyser with a detection limit of 1 ppb. The photodissociation frequency of nitrogen dioxide  $J(\text{NO}_2)$  was also monitored using a  $2\pi$  radiometer. Meteorological data were obtained by an automatic meteorological station, which recorded ambient air temperature, wind speed, wind direction and atmospheric pressure. Five-day backward trajectories have been calculated during both the experiments using a global transport model  $\text{TM}_2$  with a resolution of  $2.5^\circ \times 2.5^\circ$  (Ramonet et al., 1996).

3. Results and discussion

3.1. Short-term DMS variation

One hundred and nineteen measurements of atmospheric DMS have been performed in 1997 between 1 September and 6 September during two periods (from 1 September at 18:00 to 3 September at 2:00 and from 5

September at 7:00 to 6 September at 18:00). Figs. 2a and b present a quick meteorological outlook: wind speed, and direction and  $J_{(NO_2)}$  as an indicator of total radiation during the whole period. Wind direction shows no significant change during the whole period with winds originating from N/NW directions. Air masses of 5-day back trajectory analysis confirmed the above observation. Indeed during the first period

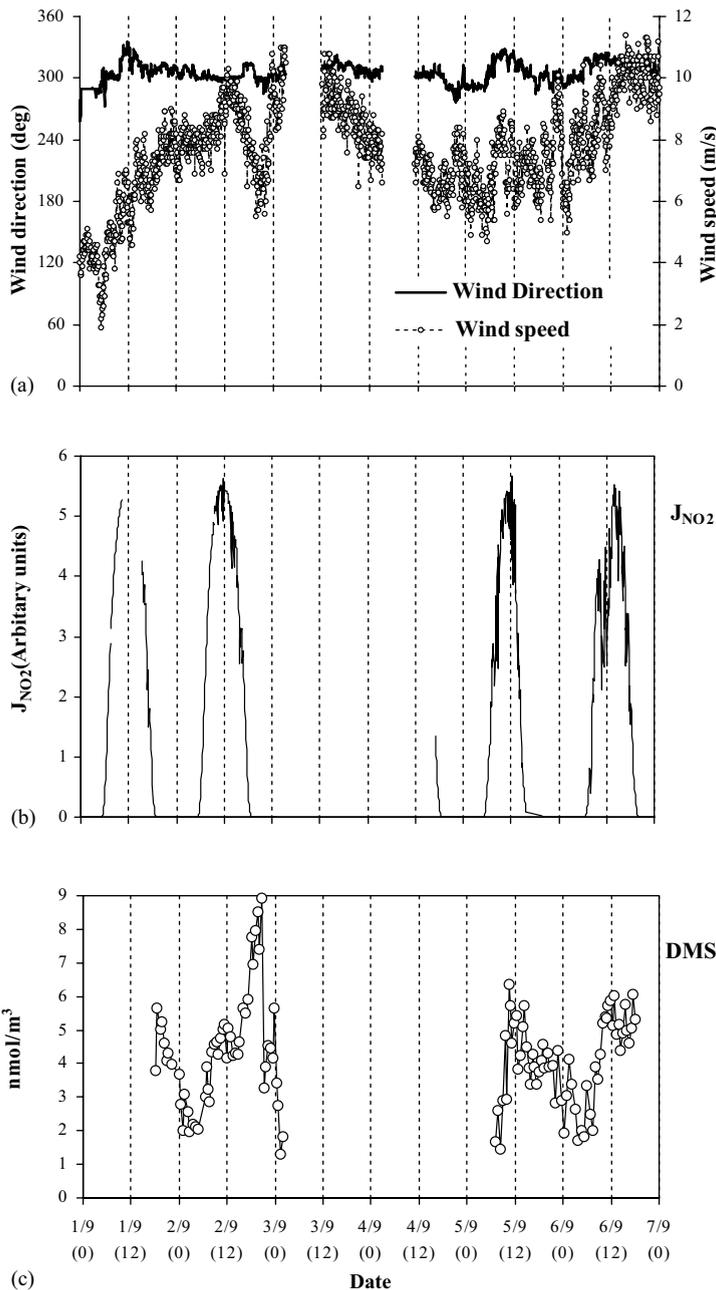


Fig. 2. Variation of (a) wind speed (in  $m s^{-1}$ ) and direction (in  $^{\circ}$ ), (b) photodissociation frequency of  $NO_2$  (in arbitrary units) and (c) atmospheric DMS (in  $nmol m^{-3}$ ) during the period of 1–8 September 1997.

the air masses originated from NW Europe and during the second period from N/NE sectors (Turkey and Bulgaria). Wind speed was quite high during the two experiments with mean value of the order of  $8 \text{ m s}^{-1}$ . Finally, the measured  $J(\text{NO}_2)$  show that generally sunny conditions with only few passages of clouds encountered during the experiment.  $\text{O}_3$  ranged from 53 to  $83 \text{ ppb}_v$  during the first period and from 60 to  $68 \text{ ppb}_v$  during the second one indicating intensive photochemical activity in the region. During the two intensive campaigns DMS concentrations ranged between 1.30 and  $8.94 \text{ nmol m}^{-3}$  (with a mean of  $4.30 \pm 1.47$ , Fig. 2c).

The atmospheric DMS concentrations observed during the two intensive periods are in good agreement with the long-term measurements performed during the 1997–1999 period (see Section 3.2). These values are higher compared to the values reported by Ganor et al. (2000) that range between 0.54 and  $0.91 \text{ nmol m}^{-3}$  and have been measured just above the sea level in Israel and under low wind speed conditions around noon when DMS oxidation is expected to be high. However, our mean observed atmospheric DMS concentrations are in line with the measured seawater DMS and the observed high wind speed as will be discussed in detail in Section 3.2.1. The mean atmospheric DMS concentrations measured at Finokalia during the two intensive studies agree quite well with the values reported by Pio et al. (1996) for the Portuguese coast during summer/autumn as well as with other reported observations in the remote marine atmosphere (see Table 1).

### 3.1.1. Diurnal variation of atmospheric DMS

Several authors reported that wind speed is a key factor regulating the atmospheric DMS levels. From Figs. 2a and c it is clear that although in few cases atmospheric DMS concentrations follow the wind speed change, however, no quantitative correlation can be established between these two parameters. This result indicates that factors other than wind speed regulate the short-term variability of atmospheric DMS in the Eastern Mediterranean. The mean diurnal variation of DMS during the 4-day period is depicted in Fig. 3. To subtract the day-to-day variability in DMS concentrations, relative DMS concentrations (the ratio of DMS concentration at a given time to the mean diurnal value) are reported in this figure. The observed DMS diurnal variation has an amplitude of 3, much higher to that reported for the remote marine atmosphere (1.2–1.7; Andreae et al., 1985; Ayers et al., 1995; Sciare et al., 2000a). Fig. 3 clearly shows a nighttime minimum in DMS concentrations. This minimum is pronounced (amplitude of  $>2$ ) and could be explained by the presence of  $\text{NO}_3$  radicals, which are highly reactive towards DMS. Simple calculations based on the ratio of the reaction rates of DMS with OH and  $\text{NO}_3$  radicals, respectively, indicate that 1–3  $\text{ppt}_v$  of  $\text{NO}_3$  could account for such night DMS depletion. Even much higher  $\text{NO}_3$  levels (up to about 300  $\text{ppt}_v$ , mean = 25  $\text{ppt}_v$ ) have been measured in the area in July 2000 (Sebastian et al., 2001). In the early morning, DMS levels increase rapidly until 11:00. Then, a slow decrease is observed to occur at 16:00, followed by an increase to

Table 1  
Comparison of the results of this work with other species reported in the literature

	Value	Location	Period	Reference
Gas $\text{CH}_3\text{SCH}_3$ ( $\text{nmol m}^{-3}$ )	$2.35 \pm 1.38$	Finokalia	05/97–10/99	This work
	0.18–0.91	Mediterranean coast/Israel	08/95	Ganor et al. (2000)
	1.9–24.2	Atlantic coast/Portugal	11/93–08/94	Pio et al. (1996)
	1.81	NW Scotland, Eire	1989–1990	Davison and Hewitt (1992)
	$2.29 \pm 1.79$	Cape Grim, Tasmania	11/88–03/93	Ayers et al. (1995)
	3.75	New Zealand	1990–1992	Wylie and de Mora (1996)
	1.55–23.3	Amsterdam Island	1990–1999	Sciare et al. (2000b)
	$0.266 \pm 0.154$	Finokalia	10/96–09/99	This work
	$0.470 \pm 0.30$	Finokalia	03/94–04/95	Mihalopoulos et al. (1997)
	$0.48 \pm 0.21$	Mediterranean coast/Israel	08/95	Ganor et al. (2000)
Aerosol $\text{CH}_3\text{SO}_3^-$ ( $\text{nmol m}^{-3}$ )	0.621	Atlantic coast/Portugal	11/93–08/94	Pio et al. (1996)
	0.188	NW Scotland, Eire	1989–1990	Davison and Hewitt (1992)
	0.1–1.1	N Sea and N Atlantic	7/85–7/87	Watts et al. (1990)
	0.36	New Zealand	1990–1992	Wylie and de Mora (1996)
	$41.0 \pm 17.4$	Finokalia	10/96–09/99	This work
	$85.12 \pm 86.2$	Finokalia	03/94–04/95	Mihalopoulos et al. (1997)
	$41.8 \pm 16.6$	Mediterranean coast/Israel	08/95	Ganor et al. (2000)
	56–128	Israel (coastal and inland areas)	1984–1993	Luria et al. (1996)
Aerosol nss- $\text{SO}_4^{2-}$ ( $\text{nmol m}^{-3}$ )	56.3	Antalya	03/92–12/93	Gullu et al. (1998)
	41.26	Atlantic coast/Portugal	11/93–08/94	Pio et al. (1996)

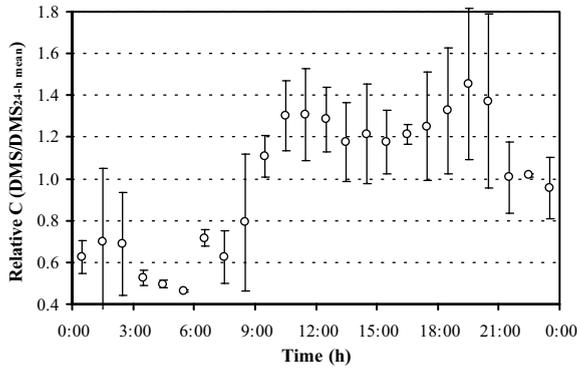


Fig. 3. Mean diurnal variation of atmospheric DMS during the 4-day intensive experiment. Relative DMS concentrations (ratio of DMS concentration at a given time to the 24-h mean value) are reported. Bars correspond to standard deviation ( $1\sigma$ ).

reach the highest levels of DMS around 20:00 (local time). The pattern of the diurnal DMS variation observed during the two intensive campaigns at Finokalia is in agreement with the observations by Andreae (1985) in the marine atmosphere under continental influence.

### 3.2. Long-term variation of atmospheric DMS

Fig. 4a presents the variation of daytime atmospheric DMS at Finokalia during the 30-month period of the study (May 1997–October 1999), on the basis of the 137 atmospheric DMS measurements that have been performed. Dimethylsulfide concentrations range from 0.3 to  $8.9 \text{ nmol m}^{-3}$  (mean = 2.35 and median = 2.08) and present a well distinguished seasonal variation (Fig. 4b). The highest values are observed during summer ( $3.74 \pm 0.81$ ) and the lowest in winter ( $0.87 \pm 0.23$ ), in good agreement with the reported observations in the remote marine atmosphere (Ayers et al., 1995; Sciare et al., 2000b; Table 1). Since DMS presents an important diurnal variation (see Section 3.1.1), the above DMS levels could be considered only as characteristic of daytime values.

Fig. 5 presents the variation of atmospheric DMS in conjunction with sea-surface temperature. A very significant correlation is observed between atmospheric DMS and sea-surface temperature (Fig. 5). This observation is in good agreement with the observations made by Sciare et al. (2000b) around Amsterdam Island in the Southern Indian Ocean, suggesting that the long-term variability in atmospheric DMS concentrations at Amsterdam Island could be explained by changes in sea-surface temperature. Although our data set is smaller than that reported by Sciare et al. (2000b), our results

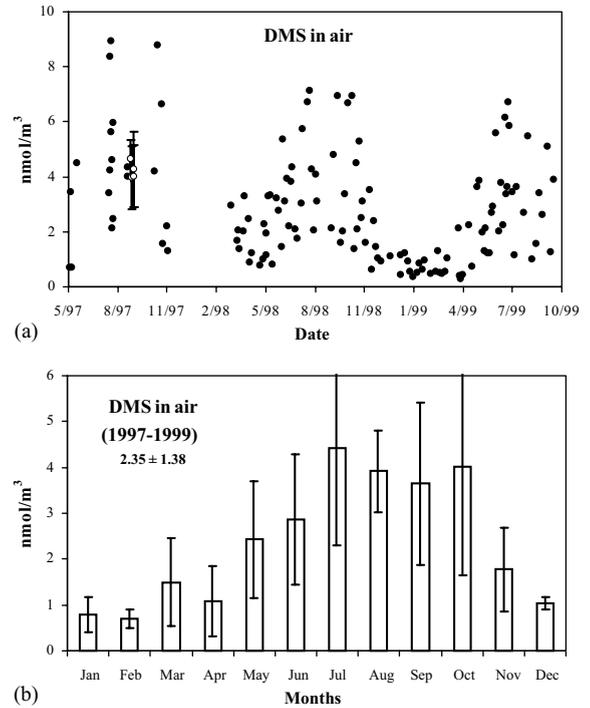


Fig. 4. Variation of atmospheric DMS during the sampling period: (a) all the data set and (b) seasonal variation of the monthly mean concentrations. Bars correspond to standard deviation ( $1\sigma$ ) of either diurnal (4a) or monthly (4b) data sets.

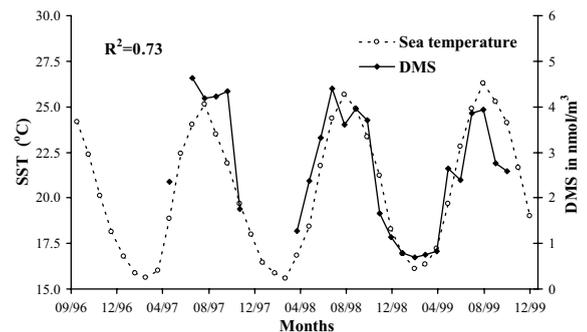


Fig. 5. Co-variation of monthly mean sea-surface temperature and DMS.

support the hypothesis that the DMS/surface temperature relationship could have more global significance.

#### 3.2.1. Reconciliation of atmospheric DMS concentrations with sea–air fluxes

Sea-to-air DMS fluxes around Crete island required to explain the measured atmospheric DMS concentrations are calculated by using a 0-D model following the approach reported by Ayers et al. (1995) for the Cape Grim observations. Seawater DMS flux was deduced

from the observed atmospheric DMS concentrations as follows:

$$F = CHt^{-1} - E,$$

where  $F$  is the flux of DMS from the seawater to the atmosphere,  $C$  the atmospheric monthly mean DMS concentration,  $t$  the DMS lifetime  $= (K_{OH}[OH])^{-1}$ : for the calculation of the DMS lifetime, only the reaction with OH radicals is taken into account. This assumption is valid since for the expected  $\text{NO}_3$  levels (Sebastian et al., 2001; see also Section 3.1.1) DMS lifetime is estimated from few minutes to 1–2 h and thus will mainly influence the nighttime levels of DMS. Note that no DMS measurements have been performed at night during the long-term study. The OH concentrations used are those calculated by a 3-D global model study (Houweling et al., 1998). The reaction rate  $K_{OH+DMS}$  is taken from Hynes et al. (1986).  $H$  the height of the boundary layer, deduced from radiosoundings performed each day by the local meteorological station. The mean summertime value was 1500 m.  $E$  the entrainment flux of DMS from the troposphere to the boundary layer, calculated as proposed by Ayers et al. (1995).

The thus modeled 0-D DMS fluxes have been compared with those calculated using seawater DMS concentrations measured during eight oceanographic cruises performed in the area from March 1997 to May 1998, wind speed and SST from climatological data (Kouvarakis et al., 2001b). The comparison is limited to the dry period when seawater DMS concentrations present their maximum values with small variations and intensive photochemistry occurs in the atmosphere of the Mediterranean. Fig. 6 presents the results of this comparison. A quite good agreement ( $\pm 30\%$ ) was found between the fluxes derived from the atmospheric

DMS concentrations by using the 0-D model and those calculated on the basis of the seawater DMS fluxes during the dry period. Therefore, the observed atmospheric DMS levels can be explained by the sea–air DMS fluxes derived from the seawater DMS observations and the atmospheric chemical destruction of DMS by OH radicals.

### 3.3. Seasonal variation of aerosol sulfur species (*nss-SO<sub>4</sub><sup>2-</sup>* and MSA)

Fig. 7a presents the variation of MSA concentration in aerosols observed at Finokalia from October 1996 to September 1999. Methanesulfonic acid ranges from 0.04 to 0.99  $\text{nmol m}^{-3}$ . As its precursor DMS, MSA presents a seasonal variation with the highest values during summer and a summer to winter ratio of about 10. Both the concentrations and the seasonal amplitude of MSA are consistent with previous studies performed at Finokalia (Mihalopoulos et al., 1997) or in remote marine areas of the world (Table 1). Methanesulfonic acid follows quite well the general pattern of atmospheric DMS; however, no correlation between the two data sets exists on a point-by-point basis. The lack of such correlation is evident mainly in spring 1998 and 1999 when MSA presents its maximum, which is due to the spring algal bloom and seen in the DMS concentrations in seawater (Bardouki et al., 2000; Kouvarakis et al., 2001b). A close examination of the DMS/MSA molar ratio shows ratios of about 4 during spring, whereas during the rest of the dry period the ratio ranges from 8 to 10. Similar DMS/MSA ratio has been reported for the remote marine atmosphere by Ayers et al. (1991;  $\sim 8$  at Cape Grim) and by Wylie and de Mora (1996; ratios ranging from 8 to 13 in New

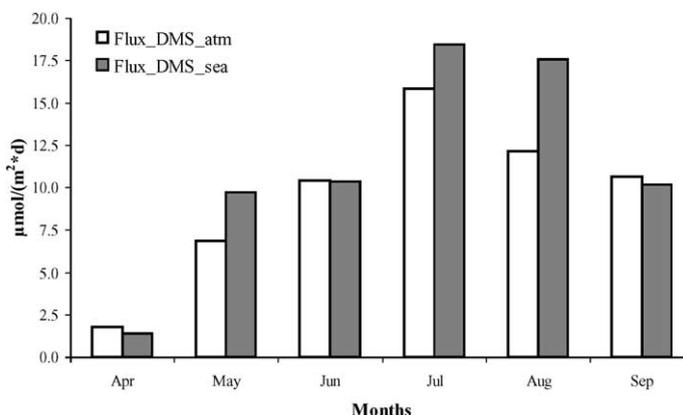


Fig. 6. Comparison between the modeled and calculated DMS fluxes during spring/early autumn period. The modeled DMS fluxes (Flux DMS Atm) have been calculated on the basis of the atmospheric DMS concentrations and OH concentrations taken from a global 3-D model (see text). Dimethylsulfide fluxes (Flux DMS Sea) have been also calculated using measured seawater DMS concentrations and wind speed from climatological data. Units are in  $\mu\text{mol m}^{-2} \text{d}^{-1}$ .

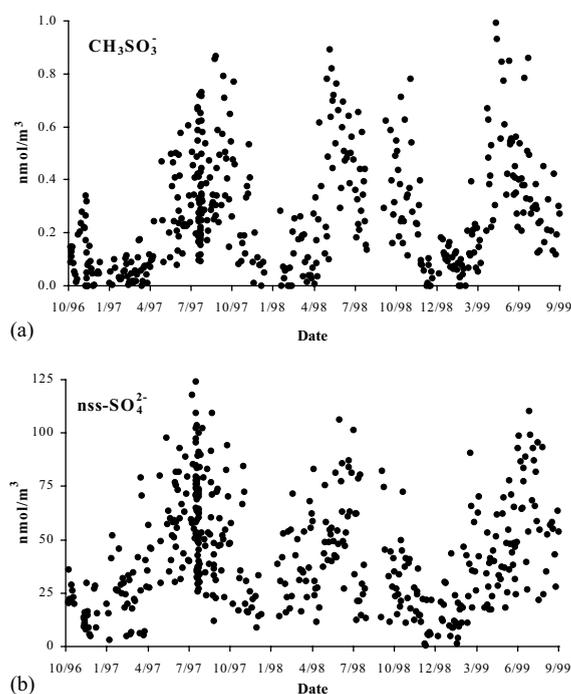


Fig. 7. Temporal variation of (a) particulate MSA and (b)  $\text{nss-SO}_4^{2-}$  measured during the 1996–1999 period.

Zealand). The lowest DMS/MSA ratios indicate more efficient oxidation of DMS to MSA and are deduced during spring when local influence is expected to be the highest due to the low wind speed and wind origin, since during that period air masses travel a part of the island before reaching Finokalia (Kouvarakis et al., 2000). Note that Mihalopoulos et al. (1992) reported a DMS/MSA ratio of 3 during an experiment performed at a coastal area in French Brittany in summer 1989 under prevailing continental winds. Thus, the presence of elevated levels of  $\text{NO}_x$  at Finokalia could account for this higher turnover of DMS to MSA during spring, in agreement with the experiments by Yin et al. (1990). Watts et al. (1990) found that more MSA is produced in air masses with both remote and polluted components and proposed that the presence of anthropogenically derived initiators promote the oxidation of DMS to MSA in agreement with our observations.

Fig. 7b presents the variation of aerosol  $\text{nss-SO}_4^{2-}$  at Finokalia calculated using  $\text{Mg}^{2+}$  or  $\text{Na}^+$  as a seawater tracer. Note that both approaches lead to very similar results (within 10%). Non-sea-salt sulfate ranges from 0.6 to  $123.9 \text{ nmol m}^{-3}$  and presents a seasonal variation with the highest values during summer and a winter ratio of 4. Both the concentrations and the seasonal amplitude of  $\text{nss-SO}_4^{2-}$  are consistent with previous studies performed in the Eastern Mediterranean (Table 1).

### 3.3.1. Variability of the $\text{MSA/nss-SO}_4^{2-}$ ratio

Several authors reported that the  $\text{MSA/nss-SO}_4^{2-}$  ratio varies both seasonally and latitudinally with higher values at higher latitudes and during summertime (see for instance, Bates et al., 1992b; Saltzman et al., 1986; Savoie and Prospero, 1989). Based on aerosol data collected during an oceanographic cruise and under pure marine conditions, Bates et al. (1992b) proposed an equation relating the  $\text{MSA/nss-SO}_4^{2-}$  ratio with the inverse of the temperature (high ratios at low temperatures). Thus, the relative contribution of biogenic and anthropogenic/continental sulfate can be performed by comparing the theoretical  $\text{MSA/nss-SO}_4^{2-}$  ratio calculated by applying the Bates et al. (1992b) equation with that calculated on the basis of MSA and  $\text{nss-SO}_4^{2-}$  observations. Figs. 8a and b present the seasonal variability of  $\text{MSA/nss-SO}_4^{2-}$  ratio (8a) and the seasonal variability of the biogenic sulfur fraction deduced from our MSA and  $\text{nss-SO}_4^{2-}$  data, the variation of temperature from climatological data and Bates et al. (1992a) Eq. (8b). For this, first the biogenic  $\text{nss-SO}_4^{2-}$  corresponding to the measured MSA is calculated on the basis of Bates et al. (1992b) equation and the climatologically derived temperature. The biogenic sulfur part derived as the ratio of the thus calculated biogenic  $\text{nss-SO}_4^{2-}$  to the measured  $\text{nss-SO}_4^{2-}$  ranges from 1% during winter to 17% during summer. These figures are in agreement with the results reported by Mihalopoulos et al. (1997) based on 45 measurements conducted during the period March 1994–April 1995. However, the above estimations have to be seen with caution since (i) the theoretical background governing the Bates et al. (1992a) equation is still under debate and (ii) as the Bates et al. (1992a) equation was derived for the lower temperatures than those occurring during summer in the Eastern Mediterranean. Other approaches like use of sulfur isotopes or performing a sulfur budget will probably allow obtaining a more clear idea and comparing the various estimations between them.

## 4. Conclusion

During a 3-yr period atmospheric DMS levels as well as aerosol concentrations of MSA and  $\text{nss-SO}_4^{2-}$  have been monitored in the Eastern Mediterranean. The following conclusions can be drawn from this study:

- Daytime atmospheric DMS concentrations range from 0.3 to  $8.9 \text{ nmol m}^{-3}$  with an average value of  $2.35 \text{ nmol m}^{-3}$ , in good agreement with reported observations in the remote marine atmosphere (Table 1). The highest DMS values occur during summer as a result of elevated DMS concentrations in seawater and high wind speed.

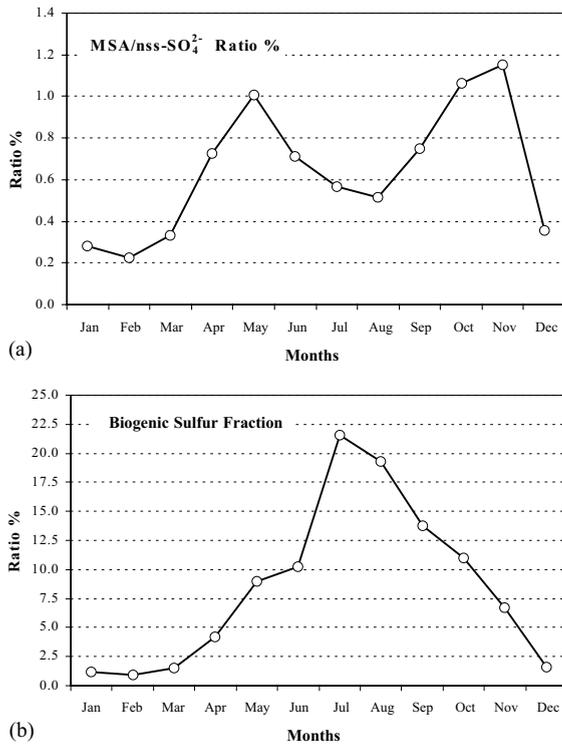


Fig. 8. (a) Seasonal variability of MSA/nss-SO<sub>4</sub><sup>2-</sup> ratio (%) and (b) seasonal variability of the biogenic sulfur fraction (%) derived from the observed MSA and nss-SO<sub>4</sub><sup>2-</sup> concentrations (see text).

- A diurnal DMS trend in the atmosphere has been observed whereby the highest DMS levels occurred in the late afternoon hours and the minimum during nighttime. The nighttime minimum could be explained by the presence of NO<sub>3</sub> radicals, which are highly reactive towards DMS. Simple calculations indicate that NO<sub>3</sub> levels of about 1–3 ppt<sub>v</sub> could explain such nighttime DMS depletion.
- A quite good agreement ( $\pm 30\%$ ) was found between the fluxes derived from the atmospheric DMS concentrations by using the 0-D model and those calculated on the basis of the seawater DMS fluxes during the dry period. Therefore, the observed atmospheric DMS levels can be explained by the sea–air DMS fluxes derived from the seawater DMS observations and the atmospheric chemical destruction of DMS by OH radicals.
- Monthly atmospheric DMS concentrations are significantly correlated with sea-surface temperature, suggesting that the long-term variability in atmospheric DMS concentrations could be explained by changes in sea-surface temperature. This result is in good agreement with the observations by Sciare et al.

(2000b) around Amsterdam Island in the Southern Indian Ocean.

- Aerosol MSA concentrations also vary seasonally from  $0.064 \pm 0.013$  in winter to  $0.378 \pm 0.043$  nmol m<sup>-3</sup> in summer. During the 3-yr period the DMS/MSA molar ratio was quite constant, around 8, and in agreement with the figures reported for the remote marine atmosphere. During spring this ratio was significantly lower probably due to a more intensive oxidation of DMS to MSA.
- On the basis of the measured MSA/nss-SO<sub>4</sub><sup>2-</sup> and the ambient temperature, the biogenic sulfur contribution has been estimated to range from 1% during winter to 17% during summer.

### Acknowledgements

We thank the European Commission, Environment Programme, (ENK2-CT-1999-00033) and the University of Crete (ELKE) for financial support and M. Kanakidou and the two anonymous reviewers for helpful remarks.

### References

- Andreae, M.O., Ferek, R.J., Bermond, F., Byrd, K.P., Engstrom, R.T., Hardin, S., Houmère, D., LeMarrec, F., Raemdonck, H., Chatfield, R.B., 1985. Dimethylsulfide in the marine atmosphere. *Journal of Geophysical Research* 90 (12), 891–900.
- Ayers, G.P., Ivey, J.P., Gillett, R.W., 1991. Coherence between seasonal cycles of dimethyl sulphide, methanesulphonate and sulphate in marine air. *Nature* 349, 404–406.
- Ayers, G.P., Bentley, S.T., Ivey, J.P., Forgan, B.W., 1995. Dimethylsulfide in marine air at Cape Grim, 41°S. *Journal of Geophysical Research* 100, 21013–21021.
- Baboukas, E.D., Kanakidou, M., Mihalopoulos, N., 2000. Carboxylic acids in gas and particulate phase above the Atlantic Ocean. *Journal of Geophysical Research* 105, 14459–14471.
- Bardouki, H., Spatial and seasonal variability of DMS(X) species in the Eastern Mediterranean Sea. Master Thesis, University of Crete, 2000.
- Barnes, I., Becker, K.H., Patroescu, I., 1996. FTIR products study of the OH initiated oxidation of dimethyl sulphide: observation of carbonyl sulphide and dimethyl sulphoxide. *Atmospheric Environment* 30, 1805–1814.
- Bates, T.S., Lamb, B.K., Guenther, A., Dignon, J., Stoiber, R.E., 1992a. Sulfur emissions to the atmosphere from natural sources. *Journal of the Atmospheric Chemistry* 14, 315–337.
- Bates, T.S., Calhoun, J.A., Quinn, P.K., 1992b. Variations in the methanesulfonate to sulfate molar ratio in submicrometer marine aerosol particles over the South Pacific Ocean. *Journal of Geophysical Research* 97, 9859–9865.

- Charlson, R.J., Lovelock, J.E., Andreae, M.O., Warren, S.G., 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate: a geophysiological feedback. *Nature* 326, 655–661.
- Davison, B.M., Allen, A., 1994. A method for sampling dimethylsulfide in polluted and remote marine atmospheres. *Atmospheric Environment* 28, 1721–1729.
- Davison, B., Hewitt, N., 1992. Natural sulphur species from the North Atlantic and their contribution to the United Kingdom sulphur budget. *Journal of Geophysical Research* 97, 2475–2488.
- Ganor, E., Foner, H.A., Bingemer, H.G., Udisti, R., Setter, I., 2000. Biogenic sulphate generation in the Mediterranean Sea and its contribution to the sulphate anomaly in the aerosol over Israel and the Eastern Mediterranean. *Atmospheric Environment* 34, 3453–3462.
- Gullu, G., Olmez, I., Aygun, S., Tuncel, G., 1998. Atmospheric element concentrations over the Eastern Mediterranean Sea: factors affecting temporal variability. *Journal of Geophysical Research* 103, 21943–21954.
- Houweling, S., Dentener, F., Lelieveld, J., 1998. The impact of nonmethane hydrocarbon compounds on tropospheric chemistry. *Journal of Geophysical Research* 103, 10673–10696.
- Hynes, A.J., Wine, P.H., Semmes, D.H., 1986. Kinetics and mechanisms of OH reactions with organic sulfides. *Journal of Physical Chemistry* 90, 4148–4156.
- Jensen, N.R., Hjorth, J., Lohse, C., Skov, H., Restelli, G., 1991. Products and mechanism of the reaction between  $\text{NO}_3$  and dimethylsulfide in air. *Atmospheric Environment* 25A, 1897–1904.
- Kouvarakis, G., Tsigaridis, K., Kanakidou, M., Mihalopoulos, N., 2000. Temporal variations of surface regional background ozone over Crete Island in Southeast Mediterranean. *Journal of Geophysical Research* 105, 4399–4407.
- Kouvarakis, G., Doukelis, Y., Mihalopoulos, N., Rapsomanikis, S., Sciare, J., Blumthaler, M., 2001a. Chemical, physical and optical characterization of aerosol during PAUR II experiment. *Journal of Geophysical Research*, in press.
- Kouvarakis, G., Bardouki, H., Mihalopoulos, N., 2001b. Sulfur budget above the Eastern Mediterranean: relative contribution of anthropogenic and biogenic sources. *Tellus*, submitted for publication.
- Luria, M., Peleg, M., Sharf, G., Siman tov-Alper, D., Spitz, N., Ben Ami, Y., Gawii, Z., Lifschitz, B., Yitzchaki, A., Seter, I., 1996. Atmospheric sulfur over the Eastern Mediterranean region. *Journal of Geophysical Research* 101, 25917–25930.
- Mihalopoulos, N., Nguyen, B.C., Boissard, C., Campin, J.M., Putaud, J.P., Belviso, S., Barnes, I., Becker, K.H., 1992. Field study of dimethylsulfide oxidation in the boundary layer: variations of dimethylsulfide, methanesulfonic acid, sulfur dioxide, non sea salt sulfate and Aitken nuclei at a coastal site. *Journal of the Atmospheric Chemistry* 14, 459–477.
- Mihalopoulos, N., Stephanou, E., Kanakidou, M., Pilitsidis, S., Bousquet, P., 1997. Tropospheric aerosol ionic composition above the Eastern Mediterranean Area. *Tellus B*, 314–326.
- Nguyen, B.C., Mihalopoulos, N., Belviso, S., 1990. Seasonal variation of atmospheric dimethylsulfide at Amsterdam island in the Southern Indian Ocean. *Journal of the Atmospheric Chemistry* 11, 123–143.
- Pio, C.A., Cerqueira, M.A., Castro, L.M., Salgueiro, M.L., 1996. Sulphur and nitrogen compounds in variable marine/continental air masses at the southwest European coast. *Atmospheric Environment* 30, 3115–3127.
- Putaud, J.P., Davison, B.M., Watts, S.F., Mihalopoulos, N., Nguyen, B.C., Hewitt, C.N., 1999. Dimethylsulfide and its oxidation products at two sites in Brittany (France). *Atmospheric Environment* 33, 647–659.
- Platt, U., Le Bras, G., Poulet, G., Burrows, J.P., Moortgat, G., 1990. Peroxy radicals from nighttime reaction of  $\text{NO}_3$  with organic compounds. *Nature* 348, 147–149.
- Ramonet, M., Le Rouley, J.C., Bousquet, P., Monfray, P., 1996. Radon-222 measurements during the TROPOZ II campaign and comparison with a global atmospheric transport model. *Journal of the Atmospheric Chemistry* 23, 107–136.
- Saltzman, E.S., Savoie, D.L., Prospero, J.M., Zika, R.G., 1986. Methanesulfonic acid and non-sea salt sulfate in Pacific air: regional and seasonal variations. *Journal of the Atmospheric Chemistry* 4, 227–240.
- Savoie, D., Prospero, J., 1989. Comparison of oceanic and continental sources of non-sea-salt sulphate over the Pacific Ocean. *Nature* 339, 685–687.
- Sciare, J., Baboukas, E., Kanakidou, M., Krischke, U., Belviso, S., Bardouki, H., Mihalopoulos, N., 2000a. Spatial and temporal variability of atmospheric sulfur containing gases and particles during the ALBATROSS campaign. *Journal of Geophysical Research* 105, 14433–14448.
- Sciare, J., Mihalopoulos, N., Dentener, F.J., 2000b. Interannual variability of atmospheric dimethylsulfide in the Southern Indian Ocean. *Journal of Geophysical Research* 105, 17257–17265.
- Sebastian, O., Geyer, A., Hoenninger, G., Mihalopoulos, N., Sciare, J., Platt, U., 2001. The role of nitrate radicals and halogen oxides in the oxidation of dimethyl sulphide in the moderately polluted Mediterranean area—first results of the CRETE 2000 field Campaign. Poster presented at the EGS meeting, Nice, March.
- Watts, S.F., Brimblecombe, P., Watson, A., 1990. Methanesulphonic acid, dimethyl sulfoxide and dimethyl sulphone in aerosols. *Atmospheric Environment* 24, 353–359.
- Wayne, R.P., et al., 1991. The nitrate radical: physics, chemistry and the atmosphere. *Atmospheric Environment* 25A, 1–203.
- Wylie, D., de Mora, S., 1996. Atmospheric dimethylsulfide and sulfur species in aerosol and rainwater at a coastal site in New Zealand. *Journal of Geophysical Research* 101, 21041–21049.
- Yin, F., Grosjean, D., Seinfeld, J.H., 1990. Photooxidation of dimethylsulfide and dimethyldisulfide: mechanism development. *Journal of the Atmospheric Chemistry* 11, 309–364.
- Yvon, S.A., Saltzman, E.S., Cooper, D.J., Bates, T.S., Thompson, A.M., 1996. Atmospheric sulfur cycling in the tropical Pacific marine boundary layer ( $12^\circ\text{S}$ ,  $135^\circ\text{W}$ ): a comparison of field data and model results. 1. Dimethylsulfide. *Journal of Geophysical Research* 101 (3), 6899–6909.