



**HAL**  
open science

# Diurnal and seasonal variation of atmospheric dimethylsulfoxide at Amsterdam Island in the southern Indian Ocean

J. Sciare, M. Kanakidou, N. Mihalopoulos

► **To cite this version:**

J. Sciare, M. Kanakidou, N. Mihalopoulos. Diurnal and seasonal variation of atmospheric dimethylsulfoxide at Amsterdam Island in the southern Indian Ocean. *Journal of Geophysical Research: Atmospheres*, 2000, 105 (D13), pp.17257-17265. 10.1029/1999JD901186 . hal-03123391

**HAL Id: hal-03123391**

**<https://hal.science/hal-03123391>**

Submitted on 28 Jan 2021

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Diurnal and seasonal variation of atmospheric dimethylsulfoxide at Amsterdam Island in the southern Indian Ocean

J. Sciare

Laboratoire des Sciences du Climat et de l'Environnement, CEA Orme des Merisiers, Gif-sur-Yvette, France

M. Kanakidou and N. Mihalopoulos

Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, Heraklion, Greece

**Abstract.** Atmospheric dimethylsulfoxide (DMSO), an important dimethylsulfide (DMS) oxidation by-product, has been monitored on a daily basis at Amsterdam Island in the southern Indian Ocean during three periods (January–September 1997, January–June 1998, and January–October, 1999). In addition, during an intensive experiment carried out in January 1998, DMSO diurnal variation has been studied in conjunction with parallel measurements of atmospheric DMS. Monthly average atmospheric DMSO mixing ratios range from 0.3 to 5.8 parts per trillion by volume and present a well-distinguished seasonal cycle with a minimum in winter and a maximum in summer similar to that observed for atmospheric DMS simultaneously measured. DMSO presents also a well-distinguished diurnal variation with maximum values around 0900 and minimum during night. A photochemical box model using measured atmospheric DMS concentrations as input data reproduces quite well the diurnal variation of DMSO when assuming a 50% yield from the DMS+OH addition channel [Hynes and Wine, 1996]. However, in absolute terms the simulated DMSO concentrations were about a factor of 2 higher than those measured. Photochemically driven heterogeneous losses of DMSO on aerosol and/or clouds could account for this difference.

### 1. Introduction

In the recent years it has been proposed that the emission of dimethylsulfide (DMS) from the oceans, through its oxidation products, may play an important role in regulating climate in the remote marine atmosphere [Charlson *et al.*, 1987]. Indeed, DMS has tentatively been identified as the major precursor of condensation nuclei (CN) and eventually cloud condensation nuclei (CCN) in remote marine regions [Ayers *et al.*, 1991; Andreae *et al.*, 1995]. However, its role as a climate regulator remains unknown. The effect of DMS on the climate is critically dependent on the production of gas phase sulfuric acid ( $\text{H}_2\text{SO}_4$ ) since methanesulfonic acid (MSA), another main oxidation end-product of DMS, is not expected to form new particles [Kreidenweiss and Seinfeld, 1988]. It is thus important to define the factors controlling the relative yields of MSA and  $\text{H}_2\text{SO}_4$  in the oxidation of DMS for a comprehensive understanding of the possible sulfur-climate interactions. In the recent years the picture of the oxidation scheme of DMS became more complicated since dimethylsulfoxide (DMSO) has been firmly established as an important product of the OH and halogen oxide (XO) initiated DMS oxidation [Barnes *et al.*, 1994; Hynes and Wine, 1996; Toumi, 1994]. These studies demonstrated that DMSO is produced from the OH-initiated atmospheric oxidation of DMS through the addition channel, with a yield of approximately 30% of the total reaction at 298 K and as high

as 70% at low temperatures [Barnes *et al.*, 1994, 1996; Hynes and Wine, 1996]. In the case of XO-initiated atmospheric DMS oxidation, DMSO yield is expected to be around 100% [Barnes *et al.*, 1991]. Thus understanding of DMSO fate in the marine atmosphere is important for a better evaluation of the climatic role of biogenic sulfur cycle. DMSO can also play an important role in the DMS cycling in the seawater [Hatton *et al.*, 1996; Kieber *et al.*, 1996; Simo *et al.*, 1998]. However, because of the high solubility of DMSO, seawater does not represent an atmospheric source of DMSO.

In the atmosphere, DMSO has been detected in the aerosol phase [Watts and Brimblecombe, 1987; Watts *et al.*, 1990; Sciare *et al.*, 2000], in gas phase [Berresheim *et al.*, 1993, 1998], and in rainwater [Andreae, 1980a, b; Sciare *et al.*, 1998]. The first results on the diel variation of DMSO were reported by Berresheim *et al.* [1993, 1998] in the north-western United States and Antarctica, respectively, during a 1- and 3-day period of continuous measurements with 10-min averaged time series. As noticed by Berresheim *et al.* [1998] for the work conducted in Antarctica, due to the low OH concentrations, aerosol loss and/or surface deposition was a much more important sink for DMSO compared to photochemistry. With the exception of these works, no systematic studies on atmospheric DMSO were carried out for long time periods. Thus no indications on a possible DMSO seasonal variation or amplitude exist. This paper presents the first 25-month series of DMSO measurements (from January to September 1997, from January to June 1998, and from January to October 1999) in conjunction with atmospheric DMS measured simultaneously. To understand the factors controlling the atmospheric DMSO concentration at Amsterdam Island, we also investigated its short-term variation

Copyright 2000 by the American Geophysical Union.

Paper number 1999JD901186.  
0148-0227/00/1999JD901186\$09.00

(measurements in January 1998) in conjunction with that of DMS, its precursor, by using a time resolution of about 1-2 hours. The results of DMSO diurnal variation have been critically compared with the output of a photochemical box model using measured atmospheric DMS as input data.

## 2. Experiment

Amsterdam Island (37°50'S-77°30'E) is located in the prevailing westerlies of the southern Indian Ocean. The nearest lands upwind are South Africa and Madagascar, about 3400 km and 5000 km to the northwest, respectively. More details on the meteorological conditions occurring in this area are given by Polian *et al.* [1986].

Atmospheric DMSO was sampled from the top of the building of the Laboratory of Geophysics situated 100 m south of the base. During the intensive campaign in January 1998, DMSO sampling was performed from 0500 to 2400 local time and on a 1-2 hour basis. During the rest of the year the DMSO sampling was centered on the DMS sampling time (0800 local time) and with 2-6 hour time step depending on the season. DMSO was collected using the refluxing sampling technique described by Cofer *et al.* [1985]. Air with flow rate of around 15 L min<sup>-1</sup> is drawn through a Teflon filter (porosity of 0.5 μm) to remove aerosol particles and create a mist with the water present in the Cofer mist chamber. Twenty (20) mL of pure water, lightly acidified to stabilize better the trapped DMSO, is used in the Cofer chamber. DMSO analysis was performed by reduction of DMSO to DMS using sodium borohydride (NaBH<sub>4</sub>) as described by Andreae [1980a]. This method has also been adapted and successfully improved for nano-molecular aqueous DMSO determinations [Simo, 1998; Sciare and Mihalopoulos, 2000]. The DMS produced from DMSO reduction was trapped on Tenax GC at -80°C for 15 min and subsequently analyzed following the method described by Nguyen *et al.* [1990]. Tests performed by retreating and reanalyzing the same sample did not show any detectable amounts of DMS, indicating quantitative reduction of DMSO, removal of DMS during the described procedure and negligible blank values. Evaluation of the sampling procedure using two Cofer chambers operating in parallel and in series, respectively, showed that (1) the reproducibility in the sampling procedure was of the same order of magnitude as that in the DMSO determination, that is, 6% and (2) the sampling efficiency was found to be 85 ± 7%. The technique was also checked for both positive and negative interference. It was found that possible artifacts from reactions of DMS or DMSO with H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> were negligible in the remote atmosphere. DMSO analyses were performed within a few hours of the collection. Until the analysis the samples were kept refrigerated. Several tests showed that DMSO is stable for at least 40 days under the conditions used for conservation (acidified samples by addition of HCl, stored at 4°C). Atmospheric dimethylsulfone (DMSO<sub>2</sub>), a presumable oxidation product of DMSO existing in the marine atmosphere at levels lower or at least comparable to the DMSO, could be also trapped concurrently with atmospheric DMSO in our Cofer chambers. Thus the reduction of DMSO<sub>2</sub> to DMS using the NaBH<sub>4</sub> pellets has been examined and was found to be less than 1%, implying that DMSO<sub>2</sub> reduction to DMS has a nonsignificant impact in our measured DMSO concentrations.

The reproducibility of the technique was estimated to be of the order of 6%. The absolute accuracy defined as the sum of the accuracy in the DMSO reduction to DMS and the sampling efficiency was estimated to be of the order of 20%. More details on the sampling, analysis and method evaluation are given by Sciare and Mihalopoulos [2000].

Atmospheric DMS has been sampled on a daily basis at "Pointe Bénédicte" station, 2 km upwind of the base, since 1989. More details on the technique are given by Nguyen *et al.* [1990]. Mean error of the DMS analysis was estimated to be of the order of 5%. During the intensive experiment of January 1998, DMS sampling was also performed at the same place with DMSO. DMS measurements at this site show no significant difference (less than 5%) compared to the DMS observed at "Pointe Bénédicte" (J. Sciare *et al.*, Short term variability of atmospheric dimethylsulfide and its oxidation products at Amsterdam Island during summer time, submitted to *J. Atmos. Chem.*, 2000, hereinafter referred as Sciare *et al.*, submitted manuscript, 2000). All meteorological parameters used in this paper were provided by the local meteorological station (referenced as WMO/61996).

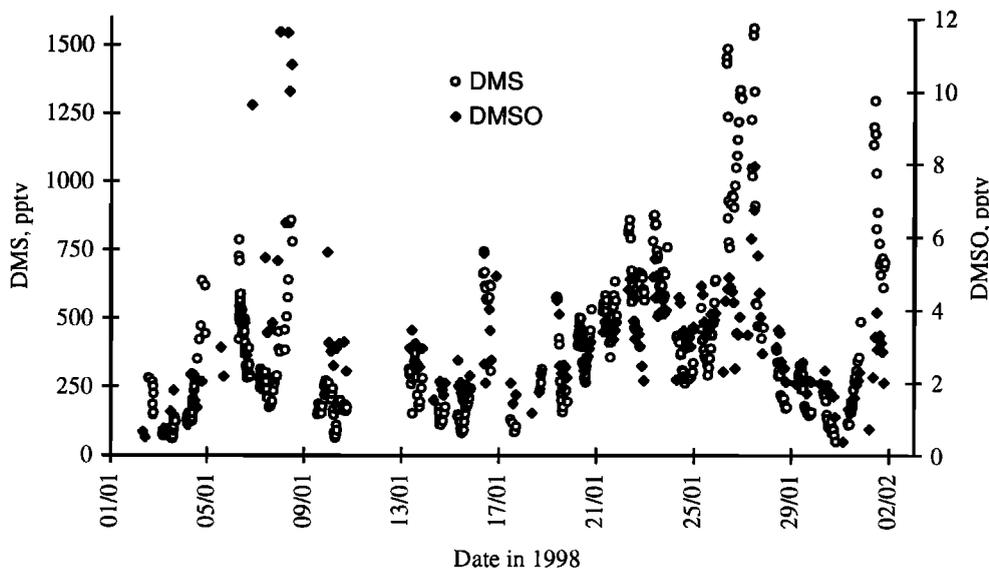
## 3. Results and Discussion

### 3.1. Short-Term DMSO Variation

One hundred ninety-one (191) measurements of atmospheric DMSO have been performed between January 2 and February 2, 1998. DMSO mixing ratios ranged between 0.36 parts per trillion by volume (pptv) and 11.6 pptv (mean equal to 3.2 pptv; standard deviation equal to 1.7 pptv). During this period, atmospheric DMS mixing ratios ranged between 65 pptv and 1460 pptv (mean equal to 430 pptv; standard deviation equal to 290 pptv; Figure 1). DMSO follows quite well the DMS variations although DMS and DMSO are not significantly correlated ( $r^2=0.21$ ).

Our measured DMSO concentrations fall in the range of the values reported by Berresheim *et al.* [1993, 1998]. Indeed, during the experiment performed by these authors at a Pacific coastal site in northwestern United States in April, the corresponding DMSO mixing ratios ranged between <0.5 pptv and 3.2 pptv, with a DMS/DMSO ratio of the order of 16 [Berresheim *et al.*, 1993]. At a coastal site in Antarctica, Berresheim *et al.* [1998] reported atmospheric DMSO mixing ratios ranged from <0.2 pptv to 25 pptv with a mean DMS/DMSO ratio of about 50. However, during our experiment the mean DMS/DMSO ratio was 134±79 significantly higher than those reported in the previous studies. This could reflect the different temperatures encountered during our experiment.

Atmospheric DMSO has been also reported in the equatorial Pacific by Bandy *et al.* [1996]. However, the reported values (10-50 pptv) are very high relative to the measured DMS levels and the air temperature. Indeed, under these experimental conditions DMSO values of the order of 1-2 pptv are expected (based on a DMSO yield of 50% from the addition channel of the DMS+OH reaction). The significantly higher measured DMSO values (up to a factor of 20) could indicate either intrusion of air rich in DMSO from higher altitudes (lower temperatures as in Antarctica) and/or presence of significant amounts of XO radicals which are known to exclusively produce DMSO when reacting with DMS [Barnes *et al.*, 1991].



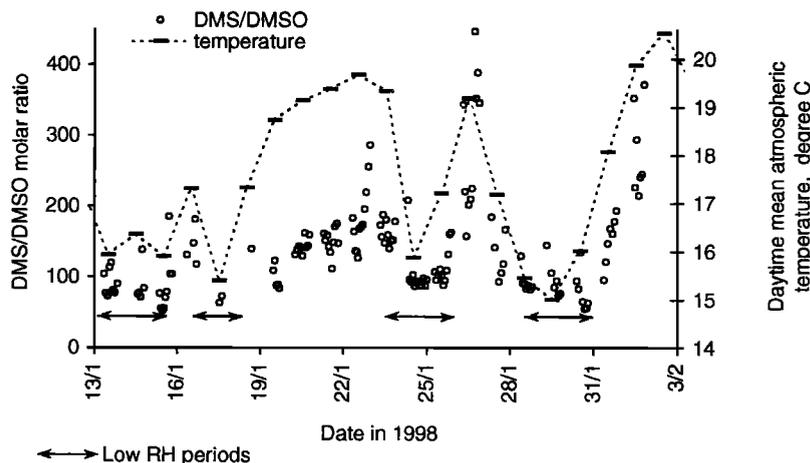
**Figure 1.** Variation of atmospheric DMS and DMSO mixing ratios for the period January 1 to February 2, 1998.

**3.1.1. Temperature variation.** As discussed in the introduction, DMSO is produced by the OH-initiated oxidation of DMS through the addition channel, which is temperature-dependent. Thus DMSO production and especially the DMS/DMSO ratio is also expected to be temperature-dependent. Figure 2 shows the DMS/DMSO variation during the period January 13 to February 2 1998, when quasi-continuous measurements of DMSO were performed. The DMS/DMSO ratio followed the temperature variation quite well. DMS/DMSO ratio ranges from 450 down to 50 for temperature changes from 21°C to 15°C, respectively. On the basis of the temperature dependence of the addition and the abstraction channels proposed by *Hynes et al.* [1986], changes by up to a factor of 1.5 are expected in the branching ratio and thus in the DMS/DMSO ratio (varying from 68-46) for the above temperature range. Although the agreement between the expected and observed DMS/DMSO ratios in the low temperatures is reasonably good, in the higher temperatures the difference is up to factor of 6. Factors other than temperature could account for this difference.

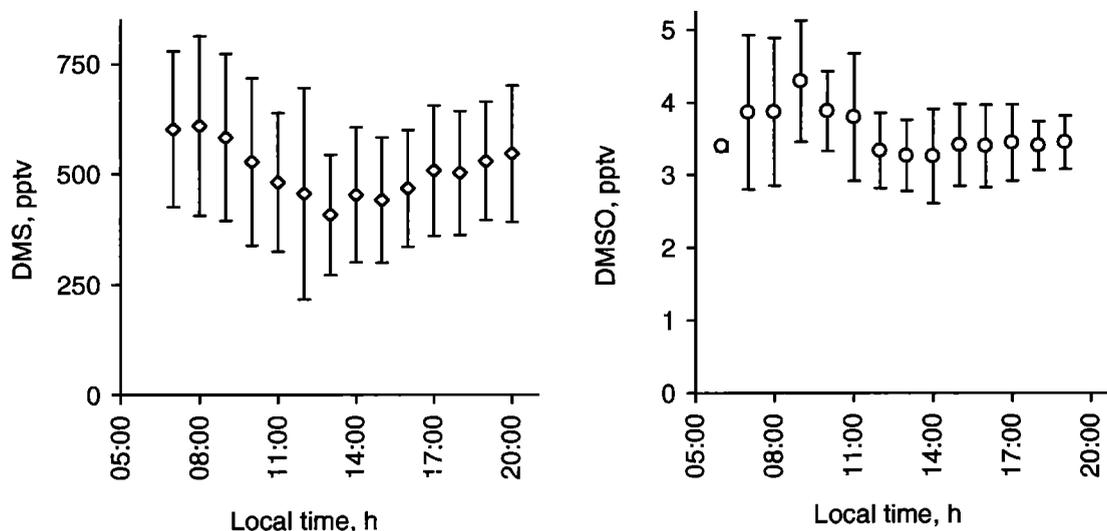
*Berresheim et al.* [1998], during their experiment performed in Antarctica, have reported that most of the time the important changes in the DMSO concentration have been associated with sharp changes in the dew point, indicating transport from the free troposphere (FT). Thus entrainment from the FT, where air temperature is significantly lower than in the marine boundary layer (MBL), could influence the partitioning between the addition and abstraction channels and thus the DMS/DMSO ratio.

*Watts et al.* [1987] reported that DMSO is highly water-soluble. Thus changes in RH are expected to influence the partition of DMSO between the gas and liquid phase, and therefore the DMS/DMSO ratio.

During our experiment the lowest dew point was associated with the lowest relative humidity (RH), air temperature, and south wind sectors, which occurred after the passage of fronts. Similarly, the highest dew point, RH, and air temperature were associated with north wind sectors. This situation could partly explain the large deviations between measured and calculated DMS/DMSO ratios especially during



**Figure 2.** Variation of DMS/DMSO ratio and temperature during the period January 13 to February 2, 1998. The arrows indicate periods of low relative humidity (RH).



**Figure 3.** Diurnal variation of (a) DMS and (b) DMSO mixing ratios calculated from a 6-day period (January 20-25, 1998). Error bars correspond to one standard deviation of the data.

the events associated with air masses coming northern of Amsterdam Island. Since all of the above mentioned parameters (RH, temperature, etc.) were more or less correlated, the relative contribution of each one on the DMS/DMSO ratio could not be evaluated separately.

**3.1.2. Diurnal variation.** Figures 3a and 3b present the mean diurnal variation of DMS and DMSO with their standard deviation obtained during a 6-day period (January 20-25, 1998) characterized by high insolation and stable wind speed and direction. DMS diurnal variation presents a maximum of 610 pptv at 0800 local time (2 hours after the sunrise) and a minimum of 408 pptv at 1300 (Figure 3a). Such variation, in line with the DMS + OH reaction, has been also observed for the remote marine atmosphere [Andreae *et al.*, 1985; Ayers *et al.*, 1995; Sciare *et al.*, submitted manuscript, 2000]. The diurnal pattern of DMSO is quite different from that of DMS (Figure 3b). DMSO is increasing after sunrise to reach its maximum of 4.3 pptv around 0900 (local time), following by a regular decrease to 3.3 pptv at 1300, and finally it remains at these levels until night. The DMSO maximum, which is shifted compared to that of DMS by 1-2 hours, can be explained by the DMS photooxidation. At this time of the day the DMSO lifetime with respect to its reaction with OH varies between 2 and 3 hours. The DMSO decrease in the afternoon can result from both the decrease in DMS levels and the increase in OH concentrations. It is worthwhile noting that DMSO reacts with the OH radicals at least 10 times faster than DMS [Urbanski *et al.*, 1998]. Berresheim *et al.* [1998] claim that due to the low OH radicals (at least a factor of 5 lower than those calculated by the chemistry zero-dimensional (0-D) model described below for Amsterdam Island), downward mixing from the free troposphere was the main mechanism controlling the DMSO variations in Antarctica. Thus the DMSO diurnal variation observed during our experiment is difficult to compare with their results. However, our DMSO diurnal variation is similar to that simulated by Hynes and Wine [1986] and, as will be shown further, can be partly explained by the diurnal variation of DMS.

### 3.2. Seasonal Variation of DMSO

Using the Cofer mist chamber technique, a 25-month record of atmospheric DMSO has been performed at Amsterdam Island to determine its seasonal variation (January-September 1997, January-July 1998, and January-October 1999). Figure 4a presents the daily atmospheric DMSO variation during the whole period. For comparison, daily atmospheric DMS variation is also plotted in the same figure.

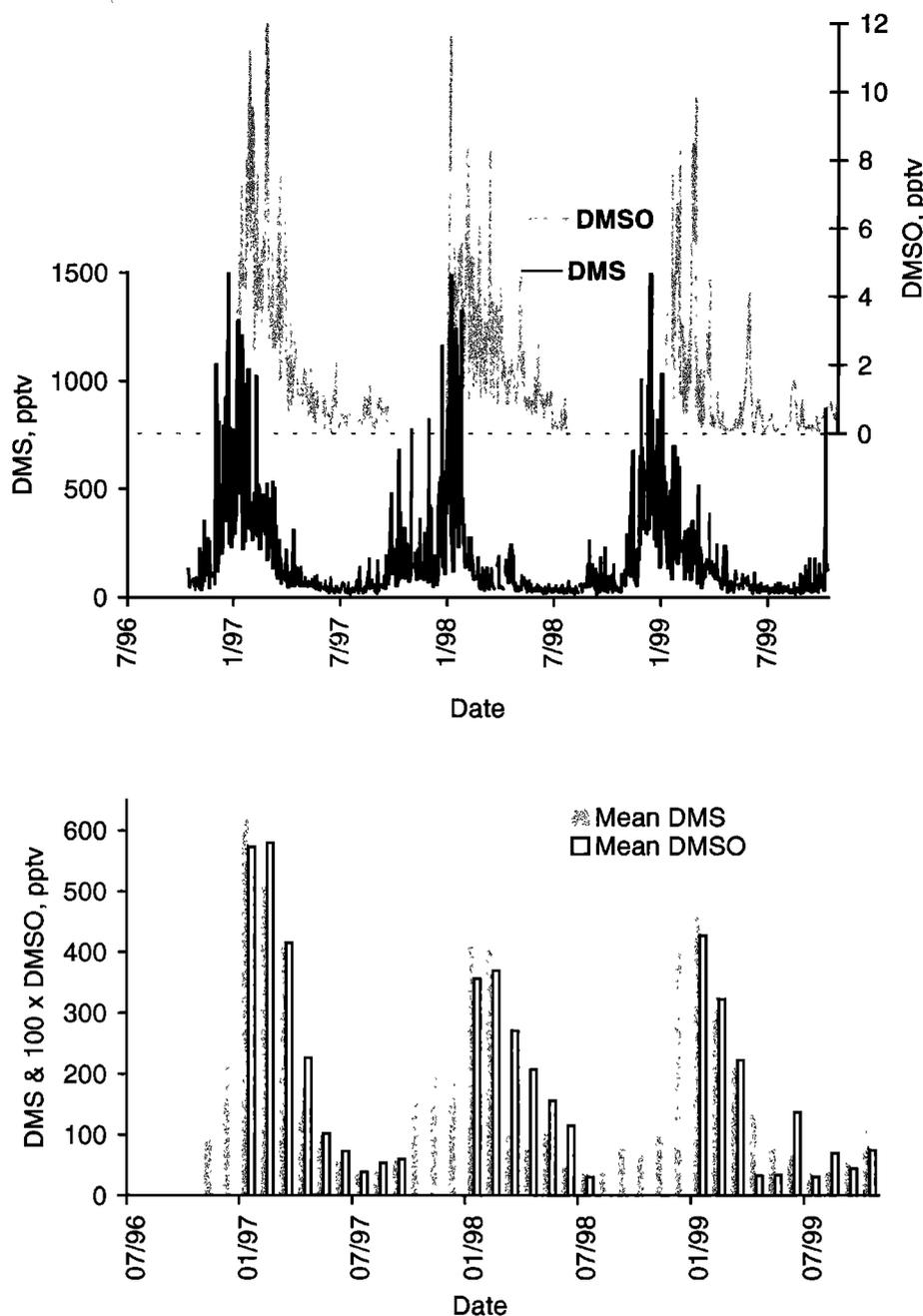
Although very few DMSO values exist during springtime, the DMSO trend is similar to that of DMS, with maxima in Austral summer (January-March: 0.2-14.9 pptv; mean equal to 3.8 pptv) and minima in winter (July-September: 0.1-1.4 pptv; mean equal to 0.5 pptv). At the same time, the corresponding values for DMS were 32-1760 pptv (mean equal to 396 pptv) during summer and 14-177 pptv (mean equal to 44 pptv) during winter. Figure 4b shows monthly mean values for DMS and DMSO for the whole period. Despite the month-to-month variations, DMS and DMSO seasonal trends were comparable with the highest values reported during summer 1997. The amplitude of the seasonal cycle of DMS was found to be around 9, that is, slightly higher than for of DMSO (7.5). Changes in the air temperature could account for the difference in the amplitude of the seasonal cycles of DMS and DMSO.

Figure 5 presents the monthly mean DMS/DMSO ratio during the whole period as well as the expected mean DMS/DMSO ratio calculated using the following equation which considers only reaction with OH radicals:

$$[\text{DMS}] / [\text{DMSO}] = (K_{\text{OH-DMSO}}) / (K_{\text{OH-DMS}} \times \text{br-ratio} \times 0.5) \quad (1)$$

where (1)  $K_{\text{OH-DMSO}}$  is the rate coefficient for the OH+DMSO reaction equal to  $8.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  as proposed by Urbanski *et al.* [1998], (2)  $K_{\text{OH-DMS}}$  is the rate coefficient of the OH+DMS reaction as proposed by Hynes *et al.* [1986], (3) br-ratio is the temperature dependence of branching ratio of the addition and the abstraction channels as proposed by Hynes *et al.* [1986], and (4) a DMSO yield of 0.5 from the addition channel of DMS+OH reaction has been used [Hynes and Wine, 1996].

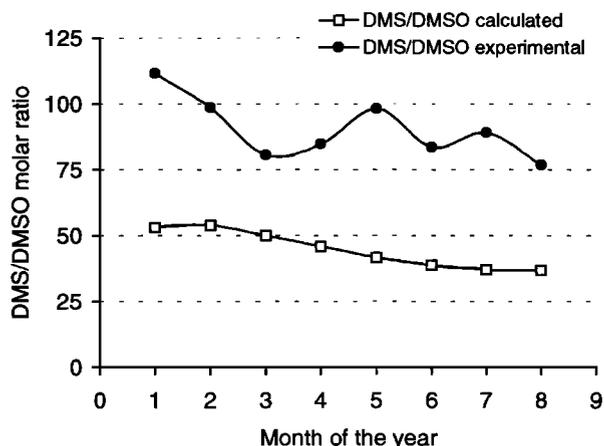
Thus following equation (1) and due to the small amplitude of temperatures at Amsterdam Island over the year (11.3-17.5°C),



**Figure 4.** (a) Daily and (b) monthly mean variation of atmospheric DMSO and DMS mixing ratios during the 25-month record period.

the mean DMS/DMSO ratio is expected to vary from 37 during winter to 54 during summer. Figure 5 shows that the measured monthly mean DMS/DMSO ratios are well above these values, especially during summer when the deviation is more than a factor of 2. Note that on a daily basis during summer the amplitude in the measured DMS/DMSO ratio never exceeded 20%. Thus, if the above kinetic data and especially the DMSO yield from the addition channel are correct, then pathways other than the OH+DMSO reaction have to be involved in the atmospheric DMSO cycle. Since DMSO is water-soluble, it can be removed from the atmosphere through wet deposition. *Sciare et al.* [1998] measured the DMSO concentration in rainwater and found that it follows a seasonal cycle in line with that of the

atmospheric DMS. However, removal of atmospheric DMSO through wet-deposition cannot explain the high DMS/DMSO ratios since the precipitation frequency is not the same during summer and winter. Indeed, during the intensive campaign performed in January 1998 and previously discussed in detail, although three rain events occurred on January 13, 24, and 27, respectively, the DMS/DMSO ratio remained very high. Analysis of the field measurements performed both in the Antarctic and equatorial Pacific boundary layer suggests that 60-80% and 25-33%, respectively, of the DMSO is removed by heterogeneous processes [Urbanski *et al.*, 1998]. An analysis of our data indicates that 38-58% of atmospheric DMSO could be removed by heterogeneous processes at Amsterdam Island.



**Figure 5.** Comparison between the measured and calculated monthly mean DMS/DMSO ratios.

### 3.3. Photochemical Processes Controlling the DMSO Oxidation Scheme: 0-D Chemical Model Simulations

To analyze the factors controlling the diurnal variation of DMSO as depicted in Figure 3b and to improve our understanding of the photochemical processes controlling DMS and DMSO oxidation, a chemical box model has been used. The commercially available software FACSIMILE [Curtis and Sweetenham, 1988], which uses automatic time step selection and error control, was used to solve the differential equations with a high accuracy as required for chemistry studies. The chemistry model is a condensed chemical mechanism, which, in addition to the background  $O_3/NO_x/OH/CO$  and  $CH_4$  chemistry, also takes into account the oxidation chemistry of  $C_1$ - $C_5$  nonmethane hydrocarbons (NMHC) including isoprene and sulfur compounds. The chemical scheme is presented in detail by Sciare *et al.* [2000].

**3.3.1. Input parameters.** For this study, the model has been initialized by monthly mean observed  $O_3$  mixing ratios of 13.3 ppbv [Gros *et al.*, 1998] and NMHC values measured in January by Touaty *et al.* [1996]. A marine boundary layer height of 1150 m has been used following observations by radiosoundings on the island. For the simulations, atmospheric pressure has been kept constant at 1020.9 hPa, whereas temperature, relative humidity, and carbon monoxide mixing ratios vary hourly over the simulated period of 6 days (January 20-25). Hourly varying photolysis rates calculated off-line by a radiation model [Brühl and Crutzen, 1988] are used for this study.

A range of DMS fluxes of 16-18  $\mu\text{mol m}^{-2} \text{d}^{-1}$  has been adopted to drive DMS diurnal variations. However, to eliminate any possible discrepancy due to uncertainties in the DMS simulated levels, the observed hourly varying DMS mixing ratios were adopted in the version of the model used for the study of DMSO chemistry. Entrainment of  $O_3$  from the free troposphere (FT) has been parameterized using an entrainment velocity of 0.6 cm/s and assuming a mean  $O_3$  FT mixing ratio of 23.8 ppbv [Gros *et al.*, 1998]. For DMS a loss rate of  $1.5 \times 10^{-6} \text{ s}^{-1}$  from the boundary layer to the FT has been assumed [Ayers *et al.*, 1995].

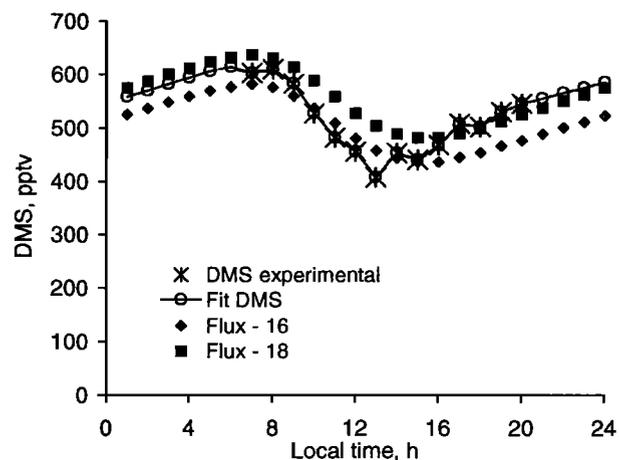
Deposition velocities of 0.87 cm/s, 0.1 cm/s, 1 cm/s, 0.1 cm/s, and 1 cm/s have been adopted for  $SO_2$ ,  $SO_4^-$  small particles,  $SO_4^-$  large particles, MSA, and DMSO, respectively

[Sciare *et al.*, 2000]. A spin-up time of 2 days has been used to equilibrate the model.

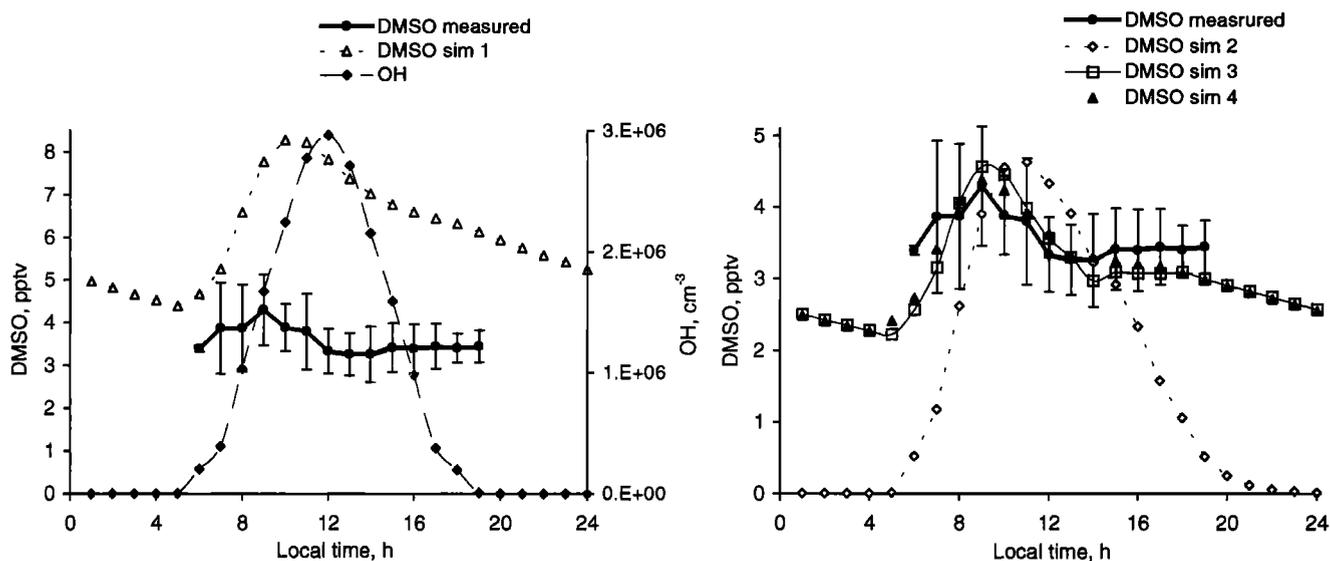
**3.3.2. Chemical model results and discussion.** The simulated mean diurnal variation of DMS is shown in Figure 6 and compared with observations. The "best fit" has been obtained by using DMS fluxes of 16-18  $\mu\text{mol m}^{-2} \text{d}^{-1}$ . This range of fluxes is slightly higher than the range of 7-14 proposed by Sciare *et al.* [1999] for Amsterdam Island and for the month of December. However, if we consider that the mean atmospheric DMS during January 1998 is about 50% higher compared to December 1997, it is reasonable to assume higher DMS fluxes in January than in December. As shown in Figure 6, the chemical model is able to simulate relatively well the general diurnal trend of DMS with a maximum in the morning hours and a minimum in the afternoon.

To eliminate any discrepancy resulting from the small deviations of DMS calculated values from the observations, the hourly mean DMS observations are used to force the model for the study of DMSO. In Figure 7a the measured DMSO concentrations are compared with the model results (DMSO simulation (sim) 1). Although the model is able to reproduce relatively well the DMSO diurnal variation, in absolute values there is a difference of up to a factor of 2 between observations and simulations. Since DMS is fitted to observations, this difference implies a smaller production rate or a higher loss rate of DMSO than used in the model. To investigate this, three additional simulations have been performed and reported in Figure 7b with the measured DMSO:

1. A heterogeneous loss of DMSO has been taken into account day and night with a rate of  $2 \times 10^{-4} \text{ s}^{-1}$  (DMSO sim 2, Figure 7b). This is between the rate of  $2.6 \times 10^{-4} \text{ s}^{-1}$  suggested by Davis *et al.* [1999] for the equatorial region and the  $1.4 \times 10^{-4} \text{ s}^{-1}$  given by the same group for Antarctica [Davis *et al.*, 1998].
2. A heterogeneous loss of DMSO has been introduced proportional to the OH concentration with a pseudo first-order rate taken equal to  $2.4 \times 10^{-10} [\text{OH}] \text{ s}^{-1}$ , [OH] being the concentration of OH radical (DMSO sim 3, Figure 7b).
3. The DMSO yield of the reaction of DMS with OH (addition channel) has been reduced to 25% (crosses) instead of 50% in the "basic" simulation (DMSO sim 4, Figure 7b).



**Figure 6.** Comparison between the simulated and observed diurnal variations of DMS.



**Figure 7.** Comparison between the simulated and observed diurnal variations of DMSO. Refer to the text for conditions encountered in simulations (sim) 1, 2, 3, and 4. Error bars correspond to one standard deviation.

As it can be seen in Figure 7b, when heterogeneous loss is taken into account to occur day and night (DMSO sim 2), that is, being nonphotochemically regulated, the model calculates daytime DMSO concentrations of very close to those observed. However, contrary to observations, a very strong depletion of DMSO is computed late afternoon and during night, when DMSO photochemical production stops, whereas its heterogeneous loss remains active. The OH concentrations plotted in Figure 7a indicate the photochemical activity period. Therefore the DMSO observations indicate the absence of a significant nighttime heterogeneous loss of DMSO.

Focusing on the results of the third simulation (DMSO sim 3), considering a heterogeneous loss linked to the photochemical activity in the atmosphere, that is, mainly during daytime, it can be seen that a relatively good agreement can be achieved between calculations and observations of DMSO during both day and night. For this simulation the pseudo first-order rate of this reaction assumed to be regulated by photochemistry maximizes around noon ( $7 \times 10^{-4} \text{ s}^{-1}$ ) and minimizes ( $1.5 \times 10^{-7} \text{ s}^{-1}$ ) during night. As expected, similar results can be obtained when reducing the DMSO yield of the reaction of DMS with OH to half the initially adopted value, that is, assume that only 25% of this reaction is producing DMSO (DMSO sim 4). However, there is some evidence [Arsene *et al.*, 1999] that DMSO yield from DMS reaction with OH might be even higher than the 50% adopted in this study. Therefore a heterogeneous loss of DMSO controlled by photochemistry (DMSO sim. 3) appears as the most probable explanation of the observed DMSO levels.

Indeed, little is known about the fate of DMSO in the heterogeneous phase. On the basis of the sticking coefficients reported by De Bruyn *et al.* [1994], Berresheim *et al.* [1998] has calculated DMSO uptake rates at 275 K of the order of  $6.5 \times 10^{-5} \text{ s}^{-1}$  which corresponds to gas phase DMSO lifetime of the order of 4.3 hours. This lifetime is smaller than the 9.3 hours reported for Antarctica by these authors for the gas phase reaction of DMSO with OH radicals. Bardouki *et al.*

[1999] have shown that although DMSO is quite stable in the liquid phase versus pH, temperature, and reactions with  $\text{H}_2\text{O}_2$ , it reacts very fast with OH radicals producing methanesulfinic acid (MSIA), which reacts further to give methanesulfonic acid (MSA). These authors have also calculated that the reaction of DMSO with respect to OH radicals in the liquid phase could be comparable or even faster than the gas phase reaction of DMSO with OH radicals. This reaction driven by photochemistry can also take place on aerosol particles, although their water content is lower than that of the cloud droplets. The above mechanisms comprise significant heterogeneous loss of atmospheric DMSO and could thus explain the important difference between the observed and the simulated DMSO levels based on gas phase chemistry.

#### 4. Conclusions

Atmospheric DMSO concentrations have been measured during a 25-month period at Amsterdam Island in the southern Indian Ocean. To our knowledge, this is the first study of the seasonal variation of this important DMS oxidation intermediate in the marine atmosphere. DMSO was found to follow a well-established seasonal pattern in line with that of DMS, its precursor. However, the DMS/DMSO ratio was also changing seasonally with values higher during the summer and lower during the winter. An analysis of our data indicates that temperature and heterogeneous processes could account for about 50% of this pattern each. The diurnal variation of DMSO has been studied during an intensive experiment performed in January 1998. DMSO presents a diurnal variation for which the trend can be simulated on the basis of actual knowledge on DMSO production through the addition channel of the OH-initiated reaction of DMS. However, in absolute terms there is a difference of more than a factor of 2 between the simulated and the measured DMSO values. Photochemically driven heterogeneous losses of DMSO on aerosol and/or clouds could account for this difference. Alternatively, the DMSO yield from the addition

channel could be a factor of 2 less than that proposed by Hynes and Wine [1996].

**Acknowledgments.** This work has been supported by the Institut Français pour la Recherche et la Technologie Polaire (IFRTP), the Centre National de la Recherche Scientifique (CNRS), the Commissariat à l'Énergie Atomique (CEA), and the European Union (ENV4-CT97-0410 and MSA3-CT97-5044).

## References

- Andreae, M.O., Determination of trace quantities of dimethylsulfoxide in aqueous solutions, *Anal. Chem.*, **52**, 150-153, 1980a.
- Andreae, M.O., Dimethylsulfoxide in marine and freshwater, *Limnol. Oceanogr.*, **25**, 1054-1063, 1980b.
- Andreae, M.O., R.J. Ferek, F. Bermond, K.P. Byrd, R.T. Engstrom, S. Hardin, D. Houmère, F. LeMarrec, H. Raemdonck, and R.B. Chatfield, Dimethylsulfoxide in the marine atmosphere, *J. Geophys. Res.*, **90**, 891-900, 1985.
- Andreae, M.O., W. Elbert, and S.J. de Mora, Biogenic sulfur emissions and aerosols over the tropical South Atlantic, 3, Atmospheric dimethylsulfoxide, aerosols, and cloud condensation nuclei, *J. Geophys. Res.*, **100**, 11,335-11,356, 1995.
- Arsene, C., I. Barnes, and K.H. Becker, FT-IR product study of the photooxidation of dimethyl sulphide: Temperature and O<sub>2</sub> partial pressure dependence, *Phys. Chem.*, **1**, 5463-5470, 1999.
- Ayers, G.P., J.P. Ivey, and R.W. Gillett, Coherence between seasonal cycles of dimethyl sulphide, methanesulphonate and sulphate in marine air, *Nature*, **349**, 404-406, 1991.
- Ayers, G.P., S.T. Bentley, J.P. Ivey, and B.W. Forgan, Dimethylsulfoxide in marine air at Cape Grim, 41°S, *J. Geophys. Res.*, **100**, 21,013-21,021, 1995.
- Bandy, A., et al., Chemistry of dimethyl sulfide in the equatorial Pacific atmosphere, *Geophys. Res. Lett.*, **23**, 741-744, 1996.
- Bardouki, H., N. Mihalopoulos, and C. Zetzsch, Kinetics and mechanism of the oxidation of dimethylsulfoxide (DMSO) by OH radicals in aqueous medium, paper presented at Sixth Scientific Conference of the International Global Atmospheric Chemistry Project, Bologna, Italy, Sept. 13-17, 1999.
- Barnes, I., V. Bastian, K.H. Becker and R. Overath, Kinetic study of the reactions of IO, BrO, ClO with dimethylsulfoxide, *Int. J. Chem. Kinet.*, **23**, 579-591, 1991.
- Barnes, I., K.H. Becker and I. Patroescu, The tropospheric oxidation of dimethyl sulfide: A new source of carbonyl sulfide, *Geophys. Res. Lett.*, **21**, 2389-2392, 1994.
- Barnes, I., K.H. Becker, and I. Patroescu, FTIR products study of the OH initiated oxidation of dimethyl sulphide: Observation of carbonyl sulphide and dimethyl sulphoxide, *Atmos. Environ.*, **30**, 1805-1814, 1996.
- Berresheim, H., D.J. Tanner, and F.L. Eisele, Real-time measurement of dimethyl sulfoxide in ambient air, *Anal. Chem.*, **65**, 84-86, 1993.
- Berresheim, H., F.L. Eisele, D.J. Tanner, D.S. Covert, L. McInnes, and D.C. Ramsey-Bell, Measurements of dimethyl sulfide, dimethyl sulfoxide, dimethyl sulfone, and aerosol ions at Palmer Station, Antarctica, *J. Geophys. Res.*, **103**, 1629-1637, 1998.
- Brühl, C., and P.J. Crutzen, Scenarios of possible change in atmospheric temperatures and ozone concentrations due to man's activities, estimated with a one-dimensional coupled photochemical climate model, *Clim. Dyn.*, **2**, 173-203, 1988.
- Charlson, R.J., J.E. Lovelock, M.O. Andreae, and S.G. Warren, Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, *Nature*, **326**, 655-661, 1987.
- Cofer, W.R., V.G. Collins, and R. Talbot, Improved aqueous scrubber for collection of soluble atmospheric trace gases, *Environ. Sci. Technol.*, **19**, 557-560, 1985.
- Curtis, A., and W. Sweetenham, FACSIMILE/CHEKMAT users manual, *AERE-R12805*, Harwell Lab., Oxfordshire, England, United Kingdom, 1988.
- Davis, D., G. Chen, P. Kasibhatla, A. Jefferson, D. Tanner, F. Eisele, D. Lenschow, W. Neff, and H. Berresheim, DMS oxidation in the Antarctic marine boundary layer: Comparison of model simulations and field observations of DMS, DMSO, DMSO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>(g), MSA(g), and MSA(p), *J. Geophys. Res.*, **103**, 1657-1678, 1998.
- Davis, D., et al., Dimethyl sulfide oxidation in the equatorial Pacific: Comparison of model simulations with field observations for DMS, SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>(g), MSA (g), MS, and NSS, *J. Geophys. Res.*, **104**, 5765-5784, 1999.
- De Bruyn, W.J., J.A. Shorter, P. Davidovits, D.R. Wornop, M.S. Zahnister, and C.E. Kolb, Uptake of gas phase sulfur species methanesulfonic acid, dimethylsulfoxide, and dimethyl sulfone by aqueous surfaces, *J. Geophys. Res.*, **99**, 16,923-16,927, 1994.
- Gros, V., Etude des variabilités de l'ozone et du monoxyde de carbone dans la couche limite atmosphérique marine de l'hémisphère sud. Ph.D thesis, 183 pp., Univ. of Paris VII, Paris, 1998.
- Gros, V., N. Poisson, D. Martin, M. Kanakidou, and B. Bonsang, Observation and modeling of the seasonal variation of surface ozone at Amsterdam Island: 1994-1996: The role of continental sources of O<sub>3</sub> precursors, *J. Geophys. Res.*, **103**, 28,103-28,109, 1998.
- Gros, V., B. Bonsang, D. Martin, P.C. Novelli and V. Kazan, Short term carbon monoxide measurements at Amsterdam Island: Estimations of biomass burning emission rates, *Chemosphere Global Change Sci.*, **1**, 163-172, 1999.
- Hatton, A.D., G. Malin, S.M. Turner, and P.S. Liss, DMSO: A significant compound in the biogeochemical cycle of DMS, in *Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds*, edited by R.P. Kiene et al., pp. 405-412, Plenum, New York, 1996.
- Hynes, A.J., and P.H. Wine, The atmospheric chemistry of dimethylsulfoxide (DMSO): Kinetics and mechanism of the OH + DMSO reaction, *J. Atmos. Chem.*, **24**, 23-37, 1996.
- Hynes, A.J., P.H. Wine, and D.H. Semmes, Kinetics and mechanisms of OH reactions with organic sulfides, *J. Phys. Chem.*, **90**, 4148-4156, 1986.
- Kieber, D.J., J. Jiao, R.P. Kiene, and T.S. Bates, Impact of dimethylsulfoxide photochemistry on methyl sulfur cycling in the equatorial Pacific Ocean, *J. Geophys. Res.*, **101**, 3715-3722, 1996.
- Kreidenweiss, S.M., and J.H. Seinfeld, Nucleation of sulfuric-acid water and methanesulfonic acid water particles: Implications for the atmospheric chemistry of organic species, *Atmos. Environ.*, **22**, 283-296, 1988.
- Nguyen, B.C., N. Mihalopoulos, and S. Belviso, Seasonal variation of atmospheric dimethylsulfoxide at Amsterdam Island in the southern Indian Ocean, *J. Atmos. Chem.*, **11**, 123-143, 1990.
- Polian, G., G. Lambert, B. Ardouin, and A. Jégou, Long range transport of continental radon in subantarctic areas, *Tellus, Ser. B*, **178**-189, 1986.
- Sciare, J., and N. Mihalopoulos, A new technique for sampling and analysis of atmospheric dimethylsulfoxide (DMSO), *Atmos. Environ.*, **34**, 151-156, 2000.
- Sciare, J., E. Baboukas, R. Hancy, N. Mihalopoulos, and B.C. Nguyen, Seasonal variation of dimethylsulfoxide (DMSO) in rainwater at Amsterdam Island in the southern Indian Ocean: Implications on the biogenic sulfur cycle, *J. Atmos. Chem.*, **30**, 229-240, 1998.
- Sciare, J., N. Mihalopoulos, and B.C. Nguyen, Summertime seawater concentrations of dimethylsulfoxide in the western Indian Ocean: Reconciliation of fluxes and spatial variability with long-term atmospheric observations, *J. Atmos. Chem.*, **32**, 357-373, 1999.
- Sciare, J., E. Baboukas, M. Kanakidou, U. Krischke, S. Belviso, H. Bardouki and N. Mihalopoulos, Spatial and temporal variability of atmospheric sulfur-containing gases and particles during the ALBATROSS campaign, *J. Geophys. Res.*, in press, 2000.
- Simo, R., Trace chromatographic analysis of dimethyl sulfoxide and related methylated sulfur compounds in natural waters, *J. Chromatogr.*, **807**, 151-164, 1998.
- Simo, R., A.D. Hatton, G. Malin, and P.S. Liss., Particulate dimethylsulfoxide in seawater: Production by microplankton, *Mar. Ecol. Prog. Ser.*, **167**, 291-296, 1998.
- Touaty, M., B. Bonsang, M. Kanakidou, and N. Poisson, Monitoring and model comparison of the seasonal variation of tropospheric light hydrocarbons at Amsterdam Island, in *Proceedings of EUROTRAC Symposium*, pp. 613-619, Eur. Exp. On Transp. And Transformation of Environ. Relevant Trace Constituents in the Troposphere Over Eur., Southampton, England, 1996.
- Toumi, R., BrO as a sink for dimethylsulphide in the marine atmosphere, *Geophys. Res. Lett.*, **21**, 117-120, 1994.

- Urbanski, S.P., R.E. Stickel, and P.H. Wine, Mechanistic and kinetic study of the gas-phase reaction of hydroxyl radical with dimethyl sulfoxide, *J. Phys. Chem.*, *102*, 10,522-10,529, 1998.
- Watts, S.F., and P. Brimblecombe, The Henry's law constant of dimethyl sulphoxide, *Environ. Technol. Lett.*, *8*, 483-486, 1987.
- Watts, S.F., A. Watson, and P. Brimblecombe, Measurements of the aerosol concentrations of methanesulfonic acid, dimethylsulphoxide, and dimethylsulphone in the marine atmosphere of the British Isles, *Atmos. Environ.*, *21*, 2667-2672, 1987.
- Watts, S.F., P. Brimblecombe, and A. Watson, Methanesulphonic acid, dimethylsulfoxide and dimethyl sulphone in aerosols, *Atmos. Environ.*, *24*, 353-359, 1990.

---

M. Kanakidou and N. Mihalopoulos (corresponding author), Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, P.O. Box 1470, 71409 Heraklion, Greece (mihalo@chemistry.uoh.gr)

J. Sciare, Laboratoire des Sciences du Climat et de l'Environnement, CEA Orme des Merisiers, 91191 Gif-sur-Yvette Cedex, France (sciare@lsce saclay cea.fr)

(Received August 19, 1999; revised November 22, 1999; accepted December 10, 1999.)