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Subdaily variations of atmospheric dimethylsulfide, dimethylsulfoxide, methanesulfonate, and non-sea-salt sulfate aerosols in the atmospheric boundary layer at Dumont d'Urville (coastal Antarctica) during summer

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Abstract. A study of atmospheric dimethylsulfide (DMS) and dimethylsulfoxide (DMSO) was conducted on a subdaily basis during austral summer months (450 samples from mid-December 1998 to late-February 1999) at Dumont d'Urville, a coastal Antarctic site (66° 40'S, 140° 01'E). In addition, subdaily aerosol samplings were analyzed for particulate methanesulfonate (MSA) and non-sea-salt sulfate (nssSO₄²⁻). During these summer months, DMS and DMSO levels fluctuated from 34 to 2923 pptv (mean of 290 ± 305 pptv) and from 0.4 to 57 pptv (mean of 3.4 ± 4.4 pptv), respectively. Mean MSA and non-sea-salt sulfate (nssSO₄²⁻) mixing ratios were close to 12.5 ± 8.2 pptv and 68.1 ± 35.0 pptv, respectively. In two occasions characterized by stable wind conditions and intense insolation, it was possible to examine the local photochemistry of DMS. During these events, DMSO levels tracked quite closely the solar flux and particulate MSA levels were enhanced during the afternoons. Photochemical calculations reproduce quite well observed diurnal variations of DMSO when we assume an 0.8 yield of DMSO from the DMS/OH addition channel and an heterogeneous loss rate of DMSO proportional to the OH radical concentration: $0.5 \times 10^{-10} [\text{OH}] + 5.5 \times 10^{-5}$ (in s⁻¹). If correct, on a 24 hour average the heterogeneous loss of DMSO is estimated to be 2 times faster than the DMSO/OH gas phase oxidation in these regions. Very low levels of DMSO were found in the aerosol phase (less than 0.01 pptv), suggesting that an efficient oxidation of DMSO subsequently takes place onto the aerosol surface. The observed increase of MSA levels which takes place quasi-immediately after the noon DMSO maximum suggests that an heterogeneous oxidation of DMSO onto aerosols represents a more efficient pathway producing MSA compared to the gas phase DMSO/OH pathway. Since only a third of the total amount of DMSO lost can be explained by the observed enhancement of MSA levels, further studies investigating other species including methanesulfinic acid and dimethylsulfone (DMSO₂) formed during the oxidation of DMS are here needed. When katabatic winds took place, bringing continental Antarctic air at the site, enrichments of DMSO relative to DMS and MSA relative to non-sea-salt sulfate levels were observed. That is in agreement with the hypothesis of an accumulation of DMSO and probably of gaseous MSA in the free Antarctic troposphere in relation to a less efficient heterogeneous loss rate of DMSO.

1. Introduction

The sulfur cycle still represents one of the major unknown atmospheric contributor forcing the climate system. In

particular, the effect of climate changes on dimethylsulfide (DMS) emissions from the marine biota as well as the atmospheric pathways by which cloud condensation nuclei are produced from the gaseous sulfur precursors are not enough understood. Atmospheric studies of sulfur species at high southern latitudes can here help since these oceanic regions are not yet disturbed by anthropogenic SO₂ emissions and remain dominated by natural DMS emissions from the marine biota. Previous works dedicated to the sulfur cycle study in

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Antarctic regions were mainly carried out by investigating aerosol end-products of the atmospheric DMS oxidation, namely methanesulfonate (MSA) and non-sea-salt sulfate (nssSO_4^{2-}). Multiple year-round studies of these sulfur aerosols have been initiated at Mawson [Savoie *et al.*, 1993] since 1987, Neumayer [Wagenbach, 1996] since 1983, and Dumont d'Urville [Minikin *et al.*, 1998; Legrand and Wagenbach, 1999] since 1991.

Recently, a more comprehensive approach dedicated to the study of the atmospheric fate of DMS at high southern latitudes was conducted in summer 1994 at Palmer (Antarctic Peninsula) [Berresheim and Eisele, 1998] in the framework of the Sulfur Chemistry in the Antarctic Troposphere Experiment (SCATE) project. For the first time in Antarctica, the SCATE project investigated gas phase DMS, dimethylsulfoxide (DMSO), dimethylsulfone (DMSO_2), sulfuric and methanesulfonic acids. A major result of this campaign was that due to a large enough lifetime of DMS at these latitudes and the occurrence of strong vertical pumping induced by low-pressure storm systems, a large amount of DMS can be upward transported in the free troposphere. Conversely, the distribution of DMS oxidation products in the atmospheric boundary layer at the Palmer station vicinity is frequently influenced by downward mixing from the free troposphere.

The DMS/OH addition pathway is critically temperature dependent. It is faster at low temperatures and may represent as high as two thirds of the total oxidation of DMS at 273 K [Arsene *et al.*, 1999]. The fate of DMSO, a major oxidation product of the addition pathway, is thus of great concern at the high latitudes of Antarctica. In the frame of the SCATE project, it was shown that DMSO has a lifetime of a few hours, suggesting the existence of an heterogeneous uptake of this gas onto aerosols which dominates the gas phase DMSO/OH oxidation process [Davis *et al.*, 1998]. The possibility that this heterogeneous process contributes to the observed levels of particulate MSA was proposed [Jefferson *et al.*, 1998]. Such an assumption was confirmed by very recent kinetic studies which reported a MSA production from the DMSO/OH oxidation in liquid phase [Bardouki *et al.*, 1999].

Since mid-December 1998, in addition to the investigation of sulfur (MSA and sulfate) aerosols, a study of DMS and DMSO levels was conducted at Dumont d'Urville, a coastal Antarctic site. The seasonal variations of DMS, DMSO, SO_2 , and MSA and sulfate aerosol species at this site are discussed in a companion paper [Jourdain and Legrand, this issue]. It

is shown that, except when a katabatic situation took place bringing inland Antarctic air masses to the site, the atmospheric boundary layer at DDU is less influenced by downward transport with respect to the situation at Palmer. That renders easier the study of the atmospheric fate of DMS within the marine boundary layer at DDU. In this paper, based on subdaily samplings of DMS, DMSO, and sulfur aerosols, we examine in detail some events driven by the local photochemical conditions. In particular, we test the assumption of an heterogeneous loss of DMSO onto aerosols. We also discuss the origin of particulate MSA rapidly produced during these photochemical events.

2. Sampling and Methods

2.1. DMS and DMSO Gas Phase Measurements

Four hundred and fifty subdaily DMS and DMSO samplings were achieved from mid-December 1998 to end of February 1999 at Dumont d'Urville (DDU). As a mean, the frequency of DMS and DMSO samplings ranged from 5 to 12 samples per day as detailed in Table 1. DMS samplings were performed by filling 6 L electropolished stainless steel canisters by compressing air at 5 bars within several minutes. The sampling of DMSO was achieved by using a mist chamber in which air was flowed at a rate of $0.6 \text{ m}^3 \text{ h}^{-1}$ during 1 hour through an inlet Teflon filter (Gelman 47 mm). Following Sciare and Mihalopoulos [2000], mist chambers were filled with 20 mL of acidified water. Using two mist chambers placed in series, Sciare and Mihalopoulos [2000] concluded that the efficiency of the sampling device is almost quantitative and that no correction of raw data is needed. DMSO analysis was performed by reduction of DMSO to DMS using sodium borohydride as described by Andreae [1980].

DMS and DMSO analyses were achieved in the field by using a gas chromatograph (GC) equipped with a flame photometric detector (HP 6890, 393 nm). DMS was cryogenically trapped at -60°C on a tenax GC 80 loaded tube maintained in a bath of ethanol cooled by a Cryocool CC100 device. DMS was subsequently transferred to the GC by thermal desorption of the tenax trap (boiling water) as detailed by Nguyen *et al.* [1990]. Working chromatographic conditions here applied were an oven temperature of 95°C , a detector temperature of 200°C , and a gas flow rate at the flame of 30 mL min^{-1} of helium (carrier gas), 80 mL min^{-1} of air, and 55 mL min^{-1} of hydrogen. Calibrations were achieved on a daily

Table 1. Frequency of Aerosol, DMS, and DMSO Samplings Carried Out from Mid-December 1998 to March 1999 at Dumont d'Urville

Time Periods	Number of DMS Samples per Day	Number of DMSO Samples per Day	Aerosol Samples (Number per Days)
Dec. 17 - 25, 1998	1 to 3	0	2-3
Dec. 26, 1998, to Jan. 20, 1999	5 (from 3 to 8)	5 (from 3 to 8)	2-3
Jan. 21 to Feb. 5, 1999	12 (every 2 hours)	12 (every 2 hours)	4
Feb. 6 - 25, 1999	5 (from 4 to 6)	5 (from 4 to 6)	2

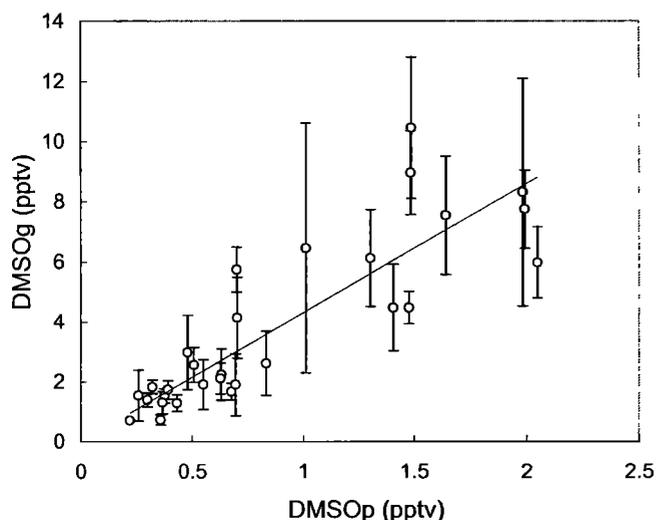


Figure 1. Comparison of mean DMSO mixing ratios observed between December 26, 1998, and January 9, 1999, using mist chamber samplings (DMSOg) with mixing ratios obtained at the same time on Whatman paper filters (DMSOp). Vertical bars refer to the variability of the multiple mist chamber sampling covering the time interval of the Whatman filter runs.

basis by the mean of a permeation tube (VICI Metronics, Santa Clara, California). This tube was calibrated against other permeation tubes used as references for the monitoring of atmospheric DMS at Amsterdam Island [Sciare *et al.*, 2000b]. This tube was checked again 1 year after (January 2000) with no detectable drift (less than 5%). Calibration range was typically from 1.18 to 3.54 ng of DMS. The detection limit was found to be close to 0.2 ng of DMS. Under these working conditions, the atmospheric DMS detection limit is close to 13 pptv when 6 L of air are sampled, as applied until the end of July. Analysis of DMS was systematically duplicated with a mean error below 5%. Note that, if necessary, the total air volume of stainless steel canisters (24 L) can be used leading to a detection limit close to 3 pptv.

For DMSO, blanks were run with a thorough washing of all glassware with Hartz mineral water commercialized in Australia. We found 0.065 ± 0.023 ng of DMSO per milliliters in this blank water. This blank value was subtracted to the DMSO content of mist chamber extracts. The DMSO detection limit (taken as twice the blank variability) is close to 0.48 pptv. Tests were performed in the field by analyzing DMSO from two mist chambers set in parallel which showed a mean error of less than 5% for 600 L of sampled air in mist chambers.

From December 20 to December 25, DMS samplings have been initiated, whereas DMSO samplings using mist chambers were not yet carried out. However, with the initial aim to investigate the DMSO level present in the aerosol phase, Whatman paper filter samples collected from mid-December to January 10 dedicated to investigation of subdaily MSA and sulfate levels (see section 2.2) were also analyzed for DMSO. As discussed in section 2.3, these paper filters collect in fact DMSO present in the aerosol phase as well as a significant fraction present in the gas phase. Since these 31 paper filter samplings were carried out from December 26 to January 9, a period over which 90 gas phase DMSO samplings were also achieved by using the mist chamber device, it is possible to estimate gas phase DMSO levels from the amount of DMSO present on the paper filters. Indeed, as depicted in Figure 1, amounts of DMSO trapped on paper filters (detection limit of 0.03 pptv) are well linearly correlated to levels of DMSO present in the gas phase ($[DMSOp] = 4.3 [DMSOg]$, with a correlation coefficient of 0.85). This relationship was therefore used to estimate gas phase levels of DMSO present at DDU from December 20 to December 25.

2.2. MSA and Non-Sea-Salt Sulfate Aerosols

In addition to daily aerosol samplings routinely carried out at the site since 1991 [Jourdain and Legrand, this issue], aerosols were also sampled with a higher frequency (2 to 4 times per day) from mid-December 1998 to February 25, 1999 (Table 1). Subdaily aerosol samplings were made on Whatman 41 filters with a flow rate of 23 L min^{-1} from mid-December to January 10 and on Teflon filters at a flow rate of 17 L min^{-1} from January 11 to the end of February. An excellent agreement is observed between subdaily samplings

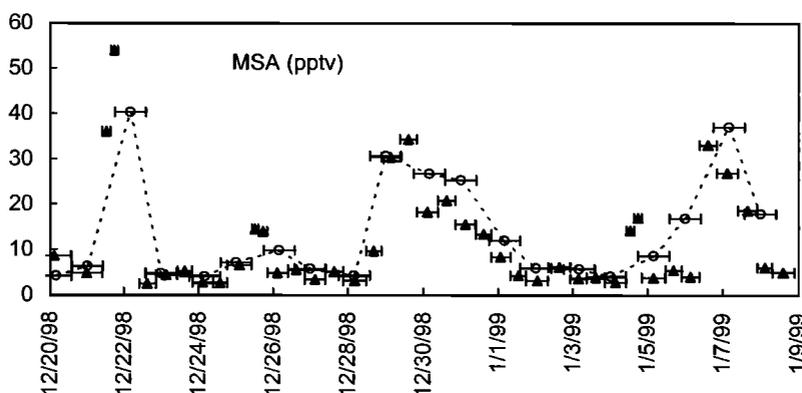


Figure 2. Comparison of MSA mixing ratios obtained using subdaily (black triangles) and daily (open circles and dashed line) aerosol samplings from December 19, 1998, to January 10, 1999, at Dumont d'Urville. Horizontal bars denote the time interval of samplings.

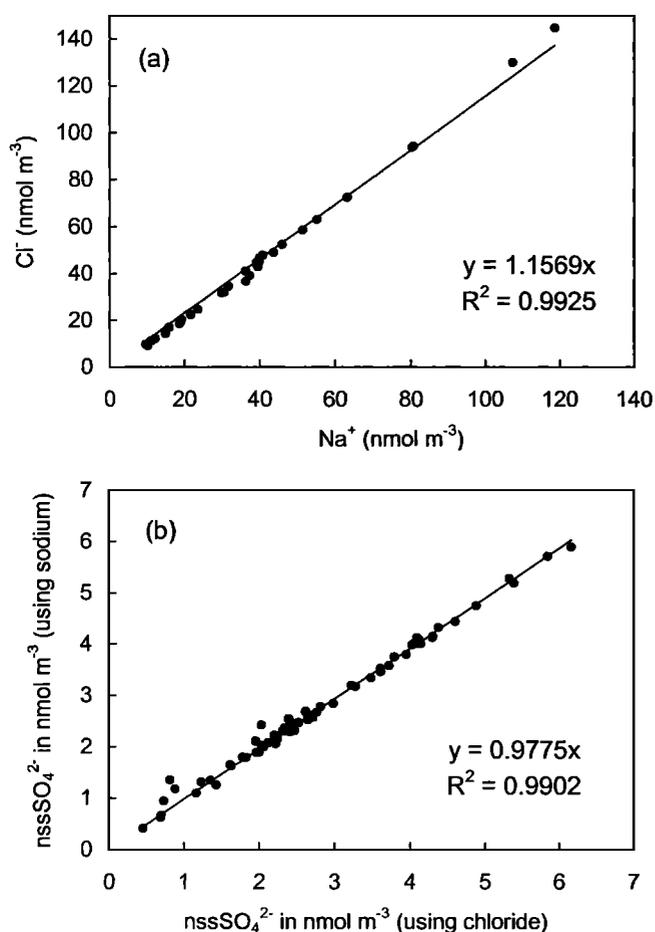


Figure 3. (a) Molar concentrations of chloride versus sodium in daily aerosols collected at DDU from December 16, 1998, to February 24, 1999. (b) Plot of nssSO_4^{2-} molar concentrations calculated using sodium and chloride as a reference for sea-salt aerosols (see section 2.2).

made on Whatman filters and corresponding daily samplings made on Teflon filters for MSA levels (Figure 2). In contrast, in a few occasions, the sulfate level measured on subdaily Whatman filters exceeded the one measured on the corresponding daily Teflon filter by more than 25 pptv. That occurred January 4 and December 21 when the wind blew from the north bringing generator exhausts towards aerosol sampling lines. As discussed by *Minikin et al.* [1998], contamination of sulfate levels at DDU by station activities, when it occurs, remains a limited phenomena (a few pptv of sulfate) on Teflon filters. In contrast, *Jourdain and Legrand* [this issue] reported that under these northern wind conditions a large contamination in SO_2 (at the level of 30 to 40 pptv) quite often takes place. Hence it is likely that SO_2 inputs from station activities led to a sulfate contamination on subdaily Whatman filters and not on Teflon filters. Thus subdaily aerosol samplings carried out from mid-December to January 10 using Whatman filters were discarded from the discussion.

Non-sea-salt sulfate levels were calculated assuming that, in contrast to the situation in winter in these coastal Antarctic regions, no fractionation of sea-salt aerosols takes place in summer (from December to February) at the site (see discussion by *Jourdain and Legrand* [this issue] and

Wagenbach et al. [1998]). Due to a possible sea-salt dechlorination, sodium is in general a better tracer than chloride of sea-salt aerosols in the atmosphere. The chloride to sodium molar ratio observed in daily aerosols collected from December 26, 1998, to February 24, 1999, at DDU is close to 1.15 (instead of 1.16 in seawater), and the nssSO_4^{2-} levels calculated using either sodium or chloride as a tracer of sea salt show little difference (Figure 3). Similar observations were made by *Jourdain and Legrand* [this issue] for preceding years (1991-1998). Thus it appears that the dechlorination of sea-salt aerosol in summer remains a limited phenomenon at this site. The absence of sea-salt dechlorination is likely related to the fact that, in contrast to observations made by *Wagenbach et al.* [1998] at other coastal Antarctic sites, the large amount of ammonia emitted by penguin colonies present there in summer ($\sim 5400 \text{ ng m}^{-3}$ [*Legrand et al.*, 1998]) limits acidification of sea-salt aerosol and the subsequent loss of HCl. Since sodium data are presently not available for winter 1999, in the following we used chloride as a reference for sea-salt aerosol. Thus the non-sea-salt sulfate concentrations (expressed in ng m^{-3}) have been calculated by subtracting the sea-salt contribution from the total sulfate level following

$$[\text{nssSO}_4^{2-}] = [\text{SO}_4^{2-}] - 0.14 [\text{Cl}^-],$$

where 0.14 represents the sulfate to chloride mass ratio in seawater.

2.3. DMSO Content of Aerosols

The amount of DMSO present in the aerosol phase was investigated on a half of daily Teflon aerosol filters (Gelman 47 mm, $0.5 \mu\text{m}$ porosity) run with a flow rate of 30 L min^{-1} during 20 hours in summer. Filters were extracted in 20 mL of acidified water (Hartz mineral water) in an ultrasonic bath (twice 15 min). Under these conditions the atmospheric DMSO detection limit is close to 0.015 pptv. The few samples collected on Teflon filters in March and April 1999 indicate a mean DMSO levels of 0.01 pptv (i.e., close to the detection limit). Such low DMSO levels clearly differ from the ones observed in December and January on paper filters (0.2 to 2 pptv; see Figure 1). We made further investigations by comparing DMSO levels observed on six Whatman and Teflon filters simultaneously run in January 2000 at DDU. Mean DMSO levels on Whatman filters are close to 1.23 ± 0.67 pptv (from 0.43 to 2.20 pptv), whereas Teflon filters indicate a mean value close to the detection limit (0.01 pptv). These observations suggest that DMSO is present in the aerosol phase at very low levels in summer (< 0.01 pptv) at DDU and that paper filters (a more hydrophilic material than Teflon) collect a significant part of DMSO present in the gas phase. Such a statement leads also to the conclusion that gas phase DMSO trapped onto Whatman paper filters does not affect significantly the levels of MSA (see section 2.2).

3. Data Presentation

Figure 4 shows subdaily DMS and DMSO mixing ratios observed at DDU from December 19, 1998, to the end of February 1999. Over this summertime period the site was most of the time exposed to winds blowing either from marine

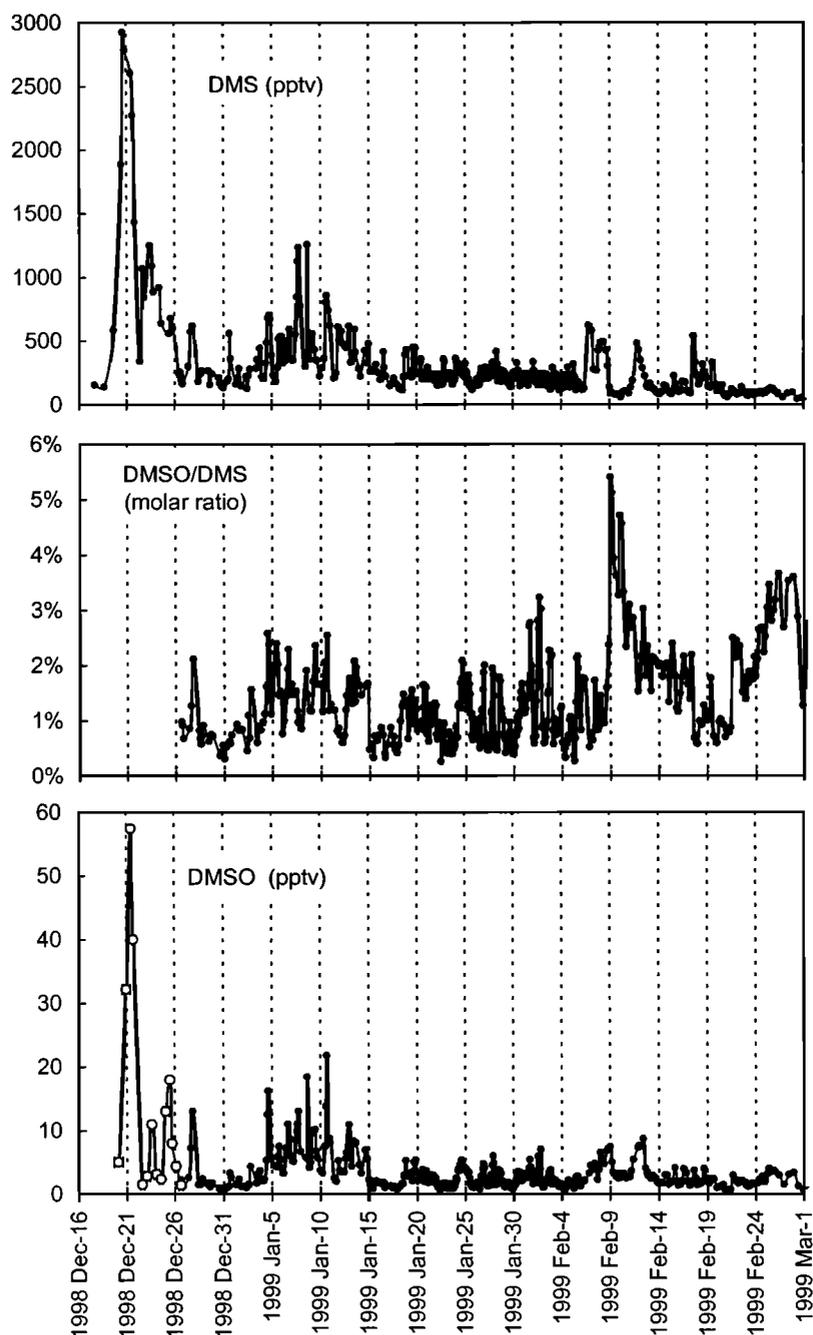


Figure 4. Subdaily DMS, DMSO mixing ratios and DMSO/DMS molar ratios observed at DDU from mid-December 1998 to late-February 1999 (see details on the sampling frequency in Table 1). For DMSO measurements, open circles refer to indirect estimations of gaseous DMSO levels made from the amount of DMSO trapped onto Whatman filters (see text), whereas solid circles refer to gas phase DMSO samplings using mist chambers.

sectors (i.e., from 270°W to 100°E; see the map in Figure 5) or glacier sectors (from 110° to 130°E). The second half of December 1998 (from December 19 to 24) was marked by the arrival of air masses coming from the open ocean. Then, during 10 days, winds brought marine air masses having been in contact with the Zélée glacier located east-southeast of the DDU site (Figure 5). Such a situation corresponds to the vicinity of a low-pressure system offshore of the station bringing marine air for a few hours to a few days over the ice

sheet. In order to estimate the time during which these marine air masses have been isolated from the open ocean, we performed air trajectory analyses. As an example, Figure 5 depicts an ensemble of air parcel trajectories arriving at or nearby DDU on January 1, 1999, at 2000 (local time (LT); i.e., UT plus 10 hours). Multiple trajectories with arrival point within 50 km of the DDU station at 940, 900, 800, and 700 hPa were computed and showed that general advection from the east along the coast is robust [Kahl, 1993].

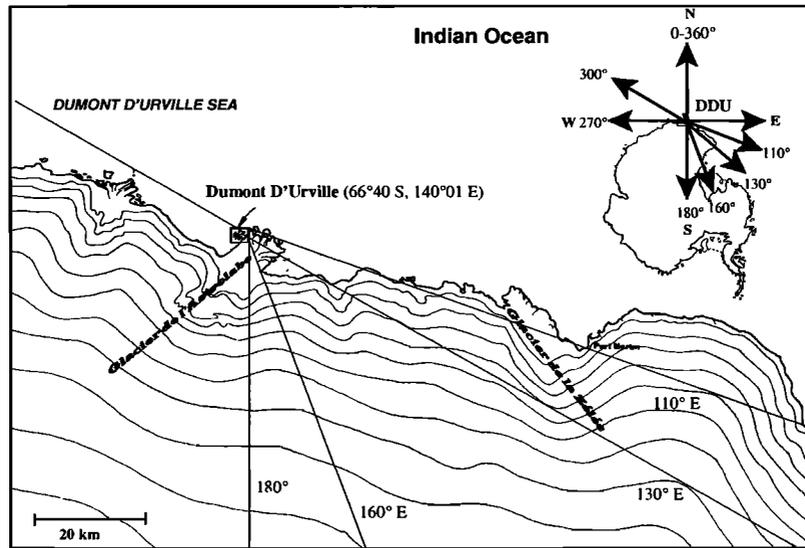


Figure 5. Map of the Terre Adélie Antarctic coast including the vicinity of the Dumont d'Urville station. Common wind directions of surface wind observed at Dumont d'Urville are from 100°E to 300°W (i.e., marine sector), from 110°E to 130°E (i.e., glacier sector), and from 140°E to 160°E (i.e., katabatic wind regime) (see text).

Isentropic trajectories were calculated from the European Centre for Medium-Range Weather Forecast, with analyses of 6-hours winds, pressures, and temperatures on a 0.5 degree grid. Figure 6 indicates that when the low-pressure system is located east of DDU, the transit time of the air mass along the coast ranges from 1 to 2 days, depending on the altitude of a trajectory. Other examples (not shown) indicate that when the low-pressure system is located offshore of DDU, a shorter transit time is observed. January 4 began a period of a week

during which marine air masses directly impacted the site. The month of February started with a marine advection between February 6 and 7 and was later on characterized by a period dominated by frequent katabatic wind regimes bringing continental Antarctic air to the site. As seen in Figure 4, over the 2 month and a half period of measurements, both DMS and DMSO levels were roughly enhanced by a factor of 2 when the wind was blowing from marine sectors (December 19 to 24, January 4 to 12, and February 6 and 7) compared with the situation of air masses having been in contact with the ice sheet arrived at the site.

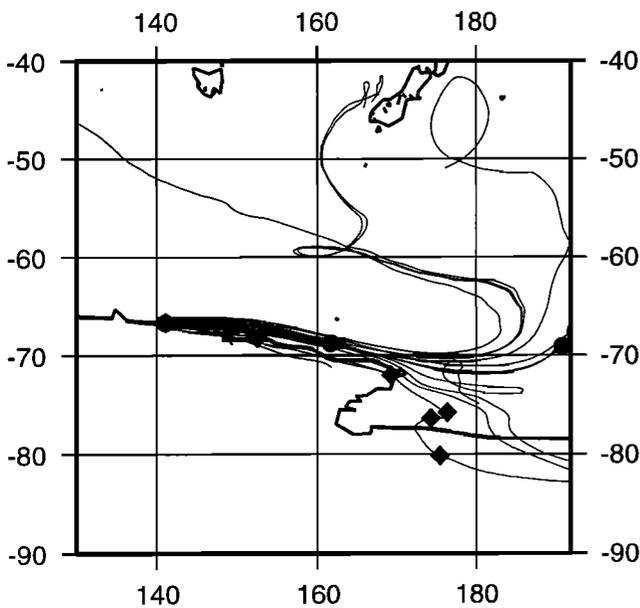


Figure 6. An isentropic trajectory ensemble for air parcels arriving at or nearby the Dumont d'Urville station on January 1, 1999, at 2000 (LT). Circles and diamonds mark the daily position of an air parcel along trajectories arriving at the 800 and 940 hPa levels above the site, respectively.

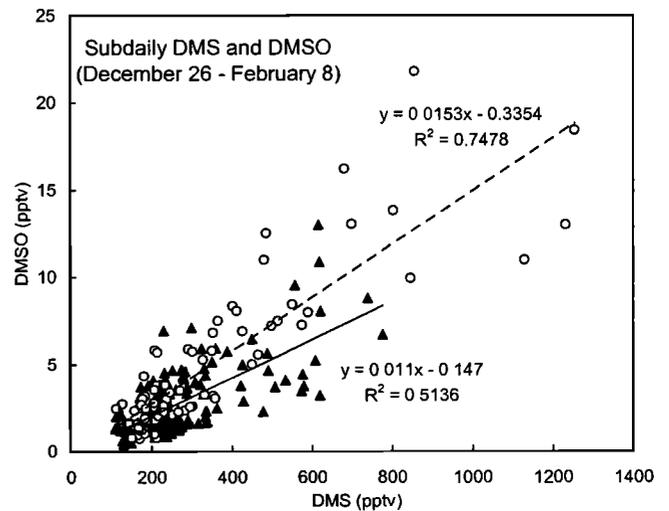


Figure 7. Subdaily mixing ratios of DMSO versus DMS at DDU from December 26 to February 8. Open circles and black triangles refer to samplings corresponding to periods of high (short-wave incident radiation, $SWR > 200 \text{ J cm}^{-2} \text{ h}^{-1}$) and low ($SWR < 50 \text{ J cm}^{-2} \text{ h}^{-1}$) sunlight conditions, respectively.

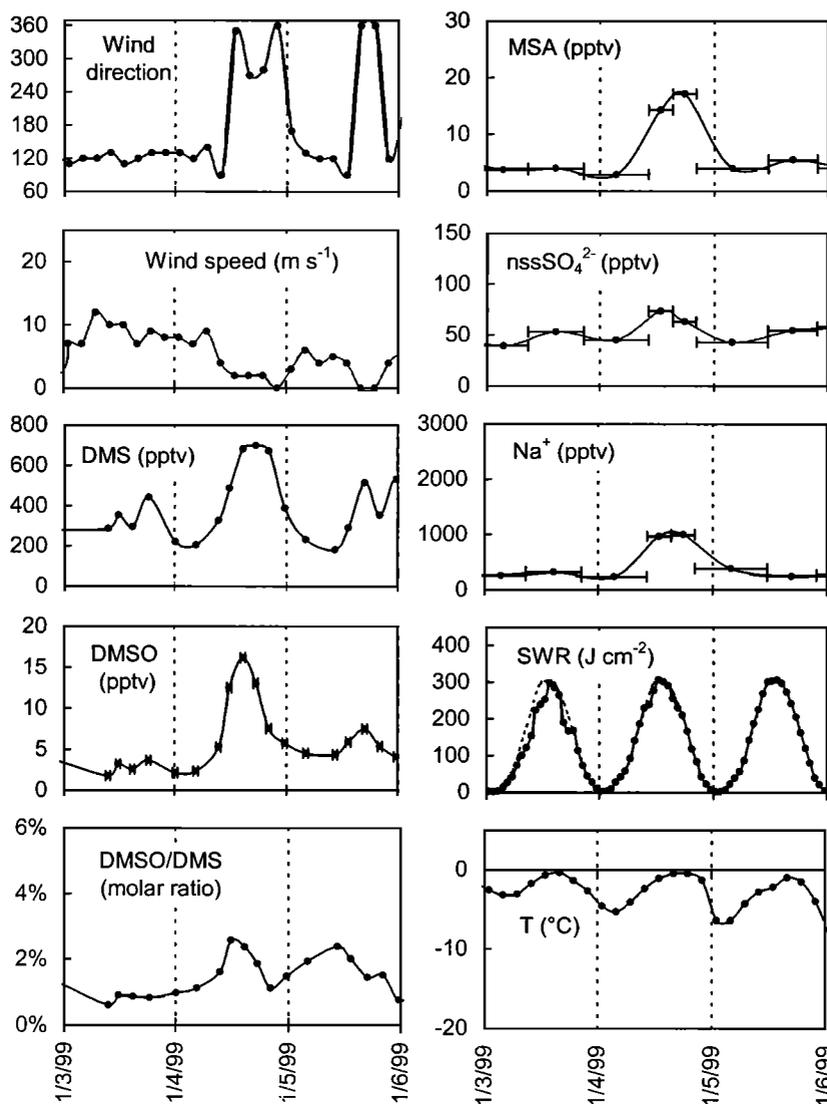


Figure 8. Time line plots for January 3 to 5, 1999: wind direction, wind speed, DMS and DMSO mixing ratios, DMSO/DMS molar ratio, MSA, nssSO_4^{2-} , and Na^+ levels on Whatman filters (see text for a possible contamination of sulfate), short wave incident radiations (SWR), and temperature.

Air trajectory analysis suggesting that winds blowing from the glacier sector correspond to a marine air mass having traveled over the ice sheet during a mean transit time of 2 days. The corresponding decrease by a factor of 2 of DMS mixing ratios with respect to those corresponding to marine air masses is consistent with a DMS lifetime of the order of a few days, which is in agreement with previous studies carried out in coastal Antarctic regions [Berresheim *et al.*, 1998]. Excluding the period from December 19 to December 26 during which DMSO was not sampled at the same time as DMS (see section 2.1) and the period of katabatic regime having started February 9, subdaily variations of DMS and DMSO levels from late-December to February 8 are well correlated ($[\text{DMSO}] = 0.014 [\text{DMS}] - 0.68$, with $R^2 = 0.63$). Such a covariance between DMS and DMSO mixing ratios first reflects the origin of air masses reaching the site, with high levels when the wind brought marine air masses to the site and lower values when the wind blew from the glacier. The

correlation is even better ($[\text{DMSO}] = 0.0153 [\text{DMS}] - 0.335$, with $R^2 = 0.75$) when samplings carried out during periods of intense sunlight conditions are considered (Figure 7), suggesting that local photochemical production of DMSO from DMS can be observed there.

DMSO has been detected at levels sometimes as high as 15 times the DMS ones in seawater [Simo *et al.*, 1997]. Examination of sea salt and DMSO atmospheric levels at DDU (not shown) reveals no significant correlation between these two components ($R^2 = 0.06$). Referring to the mean sodium mixing ratio of 940 ± 640 pptv observed from mid-December 1998 to late-February 1999 at DDU, a contribution at the level of 0.1 pptv of DMSO due to direct DMSO emissions from seawater would imply a DMSO to sodium mass ratio of the order of 3×10^{-4} and a mean DMSO seawater concentration of 52,000 nM there. That is 2 to 3 orders of magnitude higher than what is expected from summer DMS concentrations observed in seawater offshore coastal

Antarctic stations (2 nM at Palmer [Berresheim *et al.*, 1998] and up to 57 nM at DDU [Jourdain and Legrand, this issue]). Note also that DMSO measurements made on impactor runs carried out by Jourdain and Legrand [this issue] indicate a mass of DMSO close to the detection limit (i.e., ~ 0.2 ng of DMSO) on the impactor stages where 30,000 ng of sodium were present (coarse mode stages). That suggests a DMSO to sodium mass ratio lower than 6.6×10^{-6} and a DMSO seawater concentration of 1160 nM. Thus a significant contribution of primary DMSO emissions from seawater to the atmospheric DMSO levels at coastal Antarctic sites is very unlikely. A similar conclusion was drawn by Sciare *et al.* [2000c] from measurements carried out in the marine boundary layer of the Atlantic Ocean.

4. Observed Local Photochemical Production of DMS By-Products

Figure 8 presents the diurnal variations of DMS, DMSO, MSA, Na^+ , and nssSO_4^{2-} levels observed during a 3-day period of high insolation. During the second day (January 4) a marine air mass reached the site in the morning at 0900 (LT). Stable low wind speed and direction were then maintained for the rest of the day. The DMS level, close to 200 pptv early in the morning, increased between 0900 and 1400 and reached a stable value (685 ± 12 pptv) until 2000. During this time period, DMSO mixing ratios tracked the solar flux quite closely, displaying a quasi-steady state behavior. The DMSO/DMS molar ratios reached a maximum

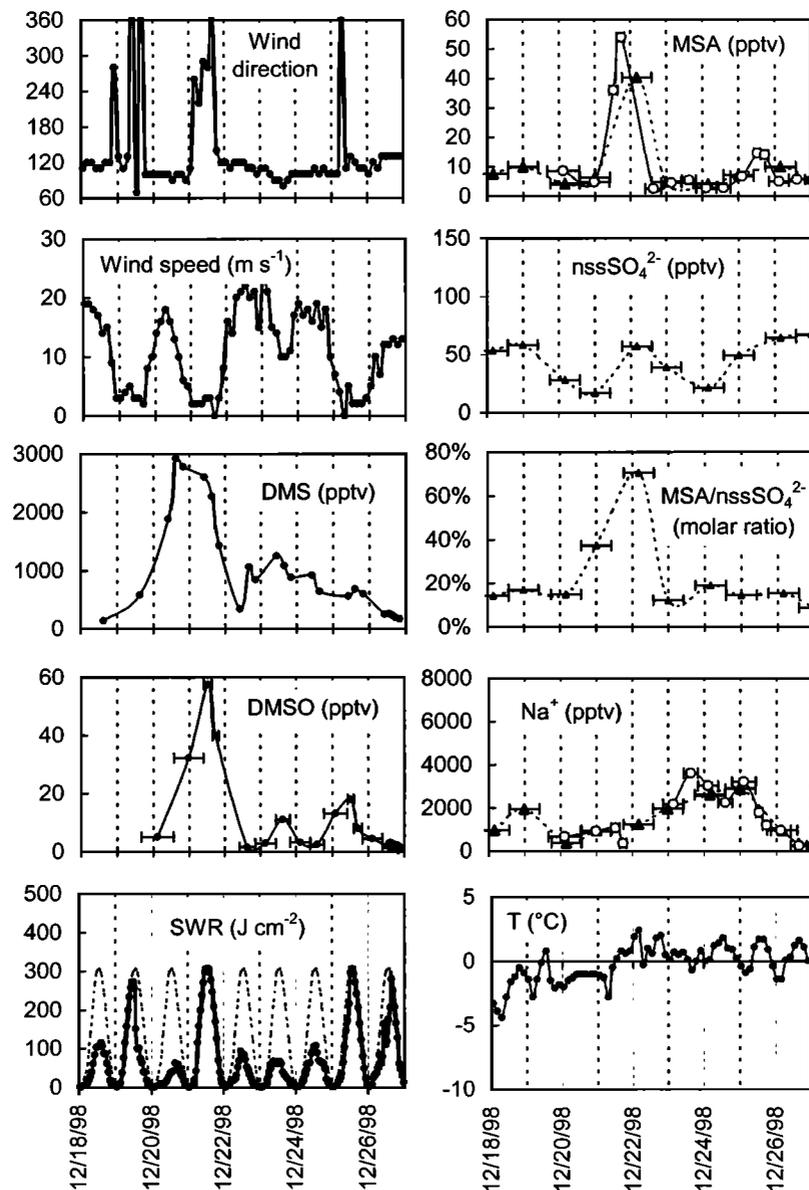


Figure 9. Time line plots for December 18 to 26, 1998: wind direction, wind speed, DMS and DMSO mixing ratios, DMSO/DMS molar ratio, short wave incident radiations (SWR), MSA and nssSO_4^{2-} levels, MSA/ nssSO_4^{2-} molar ratio, Na^+ mixing ratios, and temperature. For aerosol species the dashed lines refer to the daily sampling, the solid line (only reported for MSA and Na^+) refers to the subdaily sampling whose line was contaminated for sulfate (see text).

Table 2. DMS, DMSO, and MSA Mixing Ratios and DMSO/DMS Molar Ratios Observed During Photochemical Events Reported in This Work at DDU and by *Davis et al.* [1998] at Palmer^a

Event	Site	Reference	DMS, pptv (at Noon)	DMSO, pptv (at Noon)	MSA, pptv (Afternoon)	DMSO/DMS, %
Jan. 19, 1994	Palmer	<i>Davis et al.</i> [1998]	65	1.2	ND	1.85
Jan. 4, 1999	DDU	this work	682	16.2	15.5	2.4
Dec. 21, 1998	DDU	this work	2271	57.4	54	2.35
Dec. 25, 1998	DDU	this work	600	18.0	14	3

^a Abbreviation ND, not determined.

of 2.6% at noon, and then decreased from 2.4% at 1500 to 1.1% at 2000. During the afternoon, the MSA level reached 15.5 ± 1.3 pptv showing an increase of some 14 pptv with respect to mixing ratios observed over preceding and following nights (2.8 and 4.1 pptv, respectively). The nssSO_4^{2-} level was enhanced from 44 ± 1 pptv during these nights to 68 ± 5 pptv January 4 afternoon. However, as discussed in section 2.2, because the wind was coming from the north, the subdaily aerosol line (paper filters) has possibly been exposed to contamination by SO_2 emitted by station activities. Nevertheless, note the larger increase of MSA relative to sulfate as depicted by the change of the MSA/ nssSO_4^{2-} molar ratios from 7% at night to $23 \pm 3\%$ January 4 in the afternoon. That suggests that during this event a relatively larger amount of MSA with respect to sulfate is produced.

Although being less documented due to a lower frequency of samplings, a case with similar conditions of a marine air mass advected at the site and a day with high insolation and stable wind conditions took place December 21, 1998, as depicted in Figure 9. A marine air mass reached the DDU site from midday December 19 to late December 21 and DMS levels reached huge values (2850 ± 50 pptv) in December 20 afternoon. Such high DMS levels were maintained (from 2600 to 2300 pptv) until December 21 at noon, a day characterized by high insolation and stable low wind speed and direction (Figure 9). Again midday DMSO levels were very high, ranging from 57.4 pptv at noon to 40 pptv at 1740 December 21. Also the MSA mixing ratio during December 21 afternoon was strongly enhanced (36 pptv at noon, and 54 pptv at 1800) with respect to levels observed during nights (2.3 and 4.8 pptv). Similarly to the January 4 case, the subdaily aerosol line was contaminated by northern wind bringing pollution from the main station. However, as seen in Figure 9, the daily aerosol sampling (see the dashed line in MSA plots reported in Figure 9) partly covered the event as depicted by the high MSA level (40.8 pptv) observed between December 21 late afternoon and December 22 at 1500. At the same time the daily aerosol sampling line recorded nssSO_4^{2-} level of 57.6 pptv, a level which does not clearly differ from levels observed during nights (17 and 57.8 pptv). That clearly confirms our previous conclusion drawn from the examination of the January 4 event that the main perturbation of sulfur aerosol levels during such events mainly concern MSA rather

than non-sea-salt sulfate levels. Finally, a similar event characterized by enhancements of DMSO and MSA levels under sunny conditions when a marine air mass was advected at the site took place December 25 (Figure 9).

As seen in Table 2, these three events fit very well with the photochemical event reported by *Davis et al.* [1998] at Palmer. As discussed by *Jourdain and Legrand* [this issue], higher DMS levels observed at DDU than at Palmer are due to differences in seawater DMS content of oceanic regions offshore the two sites. Given the 10 times higher DMS level observed January 4 (as well as December 25) at DDU with respect to the case depicted by *Davis et al.* [1998] at Palmer (DMS mixing ratio of 65 pptv), the DMSO level observed at DDU during this event (16.2 pptv at noon) is in excellent agreement with the noon value of 1.2 pptv observed at Palmer (Table 2). Note also the coherence between the December 21 event characterized by a 2271 pptv DMS level (i.e., 3 to 4 times higher than the one observed January 4) and the observed DMSO mixing ratio of 57 pptv.

Although December 21 and January 4 DMS levels exhibited fluctuations possibly related to marine air mass variability or to change in source strength, the high DMSO/DMS ratios reported in Table 2 for the two events suggest that changes encountered during these events are also induced by local photochemistry. In their work, *Davis et al.* [1998] concluded that the sudden enhancement of DMSO levels at Palmer are often due to downward transport from the buffer layer. During the three events above discussed, no sudden change of the dew point was observed at the time DMSO levels were enhanced. We therefore can discard vertical transport as a main cause for observed changes there.

5. Implications for By-Products of the DMS/OH Pathways

5.1. By-Products of the DMS/OH Addition Pathway

Considering the homogeneous reaction of DMSO with OH radicals in gas phase and the levels of OH radicals calculated for coastal Antarctica, DMSO lifetime is expected to be of the order of 10 hours. The preceding pictures suggest a shorter lifetime (~ 3 hours) of DMSO as already pointed out by *Davis et al.* [1998]. In order to analyze factors controlling the

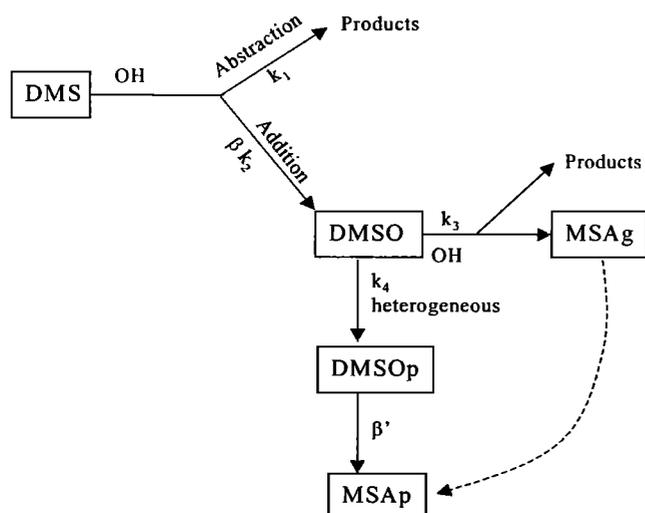


Figure 10. Abbreviated scheme of atmospheric DMSO fate in Antarctic regions. The k_1 to k_4 rate coefficients are defined in the text.

diurnal variations of DMSO depicted in Figures 8 and 9, we have first assumed that the DMSO level is controlled by its production from the DMS/OH addition pathway, and its destruction via the gas phase DMSO/OH reaction (Figure 10). Thus the time-dependent DMSO level can be calculated by solving the following equation

$$d[\text{DMSO}]/dt = \beta k_2 [\text{DMS}] [\text{OH}] - k_3 [\text{OH}] [\text{DMSO}], \quad (1)$$

with β being the yield of DMSO for the DMS/OH addition pathway, k_2 (expressed in $\text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$) is the rate coefficient for the DMS/OH addition reaction, $k_2 = (1.7 \times 10^{-42} [\text{O}_2] e^{7810/T}) / (1 + 5.5 \times 10^{-31} [\text{O}_2] e^{7460/T})$ [Atkinson *et al.*, 1997], and k_3 is the rate coefficient of the DMSO/OH reaction: $10^{-10} \text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$ [Hynes *et al.*, 1993].

First kinetic studies suggested that the yield of DMSO (β) is close to 0.5 [Hynes *et al.*, 1993]. Based on observations made at Palmer, a value close to 0.8 was proposed by Davis *et al.* [1998]. Since recent kinetic studies suggest that the DMSO yield from DMS/OH addition pathway may be higher than 0.5 [Arsene *et al.*, 1999], we have adopted the value of 0.8 proposed by Davis *et al.* [1998]. In order to account for the variability in the marine air mass, at each step, calculations were made by adjusting DMS levels to the observed ones. In addition, calculations were initiated applying an initial level of DMSO of 8 pptv, as observed at the site at 1000 when the marine input started. Figure 11 (Case a) compares observed DMSO diurnal variations and those calculated when only gas phase processes are considered following (1). It appears (Figure 11, Case a) that calculated DMSO levels at noon are overestimated by a factor of 2 with respect to observed ones, the discrepancy becoming larger in the afternoon. That clearly confirms conclusions drawn by previous studies of the existence of an heterogeneous loss of DMSO [Davis *et al.*, 1998; Sciare *et al.*, 2000a].

Introducing an heterogeneous loss rate (k_4), (1) becomes

$$d[\text{DMSO}]/dt = \beta k_2 [\text{DMS}] [\text{OH}] - (k_3 [\text{OH}] + k_4) [\text{DMSO}]. \quad (2)$$

Based on the examination of DMSO variations at the onset of sunrise, Davis *et al.* [1998] concluded that the best fit is

obtained when a yield of DMSO close to 0.8 and a heterogeneous loss rate of $2 \times 10^{-4} \text{s}^{-1}$ is assumed. As discussed by Davis *et al.* [1998], this value of k_4 corresponds to a median value of a dry aerosol surface of $10.5 \mu\text{m}^2 \text{cm}^{-3}$ estimated for February at that site. Based on the size-segregated aerosol chemistry carried out by Jourdain and Legrand [this issue], we calculated a dry aerosol surface of $3.3 \mu\text{m}^2 \text{cm}^{-3}$ for January 4. Thus in the second simulation of DMSO, diurnal variations reported in Figure 11 (Case b), we applied (2) using a k_4 value of $8 \times 10^{-5} \text{s}^{-1}$ and β values of 0.8 and 0.5. These calculations reproduce fairly well the observed diurnal DMSO variations until late afternoon when a β value of 0.8 is considered. Thus our observations are essentially in good agreement with previous findings from Davis *et al.* [1998] of an heterogeneous loss rate of DMSO in the range of 10^{-4}s^{-1} during the daytime when an addition pathway DMS/OH yield of DMSO close to 0.8 is taken. However, we note (Figure 11, Case b) that around midnight the calculated DMSO value is almost twice lower than the observed one, suggesting a lower heterogeneous loss of DMSO at night with respect to the one during the course of the day. This possibility of a changing efficiency of the heterogeneous DMSO loss rate from day to night was not investigated in the previous Antarctic study from Davis *et al.* [1998] since, as previously emphasized, the boundary layer at the Palmer site is very often disturbed by input from the buffer layer rendering difficult the examination of a photochemical event over 12 hours. Such an assumption of a day/night change of the heterogeneous loss rate of DMSO onto aerosols was also suggested by Sciare *et al.* [2000a] who examined DMSO diurnal variations at Amsterdam Island (southern Indian Ocean). At DDU site, using daily and seasonal variations of OH radical concentrations simulated by the three-dimensional transport and chemistry IMAGE model [Pham *et al.*, 1995] for 1 km elevation at 66°S , the best fit between calculated and observed DMSO levels (Figure 11, Case c) is obtained when a yield of DMSO equal to 0.8 is assumed and an OH-dependent loss rate of DMSO, k_{4a} , is taken equal to $0.5 \times 10^{-10} [\text{OH}] + 5.5 \times 10^{-5}$ (in s^{-1}). This expression of the loss rate (k_{4a}) indicates a DMSO loss rate close to 10^{-4}s^{-1} at noon (assuming a noon OH radical concentrations of $9 \times 10^5 \text{radicals cm}^{-3}$) and of $5 \times 10^{-5} \text{s}^{-1}$ at midnight ($10^4 \text{radicals cm}^{-3}$) in January at 66°S . Note that the corresponding 24-hour averaged value of k_{4a} ($0.75 \times 10^{-4} \text{s}^{-1}$) remains close to the value previously suggested by Davis *et al.* [1998] (1.7 to $2.4 \times 10^{-4} \text{s}^{-1}$). The dependence of the loss rate (k_4) to the OH radical level present in the gas phase is an empirical relationship which in fact likely depicts photochemical conditions controlling the amount of OH radicals present in hydrated aerosols.

As depicted in Table 2, the increase of MSA levels which takes place in the afternoon at DDU during the three photochemical events are roughly proportional to the maximum of the DMSO level. DMSO levels observed in the aerosol phase (see section 2.3) are far below the levels expected if we assume that the total amount of DMSO (DMSOp) lost from the gas phase is over a time interval Δt accumulated onto aerosols following

$$[\text{DMSOp}] = k_{4a} [\text{DMSO}] \Delta t. \quad (3)$$

For instance, in the case of January 4, with a noon DMSO mixing ratio of 16 pptv, we can expect a DMSO level in the aerosol phase built up over 4 hours of 7 pptv (i.e., almost 3

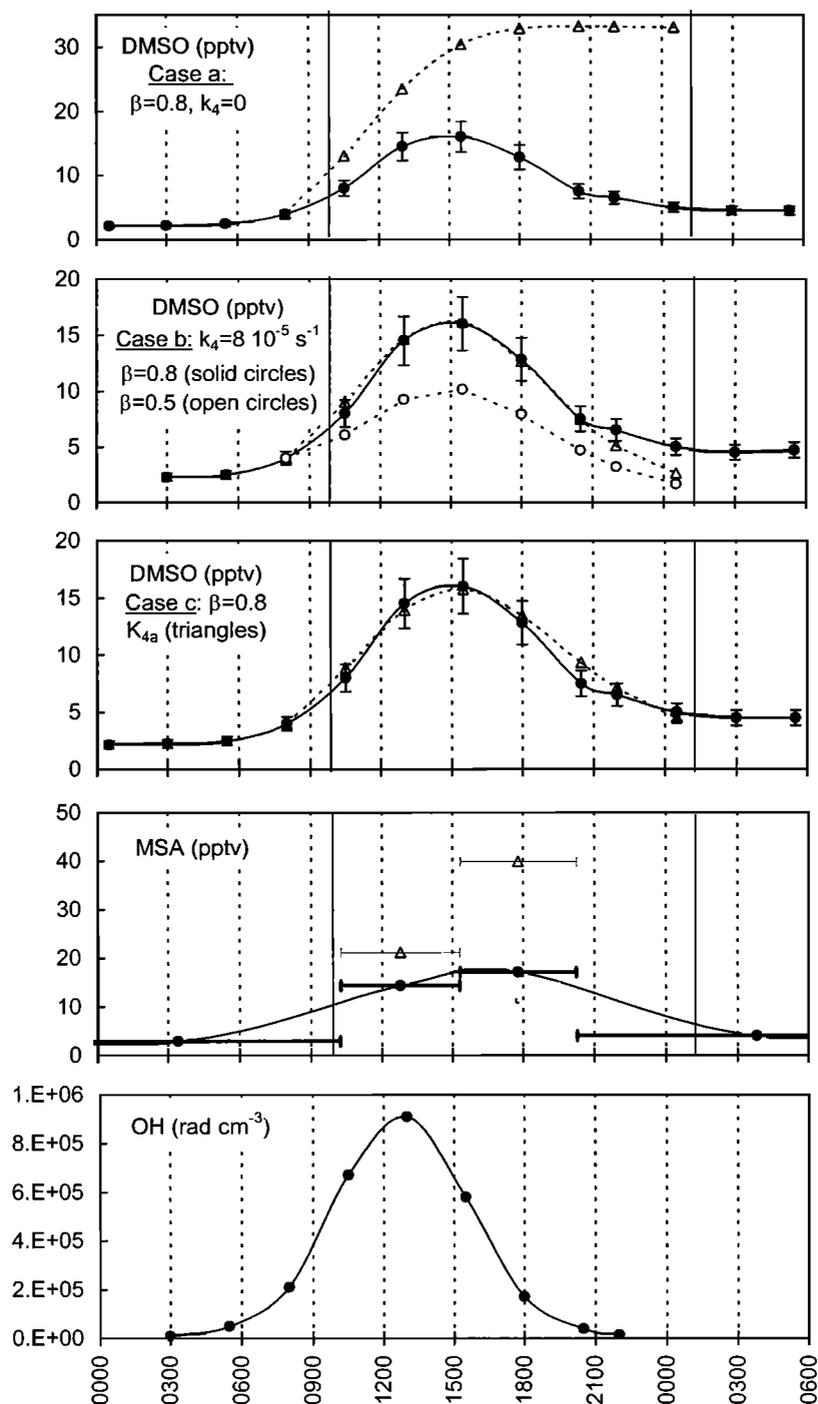


Figure 11. Calculated (open symbols) and observed (solid symbols) DMSO and MSA levels on January 4. Calculations of DMSO levels were made using (2) for three cases considering different values of the DMS/OH yield for DMSO and of the DMSO heterogeneous loss (see text). Vertical bars reported on measured DMSO plots refer to uncertainties of determinations. Expected MSA mixing ratios were calculated using (3) (see text), and horizontal bars refer to sampling intervals. Vertical solid lines depict the beginning and the end of the time period over which the wind direction remained stable. The bottom panel refers to the OH diurnal cycle used in (2). Read 1.E+06 as 1.0×10^6 .

orders of magnitude higher than the observed DMSO levels in the aerosol phase reported in section 2.3). That suggests that, after its uptake onto aerosols, DMSO is subsequently rapidly destroyed. Although the fate of DMSO in liquid phase is essentially unknown, very recent studies suggested that it reacts fast with OH radicals in the aqueous phase [Bardouki

et al., 1999]. Certainly, such reactions can also take place on hydrated aerosols. These recent kinetic studies suggest that the aqueous reaction of DMSO with OH radicals produces methanesulfonic acid (MSIA) which reacts further to produce MSA. If we assume that the total amount of DMSO lost onto aerosols has been oxidized into MSA, we calculated for the

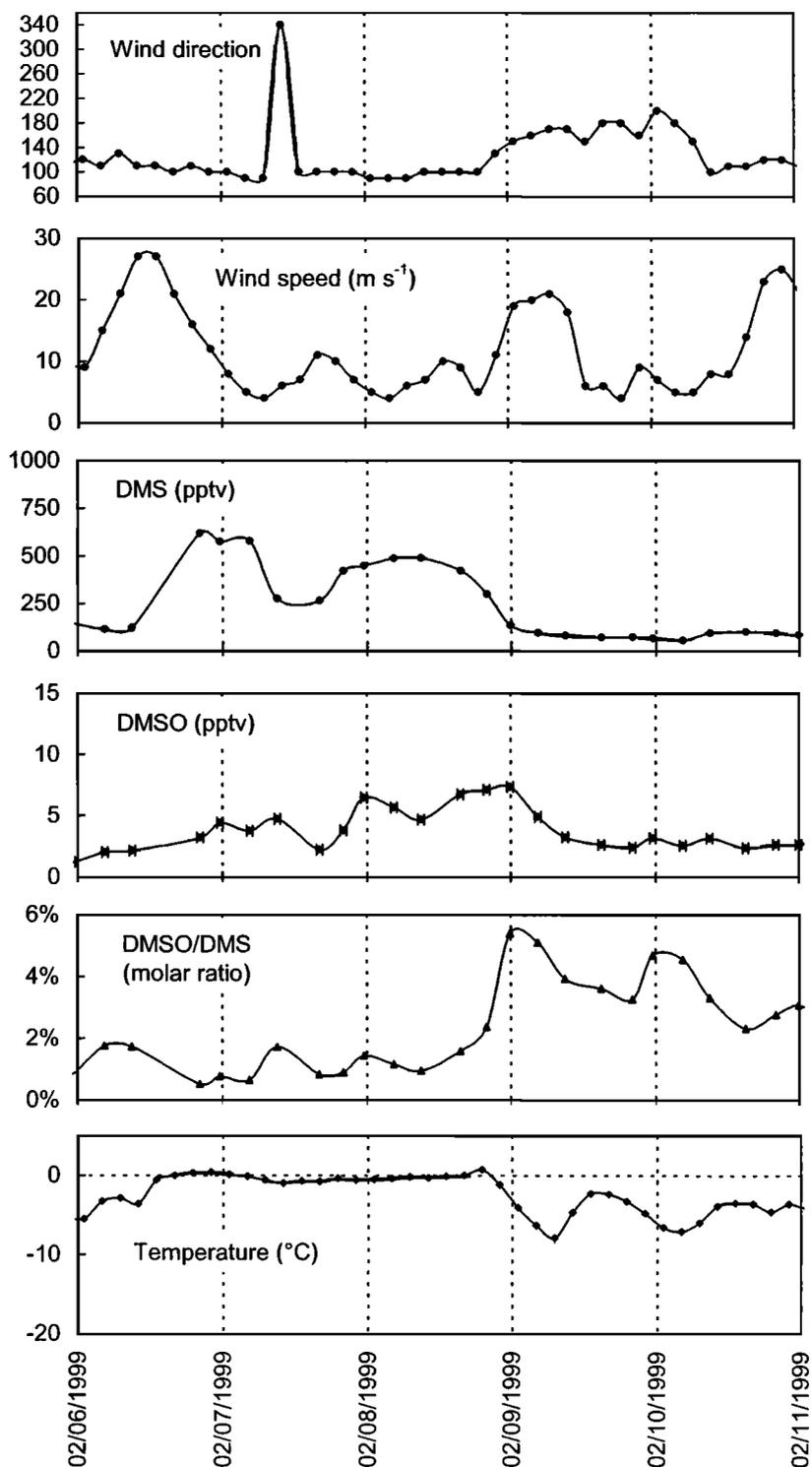


Figure 12. Time line plots for February 6 to 10, 1999: wind direction, wind speed, DMS and DMSO mixing ratios, DMSO/DMS molar ratio, and temperature.

January 4 event an increase of MSA level of some 38 pptv (Figure 11). During this event the observed MSA increase is some 3 times lower than what we can expect from a total oxidation of DMSO into MSA on aerosol ($[MSA] = [DMSOp] = k_{da} [DMSO] \Delta t$). This difference is also seen for the December 21 and 25 events as depicted in Table 2. Hence certainly a part of the total amount of DMSO trapped onto

aerosol was not fully oxidized into MSA within the few hours duration of these photochemical events. Further studies are here needed to identify and quantify some possible intermediate by-products of the heterogeneous oxidation of DMSO into MSA (methanesulfinic acid, for instance). Furthermore, investigations of $DMSO_2$ in the aerosol phase may also be useful.

5.2. By-Products of the DMS/OH Abstraction Pathway

We here discuss briefly the consistency between the observed limited production of sulfate at DDU during photochemical events and our present knowledge of the DMS chemistry. Based on a rate coefficient k_2 of 7.7×10^{-12} cm³ molecules⁻¹ s⁻¹ for the DMS/OH addition pathway and a yield for SO₂ of 0.2, *Davis et al.* [1998] suggested that the production of SO₂ via the addition DMS/OH pathway would be neglected with respect to the abstraction DMS/OH pathway. Assuming a rate coefficient for the DMS/OH abstraction pathway of 4.5×10^{-12} cm³ molecules⁻¹ s⁻¹ [*Atkinson et al.*, 1997] and a yield for SO₂ of 0.8 [*Davis et al.*, 1998], a total loss rate of SO₂ onto aerosol and ocean surface of 1.2×10^{-5} s⁻¹ [*Davis et al.*, 1998], we calculate for January 4 (DMS mixing ratios ranging from 300 to 680 pptv) a steady state SO₂ mixing ratio of 30 pptv in the afternoon. As emphasized by *Jourdain and Legrand* [this issue], such an enhancement of SO₂ mixing ratio cannot be easily detected at DDU since the low wind speed conditions encountered during photochemical events lead to pollution from the station which can disturb (up to 38 pptv) SO₂ measurements. Assuming that the total amount of SO₂ scavenged from the gas phase by aerosols is converted into particulate sulfate, we calculate that 17 pptv of sulfate can be accumulated in late afternoon during the January 4 event. That clearly represents an overestimation since a significant fraction of SO₂ is also lost at the surface ocean [*Davis et al.*, 1998]. That is qualitatively in agreement with our observation of a well-identified change of MSA levels of the order of 15 pptv (see section 5.1), whereas, if it exists, the enhancement of sulfate mixing ratio remained well below 24 pptv (section 4) during the January 4 photochemical event.

6. Katabatic Regime

The first occurrence of katabatic regime took place in 1999 during the first half of February. The time line plot from February 6 to 10 is reported in Figure 12. The three first days were characterized by air masses coming from 100°E (i.e., marine sectors). As a consequence, over these 3 days, DMS and DMSO levels peaked at more than 500 and 5 pptv, respectively, with DMSO/DMS molar ratios ranging between 1 and 2%. This situation was maintained until February 8 late afternoon with at 1900 (LT) DMS, DMSO, and DMSO/DMS molar ratio of 300 pptv, 7.1 pptv, and 2.4%, respectively. From 1900 to 2350 the wind speed was strongly enhanced from 5 to 20 m s⁻¹, and the temperature dropped from 0°C to -4°C in relation with the beginning of a katabatic situation. At that time the DMS level dropped to 136 pptv, whereas the DMSO level was still enhanced to 7.4 pptv, leading to a large increase of the DMSO/DMS molar ratio (5.4% : i.e., the largest value observed since mid-December as seen in Figure 3). DMS levels observed February 9 were the lowest encountered since mid-December 1998, reaching a minima of 56 pptv (Figure 12). Note that compared with cases of wind blowing from 110° to 130°E corresponding to the arrival of an air mass having traveling some 2 days over the ice sheet as encountered during the first half of February (DMS mixing ratio of 160 ± 35 pptv), the DMS mixing ratio observed February 9 is some 3 times lower.

This observation of an enrichment of inland Antarctic air in DMSO suggests that a different chemistry takes place in the

free troposphere over the Antarctic continent with respect to the situation in the marine boundary layer. Similarly to what was proposed in the SCATE studies for vertical transport of DMSO from the buffer layer into the boundary layer, we suggest that the free troposphere over the Antarctic continent contains higher DMSO levels due to a weakened heterogeneous loss onto aerosols. Indeed, assuming that the available surface of aerosol is 10 times lower in continental Antarctic air than in the marine boundary layer, the loss rate (k_{4a}) would be close to 0.8×10^{-5} s⁻¹ (taking into account an increase by a factor of 2 of the OH radical mixing ratio) instead of 0.67×10^{-4} s⁻¹ in the boundary layer. Assuming a 24-hour averaged OH mixing ratio of 5×10^5 radicals cm⁻³ at 5 km in February (instead of 2.3×10^5 at 1 km) which leads to a value of k_3 [OH] of 5×10^{-5} s⁻¹, the gas phase DMSO/OH reaction becomes there 5 times more rapid than the heterogeneous loss onto aerosols. Also, the lifetime of DMSO is of the order of 6 hours (i.e., 2 to 3 times longer than in the marine boundary layer). The corresponding lifetime of DMS is close to 2 days (instead of 4 days in the boundary layer). Given a typical DMS level present 2 days before the event in the marine boundary layer (~500 pptv, as observed in the marine air mass advected at DDU February 7, see Figure 12), the DMS level of 56 pptv observed February 9 would suggest a 4 days travel under sunny conditions since the air mass was over the ocean. Isentropic trajectories (not shown) indicate that the air parcel reaching DDU February 9 has been traveling over the ice sheet for more than 5 days. Having a limited confidence in trajectory information beyond 5 days, it remains difficult to derive more of a quantitative picture on lifetime of DMS and DMSO in the Antarctic free troposphere. In conclusion, the DMSO enrichment of inland Antarctic air mass may reflect differences on the atmospheric fate of DMS and DMSO leading to an accumulation of DMSO there.

7. Conclusions

This high-resolution record of DMS, DMSO, and sulfur aerosol levels gained in summer with subdaily samplings at DDU, a site which most of the time corresponds to conditions encountered in the marine boundary layer at high-southern latitudes, suggests the following conclusions:

1. A short lifetime of DMSO related to an efficient heterogeneous loss onto aerosols is here confirmed.
2. The yield of DMSO for the DMS/OH addition pathway is very likely close to 0.8.
3. The heterogeneous loss of DMSO onto aerosols is found to be photochemistry dependent.
4. The sticking of DMSO onto hydrated aerosol is followed by a rapid oxidation of DMSO at least a third of which is observed as MSA. Thus the heterogeneous uptake of DMSO onto aerosol appears to be the dominant pathway in producing particulate MSA compared to the DMSO/OH oxidation in the gas phase in the marine boundary layer of Antarctic regions.
5. A different situation likely takes place in the Antarctic free troposphere where the lower aerosol content permits an higher accumulation of DMSO in the gas phase and a subsequent larger production of gaseous MSA.

6. More progress may emerge from MSIA and DMSO₂ atmospheric measurements in both gas and aerosol phases as well as measurements of SO₂ with time resolution of a few hours.

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