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Interannual variability of dimethylsulfide in air and seawater and its atmospheric oxidation by-products (methanesulfonate and sulfate) at Dumont d'Urville, coastal Antarctica (1999–2003)

Susanne Preunkert,[1] Michel Legrand,[1] Bruno Jourdain,[1,2] Cyril Moulin,[3] Sauveur Belviso,[3] Nobue Kasamatsu,[4] Mitsuo Fukuchi,[4] and Toru Hirawake[4,5]

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[1] A multiple year-round study of atmospheric dimethyl sulfide (DMS) (from December 1998 to April 2003) as well as sulfur-derived aerosols (methanesulfonic acid (MSA) and non-sea-salt sulfate) (from March 1991 to February 2003) was conducted at Dumont d'Urville, coastal Antarctica. The three sulfur-derived species exhibit a seasonal cycle characterized by maxima in midsummer (January). Whereas the interannual variability of winter levels remains low, a strong interannual variability is shown in summer, particularly for DMS and MSA, and to a lesser extent for non-sea-salt sulfate. Over the 1998–2003 time period, January 2002 stands out with high values for all sulfur species. These interannual variabilities of atmospheric summer levels are examined in the light of seawater chlorophyll *a* content derived from Sea-viewing Wide Field-of-view Sensor (SeaWiFS) data (themselves compared to field measurements made south of 60°S), oceanic DMS levels estimated from chlorophyll *a* SeaWiFS data, and various sea-ice indices.

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1. Introduction

[2] Major uncertainties remain in quantifying the response of climate to anthropogenic forcing. Among them are the possible biogeochemical feedbacks that may reduce or strengthen the anthropogenic forcing [*Lovelock et al.*, 1972]. For instance it has been postulated that the marine biosphere may induce a feedback through dimethylsulfide (DMS) emissions [*Charlson et al.*, 1987] but there are still large uncertainties in both the sign and the amplitude of this feedback. A coupled ocean-atmosphere model forced by increasing atmospheric CO_2 suggested a negative feedback particularly at mid southern latitudes with enhanced DMS fluxes up to 30% for a doubling of CO_2 [*Bopp et al.*, 2003]. This coupled model predicts reasonably well the oceanic DMS distribution for the present-day situation except very high concentrations due to spring and summer blooms of *Phaeocystis* at high latitudes that cannot be reproduced. Therefore the response of marine biota to climate change in these regions remains essentially unknown.

[3] Information relative to the role of climatic conditions on oceanic DMS emissions at high latitudes remains either very sparse or indirect. *Curran and Jones* [2000] documented DMS concentrations in surface seawater in the Australian sector of the high-latitude Southern Ocean, but data remain rather sparse (seven voyages in spring and summer between 1991 and 1995) and documentation of the seasonal ice zone (SIZ) missed large sectors (from 100 to 140°E). *Curran et al.* [2003] found a positive correlation between methanesulfonic acid (MSA), a by-product of the atmospheric oxidation of DMS, in a coastal Antarctic ice core and 22 years satellite-derived sea-ice extent for the 80–140°E sector. Owing to a lack of long-term DMS measurements in the Antarctic Ocean such indirect information cannot be validated yet, and physical or biological parameters responsible for this link between winter sea-ice extent and summer atmospheric DMS (hence MSA) are not clearly understood. Climatological distributions of sea-surface DMS concentrations are an alternative to the lack of field observations but a review of available DMS climatologies revealed large discrepancies between them at high southern latitudes [*Belviso et al.*, 2004a].

[4] The present study examines the atmospheric record of DMS, and sulfur-derived aerosol (MSA and SO_4) from end 1998 to beginning of 2003 at the coastal Antarctic site of Dumont d'Urville (DDU) in terms of seasonal and interannual variability's. In order to investigate the concurrent

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interannual variability of the marine biota in the sector of the Southern Ocean offshore DDU, series of surveys (seawater DMS and chlorophyll a) were performed offshore DDU during austral summers 2001–2002 and 2002–2003. These surveys offered the possibility to evaluate (1) the accuracy of chlorophyll *a* data derived from satellite-based, Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and (2) the validity of seawater DMS derived from chlorophyll *a* following the work of *Belviso et al.* [2004b]. Finally, we examine the possible link between sea ice (sea-ice melting and various sea-ice extent indices) and the marine biota of these high-latitude regions, as suggested by previous studies.

2. Site, Sampling, and Methods

2.1. Site Presentation

[5] Atmospheric samplings were performed at the DDU station (66°40'S, 140°01'E, 40 m above the sea level), a small island located 1 km offshore the coastline of the Antarctic continent. The ocean around the site is generally free of ice from beginning of December to end of February and the ice extent rarely exceeds 500 km during the rest of the year (on average 370 km from April to November since 1991) (data from National Snow and Ice Center, University of Colorado, Boulder, data available at: http://www.nsidc.org). A detailed description of the sampling site and its mean climatology is given by *Wolff et al.* [1998] and *König-Langlo et al.* [1998]. The sampling site is located upwind of the station buildings, preventing sampling from contamination by human activities under usual wind conditions. The influence of human activities (diesel exhaust, heating devices, and waste incineration) on atmospheric aerosol sampling has been examined elsewhere for summer time [*Minikin et al.*, 1998] and wintertime [*Jourdain and Legrand*, 2002]. A contamination caused by human activities in the order of a few tens of nanograms per cubic meter of sulfate sometimes occurs when the site experiences episodes of low wind conditions. Emissions of ornithogenic soils related to the presence of large colonies of Adelie penguins in summer [*Legrand et al.*, 1998] has to be considered carefully since they contain Na, Cl, and SO_4 [*Jourdain and Legrand*, 2002].

2.2. Aerosol Analysis

[6] Aerosols are collected at DDU on a continuous basis since March 1991 [*Jourdain and Legrand*, 2002]. A sampling interval of 1 and 2 days is applied from end October to early April, and during the remaining winter months, respectively (i.e., ~270 samples per year). Aerosols are collected on Gelman Zefluor (47 mm diameter, 0.5 μm pore size) filters at a flow rate of 1.7 m^3 h^{-1}. Since 1999 filters are precleaned individually in three high-purity methanol bathes to avoid a potential contamination of NH_4NO_3 that occurred sporadically on factory delivered filters. The filter holder is set up at 2 m above ground and is protected from direct impaction of blowing snow and very large sea-salt particles by a stainless steel cylindrical device. After sampling, filters are stored in polycarbonate vials sealed in polyethylene bags and kept in the darkness at −18°C until analysis. Periodically, a filter field blank was achieved by running the sampling line for 10 seconds.

[7] Most of filters collected between March 1991 and February 2003 (~2800 samples) were extracted and analyzed for anions (MSA, Cl, and SO_4) at DDU by using ion chromatography (Dionex DX500 equipped with an AS11 column) as detailed by *Minikin et al.* [1998]. Cations (Na, NH_4, and K) were analyzed on the remaining sample extract (kept frozen at −18°C) after being shipped back to the laboratory (LGGE in Grenoble). Analytic conditions for cation analysis are given by *Legrand et al.* [1993]. Given the typical volume of sampled air (35 m^3 in summer and 70 m^3 in winter), the field blanks remain insignificant (< 1 ng m^{-3} for MSA, 1 ng m^{-3} for Cl, SO_4, and K, and 6–7 ng m^{-3} for NH_4 and Na). The accuracy of aerosol analysis is determined by the accuracy of ion chromatography, which is typically 5%.

[8] Resulting from precipitation of mirabilite (Na_2SO_4, $10H_2O$) during freezing of seawater, a depletion of sulfate relative to sodium (or chloride) in atmospheric sea-salt particles was identified in winter at high latitude [*Wagenbach et al.*, 1998]. The temporal occurrence and intensity of this fractionation process was investigated at DDU by studying the size segregated composition of particles collected over 2 years on a 11 stage impactor (cut-off sizes from 0.08 to 7.7 μm) [*Jourdain and Legrand*, 2002]. It was shown that at DDU the SO_4 to Na mass ratio is 0.13 in airborne sea-salt aerosols from May to October. As recommended by *Jourdain and Legrand* [2002], the non-sea-salt sulfate ($nssSO_4^{2-}$) level was calculated by applying this ratio to bulk aerosol filters collected from March to October. From November to February the $nssSO_4^{2-}$ level was calculated using the SO_4 to Na mass ratio of seawater (0.25).

[9] As detailed by *Jourdain and Legrand* [2002] emissions from ornithogenic soils contribute to the Na level by ~70 ng m^{-3} in summer (i.e., ~15% of total sodium). Ornithogenic soils also contribute to the summer SO_4 level (~60 ng m^{-3}, i.e., ~17% of total sulfate). When the contribution of ornithogenic soils to Na and SO_4 levels is neglected, the summer level of $nssSO_4^{2-}$ is overestimated by up to 45–50 ng m^{-3} (i.e., 30% of total $nssSO_4^{2-}$). In this work, Na and $nssSO_4^{2-}$ summer concentrations were corrected from ornithogenic soils inputs following *Jourdain and Legrand* [2002]. Briefly, the contribution of Na from ornithogenic emissions ($[Na^+_{or}]$) is derived from the concurrent potassium contribution ($[K^+_{or}]$) following:

$$\left[Na^+_{or}\right] = 1.82\left[K^+_{or}\right], \quad (1)$$

$$\left[K^+_{or}\right] = ([K^+] - 0.037^*[Na^+])/0.993. \quad (2)$$

The ornithogenic contribution of sulfate $[SO_4^{2-}{}_{or}]$ is calculated as

$$\left[SO^{2-}_{4or}\right] = 1.5\left[K^+_{or}\right]. \quad (3)$$

[10] Contamination of the order of a few ng m^{-3} of sulfate related to DDU station activities have been identified by *Minikin et al.* [1998]. Given the SO_4^{2-} levels of a few hundreds of ng m^{-3} observed in summer, the potential SO_4^{2-}contamination originating from the DDU station can be neglected at that season. The lower winter levels, however, can be impacted by station activities and were here inspected. Following *Jourdain and Legrand* [2002],

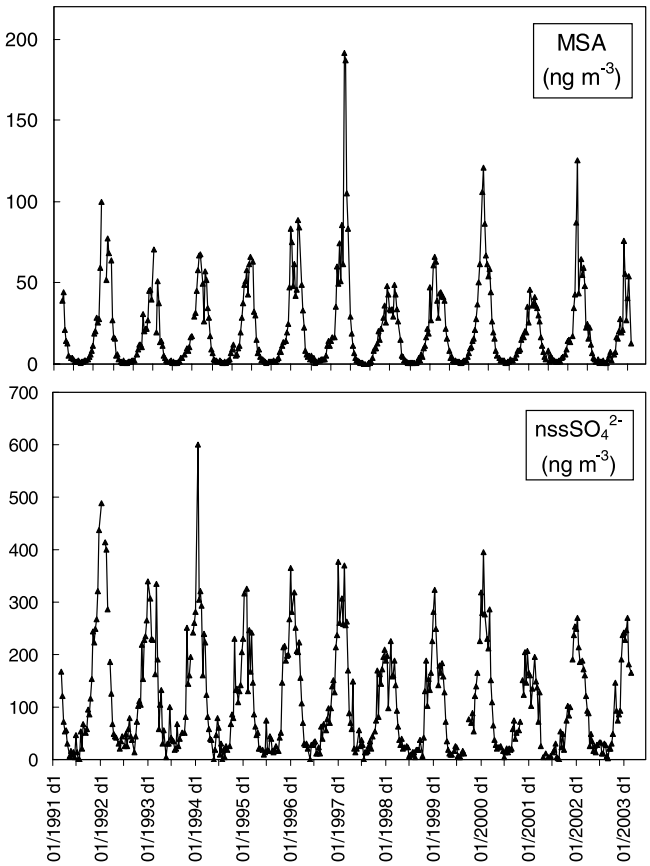

Figure 1. Ten-day average atmospheric concentrations of particulate methanesulfonic acid (MSA) and non-sea-salt sulfate observed at Dumont d'Urville (DDU) from March 1991 to February 2003. Non-sea-salt sulfate values have been corrected from the contribution of local emissions by ornithogenic soils (see section 2.2).

samples showing $nssSO_4^{2-}$ values 2 times higher than the mean winter level (i.e., ~40 ng m^{-3}) at days with low wind speeds (<5 m s^{-1}) were suspected to be contaminated and discarded from the data set (a mean of three samples each winter). The year-round 1991–2003 aerosol records (10-day averages) of MSA and $nssSO_4^{2-}$ are reported in Figure 1.

2.3. Atmospheric DMS and DMSO Analysis

[11] DMS and DMSO air samplings and analysis started at DDU in December 1998. Data collected until July 1999 have already been presented by *Jourdain and Legrand* [2001] and *Legrand et al.* [2001]. Hereafter, the data set was extended to April 2003. One or two DMS and DMSO samplings were performed each day between March and October whereas a minimum of 3 daily samplings was done from December to February (i.e., ~550 samples per year). More sub daily samplings were done in 1999 (1200 samples) and 2000 (870 samples) to document photochemical events [see *Legrand et al.*, 2001].

[12] DMS samplings are done by pressurizing an electro polished stainless steel canister of 6 L up to 4 bars during a few minutes with a membrane pump (Millipore, model XX5522050). Analyses were achieved within a week after sampling with a gas chromatograph equipped with a flame photometric detector (HP6890, 393 nm). DMS is cryogenically trapped at −60°C on a Tenax sample loop maintained in an ethanol bath. DMS is subsequently transferred to the GC by thermal desorption of the Tenax trap (boiling water) as detailed by *Nguyen et al.* [1990]. Working conditions of gas chromatography are detailed by *Legrand et al.* [2001]. Daily calibrations were achieved using a permeation tube (VICI Metronics, Santa Clara, California) thermostated at 30°C. The permeation tube was calibrated and afterward checked for its stability (drift of less than 5% after one year) against permeation tubes used as references for the atmospheric DMS monitoring at Amsterdam Island [*Sciare et al.*, 2000]. The detection limit is close to 0.2 ng, leading to an atmospheric detection limit of 13 pptv when 6 L of air are sampled. From July to November a larger air volume was sampled (up to 35 L) if necessary, leading to a detection limit close to 2 pptv.

[13] The sampling of DMSO was achieved by using a mist chamber in which air was flowed at a rate of 0.6 m^3 h^{-1} during one hour through an inlet Teflon filter (Gelman Zeflour, 47 mm, 0.5 μm pore size). Following *Sciare and Mihalopoulos* [2000], mist chambers were filled with 20 mL of acidified water. Analyses were performed by reduction of DMSO to DMS using $NaBH_4$ as described by *Andreae* [1980]. Blanks were run with a thorough washing of all glassware with mineral water. We found 0.037 ± 0.018 ng of DMSO per mL in this blank water, which was subtracted to the DMSO content of mist chamber extracts. The DMSO detection limit (taken as twice the blank variability) is close to 0.37 pptv.

[14] Figure 2 shows that DMSO mixing ratios remain rather similar over the 4 winters of the record (change by

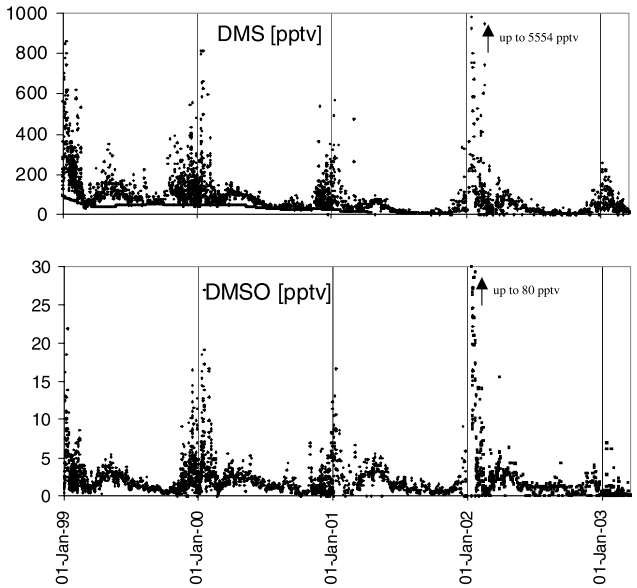

Figure 2. Atmospheric dimethyl sulfide (DMS) and dimethylsulfoxide (DMSO) mixing ratios (raw data in pptv) observed at DDU from December 1998 to April 2003. The solid line (December 1998 to February 2001) reported along with DMS data is the 1% percentile of a robust spline (see section 2.3).

Table 1. Mean Levels of Chloride, DMS, and DMSO in Early and Late Winter of 1999 and the Three Following Years

	Cl^-, ng m^{-3}	DMS, pptv	DMSO, pptv
May 1999	953 ± 507	143 ± 59	2.8 ± 1.0
May 2000–2002	563 ± 297	64 ± 23	2.6 ± 1.0
August 1999	105 ± 10	86 ± 44	1.2 ± 0.4
August 2000–2002	561 ± 274	24 ± 16	1.2 ± 0.7

less than 5%), while DMS ones were surprisingly larger during winter 1999 compared the other winters. The winter DMS levels in 1999 exceed those of following winters by 60 to 80 pptv (Table 1). In their initial study of DMS and DMSO at DDU covering the first part of the record (December 1998 to July 1999), *Jourdain and Legrand* [2001] proposed that these relatively high DMS values in winter 1999 (particularly in May) were related to an unusual high marine input as suggested by Cl concentrations twice higher in May 1999 than over preceding years. As seen in Table 1, this argumentation fails, however, if DMS data from August 1999 and later on (not available in the work of *Jourdain and Legrand* [2001]) are considered, since no overall correlation between Cl and DMS winter values can be detected.

[15] The origin of this large winter DMS values in 1999 was incidentally found end of 1999 when the pressurizing of a canister lasted for 10 hours instead of a few minutes (over wintering people have forgotten to stop sampling). The DMS mixing ratio measured in this canister was 10, 600 pptv suggesting that the membrane of the pump released a sulfur species detected as DMS by the gas chromatograph (J. Sciare, personal communication, 1999). This was confirmed by running over 2 months a new pump in parallel to the original pump used since December 1998. Indeed the new pump (switched on continuously) led to a systematic overestimation of DMS (up to 60 pptv) at the beginning, which gradually decreased over time to disappear 2 months later. The original pump used since 1998 and its membrane was never changed until now. To estimate the bias caused by the pump membrane at the beginning of the record, we examine the offset of the DMS record from end 1998 to March 2001 (1% percentile of a robust spline [*Bloomfield and Steiger*, 1983] reported in Figure 2). The offset, which ranges from 100 pptv in December 1998 to 20 pptv in January 2001, was subtracted from the raw data set. However, even corrected data indicate higher DMS levels in winter 1999 (62 ± 59 pptv from March to November 1999) compared to the following winters (30 ± 25 pptv). Since we cannot conclude if this difference is real or not, we based following discussions on winter levels discarding winter 1999. Given the rather high summer DMS levels (140 ± 414 pptv) with respect to the offset range, all summer data were considered although a slight overestimate is possibly for summer 1998–1999, in a lesser extent for 1999–2000. This will, however, not affect the discussion on the interannual summer variability.

[16] To control the reliability of DMS sampling achieved by pressurizing air in a canister, DMS sampling were also achieved once per month since 2001 by sucking ambient air directly through the Tenax sample loop of the gas chromatograph. This online sampling cannot be applied on a daily basis since it requires several hours and the Tenax sample has to be analyzed immediately after sampling. Comparison between canister and online sampling procedures showed a very good agreement ([DMS] canister = 0.97 [DMS]online with R^2 = 0.94 for 50 samples).

[17] Atmospheric DMS sampling was regularly achieved each day at 1000 UT. As mentioned above, intensive experiments (up to 10 daily samplings covering also the nighttime) were performed in summers 1999 and 2000 to document photochemical events [*Legrand et al.*, 2001]. Comparison between daily mean and 1000 UT values indicates that in summer DMS values measured at 1000 UT are about 12% lower than daily average. This difference is likely due to the fact that in December and January, DMS levels are often higher in the afternoon when sea-breeze brings more DMS at the site [*Legrand et al.*, 2001]. In winter no difference can be identified when comparing data at 1000 UT and 28 daily winter means. Thus daily DMS sampling achieved at 1000 UT depicts quite well daily mean values at DDU. To avoid any bias related to the variable number of daily samplings in discussing the long-term DMS record, we will therefore consider only DMS data obtained from sampling done at 1000 UT (Figure 3).

2.4. Measurements of DMS, $DMSP_t$, and Pigments in Seawater

[18] The content of DMS and its metabolic precursor, dimethylsulfoniopropionate (DMSP) were determined in seawater samples collected in summers 2002 and 2003 during transects done from 61°S to 66°26′ S along 140°E. In 2002 samplings were carried out during cruise KH01-3 (R/V Hakuho-Maru, January 2002) [*Terazaki et al.*, 2003]

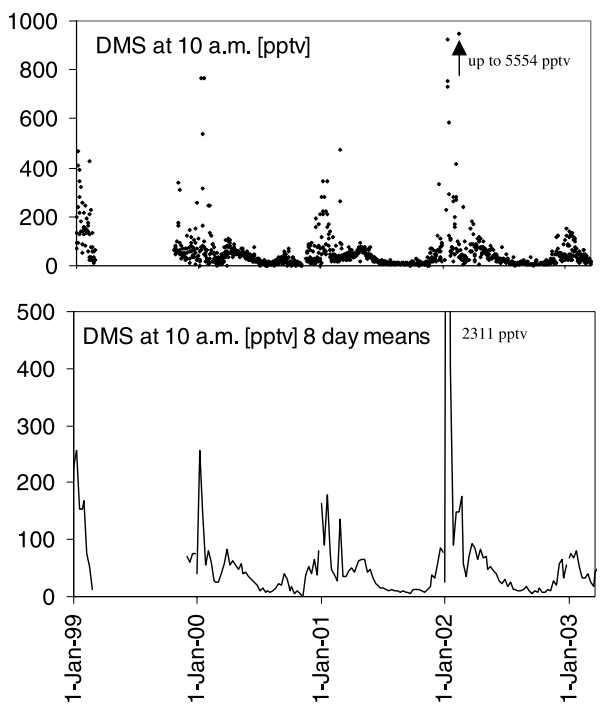

Figure 3. Corrected atmospheric DMS mixing ratios observed at 1000 UT at DDU (see section 2.3): (top) daily resolution and (bottom) 8-day averages.

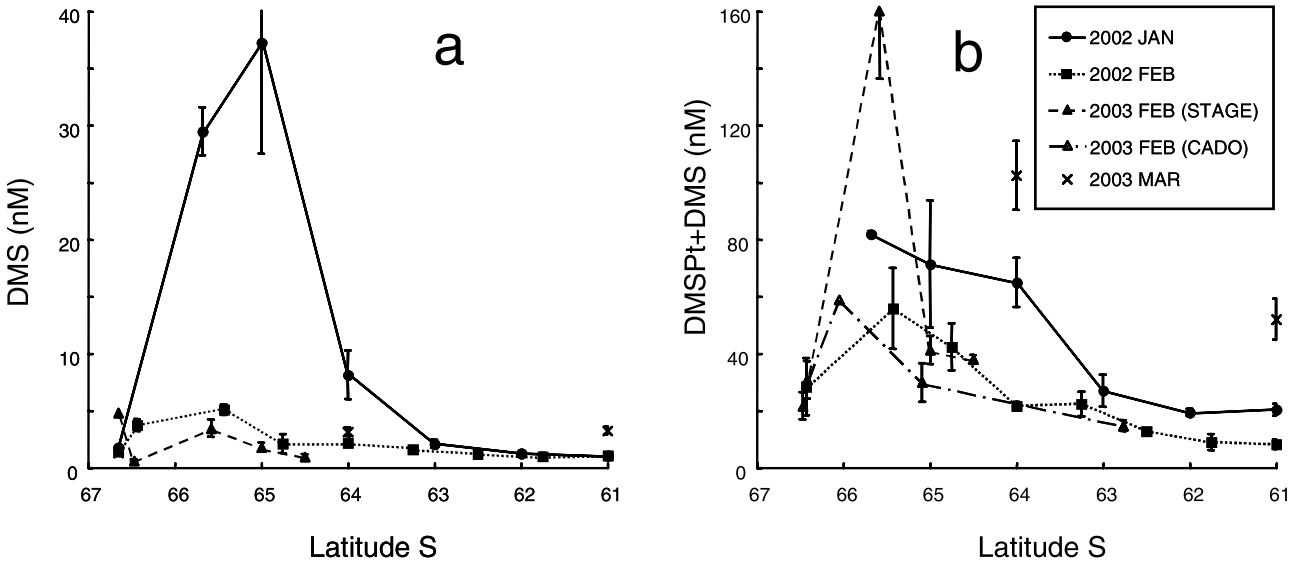

Figure 4. (a, b) DMS and (DMSPt + DMS) seawater content measured from the coast to the open sea along 140°E.

and the 43rd Japan Antarctic Research Expedition (JARE) Marine Science Cruise (R/V Tangaroa, February 2002). In summer 2003, samplings were carried out on RT/V Umitaka-Maru (February 2003) and on R/V Tangaroa chartered by JARE-44 (cruise STAGE, March 2003). Samples were collected at 10 or 11 different depths between 2 and 200 m with a rosette sampler equipped with 12 L Niskin bottles and a CTD probe (SeaBird SBE911 plus). DMS samples were transferred with glass syringes of 100 mL from Niskin bottles to avoid gas exchange. DMS was analyzed with a purge and trap device as described by *Kasamatsu et al.* [2004]. For total DMSP ($DMSP_t$) plus DMS concentration ($DMS(P)_t$), an aliquot of 4–14 mL of seawater was poured into a 30 mL serum bottle containing 4 mL of 6 M NaOH. This alkali treatment permits the cleavage of $DMSP_t$ into gaseous DMS. Serum bottles were purged with pure N_2 after storage at 4°C for at least 24 hours to complete the cleavage.

[19] Seawater samples were also collected along 140°E during the cruise CADO/OISO carried out on board R/V Marion Dufresne in February 2003 [*Beucher et al.*, 2004]. A 8 mL aliquot of unfiltered whole water taken from a rosette sampler was transferred to nonsilanated glass tubes, treated with cold alkali (200 μL of 20M NaOH), sealed with a Teflon faced septa and allowed to sit at room temperature for 2 months until samples are back to the laboratory. Then the content of a sample tube was drawn into a plastic syringe and immediately injected into a sparging device through a Teflon faced septa. Sparged samples with He for 10 min at 70 mL min^{-1} were cryotrapped on liquid N_2 in a 0.16 mm diameter FEP-Teflon loop. The trap was heated to 95°C, and its content was immediately injected onto the Poraplot Q capillary column (Chrompack). Water vapor had been previously removed using a Permapure minidryer (model MD050–72F). $DMS(P)_t$ was analyzed using a Varian 3800 gas chromatograph equipped with a Pulsed Flame Photometric Detector (PFPD). DMS was calibrated from base-treated DMSP standards (Kiadis BV, Netherlands) [*Christaki et al.*, 1996] prepared in the laboratory, in 8 mL glass tubes sealed with Teflon faced septa.

[20] Measurements of dissolved DMS in seawater beneath sea ice in winter were also occasionally performed in the vicinity of DDU (in general 3 km north of the station). After sampling in a bucket, seawater was passed through a glass fibber filter (Whatman GF/F, Ø47 mm) in a 20 mL vial filled up to prevent from DMS lost (degassing). Samples were stored at 4°C and analyzed within a few hours. The seawater samples were degassed with a 200 mL min^{-1} He flow up stream in line the Tenax sample loop maintained at −60°C.

[21] In two JARE cruises, water samples for chlorophyll *a* measurements were filtered through Whatman GF/F filters. Chlorophyll *a* was extracted in dimethylformamide [*Suzuki and Ishimaru*, 1990] for 24 h at approximately −80°C. Concentrations of chlorophyll *a* were determined onboard the ship with a model 10AU Turner Designs fluorometer using a method described by *Parsons et al.* [1984].

[22] In January and February 2002, DMS maxima of variable intensities (from 5 to 35 nM) were not observed near shore but further offshore between 65°S and 66°S (Figure 4). In February 2003, maximum DMS levels were recorded in the same area but also near-shore. The distribution of DMS(P)t further confirms the existence of important gradients from the coast to the open sea (Figure 4). Hence DMS(P)t and DMS are not homogeneously distributed in the seasonal ice zone off DDU, and only satellite estimates can provide insight into the spatiotemporal variability of DMS concentrations in the SIZ.

2.5. Chlorophyll *a* and DMS in Seawater: Field Measurements Versus Estimates From Satellite Observations

[23] The algorithm of *Belviso et al.* [2004b] was used to estimate sea-surface DMS levels from chlorophyll *a* data derived from SeaWiFS. The parameterization is based on chlorophyll *a* (from SeaWifs) and an index of the community structure of marine phytoplankton (Fp-ratio). The Fp-

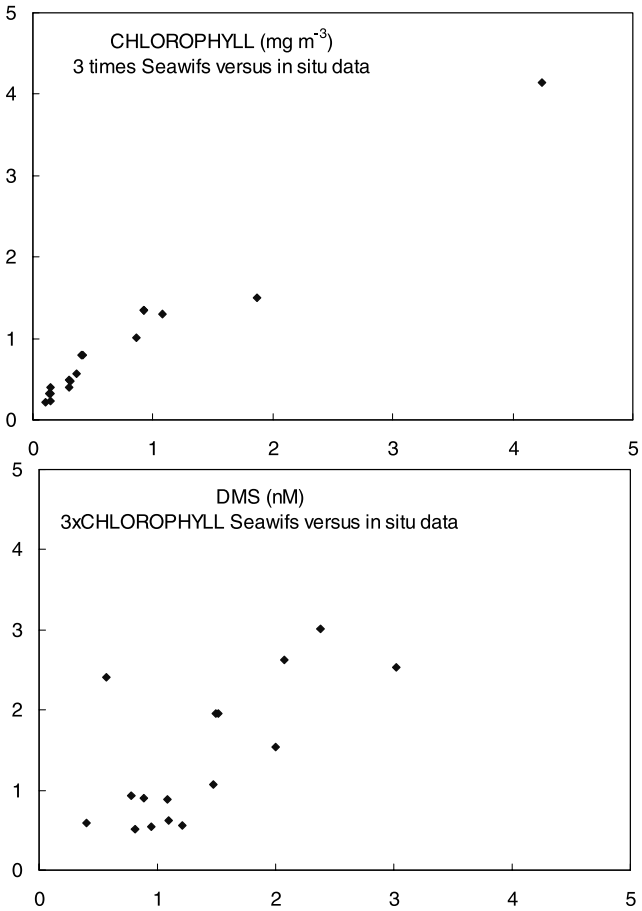

Figure 5. (top) Chlorophyll *a* in seawater (estimated from Sea-viewing Wide Field-of-view Sensor (SeaWiFS) data versus in situ measurements) and (bottom) estimated seawater DMS from SeaWiFS data versus in situ measurements, south 60°S along 140°E.

ratio represents the proportion of microphytoplankton within the whole phytoplankton community, and is determined again from the sea WiFs chlorophyll *a* content.

[24] No chlorophyll data are available either during total night (high solar zenith angle), or cloudy conditions, or sea-ice coverage. At the latitudes investigated in this work, total night never occurs and lack of data is due to the presence of sea ice or cloud. In this study we have considered monthly mean value only when satellite data cover at least 30% of the considered surface at very high latitudes (62 to 66°S) (i.e., from September–October to April) and 40% in the 58–66°S belt (i.e., from September–October to April). At grid points for which no satellite information is available owing to sea ice, a zero seawater DMS concentration was assumed in calculating average values. Since, however, the sea ice in this oceanic sector always contain large fraction of open water averages calculated in this way may be underestimated. A sensitivity test in which the zero values were discarded indicated that underestimation up to 30% is possible in spring and fall.

[25] SeaWiFS-based chlorophyll *a* levels were compared to spatially and temporally coincident in situ measurements of chlorophyll *a* carried out during the JARE transects along 140°E and 110°E in summer 2002 and 2003. As seen in Figure 5, satellite-derived chlorophyll *a* concentrations appear strongly underestimated at high southern latitudes (a factor of 3). This difference is in agreement with previous studies carried out at high latitudes (*Mitchell* [1992] along 60°W and *Hirawake et al.* [2000] along 140°E). DMS concentrations computed by applying the algorithm of *Belviso et al.* [2004b] to 3 times SeaWiFS-based chlorophyll *a* levels show a very good agreement with concomitant in situ measurements in the seasonal ice zone off DDU (Figure 5). This comparison remains, however, restricted to a short summertime period and a rather narrow oceanic sector and cannot thus be generalized to other regions of the Antarctic Ocean. Maps of monthly mean oceanic DMS levels were therefore computed for the duration of SeaWiFS observations using original and corrected (as 3 times raw data) chlorophyll *a* data. Note also that an increase by a factor of 3 of chlorophyll *a* does not lead to an increase by a factor of 3 of oceanic DMS levels, since the DMS algorithm from *Belviso et al.* [2004b] contains several nonlinear relationships and two thresholds.

3. Interannual Variability of the Atmospheric Sulfur Cycle

[26] The four sulfur-derived atmospheric species investigated in this work exhibit well-marked seasonal cycle with summer maxima. Whatever the species, winter values exhibit rather low interannual variability (see Figure 1 for MSA and $nssSO_4$, Figures 2 for DMSO, and Figure 3 for DMS). In contrast, a large interannual variability is seen in summer for DMS, and MSA, to a lesser extent for $nssSO_4$. Considering the time period over which aerosol and DMS data are available, the summer 2001–2002 clearly stands out with highest concentrations of DMS as well as MSA. Given the difference in the summer atmospheric lifetime of DMS, close to a day, compared to a few days or more for sulfur aerosol (MSA and sulfate), in the following we will investigate the cause of interannual summer variability of aerosol and DMS separately.

3.1. Interannual Variability of MSA and $nssSO_4$

[27] As seen in Figure 1, the extended year-round aerosol record (1991–2003) is consistent with data previously presented by *Jourdain and Legrand* [2002] showing well-marked summer maxima for both MSA and $nssSO_4$. Discarding the 1991–1993 years over which a significant impact of the 1991 Pinatubo volcanic eruption on sulfate level was identified [*Legrand and Wagenbach*, 1999], rather similar winter levels (May–September) are observed over the whole record (2 ± 1 ng m^{-3} for MSA, 23 ± 12 ng m^{-3} for $nssSO_4$). In summer (December–February) a larger interannual variability is observed with low values in 1997–1998, 2000–2001, and 2002–2003 (35 ng m^{-3} of MSA, 182 ng m^{-3} of $nssSO_4$) and high values in 1996–1997, 1999–2000, and 2001–2002 (73 ng m^{-3} of MSA, 247 ng m^{-3} of $nssSO_4$). The atmospheric level of MSA and $nssSO_4$ at coastal Antarctic sites was already discussed by *Minikin et al.* [1998], who concluded that the strong seasonality is driven by the summer recovery of a dominant marine biogenic sulfur source (DMS) following the sea-ice retreat. While DMS emissions mainly act in summer, in

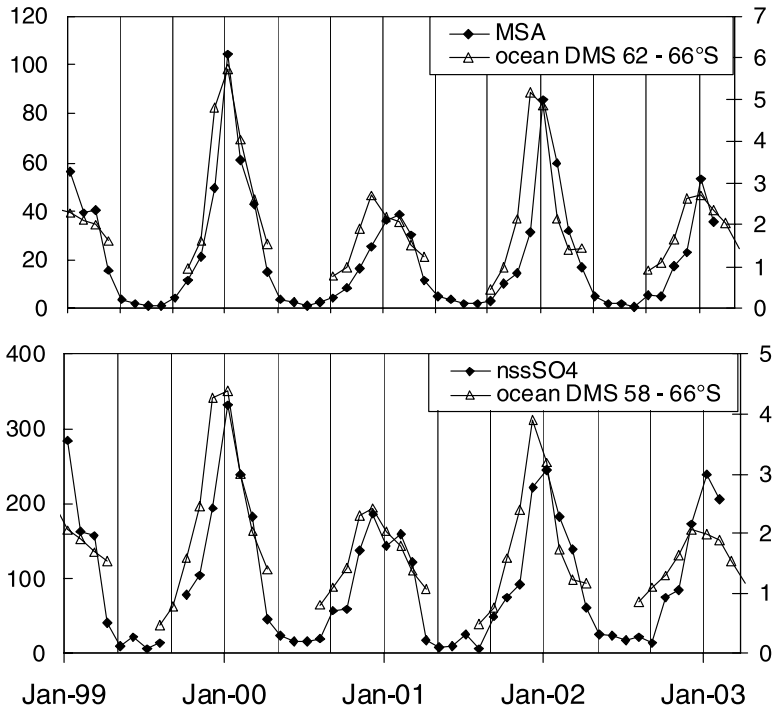

Figure 6. Comparison between monthly mean atmospheric concentrations of MSA and $nssSO_4$ at DDU (left scale in ng m^{-3}) and seawater DMS contents in the austral ocean (60–160°E) estimated from corrected (see section 2.5) SeaWiFS data (right scale in nM).

winter other $nssSO_4$ sources might be significant (stratospheric input and/or long range transport from continents) [*Minikin et al.*, 1998] in addition to possibly a local oxidation of DMS by oxidants like NO_3 or O_3 [*Jourdain and Legrand*, 2002].

[28] Since the only relevant source of sulfur species at coastal Antarctic in summer is the marine biota, possible origins of the interannual summer changes would be due to changes of either DMS sea-to-air flux or atmospheric oxidants. The DMS sea air flux depends on oceanic DMS concentrations and the transfer velocity coefficient (kw), kw being a strong nonlinear function of wind speed. On the basis of a 3-D chemistry-transport model, *Sciare et al.* [2000] investigated the cause of observed interannual variability of atmospheric DMS over 10 years at Amsterdam Island (Indian Ocean, 37°S and 77°E). The authors concluded that the large year to year variability of the seasonal atmospheric DMS cycle can be explained neither by changes of meteorological parameters controlling the kw factor nor by changes of atmospheric oxidants, but only by changes in oceanic DMS concentrations. Similarly, *Kettle and Andreae* [2000] estimated, on the basis of 15-year meteorological data, that interannual variations of wind speed and sea surface temperature induce changes of less than 10% in the DMS sea air flux. They suggested that greater interannual variations of sea air flux are caused by variations of seawater concentrations.

[29] Given the preceding conclusion that meteorological conditions (insulation, temperature, and wind speed) weakly impact interannual summer variability of sea air DMS flux and atmospheric oxidation of DMS into aerosol we examine in the following how far interannual variations of seawater DMS modulate atmospheric MSA and $nssSO_4$ level. Seawater DMS level derived from SeaWiFS data (corrected and original) for different oceanic area were matched with atmospheric $nssSO_4$ and MSA records at DDU. In view of zonal wind and atmospheric lifetime of MSA and $nssSO_4$ (a few days) a large longitudinal sector (60–160°E) was here considered. As seen in Figure 6 high levels of MSA, to a lesser extent $nssSO_4$, in summers 1999–2000 and 2001–2002 compared to the three other summers are clearly seen in seawater DMS levels estimated from corrected SeaWiFS data. Whatever the used SeaWiFs data (corrected or original), atmospheric MSA levels at DDU tend to co-vary with the seawater DMS level averaged over the sector south of 62°S. A better match between oceanic DMS and the relatively weak interannual variations of atmospheric $nssSO_4$ at DDU is obtained when oceanic area located further north (i.e., latitudes up to 58°S) is considered. Such a difference in source regions influencing the two aerosol species may be due to the fact that it needs more time to produce sulfate (via SO_2) than MSA (via DMSO) from DMS [*Davis et al.*, 1998; *Legrand et al.*, 2001]. This finding is also consistent with the conclusion drawn by *Minikin et al.* [1998] from records gained at several coastal Antarctic sites. In this last study the interannual summer variability was not investigated versus chlorophyll since available data from satellite Nimbus 7 stopped in 1986 (i.e., several years before the start of aerosol record at investigated sites). Instead, authors scrutinized the timing of mean seasonal cycle of MSA and $nssSO_4$ with monthly mean chlorophyll data available from Nimbus 7 between 1978 and 1986. They observed a larger increase for MSA than $nssSO_4$ from November to January which coincides with a

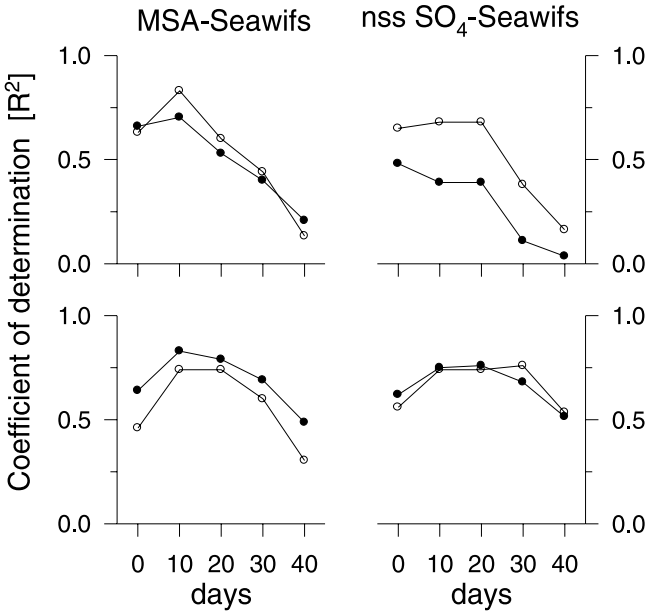

Figure 7. Coefficients of determination (R^2) of linear regressions between seawater DMS estimated from SeaWiFS and atmospheric (left) MSA records at DDU over 1999–2003 and (right) $nssSO_4$ records at DDU over 1999–2003. Correlations were made considering (top) original SeaWiFS data as well as (bottom) corrected ones. Open circles refer to full summer months (November–February), and solid circles refer to all months over which satellite data were available (August–April for $nssSO_4$ and September–April for MSA).

large increase of chlorophyll *a* south of 60°S. However, if regions located farther north are considered, the increase of chlorophyll *a* is weaker and similar to sulfate change. Note that such a difference in the seasonality of MSA and $nssSO_4$ is here confirmed by the 1999–2003 record with a mean increase of MSA from November to January of 4.4 instead of 2.3 for $nssSO_4$ (Figure 6).

[30] A detailed examination of correlations between SeaWiFS-derived data and atmospheric aerosol record at DDU was done by examining the correlation coefficient (R^2) of linear regressions and considering a potential time lag (from 0 to 40 days) between seawater DMS levels and atmospheric DMS by-products (Figure 7). Whatever the considered time periods (November–February or September–April), the correlation is very good for MSA and reaches a maximum for a lag time of 10 days (R^2 ranging between 0.7 and 0.83). For $nssSO_4$ both a reduction of the time period to November–February and the use of corrected SeaWiFS data strongly improve the correlation, which reaches a maximum ($R^2 = 0.75$) with a lag time of 10–20 days (Figure 7). The order of magnitude of these delays as well as the fact that the lag is a bit larger for $nssSO_4$ than for MSA is rather consistent with time needed for air-sea exchange, atmospheric transport and oxidation processes between the source region and the DDU site.

3.2. Interannual Variability of DMS

[31] Mean winter DMS levels (June–October) exhibit rather constant values at DDU (from 13 pptv in 2001 to 16 pptv in 2002). A far larger interannual variability is observed for the summer maximum in January. During summer 2002, exceptionally high daily DMS values (up to 5000 pptv) were observed 12 and 16 January and raise the monthly mean value by more than a factor of 2 (800 pptv instead of 337 pptv). Owing to clouds, no satellite data were available for these few days of extreme DMS levels, but on 2 January a very high chlorophyll level (up to 20 mg m^{-3}, 36 nM of DMS) was detected by the satellite in the vicinity of DDU, which may be responsible for this extreme DMS events during the first part of January 2002. *Jourdain and Legrand* [2001] have already observed a sudden increase of DMS level in December 1998 (up to 3000 pptv) coinciding with arrival of air masses from open ocean and extremely high DMS (60 nM) concentrations in the ocean near DDU. Excluding these 2 days of extreme values, the mean January DMS level at DDU is of 170 ± 180 pptv between 1999 and 2003. During an intensive campaign, performed in January–February 1994 at Palmer Station (64° 46′S, 64° 04′W), *Berresheim et al.* [1998] observed a mean atmospheric DMS mixing ratio of 120 pptv. This mean January–February level is in the range of values observed at DDU (from 60 pptv in 2003 to 244 pptv in 2002).

[32] The DMS value in January 2002 is more than 3 times higher than those in January 2000 and 2003 (Figure 8). This interannual summer variability is thus even higher than the one already pointed out for MSA (section 3.1).

[33] The high daily variability of atmospheric DMS was already discussed by *Jourdain and Legrand* [2001] in relation with very different atmospheric regimes taking place at DDU: (1) katabatic wind bringing continental air from inland to the site, (2) low-pressure systems passing offshore DDU bringing marine air traveling along the margin ice sheets area for a few hours to a few days (tangential air masses), and (3) air masses directly advected from the open ocean (marine air masses). Since the lifetime of DMS is limited to a few days in coastal Antarctic regions [*Berresheim et al.*, 1998; *Legrand et al.*, 2001], atmospheric levels will be strongly controlled by rather local emissions compared to regions influencing the atmospheric budget of MSA and $nssSO_4$. Therefore the rather high daily variability of DMS compared to MSA and $nssSO_4$ observed during summer is not surprising and the DMS atmospheric record at DDU was compared with the smallest reliable area available in SeaWiFS data (an area of 72,000 km^2 located in the northern vicinity of DDU, 138–142°E and 64–66°S). To increase the significance of comparison we exclusively considered atmospheric DMS levels for days during which the SeaWiFS satellite saw more than ~10% of the area of concern from November to April (i.e., 53% of days) and days corresponding to marine and marine plus tangential regimes (i.e., 32% and 84% in summer and 16% and 54% in autumn, respectively). As seen in Figure 8 (for the example of corrected SeaWiFs data), the high atmospheric DMS value in January 2002 is clearly seen in the seawater DMS series. Most of time the absolute atmospheric DMS maximum in January is seen in seawater DMS estimated from SeaWiFS (whatever corrected or original data are used), but the correlation ($R^2 < 0.55$, not shown) is systematically weaker than those obtained when comparing MSA or $nssSO_4$ with seawater data. This may be partly because the seasonal cycle of atmospheric DMS is characterized by

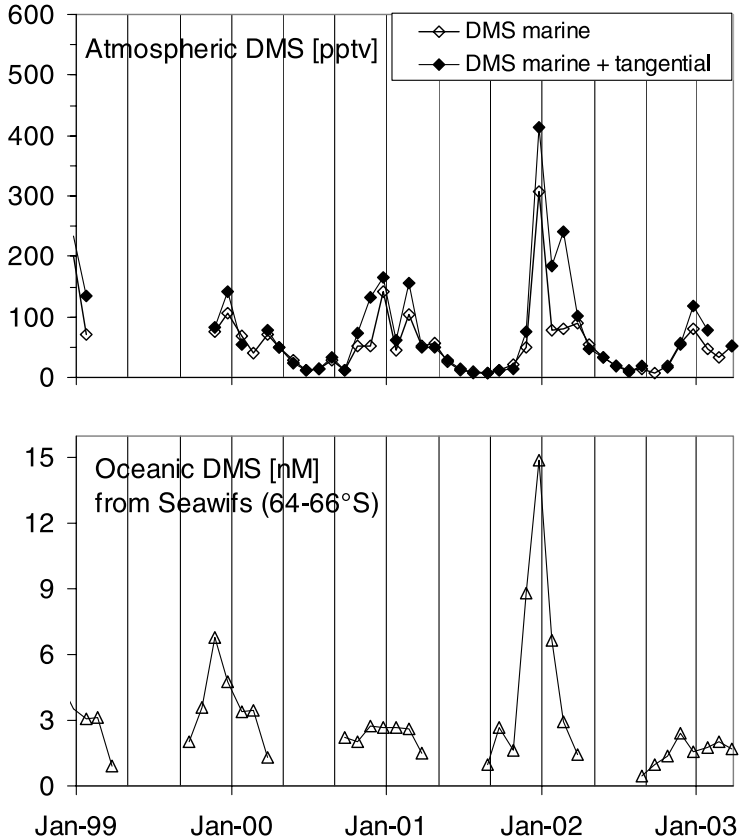

Figure 8. Comparison between (top) monthly mean atmospheric mixing ratios of DMS observed at DDU considering marine and marine plus tangential air masses and (bottom) seawater DMS concentrations in the austral ocean (138–142°E) estimated from corrected (see section 2.5) SeaWiFS data.

an absolute maximum in midsummer (January) followed by a secondary maximum around April (Figure 3, see also discussion in section 4), which is not related to seawater DMS change (Figure 8). Contrarily to what was observed with MSA and $nssSO_4$ the correlation coefficient between atmospheric and seawater DMS is, as expected, maximum without any time lag.

4. Discussion of Reliability of Seawater DMS Data

[34] The derived seawater DMS content between 64 and 66°S in January range from 2.5 nM using original SeaWiFS data and 5.5 nM using corrected ones. These values are in the order of magnitude of those measured by *Berresheim et al.* [1998] in the vicinity of Palmer (1.9 ± 0.8 nM). Similarly a mean seawater DMS value was simulated for eastern Antarctic sea-ice zone in January (2.9 nM) by *Gabric et al.* [2003] or measured (7.9 nM) by *Curran and Jones* [2000]. In contrast a far higher seawater DMS content was simulated at 65°S in January (~ 25 nM) by *Kloster et al.* [2006] using a marine ocean-atmosphere model in agreement with the climatological sea surface DMS concentration from *Kettle and Andreae* [2000].

[35] The seasonal cycle of atmospheric DMS is characterized by an absolute maximum in January followed by a secondary maximum around April (from March to May, depending of the year, Figure 3). Since this second maximum in fall is not seen in seawater DMS content, we also examine the seasonality of the sea-to-air DMS flux (Table 2). The sea-to-air DMS fluxes were calculated as the product of the sea-to-air DMS transfer velocity (kw) and the seawater DMS content estimated from both corrected and original SeaWiFS data. Among existing formulations of kw [e.g., *Wanninkhof*, 1992; *Nightingale et al.*, 2000; *Liss and Merlivat*, 1986] the one of *Liss and Merlivat* [1986] was here used because it has already produced excellent estimates of DMS fluxes in previous studies dealing with the southern ocean regions [*Ayers et al.*, 1995; *Sciare et al.*, 2000; *Gabric et al.*, 2003]. To calculate kw, sea surface temperature blended from ship and buoy over the 1950–1979 period [*Reynolds and Smith*, 1994] and wind speed from ECMWF analyses over 1980–1989 [*Trenberth et al.*, 1989] were used. The Schmidt numbers were calculated following *Saltzman et al.* [1993]. As seen in Table 2, although kw values are higher from February to April than in January, the enhancement is too weak to provide a secondary maximum of the sea-to-air fluxes in late summer. One possibility is that the secondary maximum in late summer results from an increased DMS atmospheric lifetime resulting from a drop of the oxidant concentrations at that period [*Cosme et al.*, 2002]. In addition, the longer

Table 2. Compilation of Monthly Mean DMS Sea Air Flux and Related Parameters Around DDU and in East Antarctic Southern Ocean

	DDU Region (138–142°E, 64–66°S)[a]					East Antarctic Southern Ocean (125–140°E, 60–65°S)[b]	
Month	Sea DMS, nM	Sea DMS_{cor}, nM	Kw, cm h^{-1}	Sea Air Flux, μmol m^{-2} d^{-1}	Sea Air $Flux_{cor}$, μmol m^{-2} d^{-1}	Sea DMS, nM	Sea Air Flux, μmol m^{-2} d^{-1}
Sep	0.6 ± 0.3	0.7 ± 0.4	8.3	1.2 ± 0.5	1.4 ± 0.7	0.9	1.7
Oct	0.7 ± 0.3	2.0 ± 0.7	6.0	1.0 ± 0.4	2.9 ± 1.0	1.0	2.0
Nov	1.2 ± 0.2	2.1 ± 1.1	4.9	1.5 ± 0.2	2.5 ± 1.0	1.4	2.3
Dec	2.3 ± 0.9	5.2 ± 3.3	5.0	2.7 ± 1.1	6.3 ± 3.8	2.0	3.5
Jan	2.3 ± 1.8	5.5 ± 5.4	5.7	3.2 ± 2.5	7.4 ± 7.3	2.9	4.7
Feb	1.6 ± 0.8	3.5 ± 1.9	7.3	2.8 ± 1.4	6.1 ± 3.2	3.6	5.5
Mar	1.4 ± 0.5	2.8 ± 0.5	7.4	2.4 ± 0.8	5.0 ± 1.0	3.6	6.1
Apr	0.8 ± 0.3	1.4 ± 0.3	7.2	1.4 ± 0.5	2.4 ± 0.5	3.0	6.5
Jun–Aug[c]	0.6 ± 0.3	0.6 ± 0.3	7.0	0.9 ± 0.5	0.9 ± 0.5	1.3	2.9

[a]Data are from 1999–2003 (this study).
[b]Data are from 1997–2001 [*Gabric et al.*, 2003].
[c]Data are based on nine DMS analyses made in seawater samples collected offshore DDU under the sea-ice cover in winters 2001, 2003, and 2003.

DMS lifetime may also permit contributions of DMS blooms having occurred over other high-latitude oceanic sectors. Such events were observed at least until end of April in the Drake Passage, offshore the Antarctic peninsula [*Berresheim*, 1987].

[36] On the basis of a marine production model of DMS and a GCM model, *Gabric et al.* [2003] predicted rather similar (within a factor of 2) summer DMS flux between 60 and 65°S than the SeaWiFS one but with an absolute maximum in April (Table 2). Whereas their simulations predicted highest chlorophyll *a* content in December–January, in agreement with SeaWiFS data, they simulated a DMS seawater peak end of February succeeding the phytoplankton peak by over a month. They suggested that the maximum sea-to-air flux in April is due to combination of changing wind speed, sea-surface temperature and oceanic mixed layer depth.

[37] Inconsistencies between atmospheric DMS levels at DDU and simulated seawater DMS levels (or sea-to-air fluxes) available in the literature exist not only with regard to the seasonal cycle but also for summer values. The consistency between observed atmospheric DMS level and seawater DMS (or sea-to-air fluxes) in the vicinity of DDU can be examined by using a simple box model for which the time-dependent concentration of DMS, undergoing surface emission, atmospheric chemical conversion, and ventilation to the free troposphere (but not dry deposition), is calculated as following:

$$d[DMS]/dt = F_{DMS}/H + S_{DMS} + V_{DMS}/H. \quad (4)$$

H is the height of the boundary layer, F_{DMS} the sea to air flux, S_{DMS} the rate of chemical oxidation of DMS, and V_{DMS} the boundary layer flux into the troposphere of DMS.

[38] In calculations, S_{DMS} is only related to the oxidation of DMS by OH radicals; that is,

$$S_{DMS} = -k[OH][DMS], \quad (5)$$

where k is the appropriate rate constant taken as 11.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 273K (as the sum of abstraction and addition pathways) [*Atkinson et al.*, 1997] (see also the review from *Barnes et al.* [2006]) and applied to a mean daily [OH] of 3.4×10^5 radicals cm^{-3} in January as simulated by the three-dimensional transport and chemistry model IMAGE [*Pham et al.*, 1995] for 1 km elevation at 66°S.

[39] The V_{DMS} term is set as constant adapted from measurements of the vertical concentration distribution of DMS made over the southern ocean of Australia [*Berresheim et al.*, 1990]:

$$V_{DMS} = 0.085[DMS](3000 - H)/H\ . \quad (6)$$

The DMS sea air flux was calculated by using a boundary layer height (H) as the one observed at Amsterdam Island [*Sciare et al.*, 2000] from September to April (1360 ± 85 m).

[40] Given the fact that DDU is located at the border of the considered oceanic sector, the mean atmospheric DMS level derived over individual summers using equations 4 to 6 and either the original SeaWiFS data (113 ± 50 pptv) or corrected ones (240 ± 135 pptv) are in the range of atmospheric observations made at DDU (124 ± 51 pptv for marine DMS and 91 ± 34 pptv for marine plus tangential DMS). In terms of sea-to-air flux whereas our estimation are consistent with those from *Gabric et al.* [2003] it is clear that if applied to seawater DMS levels derived by *Kloster et al.* [2006] or *Kettle and Andreae* [2000] would lead to sea-to-air fluxes at least 4 times higher and consequently DMS atmospheric mixing ratios in the range of 1000 pptv.

5. Role of Sea Ice on the Sulfur Cycle

[41] Preceding discussions indicate that the strong maximum of atmospheric sulfur species levels observed at DDU is mainly driven by the strong seasonal cycle in phytoplankton at high southern latitudes with highest biomass achieved at that time. Several recent studies suggested that apart the amount of phytoplankton, the sea-ice extent and melting of sea ice also influences oceanic and atmospheric DMS levels. These findings are discussed in the following paragraphs.

[42] From the observation of an aerosol optical depth maximum preceding the recovery of chlorophyll *a* by two months in early spring south of 60°S in the east Antarctic sector, *Gabric et al.* [2005] postulated that sea-ice melting and associated release of sea-ice algae is important for the sulfur aerosol budget. Our finding of a good correlation between the seasonal cycle of chlorophyll *a* and sulfur

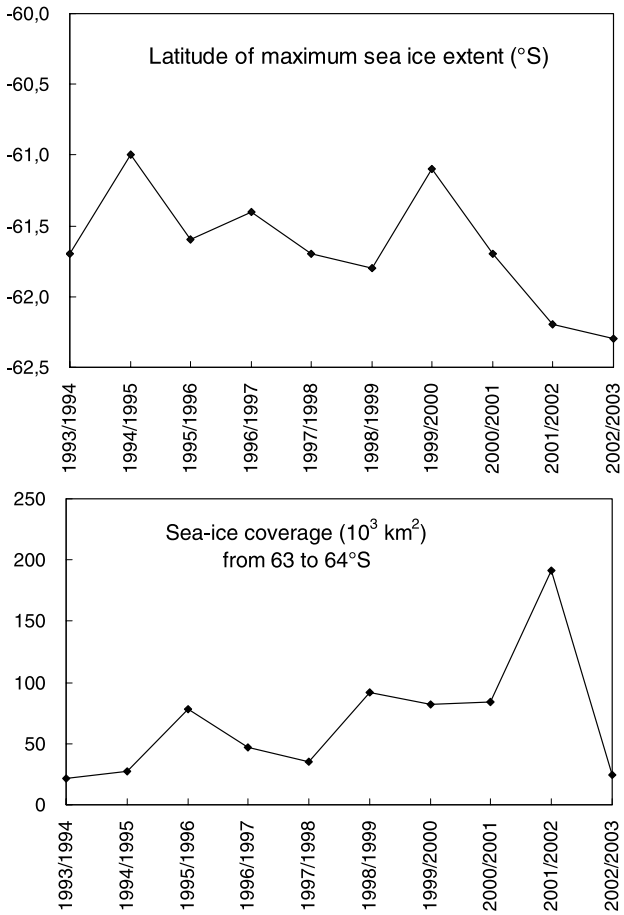

Figure 9. Interannual variations of sea-ice indices (138–142°E). (top) Latitude of maximum sea-ice extent (the coverage area by more than 15% of sea ice) and (bottom) the coverage area by sea ice of less than 50% in concentration between 63° and 64°S during the period from the day of the maximum ice extent to 31 January.

aerosols characterized by an absolute maxima in January (section 3.1) and the absence of an increase in early spring detected in the atmospheric records does not support the idea that a significant sea-ice melting sulfur source exists in early spring in the east Antarctic sector south of 60°S. Since the study of *Gabric et al.* [2005] only considered the aerosol optical depth without concurrent study of aerosol chemistry we cannot exclude that sea-salt input might be responsible for this early spring AOD peak independently of a biogenic sulphur source.

[43] The positive correlation between MSA in a coastal Antarctic ice core and 22 years satellite-derived sea-ice extent for the 80–140°E sector found by *Curran et al.* [2003] can be directly tested by checking the DDU atmospheric records and several sea-ice indices. In Figure 9 we report the latitude of the annual maximum extent of sea ice (concentration of sea ice of more than 15%) between 138° and 142°E [*Cavalieri*, 1992; *Parkinson et al.*, 1999]. Over the 1998–2003 time period, the sea-ice extent was maximum in winter 1999 and far more limited during winters 2001 and 2002. Therefore the high atmospheric DMS level seen at DDU in January 2002 cannot be attributed to a large sea-ice extent during the preceding winter. One possibility for this discrepancy between atmospheric DMS observations and the MSA ice core study from *Curran et al.* [2003] would be related the longer atmospheric lifetime of MSA with respect to DMS. However, the MSA atmospheric record shows high values in January 2000 and January 2002 which do not coincide with larger sea-ice extension over preceding winters (Figure 9) and over the 1994–2003 time period the correlation between MSA at DDU and maximum sea-ice extent remains very poor ($R^2 = 0.05$).

[44] Similarly, an absence of correlation between annual chlorophyll *a* south of 64°S along 140°E and sea-ice indices was already found by *Hirawake et al.* [2005] over 1998–2003 with in particular no relation between sea-ice extent and the large bloom observed in January 2002. In contrast, the latter authors found a good correlation between chlorophyll *a* and the coverage area by sea ice of less than 50% in concentration between 63 and 64°S during the period from the day of the maximum ice extent to 31 January. From that authors concluded that the heavy ice pack present forms an eddy-like distribution between 63 and 64°S which contributes to the sea ice scattering to smaller pieces and melting by enhancement of received insolation, and the melt water acts on water column stability concerned phytoplankton growth. Following *Hirawake et al.* [2005], we report in Figure 9 the coverage area by sea ice of less than 50% in concentration between 63 and 64°S during the period from the day of the maximum ice extent to 31 January. Over the 1998–2003 time period, summers 2001–2002 and 2002–2003 stand out with high and low sea-ice coverage between 63 and 64°S, respectively, in agreement with the highest and lowest value of atmospheric DMS level at DDU (see Figure 8).

6. Summary

[45] The year-round atmospheric records of sulfur-derived aerosol (1991–2003), and of DMS (1999–2003), gained at DDU indicate large interannual changes in summer time. From 1991 to 2003, MSA and $nssSO_4$ summer values were high in 1996–1997, 1999–2000, and 2001–2002 (73 ng m^{-3} of MSA, 247 ng m^{-3} of $nssSO_4$) and low in 1997–1998, 2000–2001, and 2002–2003 (35 ng m^{-3} of MSA, 182 ng m^{-3} of $nssSO_4$). Consistently with the aerosol record, over the 1999–2003 time period the DMS value in January 2002 is more than 3 times higher than in January 2003.

[46] Comparison of satellite data with spatially and temporally coincident in situ measurements of chlorophyll *a*, carried out during the JARE transects along 140°E and 110°E, clearly indicates that satellite-derived chlorophyll *a* concentrations are underestimated by a factor of 3 at high southern latitudes. DMS oceanic concentrations computed by applying the algorithm of *Belviso et al.* [2004b] to 3 times SeaWiFS-chlorophyll *a* raw data show a very good agreement with concomitant in situ measurements in the seasonal ice zone offshore DDU.

[47] On this basis, seawater DMS levels estimated from SeaWiFS data for different oceanic areas were matched with atmospheric DMS, $nssSO_4$ and MSA records at DDU over the 1999–2003 time period. The DMS atmospheric record at DDU co-varies rather well with oceanic DMS levels of an area of 72,000 km^2 located in the northern vicinity of DDU,

138–142°E and 64–66°S. Atmospheric MSA levels tend to co-vary with the seawater DMS level-averaged over the sector (60–160°E) south of 62°S. A better match between oceanic DMS and the relatively weak interannual variations of atmospheric $nssSO_4$ at DDU is obtained when oceanic area located further north (i.e., latitudes up to 58°S) is considered. For all sulfur species, January 2002 stands out with high values that are clearly depicted by estimated oceanic DMS levels. Furthermore, it has to be emphasized that atmospheric DMS levels at DDU are more consistent with high-latitude oceanic concentrations in the range of 2 to 6 nM in summer (at least in the east Antarctic sector) than those previously suggested in the range of 25 nM.

[48] Finally, atmospheric records at DDU do not confirm that the sulfur cycle in this region is simply modulated by the amount of sea ice formed in winter and retreating in summer. The relation between sea ice, chlorophyll *a* and the sulfur cycle appears to be more complex than previously assumed, and at least for atmospheric DMS concentrations seem to be influenced by the coverage of sea-ice pack in the Antarctic divergence zone.

[49] **Acknowledgments.** National financial support and field logistic supplies for over winter and summer campaigns at DDU were provided by Institut Paul Emile Victor (IPEV) within the program 414. This work was also partly funded by the Centre National de la Recherche Scientifique (CNRS-INSU) within the program PNCA. We are grateful to the overwinter staff who took care of measurements at DDU (1999–2002). Thanks a lot to Makoto Terazaki, Hiroshi Ogawa, Takashi Ishimaru, Tsuneo Odate, and the crew of the R/V *Hakuho-Maru,* R/V *Tangaroa,* and RT/V *Umitaka-Maru* for their marvelous hospitality in the Southern Ocean. Finally, we would like to thank the two anonymous reviewers of the manuscript for their helpful comments.

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