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Biogenic sulfur compounds in seawater and the atmosphere of the Antarctic region

By R. STAUBES and H.-W. GEORGII, *Institute of Meteorology and Geophysics, Johann Wolfgang Goethe University, 6000 Frankfurt/Main 1, Germany*

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ABSTRACT

Shipboard measurements of dimethyl sulfide (DMS), carbonyl sulfide (COS) and carbon disulfide (CS_2) in seawater and the marine boundary layer were performed during a cruise between Punta Arenas (Chile) and Cape Town (South Africa) through the Weddell Sea in November/December 1990. The DMS concentrations in seawater averaged to 71 ngS/l, atmospheric DMS mixing ratios showed a range between 2 and 1048 pptv. In the Weddell Sea where DMS mixing ratios as low as 24 pptv on the average were observed, the extensive ice cover seemed to minimize the gas exchange between seawater and the overlying atmosphere. The COS levels in seawater showed a mean of 3.5 ngS/l with minor variability. Atmospheric COS mixing ratios measured over the Weddell Sea averaged to 453 ± 43 pptv. In contrast, COS concentrations during advection processes of continental air masses over the Drake Passage were evidently higher with a mean of 628 ± 42 pptv. The concentrations of CS_2 in the remote marine boundary layer were below the detection limit of 7 pptv, with enhanced concentrations of about 35 pptv observed in air masses influenced by continental inputs. CS_2 values in surface seawater were mostly below the detection limit of 0.43 ngS/l with few exceptions revealing CS_2 values between 0.48 and 1.43 ngS/l. In 91% of all seawater samples taken during this cruise CS_2 were not found in detectable concentrations.

1. Introduction

The chemistry of biogenic sulfur compounds and their importance to regional pollution and global climatic effects is currently the subject of much interest and uncertainty. To determine the perturbations of the natural sulfur cycle caused by anthropogenic sulfur emissions it is necessary to calculate background concentrations of biologically produced sulfur compounds.

The dominant natural sulfur source is the oceanic emission of biogenic sulfur compounds which constitutes a major portion of the total global atmospheric sulfur burden. Measurements in different regions of the World's oceans have shown that DMS is the predominant form of biogenic sulfur transferred from the ocean to the atmosphere (Andreae, 1986; Bates et al., 1987). DMS is produced in surface seawater by metabolic processes in certain phytoplankton species (Turner et al., 1988; Keller et al., 1989; Leck et al., 1990). This is the reason for the large variations of the DMS concentrations observed in surface seawater and thus the difficulty in calculating global annual DMS fluxes from the World's oceans. Moreover, large uncertainties are caused by the lack of measurements from Polar Regions. Andreae and Raemdonck (1983) estimated a flux of 40 ± 20 TgS(DMS)/yr into the atmosphere which accounts for 80–95% of the gaseous sulfur flux from the oceans and about one half of the estimated natural sulfur flux per year. Emitted into the atmosphere DMS is rapidly oxidized by OH and NO_3 radicals to SO_2, methane sulfonic acid (MSA) and, via SO_2 oxidation, to non-sea salt sulfate as major reaction products (Grosjean and Lewis, 1982; Bürgermeister and Georgii, 1991). These compounds are important factors in cloud chemistry and global climate as contributors to cloud condensation nuclei (Charlson et al., 1987).

Quite recently, a further effect of a biogenic sulfur compound on global climate is discussed: the

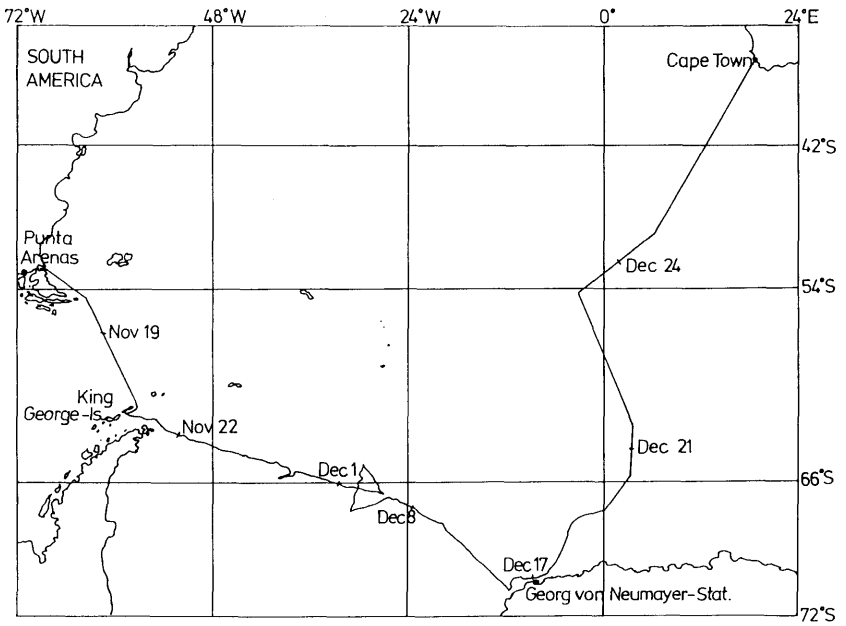

Fig. 1. Cruise track of the R/V "Polarstern" Expedition from Punta Arenas (Chile) to Cape Town (South Africa) in 1990.

enhancement of the stratospheric sulfate aerosol layer caused by an increase of the atmospheric COS concentration. Due to its long tropospheric lifetime of 2–7 years (Johnson and Harrison, 1986) COS diffuses into the stratosphere, where it is photolyzed and oxidized to sulfate. Turco et al. (1980) have speculated that anthropogenic emissions of COS may cause measurable changes in the Earth's climate within the next century. Recent measurements of atmospheric COS showed an interhemispheric ratio of 1.05 between the northern and the southern hemisphere (Khalil and Rasmussen, 1984), whereas Bingemer et al. (1990) found a significant increase of the tropospheric COS concentrations in the northern hemisphere compared to the southern hemisphere during measurements over the Atlantic Ocean in 1987. Besides anthropogenic COS emissions due to fossil fuel burning and industrial release (Khalil and Rasmussen, 1984) atmospheric COS is also emitted from natural sources. One, if not the most important natural COS source is its emission from seawater. Andreae (1985) assumed a flux of 0.4 ± 0.2 TgS(COS)/yr from the global ocean surface which accounts for 35–50% of the whole natural COS flux. COS is considered to be produced in seawater by photolysis of yet unidentified organic matter (Ferek and Andreae, 1984). Measurements of CS_2 in seawater (Kim and Andreae, 1987; Cooper and Saltzman, 1991) indicate that the oceans are a minor source of atmospheric CS_2. The oxidation of atmospheric CS_2 to COS is considered to be a further source of COS to the atmosphere.

In this paper, we report on measurements performed during a cruise with the German research vessel "Polarstern" from Punta Arenas (Chile) to Cape Town (South Africa) through the Weddell Sea in November/December 1990. The cruise track is given in Fig. 1. The concentrations of DMS, COS and CS_2 were determined simultaneously in surface seawater and the overlying atmosphere.

2. Experimental

Air concentrations of DMS, COS and CS_2 were measured 4 times a day at 6-h intervals. The samples were collected at the foremost edge of the upper deck of the ship, about 21 m above the sea level. To prevent contamination of the samples due to an influence of sources located on the ship sam-

ples were taken only when a wind vane indicated wind from the forward sector. The air sampled was enriched cryogenically at the temperature of liquid argon (−185°C) in U-shaped glass sample loops sealed with high vacuum glass valves. Oxidants were removed from the sample by using glass tubes filled with 5% Na_2CO_3 on Anakrom C22 upstream of the cryotraps. The efficiency of these scrubber tubes has been tested during the field measurements by DMS standard additions to natural air. The recovery proved to be $95.2 \pm 7.7\%$ ($n = 16$). Scrubbers were replaced when at most 10 liters of air had passed through them. Two independent sampling channels were used in parallel to allow either the collection of duplicate DMS samples operated with oxidant scrubbers and duplicate COS and CS_2 samples which were taken without prefilters. Sample volumes were generally in the range of 2.5–7.5 l with a flow rate of 0.5 l min^{-1}.

Simultaneously to the determination of atmospheric DMS and COS the concentrations of these compounds in surface seawater has been examined. Seawater was obtained from the ship's continuous sea water pumping system. Samples were injected into a gas stripping column after passing through a glass fiber filter to remove algal cells. The removal of algal cells from seawater was necessary to prevent a DMS enhancement in the sample due to the breakup of organisms in the glass column as reported by Turner et al. (1990). A glass frit on the bottom of the column allows the sulfur-free purge gas nitrogen to bubble through the sampled water. Thus the volatile compounds are stripped from the seawater into the nitrogen stream which subsequently passes through a cryotrap immersed in liquid argon to enrich the sulfur compounds. No detectable sulfur blanks had been shown when reanalyzing purged seawater. To avoid storage artifacts surface seawater samples were analyzed immediately after collection.

Analysis of both air and seawater samples were performed using a gaschromatographic system equipped with a flame photometric detector. Baseline separation of the sulfur gases in particular CO_2 (retention time: 0.49 min) and COS (r.t.: 1.38 min) as well as DMS (r.t.: 5.95 min) and CS_2 (r.t.: 6.76 min) was achieved using a $4.6' \times 1/8''$ Carbopack BHT 100 column packed in Teflon (Supelco Inc.). The temperature program of the column started at 40°C heating up to 80°C at a rate of 25°C/min. The system was calibrated by using gravimetrically determined permeation tubes. The sensitivity was 3.5 pptv of DMS and COS, respectively, and 7 pptv CS_2 in atmospheric samples (sample volume: 7.5 l) and between 0.26 and 0.43 ngS/l of COS, DMS and CS_2 in seawater samples (sample volume: 50 ml). The precision of the method is 6.4%. Further details on the analytical system have been described elsewhere (Staubes et al., 1989). From each seawater sample, 200 ml were preserved by adding 4 ml of a neutralized formaldehyde solution, from which cell counts were conducted in the laboratory using the technique described by Utermöhl (1958).

3. Results and discussion

3.1. DMS in seawater

The results of the DMS measurements in seawater is given in Fig. 2. The concentration of DMS in surface seawater samples taken during this cruise ranged from 12 to 240 ngS/l with a mean of 71 ngS/l (S.D. 52.3 ngS/l, $n = 126$). Fig. 3 show the data on phytoplankton distribution together with mean DMS seawater concentrations summarized by separating the measured area into 5 characteristic sections.

In the Drake Passage, which was crossed during 18–20 November, the obtained DMS values averaged to 61.4 ngS/l (range: 40.6 to 71.8 ngS/l; S.D. = 15.4 ngS/l, $n = 12$). These concentrations are consistent with low primary productivity in the Antarctic and Subantarctic region during austral spring relative to summer conditions. Biological data obtained during the cruise showed that the primary production had not yet developed the peak of the summer season, cell counts showed a poor state of growth of the phytoplankton community, which was dominated by Bacillariophycaea (mainly Nitzschia spp.) and Dinophyceae (mainly Gymnodinium). The observed DMS values were in good agreement with average DMS concentrations of 61 ngS/l measured by Berresheim et al. (1989) during several ship's cruises in the Drake Passage in austral fall 1986. Considerably higher DMS concentrations have been observed by Deprez et al. (1986) in a coastal area at Davis Bay (66°S, 131°E) during the summer phytoplankton bloom. The mean seawater DMS concentration taken in the Weddell

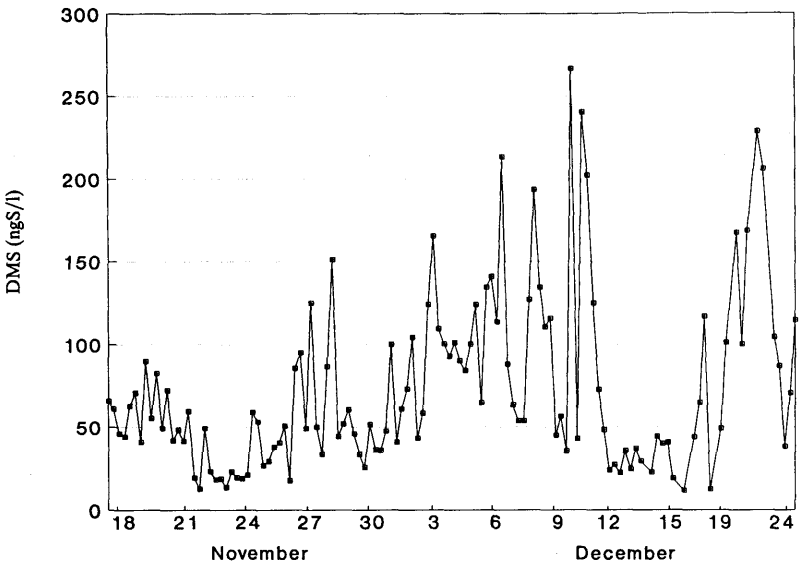

Fig. 2. DMS distribution in seawater during the "Polarstern" transect from 18 November to 24 December 1990.

Sea between 21 November and 17 December was 74.5 ngS/l (S.D. = 51.74 ngS/l, $n = 99$), thus slightly enhanced compared to average values observed in the Drake Passage. With growing numbers of phytoplankton individuals the DMS concentrations showed a slight increase from the western to the eastern part of the Weddell Sea. However, with further approach to the Atka Bight and the Georg-von-Neumayer Station (15°–8° W, 70° S) the seawater DMS concentrations decreased to a mean of 29 ngS/l (12–17 December). In this region, the ship crossed an extensive ice layer with an abundant plankton growth in the ice but minimum phytoplankton distribution in the water column. After passing the Weddell Sea, the DMS concentrations in seawater between Atka Bight

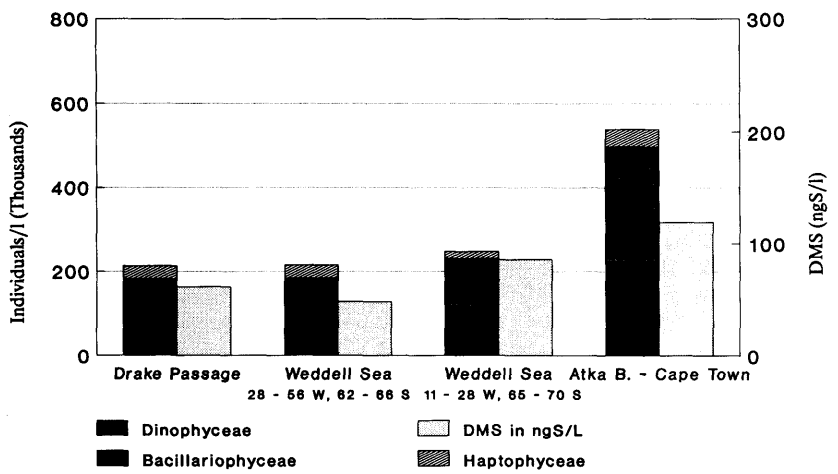

Fig. 3. Distribution of various phytoplankton spezies during the cruise of "Polarstern" from Punta Arenas to Cape Town.

and Cape Town increased to 120.1 ngS/l on the average (standard dev.: 60.5 ngS/l), maximum values of 230 ngS/l were observed on 21 December.

Several attempts to correlate DMS seawater concentrations with the distribution of phytoplankton species showed different results. A close relation of seawater DMS with phytoplankton abundance was reported by Bürgermeister et al. (1990), who found a significant correlation between dissolved DMS and the number of Dinophyceae and the sum of Bacillariophyceae in the Atlantic Ocean, and Barnard et al. (1984) and Holligan et al. (1987), who found a strong correlation between seawater DMS and the cell density of the Haptophyte Phaeocystis pouchetii in the Bering Sea and in frontal regions in the vicinity of the British Isles, respectively. However, Leck and Rodhe (1991) observed no simple correlation of DMS seawater values with the phytoplankton distribution in the seas surrounding Scandinavia.

Our study reveals a correlation between seawater DMS and the numbers of Bacillariophyceae on the 95% significance level ($r = 0.377$, $n = 98$). The Bacillariophyceae, in particular the spezies Nitzschia, Chaetoceros and Rhizosolenia constituted 40–49.5% of the total phytoplankton biomass. Fig. 4 shows plots of the DMS concentration in surface seawater against the numbers of the Bacillariophyceae (Fig. 4a), the Dinophyceae (Fig. 4b) and the Haptophyceae (Fig. 4c), which in sum account for 80–90% of the total amount of phytoplankton cells observed during this cruise. No significant correlations between DMS and the number of Dinophyceae and Haptophyceae, respectively, could be observed. A weak correlation between DMS and the Dinophyceae could only be found when the averaged data of the 4 different sections of the cruise was used ($n = 4$, $r = 0.916$).

Keller et al. (1989) showed in a comprehensive laboratory study that Bacillariophyceae are minor DMS producers compared to Haptophyceae and Dinophyceae. This observation has been made on temperate and tropical organisms. However, due to the ability of the Bacillariophyceae to form dense blooms in polar regions, the role of this taxonomic plankton class may not be ignored, as also indicated by the results of this study.

3.2. *Atmospheric DMS*

The results of the DMS measurements in the atmosphere are shown in Fig. 5. Atmospheric

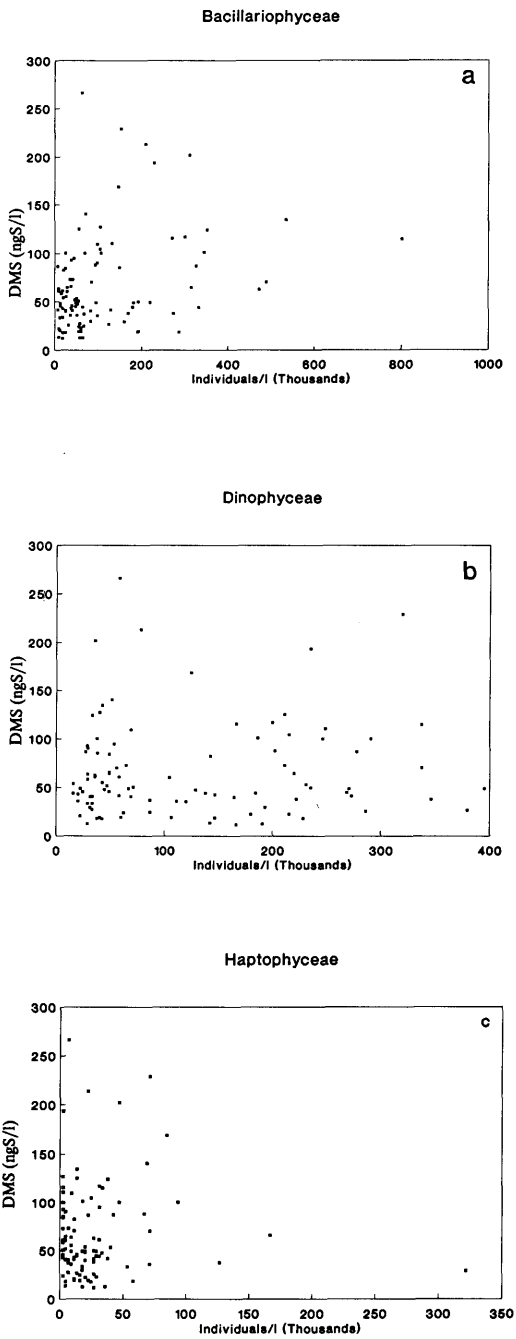

Fig. 4. Scatter diagram of the concentration of DMS vs. different phytoplankton spezies in surface seawater from the "Polarstern" cruise. (a) Bacillariophyceae, (b) Dinophyceae, (c) Haptophyceae.

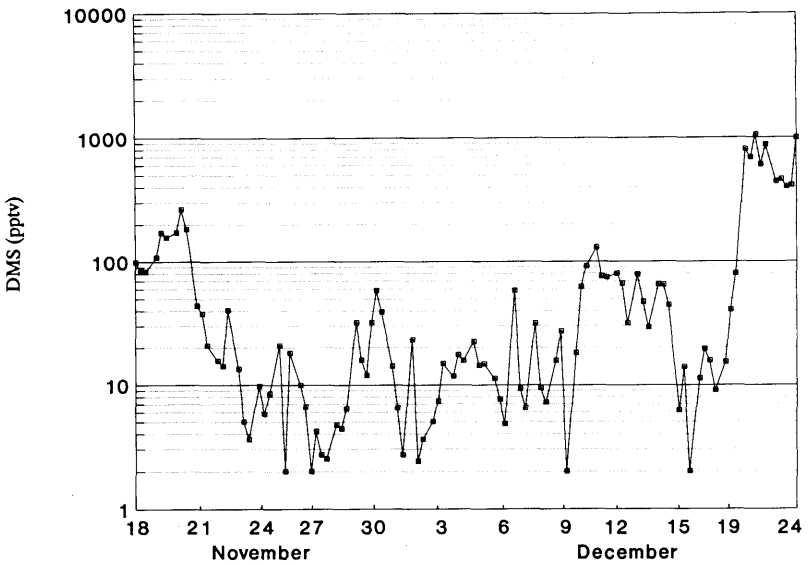

Fig. 5. DMS mixing ratios in the marine boundary layer between Punta Arenas and Cape Town from 18 November to 24 December.

DMS mixing ratios showed a range between 3 and 1048 pptv with significant differences between the individual measuring areas.

DMS mixing ratios in the marine atmosphere over the Drake Passage averaged to 147 pptv (S.D.: 60 pptv). These concentrations, which are slightly enhanced compared to the global average over the World's oceans of 113 pptv estimated by Andreae et al. (1985), were most likely caused by an effective gas stripping of DMS from seawater to the atmosphere caused by high wind speeds in this area. The meteorological situation was characterized by several lows passing the Drake Passage quickly and effected the ship with northerly to northwesterly winds with wind speeds up to 21 m/s.

The atmospheric DMS mixing ratios dropped drastically when the ship enters the Weddell Sea on 21 November. During that day the wind calmed to 8–11 m/s and turned from Northwest to Southeast. Nearly simultaneously the DMS concentration in the atmosphere decreased considerably from the average of 147 pptv in the Drake Passage to a mean of 23.7 pptv in the Weddell Sea. The overall very low DMS concentrations obtained in the marine boundary layer over the Weddell Sea suggest a significant lowering of the gas exchange between seawater and the overlying atmosphere caused by the extensive ice coverage of the Weddell Sea (see below). The DMS mixing ratios measured in the Weddell Sea never exceeded 50 pptv, exceptionally enhanced concentrations up to 30 pptv were only observed between 10–14 December. In this period, a dynamic high pressure system developed above the Antarctic continent causing strong inversion with fog and light winds. During those weather conditions DMS concentrations of 63.8 pptv on the average were found, thus a 4.5 times higher value than the mean of 14.1 pptv obtained during the remaining measurements in the Weddell Sea. These enhanced concentrations might be caused by the reduction of photochemical activity during the fog episod and/or suppressed vertical mixing in the boundary layer during stable conditions. Data obtained by Berresheim (1987) and Bates et al. (1990) indicate a strong dependence of atmospheric DMS concentrations on the boundary layer height showing a significant dilution of the DMS distribution with increasing mixed layer height. With rising wind speeds and decomposing of the fog the atmospheric DMS concentrations again decreased to a mean of 11 pptv on the average from 15–17 December.

After reaching ice-free waters at 68°S, 4°W on 20 December, the atmospheric DMS concentrations showed a mean of 671 pptv, thus an increase by a factor of 28 compared to the Weddell Sea values. Maximum concentrations up to 1048 pptv were measured on 21 December, simultaneously to maximum DMS concentrations in seawater. This strong increase of atmospheric DMS concentrations were possibly the result of increasing wind speeds up to 20 m/s and maximum DMS levels in seawater and, hence, increasing air-sea exchange rates.

3.3. DMS flux estimates

The flux of a gas across an air-water interface can be calculated by using a stagnant film model described in detail by Liss (1973), using the equation

$$F = -K(c_a/H - c_w),$$

F = flux rate, K = piston velocity, c_a = concentration in air, c_w = concentration in seawater, H = Henry's law constant.

K is calculated in the same way as described by Berresheim (1987) using an empirical formula for the radon piston velocity given by Smethie et al. (1985). The radon piston velocities can be transformed to DMS piston velocities and adjusted for actual seawater temperatures by using following relationships:

$$K \sim (\mu/D)^{-2/3} \quad \text{and} \quad \mu D/T = \text{const.}$$

μ = kinematic viscosity of seawater, D = molecular diffusivity of the solute gas.

The uncertainties by using the described method to calculate DMS flux rates are within a factor of 2 (Andreae, 1986; Smethie et al., 1985).

The DMS flux from seawater to the atmosphere over the Drake Passage averaged to 265 ± 43 ngS $m^{-2} min^{-1}$. This is evidently higher than values reported by Berresheim (1987) who calculated a mean sea-to-air flux of 98 ngS $m^{-2} min^{-1}$ in the Drake Passage during austral fall at similar DMS concentrations in seawater but drastically lower wind speeds. Corresponding to evidently higher DMS concentrations in the surface ocean between Atka Bight and Cape Town but lower wind speeds (8 ± 2 m/s) compared to values observed in the Drake Passage (mean wind speed 12.8 ± 2.9) the DMS flux rates in this region showed slightly enhanced values of 303 ngS $m^{-2} min^{-1}$ on the average. The observed flux rates are somewhat lower than the global average DMS flux from the oceans of 395 ngS $m^{-2} min^{-1}$ (Andreae et al., 1985), which is based on a surface seawater temperature of 20°C. However, the global DMS flux estimates were obtained mostly from summer data from productive ocean areas, whereas the flux rates presented here were calculated from spring data. It is likely that much higher DMS emissions occur during summer due to higher surface seawater DMS concentrations.

Due to the ice coverage of the Weddell Sea the film model could not be used to calculate DMS flux rates from the Weddell Sea. Therefore, a rough estimate of the DMS flux rates was done by using the relationship:

$$F = hc_a/t.$$

h = mixed layer height (considered to be 1.5 km), t = atmospheric residence time of DMS.

Using the mean residence time of DMS in the remote Southern hemisphere of 6.5 days estimated by Berresheim (1987) we calculated a very low sea-to-air flux of 3.9 ± 2 ngS $m^{-2} min^{-1}$ in the Weddell Sea. This indicates an evident reduction of the gas exchange between seawater and the atmosphere due to the extensive ice coverage of the Weddell Sea.

3.4. COS and CS_2 in seawater

The results of the COS measurements in seawater are given in Fig. 6. The concentrations showed an overall mean of 3.5 ngS/l accounting for 5% of the averaged DMS concentration obtained during this transect. Exceptionally high COS values were found between 65°S, 37°–34°W, on 28 and 29 November, west of the center of the Weddell Gyre. This conspicuous increase could not be related to any additionally monitored biological and meteorological parameter like water temperature, ice cover, insolation and phytoplankton distribution. To assure that there was no contamination we checked the whole seawater degassing system and found no COS blanks; from several seawater samples taken during this period we degased and analyzed two of them to confirm the results. COS determined from seawater samples collected in the Atlantic Ocean in a lati-

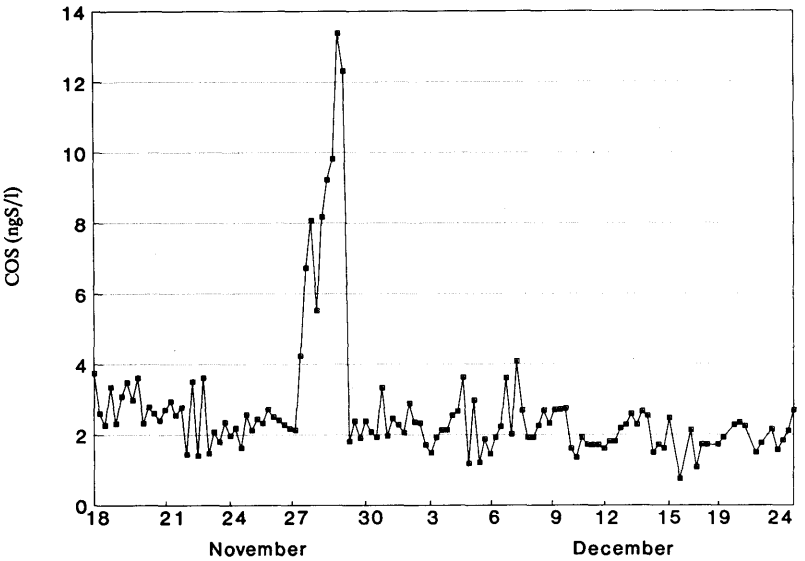

Fig. 6. COS distribution in seawater during the "Polarstern" transect from 18 November to 24 December 1990.

tudinal range between 50° N and 52° S and in the European Ice Sea between 70° N and 82° N during shipboard measurements in 1990 (Staubes and Georgii, unpublished data, will be reported in a future publication) showed similar average concentrations. However, such a hot spot as found in the Weddell Sea was not observed during any of these cruises. The minor variability of COS in seawater throughout these wide latitudinal range suggests that COS is distributed fairly homogeneous throughout the World's oceans.

The CS_2 distribution in seawater showed from 126 collected seawater samples 115 to be under the detection limit of 0.43 ngS/l. The remaining 11 samples revealed CS_2 values between 0.48 and 1.43 ngS/l with highest concentrations obtained on 28 and 29 November, when maximum COS values were found, too. Those generally very low CS_2 concentrations suggest that the CS_2 emissions from seawater do not contribute significantly to the atmospheric CS_2 distribution. This is consistent with results reported by Kim and Andreae (1987). They measured the CS_2 content of surface seawater on ship cruises in the North Atlantic and found CS_2 concentrations of 0.32 ngS/l in open ocean seawater.

3.5. COS and CS_2 in the marine boundary layer

The distribution of atmospheric COS during the transect is given in Fig. 7. In the Drake Passage the atmospheric COS concentrations showed a very high mean value of 628 pptv (standard deviation: 42 pptv). In this region north-westerly winds were predominant, highly influenced by anthropogenic inputs from the South American continent which was confirmed by relatively high CS_2 concentrations (see below) and NO_3 aerosol concentrations of 380–460 ng/m^3.

In the remote atmosphere over the Weddell Sea between 55° W and 30° W in a latitudinal range between 63° S and 67° S the atmospheric COS mixing ratios dropped to 453 pptv on the average. The atmospheric COS concentrations began to decrease on 23 November, after the wind direction had already changed from northwest to southeast on 21 November. During the whole period from 23 November to 6 December southwesterly to southeasterly winds prevailed, suggesting minor manmade perturbations. On 6 December the wind changed from strong southerly wind with force up to 22 m/s to light winds with variable wind directions predominantly from west. On 9 December the wind turned to north with wind speeds of 16 m/s. In this period we measured a remarkable increase of the atmospheric COS concentrations from about 420 pptv to 540 ppt on the average. This may be caused by a long-range transport of air influenced by continental inputs into the Antarctic region. With calming of the wind on 11 December and variable wind directions the

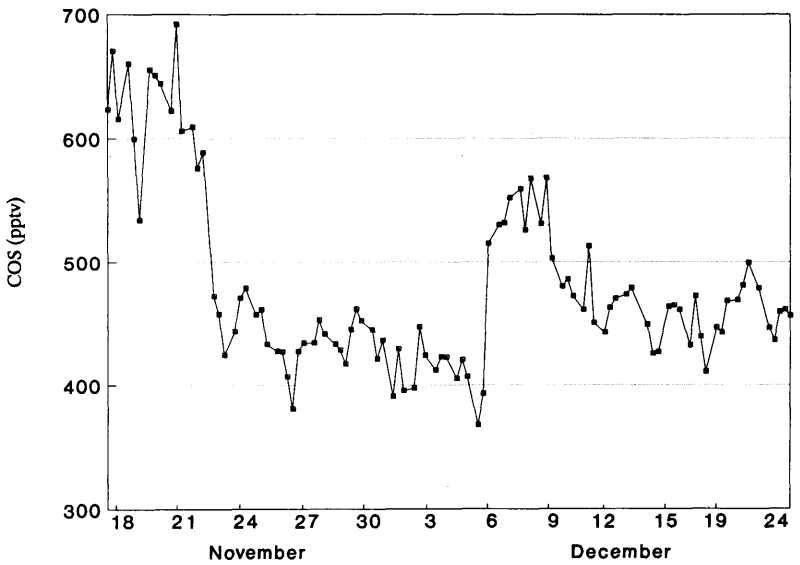

Fig. 7. COS mixing ratios in the marine boundary layer between Punta Arenas and Cape Town from 18 November to 24 December 1990.

COS mixing ratios decreased and remained at a level of 458 ± 22 pptv until the end of the cruise.

The atmospheric COS mixing ratios measured in the Antarctic region were evidently lower than those observed during a cruise in the Atlantic Ocean (50°N to 52°S) in October/November 1990, where we found an overall average of 571.5 pptv. COS measurements in the Atlantic Ocean between 30°S and 30°N reported by Bingemer et al. (1990) showed an average around 450 pptv in the remote marine air masses of the southern hemisphere and increased evidently in the northern hemisphere, showing an enhancement of 60 ppt per 10 degree latitude between 25°N and 45°N. Bingemer et al. (1990) concluded from their data that sources located on the continents, namely anthropogenic activities, contribute significantly to the global atmospheric COS cycle. The strong decrease of atmospheric COS concentrations in the remote Antarctic region observed in this study support the findings of Bingemer et al. (1990).

Atmospheric CS_2 could only be detected from 18–20 December in the Drake Passage showing an average atmospheric mixing ratio of 34.8 ± 7.5 pptv. After passing King George Island (62°S, 58°W) the CS_2 concentrations dropped under the detection limit of 7 pptv and did not increase to measurable values until the end of the transect. A rapid decrease of atmospheric CS_2 concentrations with distance from land to a few pptv was also reported by Kim and Andreae (1987) and Cooper and Saltzman (1991).

4. Conclusions

During the transect between Punta Arenas and Cape Town DMS concentrations in seawater were measured to be in the range between 12 ngS/l and 240 ngS/l with a mean of 71 ngS/l. A comparison with the phytoplankton distribution revealed a good agreement of the DMS values with the number of the Bacillariophyceae in seawater. Atmospheric DMS mixing ratios showed a range between 3 and 1048 pptv. Minimum concentrations of 24 pptv on the average were measured over ice-covered areas of the Weddell Sea. DMS flux rates ranged from a minimum of 3.8 ngS m^{-2} min^{-1} in the Weddell Sea to maximum values around 300 ngS m^{-2} min^{-1} observed in the ocean area between Atka Bight and Cape Town (South Africa). COS in seawater showed an overall homogeneous distribution with a mean of 3.5 ngS/l, which is comparable to values observed in temperate latitudes of the Atlantic and high latitudes

of the northern hemisphere. COS mixing ratios in the remote atmosphere over the Weddell Sea averaged to 453 ± 43 pptv, which was evidently lower than the mean COS concentrations of 628 ± 42 pptv measured in air masses highly influenced by continental inputs over the Drake Passage. CS_2 in seawater as well as in the overlying atmosphere could only be observed in a limited number of samples in detectable concentrations.

5. Acknowledgements

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