Dimethylsulfide Measured in the Western Pacific and the Southern Indian Ocean

By Seizi Koga, Hiroshi Tanaka

Water Research Institute, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan

and

Masahiko Hayashi

Solar Terrestrial Environment Laboratory, Nagoya University, Toyokawa 442, Japan

(Manuscript received 6 July 1992, in revised form 19 November 1992)

Abstract

Dimethylsulfide was measured in the atmosphere and the ocean water from 28 December 1990 to 13 March 1991 in the western Pacific Ocean. Mean DMS concentration in the atmosphere was low west of 180° longitude on the equator (11 pptv) as well as the temperate North Pacific Ocean (9 pptv). Atmospheric DMS concentration along 160°W was nearly uniform at about 42 pptv from 15°N to the equator. Sharp increases of atmospheric DMS concentration appeared south of the equator along 160°W and 180°, and the atmospheric DMS concentration reached approximately 95 pptv around (5°S, 160°W). Concentrations of DMS in the surface seawater were also high south of the equator, and the maximum value was 1.85 nmol L⁻¹ at (5°S, 180°). Simultaneous measurement of atmospheric and oceanic DMS was made at an interval of 6 hours on the track from (6°S, 179°W) to (11°S, 175.5°W). While the concentration of DMS in the surface seawater was quite uniform at 1.26 nmol L⁻¹, the atmospheric DMS concentration varied diurnally with a mean value of 76 pptv.

Observed DMS concentrations in the atmosphere and the ocean, together with model simulations, demonstrate that the main processes controlling the concentration and diurnal variation of atmospheric DMS are the magnitude of DMS flux from the ocean to the atmosphere and the oxidation reaction with the hydroxyl radical (OH) in the daytime. The reaction with the nitrate radical (NO₃) at night is also important, because it decreases the amplitude of the DMS diurnal variation. In addition, wind speed seems to be an important factor regulating the DMS flux.

Another measurement of atmospheric DMS was conducted during 3–12 December 1990 in the southern Indian Ocean. North of 50°S, the atmospheric DMS concentration was approximately 60 pptv, but south of 50°S it drastically increased up to 460 pptv poleward. High DMS concentration in the ocean and low OH concentration due to stormy weather are considered as possible causes of the high atmospheric DMS concentration.

1. Introduction

The ocean is a reservoir containing a tremendous amount of sulfur compounds and also plays an important role, through sea-to-air gas transfer, in the global biogeochemical sulfur cycle (Andreae, 1986). Marine algal species synthesize organo-sulfur compounds in the seawater. Oceanic dimethylsulfide (DMS) is likely to be produced by enzymatic cleavage of β -dimethylsulfoniopropionate [DMSP or (CH₃)₂S⁺CH₂CH₂COO⁻] in marine algae and phytoplankton (Kadota and Ishida, 1972; Reed, 1983; Vairavamurthy *et al.*, 1985; Turner *et al.*, 1988).

Dimethylsulfide constitutes more than 97 % of the total reduced volatile sulfur in the surface seawater (Cline and Bates, 1983), and is also likely to be responsible for the "odor of the sea". The most recent model calculation predicts the mean sea-to-air flux of DMS to be 0.5 Tmol year⁻¹ (Bates *et al.*, 1987).

It has been suggested that atmospheric DMS is initially oxidized by the hydroxyl radical (OH) and the nitrate radical (NO₃) (Andreae, 1986). Also, the reaction of DMS with the IO radical was recently proposed as another oxidation pathway (Barnes *et al.*, 1987; Martin *et al.*, 1987). The oxidation of atmospheric DMS seems to be the predominant source of sulfur dioxide (SO₂) and methanesulfonic

Fig. 1. Cruise track of the *R/V Natsushima*. The period of the cruise was from 28 December 1990 to 13 March 1991. Numbered circles refer to the locations where the seawater samples were collected.

acid (MSA or $\text{CH}_3\text{SO}_3\text{H}$) in the marine troposphere (Naguyen *et al.*, 1983; Hatakeyama *et al.*, 1985; Andreae *et al.*, 1985; Saltzman *et al.*, 1986). Non-sea-salt sulfate (nss-SO_4^{2-}), which is the end product of the DMS oxidation, is the major contributor to cloud condensation nuclei (CCN). The number concentration of CCN controls cloud albedo (Charlson *et al.*, 1987) and water circulation over the ocean.

Despite the importance of DMS in the global sulfur budget and cloud formation, spatial distribution of atmospheric DMS near the sea surface is not yet well known in the remote marine atmosphere. Ship-board measurements of DMS concentrations in the atmosphere and the ocean were conducted on board the *R/V Natsushima* in the western Pacific Ocean from 28 December 1990 to 13 March 1991. Atmospheric DMS concentration was also measured on board the *R/V Shirase* in the Indian sector of the Southern Ocean during 3–12 December 1990.

This paper presents the variation of atmospheric DMS concentration observed during the cruises traversing oligotrophic and upwelling areas. In addition, we will discuss the processes regulating atmospheric DMS concentration in association with DMS flux from the ocean.

2. Sampling and analytical methods

During the *R/V Natsushima* cruise (see Fig. 1), atmospheric samples were collected on the deck at approximately 10 m height above the sea surface, on the moving ship and in fair weather. During the *R/V Shirase* cruise (see Fig. 2), all the atmospheric samples were sucked through Teflon tubing and collected in the room.

Air samples of 2.7 to 35.0 L were collected with an air flow rate of 430 to 550 mL min^{-1} , depending on concentration. The samples were sucked first through cellulose nitrate filters (25 mm diameter;

Fig. 2. Cruise track of the *R/V Shirase*. The period of the cruise was from 3 to 12 December 1990.

nominal pore size, $0.45 \mu\text{m}$) to reduce particulate matter. Then water vapor was removed through a Teflon loop being kept at -65°C with ethanol and a Perma pure dryer of Nafion tubing. Finally, the samples were adsorbed on Chromosorb 101 (4 mm ID, 6 cm long) set within a U-shaped Teflon tube at a temperature of -65°C , and analyzed at the ship-board laboratory as soon as possible.

During the *R/V Natsushima* cruise, seawater samples were collected with buckets and Niskin bottles of 5 L at depths of 0, 10, 25, 50, 75, 100, 150, and 200 m. After the samples of 10 to 45 mL were filtered through cellulose nitrate filters (25 mm diameter; nominal pore size, $0.45 \mu\text{m}$) with syringes to remove algal cells and other detritus, these were purged to strip volatile compounds for 10 minutes

with ultra-pure helium at 60 mL min^{-1} . The gas stream containing water vapor was passed through a Perma pure dryer, and the volatile compounds were adsorbed on Chromosorb 101 at a temperature of -65°C .

The volatile compounds were desorbed rapidly from Chromosorb 101 by immersing the U-shaped Teflon tube into silicon oil at a temperature of about 200°C , and were transferred to a column of 3 mm ID and 3 m long made of Teflon. The sulfur compounds were measured by gas-chromatography with a flame photometric detector, and were identified on the basis of retention time. During the *R/V Natsushima* cruise, the chromatographic column was filled with a 25 % β , β' -ODPN on 60/80 mesh Uniport, and was set in a Yanaco G2800. Helium was used as a carrier gas with a flow rate of 50 mL min^{-1} and the column temperature was kept at 50°C . During the *R/V Shirase* cruise, the column was filled with a 25 % 1.2.3. tris (2 cyanoethoxy) propane on 80/100 mesh Shimalite (AW-DMCS) and was set in a Shimadzu GC-8A. Nitrogen was used as a carrier gas with a flow rate of 30 mL min^{-1} and the column temperature was kept at 80°C . The calibration of the chromatographic system (Yanaco G2800) was performed by injecting 20–400 μL volumes of a standard gas of DMS (4.9 ppm). A DMS standard solution diluted with benzene was prepared for the calibration of a Shimadzu GC-8A. The analytical error of DMS concentration is less than 3 %. The recoveries of DMS are 100 % for the air samples. The recovery of DMS from seawater was measured by adding a known DMS in benzen to seawater and was more than 90 %. The detection limit of DMS is about 180 pg for a Yanaco G2800 and is about 40 pg for a Shimadzu GC-8A. Here, atmospheric DMS concentrations were counted in units of parts per trillion by volume (pptv) under the condition of 25°C and 1013 hPa, so that 1 nmol m^{-3} corresponds to a mixing ratio of 24.5 pptv.

3. Results of observations in the western Pacific Ocean

3.1 Atmospheric DMS

Figure 3a plots the atmospheric DMS concentration in the western Pacific Ocean against the latitude. The sampling was made in the daytime between 9 am and 7 pm. The concentrations over the temperate North Pacific Ocean were less than 23 pptv with a mean value of 9 pptv (standard deviation $\sigma = 5.8$ for sample number $n=13$). The concentration of DMS between 15°N and the equator along 160°W was rather uniform around the value of 42 pptv ($\sigma=7.2$, $n=10$). Atmospheric DMS concentration over the equatorial and the North Pacific (from the equator to Hawaii) averaged 125 pptv in the summer season, according to Andreae and Raemdonck (1983). The observed concentrations of

DMS were considerably lower than those obtained by Andreae and Raemdonck (1983) over the North Pacific Ocean. This difference may be attributed to the fact that our observation was conducted in the winter season when primary productivity is usually low. However, a sharp increase was found after crossing the equator. The maximum value was 95 pptv around (5°S , 160°W). A similar variation was also found along the International Date Line, and the maximum value was 68 pptv around (4°S , 180°). No latitudinal variation was found in the region along 160°E , and the DMS concentration was almost identical to that observed over the temperate North Pacific Ocean. The DMS concentration on the equator monotonically decreased westward (see Fig. 3b). West of the Date Line, the concentration was uniform with a mean value of 11 pptv ($\sigma=2.6$, $n=6$), similar to the lower limit ($0.3 \text{ nmol m}^{-3} = 7.4 \text{ pptv}$) at Amsterdam Island ($37^\circ 50'\text{S}$, $77^\circ 31'\text{E}$) in Winter 1987 (Nguyen *et al.*, 1990).

3.2 Oceanic DMS

During the cruise from Guam to Kobe (see Fig. 1), the DMS concentrations in the surface seawater were 0.6 nmol L^{-1} at most (see Table 1), which is lower than the mean value of 0.7 nmol L^{-1} observed by Bates *et al.* (1987) in the region between 20°N and 35°N in the winter season. The concentration of DMS in the surface seawater at station 3 (0° , 160°W) was 0.83 nmol L^{-1} , much lower than that observed by Andreae and Raemdonck (1983) and Bates *et al.* (1987) near the equator. The concentration of DMS in the equatorial Pacific Ocean decreased westward (see the middle panel in Fig. 4), which is also shown in the above two papers. At stations 4 (5°S , 160°W) and 8 (5°S , 180°), the concentrations of DMS were significantly higher than those at the other stations. These concentrations are identical with the average value of 1.88 nmol L^{-1} in the equatorial region (0 – 5°N , 180 – 120°E) (Bates *et al.*, 1987) (see Table 1). A similar value was found by Andreae and Raemdonck (1983) in the North Pacific Ocean (5°N – 20°N , 140°W). Figure 5 shows the vertical profiles of DMS at Stations 2 (5°N , 160°W), 3, and 4, as well as the distributions of nitrate (NO_3^-) and phosphate (PO_4^{3-}). The DMS concentrations at Stations 4 and 8 (not shown in Fig. 5) were almost uniform through the depth down to 80 m, and then sharply decreased to undetectable levels at around 200 m. These profiles are similar to those obtained by Barnard *et al.* (1982) and Andreae (1986). They reported that the DMS concentration was highest in the euphotic zone and decreased downward to the depth of 1 % light penetration. However, similar results were not found at other stations. Vertical profiles of NO_3^- concentration showed a minimum at the depths of 40–80 m at stations 3, 4, 5 (0° , 165°W), 6 (0° , 170°W), and 7 (0° , 175°W). Nutri-

Fig. 3. (a) Latitudinal distributions of atmospheric DMS concentration over the western Pacific Ocean. The arrow indicates the mean value of the atmospheric DMS concentrations measured in the region from (6°S, 179°W) to (11°S, 175.5°W). (b) Longitudinal distribution of atmospheric DMS concentration along the equator from 160°W to 160°E.

ents in the sub-surface layer were not completely consumed by photoplankton.

Bates *et al.* (1987) pointed out that a maximum concentration of DMS in the surface seawater slightly south of the equator is associated with a southward displacement in the Intertropical Convergence Zone, the southeast trade winds, and the equatorial upwelling caused by the El Niño Southern Oscillation (ENSO) event. Although the period of our cruise is before the ENSO event, high concentrations of DMS, NO_3^- , and PO_4^{3-} were already located south of the equator (see Figs. 4 and 6). Judging from the vertical profiles of NO_3^- concentration, the sub-surface seawater above 80 m depth at Stations 3, 4, 5, 6, and 7 were likely to be transported by horizontal advection from the upwelling region slightly north of the equator. The seawater originated from the nutrient-rich waters of the South Pacific sub-tropical gyre. An Ekman convergence region was situated between the south equatorial

current flowing westward south of 5°N and the equatorial countercurrent flowing eastward between 5°N and 10°N. Therefore, nutrient-impoverished water would be found between north of the equator and the Ekman convergence zone.

4. Flux of DMS to the atmosphere in the equatorial region

The DMS flux from the ocean to the atmosphere was estimated from the data obtained during the cruise in the western Pacific Ocean. The basic equations of gas exchange are described in detail by Liss and Slater (1974) and Liss and Merlivat (1986). According to their gas exchange models, the DMS flux can be simply written as

$$F_{\text{DMS}} = k_{\text{DMS}}[\text{DMS}]_w, \quad (1)$$

where F_{DMS} is the DMS flux, k_{DMS} the exchange coefficient of DMS in the liquid phase, and $[\text{DMS}]_w$ the concentration of DMS in the surface seawater.

Table 1. Calculated fluxes and exchange coefficients of DMS, and observed DMS concentrations in the surface seawater.

Station Number	Location	Date	*Wind Speed (m s ⁻¹)	DMS Exchange Coefficient (m d ⁻¹)	DMS Concentration (nmol L ⁻¹)	DMS Flux (μmol m ⁻² d ⁻¹)	
1	10°N	160°W	16 Jan	5.5	1.26	0.93	1.17
2	5°N	160°W	18	7.3	2.39	1.09	2.61
3	0°	160°W	19	7.9	2.69	0.83	2.23
4	5°S	160°W	21	7.5	2.51	1.58	3.97
5	0°	165°W	23	7.0	2.15	0.76	1.64
6	0°	170°W	24	5.4	1.23	0.64	0.79
7	0°	175°W	25	5.2	1.14	0.63	0.72
	5°S	180°	26	4.4	0.65	1.85	1.21
	5°S	180°	27	5.6	1.39	1.83	2.54
	5°S	180°	27	6.7	2.08	1.78	3.70
8	5°S	180°	7 Feb	6.4	1.89	1.62	3.06
	3°S	180°	7	6.3	1.83	0.74	1.35
9	0°	180°	8	3.8	0.25	0.69	0.17
	3°N	180°	9	5.3	1.20	0.65	0.78
10	5°N	180°	9	8.3	3.00	0.51	1.53
11	0°	175°E	11	1.9	0.07	0.86	0.06
12	0°	170°E	12	5.8	1.55	0.81	1.26
13	0°	165°E	14	7.6	2.64	0.48	1.27
14	5°S	160°E	15	4.5	0.70	0.77	0.54
	2°S	160°E	16	5.5	1.36	0.95	1.29
15	0°	160°E	17	7.0	2.27	0.36	0.82
	2°N	160°E	18	7.0	2.27	0.29	0.66
16	5°N	160°E	18	7.7	2.70	0.44	1.19
	0°07'N	147°04'E	26	6.1	1.70	0.24	0.41
	1°58'N	146°59'E	27	8.0	2.89	0.33	0.95
	20°53'N	140°58'E	7 Mar	6.7	1.92	0.21	0.40
	22°02'N	140°28'E	7	9.4	3.49	0.56	1.95
	24°32'N	139°22'E	8	2.5	0.08	0.22	0.02
	25°40'N	138°34'E	8	3.0	0.09	ND	—
	27°10'N	138°08'E	9	4.0	0.31	ND	—
	27°46'N	137°52'E	9	9.4	2.69	0.26	0.77

*Wind Speed in this table indicates a mean value of wind speed for 12 hours before atmospheric DMS is measured.

The exchange coefficient, k_l (cm hr⁻¹), is dependent on the wind speed, u (m s⁻¹), at 10 m height above the water surface (Liss and Merlivat, 1986);

$$k_l(u) = 0.17u \quad u \leq 3.6, \quad (2)$$

$$k_l(u) = 2.85u - 9.65 \quad 3.6 < u \leq 13, \quad (3)$$

$$k_l(u) = 5.9u - 49.3 \quad u > 13. \quad (4)$$

The equations have been applied to CO₂ at a temperature of 20°C. When we apply k_l to DMS, the value of k_{DMS} at a given temperature is derived from the equation;

$$k_{DMS} = k_l(u) Sc_{CO_2}^{\alpha}(20) Sc_{DMS}^{-\alpha}(t), \quad (5)$$

where $Sc_{CO_2}(20)$ is the Schmidt number of CO₂ at 20°C, $Sc_{DMS}(t)$ the Schmidt number of DMS at t °C. The Schmidt number is given by ν/D and is dependent on temperature, where ν is the kinematic viscosity and D the molecular diffusivity. Here, α is $-2/3$ for Eq. (2) and $-1/2$ for Eqs. (3) and (4).

Molecular diffusivity of DMS is given by Wilke and Chang (1955) and Hayduk and Laudie (1974).

The estimated F_{DMS} from Eq. (1) and k_{DMS} from Eq. (5) are shown in Table 1 and Fig. 4 (see the top and bottom panels). The mean value of the exchange coefficient is 1.73 m d⁻¹ ($\sigma=0.81$, $n=22$) in the equatorial region (5°N–5°S, 160°E–160°W), which is close to 1.85 m d⁻¹ in the winter season estimated by Bates *et al.* (1987). However, most of the DMS concentrations in the surface seawater do not exceed 1 nmol L⁻¹ and are less than 1.88 nmol L⁻¹ (0–5°N, 180–120°E) observed by Bates *et al.* (1987). Thus, our estimated mean value of DMS flux, 1.52 μmol m⁻² d⁻¹ ($\sigma=1.0$, $n=22$), is less than their mean value of 3.48 μmol m⁻² d⁻¹ in the winter season.

Once emitted to the atmosphere from the ocean, DMS initially reacts with OH and NO₃ (Andreae, 1986). The temporal variation of DMS concentration in the atmosphere is given by the following

Fig. 4. Distributions of observed DMS concentration in the surface seawater, the estimated DMS flux, and the DMS exchange coefficient. Small arrows indicate the mean values of the observed DMS concentration in the surface seawater, the estimated DMS flux, and the DMS exchange coefficient from (6°S, 179°W) to (11°S, 175.5°W). Large arrows indicate the mean values of the DMS concentration in the surface seawater, the DMS flux, and the DMS exchange coefficient obtained by Bates *et al.* (1987) in the equatorial region (0°–5°N, 180°–120°E) in the winter season.

equation;

$$\frac{\partial [\text{DMS}]_a}{\partial t} = \frac{F_{\text{DMS}}}{h} - (k_{\text{OH}}[\text{OH}] + k_{\text{NO}_3}[\text{NO}_3]) [\text{DMS}]_a, \quad (6)$$

where $[\text{DMS}]_a$ is the DMS concentration in the atmosphere, h the thickness of the atmospheric surface mixing layer, k_{OH} and k_{NO_3} the reaction rates of DMS with OH and NO_3 , respectively, and $[\text{OH}]$ and $[\text{NO}_3]$ the concentrations of OH and NO_3 in the atmosphere, respectively. Concentrations of OH and NO_3 strongly depend on radiant flux and NO_x ($\equiv \text{NO} + \text{NO}_2$) concentration. The IO radical generated in the daytime is also proposed as an important oxidant for DMS oxidation (Barnes *et al.*, 1987; Martin *et al.*, 1987). However, the reaction of DMS with IO is excluded from the equation, because the concentration of IO is not well known. If we assume a steady state, the stationary value of $[\text{DMS}]_a$ is written as

$$[\text{DMS}]_a = \frac{F_{\text{DMS}}}{h(k_{\text{OH}}[\text{OH}] + k_{\text{NO}_3}[\text{NO}_3])}. \quad (7)$$

The box model of Koga and Tanaka (1992) was applied to simulate the observed DMS concentration in the atmosphere. Total ozone content over the sea was assumed to be 250 DU on the equator (McCartney, 1976). The concentrations of CH_4 , CO, and H_2 were fixed at 1.7 ppmv, 60 ppbv (Heidt *et al.*, 1980), and 550 ppbv (Warneck, 1988), respectively. Vertical profiles of meteorological elements were measured by radiosondes during the cruise. The air temperature of 25°C and relative humidity of 75% were taken from meteorological data. The atmospheric surface mixing layer was 600 m in thickness, which is defined as a layer with constant potential temperature. Since the air temperature does not change rapidly in the equatorial region, k_{OH} and k_{NO_3} are assumed to be constant at 6.1×10^{-12} and $1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. These values are given for k_{OH} from Hynes *et al.* (1986)

Fig. 5. Vertical distributions of DMS, nitrate and phosphate at stations 2 (5°N, 160°W), 3 (0°, 160°W), and 4 (5°S, 160°W).

Fig. 6. Latitudinal distributions of nitrate, phosphate, and temperature in the surface seawater.

and for k_{NO_3} from Dlugokencky and Howard (1988).

Figure 7 shows that there is a good correlation between the observed atmospheric DMS concentration in the equatorial region and the DMS flux estimated from the gas exchange model. The atmospheric DMS concentrations are the values measured within 1° in latitude and longitude from the stations where the seawater samples were collected. Three broken lines denote diurnally averaged atmospheric DMS concentration versus DMS flux. The dashed line A shows the relationship when the reaction of DMS with NO_3 is omitted. B and C include the reaction of DMS with NO_3 , but the initial NO_x concentrations are assumed to be 35 pptv for B and 70 pptv for

Fig. 7. Relationship between the atmospheric DMS concentrations observed in the equatorial region and the predicted fluxes of DMS. The triangle refers to the mean value of DMS concentration observed from (6°S, 179°W) to (11°S, 175.5°W).

C. The concentration of NO_x , 35 pptv, is determined from measurements over the central Pacific Ocean (McFarland *et al.*, 1979; Noxon, 1983). Most of the points are located in the area between lines A and C except for the region of small DMS flux. This suggests that NO_x concentration was less than 70 pptv and that the value of $h (k_{\text{OH}}[\text{OH}] + k_{\text{NO}_3}[\text{NO}_3])$ was almost constant during the cruise. Therefore, atmospheric DMS concentrations over the equatorial Pacific are, under the clear sky conditions, proportional to the DMS flux. The concentration of DMS in the surface seawater measured at Station 3 was 0.83 nmol L^{-1} , which is similar to that at Station 11 (0°, 175°E). However, k_{DMS} was larger at Station 3 than at station 11 due to the strong wind speed (see Table 1). The concentrations of DMS in the at-

Fig. 8. Diurnal variation of DMS concentration observed from (6°S , 179°W) to (11°S , 175°W). Vertical bars show the range between the maximum and minimum at each given time. Three data values are averaged at each time. Thin lines correspond to the predicted diurnal variations of DMS, OH, and NO_3 in the atmosphere, (a) when the reaction of DMS with NO_3 is excluded from the model, (b) when the reaction of DMS with NO_3 is included. The initial NO_x concentration is 35 pptv.

mosphere were approximately 46 pptv around Station 3 and 11 pptv around Station 11 (see Fig. 3b). The flux of DMS evidently depends on wind speed. The correlation between atmospheric DMS concentration and wind speed was also suggested from the observations of Bates *et al.* (1990) and Nguyen *et al.* (1990). The distribution of atmospheric DMS concentration in the equatorial region can probably be interpreted from the difference of DMS flux depending on the wind speed, as shown in Eq. (7).

5. Diurnal variation of atmospheric DMS observed from 6°S to 11°S

Simultaneous measurements of DMS concentration in the surface seawater and in the atmosphere were conducted at an interval of 6 hours on the track from (6°S , 179°W) to (11°S , 175.5°W) during the cruise to Western Samoa. While the diurnal variation was observed in the atmospheric DMS concentration, the oceanic DMS concentration was fairly uniform with a mean value of 1.26 nmol L^{-1} ($\sigma = 0.23$, $n=12$), which is comparable to the average value of 1.06 nmol L^{-1} between 5°S and 20°S along 170°W (Bates *et al.*, 1987). The mean value of estimated DMS flux was $2.02 \mu\text{mol m}^{-2} \text{ d}^{-1}$ ($\sigma = 1.13$, $n=12$). The observed maximum-to-minimum concentration ratio of atmospheric DMS was 1.4 with a mean value of 76 pptv (see Fig. 8). The ratio is similar to the previously measured values in the remote marine atmosphere (Andreae and Raemdonck, 1983; Andreae *et al.*, 1985; Berresheim, 1987; Salt-

man and Cooper, 1988).

When the initial NO_x concentration and the DMS flux are assumed to be 35 pptv and $2.0 \mu\text{mol m}^{-2} \text{ d}^{-1}$, respectively, the predicted maximum to minimum ratio is 1.7 (see the line *b* in Fig. 8). This value is close to the ratio of 1.4 from the field data. The observed minimum concentration of DMS in the late afternoon is attributed to the reaction with OH. When the reaction of DMS with NO_3 is omitted, the predicted maximum-to-minimum ratio becomes 1.9 (see the line *a* in Fig. 8). The rate of increase of DMS concentration at night is smaller in the field data than in the line *a*. The observed gradual increase of DMS concentration can be explained by the reaction with NO_3 . Nighttime oxidation by NO_3 probably prevents further increase of DMS concentration. The concentration and diurnal variation of DMS in the atmosphere are primarily related to the reaction of DMS with OH. But the effect of oxidation by NO_3 cannot be ignored, because it leads to a decrease the maximum-to-minimum ratio.

6. Atmospheric DMS over the southern Indian Ocean

Atmospheric DMS concentrations were measured during the *R/V Shirase* cruise in the southern Indian Ocean. The concentrations of DMS were about 60 pptv in the mid-latitude region (see Fig. 9a). Berresheim *et al.* (1990) reported that the atmospheric DMS concentration near the sea surface ranged from 15 to 60 pptv on the western side of Tasmania in early December. The period of their measurement is the same as that of the *R/V Shirase* cruise. Andreae *et al.* (1985) reported that the average value of DMS concentration was 125 pptv at Cape Grim ($40^{\circ}40'\text{S}$, $144^{\circ}44'\text{E}$), Tasmania in January. This value is higher than the values of the present study and Berresheim *et al.* (1990). The difference may result from the seasonal variation of DMS production in the ocean. Chlorophyll *a* in the surface seawater has a maximum concentration in the Antarctic Convergence Zone (around 55°S) in the middle to late December. In addition, standard deviations of the mean surface chlorophyll *a* are very large in the Antarctic Convergence Zone and south of 63°S , which shows complicated hydrographic conditions (Fukuchi, 1980). South of 50°S , the atmospheric DMS concentration increased toward higher latitudes. The drastic variation from 50 to 55°S may be related to the patchiness of phytoplankton density. The steep dip of DMS concentration around 57°S may be caused by a remarkable decrease of surface chlorophyll stock. Unfortunately, we could not measure the concentration of DMS in the surface seawater and therefore cannot estimate the flux of DMS.

The reaction rate, k_{OH} , varies within a relatively small temperature range, because the rate of the

Fig. 9. (a) Latitudinal distribution of the atmospheric DMS concentration over the southern Indian Ocean measured from the *R/V Shirase*. Arrows indicate the values observed at noon. (b) Latitudinal distribution of the estimated DMS exchange coefficient, wind speed, air temperature, and surface water temperature.

addition reaction of OH with DMS monotonically increases with decreasing air temperature (Hynes *et al.*, 1986). Air temperatures were 20°C at 30°S and 0°C at 60°S during the cruise of the *R/V Shirase* (see Fig. 9b). Thus, the reaction rates are estimated as $6.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 30°S and $11.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 60°S from the formula given by Hynes *et al.* (1986). Diurnally averaged [OH] at 30°S and 60°S, according to the model of Koga and Tanaka (1992), are estimated as 1.8×10^6 and $0.9 \times 10^6 \text{ molecules cm}^{-3}$, respectively. $k_{\text{NO}_3}[\text{NO}_3]$ is usually smaller than $k_{\text{OH}}[\text{OH}]$ due to low NO_x concentration in the remote marine atmosphere (McFarland *et al.*, 1979; Noxon, 1983). Consequently, the value of $h (k_{\text{OH}}[\text{OH}] + k_{\text{NO}_3}[\text{NO}_3])$ shows no significant latitudinal distribution, if the thickness of the atmospheric surface mixing layer is assumed to be constant. This suggests that, un-

der clear sky conditions, the observed atmospheric DMS concentration is proportional to the DMS flux. The weather was fine north of 55°S. Exchange coefficients north of 40°S are larger than those between 40°S and 50°S (see Fig. 9b). Therefore, under the condition that DMS concentrations in the seawater are relatively low north of 40°S, DMS fluxes can remain constant independent of latitude. This is probably the reason for the uniformity of atmospheric DMS concentration north of 50°S. High concentrations of DMS, exceeding 400 pptv, were observed around 61°S. Precipitation occurred frequently south of 55°S. Since any remarkable increase is not found in the exchange coefficients of DMS in this region (Fig. 9b), the high DMS concentrations in the atmosphere are caused by either reduced OH concentrations due to weak radiation flux (Nguyen *et al.*, 1990) or increased DMS concentration in the ocean.

7. Summary and conclusions

Measurements of atmospheric and oceanic DMS concentrations in the western Pacific Ocean were conducted in the winter season when the primary productivity is usually low. Atmospheric DMS concentration was approximately 10 pptv over the temperate North Pacific Ocean. Also, a similar value was observed west of 180° longitude on the equator. Elevated atmospheric and oceanic DMS concentrations were observed around 5°S east of 180° longitude. The atmospheric DMS concentration reached 95 pptv around (5°S, 160°W). The maximum concentration of DMS in the surface seawater was 1.85 nmol L⁻¹ at (5°S, 180°).

The mean concentration of atmospheric DMS from (6°S, 179°W) to (11°S, 175.5°W) was 76 pptv. The concentration varied diurnally by a factor of 1.4 in the maximum-to-minimum ratio, whereas oceanic DMS concentration was almost stationary in time with a mean value of 1.26 nmol L⁻¹. The mean concentration and the diurnal variation of DMS in the remote marine atmosphere probably depend on the magnitude of the DMS flux from the ocean and the oxidation processes through the reactions of DMS, primarily with OH and secondarily with NO₃. In addition, the DMS flux evidently depends on the wind speed.

Another observation of the atmospheric DMS was conducted during the summer season in the southern Indian Ocean. Atmospheric DMS concentrations north of 50°S were uniform around 60 pptv, while south of 50°S they increased with increasing latitude. High DMS concentrations in the atmosphere south of 55°S may be due to the low OH concentration and/or due to the high DMS concentration in the ocean.

Obviously there were regional deviations of atmospheric DMS concentration in both hemispheres. If the number density of CCN is primarily controlled by the oxidation process of DMS in the remote marine atmosphere, CCN should also be correlated to MSA concentration. Ayers and Gras (1991) found in Tasmania that mutual relationships occur among concentrations of CCN, DMS, and MSA. They suggested that there is another source of CCN besides the biogenic source. It is very important to determine what percentage of CCN is produced by the biogenic DMS in the remote marine atmosphere.

Acknowledgements

We thank Prof. A. Sumi for giving us the opportunity to participate in the N91-01 Natsushima cruise for the JAPACS Project. The authors wish to thank Dr. K. Matsunaga for technical advice, and Dr. S. Aoki and Mr. Y. Minami for their sincere support of our observations. We also thank Dr. Y. Suzuki for his helpful advice. We are thankful to Mr. K. Ando

for his arrangement of the observations, and to the officers and crews of the *R/V Natsushima* and the *R/V Shirase* for their extensive cooperation. We are indebted to Dr. T. Fujitani and Dr. Haginoya for providing meteorological data from the *R/V Natsushima* cruise. This research was supported by the Nagoya University research fund, for which we thank Prof. N. Handa, and a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References

- Andreae, M.O., 1986: The ocean as a source of atmospheric sulfur compounds. *in The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Ménard, 331–362, D. Reidel, Dordrecht.
- Andreae, M.O., R.J. Ferek, F. Bermond, K.P. Byrd, R.T. Engstrom, S. Hardin, P.D. Houmère, F. LeMarrec, H. Raemdonck, and R.B. Chatfield, 1985: Dimethyl sulfide in the marine atmosphere. *J. Geophys. Res.*, **90**, 12891–12900.
- Andreae, M.O. and H. Raemdonck, 1983: Dimethyl sulfide in the surface ocean and the marine atmosphere: A global view. *Science*, **221**, 744–747.
- Ayers, G.P. and J.L. Gras, 1991: Seasonal relationship between cloud condensation nuclei and aerosol methanesulphonate in marine air. *Nature*, **353**, 834–835.
- Barnard, W.R., M.O. Andreae, W.E. Watkins, H. Binge and H.-W. Geogii, 1982: The flux of dimethylsulfide from the oceans to the atmosphere. *J. Geophys. Res.*, **87**, 8787–8793.
- Barnes, I., K.H. Becker, P. Carlier and G. Mouvier, 1987: FTIR study of the DMS/NO₂/I₂/N₂ photolysis system: The reaction of IO radicals with DMS. *Int. Chem. Kinetics*, **19**, 489–501.
- Bates, T.S., J.E. Johnson, P.K. Quinn, P.D. Goldan, W.C. Kuster, D.C. Covert and C.J. Hahn, 1990: The biogeochemical sulfur cycle in the marine boundary layer over the northeast Pacific Ocean. *J. Atmos. Chem.*, **10**, 59–81.
- Bates, T.S., J.C. Cline, R.H. Gammon and S.R. Kelly-Hansen, 1987: Regional and seasonal variations in the flux of oceanic dimethylsulfide to the atmosphere. *J. Geophys. Res.*, **92**, 2930–2938.
- Berresheim, H., M.O. Andreae, G.P. Ayers, R.W. Gillett, J.T. Merrill, V.J. Davis and W.L. Chameides, 1990: Airborne measurements of dimethylsulfide, sulfur dioxide, and aerosol ions over the Southern Ocean south of Australis. *J. Atmos. Chem.*, **10**, 341–370.
- Berresheim, H., 1987: Biogenic sulfur emissions from the Subantarctic and Antarctic Oceans. *J. Geophys. Res.*, **92**, 13245–13262.
- Charlson, R.J., J.E. Lovelock, M.O. Andreae and S.G. Warren, 1987: Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature*, **326**, 655–661.
- Cline, J.D. and T.S. Bates, 1983: Dimethyl sulfide in the equatorial Pacific Ocean: A natural source of sulfur to the atmosphere. *Geophys. Res. Lett.*, **10**, 949–952.

- Dlugokencky, E.J. and C.J. Howard, 1988: Laboratory studies of NO₃ radical reactions with some atmospheric sulfur compounds. *J. Phys. Chem.*, **92**, 1188–1193.
- Fukuchi, M., 1980: Phytoplankton chlorophyll stocks in the Antarctic Ocean. *J. Oceanogr. Soc. Japan*, **36**, 73–84.
- Hatakeyama, S., K. Izumi and H. Akimoto, 1985: Yield of SO₂ and formation of aerosols in the photo-oxidation of DMS under atmospheric conditions. *Atmos. Environ.*, **19**, 135–141.
- Hayduck, W. and H. Laudie, 1974: Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions. *Am. Inst. Chem. Eng. J.*, **20**, 611–615.
- Heidt, L.E., J.P. Krasnec, R.A. Lueb, W.H. Pollock, B.E. Henry, P.J. Crutzen, 1980: Latitudinal distributions of CO and CH₄ over the Pacific. *J. Geophys. Res.*, **85**, 7329–7336.
- Hynes, A.J., P.H. Wine and D.H. Semmes, 1986: Kinetics and mechanism of OH reactions with organic sulfides. *J. Phys. Chem.*, **90**, 4148–4156.
- Kadota, H. and Y. Ishida, 1972: Production of volatile sulfur compounds by microorganisms. *Ann. Rev. Microbiol.*, **26**, 127–138.
- Koga, S. and H. Tanaka, 1992: Numerical study of oxidation process of dimethylsulfide in the marine atmosphere. submitted to *J. Atmos. Chem.*
- Liss, P.S. and L. Merlivat, 1986: Air-sea gas exchange rates: Introduction and synthesis. in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Ménard, 113–127. D. Reidel, Dordrecht.
- Liss, P.S. and P.G. Slater, 1974: Flux of gases across the air-sea interface. *Nature*, **247**, 181–184.
- McFarland, M., D. Kley, J.W. Drummond, A.L. Schmeltekopf and R.H. Winkler, 1979: Nitric oxide measurements in the equatorial Pacific region. *Geophys. Res. Lett.*, **6**, 605–608.
- McCartney, E.J., 1976: *Optics of the Atmosphere: Scattering by Molecules and Particles*, 89, Wiley and Sons, New York.
- Martin, D., J.L. Jourdain, G. Laverdet and G. Le-Bras, 1987: Kinetic study of the reaction of IO with CH₃SCH₃. *Int. Chem. Kinetics*, **19**, 503–512.
- Nguyen, B.C., N. Mihalopoulos and S. Belvies, 1990: Seasonal variation of atmospheric dimethylsulfide at Amsterdam Island in the southern Indian Ocean. *J. Atmos. Chem.*, **11**, 123–141.
- Nguyen, B.C., B. Bonsang and A. Gaudry, 1983: The role of the ocean in the global atmospheric sulfur cycle. *J. Geophys. Res.*, **88**, 10903–10914.
- Noxon, J.F., 1983: NO₃ and NO₂ in the Mid-Pacific troposphere. *J. Geophys. Res.*, **88**, 11017–11021.
- Reed, R.H., 1983: Measurement and osmotic significance of β -dimethylsulphonio propionate in marine algae. *Mar. Biol. Lett.*, **4**, 173–181.
- Saltzman, E.S. and D. Cooper, 1988: Shipboard measurements of atmospheric dimethylsulfide and hydrogen sulfide in the Caribbean and Gulf of Mexico. *J. Atmos. Chem.*, **7**, 191–209.
- Saltzman, E.S., D.L. Savoie, J.M. Prospero and R.G. Zika, 1986: Methanesulfonic acid and non-sea-salt sulfate in Pacific air: Regional and seasonal variation. *J. Atmos. Chem.*, **4**, 227–240.
- Turner, S.M., G. Malin, P.S. Liss, D.S. Harbour and P.M. Holligan, 1988: The seasonal variation of dimethyl sulfide and dimethylsulfonylpropionate concentrations in nearshore waters. *Limnol. Oceanogr.*, **33**, 364–375.
- Vairavamurthy, A., M.O. Andreae and R.L. Iverson, 1985: Biosynthesis of dimethylsulfide and dimethylpropiothetin by *Hymenomonas carterae* in relation to sulfur source and salinity variations. *Limnol. Oceanogr.*, **30**, 59–70.
- Warneck, P., 1988: *Chemistry of the Natural Atmosphere*, 115, Academic Press. San Diego.
- Wilke, C.R. and P. Chang, 1955: Correlation of diffusion coefficients in dilute solutions. *Am. Ind. Chem. Eng. J.*, **1**, 264–270.

西部太平洋および南部インド洋において測定されたジメチルサルファイド

古賀聖治・田中 浩

(名古屋大学水圏科学研究所)

林 政彦

(名古屋大学太陽地球環境研究所)

1990年12月28日から1991年3月13日まで、海洋科学技術センター所属の観測船「なつしま」に乗船し、西部太平洋における大気中および海水中のジメチルサルファイド(DMS)の濃度測定を行った。大気DMS濃度の平均値は、経度180°以西の赤道(11pptv)では北部太平洋海域(9pptv)と同様に低濃度であった。160°Wの15°Nから赤道までは、大気DMS濃度は約42pptvでほぼ一様であった。大気DMS濃度の急激な増加が、160°Wと経度180°に沿う海域の赤道の南側で観測され、(5°S, 160°W)付近で大気DMS濃度は約95pptvに達した。表面海水中のDMS濃度も赤道の南側で高く、最高値は(5°S, 180°)で1.85nmol L⁻¹を示した。大気中と表面海水中のDMS濃度の同時観測を6時間間隔で、(6°S, 179°W)から

(11°S, 175.5°W) まで行った。DMS 濃度は、表面海水中では 1.26nmol L^{-1} でほぼ一様であったが、大気中では日変化が観測された。この時の大気 DMS 濃度の平均値は 76pptv であった。

大気 DMS の濃度と日変化は、海面から大気への DMS フラックスの強さと、昼間の OH ラジカルとの酸化反応によって説明できることが、観測結果とモデル計算に基づいて示された。夜間の NO_3 ラジカルとの反応もまた重要であり、DMS 濃度の日変化に関する振幅を減少させる役目を担っている。さらに、風速はおそらく DMS フラックスを規定する重要な因子であろう。

南部インド洋においても、1990 年 12 月 3 日から 12 日まで、観測船「しらせ」船上で大気中の DMS 濃度を測定した。濃度は、50°S 以北では約 60pptv であったが、それ以南では 460pptv まで高緯度に向かって急激に増加した。海水中の高い DMS 濃度と暴風雨圏での低い OH 濃度が、大気中の高い DMS 濃度の原因であると考えられる。