

Flux of dimethylsulfide in the Jiaozhou Bay, China*

Hu Min, Tang Xiaoyan

Center of Environmental Sciences, Peking University, Beijing 100871, China

Li Jinlong, Yu Zhongju

Department of Technical Physics, Peking University, Beijing 100871, China

Abstract— Seasonal measurements of dimethylsulfide (DMS) in surface waters were carried out during 1993–1994 in the Jiaozhou Bay. A seasonal variation is observed for DMS concentrations in seawater, ranging from 0.6 to 8.97 nmol S/L with the highest values in spring. A factor of 4 was measured for DMS concentrations with mean concentrations of 5.85 nmol S/L or 6.58 nmol S/L in spring and 1.40 nmol S/L in winter. A sea-to-air flux of DMS also showed a seasonal variation.

Keywords: dimethyl sulfide; flux; seawater; atmosphere.

1 Introduction

Oceanic dimethylsulfide (CH_3SCH_3 , DMS) is likely to be produced by enzymatic cleavage of dimethylsulfoniopropionate (DMSP) which is an important compound in osmoregulation of phytoplankton cells (Turner, 1988). The sea surface layers are always supersaturated with DMS, which implies a net flux to the atmosphere. Andreae (Andreae, 1986) estimated that the gaseous sulfur flux from the ocean to the atmosphere lies between 1.1 and 1.6 t mol/a, and that the flux of DMS is 1.1 t mol/a. If the natural sulfur cycle is taken precisely into account, the impact of human activity to the earth's environment can be further understood.

Atmospheric DMS is initially oxidized by OH in the daytime and nitrate radical (NO_3) at night (Andreae, 1986; Yin, 1990). The oxidation of atmospheric DMS seems to contribute largely to the formation of aerosol particles containing non-sea-salt sulfate (nss-SO_4^{2-}) in the marine troposphere (Saltzman, 1988; Savoie, 1989). It is hypothesized by Charlson *et al.* (Charlson, 1987) that an increase of DMS flux would increase the number density of cloud concentration nuclei (CCN), thus enhancing cloud albedo. The enhancement would subsequently decrease seawater temperature, and would consequently decrease marine productivity and DMS emission. It is essentially important to elucidate quantitatively the relationship between DMS emissions and CCN composed of nss-SO_4^{2-} in the marine troposphere, not

* This work was supported by the National Natural Science Foundation of China

only for the global biogeochemical sulfur cycle but also for the global climate change.

Measurements of DMS concentrations along the coastline of China and estimations of DMS fluxes are necessary for predicting DMS roles in acid precipitation and provide important information regarding climate change.

In this paper we present results of measurements taken over 2 year periods in order to know the variation of DMS in seawater and assess the sea-to-air flux of DMS in the Jiaozhou Bay.

2 Determination of DMS in sea water

DMS determination method (Hu, 1995) was set up based on international literature (Andreae, 1983; Line, 1983; Bates, 1987; Burgermeister, 1990). A sea water sample of 50 ml was purged with pure nitrogen gas flow of 20 to 30 ml per minute for a period 35 minutes. Before entering the cryotrap the gas stream was dried by a Teflon tube immersed into an ice-salt bath (-10°C) to prevent icing. This gas was then passed through a U-tube packed with chromosorb R and immersed in liquid nitrogen. After collection, the DMS samples were analyzed by gas chromatography with flame photometric detection as soon as possible. The cryotrap (liquid N_2) was connected to the gas chromatographic system via six-way-valve purged with dry nitrogen gas. The column used was $2\text{m} \times 3\text{mm}$ Carbopake B/1.5% XE-60/1.0% H_3PO_4 , 60–80 mesh, packed in teflon tubing. The liquid N_2 was removed and the trap heated at around 90°C by a glycerine bath, then DMS was released and injected into the GC for separation and detection. Maximal desorption of DMS without interferences due to water vapor released from the cold trap was achieved at 90°C .

Calibration of the DMS chromatographic system is performed by injecting a few microliters in the range of 2.0–30.0 ng of DMS in ethylene glycol into 50ml of degassed sea water. The standard was purged with pure nitrogen gas into the cryotrap and analyzed in the same manner as the sea water samples. Concentrations of DMS were expressed as standard.

The accuracy and precision for DMS measurement method are 10% and 12%, respectively, based on replicate analyse ($n=10$) of samples and comparison with the standards.

3 Results and discussion

3.1 DMS concentration in sea water

Sea water samples were obtained from sea surface water and transferred, after measuring the temperature, into a polyvinyl chloride bottle. The surface samples were analyzed by the method mentioned above as soon as possible to avoid possible storage artifacts.

Measurements of DMS in sea water were carried out in Jiaozhou Bay between January 1993 and the end of September of 1994. The sampling locations are shown in Fig. 1.

Measurement results of DMS in the Jiaozhou Bay are shown in Table 1. In 1993 lowest DMS concentrations occurred in winter, ranging from 0.6 to 3.69 nmol S/L with a mean of 1.40 nmol S/L. The highest DMS concentrations were measured in summer, ranging from

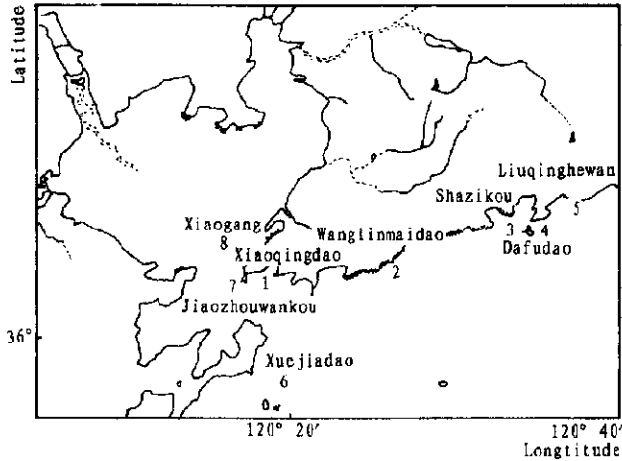


Fig. 1 Map of Jiaozhou Bay
Numbers refer to the sampling locations

3.92 to 6.94 nmol S/L with a mean of 5.85 nmol S/L. As the same, in 1994 DMS concentrations increased in spring, ranging from 3.60 to 8.97 nmol S/L with a mean of 6.58 nmol S/L, then DMS concentrations decreased in autumn ranging from 1.24 to 3.29 nmol S/L with a mean of 1.94 nmol S/L.

Table 1 DMS concentrations (nmol S/L) in the Jiaozhou Bay

Station	Winter 1993,1	Spring 1993,5	Summer 1993,7	Autumn 1993,10	Spring 1994,4	Autumn 1994,9
1	no data	6.76	4.08	3.29	8.76	1.69
2	0.90	3.92	6.16	3.35	7.79	3.16
3	0.80	6.40	no data	no data	6.74	3.29
4	3.69	6.32	no data	no data	8.97	1.24
5	0.98	4.61	no data	no data	5.44	1.19
6	0.85	6.94	3.27	no data	7.02	2.00
7	no data	5.87	no data	no data	3.60	1.37
8	no data	6.06	no data	no data	4.34	1.52
Avg.	1.40	5.85	4.50	3.32	6.58	1.94

A seasonal variation of the oceanic DMS was served in the Jiaozhou Bay with a maximum in spring and a minimum in winter (Table 2). In 1993 DMS concentrations varied by a factor of 4 between spring and winter, with mean concentrations of 5.85 and 1.40 nmol S/L, respectively. DMS concentrations in each sampling station also showed obvious seasonal variation. Difference in DMS concentrations among the sampling stations even in the same season may be due to the difference in the phytoplankton production and species.

Table 2 Sea-to-air flux of DMS in the Jiaozhou Bay

Station	Winter	Spring	Summer	Autumn	Spring	Autumn
	1993.1	1993.5	1993.7	1993.10	1994.10	1994.9
<i>T</i>	4	10	24	20	10	24.2
<i>D</i> , $\times 10^{-5}$	0.527	0.676	1.105	0.971	0.676	1.112
<i>K</i>	1.215	0.939	0.781	1.256	1.212	1.063
<i>C</i>	1.40	5.85	4.50	3.32	6.58	1.94
<i>F</i>	1.70	5.49	3.51	4.17	7.97	2.06

Notes: sea water temperature (*T*, °C), coefficient of molecular diffusion of DMS (*D*, 10^{-5} , cm^2/s), exchange constant (*K*, m/d), DMS concentration (*C*, nmol S/L), and sea-to-air flux of DMS (*F*, $\mu\text{mol}/(\text{m}^2, \text{d})$)

It seems that DMS produced by biological activity phytoplankton and zooplankton in surface seawater were consistent with phytoplankton activity. Fig. 2 shows the primary productivity of phytoplankton as well as chlorophyll-a concentrations as phytoplankton biomass in the Jiaozhou Bay (Guo, 1992). It is evident that when phytoplankton blooms in spring, high DMS concentrations are measured, however, when phytoplankton declines, minimum DMS concentrations are observed.

3.2 Flux of DMS from the ocean to the atmosphere

The model of Liss and Slater (Liss, 1974) was used to predict the sea-to-air flux of DMS. In this model the flux between liquid and gas phase is determined by the rate of molecular diffusion across a stagnant film with the thickness *Z*. The concentrations in the gas and liquid phase are C_g and C_l , respectively. The transfer rate is determined by the exchange constant *K*,

$$F = K(C_g/H - C_l) = D/Z(C_g/H - C_l),$$

where, *H* is Henry's law constant; *D* is coefficient of molecular diffusion of gas in stagnate layer. In the case of DMS, the atmosphere is highly under saturated with respect to the co-existing sea water ($H=0.3 \text{ g per cm}^3 \text{ air/g per cm}^3 \text{ water}$), so that $C_g/H \ll C_l$, and thus $F = -K \times C_l$.

Different approaches have been used to obtain the exchange constant *K*. Here Kromer method (1979) is applied. Based on field experiments with the radon method, Kromer gives a bilinear function for the dependence of K_{Rn} on *V*:

$$K_{Rn} = 0.075 \times V \quad (0 < V < 4 \text{ m/s}),$$

$$K_{Rn} = 0.72(V - 4) + 0.3 \quad (V > 4 \text{ m/s}).$$

The exchange constants obtained by this method for radon were then converted. Assuming that the salinity of sea water in the Jiaozhou Bay is 30‰, and averages of wind velocity measured for several years are applied to estimate DMS flux (Fig. 2). It was evident that a seasonal variation of the sea-to-air flux of DMS was observed with a maximum in spring and minimum in winter in the Jiaozhou Bay (Table 3).

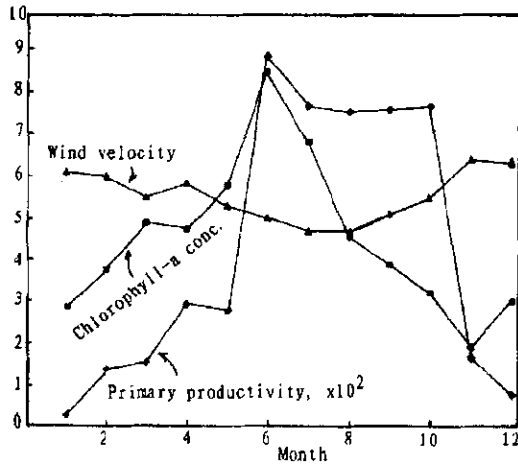


Fig. 2 Chlorophyll-a concentrations (mg/m^3), primary productivity ($\text{mg C}/(\text{m}^2 \cdot \text{d})$) and wind velocity (m/s) in the Jiaozhou Bay

Table 3 Comparison of DMS concentrations and fluxes with North Pacific data (Bates *et al.*, 1987)

Region	Time	DMS conc. ,	Flux.
		nmol S/L	$\mu\text{mol}/(\text{m}^2 \cdot \text{d})$
N. Pacific, 35—50°N	Nov. — April	0.66	2.21
N. Pacific, 20—35°N	Nov. — April	0.72	2.15
Jiaozhou Bay	Dec. — Feb.	1.40	1.70
Jiaozhou Bay	March—May	5.85/6.58	5.49/7.97
N. Pacific, 35—50°N	May—Oct.	2.22	4.96
N. Pacific, 20—35°N	May—Oct.	2.15	5.14
Jiaozhou Bay	June—Aug.	4.50	3.51
Jiaozhou Bay	Sept. —Nov.	3.32/1.94	4.17/2.06

4 Conclusions

The estimated fluxes in the Jiaozhou Bay are compared with the values reported in the literature by Bates *et al.* (Bates, 1987) in Table 3. The conclusion is that DMS fluxes from the Jiaozhou Bay are close to values for the North Pacific in the zone 20—50°N. The fluxes in the Chinese waters are slightly higher than the North Pacific values, probably because the rate of primary production in the Jiaozhou Bay is higher than that in the other seas in this temperature zone. Furthermore the average values for the Chinese waters are clearly influenced by strong maximum in the spring due to a strong development of phytoplankton in this period.

References

- Andreae MO, Barnard WR. *Anal Chem*, 1983;55:612
- Andreae MO. The role of air-sea exchange in geochemical cycling Dordrecht: D Reidel. 1986;311
- Bates TS, Cline JD, Gammon RH, Kelly-Hansen SR. *J Geophys Res*, 1987;92:2930
- Burgermeister S, Zimmermann RL, Georgii HW, Bingemer HG, Kirst GO, Janssen M, Ernst W. *J Geophys Res*, 1990; 95:20607
- Charlson RJ, Lovelock JE, Andreae MO, Warren SG. *Nature*, 1987; 326:655
- Cline JD, Bates TS. *Geophys Res Lett*, 1983; 10:949
- Guo Yujie, Yang Zheyu. *Ecology and biological resources in the Jiaozhou Bay, Beijing: Science Press, 1992*
- Hu Min. *Environmental Chemistry*, 1995; 14(2):157
- Krome B, *Gasaustausch Zwischen Atmosphere und Ozean-Feldmessungen mit der Radonmethode, Ph. D thesis, Univ. of Heidelberg, 1979*
- Liss P Sand Slater PG. *Nature*, 1974; 247:181
- Saltzman ES, Cooper D. *J Atmos Chem*, 1988;7:191
- Savoie DL, Prospero JM. *Nature*, 1989;339:685
- Turner SM, Malin G, Liss PS, Harbour DS, Holligan PM. *Limnol Oceanogr*, 1988;33:364
- Yin F, Grosjean D, Seinfeld JH. *J Atmos Chem*, 1990; 11:309

(Received July 16, 1995)