

This article was downloaded by: [North Carolina State University]

On: 18 November 2014, At: 11:02

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Chemical Engineering Communications

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcec20>

THE EMISSION RATE OF DIMETHYL SULFIDE AT THE ATMOSPHERIC-OCEANIC INTERFACE

VINEY P. ANEJA^a & JOHN H. OVERTON^b

^a Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC, 27695

^b 1911 Fountain Ridge Road, Chapel Hill, NC, 27514

Published online: 06 Apr 2007.

To cite this article: VINEY P. ANEJA & JOHN H. OVERTON (1990) THE EMISSION RATE OF DIMETHYL SULFIDE AT THE ATMOSPHERIC-OCEANIC INTERFACE, Chemical Engineering Communications, 98:1, 199-209, DOI: [10.1080/00986449008911570](https://doi.org/10.1080/00986449008911570)

To link to this article: <http://dx.doi.org/10.1080/00986449008911570>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Chem. Eng. Comm. 1990, Vol. 98, pp. 199–209
Reprints available directly from the publisher.
Photocopying permitted by license only.
© 1990 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

THE EMISSION RATE OF DIMETHYL SULFIDE AT THE ATMOSPHERIC-OCEANIC INTERFACE

VINEY P. ANEJA

*Department of Marine, Earth, and Atmospheric Sciences
North Carolina State University
Raleigh, NC 27695*

and

JOHN H. OVERTON

*1911 Fountain Ridge Road
Chapel Hill, NC 27514*

(Received March 12, 1990; in final form July 25, 1990)

Dimethyl sulfide appears to be present everywhere in the surface ocean, is readily transferred into the marine atmosphere, and may account for about 30% of the natural component of the overall sulfur budget in the atmosphere. To investigate the apparent discrepancies between measured DMS fluxes, and theoretical predictions, we have examined the transport of DMS across the marine-atmosphere interface. An analysis of vertical flux was performed with a two-film model for the transport of DMS across the marine-atmosphere interface with chemical reactions. The photosensitized oxidation of DMS, its reaction with hydrogen peroxide in the aqueous film, and reactions with nitrate and hydroxyl radicals in the gas film have negligible effect on the DMS flux to the marine atmosphere. However, the flux of DMS into the atmosphere is most sensitive to the liquid-film thickness but not to changes in temperature and gas-film thickness. Model calculations showed that if the liquid-film thickness increases from 35 μm (turbulent sea conditions) to 200 μm (calm sea conditions), the flux of DMS reduces from 290 to 55 $\mu\text{g S m}^{-2} \text{ day}^{-1}$ at an ocean temperature of 15°C for a constant gas-film thickness of 0.3 cm.

KEYWORDS Dimethyl sulfide Emission Atmospheric Ocean Interface.

INTRODUCTION

Dimethyl sulfide (DMS) is gaining increasing importance as the principal source of volatile sulfur to the marine atmosphere, and it may control the concentration of SO_2 in the remote marine atmosphere (Houmère *et al.*, 1985). It is readily emitted across the sea-air interface due to its volatility. DMS was discovered in the surface ocean by Lovelock *et al.* (1972). They suggested that DMS may be the biogenic sulfur species that balances the global sulfur budget in contrast to hydrogen sulfide, which had been speculated as the biogenically produced missing link at the time. The DMS emitted naturally by oceanic waters into the atmosphere is now being suggested as the cause of decreased pH of precipitation and cloud nuclei measured in remote areas over the ocean (Miller and Yoshinaga, 1981; Galloway *et al.*, 1982), owing to the formation of sulfate (SO_4^{2-}) from DMS oxidation (Luria *et al.*, 1986). It has also been suggested that its gaseous oxidation products may be a source of cloud condensation nuclei, leading to increased

aerosol albedo over the ocean (Charleson *et al.*, 1987), which may then lead to global climate change. Therefore, the role of DMS in the global atmospheric sulfur cycle may well be more important than has been thought of thus far. Hence determination of DMS flux from oceanic surface into the atmosphere is desirable in order to permit accurate assessment of the relative roles of anthropogenic and biogenic sulfur sources in contributing to atmospheric sulfate formation, which may influence environmental acidification and global climate change.

DMS is produced in oceanic waters by both benthic and planktonic marine organisms (Challenger, 1951; Dacey and Wakeham, 1986) suggesting that it may be ubiquitous in the surface ocean (Barnard *et al.*, 1982). It is thought to originate from the decomposition of dimethyl-sulfoniopropionate (DMSP) produced by marine organisms, in particular, phytoplankton. Dacey and Wakeham (1986) have suggested that the release of DMS by phytoplankton is enhanced when zooplankton grazes on phytoplankton. Its concentration in the upper layer of the ocean varies between a few nanograms of S per liter to about a few micrograms of S per liter (Lovelock *et al.*, 1972; Barnard *et al.*, 1982; Andreae and Raemdonck, 1983; Cline and Bates, 1983; Nguyen *et al.*, 1978, 1983). Based on DMS concentration in the atmosphere and its Henry's Law constant in sea water, oceanic DMS concentration is greatly in excess of those that would be in equilibrium with atmospheric values (Dacey *et al.*, 1984). The DMS surface concentration distribution is highly non-uniform; its average concentration is approximately 100 nanograms of S per liter. It has been observed that the concentration of DMS is dependent on diurnal (Andreae and Barnard, 1984), and seasonal variations (Turner and Liss, 1985), and on depth and location (Andreae and Raemdonck, 1983).

Liss and Slater (1974) made preliminary estimates of DMS sea-to-air flux based on limited data. However, the first known direct measurements of DMS biogenic fluxes from a marine environment (i.e., salt marsh) were made by Aneja (1975) and Hill *et al.* (1978). These measurements were made at low tide in a salt marsh on Long Island, NY. DMS fluxes varied within the range of 2700 to 10,000 $\mu\text{g m}^{-2} \text{day}^{-1}$, far in excess (about 100 $\mu\text{g m}^{-2} \text{day}^{-1}$) of DMS release from an open oceanic surface. The high values at low tide seem to reflect the biogenic activity that perhaps goes on at the source.

DMS may be removed from the oceanic surface waters by either physical, chemical, and biological pathways or any combination of these pathways. Figure 1 illustrates the various pathways for DMS removal. Some of them have been studied by Brimblecombe and Shooter (1986).

The physical transfer is perhaps best accomplished by either transfer of DMS to the atmosphere (pathway i), or transport to the deep ocean (pathway ii), or DMS adsorption/absorption on settling particles thus providing an effective mechanism for transporting the sulfide to the deep ocean (pathway iii).

The removal of DMS from the oceanic surface waters by chemical processes may be accomplished in a variety of ways; two processes being removal of DMS through complexing with metal ions (pathway iv), or removal of DMS through oxidation by metal ions (pathway v) such as Fe(III) or Cr(VI) (Srinivasan *et al.*, 1985). At the present time, however, there is little kinetic data in the literature

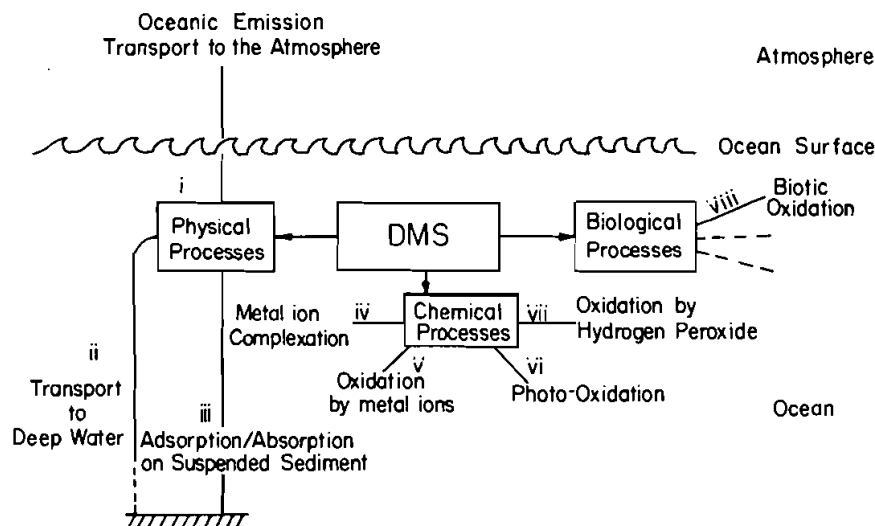


FIGURE 1 Some possible removal mechanisms for DMS from the oceanic surface waters.

for its reactions with transition metals in aqueous alkaline media such as oceanic waters. Also, the metal ion concentrations may be too small to make these pathways competitive. Although chemically stable, DMS appears to be quite readily photo-oxidized in the presence of photosensitizers (pathway vi). Brimblecombe and Shooter (1986) have shown that photosensitizers (methylene blue, Rose bengal, humic acid) in sea water can photo-oxygenate aqueous DMS in sunlight with a first order rate constant of $2.4 \times 10^{-5} \text{ sec}^{-1}$. Hydrogen peroxide (H_2O_2) has been shown to be present in oceanic waters (Zika *et al.*, 1985). It exhibits surface maxima of about $2 \times 10^{-7} \text{ mol l}^{-1}$ and decreasing concentrations with depth. It may be generated by photochemical or photobiological reactions in the top meter of the oceanic surface (see review by Zafriou *et al.*, 1984), deposition of oxidants, and by direct deposition from the atmosphere. The concentration of H_2O_2 from each of those processes is dependent upon the UV intensity in either the surface water and atmosphere. DMS may be removed from the oceanic surface water (pathway vii) by oxidation by H_2O_2 (Adewuyi and Carmichael, 1986) with an effective first order rate constant of about $7 \times 10^{-9} \text{ sec}^{-1}$ (Appendix A).

In addition to these removal mechanisms for DMS from the oceanic surface waters, it is also possible that DMS is lost through biological reactions (pathways viii). Andreae (1980) has hypothesized that biotic processes may be responsible for the oxidation of DMS to dimethylsulfoxide (DMSO) which was detected at concentrations ($10\text{--}20 \text{ n mol l}^{-1}$) substantially in excess of those of DMS in coastal waters. He suggests that DMSO is further oxidized to sulfate ion. The major pathway has not been established and there may be other biological removal pathways for DMS.

In the atmosphere, DMS may encounter three processes for its depletion. It may be removed chemically by oxidization (Cox and Sandalls, 1974; Atkinson *et*

al., 1978; Graedel, 1979; Panter and Penzhorn, 1980; Winer *et al.*, 1984) or removed by dry and wet deposition. We assumed that gas-phase oxidation process is the major pathway of removal in the gas film.

In an effort to understand the results of apparent inconsistent experimental and modeling efforts, concerning the flux of DMS from the ocean, and thus the role of DMS in the global sulfur cycle; and its possible role in the Earth's albedo change; we have performed an analytical investigation of one of the primary sources of sulfur in the atmosphere, i.e., emission of DMS from oceanic waters to the atmosphere. The major focus of this study is to determine the role of known chemical reactions on DMS mass transfer at the ocean-atmosphere interface. Analytical investigations using a thin-film model for mass transfer coupled with aqueous and gaseous phase chemical reactions of DMS have been explored to assess the role of chemistry. An alternate approach, surface renewal theory, would give approximately the same results (Danchwerts, 1970). We have ignored: (a) all biological removal processes for DMS, for there exists uncertainty in their use; (b) removal by catalytic metal ion reactions; and (c) production processes in the thin film.

PHYSICO-CHEMICAL MODEL

The principal characteristics of our transport model (Figure 2) is the two-layer model of a gas-liquid interface for exchange between water and air (Whitman, 1923; Liss and Slater, 1974). The interface between the two phases is often considered as a two-layered (film) system. Each layer is a laminar surface layer of thickness δ_i (liquid phase, $i=l$; and gas phase, $i=g$) extending from the gas-liquid interface to the well-mixed region in the interior of the ocean and the atmosphere (Figure 2). All the resistance to mass transfer across the interface is due to the layers in which transport is by molecular processes. This transport model is coupled with the DMS chemical reactions both in the liquid and gas

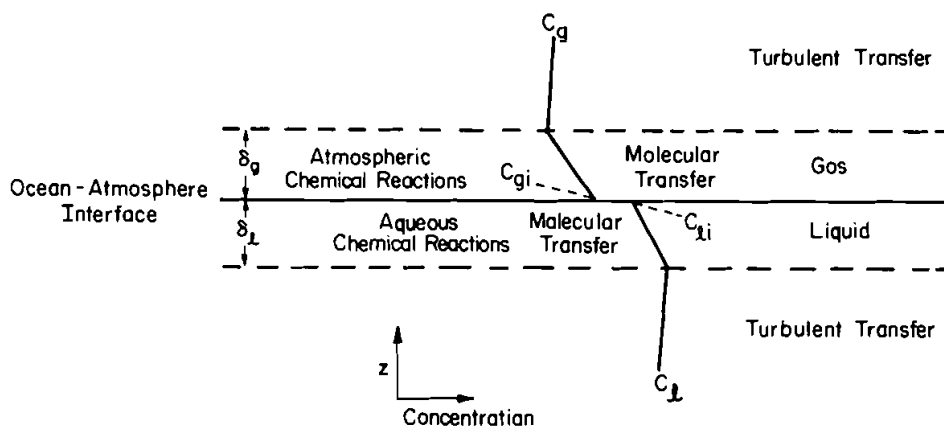


FIGURE 2 Two-layer model of a gas-liquid interface. Mass transfer only in vertical direction.

films. In the aqueous film we have considered DMS reactivity with H_2O_2 (Adewuyi and Carmichael, 1986) and its photo-oxidation (Brimblecombe and Shooter, 1986). In the gas film the chemical removal of DMS occurs via reactions with nitrate (NO_3) (Winer *et al.*, 1984) and hydroxyl (HO) (Atkinson *et al.*, 1978) radicals. Account is also taken for day and night time reactivities.

We have assumed steady state mass transport with chemical reactions. Hence

$$D_i \frac{d^2 C_i}{dZ^2} = k_{1i} C_i \quad (1)$$

where,

- C_i = DMS concentration
- D_i = molecular diffusion coefficient
- Z = vertical direction
- k_{1i} = 1st order rate constant
- δ_i = film thickness
- $i = l$ or g
- l = liquid phase
- g = gas phase

In the liquid phase the boundary conditions are:

$$Z = 0: C_l(0) = C_l \quad (2a)$$

$$Z = \delta_l: C_l(\delta_l) = C_{li} \quad (2b)$$

In the gas phase the boundary conditions are:

$$Z = 0: C_g(0) = C_{gi}, \quad (3b)$$

$$Z = \delta_g: C_g(\delta_g) = C_g \quad (3c)$$

The solutions to Eq. (1) with boundary conditions (2) and (3) are: For liquid film,

$$C(Z) = \frac{\{[\exp(\alpha_l Z) - \exp(-\alpha_l Z)]C_{li} - [\exp(\alpha_l(Z - \delta_l)) - \exp(-\alpha_l(Z - \delta_l))]\}C_l}{[\exp(\alpha_l \delta_l) - \exp(-\alpha_l \delta_l)],} \quad (4a)$$

where

$$\alpha_l = \sqrt{k_{1l}/D_l}$$

For gas film,

$$C(Z) = \frac{\{[\exp(\alpha_g Z) - \exp(-\alpha_g Z)]C_g - [\exp(\alpha_g(Z - \delta_g)) - \exp(-\alpha_g(Z - \delta_g))]\}C_{gi}}{[\exp(\alpha_g \delta_g) - \exp(-\alpha_g \delta_g)],} \quad (4b)$$

where

$$\alpha_g = \sqrt{k_{1g}/D_g}$$

RESULTS AND DISCUSSION

Based on the values of the physico-chemical parameters (Table I), the exponents, $\alpha_i \delta_i$, in Eqs. (4a) and (4b) are estimated to be $< 0.03 \text{ cm}^{-1}$ in both films. Substituting these values in Eqs. (4) we ascertain that chemical reactions have negligible effect on the fluxes of DMS through the oceanic gas-liquid interface. This finding is in agreement with the implicit assumption of Barnard *et al.* (1982) and Andreae and Raemdonck (1983) assumption of no effective chemical reactions in the gas and liquid films. However, because of the uncertainty in the values of the chemical rate constants, the range of the values of these parameters for which there would be only an insignificant reduction in the flux of DMS is of interest. Calculations show that increasing k_{1g} alone or k_{1l} alone by factors of up to 500 and 33,000, respectively, reduce the flux of DMS by less than 20% (at 15°C). Considering the components of k_{1l} (see Appendix A), either the photo-oxidation rate or the product of $k_{2[\text{H}_2\text{O}_2]}$ and $[\text{H}_2\text{O}_2]$ could be increased by factors of 10^8 or 33,000, respectively, without significant reduction (less than 20%). The components of k_{1g} , $k_{2[\text{NO}_3]} [\text{NO}_3]$ and $k_{2[\text{OH}]} [\text{OH}]$, could be increased by factors of 500 and 17,000, respectively. No doubt for the chemical reactions considered in this paper, some of the increases that would cause a significant effect (greater than 20% decrease) on the flux are too large to be realized. However, considering the paucity of relevant data, other chemical reactions or mechanisms with rates sufficient to reduce the DMS flux to the atmosphere can not be ruled out at this time.

Based on model simulations, Luria and Meagher (1986) estimated DMS oceanic emission rate of $60 \mu\text{g S m}^{-2} \text{ day}^{-1}$. Also model calculations by Luria *et al.* (1986) suggested that the Gulf of Mexico area emission of DMS is approximately $100 \mu\text{g S m}^{-2} \text{ day}^{-1}$. We therefore readily see that Luria and Meagher (1986) DMS emission rates estimates are about one-fifth and Luria *et al.* (1986) value is one-third of the DMS emission rate estimate made by Andreae and Raemdonck (1983) for the remote oceans, $290 \mu\text{g S m}^{-2} \text{ day}^{-1}$. This apparent discrepancy in the estimate of DMS flux between the model simulation of Luria and Meagher (1986) and Luria *et al.* (1986), and the thin-film model approach of Andreae and Raemdonck (1983) may have its origins in the assumption of no effective chemical or biological reactions in the thin films. However, our

TABLE I

Physico-chemical parameters for DMS transport in liquid and gas films

i	δ_i (cm)	D_i ($\text{cm}^2 \text{ sec}^{-1}$)	k_{1i} (sec^{-1})	$\alpha_i \delta_i$ (cm^{-1})
l	0.02 ^a	1.3×10^{-5}	2.4×10^{-5b}	0.027
g	0.29 ^c	0.13	$< 1.3 \times 10^{-3d}$	0.029

^a Quinn and Otto (1971).^b Appendix.^c $\delta_g = 0.29 \text{ cm} \approx D_{\text{H}_2\text{O}}/k_{g(\text{H}_2\text{O})}$; $D_{\text{H}_2\text{O}} = 0.249 \text{ cm}^2/\text{sec}$ (15°C, Reid *et al.*, 1977); $k_{g(\text{H}_2\text{O})} = 0.833 \text{ cm/sec}$ (Liss & Slater, 1974).^d See Appendix A.

TABLE II

The effect of changing temperature and liquid film thickness on DMS flux (Gas-Film thickness, δ_g , is assumed constant = 0.3 cm)^c

Temperature °C	Liquid-film thickness, δ_l^d microns	Henry's Law constant, H^a (moles/liter air) (moles/liter water)	Mass transfer coefficient			Flux ^{a,b} $\mu\text{g(S)}/\text{m}^2/\text{day}$
			k_g	k_l cm/hr	K^a	
5	10	0.039	1924	43.2	27.4	710
5	35 (world wide average) ^d	0.039	1924	12.3	10.6	274
5	100	0.039	1924	4.3	4.1	105
5	200	0.039	1924	2.15	2.1	54
5	1000 (calm sea) ^d	0.039	1924	0.43	0.42	11
15	10	0.059	2028	43.2	31.7	821
15	35	0.059	2028	12.3	11.2	290
15	100	0.059	2028	4.3	4.15	107
15	200	0.059	2028	2.15	2.11	55
15	1000	0.059	2028	0.43	0.42	11
25	10	0.086	2135	43.2	34.9	905
25	35	0.086	2135	12.3	11.6	299
25	100	0.086	2135	4.3	4.21	109
25	200	0.086	2135	2.15	2.12	55
25	1000	0.086	2135	0.43	0.42	11

^a See Appendix B.

^b Sea water DMS concentration assumed to be that which gives the value of 290 $\mu\text{g(S)}/\text{m}^2/\text{day}$ (Andreae and Raemdonck, 1983) at 15°C, $\delta_l = 35\mu$, and $\delta_g = 0.3$ cm.

^c $\delta_g = 0.3 = D_{\text{H}_2\text{O}}/k_{g(\text{H}_2\text{O})}$; $D_{\text{H}_2\text{O}} = 0.249$ cm²/sec (Reid *et al.*, 1977); $k_{g(\text{H}_2\text{O})} = 0.833$ cm/sec (Liss & Slater, 1974).

^d Quinn & Otto (1971).

TABLE III

The effect of changing temperature and gas film thickness on DMS flux (Liquid-Film thickness, δ_l , is assumed constant = 35 microns)

Temperature °C	Gas-film thickness, δ_g cm	Henry's Law constant, H^a (moles/liter air) (moles/liter water)	Mass transfer coefficient			Flux ^{a,b} $\mu\text{g(S)}/\text{m}^2/\text{day}$
			k_g	k_l (cm/hr)	K^a	
5	0.1	0.039	5771	12.34	11.7	303
5	0.3	0.039	1924	12.34	10.6	274
5	0.5	0.039	1154	12.34	9.7	251
5	1.0	0.039	577	12.34	8.0	206
15	0.1	0.059	6085	12.34	11.9	309
15	0.3	0.059	2028	12.34	11.2	290
15	0.5	0.059	1217	12.34	10.5	272
15	1.0	0.059	609	12.34	9.2	237
25	0.1	0.086	6405	12.34	12.1	312
25	0.3	0.086	2135	12.34	11.6	299
25	0.5	0.086	1281	12.34	11.1	287
25	1.0	0.086	640	12.34	10.1	261

^a See Appendix B.

^b See water DMS concentration assumed to be that which gives the value of 290 $\mu\text{g(S)}/\text{m}^2/\text{day}$ (Andreae and Raemdonck, 1983) at 15°C, $\delta_l = 35\mu$, and $\delta_g = 0.3$ cm.

investigation seems to indicate that the known DMS chemical reactions in the thin surface films do not reduce the DMS surface flux. Hence, other reasons may explain this apparent discrepancy: enhanced DMS reactivity in the film in the Gulf area, different remote oceanic atmospheric conditions, as yet unknown chemical or biological processes, or model assumptions.

The applicability of these results is limited by the lack of knowledge of H_2O_2 concentration in the aqueous film. The H_2O_2 concentration profiles up to the surface for a variety of conditions are not available. Theoretical estimates for the pathways by which H_2O_2 is formed and removed in the aqueous film cannot be performed because of the complex dependence upon UV spectral intensity, concentrations of natural and anthropogenic organic photochemical sensitizers and free-radical carriers, and interacting oxidation-reduction pairs (e.g., Fe(II) and Fe(III)) (Zafiriou *et al.*, 1984).

The contribution of the above mentioned physical processes may be influenced by the degree of turbulence in the ocean and the atmosphere, and their respective temperatures, both affecting the flux of DMS. A change in flux as a function of environmental conditions is presented in Tables II and III. These model sensitivity calculations show that if the liquid film thickness increases from $35\ \mu\text{m}$ (the over-all oceanic average layer thickness, Quinn and Otto, 1971), to $1,000\ \mu\text{m}$ (calm sea conditions, Quinn and Otto, 1971), the flux of DMS reduces from 290 to $11\ \mu\text{g S m}^{-2}\ \text{day}^{-1}$ respectively (Table II), at a temperature of 15°C and the gas-film thickness being assumed constant at $0.3\ \text{cm}$ (Table II). This reflects a change in emission rate of about 96%. Thus changing the liquid-film thickness modifies appreciably the flux of DMS. However, changes in gas film thickness or temperature (Table III) do not appreciably affect the flux of DMS. For example, the DMS emission rate varies between 206 to $312\ \mu\text{g S m}^{-2}\ \text{day}^{-1}$ regardless of gas film thickness and temperature changes. For oceanic conditions corresponding to the two-film model, these results indicate that the transport of DMS through the marine-atmosphere interface is probably controlled by liquid-film resistance.

ACKNOWLEDGEMENT

We thank Dr. Jack L. Durham, U.S. Environmental Protection Agency, Washington, D.C. for his help and encouragement in the preparation of this manuscript, and Professor L. Pietrafesa for the support provided; Brenda Batts for preparation of the manuscript.

REFERENCES

1. Adewuyi, Y.G., and Carmichael, G.R., "Kinetics of Oxidation of dimethyl sulfide by hydrogen peroxide in acidic and alkaline medium", *Environ. Sci. Technol.*, **20**, 10, 1017-1022 (1986).
2. Andreae, M.O., "Dimethylsulfide in marine and freshwaters", *Limnol. Oceanogr.*, **25**, 1054-1063 (1980).
3. Andreae, M.O. and Raemdonck, M., "Dimethyl Sulfide in the Surface Ocean and the Marine Atmosphere: A Global View", *Science*, **221**, 744-747 (1983).

4. Andreae, M.O., and Barnard, W.R., "The marine chemistry of dimethylsulfide", *Marine Chemistry*, **14**, 267-279 (1986).
5. Aneja, V.P., "Characterization of sources of biogenic atmospheric sulfur compounds", M.S. thesis, North Carolina State University, Raleigh, N.C. 27695 (1975).
6. Atkinson, R., Perry, R.A., and Pitts, Jr., J.N., "Rate constants for the reaction of OH-Radicals with COS, CS₂, and CH₃SCH₃ over the temperature range 299-430K", *Chem. Phys. Lett.*, **54**, 14-18 (1978).
7. Barnard, W.R., Andreae, M.O., Watkins, W.E., Bingemer, H., and Georgii, H.W., "The Flux of Dimethylsulfide From the Oceans to the Atmosphere", *Journal of Geophysical Research*, **87**, C11, 8787-8793 (1982).
8. Brimblecombe, P., and Shooter, D., "Photo-oxidation of Dimethylsulfide in aqueous solutions", *Marine Chemistry*, **19**, 343-353 (1986).
9. Challenger, F., "biological methylation", *Adv. Enzymol.*, **8**, 1269-1281 (1951).
10. Charlson, R.J., Lovelock, J.E., Andreae, M.O., and Warren, S.G., "Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate," *Nature*, **326**, 655-661 (1987).
11. Cline, J.D. and Bates, T.S., "Dimethyl sulfide in the equatorial Pacific Ocean: a natural source of sulfur to the atmosphere", *Geophys. Res. Lett.*, **10**, 949-952 (1983).
12. Cox, R.A., and Sandalls, E.J., "The photo-oxidation of hydrogen sulfide and dimethyl sulphide in air", *Atmos. Environ.*, **8**, 1269-1281 (1974).
13. Dacey, J.W.H., and Wakeham, S.G., "Ocean dimethylsulfide: production during zooplankton grazing on photoplankton", *Science*, **233**, 1314-1316 (1986).
14. Dacey, J.W.H., Wakeham, S.G., and Howes, B.L., "Henry's Law Constants for dimethylsulfide in freshwater and seawater", *Geophysical Research Letters*, **11**, 10, 991-994 (1984).
15. Danckwerts, P.V., *Gas-Liquid Reactions*, McGraw-Hill Book Company, New York, 276, 1970.
16. Galloway, J.N., Likens, G.E., Keene, W.C., and Miller, J.M., *J. Geophys. Res.*, **87**, 8771-8786 (1982).
17. Graedel, T.E., "Reduced sulfur emissions from the open oceans", *Geophys. Res. Lett.*, **6**, 329-331 (1979).
18. Hanna, S.R., Schulmann, L.L., Paine, R.J., and Plein, J.E., "The offshore and coastal dispersion model", Environmental Research and Technology Rep. No. 14-08-001-21138, Concord, MA, 1984.
19. Hill, F.B., Aneja, V.P., and Felder, R.M., "A technique for measurement of biogenic sulfur emission fluxes", *J. Environ. Sci Health*, **A13**(3), 199-225 (1978).
20. Houmère, P.O., LeMarrec, F., Raemdonck, H., Chatfield, R.B., Andreae, M.O., Ferek, R.J., Bermond, F., Byrd, K.P., Engstorm, R.T., and Mardin, S., "Dimethyl sulfide in the marine atmosphere", *J. Geophys. Res.*, **90**, 12891-12900 (1985).
21. Liss, P.S., and Slater, P.G., "Flux of gases across the air-sea interface", *Nature*, **247**, 181-184 (1974).
22. Lovelock, J.L., Maggs, R.J., and Rasmussen, R.A., "Atmospheric dimethyl sulfide and the natural sulfur cycle", *Nature*, **237**, 452-453 (1972).
23. Luria, M., Van Valin, C.C., Wellman, D.L., and Pueschel, R.F., "Contribution of Gulf area natural Sulfur to the North American sulfur budget", *Environ. Sci. Technol.*, **20**, 1, 91-95 (1986).
24. Luria, M., and Meagher, J.F., "Computer simulation of the oxidation and removal of natural sulfur compounds in the marine atmosphere", Proceedings of the 7th International Clean Air Congress, Sydney, Australia, August 24-29, 295-302 (1986).
25. Miller, J.M., and Toshinaga, A.M., *Geophys. Res. Lett.*, **8**, 779-782 (1981).
26. Nguyen, B.C., Gaudry, A., Bonsang, B., and Lambert, G., "Reevaluations of the role of dimethyl sulfide in the sulfur budget", *Nature*, **275**, 637-639 (1978).
27. Nguyen, B.C., Bonsang, B., and Gaudry, A., "The role of the ocean in the global atmospheric sulfur cycle", *J. Geophys. Res.*, **88**, 10903-10914 (1983).
28. Panter, R., and Penzhorn, R.D., "Alkyl sulfonic acids in the atmosphere", *Atmos. Environ.*, **14**, 149-151 (1980).
29. Srinivasan, C., Chellamani, A., and Rajogokal, S., "Mechanism of the oxidation of alkyl aryl and diphenyl sulfides by chromium (vi)", *Journal of Organic Chemistry*, **50**, 12001-12005 (1985).
30. Turner, S.M., and Liss, P.S., "Measurements of various sulfur gases in a coastal marine environment", *J. Atmos. Chem.*, **2**, 223-232 (1985).
31. Quinn, J.A., and Otto, N.C., "Carbon Dioxide Exchange at the Air-Sea Interface: Flux Augmentation by Chemical Reaction", *Journal of Geophysical Research*, **76**, 6, 1539-1549 (1971).
32. Whitman, W.G., *Chem. Metall. Engng.*, **29**, 146 (1923).

33. Winer, A.M., Atkinson, R., and Pitts, Jr., J.N., "Gaseous Nitrate Radical: Possible Nighttime Atmosphere sink for Biogenic Organic Compounds", *Science*, **224**, 156-159 (1984).
34. Zafiriou, O.C., Jousot-Dubien, J., Zepp, R.G., and Zika, R.G., "Photochemistry of natural waters", *Environ. Sci. Technol.*, **18**, 12, 358-371 (1984).
35. Zika, R.G., Moffett, J.W., Pentaene, R.G., Cooper, W.J., and Saltzman, E.S., "Spatial and temporal variations of hydrogen peroxide in Gulf of Mexico waters", *Geochemica et Cosmochimica Acta*, **49**, 1173-1184 (1985).

APPENDIX A

Aqueous Film Reactions

$$\begin{aligned}\frac{d[\text{DMS}]}{dt} &= -\{k_2[\text{H}_2\text{O}_2] + k_{1v}\}[\text{DMS}] \\ &= -(k_{1\text{H}_2\text{O}_2} + k_{1v})[\text{DMS}]\end{aligned}$$

DMS reaction with H_2O_2 :

$$k_2 = 3.3 \times 10^{-2} \text{ l/mole-sec} \quad (\text{Adewuyi and Charmichael 1986})$$

$$[\text{H}_2\text{O}_2] < 20 \times 10^{-8} \text{ mole/l} \quad (\text{Zika } et \text{ al.}, 1985)$$

$$k_{1\text{H}_2\text{O}_2} = k_2[\text{H}_2\text{O}_2] = 67 \times 10^{-10} \text{ sec}^{-1}$$

Photo oxidation of DMS:

$$k_{1v} = 2.4 \times 10^{-5} \text{ sec}^{-1} \quad (\text{Brimblecombe and Shooter 1986})$$

1st order rate constant for loss of DMS in surface water:

$$k_{1l} = k_{1v} + k_{1\text{H}_2\text{O}_2} = 2.4 \times 10^{-5} \text{ sec}^{-1}$$

Gas Film Reactions

$$\frac{d[\text{DMS}]}{dt} = -(k_{2\text{NO}_3}[\text{NO}_3] + k_{2\text{OH}}[\text{OH}])[\text{DMS}] = -k_{1g}[\text{DMS}]$$

k_2 = second order rate constant

k_1 = first order rate constant

1st order rate constant for the loss of DMS in the gas film is taken as the values given by Winer *et al.* (1984):

$$[\text{NO}_3] \leq 100 \text{ ppt}$$

$$k_{1\text{NO}_3} = k_{2\text{NO}_3}[\text{NO}_3] < 1.3 \times 10^{-3} \text{ sec}^{-1}$$

$$[\text{OH}] = 4 \times 10^6 \text{ cm}^{-3}$$

$$k_{1\text{OH}} = k_{2\text{OH}}[\text{OH}] < 4 \times 10^{-5} \text{ sec}^{-1}$$

$$k_{1g} = k_{1\text{NO}_3} + k_{1\text{OH}} \leq 1.3 \times 10^{-3} \text{ sec}^{-1}$$

APPENDIX B

$$\text{FLUX} = -K^*(C_g - HC_l)$$

$$K^* = \frac{k_g k_l}{k_l + Hk_g}$$

$$C_g = [\text{DMS}]_{\text{gas}}$$

$$C_l = [\text{DMS}]_{\text{liquid}}$$

Assume $C_g \ll HC_l$

$\therefore \text{Flux} \approx HK^*C_l$

$K \equiv HK^* = Hk_gk_l/(k_l + Hk_g)$

“Overall” mass transfer coefficient:

$$K = \frac{Hk_gk_l}{k_l + Hk_g} \text{ (cm/hr)}$$

H = Henry's law constant (Dacey *et al.*, 1984)
(moles/liter air)/(moles/liter water)

$$= \left(\text{EXP} \left[12.64 - \frac{3547}{T} \right] \right) / (RT)$$

T = temperature ($^{\circ}\text{K}$)

R = gas constant $\left(0.08208 \frac{\text{liter atm}}{\text{mole}} \right)$

k_l = liquid phase mass transfer coefficient (cm/sec)

k_g = gas phase mass transfer coefficient (cm/sec)

$k_l \equiv D_l/\delta_l$

$k_g \equiv D_g/\delta_g$

$$D_g = 0.156 \left(\frac{T}{273} \right)^{1.5} \text{ cm}^2/\text{sec}$$

$$D_l = 1.2 \cdot 10^{-5} \text{ cm}^2/\text{sec}$$