



Department of Biology

Woods Hole Oceanographic Institution

Woods Hole, MA 02543 USA

Phone: (508) 457-2000

Fax: (508) 457-2169

Telex: 951679

January 16, 1998

Dr. Ron Ferek
Program Manager
Code 322BC
Ballston Tower One
800 North Quincy Street
Arlington, VA 22217-5660

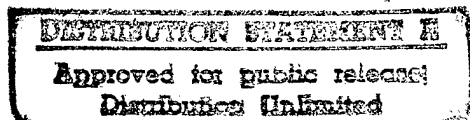
Dear Dr. Ferek:

On behalf of Dr. John W.H. Dacey and Dr. Nelson M. Frew, please find enclosed three copies of the Final Technical Report for ONR Grant N00014-95-1-0817, entitled "Laboratory Measurements of the Water/Air Flux of Dimethylsulfide Using a Wind/Wave Tank".

If there is anything else which you require, please let me know.

Sincerely,

Jane E. Marsh
Sr. Staff Assistant
Biology Department



enclosures

xc: S. Ferreira, WHOI Grant & Contract Services
ONR, Boston
Director, NRL
DTIC (2)
ONR, OCCC1

DTIC QUALITY INSURED

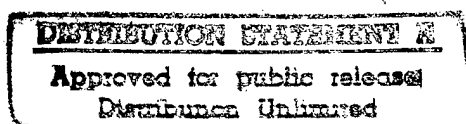
Laboratory Measurements of the Water-Air Flux of Dimethylsulfide using a Wind Wave Tank
J. W. H. Dacey and N. M. Frew

Estimating the flux of dimethylsulfide (DMS) from the ocean to the atmosphere is an important biogeochemical problem (Andreae and Crutzen 1997). Sulfur aerosols are an important contributor to optical haze in the marine atmosphere as well as a possible modulator of global climate. Shaw (1983, 1987) first suggested that atmospheric sulfur might be involved in climate regulation. Charlson *et al.* (1987) proposed that volatile organic sulfur emitted from the ocean was involved in the formation of cloud condensation nuclei, affecting the albedo and radiation balance of the earth. Charlson *et al.* (1992) estimated that the direct (backscattering and reflection of solar radiation by sulfate aerosols) and indirect (cloud albedo) effects of sulfate aerosols might counteract the climatic forcing by trace greenhouse gases. The relative roles of greenhouse gases and sulfate aerosols in global atmospheric change remain a topic of debate (Schwartz, 1988; Caldeira, 1989; Falkowski *et al.* 1992; Langner *et al.*, 1992; Kiehl and Briegleb, 1993; Bates *et al.*, 1997).

Dimethylsulfide (DMS) is the most abundant volatile sulfur compound in seawater and is widely accepted as dominating the flux of biogenic sulfur to the atmosphere: it constitutes about half of the global biogenic sulfur flux to the atmosphere (Andreae, 1990; Erickson *et al.*, 1990). The concentrations of DMS in the surface mixed layer of the ocean are orders of magnitude higher than the equilibrium concentration in the marine atmospheric boundary layer. Thus, a strong concentration gradient exists to drive a flux of DMS into the atmosphere (Andreae, 1986; Bates *et al.*, 1987). The sea-air exchange of DMS is affected by a number of physical factors, including seawater temperature, wind speed, surface turbulence and gas diffusivity (Liss and Merlivat, 1986; Wanninkhof, 1992; Saltzman *et al.*, 1993). Saltzman and Cooper (1989) concluded, based on variations in DMS concentrations in the atmospheric marine boundary layer, that DMS transfer may be slower than predicted by the standard Liss-Merlivat transfer model. A more recent assessment by Yvon *et al.* (1996) suggests that flux may be higher than these flux models predict. All estimates of DMS flux have depended on the assumption that DMS flux is water-side controlled, although the relatively high solubility of DMS suggests that its behavior may be transitional to air-side control.

The flux of gases across the air-water interface is understood to involve three transfer processes (Liss and Slater, 1974): (1) transfer from the bulk aqueous solution to the surface water film, (2) transfer from the surface water film to the surface air film, and (3) transfer from the surface air film to the bulk atmosphere. The rate of gas equilibration at the interface between air and water films is taken to be faster than transport through the sublayers on either side of the interface. The rate of transport is therefore controlled by transport to or from the interface through the viscous sublayers in the water and in the air. The relative importance of the hydrodynamics of these sublayers is determined by a number of factors.

The rate of transfer of relatively insoluble permanent gases between the water and the atmosphere is controlled by the flux through the water-side boundary layer. Mass balance equations indicate that higher gas solubility increases the significance of the air-side control of flux, as the rate of equilibration between the water and the surface air film has a disproportionate



19980126 044

impact on the fugacity on the air-side boundary. The transfer of a relatively few molecules quickly diminishes the partial pressure gradient across the interface. The fluxes of highly soluble gases, such as methylamines, ammonia and water vapor itself are controlled by flux through the air-side sublayer.

Our main objective in this project were to parameterize the flux kinetics of DMS while simultaneously measuring water-air transfer of O_2 , SF_6 , Ne, CH_4 , and He under varying wind speeds and hydrodynamic conditions. The experiments were designed to allow investigation of the air-side transfer resistance and the role of surface films in regulating DMS flux.

Experimental estimates of k_{600} for gases measured in this study are plotted in Figure 1. The data follow the non-linear pattern of increasing flux with increased wind speed familiarized by Liss & Merlivat (1986). Data in Figure 1 cannot be compared directly with the Liss-Merlivat plot since the wind speed in our tank experiment is measured at 10 cm, as opposed to 10 m elevation. Our data are revealing, however, in illustrating the source of some of the variability in laboratory and field measurements. The variability in flux we observed under similar wind speeds indicates that wind speed is not the sole factor determining flux through the sublayers. In the case of water-side controlled gas flux, the hydrodynamics of the aqueous sublayer is key, and these hydrodynamics are significantly controlled by wind stress, u_* . In the field, the relationship between u_* and u introduces some variability, since u_* depends not only on wind speed, but also on other factors such as sea state. This does not explain the variability in the wave tank, however, where the fetch is essentially infinite and the wave field is established quickly and remains constant during an experiment.

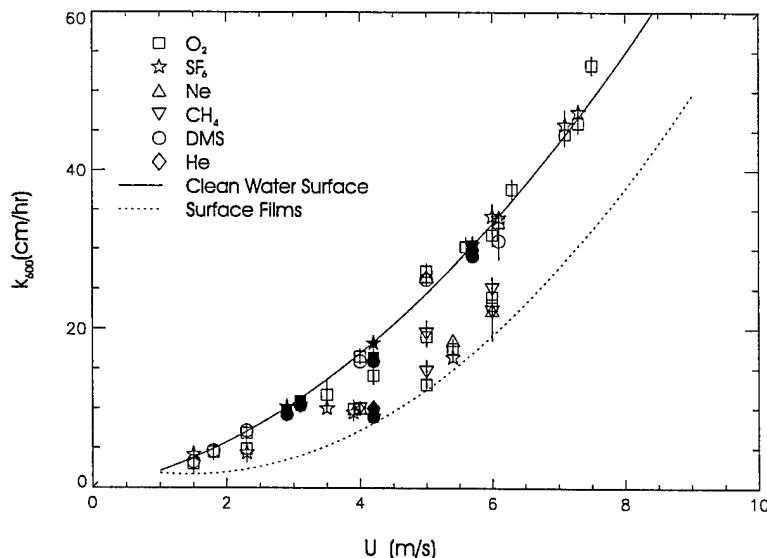


Figure 1 Laboratory wind-wave tank measurements of gas transfer velocity ($Sc=600$) versus wind speed ($z=10$ cm) for O_2 , SF_6 , Ne, CH_4 , DMS, and He. Data represented as open symbols and solid symbols were measured in fresh water and seawater, respectively. Fitted lines to the laboratory measurements of Frew *et al.* (1995) are shown for comparison. The upper bound on the data lies near the clean water data of Frew *et al.* The lower bound on the data lies near experimental data with surface films (0.03 μ M Triton-X 100). Standard errors are plotted for each point.

Other factors control the relationship between u_* and k_{600} , most notably variability in the physical characteristics of the water surface due to surfactants. Small changes in the concentration of surfactant strongly influence the hydrodynamics of the aqueous sublayer (Frew et al., 1995). This variability can be factored out through the dual-tracer design of our measurements. When the transfer velocities of gases are normalized against the transfer velocity of O_2 (all k 's corrected for diffusivity), the tight functional relationship between the fluxes of the gases becomes apparent (Figure 2). This relationship indicates that much of the variability of flux at a given wind speed is due to variability in the hydrodynamic forcing of flux. Deviations from the linear relationship of unity slope signify other processes are influencing the transfer of a gas. Careful examination indicates that DMS transfer rates lie slightly below the line at higher wind speed, meaning that DMS behaves somewhat differently than the permanent gases under the experimental temperatures and wind speeds.

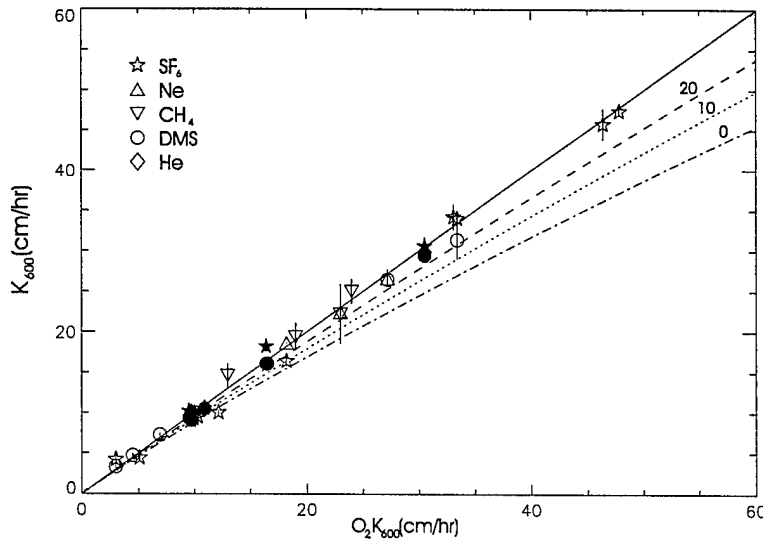


Figure 2 Laboratory wind-wave tank measurements of SF_6 , Ne, CH_4 , DMS, and He transfer velocities ($Sc=600$) versus the transfer velocity of O_2 ($Sc=600$). Data represented as open symbols and solid symbols were measured in fresh water and seawater, respectively. Standard errors are plotted for each data point. The solid line represents ideal "water-side controlled" kinetics. Dashed lines represent predicted k_{600} for DMS at temperatures 0, 10 and 20C using our formulation of γ_a .

We evaluated the importance of the two boundary layers by considering the steady state condition in which the mass balance for gases at the interface is given by:

$$m_a'' = m_w'' \quad (1)$$

when the flux through the boundary layers of the air phase and water phase are equal and respectively:

$$m_a'' = k_a(c_a - C_{s,w}/\beta) \quad (2)$$

$$m_w'' = k_w(C_{s,w} - C_w) \quad (3)$$

where c_a and C_w are bulk concentrations in the air and water, $C_{s,w}$ is gas concentration at the interface between the water surface and air expressed in terms of aqueous concentration, and β is the Bunsen coefficient (expressed as the ratio C_w/c_a at equilibrium). The transfer velocities, k_a and k_w , are expressions of the hydrodynamic regime in the air and water boundary layers. We combine eqns. (1), (2), and (3) to determine the relative importance of the air-surface concentration difference to the water-surface concentration difference in controlling flux. This ratio becomes:

$$\frac{\beta c_a - C_{s,w}}{C_{s,w} - C_w} = \frac{\beta k_w}{k_a} \quad (4)$$

Using the fact that the sum of the air fraction and water fraction is unity allows equation 4 to be arranged, yielding the ratio of the air concentration difference to the total concentration difference, γ_a , given as:

$$\gamma_a = \frac{\beta c_a - C_{s,w}}{\beta c_a - C_w} = \frac{1}{1 + k_a/\beta k_w} \quad (5)$$

γ_a is the air-side gradient fraction, defined as the gas concentration gradient across the air-side sublayer layer as a fraction of the entire gradient from the bulk water to the bulk air. When k_a is small, or when solubility is high, γ_a approaches unity. As such, therefore, γ_a is a measure of the error in assuming the flux is water-side controlled. To date, k_a and k_w have not been

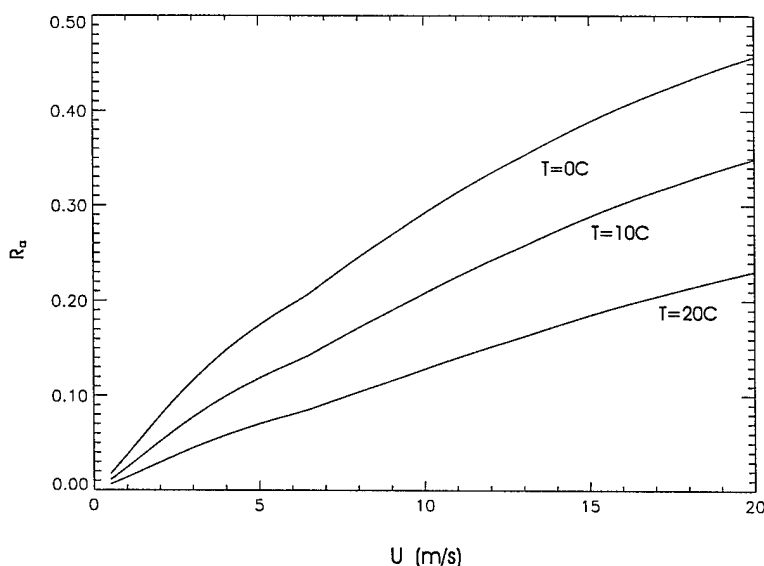


Figure 3 The air-side gradient fraction, γ_a , for DMS as a function of wind speed at temperatures 0, 10, and 20°C in seawater are shown. γ_a is determined from β , k_w , and k_a as shown in equation 5. Values of β come from Dacey *et al*, 1984. Values of k_w and k_a are determined from tank experiments. The value of k_w is determined from sparingly soluble gases and the value of k_a is determined from water vapor transport (e.g., Kondo 1975). The increase in γ_a with wind speed arises because k_w increases faster with increasing wind speed than k_a . Decreasing temperature raises gas solubility, leading to an increase in γ_a .

quantified simultaneously in oceanic conditions. *In situ* values of k_a (e.g., Kondo, 1975) and k_w can be approximated from available models.

Due to the moderate solubility of DMS (Dacey et al., 1984), γ_a becomes significant at lower water temperatures. Also, increasing wind speed has a greater influence on the aqueous sublayer than on the air-side sublayer, with the result that k_a becomes increasingly important at higher wind speeds. These findings are summarized in Figure 3, which shows the influence of temperature and wind speed on γ_a . We conclude that air-side control may be a significant factor in higher latitudes where DMS is commonly found at high concentrations in surface water (Berresheim, 1987), and where both low temperatures and high winds are typical. As γ_a approaches 0.4, conventional flux models based on wind speed parameterizations may overestimate DMS flux for these locales by 60%.

- Andreae, M. O. Ocean-atmosphere interactions in the global biogeochemical sulfur cycle. *Mar. Chem.* **30**,1-29, 1990.
- Andreae, M. O. The ocean as a source of atmospheric sulfur compounds. In: *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Baut-Menard, D. Reidel, Norwell, MA, 331-362, 1986.
- Andreae M.O. and P. J. Crutzen Atmospheric Aerosols: Biogeochemical sources and role in atmospheric chemistry. *Science* **276**, 1052-1058, 1997.
- Bates, T.S., J.D. Cline, R.H. Gammon and S.R. Kelly-Hansen. Regional and seasonal variations in the flux of oceanic dimethylsulfide to the atmosphere, *J. Geophys. Res.*, **92**, 2930-2938, 1987.
- Bates, TS, and P K Quinn. Dimethylsulfide (DMS) in the equatorial Pacific Ocean (1982-1996): evidence of a climate feedback? *Geophys. Res. Lett.*, **24**, 861-864, 1997.
- Berresheim, H. Biogenic sulfur emissions from the Subantarctic and Antarctic Oceans. *J. Geophys. Res.*, **92**, 13245-13262, 1987.
- Caldeira, K. Evolutionary pressures on planktonic production of atmospheric sulfur. *Nature*, **337**, 732-734, 1989.
- Charlson, R.J., J.E. Lovelock, M.O. Andreae, and S.G. Warren. Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate. *Nature*, **326**, 655-661, 1987.
- Charlson, R. J., S. E. Schwartz, J. M. Hales, R. D. Cess, J. A. Coakley, J. E. Hansen, and D. J. Hofmann. Climate forcing by anthropogenic aerosols. *Science*, **255**, 423-430, 1992.
- Dacey, J. W. H., S. G. Wakeham, and B. L. Howes. Henry's Law constants for dimethylsulfide in freshwater and seawater. *Geophys. Res. Lett.*, **11**, 991-994, 1984.
- Erickson, D. J., S. J. Ghan, and J. E. Penner. Global ocean-to-atmosphere dimethylsulfide flux. *J. Geophys. Res.*, **95**, 7543-7552, 1990.
- Falkowski, PG, Y. Kim, Z. Kolber, C. Wilson, C. Wirick, and R. Cess. Natural versus anthropogenic factors affecting low-level cloud albedo over the North Atlantic. *Science*, **256**, 1311-1313, 1992.
- Frew, N. M., E. J. Bock, W. R. McGillis, A. V. Karachintsev, T. Hara, T. Muensterer and B. Jähne. Variation of air-water gas transfer with wind stress and surface viscoelasticity. In: *Air-Water Gas Transfer*, B. Jähne and E. C. Monahan (eds.), AEON Verlag & Studio, Hanau, 529-541, 1995.

- Kiehl, J. T. and B.P. Briegleb. The relative roles of sulfate aerosols and greenhouse gases in climate forcing. *Science*, **260**, 311-314, 1993.
- Kondo, J. Air-sea bulk transfer coefficients in diabatic conditions. *J. Boundary-Layer Meteorol.*, **9**, 91-112, 1975
- Langner, J., H. Rodhe, P. J. Crutzen, and P. Zimmermann. Anthropogenic influence on the distribution of tropospheric sulphate aerosol. *Nature*, **359**, 712-716, 1992.
- Ledwell, J. J. The variation of the gas transfer coefficient with molecular diffusivity. In: *Gas Transfer at Water Surfaces*, W. Brutsaert and J. H. Gerhard (eds.), D. Reidel, Boston, 293-302, 1984.
- Liss, P.S. Gas transfer: experiments and geochemical implications. In: *Air-Sea Exchange of Gases and Particles*, P.S. Liss and W.G.N. Slinn (eds.), D. Reidel, Boston, 241-298, 1973.
- Liss, P. S. and L. Merlivat. Air-sea gas exchange rates: introduction and synthesis. In: *The Role of Air-Sea Exchange in Geochemical Cycling*, P. Buat-Menard (ed.), D. Reidel, Norwell, MA, 113-127, 1986.
- Liss, P.S. and P.G. Slater. Flux of gases across the air-sea interface, *Nature*, **247**, 181-184, 1974.
- Saltzman, E.S, D.B. King, K. Holmen, and C. Leck. Experimental determination of the diffusion coefficient of dimethylsulfide in seawater, *J. Geophys. Res.*, **98**, 16481-16486, 1993.
- Saltzman, E. S, and D. J. Cooper. Dimethyl sulfide and hydrogen sulfide in marine air. In: *Biogenic Sulfur in the Environment*, ACS Symposium Series No. 393., E. S. Saltzman and W.J. Cooper (eds.), 330-351, 1989.
- Schwartz, S. E. Are global cloud albedo and climate controlled by marine phytoplankton? *Nature*, **336**, 441-445, 1988.
- Shaw, G. E. Bio-controlled thermostat involving the sulfur cycle. *Clim. Change*, **5**, 297-303, 1983.
- Shaw, G. E. Aerosols as climate regulators: a climate-biosphere linkage? *Atmos. Environ.*, **21**, 985-986, 1987.
- Wanninkhof, R. Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.*, **97**, 7373-7382, 1992.
- Yvon, S. A., E. S. Saltzman, D. J. Cooper, T. S. Bates, and A. M. Thompson. Atmospheric sulfur cycling in the tropical Pacific marine boundary layer (12°S, 135°W): a comparison of field data and model results 1. dimethylsulfide. *J. Geophys. Res.*, **101**, 6899-6909, 1996.

Publications from this project:

McGillis, W. R., J. W. H. Dacey, N. M. Frew, E. J. Bock, and R. Nelson (in preparation)
Water-Air Flux of Dimethylsulfide

Presentations:

Dacey, J. W. H., N. M. Frew, E. J. Bock, W. R. McGillis, "Water-Air Transfer of Dimethylsulfide," ASLO Aquatic Sciences Meeting, Sante Fe, February, 1996.

Dacey - Dimethylsulfide: A geophysiology of the surface ocean. University of Connecticut Avery Point, 31 October 1997.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE January 1998	3. REPORT TYPE AND DATES COVERED Final Report 5/1/95 - 12/31/96	
4. TITLE AND SUBTITLE LABORATORY MEASUREMENTS OF THE WATER/AIR FLUX OF DIMETHYLSULFIDE USING A WIND/WAVE TANK		5. FUNDING NUMBERS N00014-95-1-0817	
6. AUTHOR(S) John W.H. Dacey and Nelson M. Frew		8. PERFORMING ORGANIZATION REPORT NUMBER W.H.O.I. Proposal No 9577	
7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES) WOODS HOLE OCEANOGRAPHIC INSTITUTION WOODS HOLE, MA 02543		10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAMES(S) AND ADDRESS(ES) ONR, Code 322BC 800 N. Quincy Street Ballston Tower One Arlington, VA 22217-5660		11. SUPPLEMENTARY NOTES	
a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The flux of dimethylsulfide (DMS) from the surface water of the ocean to the atmosphere is an important biogeochemical problem, since DMS contributes to optical haze and potentially impacts global climate by influencing earth's albedo. DMS is also an interesting gas in terms of gas exchange. The rate of flux of a gas across the air-water interface is regulated by its diffusivity and by the hydrodynamics of the two sublayers on either side of the interface. The fluxes of permanent gases are typically controlled by the rate of transport to the surface of the water film, and hence are called "water-side" controlled. The hydrodynamics of the aqueous sublayer are not as important in controlling fluxes of highly soluble gases, which are controlled by transport through the atmospheric sublayer above the interface. Our project indicates that the flux of DMS is transitional; at low wind speeds and in warm water, its flux is water-side controlled; at higher wind speeds in cold water, DMS flux has a significant component of air-side control. Under these latter conditions, flux models as they are usually applied may overestimate flux by 60%. We developed a coefficient, γ_a , to characterize the contribution of air-side control to flux.			
14. SUBJECT TERMS		15. NUMBER OF PAGES	
17. SECURITY CLASSIFICATION OF REPORT		16. PRICE CODE	
18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT	