# Water-air flux of dimethylsulfide

W. R. McGillis, J. W. H. Dacey, N. M. Frew, E. J. Bock[1], and R. K. Nelson

Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

**Abstract.** The water-air exchange of dimethylsulfide (DMS) has been measured in a laboratory wind-wave tank in fresh and seawater. To understand the transport behavior of DMS, its exchange was measured simultaneously with that of $O_2$, $SF_6$, Ne, $CH_4$, and He under varying wind speeds and hydrodynamic conditions. No unpredictable differences between fresh and seawater were found, indicating that DMS surface affinities do not exist in seawater. Results also indicate that Schmidt number corrections can be applied to DMS gas exchange. While the rate of transfer of relatively insoluble or sparingly soluble permanent gases between the ocean and the atmosphere is primarily controlled by the rate of flux through the aqueous boundary layer, interfacial mass balances indicate that increased DMS solubility increases the significance of the airside control of flux. The hypothesis that DMS transport across the water-air interface is subject to waterside control for moderate environmental conditions is supported. However, for ocean-atmospheric DMS exchange with low sea surface temperature or moderate wind speeds, there may be a significant influence by the atmospheric mass boundary layer. An atmospheric gradient fraction $\gamma_a$ applied to the waterside air-sea gas transfer velocity will correct for these effects. Estimates of ocean-atmospheric DMS transfer velocities for these conditions are provided.

## 1. Introduction

Estimating the flux of 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 and Quinn*, 1997].

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 nonanthropogenic 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, gas diffusivity [*Liss and Merlivat*, 1986; *Wanninkhof*, 1992; *Saltzman et al.*, 1993], and wave fields [*Jähne et al.*, 1987]. *Saltzman and Cooper* [1989] concluded, on the basis of variations in DMS concentrations in the atmospheric marine boundary layer, that DMS transfer may be slower than predicted by the standard Liss-Merlivat (L-M) transfer model. A more recent assessment by *Yvon et al.* [1996] suggests that flux may be higher than the L-M flux model predicts.

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 waterside boundary layer. Many previous laboratory studies explored the relationship between air-water gas transfer of a sparingly soluble gas and wind speed or wind stress [*Downing and Truesdale*, 1955; *Kanwisher*, 1963; *Hoover and Berkshire*, 1969; *Liss*, 1973; *Broecker et al.*, 1978; *Siems*, 1980; *Merlivat and Memery*, 1983; *Ledwell*, 1984; *Broecker and Siems*, 1984; *Jähne et al.*, 1985; *Wanninkhof and Bliven*, 1991; *Wanninkhof et al.*, 1991]. Mass flux balance equations indicate that higher gas solubility increases the significance of the airside control of flux. The transfer of 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 airside sublayer. The importance of the water and air boundary layers is evaluated by considering the steady state condition in which the mass flux balance for gases at the interface is given by

$$m_a'' = m_w'', \tag{1}$$

where $m''$ is the mass flux and $a$ and $w$ are the air and water boundary layers, respectively. Consistent with the formulation of *Liss and Slater* [1974], the flux through the boundary layers of the water phase and air phase are given as

$$m_w'' = k_w(C_{s,w} - C_w) \tag{2}$$

$$m_a'' = k_a(c_a - \frac{C_{s,w}}{\alpha}), \tag{3}$$

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 $\alpha$ is the Ostwald solubility 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 (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

$$\frac{\alpha c_a - C_{s,w}}{C_{s,w} - C_w} = \frac{\alpha k_w}{k_a} . \tag{4}$$

Using the fact that the sum of the air fraction and water fraction is unity allows (4) to be rearranged, yielding the ratio of the air concentration difference to the total concentration difference $\gamma_a$:

$$\gamma_a = \frac{\alpha c_a - C_{s,w}}{\alpha c_a - C_w} = \frac{1}{1 + k_a/\alpha k_w} . \tag{5}$$

The atmospheric gradient fraction $\gamma_a$ is a measure of the fraction of total concentration difference driving air-water gas transfer in the air. This quantity is expressed in terms of the air and water mass boundary layers and gas solubility.

Estimates suggest that the component of airside control in DMS flux is likely small but possibly measurable. Empirically, this possibility can be evaluated by comparing the flux of DMS with the flux of other gases known to be waterside controlled. The kinetics of flux for such gases have been described as $k_w = \beta^{-1} u_{*,w} Sc^{-n}$ by *Jähne et al.* [1987b]. Here the gas transfer velocity across the aqueous boundary layer $k_w$ is a function of the waterside friction velocity $u_{*,w}$, the Schmidt number $Sc$, and a hydrodynamic parameter $\beta$. The friction velocity is related to wind speed through the relationship $u_* = \sqrt{\tau_o/\rho} = C_d^{1/2} U$, where $U$ is the wind speed, $C_d$ is the air-water surface drag coefficient, $\tau_o$ is the surface wind stress, and $\rho$ is the density.

In the simplest case the hydrodynamics of surface water is driven solely by wind stress, and in clean water environments with long fetch, a gas transfer relationship with wind speed gives predictable results. The direct relationship of transfer velocity to wind speed breaks down when other factors influence the hydrodynamics of the aqueous sublayer. Surfactants, for example, influence the relationship between wind stress and surface water turbulence, so the simple relationship between gas transfer velocity and wind speed is obscured [*Frew et al.*, 1995; *Frew* 1997]. This variability has been incorporated into the Schmidt number exponent $n$, which ranges between 0.5 and 0.67 [*Ledwell*, 1984] and $\beta$, which ranges between 7 and 30 [*Jähne et al.*, 1987b; *Frew et al.* 1995].

The main objective in this study was to determine the parameters regulating the flux of DMS. Under varying wind speeds and hydrodynamic conditions, simultaneous measurements of water-air transfer of $O_2$, $SF_6$, Ne, $CH_4$, and He were performed. All previous in situ estimates of DMS flux assumed that DMS flux was waterside controlled, although the solubility of DMS suggests that its behavior may be transitional to airside control. The experiments of this study were designed to allow investigation of the effect of seawater on DMS surface concentration, the Schmidt number dependence, and the effect of solubility on the transfer velocities of DMS.

## 2. Experimental Description

Experiments were performed in an annular wind-wave tank with quasi-infinite fetch. The tank contained an annular polycarbonate channel (50 cm mean radius, 20 cm wide, and 40 cm deep, filled with water to a depth of 17 cm) with a choice of gas tight or open headspace, allowing both gas invasion and evasion experiments. Headspace gases were either nitrogen or air. The tank also contained multiple ports for headspace purging and the ability to sample both liquid and gas phases as well as the ability to remove surface films by surface skimming. Wind-driven waves were generated by a graphite rotor with 12 vertical graphite reinforced paddles (20 cm long, 5 cm high, and 0.1 cm thick) around the perimeter. Instrumentation in the wave tank included an acoustic current meter, a Pitot tube for air speed measurement, and YSI Endeco dissolved oxygen ($O_2$), temperature, conductivity, and pH probes. All experiments were conducted at room temperature (20°-23°C).

DMS was introduced to the tank by injecting 4-6 $\mu$L of pure (liquid) DMS through a septum directly into the water in the tank to make a solution of ~100 nM. Samples were withdrawn by syringe through a stainless steel valve: the inlet to the valve was 10 cm above the floor of the tank. Water samples (25 mL) were injected into 55 mL serum bottles which were stoppered with Teflon-lined septa. Bottles were held on a shaker table to accelerate equilibration between the aqueous solution and the headspace in the bottle, and DMS concentrations were measured by analyzing the headspace with a Sievers sulfur chemiluminescence detector. $SF_6$ was added to the tank prior to each run by injecting a 75 mL spike prepared by equilibrating distilled water with 100 ppm $SF_6$ in $N_2$ to give an initial concentration in the tank of ~$10^{-12}$M $SF_6$. Samples of 40 mL were withdrawn from the tank at intervals into 100 mL glass syringes. These were equilibrated with a 60 mL volume of ultrahigh purity $N_2$ drawn into each syringe. $SF_6$ concentration in each syringe headspace was then determined by triplicate loop injections into a gas chromatograph equipped with an electron capture detector. $CH_4$, Ne, and He were added to the water in the tank by bubbling pure gas through a fritted glass bubbler. Each gas was measured by headspace equilibration in serum bottles. $CH_4$ was measured by flame ionization detector, and Ne and He were measured by thermal conductivity detector (with He carrier for Ne assay and $N_2$ carrier for He assay).

For all gases the rate of flux was determined using the first-order rate constant for gas concentration in the water as a function of time (whether for evasion or invasion); $r^2$ for the regression lines were always greater than 0.97. Fluxes of DMS, $SF_6$, Ne, $CH_4$, and He were performed as evasion experiments in all cases, while flux of $O_2$ was measured by both evasion from and invasion into the aqueous phase. During evasion experiments a headspace flushing rate of 30 L min$^{-1}$ was sufficient to maintain low headspace concentrations for all gases but DMS. Preliminary experiments at this flushing rate yielded a suppressed transfer rate of DMS relative to the other gases. The tank mass balance ($V_H \, dC_H/dt = \alpha V_L \, dC_L/dt - RC_H$) shows that the accumulation of gas in the headspace is a result of

transfer from the water competing with a dilution from a flushing gas. $C_H$ and $C_L$ are the headspace and liquid concentrations, $V_H$ and $V_L$ are the headspace and liquid volumes, and $R$ is the flushing rate of gas containing zero DMS. For each gas in the headspace to be flushed sufficiently, $R \gg \alpha k_s A_s$ (where $k_s$ and $A_s$ are the air-water transfer velocity and air-water surface area, respectively). Unlike the other gases used in this study that are less soluble ($\alpha \leq 1$), DMS concentration in the headspace is nonzero, and a mass balance must be used in the calculations for headspace concentration to determine the total gas transfer velocity. Rates of 200 L min$^{-1}$ were required to keep DMS headspace concentrations insignificant at 20°C. This large flush rate was accomplished by pumping laboratory room air containing negligible amounts of DMS into the tank headspace.

## 3. Results and Discussion

In order to compare the transfer velocities of different gases it is useful to normalize the measured gas transfer velocity $k$ to a fixed Schmidt number $Sc$ frequently chosen to be 600, such that

$$k_{600} = k \, (\frac{600}{Sc})^{-1/2} \ , \tag{6}$$

where $Sc$ is the gas under the conditions (temperature and salinity) of the observation. In this way, variations in the mass diffusivity are factored out. A value of 600, the $Sc$ for $CO_2$ at 20°C, is used for normalization because of the importance of air-water $CO_2$ exchange at ambient temperatures. Experimental estimates of $k_{600}$ for gases measured in this study are plotted in Figure 1. The data follow the pattern of increasing flux with increased wind speed shown in previous laboratory experiments. Data in Figure 1 cannot be compared directly with in situ parameterizations since the wind speed in our tank experiment is measured at 10 cm, as opposed to a 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 water and air mass boundary layers. In the case of waterside controlled gas flux the hydrodynamics of the aqueous boundary layer is key, and these hydrodynamics are significantly controlled by the friction velocity $u_*$. 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. The wave field is established quickly and remains constant during an experiment.

Other factors control the relationship between $u_*$ and $k$, 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 [Asher and Pankow, 1986; Frew, 1997]. This variability can be factored out through the multitracer design of our measurements. When the transfer velocity of gases, corrected for mass diffusivity, are normalized against the transfer velocity of $O_2$, corrected for mass diffusivity, the tight functional relationship between the fluxes of the gases is apparent (Figure 2).

Bulk estimates of the DMS transfer velocity are similar to the estimates of He, Ne, $O_2$, $CH_4$, and $SF_6$, as shown in Figure 2. The data are Schmidt number-corrected using diffusivities for Ne and He [Jähne et al., 1987a], $O_2$ [Jähne, 1980], $CH_4$ [Wanninkhof, 1992], $SF_6$ [King and Saltzman, 1995], and DMS [Saltzman et al., 1993]. With these Schmidt numbers the apparent Schmidt number exponent calculated for this study was 0.49($\pm$.09). Deviations from the linear relationship of unity slope in Figure 2 signify other processes for a specific gas. Some discrepancies may be due to gas detection sensitivity. Other deviations are due to any process that changes the gas concentration in the aqueous air-water boundary layer. Since there is no discernible difference between freshwater and seawater runs, there is not likely to be any surface affinity of DMS on the seawater interface. This also demonstrates that DMS flux does not exhibit any significant chemical effects in fresh or
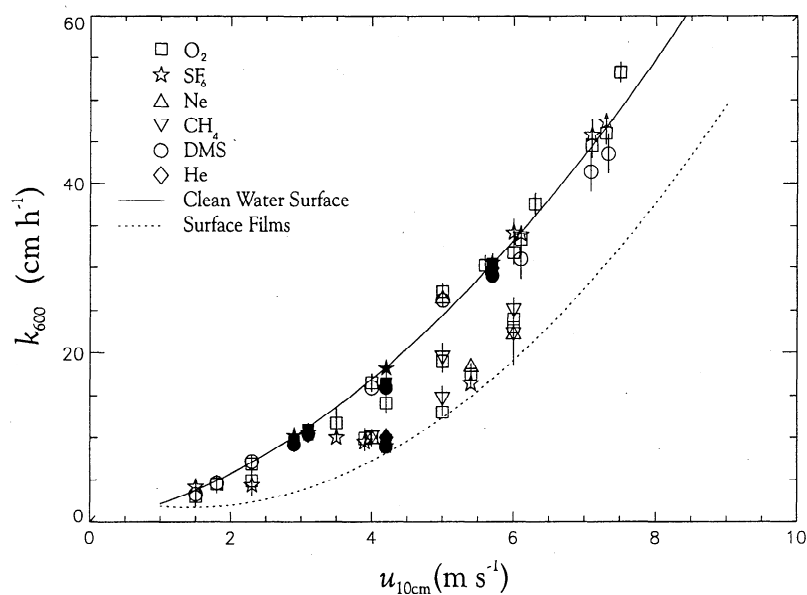


**Figure 1.** Gas transfer velocity ($Sc$=600) versus wind speed ($z$=10 cm) for $O_2$, $SF_6$, Ne, $CH_4$, dimethylsulfide (DMS), and He. Data represented as open symbols and solid symbols were measured in freshwater and seawater, respectively. Fitted lines to the laboratory measurements of *Frew et 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 µM Triton-X 100). Standard errors are plotted for each point.
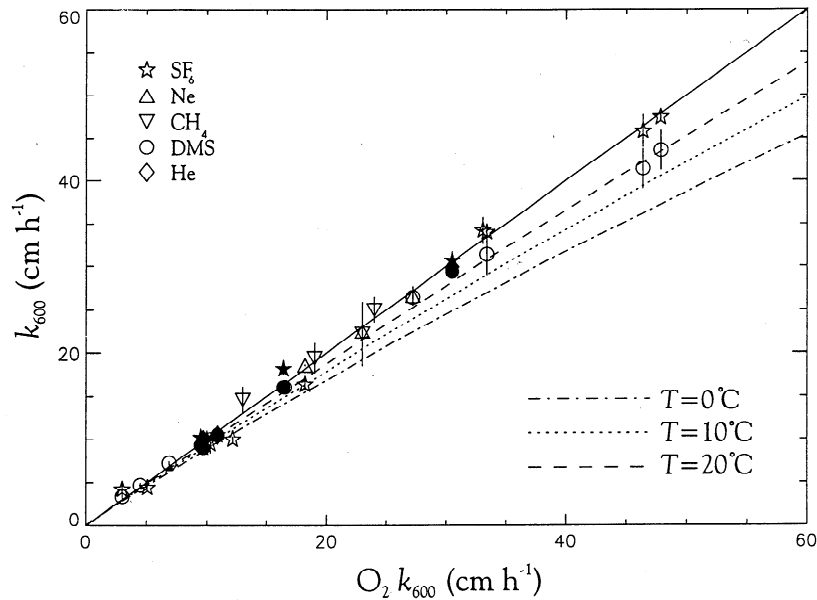
**Figure 2.** $SF_6$, Ne, $CH_4$, DMS, and He transfer velocities ($Sc$=600) versus the transfer velocity of $O_2$ ($Sc$=600). Data represented as open symbols and solid symbols were measured in freshwater and seawater, respectively. Standard errors are plotted for each data point. The solid line represents ideal waterside controlled kinetics. Dashed lines represent predicted $k_{600}$ for DMS at temperatures of 0, 10°, and 20°C using the derived $\gamma_a$.

seawater. Concentrations in the air-water boundary layer are extremely difficult to measure; therefore, studies use the bulk air and bulk water concentration gradient. The behavior of gases that undergo chemical effects in the water-air boundary layer or display an airside effect ($\gamma_a$>0) will deviate from the nonreactive, waterside controlled $O_2$ behavior.

Bulk formulations of air-water gas exchange are useful for regional and global modeling of gas fluxes. The general expression for predicting gas flux is $F=ks\Delta C$, where $F$ is the air-water gas flux, $k$ is the total gas transfer velocity, $s$ is the gas solubility in water, and $\Delta C$ is the total air-water concentration gradient. Airside effects on the total gas transfer velocity $k$ can be taken into account by correcting the waterside transfer velocity with

$$k = k_w(1-\gamma_a) \quad . \tag{7}$$

The airside gradient fraction $\gamma_a$ is defined as the gas concentration gradient across the airside boundary layer as a fraction of the entire gradient from the bulk water to the bulk air. When $k_a$ is large or when solubility is low, $\gamma_a$ approaches zero and (7) predicts the waterside control of the gas. Conversely, when $k_a$ is small or when the solubility is high, $\gamma_a$ approaches unity, and there is an insignificant waterside effect. Therefore $\gamma_a$ is a measure of the error in assuming the flux is waterside controlled. If the airside influence is significant, a $\gamma_a$ relationship can be determined using parameterizations for in situ estimates of $k_a$ and $k_w$ in terms of wind speed, gas diffusivity, gas molecular weight, and gas solubility.

In order to approximate this effect in the wind-wave tank an estimate for $k_a$ is used. *Liss and Slater* [1974] show that $k_a$ can be calculated by the relationship $k_a = k_{H_2O}(M/M_{H_2O})^{-1/2}$, where $M$ is the molecular weight of the gas. The transfer of $O_2$ is assumed to approximate $k_w$ accurately. *Dacey et al.* [1984] provide DMS solubility as a function of temperature. In linear wind-wave tanks, *Liss* [1973] and *Kondo* [1975] investigated water vapor transfer velocities as a function of wind speeds. Figure 3 shows this relationship in comparison with several measurements from the annular wind-wave tank used in this study. The measurements show

a linear relationship between $k_{H_2O}$ and wind speed. Using these laboratory observations of $k_w$ and $k_a$, $\gamma_a$ was calculated for DMS solubilities corresponding to 0, 10°, and 20° C. Values of $\gamma_a$ were used in (7) and plotted in Figure 2. The observations are in good agreement with the airside effect corresponding to temperatures used in the experiment. Although the conditions in the wave tank may not simulate field quantities, the results suggest that DMS exhibits an airside effect.

To date, $k_a$ and $k_w$ have not been quantified simultaneously in oceanic conditions, although in situ values of $k_a$ and $k_w$ can be approximated from available models. The model given by *Wanninkhof* [1992], for example, can be used for the waterside transfer velocity

$$k_w = 0.31 \ u_{10}^2 \ (Sc/660)^{-1/2} \ ; \ \frac{1}{u_{10}} \frac{dk_w}{du_{10}} = 0.62 \ (Sc/660)^{-1/2}, \tag{8}$$

where $u_{10}$ is the wind speed at 10 m. Other models and parameterizations for $k_w$ can be applied. Airside transfer velocities can be calculated from oceanic models of the water vapor transfer velocities [*Kondo*, 1975; *Liu et al.*, 1979]:

$$k_a \approx 659 u_{10}(M/M_{H_2O})^{-1/2} \ ; \ \frac{dk_a}{du_{10}} \approx 659(M/M_{H_2O})^{-1/2} \tag{9}$$

Since the error assuming a linear $k_{H_2O}$-wind speed relationship is small, the averaged value for 10 m wind speeds ranging from 2 to 20 m s$^{-1}$ is used for simplicity. Solubilities of the other gases in distilled water are taken from the critical tables; salinity effects on solubility do not affect the order of magnitude of these calculations. For oceanic conditions the Ostwald solubility coefficient for DMS is given as

$$\alpha = e^{[3525/T(°K)-9.464]} \ ; \ d\alpha/du_{10}=0 \tag{10}$$

Because of the moderate solubility of DMS [*Dacey et al.*, 1984], $\gamma_a$ becomes significant at lower water temperatures. Also, increasing wind speed has a greater influence on the aqueous
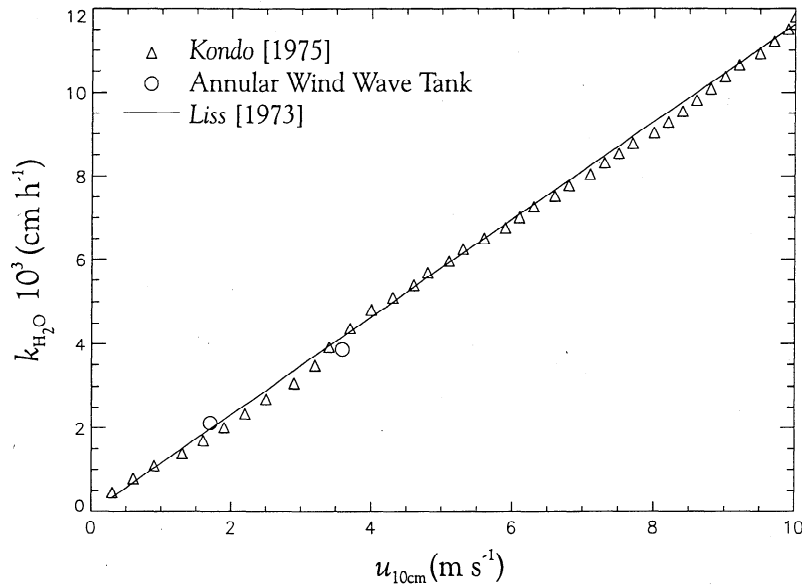
**Figure 3.** Water vapor transfer velocities as a function of wind speed ($z$=10 cm). Bulk transfer coefficients from *Kondo* [1975] are for neutral conditions. Data from the annular wind-wave tank are from mass flux balances. A line approximating the $H_2O$ transfer velocities of *Liss* [1973] is shown for comparison.

sublayer than on the airside sublayer with the result that $k_a$ becomes increasingly important at higher wind speeds. These findings are summarized in Figure 4, which shows the influence of temperature and wind speed on $\gamma_a$. For a wind speed of 5 m s$^{-1}$ at 10 m, $\gamma_a$ for He, Ne, $O_2$, $CO_2$, and DMS are $9\times10^{-5}$, $2\times10^{-4}$, $5\times10^{-4}$, $2\times10^{-2}$, and $1\times10^{-1}$, respectively. *Liss and Slater* [1974] have shown, using mean values of $k_a$ and $k_w$, that the atmospheric gradient fraction is ~0.04 on the basis of mean temperatures and mean wind speed determination.

Figure 5 shows in situ estimates of the gas transfer velocity of DMS using (7). As expected, transfer velocity increases with increasing wind speed. When the sea surface temperature (SST) is decreased, the DMS diffusivity goes down, and the solubility of DMS goes up. As the wind speed increases, the solubility effect increases with a corresponding increase in the atmospheric gradient fraction. For these reasons, airside 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
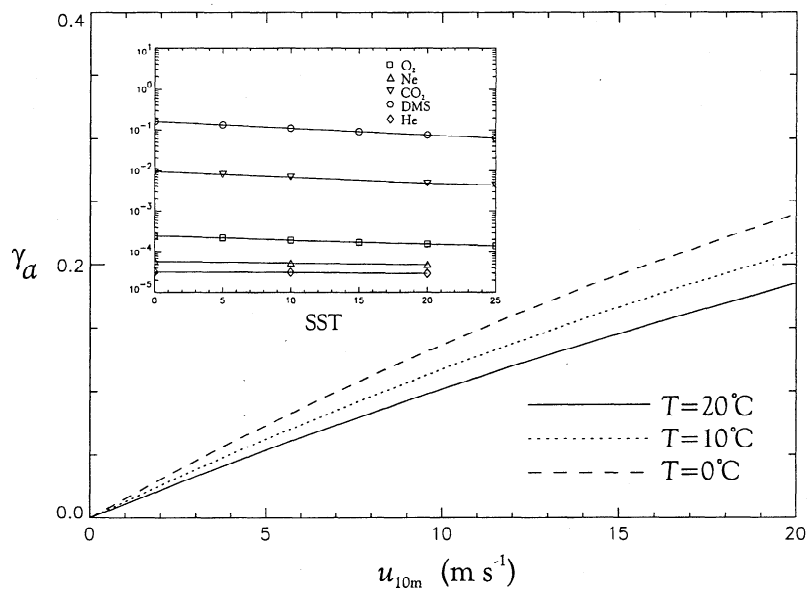


**Figure 4.** The airside gradient fraction $\gamma_a$ for DMS as a function of wind speed at temperatures 0, 10°, and 20°C in seawater are shown. The $\gamma_a$ is determined from $\alpha$, $k_w$, and $k_a$ as shown in (5). Solubilities come from *Dacey et al.* [1984]. The increase in $\gamma_a$ with 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 $\gamma_a$. The insert shows airside gradient fraction versus SST for a wind speed of 5 m s$^{-1}$ at a 10 m height. This fraction is the portion of the total water-air concentration difference that exists in the atmosphere. The gradient fraction for $O_2$, Ne, $CO_2$, and He are shown for comparison.
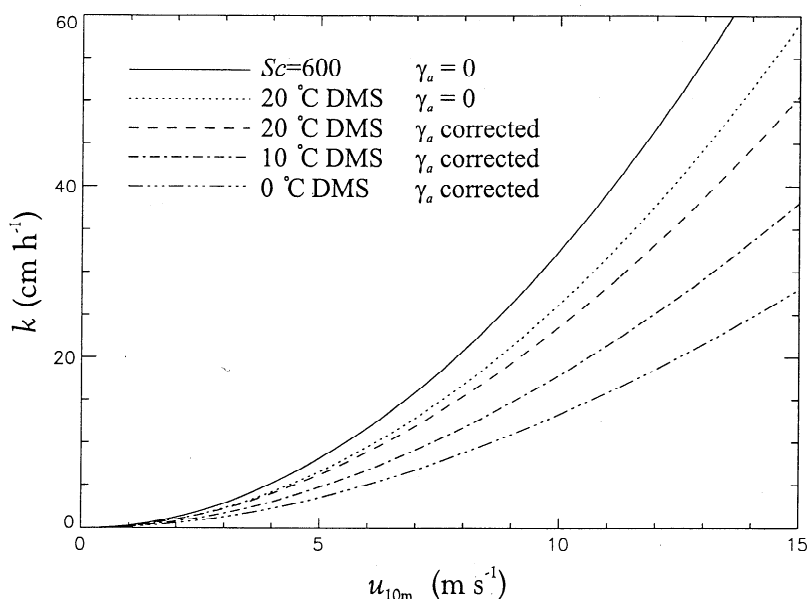
**Figure 5.** The effect of temperature on the estimate of in situ DMS transfer velocity. The $Sc$=600 for DMS at 28.6° C. For lower temperatures the $Sc$ will increase, and the gas transfer velocity will decrease. The gas transfer velocity also decreases with temperature because of the increase in $\gamma_a$.

low temperatures and high winds are typical. As $\gamma_a$ increases, conventional flux models based on wind speed parameterizations may overestimate DMS flux for these locales.

## 4. Concluding Remarks

Water-air exchange of DMS has been measured in freshwater and seawater under a range of hydrodynamic conditions. The transfer of $O_2$, $SF_6$, Ne, $CH_4$, and He was measured simultaneously and the $k$-$u$ variations observed were a result of surfactants. Results indicate that for DMS, $Sc$ corrections are applicable with no noticeable chemical effect in seawater. Results also indicate that at low SST and high wind speeds, the DMS atmospheric gradient fraction is significant. Estimates based on in situ gas and water vapor exchange indicate that the DMS transfer velocity can be significantly decreased. Hypotheses that need to be tested include comparing $k_a$ to $k_{H_2O}$, especially at reduced temperatures, and in situ validation of DMS fluxes.

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E. J. Bock and W. R. McGillis, Applied Ocean Physics and Engineering Department, Woods Hole Oceanographic Institution, Woods Hole, MA 02543. (wmcgillis@whoi.edu).

J. W. H. Dacey, Biology Department, Woods Hole Oceanographic Institution, Woods Hole, MA 02543. (jdacey@whoi.edu).

N. M. Frew and R. K. Nelson, Marine Chemistry and Geochemistry Department, Woods Hole Oceanographic Institution, Woods Hole, MA 02543. (nfrew@whoi.edu; rnelson@whoi.edu ).