Relaxed eddy accumulation measurements of the sea-to-air transfer of dimethylsulfide over the northeastern Pacific

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[1]   Gas transfer rates were determined from relaxed eddy accumulation (REA) measurements of the flux of dimethylsulfide (DMS) over the northeastern Pacific Ocean. This first application of the REA technique for the measurement of DMS fluxes over the open ocean produced estimates of the gas transfer rate that are on average higher than those calculated from commonly used parameterizations. The relationship between the total gas transfer rate and wind speed was found to be gas $k_{gas} = 0.53\ (\pm 0.05)\ U_{10}^{2}$ Because of the effect of the airside resistance, the waterside transfer rate was up to 16% higher than k_{gas}. Removal of the airside transfer component from the total transfer rate resulted in a relation between wind speed and waterside transfer of $k_{660} = 0.61\ (\pm 0.06)\ U_{10}^{2}$. However, DMS fluxes showed a high degree of scatter that could not readily be accounted for by wind speed and atmospheric stability. It has to be concluded that these measurements do not permit an accurate parameterization of gas transfer as a function of wind speed.   *INDEX TERMS:* 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 3339 Meteorology and Atmospheric Dynamics: Ocean/atmosphere interactions (0312, 4504); 4504 Oceanography: Physical: Air/sea interactions (0312); 4820 Oceanography: Biological and Chemical: Gases; 4855 Oceanography: Biological and Chemical: Plankton; *KEYWORDS:* dimethylsulfide, DMS, relaxed eddy accumulation, micrometeorology

1. Introduction

[2]   Ocean-atmosphere interactions and feedback mechanisms are key processes that need to be quantified in order to understand the role of the oceans in atmospheric chemistry and global climate. The biogenic gas dimethylsulfide (DMS), and its precursor dimethylsulfoniopropionate (mainly produced by phytoplankton of the class Prymnesiophyceae) have been the focus of international research programs since *Lovelock et al.* [1972] reported that DMS emissions from the oceans could possibly close the global sulfur budget.

[3]   Lovelock and coworkers showed that DMS was found in surface ocean waters throughout the Atlantic Ocean. Since then, it has been shown that DMS is ubiquitous in the surface waters of the oceans, in concentrations far in excess of those expected if it were in equilibrium with the atmosphere [e.g., *Kettle et al.*, 1999]. This and other studies have demonstrated that there is an efflux of DMS from the ocean to the atmosphere and that DMS could have a major impact on atmospheric chemistry. *Shaw* [1983] and more recently, *Charlson et al.* [1987], have suggested that atmospheric oxidation products of DMS are part of one of the major feedback mechanisms linking the global biosphere and climate.

[4]   DMS and its oxidation products affect atmospheric chemistry in various ways [*Andreae and Crutzen*, 1997]. Once emitted from the oceans, DMS is subject to oxidation by free radicals, such as OH and NO_3, to form a variety of products including methane sulfonic acid and sulfur dioxide, part of which in turn is oxidized to form non-sea salt sulfate, which can influence the earth's radiation budget through the formation of aerosols and clouds. Empirical evidence for a DMS-driven negative climate feedback has been found: cloud condensation nucleus (CCN) concentrations over the Southern Ocean are found to be significantly determined by DMS emissions; in turn microphysical properties of marine stratocumulus clouds are determined by atmospheric CCN concentrations; and cloud optical properties show a measurable response to observed changes in cloud microphysical properties [*Ayers and Gillett*, 2000]. In

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addition, DMS variability was found to be closely related to sea surface temperature anomalies, indicating a link between DMS and climate change [*Sciare et al.*, 2000].

[5] Even with an understanding of the dynamics of DMS in the atmosphere, current models are still unable to accurately simulate the oceanic climate feedback system. A major problem remains the uncertainty of the relative contribution of DMS to the atmospheric sulfur burden, which at least equals the uncertainty in the magnitude of the sea-to-air flux, which ranges from 15 to 33 Tg S yr^{-1} [*Kettle and Andreae*, 2000].

[6] The air-sea flux can be estimated from

$$F = k_{gas}\left(C_w - C_a K_H^{-1}\right), \tag{1}$$

which is the product of the air-sea concentration disequilibrium (corrected by the appropriate solubility constant K_H) and an empirically determined exchange rate (k_{gas}), usually related to wind speed and sea surface temperature. Parameterization of k_{gas} has been based on laboratory and lake tracer data [*Wanninkhof et al.*, 1985; *Upstill-Goddard et al.*, 1990; *Clark et al.*, 1995] and on large-scale budgeting studies [*Broecker and Siems*, 1984; *Tans et al.*, 1990; *Wanninkhof*, 1992]. Commonly used are the parameterizations suggested by *Liss and Merlivat* [1986] and *Wanninkhof* [1992]. The first is based on a wind speed extrapolation from a tracer release experiment with a timescale of 1–2 days and the latter is based on mean wind speed and the global ^{14}C budget; they differ in their predictions by about a factor of 2. Consequently, a large uncertainty remains concerning the magnitude of the global trace gas flux. Local budgets, over shorter timescales, are often calculated by using the parameterization of Liss and Merlivat [e.g., *Turner et al.*, 1996; *Sharma et al.*, 1999]. However, both models [*Liss and Merlivat*, 1986; *Wanninkhof*, 1992] compute large-scale averaged fluxes; therefore exchange coefficients measured on shorter timescales and smaller spatial scales could deviate significantly from the proposed parameterizations. Indeed, field measurements of CO_2 flux, based on half-hourly measurements by eddy correlation (the most direct means of measuring gas exchange), yield transfer velocities that are significantly higher than predicted by the *Wanninkhof* [1992] model [*Jacobs et al.*, 1999]. Moreover, gas exchange rates showed a large degree of scatter when plotted versus wind speed. This implies that local processes other than wind speed that occur on timescales of an hour may affect the exchange of gases, or that the signal-to-noise ratio is low because of small fluxes and/or low precision.

[7] Recent progress in understanding the factors that influence gas exchange has come from the application of micrometeorological techniques that directly measure fluxes across the sea surface, in combination with a careful examination of sea surface properties [*Edson and Fairall*, 1998; *Fairall et al.*, 2000]. It is only recently that direct measurements of gas fluxes have become feasible at sea. Meteorological techniques are routinely used for the measurement of the fluxes of momentum and heat [*Smith et al.*, 1996], and the eddy correlation (EC) technique has been shown to be appropriate for the direct determination of the transfer velocity of CO_2 [*Jacobs et al.*, 1999; *McGillis et al.*, 2001; *Wanninkhof and McGillis*, 1999]. However, the applicability of these techniques is limited, because CO_2 fluxes are often below the limit of detection and special conditions that assure high fluxes have to be selected for reliable gas flux measurements. In contrast, DMS exhibits a strong concentration gradient between the ocean and the air, resulting in ever present fluxes out of the ocean. Once in the atmosphere, DMS is oxidized with a lifetime of hours to a few days [*Clarke et al.*, 1998; *Chin and Jacob*, 1996], which allows the determination of the flux by micrometeorological techniques that typically require time spans of less than 1 hour. These characteristics make DMS ideal for process studies of gas exchange [*Dacey and Cooper*, 1993]. However, because of the lack of fast DMS sensors, few EC measurements have been performed [*Mitchell*, 2001]. The development of techniques that are more widely applicable (such as relaxed eddy accumulation and gradient flux techniques) is an important addition to present flux measurement capabilities and will lead to a better understanding of the sensitivity of gas exchange to environmental conditions. However, the application of these techniques in the marine environment is still in its infancy, and only a few studies have aimed at oceanic measurement of DMS fluxes [*Putaud and Nguyen*, 1996; *McGillis et al.*, 2001] by using the gradient flux technique. Furthermore, intercalibrations of techniques are needed in order to understand the capabilities and limits of different methods.

[8] During the Fluxes, Air-Sea Interaction, and Remote Sensing (FAIRS) experiment, field measurements of DMS flux over the ocean were conducted by using the gradient flux (GF) and relaxed eddy accumulation (REA) techniques. Although these techniques do not measure the flux directly, their application over terrestrial systems has proven to yield accurate measurements of gas exchange. Moreover, recent experiments have indicated that the measurement of DMS fluxes with these techniques is feasible [*Zemmelink et al.*, 2002a]. The results from the FAIRS experiment are presented here in two consecutive papers, with the REA study reported in this paper.

2. Methodology

[9] The eddy correlation method involves measuring the concentration of the gas in question at the same time as measuring the vertical component of the wind speed at a frequency of 10 Hz or more. Subsequently, the flux can be calculated from the covariance between the vertical wind speed (w) and gas concentration C

$$F = \left(\overline{w'C'}\right), \tag{2}$$

where F is the flux of C, primes indicate deviation from the mean, and the overbar denotes the mean value over the sampling period. However, no fast response sensors have been available for most trace gases, and in previous decades surface exchange was mainly investigated by profile or enclosure methods. Considering the uncertainties and limitations of these methods it is generally desirable to have a more direct micrometeorological method like EC available for trace gases. In order to overcome this problem *Desjardins* [1977] proposed a modification of the EC technique, with the fast response trace gas sensor being replaced by fast response sampling valves combined with

slow analysis techniques. This technique is known as eddy accumulation (EA), in which air is drawn from the immediate vicinity of an anemometer, measuring vertical wind speed, and subsequently diverted into two accumulators on the basis of the sign of w, at a pumping rate proportional to the magnitude of w. Unfortunately, it proved that sampling air in real time at a rate proportional to the vertical wind velocity is extremely difficult to achieve [*Hicks and McMillen*, 1984; *Speer et al.*, 1985], leading *Businger* [1986] and more recently *Businger and Oncley* [1990] to suggest a relaxation of this technique.

[10] Relaxed eddy accumulation, REA, a conditional sampling technique, samples air on the basis of vertical wind fluctuations, collecting updraft air in one reservoir and downdraft air in another at a constant flow rate [*Businger and Oncley*, 1990]. Fluxes are calculated following

$$F = \beta \sigma_w \Delta C \qquad (3)$$

where β is the eddy accumulation coefficient, σ_w (m s^{-1}) is the standard deviation of the vertical wind speed, and ΔC is the mean gas concentration difference between the upward and downward moving eddies.

[11] For an ideal Gaussian distribution of the vertical wind speed the β factor is a constant (0.627), for gas transport from the earth's surface to the atmosphere [*Wyngaard and Moeng*, 1992]. However, several field experiments yielded β which were on average somewhat lower than the theoretical value found by Wyngaard and Moeng. Experimental values for β have mainly been derived from eddy correlation data sets of vertical wind speed and temperature from measurements over land. Average values of β between 0.56 and 0.60 were found [*Businger and Oncley*, 1990; *Baker et al.*, 1992; *Pattey et al.*, 1993]. However, values sometimes showed a considerable scatter with ranges from 0.2 to 0.9 [e.g., *Oncley et al.*, 1993; *Beverland et al.*, 1996].

[12] It is still uncertain whether β is constant or varies with turbulence. *Businger and Oncley* [1990] and more recently *Andreas et al.* [1998] proposed β as a general function of stability (z/L). However, only a weak systematic variation was detected and could not be reproduced by other authors [*Beverland et al.*, 1996]. Therefore a constant literature value for β (0.56–0.60) is often used or β is determined from in situ eddy correlation measurements of the sensible heat flux $\left(\overline{w'\theta'} \right)$ according to

$$\beta = \frac{\overline{w'\theta'}}{\sigma_w (\overline{\theta}_u - \overline{\theta}_d)}, \qquad (4)$$

where $\overline{\theta}_u$ and $\overline{\theta}_d$ are the average temperature in upward and downward wind directions. In this study we set β at 0.6, the surface layer value suggested by *Businger and Oncley* [1990]; we will compare the value of 0.6 with β determined in the marine environment using equation (4).

[13] Ignoring the magnitude of the vertical wind speed for conditional sampling, as with relaxed eddy accumulation, leads to smaller concentration differences between the updraft and downdraft collection reservoirs. This effect can be compensated for by the use of a sampling threshold w_0 ("deadband") around zero vertical wind speed, where neither updraft nor downdraft air is sampled. However, the optimal size of the deadband remains somewhat elusive. By

using mathematical simulations, several authors proposed a threshold value ranging between $0.6\sigma_w$ and $0.9\sigma_w$ [*Oncley et al.*, 1993; *Baker*, 2000]. However, a deadband might not be used at all [*Cobos et al.*, 2002]; or if a deadband is used it may be adjusted to σ_w [*Christensen et al.*, 2000; *Pryor et al.*, 2002] or treated as a constant value, for example, *Pattey et al.* [1993] who use 0.05 m s^{-1}, and *Hensen et al.* [1996], using 0.03 m s^{-1}. The size of the deadband is still controversial. However, a study of the effect of the size of the deadband on the measured flux was beyond the scope of this experiment and we decided to use a fixed, small, deadband of 0.03 m s^{-1}. This deadband size ranged from 0.05 σ_w to 0.09 σ_w.

[14] The deadband approach has the advantage of increasing the concentration difference between the two collection reservoirs because sampling is biased toward larger eddies (those with sufficient vertical velocity to exceed the threshold) which tend to move farther along the concentration gradient. The quantitative effect of the deadband on REA measurements is still a matter of investigation. However, it is generally accepted that the increase in concentration difference must be balanced by a decrease in β. The correction for the increased (concentration) difference has been evaluated by *Businger and Oncley* [1990] and *Pattey et al.* [1993]. Both studies found an exponential decrease of β with increasing w_0. The correction that is used in this study is derived from *Businger and Oncley* [1990], which applied to equation (3) results in

$$F = \beta \exp(-0.75 w_0 / \sigma_w) \, \sigma_w \, \Delta C. \qquad (5)$$

[15] Prior to application of the relaxed eddy accumulator in the marine environment (for measurement of DMS emissions), the performance of the system was tested against eddy correlation measurements of CO_2 flux. The tests were conducted in the Netherlands over a grass field during daytime in spring. Fluxes were calculated on a 30-min basis. Wind velocities and temperature fluctuations were measured with a sonic anemometer (A. T. I. SWS-2211/3K) mounted on a pole at 4 m above ground level. The sampling inlet was located near the sonic anemometer and air was transported to the base of the tower through 4.5 m of Dekabon tubing at a flow rate of 7.5 l min^{-1}. CO_2 and H_2O density fluctuations were measured by a fast response nondispersive infrared monitor (LICOR, Li-6262). Calibration using N_2 for zero calibration and CO_2 in air for span calibration was performed at the start and the end of the experiment, in the morning and evening respectively. The CO_2 fluxes were corrected for air density fluctuations, using sensible and latent heat fluxes [*Webb et al.*, 1980]. No rotation-of-axes correction was applied to the fluxes, in order to compare them with fluxes computed by the REA technique.

[16] The configuration of the REA system is described by *Zemmelink et al.* [2002a]; for measurement of CO_2 fluxes Teflon tubing was replaced by Dekabon tubing. Air was typically sampled over 30 min at a flow rate of 300 mL min^{-1} and collected in Tedlar bags. For the REA measurements the gas was dried and brought to equal temperature prior to analysis or mass flow measurements; hence density corrections were unnecessary. Samples were analyzed for CO_2 using the same LICOR as used for the EC measurements.
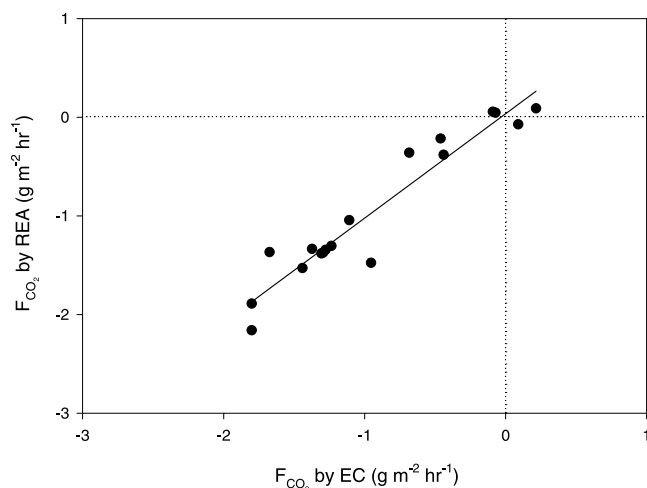
Figure 1. Comparison between relaxed eddy accumulation (REA) and eddy correlation (EC) techniques based on 30-min CO_2 flux measurements carried out over a grass field. Solid line is the regression: REA = 1.06 EC + 0.01, R^2 = 0.90. A negative flux indicates CO_2 uptake by the field.

[17] CO_2 flux measurements were conducted from 7 AM to 10 PM, and a linear regression was calculated for the 18 observations of CO_2 flux measured by REA against those measured by EC (Figure 1). Good agreement was found between the two techniques, with $F_{REA} = 1.06F_{EC} + 0.01$ (R^2 = 0.90). The agreement between REA and EC suggests that integrating the sampled air by the duration of the updraft and downdraft events with this REA system is a good approximation for CO_2 fluxes over land. Subsequently, the REA system was applied for DMS measurements over coastal areas [*Zemmelink et al.*, 2002a] and over the more remote ocean during FAIRS.

[18] Dimethylsulfide fluxes were measured during the second leg of the FAIRS experiment, which was designed to investigate the effect of ocean surface waves on remote sensing techniques and air-sea fluxes (Figure 2) [*Jessup et al.*, 2002]. DMS fluxes were measured by REA on half-hourly timescales from yearday 282.5 to 287 in the northeast Pacific (35.9°N, 123.8°W to 35.1°N, 123.1°W) during October 2000, from the Floating Instrument Platform (FLIP), using the configuration described by *Zemmelink et al.* [2002a]. Air was sampled from the vicinity of a sonic anemometer 12.75 m above the mean sea surface, at a flow rate of 300 mL min^{-1}, and collected in Tedlar bags. Oxidants were removed by KI soaked cotton [*Kittler et al.*, 1992] placed at the inlet of the collection reservoirs. The collected air was brought to equal temperature and the effect of density fluctuations on the DMS flux measurements was further avoided by drying the air on a cold finger prior to concentration of DMS onto a Tenax trap, at a flow rate of 300 mL min^{-1}. Both the cold finger and the Tenax were cooled to −15°C. Subsequently, the DMS concentration was determined by gas chromatography using a Sievers sulfur chemiluminescence detector [following *Zemmelink et al.*, 2002b]. The contents of the bags were analyzed within a day after collection. Previous tests proved that DMS remained stable for at least one week in the collection bags [*Zemmelink et al.*, 2002b]. Each sample bag contained enough air for a triplicate analysis of the DMS concentration, thus giving information on the analytical precision.

[19] Surface water was sampled with a Teflon bucket. Subsequently, a subsample of 5 mL was transferred to a sparge tube and bubbled vigorously (120 mL min^{-1}) for 5 min with inert gas (zero air). The DMS-containing air was dried, and DMS was focused onto cold Tenax (at 120 mL min^{-1}), after which it was analyzed in the same way as the air samples. Measured concentrations were used to calculate the flux from equation (5) and the transfer velocity of DMS was calculated by using

$$k_{gas} = Flux/\left(C_w - C_a K_H^{-1}\right), \tag{6}$$

where k_{gas} is the total gas transfer velocity (including the effect of both airside and waterside transfer velocities), C_w and C_a are the concentrations of DMS in the water and the air respectively, and K_H is the dimensionless Henry coefficient derived from H/RT where H is the Henry coefficient for DMS [*Dacey et al.*, 1984], R is the universal gas constant and T is the absolute temperature. The effect of the airside transfer velocity has to be removed in order to express the transfer velocity in terms of k_w, the waterside transfer velocity. A correction is applied as suggested by *McGillis et al.* [2000]:

$$k_w = \frac{k_{gas}}{(1 - \gamma)}, \tag{7}$$

where γ accounts for the effect of the airside transfer velocity. The value of γ is related to the ratio of the water and airside transfer velocities. It was calculated here from the airside transfer velocity of water vapor as suggested by *Kondo* [1975] and *Liu et al.* [1979], and the waterside transfer velocity given by the model of *Wanninkhof* [1992].

[20] The transfer velocity is compared with the *Wanninkhof* [1992] parameterization, based on the inventory
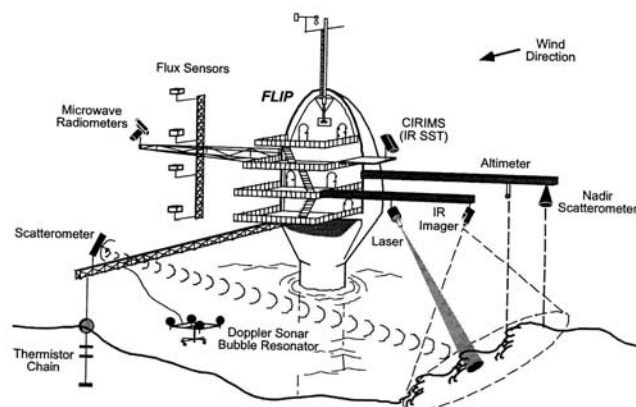

Figure 2. Instrument positioning aboard the floating instrument platform FLIP during the Fluxes, Air-Sea Interaction, and Remote Sensing experiment. The experiment was designed to investigate whether fluxes can be characterized and quantified by measuring physical control mechanisms (such as waves, bubbles, and sea surface temperature) by remote sensing instruments.
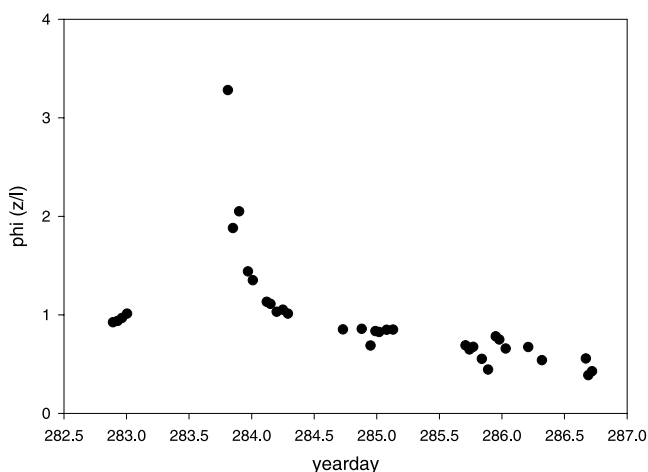
Figure 3. The atmospheric stability during the course of the experiment. Circles are the atmospheric stability expressed as phi (ϕ, a function of measurement height divided by the M-O length), where $\phi > 1$ = stable and $\phi < 1$ = unstable.

of natural and bomb-produced ^{14}C and short-term wind speed averages,

$$k_{660W92} = 0.31 \; U_{10}^2, \tag{8}$$

with the *Jacobs et al.* [1999] parameterization, based on eddy correlation measurements of CO_2 flux,

$$k_{660J99} = 0.54 \; U_{10}^2, \tag{9}$$

and with the *McGillis et al.* [2001] parameterization, also based on eddy correlation measurements of CO_2 flux

$$k_{660M01} = 3.3 + 0.026 \; U_{10}^3, \tag{10}$$

where U_{10} is the wind speed (m s^{-1}) at a height of ten meters and k_w is expressed in cm h^{-1} and normalized to a Schmidt number of 660, equivalent to the transfer velocity of CO_2 in seawater at a temperature of 20°C. For comparison with equations (8)–(10), the REA-based transfer velocities of DMS were converted to k_{660} by multiplying by $(Sc_{DMS}/660)^{1/2}$ where Sc_{DMS} is the Schmidt number of DMS [*Saltzman et al.*, 1993].

[21] To examine gas exchange rates under different atmospheric conditions, the atmospheric stability is a useful parameter. The atmospheric stability was expressed as ϕ, a function of the dimensionless ratio (z/L) of height z (12.75 m for the REA experiments) to the Monin-Obukhov length L, where L reflects the relative contribution of buoyancy and wind shear to the production of turbulence. The value of ϕ was calculated following *Dyer* [1974]: $1 + 5z/L$ for stable conditions and $(1 + 16z/L)^{-1/4}$ for unstable conditions.

3. Results

[22] Dimethylsulfide fluxes were measured during the second leg of the FAIRS experiment. At the start of the experiment the air temperature was higher than the water temperature, 16.7°C and 16.1°C respectively. At yearday 284.7–284.8 the air temperature became colder than the water, 15.2°C and 16.1°C respectively, initiating a shift from stable atmospheric conditions ($\phi > 1$) to unstable conditions ($\phi < 1$) after yearday 284.8 (Figure 3).

[23] Surface water DMS concentrations were measured several times each day and varied around 1.6 nM, showing
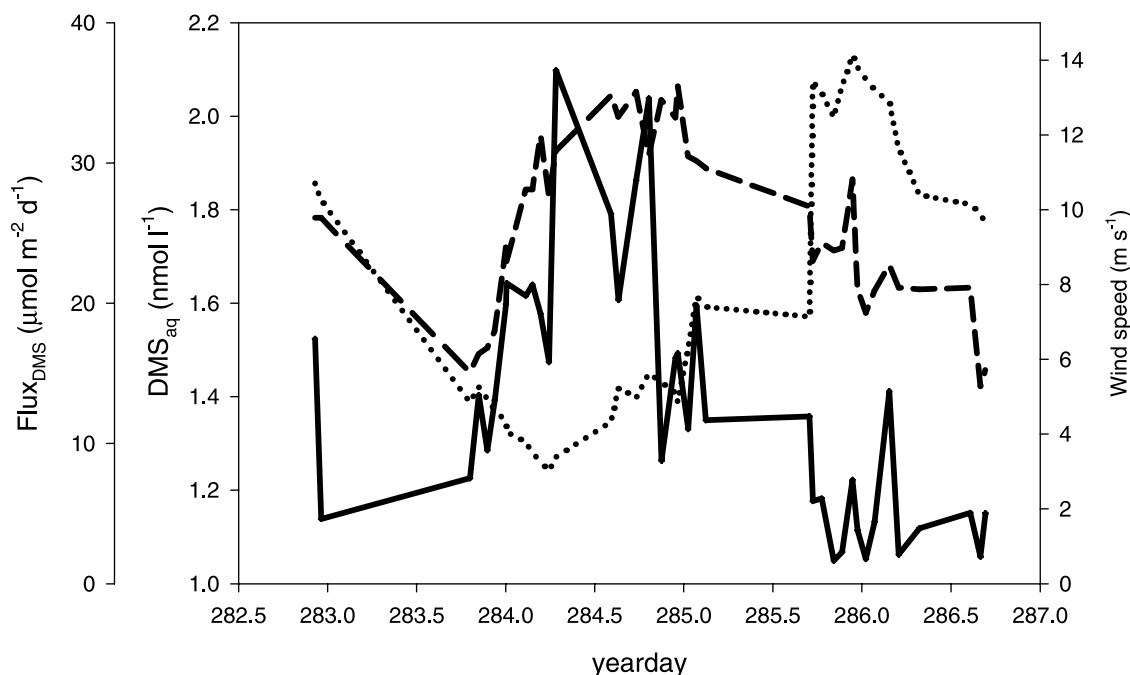

Figure 4. Wind speed (long dashed line), DMS fluxes (solid line), and aqueous DMS (dotted line) from day 282.5 to 287.
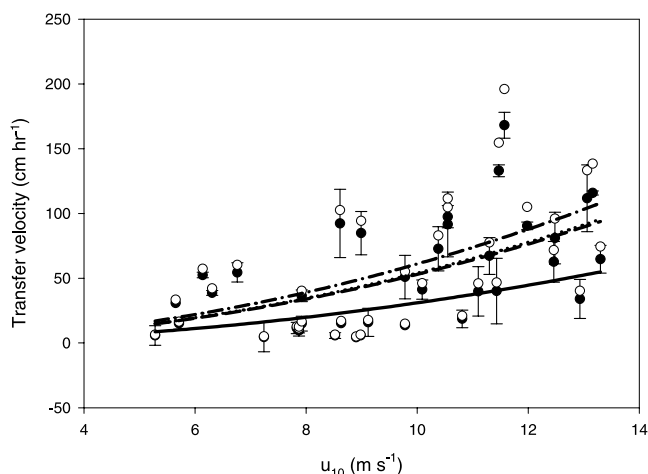
Figure 5. Gas transfer velocities converted to k_{660}. Solid circles are the total transfer velocities derived from individual flux measurements; error bars represent the standard deviations of the gas concentrations, an indication of the analytical accuracy. Open circles are waterside transfer velocities; the same error bars apply. The solid line is the parameterization proposed by *Wanninkhof* [1992]: $k_{660} = 0.31\ U_{10}^2$; the dotted line is proposed by *Jacobs et al.* [1999]: $k_{660} = 0.54\ U_{10}^2$; the dashed line is the result from the REA-DMS flux measurements, uncorrected for the airside transfer velocity: $k_{660} = 0.53\ (\pm 0.05)\ U_{10}^2$; and the dash-dotted line is the waterside transfer relationship: $k_{660} = 0.61\ (\pm 0.06) U_{10}^2$.

an increase at the end of the experiment to 2.1 nM (Figure 4). Wind speed varied between 4 and 14 m s^{-1}, with highest wind speeds from yearday 284.2 to 285.5, coinciding with neutral to unstable atmospheric conditions. Fluxes derived from the REA measurements varied between 1.9 and 37 μmol DMS m^{-2} d^{-1}, with higher fluxes during elevated wind speeds and high variability of measured fluxes even during periods of relatively constant surface water DMS concentrations and wind speed (Figure 4). Around yearday 284.8, both wind speed and fluxes decreased, coinciding with a shift in atmospheric stability toward more unstable conditions.

[24] Gas transfer velocities of DMS were computed from the combination of the DMS fluxes and the disequilibrium between the water and the air. Figure 5 shows the total gas transfer velocities and the (higher) waterside transfer velocities. The error bars in the figure represent standard deviations of replicate gas chromatographic analyses and are only attached to the total transfer velocities. The data cover a wide range of wind speeds and show a high degree of scatter that appears to increase at higher wind speed. Nevertheless, a trend of increasing k_{gas} with increasing wind speed can be observed. A fit of k_{gas} (uncorrected for the airside transfer velocity) to U_{10}^2 with zero intercept resulted in

$$k_{gas_{REA}} = 0.53\ U_{10}^2 \qquad (R^2 = 0.34). \qquad (11)$$

The 95% confidence interval for the coefficient (0.53) extends from 0.48 to 0.58, with k_{gas} and U in units of cm h^{-1} and m s^{-1}, respectively.

[25] The airside effect was removed from the total transfer velocity using the γ factor as suggested by *McGillis et al.* [2000], which is based on gas solubility and wind speed. The correction increases with increasing wind velocities (Figure 6). The waterside transfer velocity becomes

$$k_{660\,REA} = 061(\pm 0.06)\ U_{10}^2 \qquad (R^2 = 0.36). \qquad (12)$$

Equation (12) differs from the coefficient (0.31) of equation (8) as proposed by *Wanninkhof* [1992] and the cubic relation (10) from *McGillis et al.* [2001] but is close to the coefficient (0.54 ± 0.08) of the gas transfer parameterization (equation (9)) proposed by *Jacobs et al.* [1999]. However, the correlation in equation (12) is very poor as a result of the scatter observed in the gas transfer velocities.

4. Discussion

[26] From the combination of the DMS fluxes and the air/water disequilibrium we computed the gas transfer velocity of DMS, using water sampled at a depth close to the surface to estimate the disequilibrium. However, *Kieber et al.* [1996] calculated that atmospheric ventilation is the predominant removal pathway in the upper meter of the water column, which implies a strong gradient of DMS with smaller concentrations at the surface as compared to deeper water. In contrast, *Yang* [1999] observed an enrichment of DMS at the surface microlayer. Both observations illustrate that water samples taken at a particular depth may not contain equal concentrations of DMS as water at the boundary layer, which directly influences the magnitude of fluxes. However, it is extremely difficult to sample close to the boundary layer and therefore we have to accept a certain uncertainty in the surface water DMS concentration and therefore in fluxes and transfer velocities.

[27] Usually k_w is normalized to k_{660} (k_w for a Schmidt number of 660) and fitted to a function of wind speed. The k_{660} parameterization that we obtained from this approach was (within error bars) in agreement with the parameterization of *Jacobs et al.* [1999], both showing a difference of a factor 2 to 3 with commonly used gas transfer velocity
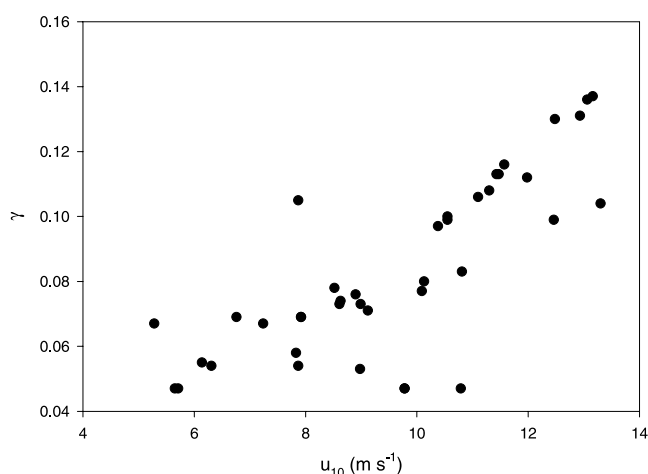

Figure 6. The gamma correction factor for the effect of the airside transfer velocity on the exchange of DMS as a function of wind speed. Gamma is calculated following *McGillis et al.* [2000].
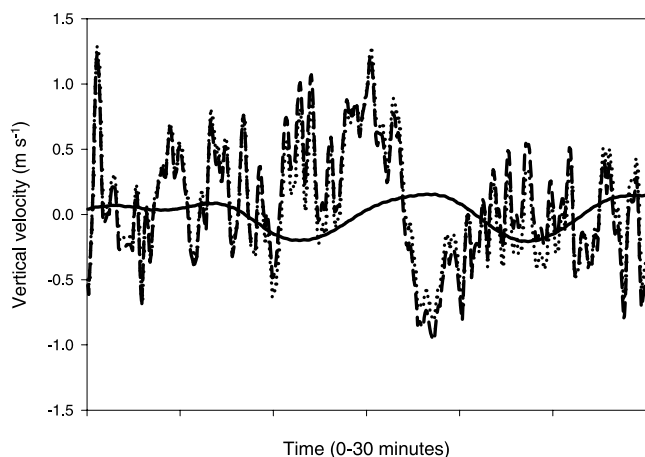
Figure 7. Effect of FLIP's motion on measured wind speed. The solid line is the vertical velocity (m s^{-1}) of FLIP during a sampling run on day 285. The dotted line is the vertical wind velocity uncorrected for the motion of the platform, and the dashed line is the true vertical wind speed, corrected for the motion of FLIP.

parameterizations [*Liss and Merlivat*, 1986; *Wanninkhof*, 1992]. *McGillis et al.* [2000] reiterated that transfer velocities derived from micrometeorological measurements of the flux of soluble gases include the effects of transfer through both air and water. In order to express k_{gas} as k_w the airside effect has to be removed. The magnitude of this correction depends on the assumed relationship between gas transfer and wind speed, as well as the solubility of the gas. The correction applied here is based on the quadratic relation between k_w and U_{10} as suggested by *Wanninkhof* [1992]. This might not be the most appropriate because the *Wanninkhof* [1992] parameterization is based on global ^{14}C budgets and cannot be expected to be representative of local processes that influence gas exchange. However, it is a reasonable intermediate choice between *Liss and Merlivat* [1986] and *Jacobs et al.* [1999]. The correction was found to be significant: around 10% at wind speeds of $7-10$ m s^{-1} increasing to a maximum of 16% at higher wind speeds.

[28] A quadratic dependence is often assumed in order to allow a direct comparison to the *Wanninkhof* [1992] relationship [e.g., *Jacobs et al.*, 1999]. An alternative is to derive a fit through the data with a varying exponent, which results in: $k_{660REA} = 0.35 * U_{10}^{2.18}$. However, the fraction of the variance that can be reproduced by assuming a dependence of k_{660} on $U_{10}^{2.18}$ remains low ($R^2 = 0.34$). The scatter in the data set is very large, over an order of magnitude at a wind speed of 11 m s^{-1}. This is not likely to be caused by poor accuracy of the REA system. Significant scatter was also observed in EC measurements of CO_2 flux conducted during the ASGAMAGE [*Jacobs et al.*, 1999] and GasEx-1998 [*McGillis et al.*, 2001] cruises, where the best fit through ASGAMAGE transfer velocities showed a correlation of 0.17. The scatter suggests that physical processes other than wind speed alone regulate gas exchange. *Bock et al.* [1999] emphasized that gas exchange is indirectly affected by wind speed. Other environmental parameters, such as waves, surface films and subsurface turbulence are intermittently linked and influence gas exchange in a more direct manner. However, explanation of the scatter in terms

of relevant physical processes in the source area of the flux is beyond the scope of this study and will only be possible when more data from the FAIRS experiment become available.

[29] Even though the REA system generated accurate measurements of CO_2 fluxes over land there still uncertainties about the accuracy of the measured DMS fluxes over water and the derived transfer velocities. The estimate of k_{660} generated by equation (12) results in exchange rates higher than previous studies using eddy correlation [*Jacobs et al.*, 1999; *McGillis et al.*, 2001] and more than twice as high as simultaneous gradient measurements of the DMS flux during FAIRS that are more in agreement with the Liss and Merlivat parameterization [*Hintsa et al.*, 2004].

[30] An overestimation of the DMS flux caused by a technical artifact of the REA system is unlikely. Sampling errors that are involved with REA are most probably confined to a mismatch between the switching of the valve that diverts the gas sample into the appropriate collection reservoir and the change of direction of w. As a result, upward moving air would be collected in the reservoir for downward moving air and vice versa. This would lead to a decrease of the concentration difference between the two reservoirs and hence an underestimation of the flux and k_w.

[31] However, there are possible situations in which REA measurements could result in an overestimation of the flux. First, a heterogeneous distribution of DMS over the sea surface could lead to horizontal transport. It is unlikely that this occurred during FAIRS, because water samples did not indicate a significantly heterogeneous distribution of DMS.
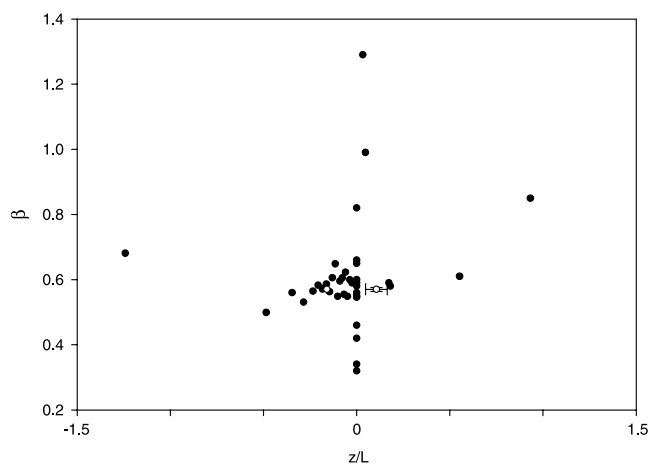

Figure 8. Estimates of the relaxed eddy accumulation coefficient β. Solid circles: the coefficient calculated as a function of stability for simulations of REA heat flux from direct correlation measurements of sensible heat flux during GasEx-2001. Here $z/L > 0$ corresponds to stable conditions, $z/L \sim 0$ corresponds to neutral conditions, and $z/L < 0$ corresponds to unstable atmospheric conditions. Open circles: REA coefficients used for the calculation of the DMS flux following $\beta \exp(-0.75w_0/\sigma_w)$, as suggested by *Businger and Oncley* [1990]. The simulations tend to converge on a mean for β around 0.58. Scatter in the calculated β increases as z/L approaches zero because both numerator and denominator in the calculation approach zero at near-neutral conditions.
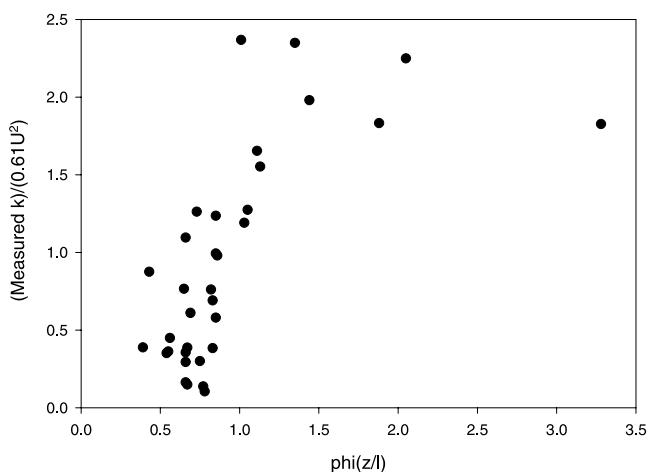
Figure 9. Deviation of the transfer velocity (k_{660}) from the mean $k_{660} = 0.61\ U_{10}^2$ versus the atmospheric stability expressed as phi (ϕ, a function of measurement height to the M-O length), where $\phi > 1$ is stable and $\phi < 1$ is unstable.

Second, if the sonic anemometer that triggers the valve is tilted and responds to the horizontal wind (u), then the measured flux will be composed of horizontally and vertically transported DMS. To avoid this problem, samples with $|\overline{w}| > 0.01 \cdot \overline{u}$ (where the bar indicates a time average) were not used for further analysis, minimizing the influence of horizontal transport on the measured flux.

[32] Vertical movement of the platform by waves and swell will affect the measured wind speeds. This is a potential source of error for the measured flux. REA measurements are very difficult to correct for the effect of platform motion, because the sampling depends on an instantaneous response of valves to wind speed changes. Figure 7 demonstrates the motion of FLIP and the effect on the vertical wind speed during a sampling run at day 285, representative of the whole experiment. Although the vertical wind speed is slightly contaminated by the motion, the effect on the magnitude, direction, and duration of w is minimal. Hence the effect of platform motion on the measured flux is negligible.

[33] The effect of atmospheric conditions on REA has been studied in terms of the value of β as a function of atmospheric stability and turbulence. Empirical estimates of β based on EC measurements over terrestrial systems yielded numbers in the vicinity of $0.56-0.58$ [*Baker et al.*, 1992; *Pattey et al.*, 1993; *Beverland et al.*, 1996; *Katul et al.*, 1996]. Following the approach of *Businger and Oncley* [1990] to correct eddy accumulation coefficients for the use of a deadband resulted in effective β values (calculated from $\beta \exp(-0.75w_0/\sigma_w)$, used in equation (5)) of 0.57 ± 0.006 in stable conditions and 0.57 ± 0.004 in unstable conditions; all falling within the above mentioned range derived from EC measurements over land by *Baker et al.* [1992], *Pattey et al.* [1993], *Beverland et al.* [1996], and *Katul et al.* [1996]. However, terrestrially derived values of β might not necessarily be the same as values over water. Moreover, *Andreas et al.* [1998] found a weak stability dependence of β for gas fluxes using turbulence data of sensible heat and results from *Businger and Oncley* [1990]. This implies that extreme stable or unstable conditions, due

to air-water temperature differences, could affect β factors. REA simulations based on EC measurements of sensible heat fluxes over the ocean, conducted during the GasEx-2001 cruise, resulted in values of β that were similar to those found by *Andreas et al.* [1998] and indicated a weak, but not significant, stability dependence (Figure 8). Averaged values of β during unstable (z/L < −0.01), neutral (where z/L approaches 0) and stable conditions (z/L > 0.01) were 0.58 (±0.04, n = 930), 0.55 (±0.41, n = 12) and 0.69 (±0.26, n = 11), respectively. Overall, the average value for β was 0.58, similar to the effective values calculated from $\beta \exp(-0.75w_0/\sigma_w)$.

[34] The data show a trend of k_{660} with atmospheric stability where k_w based on REA is lower than average during unstable atmospheric conditions and higher than average during stable conditions (Figure 9). The trend of increasing k_{660} with increasing ϕ contradicts the expected trend of relatively low fluxes during stable conditions due to suppressed turbulence, and relatively high fluxes during unstable conditions where turbulence is enhanced by buoyancy. Both REA and GF results show the same trend so this observation does not provide an explanation as to why results derived from both methods show the large discrepancy [*Hintsa et al.*, 2004]. Unfortunately, the present data set does not allow a definitive relation between k_{660} and parameters other than U_{10} and the atmospheric stability.

5. Conclusion

[35] The transfer rates presented here, based on REA measurements of DMS flux, are within the uncertainty of previously reported transfer rates that were based on EC measurements of CO_2 fluxes. However, DMS fluxes showed a high degree of scatter that could not readily be accounted by wind speed and atmospheric stability. Moreover, the REA measurements significantly deviate from simultaneous GF measurements. The relatively small data set and the lack of observations of other environmental parameters that could explain the observed scatter do not yet allow an accurate parameterization of gas transfer. More measurements and an extensive analysis of measurement techniques or environmental parameters that could affect the flux are needed to gain confidence in field measurements of gas fluxes in the marine environment.

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