

Fluxes and gas transfer rates of the biogenic trace gas DMS derived from atmospheric gradients

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[1] Gas transfer rates were determined from vertical profile measurements of atmospheric dimethylsulfide (DMS) gradients over the equatorial Pacific Ocean obtained during the GasEx-2001 cruise. A quadratic relationship between gas transfer velocity and wind speed was derived from the DMS flux measurements; this relationship was in close agreement with a parameterization derived from relaxed eddy accumulation measurements of DMS over the northeastern Pacific Ocean. However, the GasEx-2001 relationship results in gas transfer rates that are a factor 2 higher than gas transfer rates calculated from a parameterization that is based on coincident eddy correlation measurements of CO₂ flux. The measurement precision of both the profiling and eddy correlation techniques applied during GasEx-2001 is comparable; the two gas transfer data sets are in agreement within their uncertainty. Differences in the number of samples and the wind speed range over which CO₂ and DMS fluxes were measured are likely causes for the observed discrepancy.

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1. Introduction

[2] Dimethylsulfide (DMS), a biogenic gas that originates from the oceans, plays an important role in atmospheric chemistry [Andreae and Crutzen, 1997]. Observations in the marine boundary layer of the Southern Hemisphere strongly suggest that DMS and its atmospheric oxidation products participate in processes of climate regulation and the reactivity of the atmosphere [Ayers and Gillett, 2000]. Quantification of the sea-to-air flux remains a prerequisite for assessing the environmental impact of DMS. The exchange of DMS (F , mol m⁻² d⁻¹) between the ocean and the atmosphere is commonly estimated from the air-sea concentration gradient (ΔC) and an empirically determined gas transfer rate (k_{gas}),

$$F = k_{\text{gas}}\Delta C. \quad (1)$$

Most parameterizations of transfer rates are based on wind tunnel, radiocarbon, or tracer measurements, and relate k_{gas} to sea surface temperature and wind speed. Unfortunately, the most commonly applied parameterizations, of Liss and

Merlivat [1986] and of Wanninkhof [1992], differ by more than a factor of 2 in their prediction of exchange rates and therefore the flux [Kettle and Andreae, 2000]. Studies of DMS and sulfur cycling over the oceans [Putaud and Nguyen, 1996; Yvon et al., 1996] support the higher estimates of gas transfer rates. On the other hand, studies based on the use of dissolved tracer gases support lower estimates [Liss et al., 1993; Nightingale et al., 2000]. There is currently no well-constrained relationship between gas transfer rates and wind speed that can be used for the reliable prediction of in situ DMS fluxes. Liss [1999] has stated that progress is most likely to come once a micrometeorological technique is developed that can measure DMS fluxes across the sea surface.

[3] In recent years, micrometeorological techniques, such as the gradient flux (GF) and relaxed eddy accumulation (REA) techniques, have been applied for the measurement of DMS fluxes, and the subsequent derivation of the gas transfer rate [McGillis et al., 2001; Zemmeling et al., 2002; Hints et al., 2004; Zemmeling et al., 2004]. Most of these studies suggest high DMS transfer rates. However, GF and REA techniques do not allow the measurement of the absolute flux and rely on models that incorporate wind and atmospheric stability measurements. These models have been extensively tested over terrestrial systems, but their

application in the marine environment is still relatively new. Although *Edson and Fairall* [1998] concluded that Monin-Obukhov similarity theory (the basis of the GF technique) is valid over the sea, as long as it is applied above the wave boundary layer, further tests are necessary before both REA and GF can be applied with confidence at sea. The first studies that aimed at the intercalibration of REA and GF techniques, used in tandem for the measurement of DMS fluxes, resulted in different gas transfer rates between the two methods [*Hintsä et al.*, 2004; *Zemmelink et al.*, 2004]. The difference could not be attributed to experimental error. One environmental forcing factor, i.e., atmospheric stability, was also ruled out as an explanation of the discrepancy. Both sets of results were reasonable, however: REA measurements were in agreement with gas transfer velocities obtained from eddy correlation measurements of CO₂ fluxes in a shelf sea [*Jacobs et al.*, 1999] and GF measurements were in agreement with estimates based on the parameterization of *Liss and Merlivat* [1986]. It was concluded that there is at present no reason to prefer the use of one technique over the other in the marine environment.

[4] Better insight into the applicability of micrometeorological systems in the marine environment and processes that influence gas exchange will come from experiments that aim at the intercalibration of techniques and/or at the measurement of fluxes of different gases. The transfer rates of different gases (or gases at different temperatures) can then be related through the Schmidt number (Sc) using $k_a = k_b(Sc_a/Sc_b)^n$ where n is the Schmidt number dependence ($-2/3$ for smooth water surfaces, wind speed $\leq 3.6 \text{ m s}^{-1}$, and $-1/2$ for rough surfaces, wind speed $> 3.6 \text{ m s}^{-1}$). In this study we present results derived from GF measurements of DMS fluxes over the equatorial Pacific Ocean performed during the GasEx-2001 experiment. In addition, these GF results from GasEx-2001 are compared with eddy correlation measurements of the CO₂ flux conducted during the same cruise and with results from previous measurements over the northeastern Pacific Ocean. Finally, possible reasons for the discrepancy between the results of the different measurements are discussed.

2. Materials and Methods

[5] The GasEx-2001 cruise was an interdisciplinary air-sea gas exchange experiment conducted aboard the NOAA ship *Ronald H. Brown* during February 2001. The study site was in the eastern equatorial Pacific along 3°S between 125°W and 130°W.

[6] With the GF technique [*Businger et al.*, 1971], the flux is derived from the difference in concentration (C , mol m⁻³) between two or more elevations using Monin-Obukhov similarity theory [*Monin and Obukhov*, 1954],

$$C(z) = \frac{C_*}{k} \left(\ln(z) - \Psi\left(\frac{z}{L}\right) \right), \quad (2)$$

where $C(z)$ is the DMS concentration at height z (m), Ψ is the integrated flux profile function that corrects for atmospheric stability [*Paulson*, 1970], L is the Obukhov length,

and k is the von Karman constant (0.4). The value of C_* is determined from the least squares fitted slope of $C(z)$ as a function of $\ln(z) - \Psi(z/L)$, the stability-corrected height. Next the DMS flux is calculated using

$$F_{\text{DMS}} = -C_* u_*, \quad (3)$$

where u_* (m s⁻¹) is the friction velocity, derived from eddy correlation wind measurements. The uncertainty of the estimated flux is expressed in this study as the 95% confidence interval of C_* , based on the fit of C to $\ln(z) - \Psi(z/L)$. The uncertainty in u_* has not been calculated in this study but is of the same order as the uncertainty in C_* .

[7] Air was sampled at 40-min intervals using inlets at 2.5, 4, 6, and 8 m above the sea surface from a boom that extended 10 m off the bow. The elevation of the inlet at 8 m was adjustable and sometimes used to take duplicate samples at the other elevations. Sampled air was drawn at 200 mL min⁻¹ over potassium iodide oxidant scrubbers, led through 30 m of Teflon tubing and collected in Tedlar bags following the procedure described by *Zemmelink et al.* [2002]. The collected air was brought to the same temperature and the effect of density fluctuations on the DMS flux measurements was further avoided by drying the air over a cold finger prior to concentration of DMS on a Tenax trap, at a flow rate of 300 mL min⁻¹. Both the cold finger and the Tenax trap were cooled to -15°C . This is necessary for the GC analysis, and also removes the need for the Webb correction. Subsequently, the DMS concentration was determined by desorption of the DMS into a Sievers 350B gas chromatograph. Sulfur compounds were separated on a Chromosil-330 column and analyzed with a sulfur chemiluminescence detector. A triplicate analysis was conducted from each sampling bag. The concentration of DMS in the surface water was determined from water samples taken during each flux measurement. Aqueous DMS was analyzed following the procedure described by *Dacey et al.* [1998].

[8] Transfer velocities were calculated using $k_{\text{gas}} = F/(C_w - C_a/K_H)$ where k_{gas} is the total gas transfer velocity, which results from a waterside transfer velocity (k_w) and an airside transfer velocity (k_a), C_w is the waterside DMS concentration, C_a is the atmospheric DMS concentration, determined from the measurements at 2.5 m elevation, and K_H is the dimensionless Henry coefficient ($K_H = H/RT$ where H is the Henry constant of DMS calculated following *Dacey et al.* [1984], R is the universal gas constant, and T is the absolute temperature).

[9] In order to express the transfer velocity in term of k_w , the effect of the airside transfer velocity has to be removed as suggested by *McGillis et al.* [2000]: $k_w = k_{\text{gas}}/(1 - \gamma)$, where γ is the airside gradient factor affecting the flux. The value of γ is calculated from the ratio of the water and airside transfer velocities: $\gamma = 1/(1 + k_a/\omega k_w)$, with ω the Ostwald solubility coefficient for DMS from *Dacey et al.* [1984]. The airside transfer velocity (k_a) is calculated from models of water vapor transfer velocities as suggested by *Kondo* [1975] and *Liu et al.* [1979]. Waterside transfer velocities (k_w) for the γ correction are given by the model of *Wanninkhof* [1992]. The correction is on the order of 5% at wind speeds up to

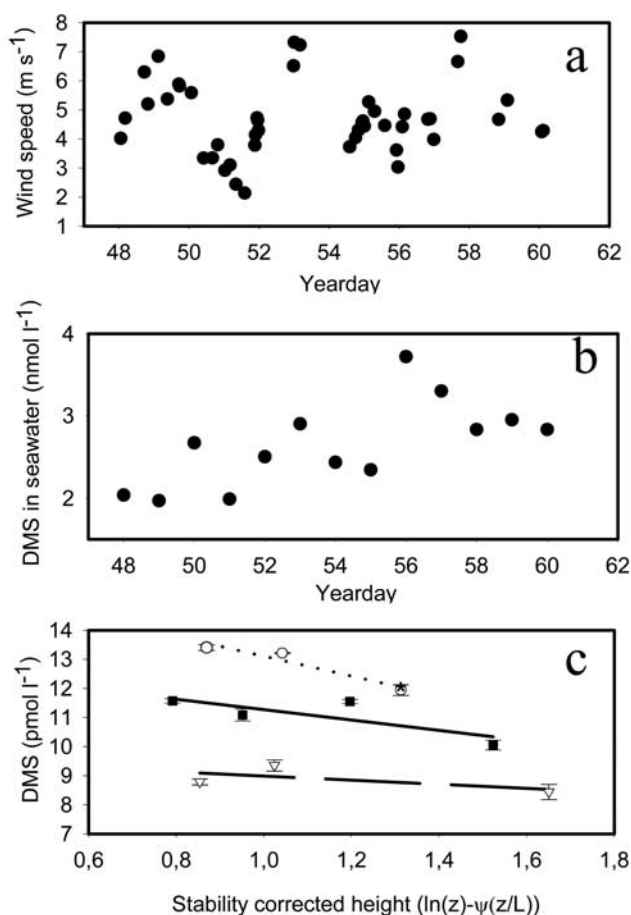


Figure 1. (a) Wind speed (m s^{-1}) at 10 m. (b) Surface water DMS concentration (nmol L^{-1}) averaged over each day. (c) Atmospheric DMS (pmol L^{-1}) as a function of the stability-corrected elevation. The dotted line is the best fit through an early morning profile (open circles), $U = 6.8 \text{ m s}^{-1}$, slope = -3.2 , $R^2 = 0.92$; the solid line is the best fit through a mid afternoon profile (solid squares), $U = 5.4 \text{ m s}^{-1}$, slope = -1.8 , $R^2 = 0.64$; the dashed line is the best fit through a mid morning profile (open triangles), $U = 5.8 \text{ m s}^{-1}$, slope = -0.1 , $R^2 = 0.43$. Error bars are 1 standard deviation from the mean. The asterisk indicates a duplicate sample taken along with the open circles.

5 m s^{-1} , 10% at $7\text{--}10 \text{ m s}^{-1}$ and 16% or more at higher wind speeds [Zemmelink *et al.*, 2004].

3. Results and Discussion

[10] The atmosphere was slightly unstable during the experiment with the water temperature higher than the air temperature: 26.9° and 26.3°C , respectively. Wind speed ranged from 2 to 7.5 m s^{-1} , averaging 5 m s^{-1} (Figure 1a). The seawater DMS concentration ranged from 2 to 3.7 nM , with an average of 2.7 nM (Figure 1b), consistent with values for this area listed in the database of Kettle *et al.* [1999] and values of approximately $2.0 (\pm 0.7) \text{ nM}$ found by Bates *et al.* [1993] in the central equatorial Pacific Ocean, while Yvon *et al.* [1996] found an average seawater DMS concentration of 4.1 nM south-west of the GasEx-2001 cruise.

[11] The average DMS concentration in 48 series of three profiles collected at 2.5 , 4 , and 6 m were 10.1 , 9.2 and 8.7 pmol L^{-1} , respectively. These atmospheric concentrations are lower than those found by Yvon *et al.* [1996] but consistent with atmospheric DMS found in the marine boundary layer remote from the continents [Andreae, 1990; Quinn *et al.*, 1993]. The decreasing DMS concentration with height (Figure 1c), confirms an efflux. However, the uncertainty at the 95% confidence interval for C_* (and therefore of the estimated flux and transfer velocities) was large, which for some measurements does not exclude the possibility of a flux of DMS into the water (Figure 2). A problem involved in the application of the gradient method is its sensitivity to flow distortion and platform motion; both become more pronounced with increasing wind speeds. The relative uncertainty of our measurements (expressed as the percentages of the flux) did not show a dependence on wind speed so we could not straightforwardly attribute the error in our flux measurements to flow distortion around the ship's hull. However, the uncertainty is not caused by the analytical procedure that was used to determine the DMS concentration in the sampled air: The reproducibility of a triplicate analysis was good, usually within 10%. In addition, DMS values deviating from a log linear slope in any one profile could not be attributed to fouling of the sample system; duplicate air samples taken from the same elevation did not show a significant difference (and the different inlets showed no signs of any systematic bias).

[12] Stochastic measurement errors may still have affected the profiles so it was decided to use all 48 measurements for further analysis. Fluxes were positive and increased with increasing wind speeds from $0.2 (\pm 4) \mu\text{mol m}^{-2} \text{ d}^{-1}$ to a maximum of $36 (\pm 21) \mu\text{mol m}^{-2} \text{ d}^{-1}$, with an average of $9.0 \mu\text{mol m}^{-2} \text{ d}^{-1}$ (Figure 2).

[13] Transfer velocities calculated from the sea surface DMS concentrations and the measured flux varied between 0.5 and 55 cm hr^{-1} . On average, transfer velocities increased with increasing wind speeds (Figure 3). The transfer velocities were on average higher than those derived from parameterizations between wind speed and

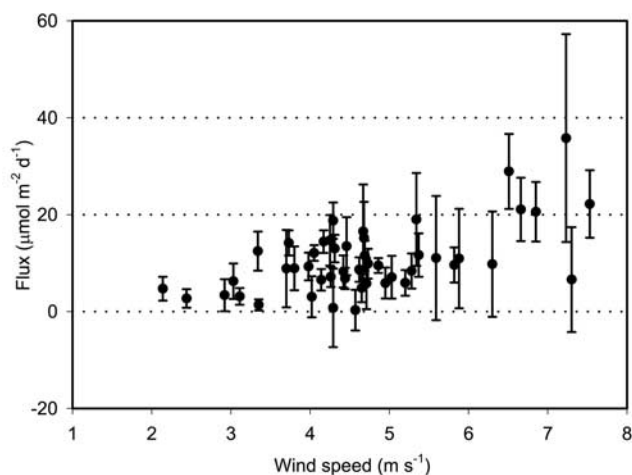


Figure 2. DMS flux ($\mu\text{mol m}^{-2} \text{ d}^{-1}$) as a function of wind speed (m s^{-1}). Error bars represent the 95% confidence interval of the best fit through the profile.

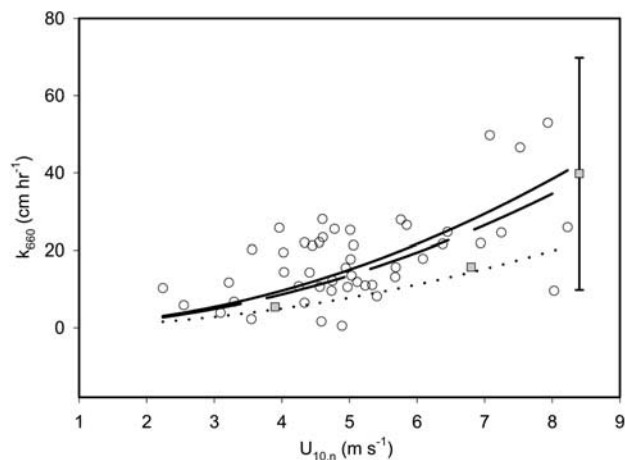


Figure 3. Open circles: gas transfer velocities (cm hr^{-1}), derived from gradient measurements of DMS fluxes during the GasEx-2001 cruise (Figure 2), versus wind speed (m s^{-1}) at 10-m elevation during neutral atmospheric conditions. The shaded squares are the average of gas transfer velocities derived from DMS gradient measurements during the GasEx-1998 cruise ($n = 3$) conducted in the North Atlantic Ocean. Transfer velocities are normalized to the transfer velocity of CO_2 in water at 20°C with a salinity of 35‰. The solid line is the quadratic fit through the GasEx-2001 results: $k_{660} = 0.60 (\pm 0.04) U_{10}^2$. The dashed line is the equation based on eddy correlation measurements of the CO_2 flux: $0.54 U_{10}^2$ by *Jacobs et al.* [1999]. The dotted line is the *Wanninkhof* [1992] fit: $k_{660} = 0.31 U_{10}^2$.

gas transfer commonly applied for the calculation of fluxes [*Liss and Merlivat*, 1986; *Wanninkhof*, 1992]. Nevertheless, the results of GasEx-2001 (hereinafter referred to as GasEx01-GF/DMS) are consistent with the high transfer velocities derived from DMS fluxes found during GasEx-1998 conducted in the North Atlantic Ocean (Figure 3, and *McGillis et al.* [2001]). Moreover, the results from DMS measurements are in agreement with transfer velocities derived from eddy correlation measurements of the carbon dioxide flux (hereinafter referred to as GasEx01-EC/ CO_2 measurements) conducted by *McGillis et al.* (Figure 4).

[14] A fit through the GasEx01-GF/DMS data using a quadratic dependence on wind speed resulted in

$$k_{660} = 0.60(\pm 0.04)U_{10}^2 \quad R^2 = 0.28, \quad (4)$$

in which k_{660} is the transfer velocity normalized to the transfer velocity of CO_2 in water with a salinity of 35‰ at 20°C and U_{10} (m s^{-1}) is the wind speed at 10-m elevation under neutral conditions. The exponent in the relationship between k_{660} and U_{10} is based on the work of *Wanninkhof* [1992], who proposed $k_{660} = 0.31 U_{10}^2$ for short-term measurements of wind speed). Equation (4) is nearly equivalent to the relation derived from relaxed eddy accumulation (REA) measurements of DMS flux over the northeastern Pacific during the Fluxes Air-Sea Interaction and Remote Sensing (FAIRS) experiment $k_{660} = 0.61(\pm 0.06) U_{10}^2$, but it is different from parameterizations obtained

from GF/DMS measurements during the same FAIRS cruise $k_{660} = 0.18 (\pm 0.03) U_{10}^2$ [*Hints et al.*, 2004; *Zemmelink et al.*, 2004] and different from the relationship derived from the GasEx01-EC/ CO_2 measurements $k_{660} = 0.28 (\pm 0.01) U_{10}^2$.

[15] On the basis of the agreement between the constants of the gas transfer relationships derived from GasEx01-GF/DMS measurements (0.60 ± 0.04) and FAIRS-REA/DMS measurements (0.61 ± 0.06), we decided to combine both data sets. It is clear that the absolute scatter of k_{660} in this merged data set increases with increasing wind speed; for a wind speed range of $2 \text{ m s}^{-1} < U < 5 \text{ m s}^{-1}$ the value of $k_{660\text{avg}} = 14 \pm 8 \text{ cm hr}^{-1}$, while for a wind speed range of $6 \text{ m s}^{-1} < U < 9 \text{ m s}^{-1}$ the value of $k_{660\text{avg}} = 30 \pm 24 \text{ cm hr}^{-1}$ (where the subscript avg refers to the average). Analysis of log transformed data, $\ln(k_{660})$ versus $\ln(U)$, showed that the relative scatter remained constant (Figure 5) and that the variance of the two transformed data sets does not significantly differ ($P > 5\%$), which implies that pooling the two data sets is legitimate.

[16] The relationship between gas transfer and wind speed derived from the best fit through the log transformed data, with zero intercept, was $k_{660} = 1.28 (\pm 0.42) U^{1.47 (\pm 0.22)}$ ($R^2 = 0.35$). Application of a quadratic fit through the ln transformed data resulted in $k_{660} = 0.48 (\pm 0.09) U_{10}^2$ ($R^2 = 0.31$; Figure 6). Both relationships are within the uncertainty of the “global average k ” determined from the atom bomb ^{14}C inventory in the ocean ($U_{10} = 7.4 \text{ m s}^{-1}$, $k = 22 \text{ cm hr}^{-1}$ [*Broecker et al.*, 1985]). Values of $k_w < 1$ were excluded from the log transformed data in order to evaluate the effect of low k_w values on the parameterization derived from $\ln(k_w)$ versus $\ln(U)$; this resulted in $k_{660} = 0.52 (\pm 0.08) U_{10}^2$.

[17] Many parameterizations of gas exchange with wind speed have been reported, and dependencies in wind speed

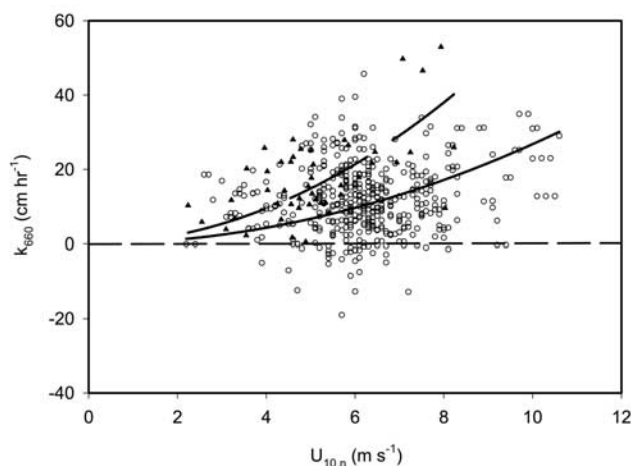


Figure 4. Gas transfer rates (cm hr^{-1}) derived from gradient measurements of DMS flux (black triangles) and eddy correlation measurements of CO_2 flux (open circles). The dashed line is the gas transfer parameterization based on DMS measurements ($k_{660} = 0.60 U_{10}^2$), and the solid line is the gas transfer parameterization based on CO_2 measurements ($k_{660} = 0.28 U_{10}^2$), derived from *McGillis et al.* [2001].

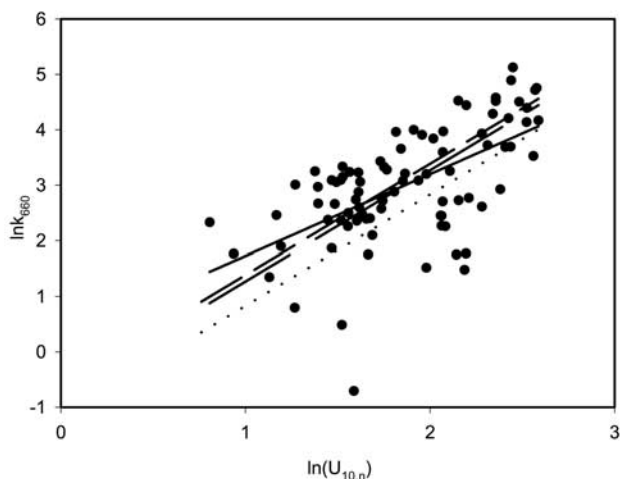


Figure 5. Ln transformed k_{660} versus ln transformed $U_{10,n}$. The solid line is the least squares fit through the data: $k_{660} = 1.28 U_{10}^{1.47}$. The short dashed line is the equation based on eddy correlation measurements of CO_2 flux: $k_{660} = 0.54 U_{10}^2$ from *Jacobs et al.* [1999]. The long dashed line is the quadratic fit through the merged data set: $k_{660} = 0.48 U_{10}^2$. The dotted line is the *Wanninkhof* [1992] fit: $k_{660} = 0.31 U_{10}^2$.

vary from linear [*Liss and Merlivat*, 1986] to quadratic and cubic [*Wanninkhof*, 1992; *Jacobs et al.*, 1999; *Nightingale et al.*, 2000; *Wanninkhof and McGillis*, 1999; *McGillis et al.*, 2001]. *Monahan and Spillane* [1984] proposed that gas

transfer is proportional to whitecap coverage and that white cap coverage scales approximately with U^3 . Laboratory studies of *Asher et al.* [1996] have shown a linear, gas-specific, dependence of gas transfer with whitecaps, implying that gas exchange could show a cubic relation to wind speed. Indeed, *Wanninkhof and McGillis* [1999] and *McGillis et al.* [2001] showed that the exchange of CO_2 over a wide range of wind speeds up to 16 m s^{-1} was described well by a cubic wind speed dependence of k . However, a cubic fit through the merged GasEx01-GF/DMS and FAIRS-REA/DMS data, in the form of $\ln y = \ln a + 3 \ln x$, did not yield a better fit with the observed data ($R^2 < 0.1$) than a quadratic fit.

[18] Using the merged data set and following the most common approach of relating k_w to the square of U_{10} it is possible to describe the exchange of DMS up to a wind speed of 13 m s^{-1} by

$$F_{\text{DMS}} = 0.48(1 - \gamma)U_{10}^2 660 / \text{Sc}_{\text{DMS}})^{-n} \Delta C \quad R^2 = 0.31, \quad (5)$$

where Sc_{DMS} can be derived from *Saltzman et al.* [1993]. This relationship between gas transfer and wind speed is in good agreement with the parameterization found by *Jacobs et al.* [1999]: $k_{660} = 0.54 (\pm 0.08) U_{10}^2$, determined from eddy correlation measurements of CO_2 flux over a shelf sea.

[19] However, it should be emphasized that although the GasEx01-GF/DMS and FAIRS-REA/DMS data are in agreement in terms of the derived parameterizations and the homogeneous variance, there is no reason to assume that the FAIRS-GF/DMS or GasEx-EC/ CO_2 results are

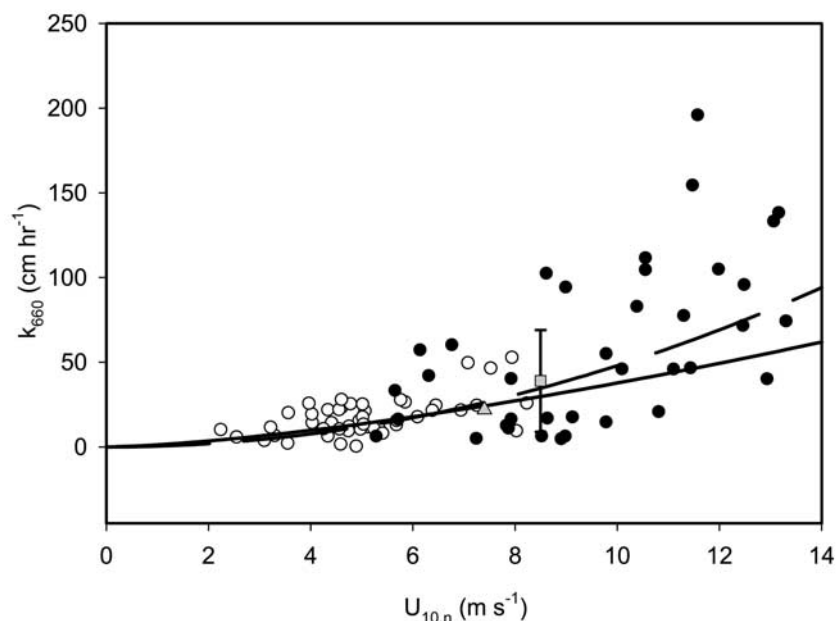


Figure 6. Merged GasEx-2001-GF (open circles) and FAIRS-REA results (solid circles). The shaded square is the average of gas transfer velocities derived from DMS gradient measurements during the GasEx-1998 cruise ($n = 3$). The shaded triangle is the global mean transfer rate determined from ^{14}C [*Broecker et al.*, 1985]. Transfer velocities are normalized to the transfer velocity of CO_2 in water at 20°C with a salinity of 35‰. The solid line is the least squares fit through the data: $k_{660} = 1.28 U_{10}^{1.47}$. The dashed line is the quadratic fit through the merged data set: $k_{660} = 0.48 U_{10}^2$.

erroneous. Moreover, the variance in the FAIRS-GF/DMS and the GasEx-EC/CO₂ data sets is not statistically different from the variance of the two other data sets ($P > 5\%$).

[20] It is questionable whether equation (5) is a valid description of gas exchange over the Pacific Ocean since it is based on measurements made in marine geographical provinces with different characteristics. Differences in environmental conditions during the FAIRS and GasEx-2001 cruises might have affected the applied techniques. The FAIRS cruise was conducted on the edge of the Californian current where the occurrence of strong winds and high swell is common, while the equatorial Pacific is typically a low wind speed area where small waves prevail. The effect of swell and waves on the applicability of REA and GF techniques, more specifically on the models that these techniques are based upon, is not yet fully understood. In addition, the Californian current is much more biologically productive, and it is likely that there are more surfactants in this area than in the equatorial Pacific. Surfactants are known to suppress gas exchange significantly [Frew, 1997].

[21] Although the GasEx01-EC/CO₂ and GasEx01-GF/DMS data sets agree, GF/DMS measurements made beyond 6 m s^{-1} suggest a strong increase of transfer rates, which depends mostly on the three DMS measurements with k_{660} above 40 cm hr^{-1} . This increase is not observed in the EC/CO₂ measurements, resulting in a discrepancy between the GasEx01-EC/CO₂ and GasEx01-GF/DMS parameterizations. The different sizes of the data sets and the larger wind speed range over which the EC/CO₂ measurements were made are likely reasons for the discrepancy between the two parameterizations. The small number of GF/DMS measurements at elevated wind speeds does not allow a conclusion other than that the data sets agree within uncertainty. However, processes such as biogeochemical conversions in the sea surface microlayer and bubble mediated transport may cause a difference in the exchange rates of two gas species; such effects are not taken into account in the parameterizations.

[22] The GasEx01 results clearly show that it is not possible to rely on the use of a single technique for the description of air-sea gas exchange. Moreover, even when it is possible to make reliable field measurements of gas fluxes, there will still be a significant degree of uncertainty when gas transfer velocities are parameterized as a function of wind speed alone. It is unlikely that this uncertainty will be reduced by more measurements alone, unless other factors controlling exchange within the source area are taken into account.

[23] It seems that most field measurements (GasEx98/01, ASGAMAGE, FAIRS) indicate higher gas transfer rates than those derived from the *Liss and Merlivat* [1986] parameterization (which can be approximated by the quadratic dependence: $k_{660} = 0.17 U^2$); this would mean that the current IPCC estimate of the CO₂ budget, which is based on the average of transfer velocities derived from *Wanninkhof* [1992] and *Liss and Merlivat* [1986], is at the low side. Moreover, studies of sulfur cycling often estimate the atmospheric burden of DMS on the basis of fluxes calculated by using the *Liss and Merlivat* [1986] parameterization of k_w as a function of wind speed. The in situ measurements during GasEx-2001 imply that the

atmospheric burden of DMS can be underestimated significantly by this approach. Gas transfer parameterizations that are derived from micrometeorological measurements of gas fluxes in the field tend to result in higher transfer rates than those based on the conventional Liss and Merlivat gas transfer parameterization. The emission of DMS from the ocean to the atmosphere could well be higher than until now was commonly thought. However, field measurements show a high degree of scatter that cannot readily be accounted for by wind speed and water temperature alone. It has to be concluded that in situ measurements do not yet permit an accurate parameterization of gas transfer as a function of wind speed.

4. Conclusion

[24] The gas transfer velocities derived from in situ measurement of DMS and CO₂ fluxes during GasEx-2001 agree within uncertainty. However, averages in the form of a functional fit of k_{660} versus U_{10} through the data sets result in a large discrepancy between parameterizations. This emphasizes the danger of relying on a single technique, or data set, to obtain gas budgets. The measurement precision of both techniques during GasEx-2001 seems to agree well, which is encouraging because it might help one or both of the techniques to improve precision and or accuracy in the future.

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