

# DMS sea-air transfer velocity: Direct measurements by eddy covariance and parameterization based on the NOAA/COARE gas transfer model

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[1] Estimates of the DMS sea-air transfer velocity ( $k_{DMS}$ ) derived from direct flux measurements are poorly modeled by parameterizations based solely on wind speed and Schmidt number. DMS and  $CO_2$  flux measurements show  $k_{CO_2}$  to be a stronger function of wind speed than  $k_{DMS}$ . The NOAA/COARE gas flux parameterization, incorporating the bubble-mediated gas transfer theory of Woolf (1997), appears to do a better job reproducing the observations for both gases, illustrating the importance of trace gas solubility in sea-air exchange. The development of gas transfer parameterizations based on physical principles is still in its infancy, but recent advances in direct flux measurement methods provide an opportunity to evaluate the success of various modeling approaches for this critical geophysical process. **Citation:** Blomquist, B. W., C. W. Fairall, B. J. Huebert, D. J. Kieber, and G. R. Westby (2006), DMS sea-air transfer velocity: Direct measurements by eddy covariance and parameterization based on the NOAA/COARE gas transfer model, *Geophys. Res. Lett.*, 33, L07601, doi:10.1029/2006GL025735.

## 1. Introduction

[2] Sea-air exchange of trace gases is an important process in atmospheric chemistry, marine biology, and climate. Fluxes of carbon dioxide ( $CO_2$ ) and dimethylsulfide (DMS) are the subject of continuing experimental and theoretical interest due to their link with global climate;  $CO_2$  exchange has obvious importance to the atmospheric carbon and radiation budgets, and DMS is the principal precursor for atmospheric sulfate aerosol and cloud condensation nuclei in remote marine regions covering large areas of the globe. Direct measurement of these fluxes has been challenging, to say the least. It is common practice to estimate the magnitude of important trace gas fluxes with simple formulations expressing gas exchange as a product of the sea-air concentration difference and a transfer velocity,  $k$  [e.g., Wanninkhof, 1992; Nightingale *et al.*, 2000; Liss and Merlivat, 1986].

[3] We recently reported success in direct measurements of the DMS sea-air flux by eddy covariance from ship platforms [Huebert *et al.*, 2004]. Exchange velocities are

derived from observations by dividing the flux by the interfacial DMS concentration difference. The apparent discrepancy between these observations and existing wind speed-dependent parameterizations motivates us to explore a more complex, physically-based model of sea-air DMS exchange. Our goals in this investigation are both improving flux estimation methods for DMS and, at a more fundamental level, understanding how differences in trace gas properties not accounted for in simple wind speed-based flux models may affect the transfer velocity.

## 2. NOAA/COARE Gas Transfer Model

[4] The flux,  $F_x$ , of trace gases between the atmosphere and ocean is characterized by a simple parameterization of the form

$$F_x = \overline{w'x'} = \alpha_x k_x (X_{wr}/\alpha_x - X_{ar}) \quad (1)$$

where the flux is by definition the mean covariance of vertical velocity fluctuations ( $w'$ ) with turbulent fluctuations of gas concentration ( $x'$ );  $\alpha_x$  is the dimensionless solubility of the gas in seawater;  $X_{wr}$  the mean concentration of the gas at some reference depth ( $z_{wr}$ ) in the ocean;  $X_{ar}$  the mean concentration of the gas at some reference height in the atmosphere; and  $k_x$  the transfer velocity. Historically,  $k_x$  has been determined experimentally; a simple wind speed dependence has often been used to describe its environmental variations [e.g., Wanninkhof, 1992].

[5] Interest in developing a more general form has led to the application of physically-based models derived from both surface renewal and turbulent-molecular diffusion theory near the air-sea interface [Soloviev and Schluessel, 1994; Fairall *et al.*, 2000]. While differing somewhat in the weighting of details, the two approaches lead to rather similar results [Fairall *et al.*, 2000, Figures 2 and 3]. Both methods assume horizontal homogeneity in a statistical sense; that is, the patchiness of the near surface layer can be dealt with statistically by averaging. Following Fairall *et al.* [2000], a transfer velocity on each side of the interface can be computed.

$$V_{ix}^{-1} = \int_0^{z_r} [K_i(z) + D_{ix}]^{-1} dz \quad (2)$$

where  $K(z)$  is the turbulent eddy diffusivity,  $D_x$  the molecular diffusivity, and subscripts  $i$  and  $x$  refer to the phase (air or water) and trace gas respectively. The total transfer velocity is given by

$$k_x = [V_{wx}^{-1} + \alpha_x V_{ax}^{-1}]^{-1} \quad (3)$$

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From surface-layer similarity theory  $K(z) \approx Kz u_*$  where  $\kappa$  is the von Karman constant ( $\kappa = 0.4$ ) and  $u_*$  the friction velocity in the fluid (air or water). Because small-scale turbulence is suppressed by dissipation, there is a region near the interface ( $z_r < \delta_{ui}$ ) where transport is dominated by molecular diffusion. The integral can be approximated as

$$V_{ix}^{-1} = \frac{1}{u_{*i}} \left[ \frac{\ln(z_{ri}/\delta_{ui})}{\kappa} + h_i S_{ci}^{1/2} \right] \quad (4)$$

where  $S_c$  is the Schmidt number for the gas in the fluid, and  $h$  is a coefficient of the molecular diffusion sublayer.

[6] *Fairall et al.* 1996a used this approach to describe the transfer of heat in the cool skin on the ocean for the TOGA COARE bulk flux model [*Fairall et al.*, 1996b, 2003] and [*Fairall et al.*, 2000] adapted it for the NOAA/COARE gas transfer model. The final version of the model [*Hare et al.*, 2004] uses

$$u_{*a} V_{ax}^{-1} = \left[ h_a S_{ca}^{1/2} + C_d^{-1/2} - 5 + \ln(S_{ca})/(2\kappa) \right] \quad (5a)$$

$$u_{*a} V_{wx}^{-1} = \sqrt{\rho_w/\rho_a} \left[ h_w S_{cw}^{1/2} + \ln(z_{wr}/\delta_{iw})/\kappa \right] \quad (5b)$$

where  $C_d$  is the atmospheric velocity drag coefficient. The factor of the ratio of density of water to air in (5b) follows from assuming the momentum flux is the same on both sides of the interface. *Hare et al.* [2004] defined

$$h_w = \frac{\Lambda}{A\varphi} \quad (6)$$

where  $\Lambda = 13.3$ ,  $\varphi$  is an empirical function to account for buoyancy-driven transfer at low wind speeds [see *Fairall et al.*, 2000], and  $A$  is a factor that is adjusted to fit measured gas transfer velocities. *Soloviev and Schluessel* [1994] suggested  $A = 1.85$  for  $\text{CO}_2$ .

[7] The final complication is accounting for bubble-mediated gas transfer in the ocean. In the NOAA/COARE model, a parameterization from *Woolf* [1997] is used

$$k_x = \left[ (V_{wx} + k_b)^{-1} + \alpha_x V_{ax}^{-1} \right]^{-1} \quad (7)$$

where  $k_b$  describes the enhancement of transfer associated with plumes of whitecap-generated bubbles

$$k_b = B V_o f \alpha_x^{-1} \left[ 1 + \left( e \alpha_x S_{cw}^{1/2} \right)^{-1/n} \right]^{-n} \quad (8)$$

Here  $f$  is the whitecap fraction, a strong function of 10 m wind speed,  $U_{10}$  [*Monahan and O'Muircheartaigh*, 1980].

$$f = 3.84 \times 10^{-6} U_{10}^{3.41} \quad (9)$$

*Woolf* [1997] gives the values  $V_o = 6.8 \times 10^{-3} \text{ m s}^{-1} = 2450 \text{ cm h}^{-1}$ ,  $e = 14$ ,  $n = 1.2$  for  $\text{CO}_2$ ; we have added the factor  $B$  which is adjusted to fit measured transfer velocities.

[8] The NOAA/COARE gas flux parameterization is principally contained in (7), with (5) and (8) representing the details. To apply the parameterization to DMS we have specified solubility and Schmidt number following *Saltzman et al.* [1993]. Due to increased solubility, the ratio

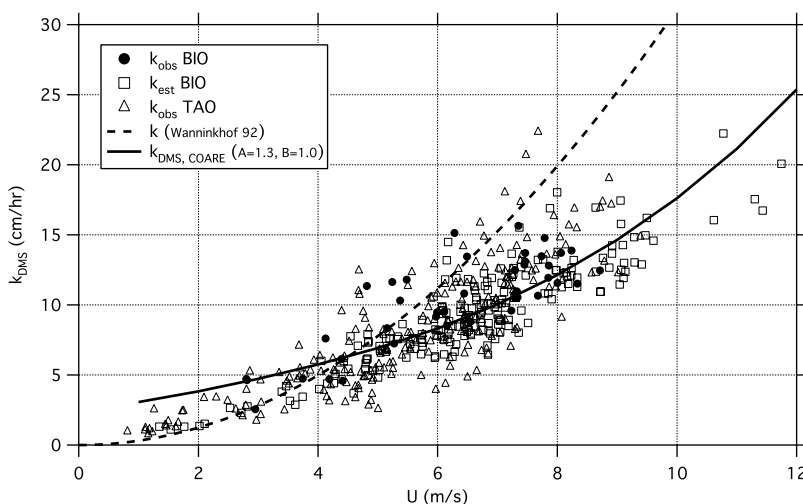
of air side resistance to water side resistance for DMS is about 0.05 versus 0.005 for  $\text{CO}_2$ . There are two adjustable factors:  $A$  for the molecular sublayer transport and  $B$  for the bubble-mediated transport. *Hare et al.* [2004] optimized the fit of the parameterization to the GasEx-1998  $\text{CO}_2$  flux measurements [*McGillis et al.*, 2001a, 2001b]. The GasEx-1998 values ( $A = 0.63$  and  $B = 2.0$ ) are certainly different from the original references ( $A = 1.85$  and  $B = 1.0$ ). For GasEx-2001 [*McGillis et al.*, 2004] the fit to the measured  $\text{CO}_2$  fluxes yields  $A = 1.3$  and  $B = 0.82$ , although the limited wind speed range of the GasEx-2001 data do not constrain the value of  $B$  very well. The difference in the 1998 and 2001 results for  $\text{CO}_2$  is striking but, given the exploratory nature of the measurements and theory, the significance is unclear and several factors may be involved. The difference could be the result of (for example) surfactants or perhaps a measurement problem (see the extensive discussion by *Hare et al.* [2004]). *Woolf* [2005] recently discussed the dependence of whitecap fraction on sea-state, and it is likely some of the variability in  $B$  accounts for error inherent in the calculation of  $f$  by wind speed alone (9), ignoring the influence of fetch, currents, and ocean depth on whitecap development.

### 3. DMS Flux Measurements

[9] The development of a mass spectrometric method for fast atmospheric DMS measurement [*Bandy et al.*, 2002], and correction algorithms for high frequency wind measurement on ship platforms [*Edson et al.*, 1998], have enabled us to deploy a DMS eddy covariance flux system on two recent research cruises. Results from the November 2003 TAO cruise on the NOAA Ship *Ronald H. Brown* were reported previously [*Huebert et al.*, 2004]. More recently, we participated on the summer 2004 Biocomplexity cruise (hereinafter BIO cruise) to the Sargasso Sea on the R/V *Seward Johnson*.

[10] A principal objective of the summer 2004 BIO cruise was a Lagrangian study of DMS production and loss in the mixed layer of persistent, large-scale eddies, commonly observed south of Bermuda. In two successive intensive experiments, drogues were deployed in anticyclonic and cyclonic eddies and followed over several days. Daily 8 AM GMT (4 AM local) hydrocasts provide a profile of DMS concentrations and physical variables, and describe the evolution of these properties over the course of the study. As a result of the Lagrangian experimental design, surface DMS concentrations exhibited little variability (at 3 m depth:  $\mu_{DMS} = 2.64 \text{ nM}$ ;  $\sigma_{DMS} = 0.41 \text{ nM}$ ). During the two intensives, DMS concentrations in the upper 10 m were essentially constant. Although a slight gradient between 3 and 10 m is discernible in the mean profiles for both eddies, it is statistically insignificant.

[11] Continuous 20 Hz mass spectral data, wind, and motion measurements were processed in hourly blocks to obtain corrected winds and atmospheric DMS mixing ratios. Fluxes were computed for overlapping 10 minute intervals by integration of DMS-vertical wind velocity ( $W$ ) cospectra and averaged to obtain hourly flux estimates. Flow distortion caused by the ship superstructure (typically a  $6^\circ$  elevation angle) is apparent in the mean winds over a broad sector of relative wind direction. A streamline rotation corrects this distortion, but when winds are clearly out-of-sector (i.e., from the stern quadrant), or when the



**Figure 1.** Observed DMS transfer velocities and model estimates. Concurrent sea water DMS measurements were not available for all hours on the BIO cruise, so values  $k_{est}$  are determined from project-mean sea water DMS concentration. Wanninkhof 92 is computed using a Schmidt number appropriate for mean BIO cruise sea water temperature and salinity ( $Sc = 655$ ).

ship is turning, severe variability in mean  $W$ , increased flow distortion, distortion of the  $W$ :DMS cospectrum, and significant signal in the  $W$ :DMS quadrature spectrum are often apparent. Subjective analysis determined the following statistical criteria are sufficient to filter out grossly corrupted flux measurements: mean relative wind direction  $\pm 120^\circ$ ; standard deviation in relative wind  $< 25^\circ$ ; mean tilt angle (from the streamline distortion correction) between  $4^\circ$  and  $10^\circ$ ; and standard deviation in vertical wind velocity  $< 0.6$  m/s.

[12] For the 3 hour period bracketing each hydrocast, DMS transfer velocities,  $k_{DMS}$ , are computed by dividing the observed flux by the 3 m sea water concentration. For other times, when no concurrent sea water DMS measurements were available,  $k_{DMS}$  is estimated by dividing the observed flux by the mean DMS concentration from all surface hydrocasts (2.64 nM @ 3 m).

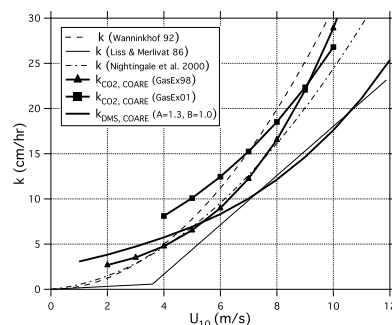
#### 4. DMS Transfer Velocity

[13] The COARE gas transfer algorithm computes  $k_{DMS}$  from basic meteorological observations, sea surface temperature, and bulk heat and momentum fluxes derived from the COARE bulk flux model. Model results and DMS transfer velocity observations are shown in Figure 1. For this figure, model exchange velocities were computed using BIO cruise project-mean meteorological data over a range of wind speeds, and thus represent a  $k$  vs.  $U$  relationship for mean BIO cruise experimental conditions. Fortunately, conditions did not vary greatly over the course of the two intensives. Exchange velocity observations from the BIO cruise are distinguished as either  $k_{obs}$  or  $k_{est}$ , depending on whether they are derived from coincident sea water DMS measurements or the project-mean DMS concentration, as explained above. Data from the TAO cruise are also shown and generally fall along the same curve.

[14] Minimal adjustments to the parameters are sufficient to obtain a subjective fit to the observations. Setting parameter  $A$  to the value from GasEx-2001 ( $A = 1.3$ ) and leaving  $B$  at the default ( $B = 1$ ) achieves a very reasonable

result (Figure 1). Because DMS has a higher solubility than  $CO_2$ , bubble-mediated transfer is much weaker and parameter  $A$  is dominant in the wind speed range of these data. There are hints in Figure 1 that observed values of  $k_{DMS}$  fall below the parameterization at low wind speeds, although the number of data points is limited. This could be eliminated by reducing  $A$ , but as a consequence the parameterization will underestimate  $k$  at higher wind speeds.

[15] At this point in the development of theory and measurements, it does not seem appropriate to attempt an optimization of  $A$  and  $B$  without more data. Differences between the model and observations at low wind speed may result from imperfections in the model, or alternately as an artifact of using 3 m DMS concentration as an estimate of surface DMS concentration, or both. It seems certain that at low wind speeds, when mixing is reduced, a significant concentration gradient could develop in the upper few meters, especially during the day when both gas exchange and photochemical destruction remove DMS from the surface layer. Reducing sea water DMS concentration from 2.6 to 1.6 nM is sufficient to bring low wind speed data into substantial agreement with the model. This question will



**Figure 2.** A comparison of various models for the exchange velocity,  $k$ , of trace gases. The NOAA/COARE parameterizations for DMS (this work) and for GasEx  $CO_2$  are shown. Other models are calculated using a Schmidt number appropriate to BIO cruise conditions ( $Sc = 655$ ).



only be resolved by near-surface sampling for dissolved DMS on future cruises, especially during light winds.

## 5. Conclusions

[16] Figure 2 presents a comparison of the NOAA/COARE parameterization for DMS with three well known gas transfer models. Also shown are the COARE algorithm-derived transfer velocities for CO<sub>2</sub> based on results from the GasEx-1998 and -2001 cruises. The parameterizations of Wanninkhof [1992] and Nightingale *et al.* [2000] postulate a quadratic dependence on  $U$ , with adjustments to the Schmidt number ( $Sc$ ) accounting for the molecular diffusivity the trace gas, yielding a rather steep dependence on wind speed. Adjustments to  $Sc$  tend to move the  $k$  vs.  $U$  curve up or down, but do not change the slope of the curve. These models therefore cannot explain the observed wind speed dependence of  $k_{DMS}$ . The Liss and Merlivat model is closer to observed  $k_{DMS}$  at moderate wind speeds, but fails to predict significant flux at low wind speeds, and is quite far from GasEx results for CO<sub>2</sub>.

[17] The best power-law fit to observed  $k_{DMS}$  is  $U^{1.3}$ , a much flatter curve than the quadratic dependence of most models. This apparently results from the greater solubility of DMS compared to CO<sub>2</sub> or in-situ tracers such as SF<sub>6</sub>, reducing the impact of bubbles on the exchange velocity. While parameters are necessary to achieve a reasonable fit (it is not yet possible to accurately describe bubble fields and evolution from first principles), the reduced dependence of  $k_{DMS}$  on breaking waves in the NOAA/COARE model arises directly from consideration of the Bunsen solubility of the trace gas.

[18] The interpretation of the parameters  $A$  and  $B$  remains somewhat uncertain, but two features of the NOAA/COARE model are notable: the cool skin parameterization prevents estimated values of  $k$  from approaching zero at low wind speeds, and the dependence on gas solubility correctly reproduces differences between the observed values of  $k$  for CO<sub>2</sub> and DMS. Woolf [1993] predicted that as trace gas solubility increases, wind speed dependence of  $k$  becomes less strong. Figure 6 of Woolf [1993] presents estimates of  $k$  vs.  $U$  for CO<sub>2</sub> and a hypothetical gas “X” with the solubility of DMS. The trend in his predicted values of  $k$  corresponds to our observations that the wind speed dependence of  $k_{DMS}$  is less than that of  $k_{CO_2}$ . Inclusion of the Woolf parameterization for bubble-mediated transfer velocity in the NOAA/COARE model thus yields better agreement with observations than parameterizations based solely on Schmidt number and a power of  $U$ .

[19] Direct flux measurements have shown simple exchange velocity formulations are not flexible enough to describe the behavior of both DMS and CO<sub>2</sub>. Models based on a quadratic fit to tracer or radiocarbon data overestimate DMS flux at high wind speeds and underestimate the flux as wind speed approaches zero. Since the impact of bubbles depends strongly on the solubility of each specific trace gas, more accurate sea-air exchange predictions will be derived from models that account for this effect.

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