

DMS Sea-Air Transfer Velocity: Direct Measurements by Eddy Covariance and Parameterization Based on the NOAA/COARE Gas Transfer Model

B. W. Blomquist

B. J. Huebert

Department of Oceanography University of Hawaii, Honolulu, Hawaii, USA

C. W. Fairall

Physical Science Division, NOAA Earth System Research Laboratory,

Boulder, Colorado, USA

D. J. Kieber

Chemistry Department, College of Environmental Science and Forestry,

State University of New York, Syracuse, New York, USA

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 CO₂ 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 *Wolf* [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.

B. W. Blomquist, B. J. Huebert, Department of Oceanography, University of Hawaii, 1000 Pope Rd., Honolulu, HI 96822, USA. (blomquis@hawaii.edu, huebert@hawaii.edu)

C. W. Fairall, Physical Science Division NOAA Earth System Research Laboratory 325 Broadway, Boulder, CO 80305-3328, USA. (Chris.Fairall@noaa.gov)

D. J. Kieber, Chemistry Department, College of Environmental Science and Forestry, State University of New York, 1 Forestry Dr., Syracuse, NY 13210, USA. (djkieber@mailbox.syr.edu)

1. Introduction

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 principle 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 (eg. *Wanninkhof* [1992]; *Nightingale et al.* [2000]; *Liss and Merlivat* [1986]).

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 Parameterization

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'); α_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]).

Interest in developing a more general form has led to the application of physically-based models derived from turbulent-molecular diffusion theory near the air-sea interface (*Soloviev and Schluessel* [1994]; *Fairall et al.* [2000]). From this theory a transfer velocity on each side of the interface can be computed (*Fairall et al.* [2000]).

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

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

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

From surface-layer similarity theory $K(z) \approx \kappa z u_*$ where κ 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 ($z_r < \delta_u$) 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.

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

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

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

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 $\Lambda = 13.3$, φ is an empirical function to account for buoyancy-driven transfer at low wind speeds, and A is a factor that is adjusted to fit measured gas transfer velocities.

Soloviev and Schluessel [1994] suggested $A = 1.85$ for CO_2 .

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

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

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

$$k_b = B V_0 f \alpha_x^{-1} \left[1 + (e \alpha_x S_{cw}^{1/2})^{-1/n} \right]^{-n} \quad (8)$$

Here f is the whitecap fraction (a strong function of wind speed). *Wolf* [1997] gives the values $V_0 = 6.8 \times 10^{-3} \text{ m s}^{-1} = 2450 \text{ cm h}^{-1}$, $e = 14$, $n = 1.2$ for CO_2 ; we have added the factor B which is adjusted to fit measured transfer velocities.

The NOAA/COARE gas flux parameterization is principally contained in (7), with (5) and (8) representing the details. 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 CO_2 flux measurements (*McGillis et al.* [2001a, b]). 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 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 CO_2 is puzzling but, given the exploratory nature of the measurements and theory, the significance is unclear. The difference could be the result of (for example) surfactants or perhaps a measurement problem (see the extensive discussion in *Hare et al.* [2004]). To apply the parameterization to DMS we have specified solubility and Schmidt number following *Saltzman et al.* [1993].

3. DMS Flux Measurements

The development of the Atmospheric Pressure Ionization Mass Spectrometer–Isotopically Labeled Standard method (APIMS–ILS) for fast atmospheric DMS measure-

ment (*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*.

A principle objective of the summer 2004 BIO cruise was a Lagrangian study of DMS production 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 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 over the course of the study (at 3 m depth: $\mu_{DMS} = 2.64$; $\sigma_{DMS} = 0.41$ nM). Figure 1 illustrates that during the two intensives, DMS concentrations in the upper 10 m were essentially constant. Although some hint of a slight gradient in the upper 10 m is visible in the mean profiles for both eddies, it is statistically insignificant.

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 W:DMS cospectra and averaged to obtain hourly flux estimates. Statistical criteria were used to eliminate flux data for hours where conditions were not optimal (Table 1).

For the 3 hour period bracketing each hydrocast, we calculate the DMS transfer velocity, k_{DMS} , by dividing the observed flux by the measured sea water concentration. For all other hours during the day, we estimate k_{DMS} by dividing the observed flux by the project mean DMS concentration (2.64 nM @ 3 m).

4. DMS Transfer Velocity

DMS transfer velocities for both TAO and BIO cruises are shown in Figure 2 along with the NOAA/COARE parameterization for k_{DMS} using BIO cruise project-mean meteorological data for model input. Data 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. Figure 3 shows residual differences between all BIO cruise k_{DMS} results and COARE model results calculated from hourly in-situ meteorological data.

A fairly good fit to the DMS data is $A = 1.3$ and $B = 1.0$, but a least squares optimization was not attempted. 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 Figures 2 and 3 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. This distortion cannot be corrected by increasing B unless one is willing to make dramatic increases to B . It is possible that deviation from the model predicted values at low wind speed is an artifact of using 3 m DMS concentration as an estimate of surface DMS concentration. At low wind speeds, when mixing is reduced,

a significant concentration gradient may exist in the upper few meters, especially during the day when both gas exchange and photochemical destruction remove DMS from the surface layer. This situation can only be remedied by near-surface sampling for dissolved DMS on future cruises, especially during light winds.

5. Conclusions

Figure 4 presents a comparison of the NOAA/COARE parameterization for DMS with three other well known gas transfer models. Also shown are the COARE algorithm-derived transfer velocities for CO₂ based on results from the 1998 and 2001 GasEx cruises. The parameterizations of *Wanninkhof* [1992] and *Nightingale et al.* [2000] use a quadratic function of U , with adjustments to the Schmidt number (Sc) accounting for the molecular diffusivity of each gas in sea water. This results in 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 shape of the curve. These models therefore fail to 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 CO₂.

The best power-law fit to observed k_{DMS} is $U^{1.3}$, a much flatter curve than the quadratic dependence of other models. This apparently results from the higher solubility of DMS compared to CO₂ or tracers such as SF₆, which reduces 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 life cycles from first principles), the

reduced impact of bubbles on k_{DMS} in the NOAA/COARE model arises directly from considering the Bunsen solubility of the trace gas.

While the interpretation of the parameters A and B remains uncertain, 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 appears to reproduce differences between the observed values of k for CO_2 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_2 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 .

Direct flux measurements have shown simple exchange velocity formulations are not flexible enough to describe the behavior of both DMS and CO_2 . Models based on a quadratic fit to tracer or radiocarbon data overestimate DMS flux at high wind speeds. Since the impact of bubbles depends strongly on the solubility of each specific trace gas, increasingly accurate sea-air exchange predictions will be derived from models that include this effect.

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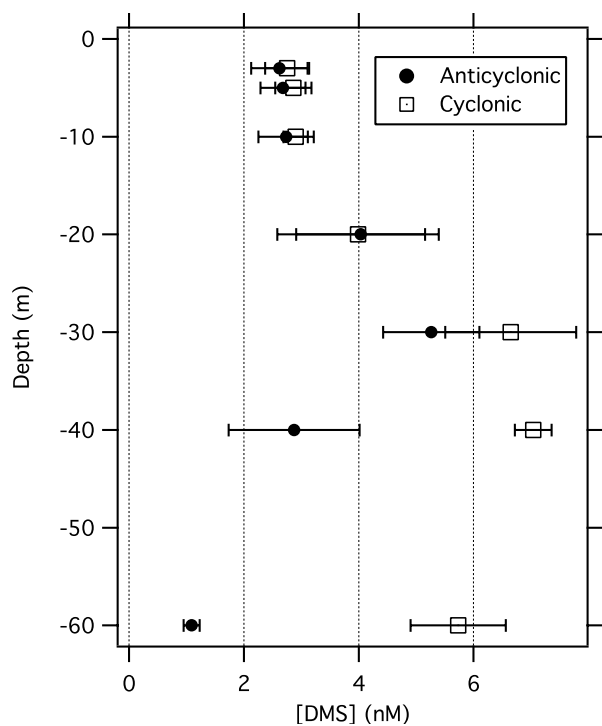


Figure 1. Sea water DMS depth profiles from the two eddies studied during the 2004 BIO cruise. Data are means from profiles collected over several days. For 3–10 m depths, $n = 14$ (cyclonic) and $n = 24$ (anticyclonic).

Table 1. Selection Criteria for DMS Flux Data^a

Metric	Criteria
$\mu_{WindDir}$ ^b	$\pm 120^\circ$
$\sigma_{WindDir}$	$< 25^\circ$
Tilt Correction ^c	$4^\circ < \beta < 10^\circ$
σ_w	$< 0.6 \text{ m/s}$

^a Based on hourly wind statistics.

^b Relative to ship's bow.

^c Elevation angle from streamline distortion correction.

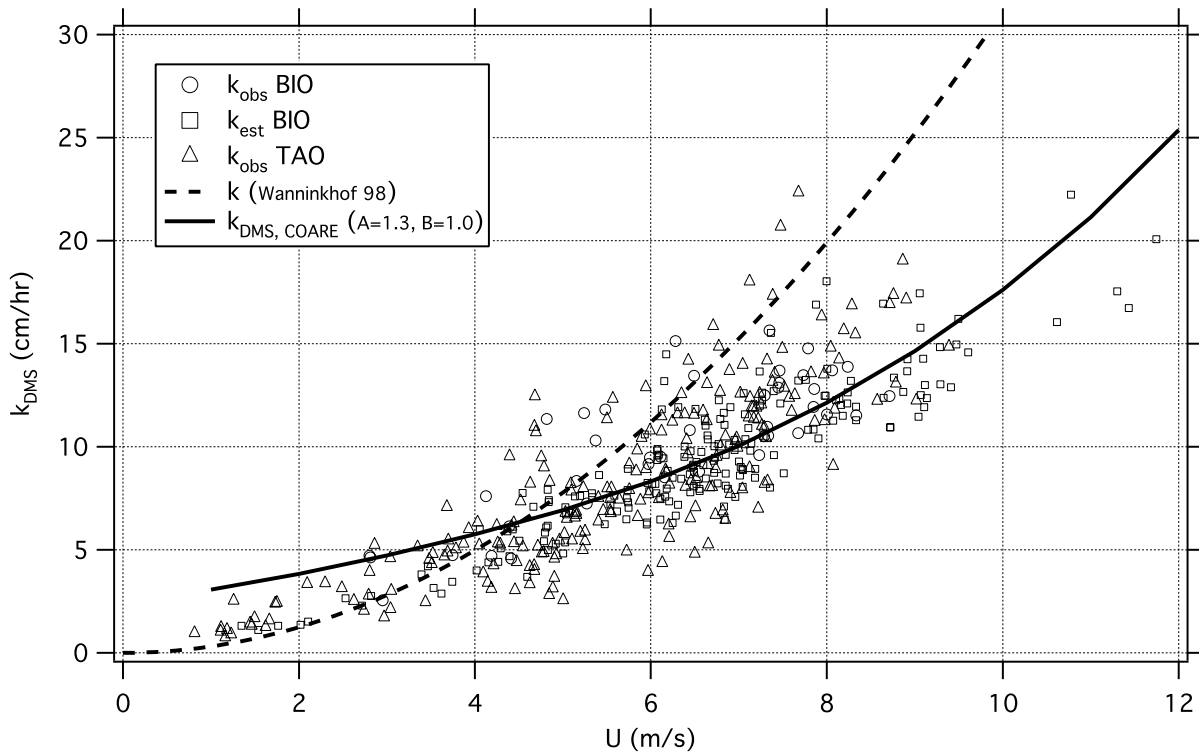


Figure 2. Observed DMS transfer velocities and model estimates. Values k_{est} from the BIO cruise are estimated using project mean sea water DMS concentration. The COARE model curve is calculated using mean meteorological data for the entire cruise.

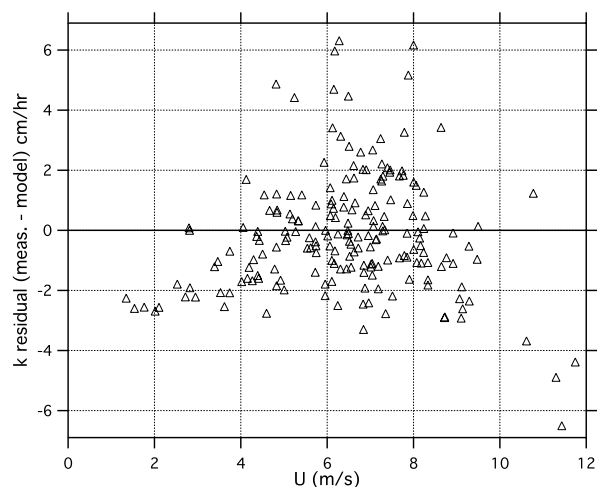


Figure 3. Residual differences between BIO cruise observed and estimated values of k_{DMS} and NOAA/COARE gas transfer model estimated k_{DMS} . Hourly average in-situ meteorological data were used for model input.

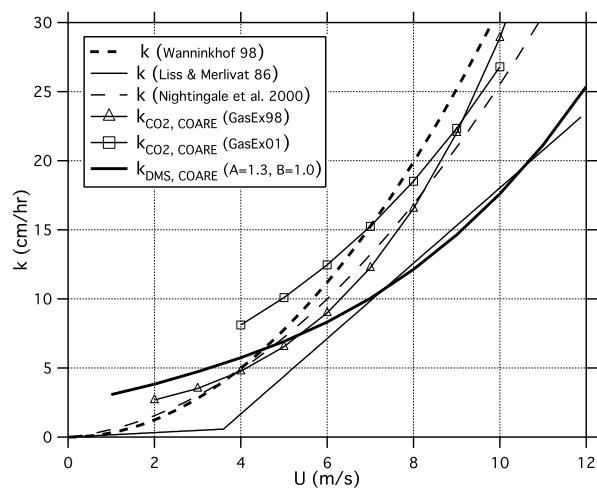


Figure 4. A comparison of various models for the exchange velocity, k , of trace gases. Optimizations for both CO_2 and DMS are shown for the NOAA/COARE parameterization.