

Measurement of the sea-air DMS flux and transfer velocity using eddy correlation

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[1] We report the successful eddy-correlation (EC) measurement of dimethyl sulfide (DMS) fluxes using an atmospheric pressure ionization mass spectrometer (APIMS). Calculated hourly transfer velocities span the range of two widely used parameterizations. The results suggest that factors in addition to wind speed also control the flux, but some of the scatter in each wind speed interval is no doubt due to measurement uncertainties. We can at last measure the flux of a marine biogenic gas on a time scale of tens of minutes, with an accuracy of tens of percent. This enables investigations into the physical controls of air-sea gas transfer common to many important trace gas species.

INDEX TERMS: 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0394 Atmospheric Composition and Structure: Instruments and techniques; 1615 Global Change: Biogeochemical processes (4805); 4504 Oceanography: Physical: Air/sea interactions (0312).
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[2] The ocean is a net source (e.g., DMS, CO, CH₄) and sink (e.g., CO₂, CFCs) of many radiatively and chemically important trace gases. Air/sea fluxes of these gases are commonly expressed as a product of the air/water concentration difference and a transfer velocity, k . *Liss and Merlivat* [1986] (hereinafter LM86), *Wanninkhof* [1992] (hereinafter W92), and others have parameterized k as a function of wind speed only. However, the scatter in tracer-loss experiments reported by *Nightingale et al.* [2000] (hereinafter N2000) suggests other factors are at least as important as wind velocity in determining k . Prior air-sea exchange studies have been limited to long timescales (days to years) by the averaging requirements of budget-type flux methods. As a consequence, studies of this type do not observe the effects of factors that vary over shorter timescales of an hour or less. Thus, the potential impact of other physical factors such as bubble and wave spectra, wave

slope, wind speed variability, and surface films have been unconstrained by observations.

[3] The most direct technique for measuring gas fluxes is eddy-correlation [*Fairall et al.*, 2000], since it utilizes the covariance of scalar concentrations (or mixing ratios) and vertical wind velocity. EC requires measurements at a sufficient rate (10–20 Hz) to adequately capture all turbulence frequencies contributing to the flux. On moving platforms, apparent wind velocities must be corrected both for flow distortion by the platform and for contamination of measured wind velocity by platform motion. *Lenschow et al.* [1981] made airborne EC measurements of the marine ozone flux in 1981. Since then, several groups [*Oost*, 1998; *McGillis et al.*, 2001] have demonstrated the ability to measure CO₂ fluxes from ships by EC, but the method is only applicable to those regions of the ocean surface with a combination of strong winds and relatively high air-sea concentration gradients (about a third of the world's oceans). Until now there have been few demonstrations of other suitably fast analytical instruments.

[4] *Bandy et al.* [2002] recently developed the APIMS isotopically labeled standard (APIMS-ILS) technique for DMS and demonstrated its utility for measuring DMS fluxes from aircraft [*Stevens et al.*, 2003]. With this method ionization of DMS is only efficient when ambient air is dried and heated. A Nafion[®] membrane air drier is therefore used in marine environments to precondition the sample air. A high concentration (1 ppbv) of triply-deuterated (d₃) DMS is continuously added to the ambient air at the sample inlet. In addition to providing an internal standard, the d₃ DMS isotopomer occupies adsorption sites in the transfer tubing and drier, reducing retention of the ambient DMS isotopomer and improving frequency response. Determination of the ambient DMS mixing ratio is not based on the intensity of the ambient DMS signal but rather on the ratio of ambient DMS to internal standard DMS signals. Thus, changes in sensitivity do not affect the accuracy of the measurement, although they can increase noise and degrade the detection limit. Because the method measures mixing ratio rather than mass concentration, density fluctuations caused by temperature and humidity [*Webb et al.*, 1980] do not affect the measured DMS flux.

[5] The biogeochemical interest in DMS is largely because sulfate from DMS influences the optical properties of marine clouds [*Charlson et al.*, 1987]. DMS is formed from dimethyl sulfonylpropionate, an osmolyte that is released when certain phytoplankton cells are ruptured [*Bates et al.*, 1994]. The concentration of DMS is highly supersaturated in sea water: a typical 2 nM DMS_{sw} concentration would have 13,000 pptv of DMS in the air above it at equilibrium, two orders of magnitude higher than the

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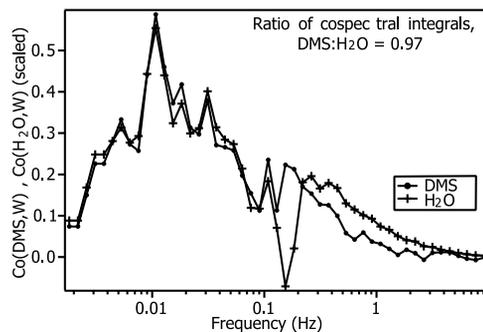


Figure 1. Three-hour averages of 10 minute power spectra for water vapor and DMS fluxes on 1 Nov. The dip in the water cospectrum at 0.2 Hz (due to the separation of the sensors) has been left uncorrected for this illustration.

~150 pptv of atmospheric DMS we encountered. Thus the air concentration has little or no influence on the emission of DMS. The atmospheric lifetime of DMS is limited to a day or so by the oxidation of DMS to SO₂, sulfate, and methanesulfonic acid in the marine boundary layer.

[6] We report here on DMS flux measurements from the NOAA Ship Ronald H. Brown, during a cruise to service TAO buoys in the eastern Equatorial Pacific (95 to 110 W and -7.5 to 7.5 N) in November of 2003. Wind velocity, platform motion, water vapor, and CO₂ measurements on these annual cruises [Cronin *et al.*, 2002] are made from the Brown's forward jackstaff, mostly while steaming. The APIMS-ILS was located in a laboratory van on the foredeck, just behind the jackstaff. We conveyed sample air through 24 m of 1.27 cm ID Teflon tubing at 120 l/min to the APIMS-ILS, where it was subsampled into the drier at 4 l/min. Although turbulent flow helped preserve high frequency variability during the 1.3 sec transit, the Nafion driers slight tendency to adsorb DMS limited the half-power response frequency to 1–2 Hz, based on laboratory measurements.

[7] On a ship, ambient wind velocity measurements are challenging. We measured wind velocity on 3 axes with a Gill sonic anemometer, located about 1 m above the DMS inlet on the jackstaff, 18 m above the sea surface. Linear acceleration and angular rotation rate were determined at the same frequency as DMS and wind velocity (20 Hz) using a triaxial set of accelerometers and angular rate sensors and subtracted from the apparent winds. Motion channels were low pass filtered at 5 Hz to eliminate mast vibration artifacts. Wind measurement methods and motion corrections have been described by Edson *et al.* [1998].

[8] From experience with CO₂ and latent heat flux measurements on this platform, 1–2 Hz response is adequate to capture almost all of the flux at 18 m above the surface. When we compare the normalized cospectra of DMS and water vapor (which ought to have similar shapes) during a 3 hour interval with relatively constant 6 m/s winds (Figure 1), we see some loss of DMS power in the 0.3–3 Hz range. Integrating both cospectra suggests that we captured 97% of the DMS flux. (This drops to 92% if we remove the 0.2 Hz dip in the water vapor cospectrum.) Thus our frequency response enabled us to capture over 90% of the DMS flux at 6 m/s wind speed. This may decrease slightly at higher wind speeds.

[9] Scalar fluxes from ships tend to be fairly insensitive to motion correction errors [Fairall *et al.*, 2000, 2003; McGillis *et al.*, 2001]. DMS fluxes should be more robust than those of CO₂, because the DMS sea/air concentration difference is large relative to the air concentration. Thus atmospheric DMS varies by tens of percent, while CO₂ fluctuations are only a fraction of a percent of the air concentration; the turbulent DMS fluctuations are therefore easier to measure accurately. In discussing the error in a single covariance flux measurement, we draw a distinction between actual biases or proportional errors in the sensors or the measurement process versus statistical sampling error associated with estimating a large scale variable from a point measurement in a finite time interval [see McGillis *et al.*, 2001, section 3]. The effects of sampling error on a mean estimate are reduced by increasing the sampling time or averaging an ensemble of independent samples. For our 1-hr measurements, sampling error tends to dominate the uncertainty of covariance flux measurements. Edson *et al.* [1998] quantified the error in scalar flux computations from ship data and found it to be 10–15% under most conditions at sea, which is comparable to land-based covariance measurements. For CO₂ flux, Fairall *et al.* [2000] found the sampling error for 30-min. fluxes to be on the order of 100%, reflecting the much weaker correlation versus noise characteristics of CO₂ over the ocean. We believe that 15–20% is a reasonable overall uncertainty for our 1-hr mean DMS fluxes.

[10] The observed DMS fluxes varied on timescales as short as 10 minutes (Figure 2), often in concert with wind speed variations, but the correlation was not perfect. This suggests that wind and seawater DMS concentration (DMS_{sw}) are not the only factors controlling the flux. We did not observe a day/night difference in fluxes like that reported for Gas Ex 2001 [McGillis *et al.*, 2004]. The nighttime flux mean was about 4% larger than the daytime mean, far less than the 10% standard errors of these means. This is consistent with the fact that the nighttime mean DMS_{sw} was about 7% larger, while the wind speed was 3% smaller.

[11] We divided the hourly-averaged flux measurements by the average of DMS_{sw} at the beginning, middle, and end of each hour to derive k for DMS. DMS_{sw} was measured each half hour by the purge-and-trap method with an

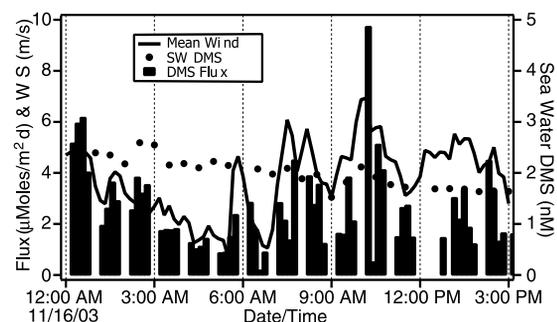


Figure 2. Seawater DMS, wind speed, and DMS flux (10 minute averages) on 16 Nov. at 8 N 101 W. The flux often responded very rapidly to changes in wind, but wind speed was clearly not the only controlling factor. Neutral 10 m wind speeds would be about 5% smaller than these 18 m winds.

automated gas chromatograph [Bates *et al.*, 2000]. The timescale of calculated transfer velocities is thus limited by the frequency of seawater measurements rather than flux data. Bates *et al.* [1987] found no measurable difference in DMS_{sw} due to sampling procedure or depth in the upper 5 m of the water column. Based on the variability during each hour and measured precision, we estimate the total uncertainty in DMS_{sw} to be about 10%.

[12] Hourly-average transfer velocities are plotted against average wind speed (WS) in Figure 3, alongside the LM86 and W92 parameterizations. Error bars represent combined uncertainty due to the flux (covariance) calculation (from equation (69) of Fairall *et al.* [2000]), the DMS_{sw} uncertainty, and atmospheric DMS uncertainty (5%). The resulting average total uncertainty in k is $\pm 15\%$. Unfortunately, adding the wind speed standard deviation as an x-axis error bar makes this plot unreadable; for most points above the W92 line the wind speed standard deviation bar intersects the W92 line. The scatter in the data looks very similar when transfer velocities are plotted against friction velocity (not shown).

[13] Binned by wind speed and averaged over 1 m/s intervals (Figure 4), our measured transfer velocities lie only slightly above the LM86 line, similar to the conclusions of N2000. Results at WS < 3 m/s generally lie above both models. The drop in k above 9 m/s may be due to the paucity of data in that range. The relative standard deviation of the mean k was between 15 and 40% in each range, reflecting a combination of both measurement uncertainties and non-wind factors' influence on transfer velocities. The range of transfer velocities for any one wind speed is comparable to the difference between LM86 and W92.

[14] It is instructive to compare our results with the GasEx-2001 [McGillis *et al.*, 2004] field program, a comprehensive study of trace gas and conventional heat/moisture transfers in the Equatorial Pacific to the West of our DMS study region. The transfer of CO₂ was investigated with direct covariance and profile methods. The CO₂ transfer velocity dependence was examined by Hare *et al.* [2004] by comparing average values with the NOAA/COARE parameterization, which had been previously tuned to the GasEx-1998 direct covariance results. The 2001 CO₂ transfer velocities exhibited a weaker wind speed dependence than the 1998 values, with 30% higher

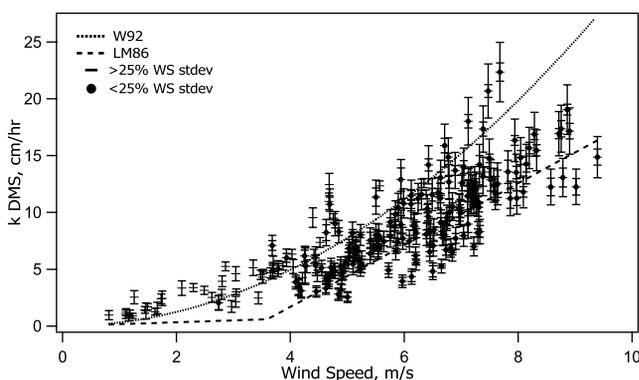


Figure 3. Measured exchange velocities vs wind speed, with the LM86 and W92 model values. Points without a dot had wind variability in excess of 25% of the mean. Error bars are the total uncertainty.

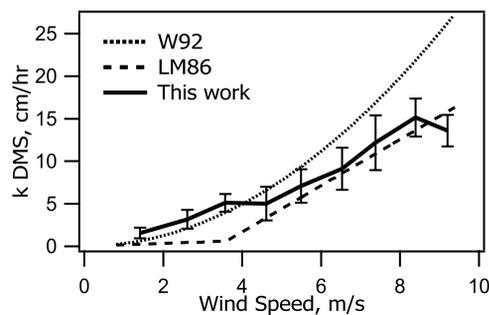


Figure 4. Average transfer velocities, binned in 1 m/s intervals of wind speed. Error bars are one standard deviation.

values at low wind speeds. The enhanced results for low wind speed were consistent with surfactant measurements that show essentially no surfactants in 2001. Our DMS results indicate a weaker wind-speed dependence than the COARE parameterization and the W92 relationship. It is not yet clear whether this difference is real, which would suggest differences in DMS and CO₂ dependences on surfactants and/or bubbles. More measurements will be required to resolve this issue.

[15] Nightingale *et al.* [2000] argued that only about half the variance in k could be explained by wind speed. The APIMS-ILS/EC flux measurement - because it is both fast and accurate - offers the potential to study those factors. It can be used in future experiments alongside measurements of bubble and wave spectra, surface films, mean square wave slope, whitecap fraction, and other physical factors to quantify those functionalities. This new technique could contribute to tremendous advances in our understanding of gas transfer at the air-sea interface.

[16] From the standpoint of gas exchange measurements, we can at last measure the transfer velocity of a biogenic gas (DMS) from the ocean to the atmosphere with an accuracy of 15–20% on time scales of less than an hour. Transfer velocities determined on short timescales can now be used by analogy to quantify physical factors controlling the exchange of many other gases, including CO₂, CH₄, and N₂O.

[17] From the standpoint of DMS, it is evident that DMS fluxes change rapidly in response to changes in wind speed and possibly a variety of factors that were not measured in this pilot experiment. At most wind speeds some hourly k values exceeded W92 and some were smaller than LM86. If in fact our measurement uncertainties were smaller than the observed variability, this demonstrates that wind is only one of the important controlling factors. When binned by wind speed and averaged, the most defensible transfer velocities (from 4–9 m/s) fall between LM86 and W92, as suggested by N2000. Thus these theories are on the right track, but need to include other important parameters.

[18] It is encouraging that the APIMS-ILS method produced results that make geophysical sense on its first ship-borne deployment. We believe it offers great promise for use in future studies of air-sea exchange.

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