Sea-to-air fluxes from measurements of the atmospheric gradient of dimethylsulfide and comparison with simultaneous relaxed eddy accumulation measurements

Eric J. Hintsa, John W. H. Dacey, Wade R. McGillis, James B. Edson, and Christopher J. Zappa

Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA

Hendrik J. Zemmelink[1]

University of Groningen, Haren, Netherlands

[1] We measured vertical profiles of dimethylsulfide (DMS) in the atmospheric marine boundary layer from R/P FLIP during the 2000 FAIRS cruise. Applying Monin-Obukhov similarity theory to the DMS gradients and simultaneous micrometeorological data, we calculated sea-to-air DMS fluxes for 34 profiles. From the fluxes and measured seawater DMS concentrations, we calculated the waterside gas transfer velocity, k_w. Gas transfer velocities from the gradient flux approach are within the range of previous commonly used parameterizations of k_w as a function of wind speed but are a factor of 2 smaller than simultaneous determinations of transfer velocity using the relaxed eddy accumulation technique. This is the first field comparison of these different techniques for measuring DMS flux from the ocean; the accuracy of the techniques and possible reasons for the discrepancy are discussed.   *INDEX TERMS:* 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 3339 Meteorology and Atmospheric Dynamics: Ocean/atmosphere interactions (0312, 4504); 4504 Oceanography: Physical: Air/sea interactions (0312); *KEYWORDS:* air-sea exchange, gas transfer, sulfur emissions

1. Introduction

[2] The composition of the atmospheric marine boundary layer (MBL) is profoundly influenced by gas exchange with the underlying ocean. Water vapor, reduced sulfur compounds, and halocarbons are among the important molecules with ocean sources. In turn, deposition to the ocean is a major sink for oxidized species, ozone, and aerosols in the MBL. The largest natural flux of reduced sulfur to the atmosphere is from dimethylsulfide (DMS). DMS is readily oxidized in the troposphere on a timescale of about a day, and the resulting sulfate contributes to the formation of cloud condensation nuclei. This can influence the local or even global climate, though the magnitude of this effect is still poorly quantified two decades after it was first hypothesized [*Shaw*, 1983; *Charlson et al.*, 1987]. In order to evaluate its impact on atmospheric chemistry and radiative forcing, the flux of DMS into the atmosphere is one of the key quantities that must be determined.

[3] Air-sea gas exchange can be written as the product of the gas transfer velocity and the disequilibrium between the water and air phases:

$$F = k_{gas} \cdot (C_w - C_a/K_H), \qquad (1)$$

where F is the flux of the gas out of the ocean, k_{gas} is the gas transfer velocity, C_w is the aqueous concentration of the gas, C_a is the concentration of the gas in the atmosphere, and K_H is the appropriate Henry's Law solubility constant. Here k_{gas} is controlled by transfer through both the air and water layers; for slightly soluble gases it is dominated by the waterside while for more soluble gases such as DMS the airside has a small effect as well. Gas transfer velocities through the aqueous surface layer (k_w) for different gases are related by their Schmidt numbers via

$$k_{w1} = k_{w2} \cdot \left(\frac{Sc_1}{Sc_2}\right)^{-n}, \qquad (2)$$

where Sc is the Schmidt number of the gas (ratio of kinematic viscosity of water to diffusivity of the gas), and

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[1]Now at Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA.

n has been determined to be 1/2 for all but the calmest conditions at sea [*Nightingale et al.*, 2000]. Thus accurate measurements of gas exchange for one gas can be used to predict k_w for any gas whose Schmidt number is known, and progress on the air-sea exchange of DMS can lead to advances in areas far beyond the fluxes and chemistry of atmospheric sulfur. In particular, k_w derived from DMS flux measurements could be used to help predict the air-sea flux of CO_2, the most important anthropogenic greenhouse gas.

[4] In recent years there have been major advances in the study of processes that affect the exchange of gases between the ocean and the atmosphere (see *Asher and Wanninkhof* [1998] for a review). However, these processes (such as bubble formation and small-scale waves) are often not taken into account in the calculation of fluxes. Most estimates of DMS air-sea exchange have been based on measurements of aqueous DMS and parameterizations of k_w as a function of wind speed, such as those by *Liss and Merlivat* [1986] or *Wanninkhof* [1992]. It is now recognized that k_w can be derived from field measurements of gas fluxes, and pioneering studies have been conducted near the air-sea interface [*Jacobs et al.*, 1999; *McGillis et al.*, 2001a, 2001b; *Nightingale et al.*, 2000], and from aircraft [*Russell et al.*, 1998; *Lenschow et al.*, 1999; *Bandy et al.*, 2002]. One advantage of using DMS for air-sea exchange studies is that the ocean is strongly supersaturated compared to the atmosphere, so the atmospheric concentration in equation (1) is usually a small correction or can even be neglected, and there is always a flux out of the ocean. Unfortunately, only relatively slow techniques for measuring DMS in the atmosphere, such as gas chromatography (GC), have been available, precluding the use of eddy correlation (the most direct method) to measure the flux until quite recently [*Bandy et al.*, 2002]. This has required the use of methods that allow slower gas analyses, such as the gradient flux (GF) or relaxed eddy accumulation (REA) techniques.

[5] Other than our preliminary experiments during the GasEx-98 cruise and at a nearshore dock [*McGillis et al.*, 2001a; *Zemmelink et al.*, 2002a], the only previous study of DMS fluxes using the GF technique was by *Putaud and Nguyen* [1996], who measured concentrations through inlets at different elevations near and over a ship. They found that on average, fluxes were significantly larger than predicted by the Liss and Merlivat or Wanninkhof parameterizations, though several profiles that showed negative fluxes (into the ocean, despite the ocean always being supersaturated) were neglected. However, that study was potentially affected by problems of flow distortion around the ship. DMS fluxes have also been measured by micrometeorological and bulk techniques from aircraft [*Russell et al.*, 1998; *Lenschow et al.*, 1999; *Bandy et al.*, 2002]. In this paper, we present new measurements of DMS flux using the GF technique from R/P FLIP, a stable oceangoing research platform. DMS fluxes were also measured with the REA technique [*Zemmelink et al.*, 2004]. We believe that these are the first simultaneous measurements of DMS air-sea exchange over the open ocean by two different techniques in the surface layer, and one of very few such compar-

isons for any gas. In this paper we present and discuss the GF results and compare them with the simultaneous REA measurements.

2. Theory and Experimental

[6] For a gas with an ocean source and an atmospheric sink, there will be a mean gradient in the lower atmosphere, decaying with elevation above the ocean surface. The lifetime of DMS is short enough that this gradient is nearly always present, yet long enough ($\sim$1 day) that the gradient in the lowest layer of the MBL is not significantly altered by oxidation. Vertical mixing by turbulent eddies causes transport of DMS down the gradient. Using Monin-Obukhov (MO) similarity theory, the flux can be expressed as

$$F \equiv -u_* C_* = \frac{-u_* \mathrm{k}}{\phi_\mathrm{m}(z/L)} \left(\frac{\partial C}{\partial \ln z} \right), \qquad (3)$$

where u_* is the friction velocity (calculated from the covariance between horizontal and vertical wind speed), C_* is the scaling parameter for a given gas, k is the von Karman constant (assigned a value of 0.4), C is the concentration of the gas, z is the height above the mean sea surface, and $\phi_m(z/L)$ is the flux profile function for mass defined as

$$\phi_m \left(\frac{z}{L} \right) = \frac{\mathrm{k}z}{C_*} \left(\frac{\partial C}{\partial z} \right), \qquad (4)$$

with L the MO length. Integration of equation (3) results in a diabatic profile for a given gas expressed as

$$C(z) = C(z_0) + \frac{C_*}{\mathrm{k}} [\ln(z/z_0) - \Psi_m(z/L)], \qquad (5)$$

where z_0 is the height at which the semilogarithmic profile goes to the surface concentration and Ψ_m is the integral of $(1 - \phi_m(z/L))/z$. Equation (5) is typically used with the gradient flux technique to determine the scaling parameter, C_*, from samples collected at different elevations. Specifically, the slope of gas concentration at different heights versus $\ln(z) - \Psi_m$ is equal to C_*/k. The scaling parameter is then combined with direct measurements of u_* to compute the flux using $F = u_* C_*$. The flux measurements can then be combined with measurements of the concentration of aqueous DMS to calculate k_{gas} by inverting equation (1).

[7] With the gradient flux (GF) technique, the key is to simultaneously and precisely measure gas concentrations at different elevations without significantly perturbing the existing gradient. Simultaneous sampling is necessary because sequential measurements are strongly affected by atmospheric variability. The experiments reported here were carried out on the port boom of R/P FLIP, a research platform designed for high stability and low wind field distortion. FLIP is essentially a floating tower that tends to align itself with the wind such that the airflow is across the port boom. This allows the gas inlets to be positioned so that they always face into the wind. One inlet was mounted above the boom and two more inlets were attached to a mast suspended from the boom, at elevations from 2.6 to 12 m. A schematic of the experimental configuration is shown in Figure 1a. Because most of its length is below the waterline,
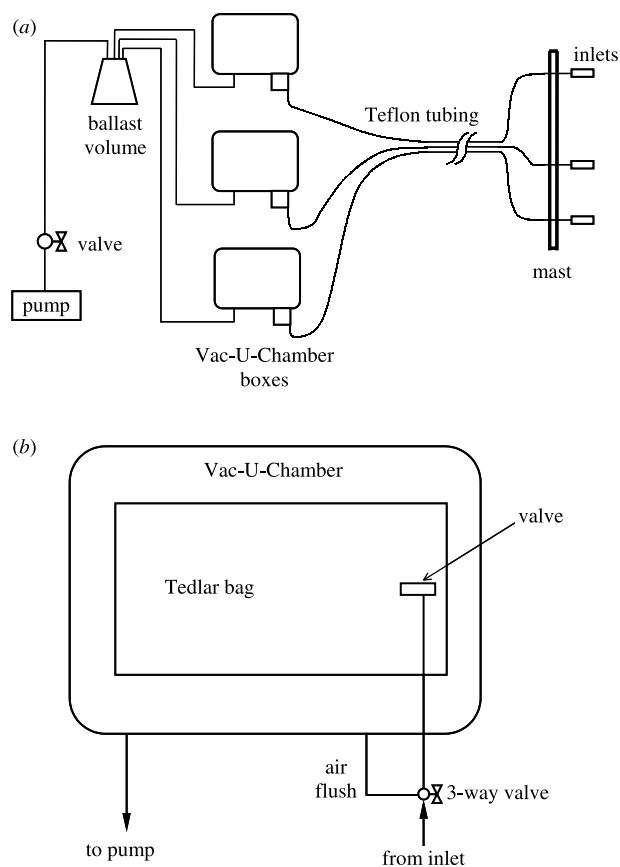
Figure 1. (a) Mast and inlet system to boxes and pump during FAIRS and (b) close-up view of a Vac-U-Chamber, sampling bag, three-way valve, and plumbing.

FLIP has relatively little motion even in rough conditions, nearly eliminating the effect of vertical motion on the inlets.

[8] The gas inlets were $7/16''$ (11 mm) i.d. Teflon tubes with KI-soaked cotton to act as an oxidant scrubber [*Kittler et al.*, 1992; *Persson and Leck*, 1994]. This removes ozone, NO_3, and other oxidants that could perturb the measured concentrations of DMS. Sampled air then flowed through about 25 m of $3/16''$ (4.8 mm) i.d. Teflon tubing to a series of Vac-U-Chambers (SKC Inc.). These are airtight boxes into which we placed 10-L Tedlar bags (SKC) used for gas sampling. The three Vac-U-Chambers could be evacuated with a single diaphragm pump, and a Nylon three-way valve on each chamber allowed us to switch from purging the gas lines to collecting air samples (Figure 1b). A ballast chamber between the pump and the boxes ensured steady flow, and a metering valve between the pump and the ballast chamber was used to control the flow. Typically, the gas lines were purged for 10 min or more, then the pressure in the ballast volume was adjusted to a level that was appropriate for the desired flow. When the pressure and flows had stabilized, the three-way valves were switched manually to send air from the inlets into the bags (as air was pumped out of the box around them, the bags would fill) at a rate of about 300 mL min^{-1} for 30 min (to average over atmospheric fluctuations). In this way, the air samples were only in contact with the oxidant trap, Teflon tubing, the Nylon three-way valves, and Tedlar bags (all determined to have

no effect on DMS), before being analyzed with a GC. A preliminary version of this setup has been described by *Zemmelink et al.* [2002a]. With multiple sets of bags, a profile could be obtained every 45 min.

[9] The air samples were dried by passing through a cold trap at $-15°C$, preconcentrated on Tenax TA at $-15°C$, desorbed by flash heating, separated on a Chromosil-330 column and analyzed with a Sievers 350B sulfur chemiluminescence detector equipped with a Model 355 burner. Chromatograms were stored on a computer and analyzed for DMS peak areas. We typically analyzed 3 1-L samples from each bag. All of the analysis steps (preconcentration, flash heating, data acquisition, etc.) were automated for one Tedlar bag at a time. The GC was calibrated with standards prepared by injecting a sample of DMS from a permeation tube into a bag filled to a known volume of zero air with an MKS flow controller. The standard bags were analyzed exactly as the air sample bags, and a calibration curve over the course of the experiments was constructed. Aqueous DMS concentrations were obtained from 5 mL water samples from a Teflon bucket lowered from the deck of FLIP. Unfiltered samples were sparged with nitrogen for five minutes, with the resulting gas samples dried and analyzed in the same way as the air samples.

[10] For the determination of fluxes by the REA method, samples are collected in two reservoirs depending on the sign of the vertical wind velocity. A threshold value of the vertical wind velocity is often used, below which air is discarded. The flux is calculated from the product of the eddy accumulation coefficient (experimentally determined to be about 0.6), the standard deviation of the vertical wind speed, and the mean concentration difference between the samples collected during upward and downward moving eddies, with a further correction for the threshold velocity. Air samples for REA were analyzed in the same manner as for GF. Further details of the REA method as applied during the FAIRS cruise are given by *Zemmelink et al.* [2004].

[11] Wind speed, wind direction, and momentum and buoyancy fluxes were measured with a Solent 3-D sonic anemometer/thermometer, relative humidity and temperature with a Vaisala RH/T probe, and water temperature at 2 m depth with a YSI thermistor. The R/P FLIP is not perfectly stationary, so the meteorological fluxes were corrected for platform motion using the approach given by *Edson et al.* [1998]. The parameters u_*, L, and Ψ_m, were calculated from these data. Other simultaneous data obtained on FAIRS included wave height, sea surface roughness, and infrared and microwave sensing of the sea surface. A detailed description of the FAIRS cruise is given by *Jessup et al.* [2002].

3. Results

[12] The Fluxes, Air-Sea Interaction, and Remote Sensing (FAIRS) cruise took place from 15 September to 15 October 2000, with DMS fluxes measured on the second leg of the cruise, starting 5 October. All of the data were obtained from 8 to 12 October (year day 283–287), during which time FLIP was drifting SE, about 200 km west of the central California coast (35.9°N, 123.8°W to 35.1°N, 123.1°W). A total of 34 profiles were collected and analyzed. A plot of wind speed and aqueous DMS for this period is shown by *Zemmelink et al.* [2004]. Winds at 10 m elevation ranged
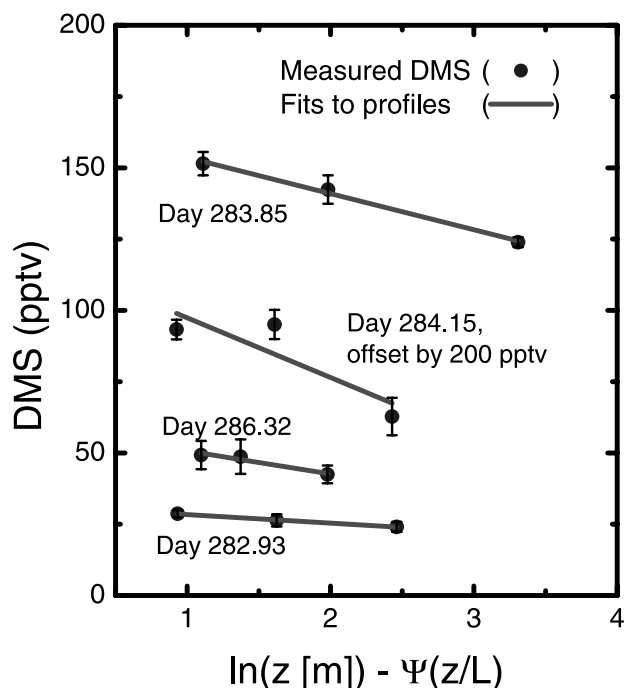
Figure 2. Profiles of DMS at different times during FAIRS, with fits of DMS mixing ratio to $\ln(z) - \Psi(z/L)$, the integral form of the flux profile function, and error bars from the standard deviations of the DMS measurements. The profile at day 284.15 has been reduced by 200 ppt to bring it onto the same scale.

from 4 to 14 m s^{-1}, reaching a maximum on day 284 then decreasing slowly for the rest of the sampling period. Atmospheric stability changed from stable to unstable conditions on day 284. Atmospheric DMS concentrations strongly tracked the wind velocity, and varied from 20 to 300 ppt over 5 days. The relative concentration differences, $\Delta C/C$, ranged from 3 to 25% over elevations of 2.6 to 12.2 m. Some representative profiles are shown in Figure 2. The measured DMS profiles did not always monotonically decrease with elevation, but the slope of concentration versus $\ln(z) - \Psi_m$ was always negative, as expected from theory and the fact that the oceans are supersaturated with respect to the atmosphere. During these experiments, the supersaturation was a factor of 9 to 100, leading to a maximum correction of 11% for the air concentration of DMS in equation (1), similar to *Putaud and Nguyen* [1996]. The precision of the DMS measurements was typically better than 3%, after averaging all replicate analyses. However, this has a large effect on the uncertainty of the slope, because gradients were only ~10% over the range of inlet elevations. The accuracy of the DMS concentrations is estimated at about 20% and is largely determined by the calibration process. This affects the DMS flux calculations; however it has little or no effect on calculations of k_{gas}, since the calibration affects the air and water concentrations equally.

[13] DMS fluxes were calculated from equations (3) and (5) using the Businger-Dyer formulations given by *Paulson* [1970]. Measurements of water vapor profiles on the first leg of the FAIRS cruise showed that this function, originally

derived from data over land surfaces, is applicable within a few percent to water surfaces during unstable conditions (C. Zappa, personal communication). The DMS concentrations were regressed against $\ln(z) - \Psi_m(z/L)$ and the slope was multiplied by u_*k to obtain the flux. Calculated DMS fluxes are plotted in Figure 3a as a function of time, along with DMS mixing ratios at 5.2 m. The waterside gas transfer velocity for each profile was calculated by inverting equation (1), with an additional term for the fraction of airside control [*McGillis et al.*, 2000]:

$$k_w = \frac{F_{DMS}}{(DMS_w - DMS_a/K_H)} \cdot \frac{1}{(1 - \gamma_a)}, \qquad (6)$$

γ_a accounts for airside control and increases for more soluble gases and higher wind speeds. In these experiments, the maximum effect was 16%, using DMS solubility data from *Dacey et al.* [1984]. For CO_2 this term is an order of magnitude smaller, and for more insoluble gases such as O_2, methane, and He it is negligible [*McGillis et al.*, 2000]. k_w was then converted to conditions with $Sc = 660$ (appropriate for CO_2 in seawater at 20°C; commonly used for
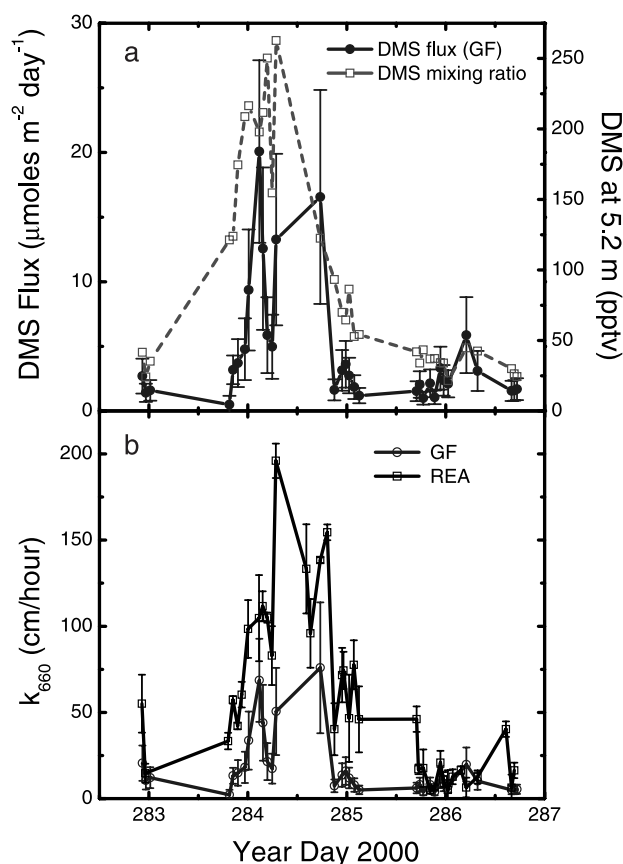

Figure 3. (a) DMS flux from the GF technique (solid circles) as a function of time during FAIRS and the mixing ratio of DMS at 5.2 m elevation (open squares). The error bars include the uncertainty from the GC analyses and the meteorological data. (b) Gas transfer velocities (k_{660}) as a function of time for the GF (circles) and REA (squares) techniques, with error bars representing measurement precision.
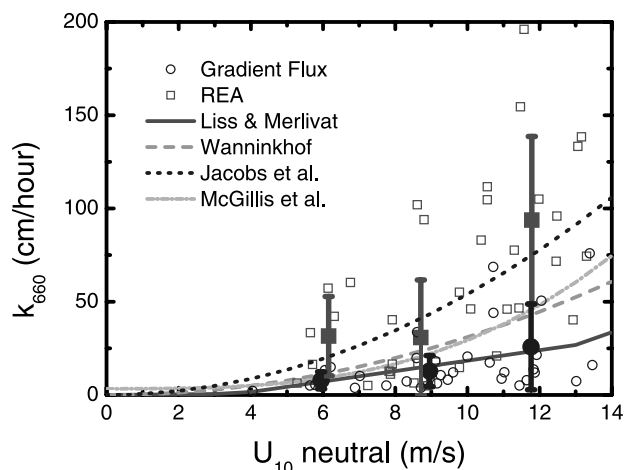
Figure 4. The k_{660} versus U_{10} (neutral) for GF (circles) and REA (squares) during FAIRS. Large solid symbols are binned and averaged data for wind speeds less than 7.5 m s^{-1}, 7.5–10.1 m s^{-1}, and greater than 10.1 m s^{-1}, and error bars represent the standard deviations for each point. Four commonly used parameterizations of transfer velocity versus U_{10} are also shown for reference.

comparison of air-sea gas transfer velocities for different gases) by

$$k_{660} = k_w \cdot \left(\frac{Sc}{660}\right)^{1/2} \qquad (7)$$

with Sc for DMS from *Saltzman et al.* [1993].

[14] Values of k_{660} are plotted versus time in Figure 3b and versus wind speed at 10 m (corrected to neutral conditions) in Figure 4, both as individual measurements and data binned and averaged with wind speed. Also shown are simultaneous measurements of k_{660} using the REA technique, and several commonly used parameterizations of k_w as a function of wind speed [*Liss and Merlivat*, 1986; *Wanninkhof*, 1992; *Jacobs et al.*, 1999; *McGillis et al.*, 2001b]. Both data sets show a fair amount of scatter, but the GF data are clearly much lower than the REA data. The average GF data are in close agreement with the Liss and Merlivat relationship and the average REA data compare better with *Jacobs et al.* [1999]. Linear regression of gas transfer velocities for the two techniques yields a slope of about 2, with a reasonable correlation ($R^2 = 0.61$) despite a fair degree of scatter (Figure 5). Some of the scatter in Figure 5 is caused by the precision of our GC analyses during FAIRS, but this does not affect the mean difference between the two techniques. The main sources of uncertainty for the GF method are the DMS analyses and the applicability of the technique itself. Because of reduced analytical precision during FAIRS compared to laboratory analyses of DMS concentrations, the (random) uncertainty of any one profile is about 30–50%. The meteorological measurements add an additional uncertainty of 10–30%. The total of all random errors is not, however, much more than 50%, as can be seen in Figure 3, where on day 285 and again on day 286, consecutive flux measurements and calculated values of k_{660} are clustered together during

similar conditions. Furthermore, this does not affect the accuracy of the profiles, and by averaging many individual values of k_{660} together, the precision can be improved. In the following section, we will discuss the possible reasons for the discrepancy between GF and REA.

4. Discussion

[15] The gas transfer velocities derived from the GF and REA experiments clearly fall within the range of reasonable values for the measured wind speeds, but there is a difference of about a factor of 2 between the two data sets. The GF data are in agreement with the parameterization of *Liss and Merlivat* [1986], while the REA data are closer to the results of *Jacobs et al.* [1999]. Previous comparisons of gas transfer velocity under different conditions (using wind speed as a transfer standard) have differed by an order of magnitude or more, and other current "state-of-the-art" intercomparisons with simultaneous measurements also show similar (factor of 2) disagreements [*Jacobs et al.*, 2002]. Only when different techniques (and data for different gases) yield agreement on gas transfer velocities can we have better confidence in their accuracy. In addition, gas exchange is a complicated process that depends on variables other than wind speed, and in all likelihood cannot be completely described by one variable. Accurate measurements of k_w will need to be coupled with simultaneous observations of conditions at the air-sea interface (wind, waves, surfactants, etc.) to derive more realistic parameterizations of air-sea exchange.

[16] Because the GF and REA experiments were carried out simultaneously and with the same trace gas analytical method, there are a number of factors that can be ruled out as the cause of any disagreement here. Both the gradient flux and relaxed eddy accumulation samples were collected in Tedlar bags and analyzed on the same gas chromatograph under exactly the same conditions. The response of the Sievers chemiluminescence detector is linear over the concentrations measured in these experiments. All samples were analyzed within 12 hours, usually within a few hours.
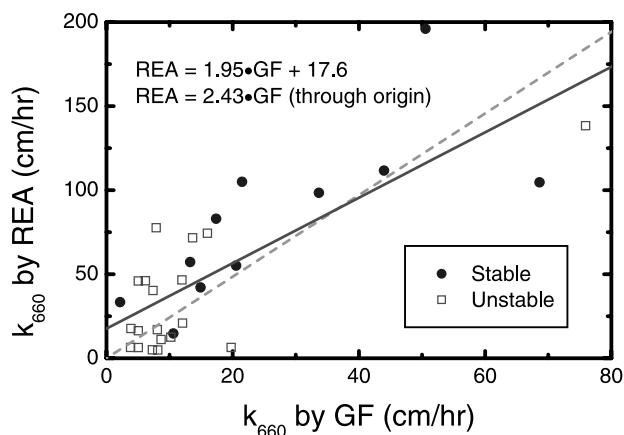

Figure 5. Gas transfer velocity (k_{660}) for REA versus GF for simultaneous data points. Solid circles are for data under stable atmospheric conditions, and open squares are for unstable conditions. Linear fits to the data are also included (solid line) and forced through the origin (dashed line).

We have previously shown that air samples can be stored in Tedlar bags for at least one week without loss of DMS [*Zemmelink et al.*, 2002b]. Because gas transfer velocities are derived from gas concentrations divided by aqueous DMS concentrations for both methods, the calibration of the GC (used for both water and air samples) affects the k_{gas} results only slightly. We have verified the relative calibrations of gas and water samples with prepared standards in the laboratory. All the materials used are compatible with DMS collection; in addition they were very similar between the GF and REA systems. The meteorological data are reasonably accurate, and contribute an uncertainty of only about 10–30% to the results. Finally, although the REA results were higher than those for GF, any errors in valve switching, etc. for REA would tend to bias it low, as discussed by *Zemmelink et al.* [2004].

[17] We are left with the possibility of problems in sampling with either GF or REA, or something inherent to one or both of the two techniques. In prior experiments [*Zemmelink et al.*, 2002a], all the GF inlets were placed at the same elevation, with good agreement in DMS concentration between the different samples. In addition, during FAIRS the average of the upgoing and downgoing REA samples (at 12.75 m) agreed well with DMS at our highest elevation (12.22 m); the small difference in elevations is negligible. From the meteorological measurements, it was determined that flow distortion was unimportant except within 1 meter of the port boom; all of the inlets for both experiments were outside this range. In addition, the error in our height measurements due to flow distortion would have to be greater than one meter in order to significantly affect the calculated flux. The interaction of winds and high waves (on the order of 1 m height on days 284–285) could conceivably distort the shape of the flux profile as described by equation (4) near the water surface. Waves would bring higher relative concentrations to the inlets at their crests, and lower concentrations over the troughs. Because of the logarithmic nature of the profile, the concentration gradient is steepest near the surface, which would tend to affect the lowest inlet most. However, this effect was checked for by using only the data from the upper two inlets (5.2 and 12.2 m elevation), which should have little or no influence from the wave roughness elements. This analysis yielded quantitatively similar results to the analysis using all three inlets.

[18] An independent estimate of the flux was derived from a one-box model assuming a boundary layer box with a depth from assimilated meteorological data (M. Chin, personal communication) and a logarithmic DMS profile up to the top of the boundary layer. The flux from the ocean was balanced by the atmospheric increase in DMS, chemical loss, and entrainment into the free troposphere. The increase in DMS was derived from data for day 284, when atmospheric DMS increased rapidly as shown in Figure 3. The chemical loss rate was calculated to be 3 ± 1 micromoles m^{-2} d^{-1} on the basis of a diurnally averaged modeled OH concentration (M. Chin, personal communication). The entrainment rate was estimated at 0.005 m s^{-1} on the basis of results of *Lenschow et al.* [1982] and *Thompson and Lenschow* [1984]. This simulation yielded a value intermediate between the average GF and REA fluxes for that day. However, the uncertainties in this calculation (particularly the increase in boundary layer height during the transition

from stable to unstable conditions) prevent it from being used as more than a factor of 2 estimate.

[19] One potential problem of the GF technique is that each inlet measures air-sea exchange from a different source footprint. Since the flux footprint extends to roughly 100 times the height, we would be vulnerable to fluctuations on spatial scales between 100 m and 1 km. However, there has been no evidence of surface DMS variability on these spatial scales. In any case, small-scale variability should average out over many profiles because some would be anomalously high and others anomalously low. The sea surface upwind of the sample inlets is unaffected by FLIP's wake since we were drifting with the currents and the surface layer was always being blown downwind of our flux footprint, so there should be no preferential vertical mixing that could possibly induce systematic variations in surface water DMS upwind of the platform. Though there was large variability in the individual flux measurements (as can be seen in Figures 3 and 4), on average the REA gas transfer velocities were about twice those by GF, with no obvious dependence on wind speed.

[20] A possible clue is that measured values of k_{660} are generally smaller during unstable conditions compared to stable conditions for the same wind speed. This can be seen most clearly in Figure 9 of *Zemmelink et al.* [2004] and is also true for the GF results, but could have been caused by some factor other than wind speed or stability. The discrepancy between GF and REA is largest during stable and near-neutral conditions (Figure 3b; days 283.5–285.5). As the atmosphere became increasingly unstable toward the end of the experiment, the REA values of k_{660} decreased and nearly reached agreement with the GF results. Inaccuracies in the MO flux profile function are another possible source of error, but the GF results were still lower than those of REA during near-neutral conditions (where Ψ makes no contribution in equation 5). Furthermore, measurements of water vapor profiles during FAIRS showed that at least for unstable conditions the Businger-Dyer parameterization of Ψ is accurate over the ocean.

5. Conclusions

[21] Sea-to-air fluxes of DMS were measured on R/P FLIP during the 2000 FAIRS cruise off the coast of California using the gradient flux and relaxed eddy accumulation techniques. Both techniques yielded reasonable results (within the uncertainty of other field measurements that are considered state of the art), but the REA data were about a factor of 2 higher than the GF data. This level of agreement is similar to the most careful comparisons of air-sea gas exchange methods [*Jacobs et al.*, 2002], and we believe that improvements in our techniques during future work will explain and/or narrow these differences. Because the GF and REA samples were analyzed identically, there is a strong suggestion that the source of the discrepancy is something inherent to one or both of the techniques.

[22] With this demonstration of the feasibility of DMS sea-to-air flux measurements, we are left with a need for further experiments comparing multiple techniques for measuring gas fluxes over the ocean, and for simultaneous experiments with different gases. We have begun prelimi-

nary work in this direction on the GasEx-2001 cruise and at the Dutch MPN (Meetpost Noordwijk) platform in the North Sea.

[23]   In future experiments, we will focus on four areas: 1) Improvements in our techniques to ensure that they are not causing errors. For GF, this includes larger and faster flows through the gas sampling lines with subsampling into bags, actively regulating the flow into the bags with flow controllers, more frequent null experiments with all the inlets at the same elevation, and experiments on wave effects with the inlets closer to the sea surface. For REA, this includes further analysis of the eddy accumulation coefficient and the threshold velocity under a wider range of atmospheric conditions, and replacing the Tedlar bags with inline gas sensors that would allow a detailed study of the effect of the threshold velocity on measured fluxes. 2) Comparison of GF and REA measurements with the eddy correlation method, for example, by using newly developed chemical ionization mass spectrometry techniques. 3) Detailed analysis of physical processes in the source area of the flux. 4) Enlarging the data set of profiles and REA measurements with an automated sampling and analysis system. We have begun work on this using a miniaturized gas chromatograph developed for small aircraft. With a much larger data set we can begin to look for differences as a function of stability, sea state, or surface conditions, which is not possible with the relatively small data set obtained from FAIRS.

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J. W. H. Dacey, J. B. Edson, E. J. Hintsa, W. R. McGillis, C. J. Zappa, and H. J. Zemmelink, Woods Hole Oceanographic Institution, MS 25, Woods Hole, MA 02543, USA. (ehintsa@whoi.edu)