14.6 SEA-TO-AIR EXCHANGE OF DIMETHYL SULPHIDE

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1. INTRODUCTION

The sea-to-air flux of dimethyl sulphide was assessed with the relaxed eddy accumulation (REA) and the gradient flux (GF) techniques over the northeastern Pacific Ocean. Measured fluxes and seawater DMS concentrations were used to calculate gas transfer velocities, k_{gas}. Gas transfer velocities derived from both techniques are within the range of commonly used parameterizations of k_{gas}. However, gas transfer rates from the GF technique are significantly smaller than simultaneous determinations of k_{gas} with REA.

The rate of gas transfer across the atmosphere-ocean interface is usually described by the bulk aerodynamic equation:

$$F = k_{gas} ([gas]_{air} - [gas]_{water}) \qquad (1)$$

where k_{gas} is the gas transfer velocity; usually derived from wind tunnel, radiocarbon, or tracer measurements and related to wind speed and sea surface temperature but not to other environmental parameters that could affect the flux. Moreover, commonly used gas transfer parameterizations yield differences up to a 100% (Wanninkhof, 1992). Ideally, gas transfer velocities should be derived from field measurements of gas fluxes, then k_{gas} can be computed directly and include all algorithms that affect gas exchange.

Recent effort has focused on the derivation of the transfer velocity from eddy correlation (EC) measurements of CO_2 fluxes, using fast meteorological and gas sensors (Jacobs et al., 1999; McGillis et al., 2001). Unfortunately, the disequilibrium between CO_2 in the water and the atmosphere is usually low, resulting in fluxes that are often at or below the limit of detection. The application of EC for CO_2 flux measurements requires the selection of specific conditions that provide large concentration differences (e.g. during phytoplankton blooms).

The biogenic gas dimethyl sulphide (DMS) exhibits a strong concentration gradient between the ocean and the atmosphere and fluxes are always evident. Field measurements of this gas would be preferable for the determination of gas transfer velocities. However, the fast detector response required for EC is beyond the present capability of gas chromatographic systems that are required to measure DMS concentrations. Other techniques, which allow the measurement of fluxes without the use of fast response sensors, will have to be developed and tested for application over the marine atmospheric boundary layer. Two such techniques are the gradient flux (GF) and the relaxed eddy accumulation (REA) methods.

The application of micrometeorological techniques for the measurement of DMS fluxes is rather new. So far only the GF technique has been applied for this purpose. Parallel use with other techniques has only been tested for trace gas measurements over terrestrial systems (Pattey et al., 1999) and indicate differences of 63% and higher between fluxes estimated by the two systems. Intercalibration of different techniques should be conducted in the marine environment as well in order to apply GF and REA to the measurement of trace gas fluxes in this environment with confidence.

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2. STUDY SITE AND TECHNIQUES

During the Fluxes, Air-Sea Interaction, and Remote Sensing (FAIRS) experiment, DMS fluxes were measured on half-hourly time scales from yearday 282 to 287 (UTC) in the Northeast Pacific (37°N, 123.2°W) during October 2000, from the Floating Laboratory Instrument Platform FLIP.

2.1 *REA flux measurements*

The REA measurements were obtained 12 meter above the sea surface. Air was sampled at a constant flow rate (300 ml min^{-1}) into two separate reservoirs (Tedlar bags), according to the sign of the vertical wind speed (upward and downward moving air). Fluxes were calculated following Businger and Oncley (1990):

$$F = \beta \sigma_w \Delta C, \text{ where } \beta = \beta_0 \, e^{(-3/4)(w_0/\sigma_w)} \qquad (2)$$

where ß is the eddy accumulation coefficient (β_0 = 0.6), w_0 the dead band velocity (0.03 m s^{-1}), σ_w the standard deviation of the vertical wind speed, and Δc the mean concentration difference between the upward and downward moving air. The eddy accumulation coefficient can also be computed from EC measurements of sensible heat fluxes:

$$\overline{w'T'} = \beta \, \sigma_w \, (\bar{T}u - \bar{T}d) \qquad (3)$$

2.2 *Gradient flux measurements*

The GF samples were obtained from 2.5, 6 and 12 meter elevation at a flow rate of 300 ml min^{-1} and stored in Tedlar bags. GF DMS fluxes were computed using the following set of equations (Paulson, 1970):

$$F = -u_* \, k \, \Delta C / [\ln(z_2 / z_1) - \Psi_2 + \Psi_1] \qquad (4)$$

with $\Psi = -5z/L$ for stable conditions and $\Psi = 2\ln((1+x^2)/2)$ for unstable conditions (where $x = (1-16z/L)^{1/4}$), where k is the van Kármán constant (0.4), u_* (m s^{-1}) is the friction velocity calculated using momentum flux, z is the measurement height, and L is the Monin-Obukhov length calculated using the momentum and sensible heat fluxes.

2.3 *Gas analytical procedure*

DMS from water and air samples was focussed on Tenax cooled to -15°C and analyzed using a Sievers gas chromatograph equipped with a sulfur chemiluminescence detector following the procedure described in Zemmelink et al. (2002). The effect of density fluctuations on our flux measurements was avoided by equalizing the temperature in the collection bags and drying the air on a cold finger prior to concentration of DMS onto Tenax, with both the cold finger and the Tenax cooled to –15˚C.

2.4 *Estimation of the transfer velocity*

Surface water DMS was determined by sparging 5 ml of water with nitrogen. Measured concentrations were used to calculate the transfer velocity of DMS using the following equation:

$$k_{gas} = \text{flux} / (C_w - C_a H^{-1}) \qquad (5)$$

where C_w and C_a are the concentrations of DMS in the water and the air respectively, and H is the Henry's law coefficient for DMS (Dacey et al., 1984). In order to account for the effect of the airside control on the exchange of soluble gases, a correction is applied as suggested by McGillis et al. (2000).

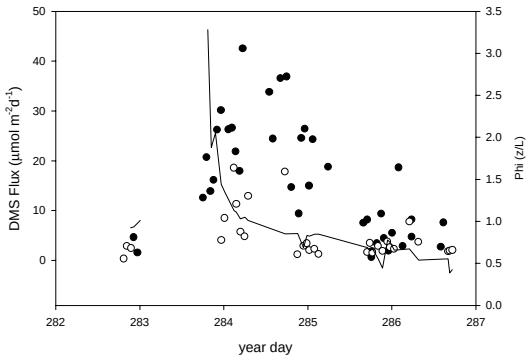

Figure 1. DMS fluxes (µmol m-2 d-1) derived from REA measurements (black dots) and GF measurements (white dots). Solid line is atmospheric stability (phi) evaluated at 10 m elevation.

3. RESULTS AND DISCUSSION

Fluxes measured with REA and GF traced each other reasonably well (Fig. 1) with elevated fluxes from year day 283.8 until 285.6. This period had elevated wind speeds as compared to the other days (Fig 2). Fluxes derived from the REA measurements were on average more than two times higher than fluxes derived from the GF measurements, with the largest differences around day 284 and 285. Although atmospheric stratification changed from stable to unstable conditions within this time frame (Fig. 2), there is no clear relation with the difference between REA and GF results and atmospheric stability. Consequently, the correction to neutral conditions using the integrated Monin-Obukhov flux-profile function is not likely to be the source of the discrepancy. Moreover, measurements of water vapor profiles during FAIRS showed that at least for unstable conditions the Dyer (1974) parameterization of Ψ is accurate (results not shown).

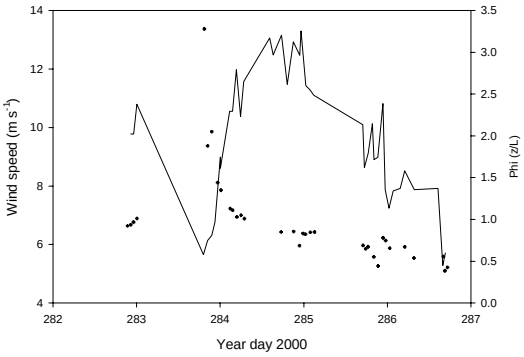

Figure 2. Timeseries of wind speed (m s-1) and atmospheric stability (data points).

The effect of atmospheric conditions on REA has been studied in terms of the value of β as a function of atmospheric stability and turbulence. Empirical estimates of β based on EC data sets of measurements over terrestrial systems yielded values in the vicinity of 0.56-0.58 (Baker, 1992; Pattey et al., 1993; Beverland et al., 1996; Katul et al., 1996). Values calculated using equation 2 resulted in eddy accumulation coefficients of 0.57 +/- 0.005, all within the expected range. Andreas et al. (1998) found a weak stability dependence of β for gas fluxes using turbulence data of sensible heat and results from Businger and Oncley (1990). REA simulations based on EC measurements of sensible heat fluxes over the ocean, conducted during the GasEx 2001 cruise, resulted in values of β that were similar to those found by Andreas et al. (1998) and indicated a weak, but not significant, stability dependence (Fig. 3).

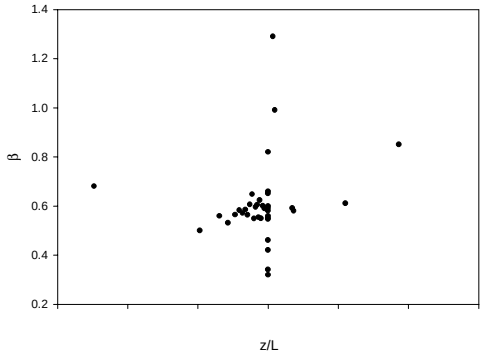

Figure 3. Relaxed eddy accumulation coefficients for sensible heat fluxes as a function of stability.

Averaged values for β during unstable, neutral and stable conditions were 0.58 (+/- 0.34, n = 930), 0.55 (+/- 0.14, n = 12) and 0.69 (+/- 0.26, n = 11) respectively. Overall, the average value for β was 0.58, similar to the values based on equation 2.

As a consequence, the difference between transfer velocities derived from the REA and GF flux measurements is large (Fig. 4). However, previous comparisons of gas transfer velocities differed by an order of magnitude and other current state-of-the-art measurements show a scatter of a factor of 2 or more (e.g. Jacobs et al., 1999), similar to the difference between the parallel measurements presented here. Thus, neither data set provides definitive a single particular parameterization of k_{gas} that is commonly used for the calculation of gas transfer over the ocean-atmosphere interface.

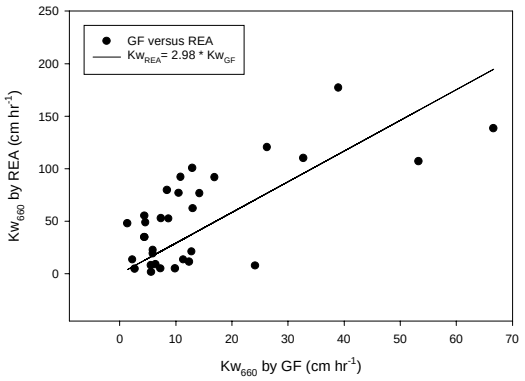

Figure 4. Transfer velocities (cm h-1) derived from REA measurements versus GF measurements.

4. SUMMARY

Measured REA and GF provided reasonable results although REA resulted in values of fluxes and k_{gas} more than a factor two higher than the GF values. This level of agreement is comparable to the discrepancies found between models that are commonly used for the determination of transfer velocities and gas fluxes.

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