

Interactive comment on “Determining the sea-air flux of dimethylsulfide by eddy correlation using mass spectrometry” by B. W. Blomquist et al.

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We are grateful to the Reviewer for taking time to comment on the manuscript. Typographical errors are easily corrected. We will address content-related comments in order, quoting the comments in *italic* for convenience.

Pg. 1974, line 16- “...rapid changes in mean DMS mixing ratio...”, DMS has a lifetime in the atmosphere on the order of one day while the flux measurements are made on the order of one hour. What rapid changes have been seen and are they really significantly affecting the measured flux?

As discussed in Section 5.2, ignoring chemical loss is unlikely to present a problem. It is possible to observe rapid changes in mean DMS mixing ratio in the vicinity of blooms

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associated with mesoscale features such as upwelling regions or current boundaries. Whether advective flux under these conditions will significantly bias the surface flux estimate can be qualitatively assessed as discussed in Sec 5.2. It may be wise to exclude periods when $d\bar{c}/dt$ becomes a significant fraction of F_0/z , where F_0 is approximated from the observed wind speed, sea water dms concentration, and an assumed transfer velocity.

Pg. 1974, line 18- “In addition, bias in surface flux estimates...”, It seems that this statement is in direct contrast to the previous statement that says rapid changes in mixing ratio affect the measured flux. Maybe I am missing the difference between the changes of DMS mixing ratio with height vs. the changes in the mean DMS mixing ratio?

Here we assume flux divergence is controlled by the relative magnitudes of surface flux and entrainment at the inversion. In discussing the errors from flux divergence, the advective flux is assumed to be negligible. Admittedly, flux divergence is difficult to evaluate without measurements throughout the air column. Fortunately it contributes little error under most conditions.

Pg. 1975, line 15-should maybe include references to Simo and/or Saltzman manuscripts (I believe Simo, 1998 and Simo and Dachs, 2002, Simo and Pedros-Alio, (year?), Cooper and Saltzman, 1991, deBruyn et al., 2002) in the list of GC-FPD and GC-MS DMS measurements

The list is not meant to be exhaustive and these methods have been used in many more field programs over the years than cited by the reviewer. A useful early reference for DMS which includes most of the principle groups active in method development, including Saltzman, Bandy, Andreae, Ferek, and Johnson is the CITE-3 study (Gregory et. al. JGR 98, D12, 23373-23388, 1993). Citations in the Gregory93 paper, as well as companion papers in the same volume, should give the reader a thorough background on early DMS analytical methods and we will add it to the list.

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Pg. 1976, line 11-missing a Hints gradient flux reference (Hints et al., 2004)

The Hints 2004 paper is a companion to the Zemmeling 2004b reference and we can add it.

Pg. 1976, line 24-missing a reference to McGillis et al., 2004 and there are two new references to CO₂ open ocean EC, Taddei et al., 2009 and Miller et al., 2009. EC has also been performed at sea for acetone, Marandino et al., 2005 and Taddei et al., 2009.

Again, the list isn't meant to be exhaustive since CO₂ flux is not the principle subject here, but we can add the more recent CO₂ references.

Pg. 1976, line 27-29-have all of these campaigns resulted in published manuscripts?

We will add references and include manuscripts currently in process if accepted before the final revised version of this paper is submitted.

Pg. 1979, Section 2.2-There is no discussion of the potential to saturate the DMSH+ signal (i.e. no increase in DMSH+ counts with corresponding increase in DMSH+ mixing ratio) in the presence of insufficient H₃O+ (very dry conditions of a clean air generator or low relative humidity, or many trace gases in the air stream competing for the proton from the hydronium ion). Have the authors experienced this? It seems that lines 23-25 on page 1980 are referring to this phenomenon but it is not explicitly stated.

Ionization equilibria in zero air are likely quite different than in ambient air due to much lower water concentration and an absence of DMS. So, any background species at the same mass as DMS, even if it exists at the same concentration in zero air and ambient air, which is not certain, will not necessarily have the same absolute signal strength (count rate). So, subtraction of a zero air background signal from the ambient air signal is problematic. The gold adsorption method for blanking is better, but we must assume the background species itself is not removed by the gold. Also, as mentioned in the text, removal of DMS can itself alter the ionization equilibria somewhat, potentially biasing the background measurement. But as long as the backgrounds are small, the resulting

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error will not be significant.

Saturation of the DMS signal, or nonlinearity in the signal strength with respect to the actual mixing ratio, if it occurs, is not a critical concern. The measurement is based on the *ratio* of ambient and standard signals, not absolute signal strength. We merely require sufficient signal to get adequate precision for the ratio measurement. Even if the signal is completely saturated, the isotopomer ratio will reflect the relative concentration difference between ambient and internal standard species. This is the principle advantage of the isotopic internal standard and the main reason the technique works well for high rate ambient measurements.

Pg. 1981, line 27-stipulate that they are referring to counting (Poisson distribution) statistics when they say "...theoretical noise..."

As mentioned in the response to review 1, we will be submitting a revised version of this section...

Pg. 1982, line 10-Do the authors record their mass flow controller (mfc) output signals?

We mention in Appendix Section A4 that flows are recorded as DC voltages by the data acquisition system. We can add that at least once a day flows are stopped to record a period of meter zero data.

Pg. 1982, line 19-The perm tube is brought to the field for in situ standard cylinder calibration. This device would have to be shipped, presumably, without gas flowing over it and without temperature control. How trustworthy is field calibration using the perm tube after such shipment? Do the authors weigh the perm tube at sea to check stability?

The manufacturer states the tubes may be stored at ambient temperature (or even frozen) and returned to equilibrium without affecting the calibrated permeation rate. This claim may be debatable, but in practice we don't often notice a significant difference between calibrations at sea and in the lab. Where there is a difference, the

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lab calibration data is preferable to the calibrations done at sea. At sea the tubes are maintained under constant flow and at temperature, so presumably they will come to adequate equilibrium within a few days. Weighings are done for a primary calibration in the lab prior to a cruise but are not possible at sea due to ship motion.

Pg. 1982, line 20-Figure 12 is referred to out of order

We will simply refer to the appendix here rather than the figure.

Pg. 1985, Section 3.2-there is no mention of the pipeline delay in the sonic anemometer data stream. Do Gill anemometers have a pipeline delay, like Campbells?

The sonic signals are recorded as analog data with little or no delay.

Pg. 1986, line 1-Is there a reference for the lag correlation procedure employed here?

Computing the correlation coefficient as a function of lag time is a standard method, similar to autocorrelation but for two variables. Most data analysis software (e.g. Matlab or IgorPro) has built-in functions to perform this computation.

Pg. 1987, line 10 and Figure 5-I don't quite understand this. In order to compare measured fluxes to Kaimal et al., 1972 you must normalize your measured cospectrum to the covariance and plot with the idealized Kaimal potential temperature cospectrum computed using the equation in the Kaimal et al., 1972 publication.

This is merely meant to introduce a degree of uncertainty in the expected shape of a cospectrum. Based on the empirical results in Kaimal 72, cospectra do not have a well defined form beyond the inertial subrange under unstable conditions ($z/L < 0$). So, to the extent we may experience unstable atmospheric conditions at sea, we do not necessarily expect a well behaved cospectral shape below the inertial subrange. In addition, sampling issues give rise to considerable random variability at these frequencies.

Perhaps we should say "Covariance spectra in the atmospheric surface layer exhibit a

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distinctive form under neutral or stable conditions which is a function of wind speed, measurement height and atmospheric stability (Kaimal et al., 1972). The theoretical shape for the cospectrum is not well defined at low frequencies for unstable conditions, however, and this cospectral region is further affected by random noise over short averaging periods."

Pg. 2000, line 6-It is true that low frequency noise will average out when all records are considered together. However, I do not understand how the authors compute their k values for a k vs. U plot? Are the k values computed over one hour or less? Do the k values contain contamination from low frequency noise?

Transfer velocity is not a topic of this paper, but yes, k values computed from observed flux and sea water dms concentration will exhibit scatter contributed by low frequency noise in the flux measurement.

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