

***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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Revised Section 6.1: Flux Error

The uncertainty in covariance of vertical velocity, w , and some scalar, c , may be expressed as

$$\Delta F_c = \frac{a \sigma_w \sigma_c}{\sqrt{T / \min(\tau_w, \tau_c)}} \quad (1)$$

where σ is the standard deviation, τ is the integral (decorrelation) time scale, T the sample integration time, and a is a constant variously reported as 1 or 2 (e.g. Fairall, 2000 or Lenschow and Kristensen, 1985). The constant a in this form reflects the

uncertain nature of the relationship, arising from approximations to the form of the autocorrelation functions and the interactions of the two variables. Because there are two variables here, there are two time scales. The appropriate time scale is generally taken to be the shorter of the two (generally τ_w) or as the square root of the product of the two, τ_{wc} .

We assume the wind speed measurement is relatively noise-free, but the scalar measurement is often subject to multiple sources of variance. Assuming the sources of variance are independent, we may expand (1) to the following form.

$$\Delta F_c = \frac{a \sigma_w \sigma_{c_a}}{\sqrt{T/\tau_{wc_a}}} \left[1 + \frac{\sigma_{c_n}^2 \tau_{c_n}}{\sigma_{c_a}^2 \tau_{wc_a}} \right]^{1/2} \quad (2)$$

Here we consider two sources of variance in c , atmospheric turbulence (c_a) and white noise (c_n). We have normalized by the first process and allow a different time scale and variance for each process.

There are various approaches for determining the integral time scales, τ_x , defined as the integral of the autocorrelation function of x .

$$\tau_x \equiv \frac{1}{\sigma_x^2} \int_0^\infty R_x(t) dt \quad (3)$$

In the surface layer, τ_w is often approximated as in (4) where z is the observation height and $\overline{u_r}$ the relative wind speed.

$$\tau_w = b z / \overline{u_r} \quad (4)$$

The coefficient b is fairly uncertain, but is a function of (z/L); on the order of 10 in unstable conditions and 3 in near-neutral conditions. The integral time scale may also

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be estimated from the peak frequency (f_{max}) in the w variance spectrum or, alternately, the wc cospectrum.

$$\tau_x = 1/2\pi f_{max} \quad (5)$$

We can also compute the integral time scale for of band-limited white noise arising from electronic noise or Poisson counting statistics, τ_{cn} . Band-limited white noise is characterized by a constant variance-spectral value from $f = 0$ to a maximum frequency, f_x .

$$\Phi_{cn}(f) = \Phi_{cn} \quad f < f_x \quad (6a)$$

$$\Phi_{cn}(f) = 0 \quad f > f_x \quad (6b)$$

We could compute the autocorrelation function of the noise (Fourier transform of the spectrum) and integrate to get τ_{cn} , as in (3). However, in this case it is simpler to use the relationship between the integral time scale and the value of the variance spectrum at $f = 0$.

$$\sigma_{cn}^2 \tau_{cn} = \frac{\Phi_{cn}(0)}{4} = \frac{\Phi_{cn}}{4} \quad (7)$$

Substitution of (7) into (2) yields the following expression for the absolute error of the covariance.

$$\Delta F_c = \frac{a \sigma_w \sigma_{ca}}{\sqrt{T/\tau_{wc_a}}} \left[1 + \frac{\Phi_{cn}}{4 \sigma_{ca}^2 \tau_{wc_a}} \right]^{1/2} \quad (8)$$

Some parameters in (8) are stability dependent. Monin-Obhukov similarity scaling may be used to show the stability dependence of variances through the following relationships, where L is the Obukhov length in meters and u^* is the friction velocity.

$$\sigma_w = 1.25 u^* f_w(z/L) \quad (9a)$$

$$\sigma_{c_a} = \frac{\overline{w'c'}}{u^*} 3.0 f_c(z/L) \quad (9b)$$

Following (4), an empirical relationship may be used to describe the stability dependence of τ_{wc_a} , where b is now a constant.

$$\tau_{wc_a} = b \frac{z}{u_r} f_\tau(z/L) \quad (10)$$

The functions f_w and f_c are similarity relationships describing z/L dependence.

$$f_w(z/L) = (1 + 3|z/L|)^{1/3} \quad z/L < 0 \quad (11a)$$

$$f_w(z/L) = 1 + 0.2 z/L \quad z/L > 0 \quad (11b)$$

$$f_c(z/L) = (1 + 20|z/L|)^{-1/3} \quad z/L < 0 \quad (12a)$$

$$f_c(z/L) = 1 + 1.0 (z/L)^{1/2} \quad z/L > 0 \quad (12b)$$

One coauthor (Fairall) has studied the stability dependence of τ_{wc} using flux observations made from R/P Flip during the SCOPE field program, in an Eastern Pacific

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stratocumulus regime. Estimates of τ_{wc} were obtained from the f_{max} of cospectra ($f C_{wc}(f)$) and individual variance spectra (where $f_{max} = \sqrt{f_{max,c} f_{max,w}}$). A fit to these data yields a value of $b = 2.8$ in (10) and the following empirical relationship for $f_{\tau}(z/L)$.

$$f_{\tau}(z/L) = [\min(5, \max(0.5, (1 + 0.6z/L)))]^{-1} \quad (13)$$

Equations (9-13) allow an estimate of ΔF_c from (8) in terms of u^* , L , Φ_{c_n} and $\overline{u_r}$. Figure 8 shows the stability dependence of Eq. (8) for typical conditions: $z = 18$ m, $\overline{u_r} = 8$ m s⁻¹, $u^* = 0.28$ m s⁻¹, $F_0 = 1$ pptv m s⁻¹ (3.6 μ moles m⁻² d⁻¹), and $\Phi_{c_n} = 4$ pptv² Hz⁻¹. In general, uncertainty is much larger under stable atmospheric conditions ($z/L > 0$) and for this example the contribution from white noise is seen to be less than 10% of the total error.

For DMS several parameters in (8) are conveniently estimated directly from the measurements. The turbulent variance in DMS, σ_{ca} , may be estimated as the square root of the second point in DMS autocovariance, as illustrated in Figure 4, and σ_w is computed directly from motion corrected wind data. Φ_{c_n} in (8) may be estimated as the mean of the DMS variance spectrum from 5 to 10 Hz, where white noise from counting statistics predominates. For the APIMS, Φ_{c_n} is typically in the range of 1-7 pptv² Hz⁻¹. Accurate determination of τ_{wc} from a single cospectrum or variance spectrum is subject to considerable uncertainty, however, and we therefore use the empirical relationships in (10) and (13).

Figure 9 shows a comparison between error computed from hourly observations via Eq. (8) and the observed relative standard deviation (RSD) of the observations versus 10-meter neutral wind speed, U_{10N} , during the Southern Ocean GASEX project. Obukhov length (L) and U_{10N} are obtained from standard output of the NOAA COARE bulk flux model (Fairall et al., 1996, 2003). To compensate for additional environmental sources of variance in the observations, we have normalized the observed flux and

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computed flux error to sea water DMS concentration, and further restrict observations to a narrow sea surface temperature range (SST = 4-7 deg C). Computed error is further normalized to yield relative error. Figure 8 therefore presents the relative error and observed RSD in DMS transfer velocity ($\Delta k_{DMS}/k_{DMS}$) over a limited temperature range, binned by wind speed (n=329). We find the computed error is in general agreement with the observed RSD of the observations when the constant $a = 2$ in Eq. (8).

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Fig. 8. Computed absolute flux error as a function of atmospheric stability (z/L). Error is computed from Equations (8-13) for the following conditions: $z = 18$ m, $\overline{u_r} = 8$ m s⁻¹, $u^* = 0.28$ m s⁻¹, $F_{0,dms} = 1$ pptv m s⁻¹ (3.6 μ moles m⁻² d⁻¹), and $\Phi_{c_n} = 4$ pptv² Hz⁻¹. The contribution of noise from the second term in Eq. (8) is small, but becomes a larger fraction of the total for unstable conditions ($z/L < 0$).

Fig. 9. Computed relative error and RSD of the observations from the Southern Ocean GASEX project. Flux results were selected for a narrow range of sea surface temperatures (4-7 deg C). Error was computed for each hourly observation ($n=329$) from equation (8) with constant $a = 2$. Observed flux and computed error were normalized to the observed sea water DMS concentration, yielding transfer velocity: k_{dms} and Δk_{dms} . Absolute error was further normalized to yield relative error and the RSD of the observations was computed. These results were binned by the 10-meter neutral stability wind speed, U_{10N} . The binned computed error (red line) is in general agreement with observed relative standard deviation of the binned observations (blue symbols). The white noise error contribution from the second term in (8) (green line) is less than 20 percent of total uncertainty for this data set.

The figures can be found on the next pages.

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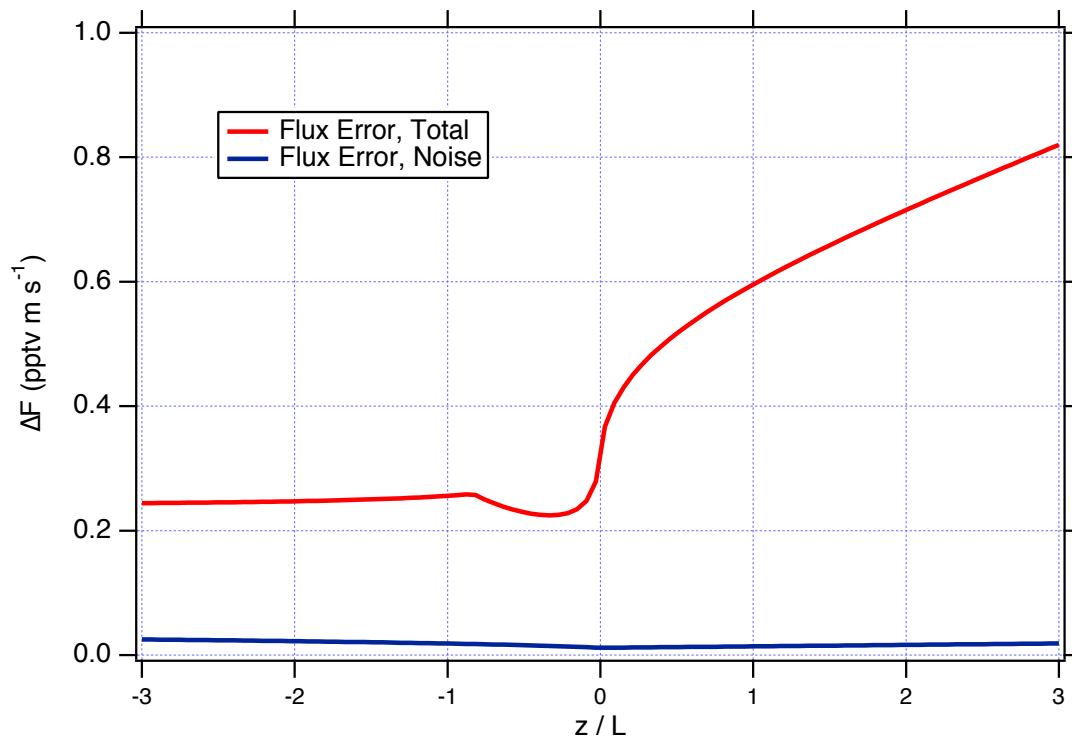
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Fig. 8.

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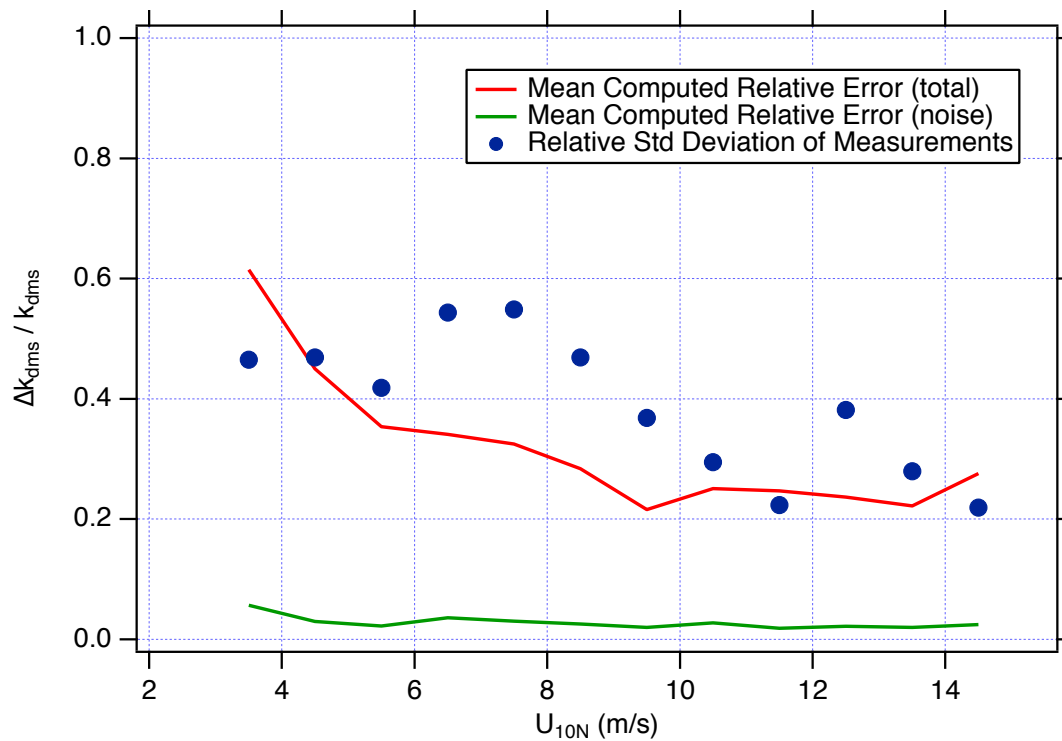


Fig. 9.

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