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**Atmospheric Measurement Techniques Discussions**

# *Interactive comment on* "Direct measurement of the oceanic carbon monoxide flux by eddy correlation" *by* B. W. Blomquist et al.

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## Response to Anonymous Referees

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We would like to thank the reviewers for commenting on the paper and will address their general and specific comments as clearly as possible.

### 1 General Comments, Referee 1

*With respect to data quality and error issues:* We agree the data set presented here is indeed brief. The CO analyzer was borrowed from the manufacturer for this work and we were only able to deploy it on a short test cruise. Our intent in submitting this article is to 1) present evidence that air-sea flux measurements of CO are feasible with current state-of-the-art instrumentation, and 2) examine the error related to departure from stationary conditions (as reference, see Businger (1986)). In the first case, the development of an eddy correlation flux method is significant because CO is an interesting tracer for a variety of biological, photochemical and physical processes in the ocean surface mixed layer. CO also presents an ideal low solubility species for the study of air-sea gas transfer in-situ. The second point with respect to stationarity is of wider interest, as the effects of non-stationarity in CO may illustrate similar chal-

lenges to flux measurement of other long lived trace gases with comparatively high background atmospheric concentrations.

The cospectrum is noisy, indicative of a flux measurement near the detection limit. This is often the case for trace gas fluxes over the ocean, and many hours of data may be required to reveal the expected features of a classic surface flux cospectrum. In this case the cospectrum in Figure 5 is the average of a about 35 selected early afternoon 10-min data segments. The cospectrum integral is positive as expected, but the shape is dominated by noise. The variance spectrum (Figure 1 in the paper) is a mean of more than 400 spectra and clearly shows the expected -5/3 dependence from turbulent dissipation.

To investigate the error issue in greater detail, we recently completed an analysis of theoretical flux error as a function of air-sea concentration gradient ($\Delta P_{CO}$) and wind speed ($u$). Flux error may be specified as a function of variance in both wind and scalar measurements, where the scalar (CO) variance is composed of an atmospheric vertical turbulent flux component ($\sigma^2_{co_a}$) and an "other noise variance" component, $\sigma^2_{co_n}$ (e.g. analyzer white noise, etc.), and T is sampling time in seconds (after Fairall et al. (2000)).

$$\delta F_{co} = \frac{2\,\sigma_w}{\sqrt{T}} \left[ \sigma^2_{co_a} \tau_{w\,co} + \sigma^2_{co_n} \tau_{co_n} \right]^{1/2} \tag{1}$$

The two terms are assumed to be independent, with characteristic integral time scales ($\tau$). From nighttime flux measurements under conditions where $\Delta P_{CO}$ is very low (and therefore $\sigma^2_{co_a} \sim 0$) we can solve (1) for the "other noise" variance term. Then, using similarity relationships to represent $\sigma^2_{co_a}$, $\sigma_w$ and $\tau_{w\,co}$, and employing empirical functions for the stability dependence of these parameters (Blomquist et al. (2010)), we derive an expression for error as a function of flux magnitude and wind speed. This can be further extended to a relationship between $\Delta P_{CO}$ and $u$ (2) by assuming an arbitrary error condition (e.g. $\delta F/F = 1$, or 100% error) and a wind speed dependent model for the gas transfer coefficient. (The entire derivation is rather lengthy, but can



be presented in the text or appendix of the article if the editor wishes).

$$\Delta P_{CO} = \frac{2 \times 1.25 u_*\, f_w(z/L)}{\alpha\, k(u)\, \sqrt{3600}} \left[ \left( \frac{3\, F_c\, f_c(z/L)}{u_*} \right)^2 \frac{2.8\, z\, f_\tau(z/L)}{\overline{u_r}} + 0.00041 \right]^{1/2} \tag{2}$$

Here, $F_c$ is the CO flux, $f_i(z/L)$ are functions defining stability dependence (unity for neutral conditions), $z$ is measurement height, $L$ is the Obukhof length, $u_*$ is friction velocity, $\overline{u_r}$ is mean relative wind speed, $\alpha$ is dimensionless solubility, and $k(u)$ is the gas exchange transfer coefficient. For CO, $k(u)$ may be estimated from a cubic wind speed dependence as in Edson et al. (2011).

The relationship between $\Delta P_{CO}$ and $u$ from (2) is shown in Figure 1 below. This curve should be a theoretical limit under ideal stationary conditions (the similarity functions assume stationarity) but in fact may be an upper limit, as $\sigma^2_{co_a}$ is not exactly zero in the empirical determination of the "other error" and some additional variance arising from non-stationarity may also be present. We also note that, other things being equal, as SST decreases so does $\Delta P_{CO}$ and error conditions for the flux measurement become more stringent.

Peak early afternoon conditions for this field trial ($\Delta P_{CO} = 1700$ ppb, $u = 10$ m/s) lie a factor of 3 above the curve in Figure 1 below, implying an expected error of 33% for hourly mean flux. This is approximately the observed error in peak afternoon mean hourly flux values from Figure 3 of the article (22 - 37% relative error at 1-3 PM local time). Values in this figure represent the average of all valid 10-minute flux measurements for each hour over two days, but in some cases the hourly means include only a little more than one hour of actual sampling time due to the selection process described in the article and illustrated in Figure 4. The effects of non-stationarity were significant. Removing 10-minute flux values which exhibit excessive horizontal flux or $\partial CO/\partial t$ (Figure 4 in the article) is critical to reducing error to near the theoretical limit and resolving the diel cycle.

In practice, ideal stationarity is never realized in the field. The question "How much

non-stationarity is too much?" is an interesting one. The answer probably depends on the nature of the scalar and the scientific question to be addressed. Criteria are often somewhat subjective. In this case, 10-minute values plotted in Figure 4 of the article show a clear central cluster surrounded by a widely scattered cloud of outliers. Limits were chosen to include the densest portion of the central cluster. Furthermore, it is apparent from this figure that $\partial CO/\partial t$ shows the greatest range as an indicator of non-stationary conditions, but it is not always sufficient. Some samples exhibit significant horizontal turbulent flux and low $\partial CO/\partial t$. It therefore seems wise to examine stationarity from a variety of perspectives.

The comparison between CO and DMS flux measurements in Table 1 is meant to illustrate potential stationarity issues for gases such as CO with long atmospheric lifetimes, relatively high mean background concentrations, and vigorous sources and sinks. The magnitude of the air-sea CO flux is small enough that even modest horizontal atmospheric gradients generate scalar variance from horizontal turbulent diffusion many times greater than the variance from surface flux, leading to longer required integration times and more stringent selection criteria. The magnitude of DMS surface flux is similar to CO, as shown in Table 1, but the atmospheric lifetime of DMS is much shorter and the mean background concentration is 1000 times less. For DMS, turbulent diffusion of horizontal gradients is therefore less problematic.

We feel the results presented, obtained under challenging conditions, demonstrate the feasibility of CO flux measurements from ships. In locations where seawater CO concentrations are higher (e.g. high latitudes in summer or Pacific equatorial regions) measurement precision should be improved. Furthermore, the analysis of expected error and stationarity issues leads to generally important conclusions which may be pertinent to flux measurement of other long lived trace gases, such as carbon dioxide.



## 2 Specific Comments, Referee 1

We can certainly add detail on the experimental setup. The sampling inlet, wind and motion measurement system, data acquisition system, and flux computation methodology are identical to the description presented in our DMS manuscript (Blomquist et al. (2010)). This was cited, but we can specify the details explicitly if the editor prefers. With respect to the referee's questions:

1) *What was the anemometer used? How far the air inlet was from the anemometer and was it covered with a mesh?* The anemometer was a Gill model R2 mounted at the top of a 10m tower on the ship's bow deck. The air sampling inlet and 6-channel motion system were mounted 0.8m below the sonic volume. Mesh was not used.

2) *The method to calculate flux values is different than typically used in EC measurements so a reference would be good in the manuscript or more detailed description of data handling.* Flux was computed as the integral of the cospectrum as described in paragraph 3 of Section 3, where wind data are corrected for ship motion (Edson et al. (1998)) and an hourly 3 second pulse of nitrogen into the inlet tip facilitates synchronization of the two signals. The spike in the CO response recorded by the analyzer is aligned with the pulse trigger recorded by the data system on the same time base with wind and motion. Inlet lag time was measured at $\sim$1.6 seconds.

3) *Was any of the hours removed by unstationary conditions? Were other flux quality tests done?* The stationarity criteria are described in the article and the response above and illustrated in Figure 4 of the article. Other selection criteria to improve flux quality are described in paragraph 4 of Section 3.

4) *What was the data coverage over the two day period?* Data acquisition was continuous, but roughly one-third of the 10-minute flux values over the 2 day period were eliminated, primarily on the basis of relative wind direction and stationarity criteria.

5) *Were the measurements above the detection limit of the instrument?* For CO, be-

cause the background atmospheric concentration is so large (100 ppb or more), measurements are always well above the detection limit of the analyzer. The more critical parameter is precision (signal-to-noise) and in that respect the current generation of infrared absorption laser spectrometers offer a significant improvement (Figure 1 in the article).

6) *No information about the tube attenuation is given or if it was corrected and if it was not corrected, what kind of errors does it bring to the flux values.* The inlet system has been used extensively for DMS and the transfer characteristics studied in detail (Blomquist et al. (2010)). At flow rates $\geq$ 80 $L\ min^{-1}$, frequency attenuation in the main sample line is not significant; the half-power frequency is $\sim$ 10 Hz. The Nafion air dryer produces the greatest signal attenuation, lowering the half-power to $\sim$ 1-2 Hz. The actual frequency response of the CO analyzer in this configuration is quoted by the manufacturer at 1-2 Hz as well.

Using this inlet system for DMS we have consistently found a flux attenuation correction of 4-5% at wind speeds comparable to this test. We therefore applied the same correction to the CO flux. A more thorough examination of flux losses is warranted, but we did not have the analyzer long enough to complete these tests. The bias error associated with imprecision in this correction is unlikely to alter the conclusions of this report.

7) *Part of the experimental part is in strange locations: text related to flux calculation methodology (P4813, L1-13) should not be in the results part.* We agree, and can move this text to the experimental section, adding additional detail given above and hopefully avoiding potential confusion.

8) *The used time averaging is not clear throughout the manuscript and in some cases 10- or 30-min flux values are used.* As described in the text, all flux is computed in 10-minute data segments. Subsequent averaging to hourly time scales, or hourly bin averaging to a 24 hour diel cycle, is done from 10-minute flux values with out-of-sector



wind and non-stationary periods eliminated.

9) *P4813, L18: Equation should be given.* The transfer coefficient at the reference Schmidt number 660 ($k_{660}$) is computed as

$$k_{co,660} = \frac{F_{co}}{\alpha_{co}\,\Delta P_{co}} \left( \frac{Sc_{co}}{660} \right)^{1/2} \tag{3}$$

where $F_{co}$ is the flux in ppb m/s, $\alpha_{co}$ the dimensionless solubility of CO in seawater at ambient SST, $\Delta P_{co}$ the interfacial concentration gradient in ppb, and $Sc_{co}$ is the Schmidt number for CO in seawater at ambient SST and salinity.

10) *P4814, L11: Variables in the equation are not listed.* Variables in this equation are defined in equations 1 and 2 above. Once these are added to the manuscript the meaning will be clear. We will alter the notation $c'$ to $co'$ to be clear the equation refers to the scalar (CO) concentration.

11) *P4814, L12-17: In the manuscript comparisons are made to DMS flux measurements from different time. DMS is not explained and the whole comparison between DMS and CO remains unclear. Also no error limits for the different values in Table 1 are given.* The comparison with DMS flux, as described in the text and in this response above, is solely to illustrate error arising from non-stationary conditions for gases with a high background concentration, like CO. The air-sea flux for these gases is often quite small compared to the potential magnitude of other turbulent diffusion processes in the atmosphere.

12) *Figures 1 and 5: How many 10-min samples were used in the plots?* As mentioned above, roughly one-third of the 10-minute flux values were eliminated. There were about 600 10-minute values (remember, they overlap in time by 50%). About 400 10-minute spectra were averaged in Figure 1. For Figure 5, only selected 10-minute spectra from 1-3 PM local time were averaged ($N = 35$). This is why the Figure 5 cospectrum is much noisier than the variance spectrum in Figure 1. We can make this

clear in the caption to the figures. Figure 5 is meant to illustrate that after eliminating periods of excessive non-stationarity, the magnitude of horizontal flux is still several times greater than the vertical flux.

## References


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