**Response to reviewer's comments on MS # amt-2009-33 by Bariteau et al.**

We appreciate the constructive comments by both anonymous referees and by M. Gallagher on our manuscript. Their contributions have been very helpful in further improving our paper. We have rewritten the manuscript incorporating most of their suggestions. Below, we provide a point by point response to the raised questions. For clarity, we first list the referee comment, and then our response (Authors' Response) in the following.

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Anonymous Referee #1

*General comments: This is a very detailed and thorough description of an eddy covariance technique for measuring ozone deposition on ship platforms. The authors are very meticulous in their description and analysis of the data. There is nothing necessarily new in either the ozone instrumentation or in the analysis of the eddy covariance flux data; it is just done very well and extremely carefully. This concern for detail is necessary to obtain quality ship-borne ozone flux measurements since the fluxes tend to be very small and can be overwhelmed by improper corrections or biases introduced by ship motions, etc. It is well-written and the figures adequately convey the authors' points. This paper merits publication with only a few minor considerations.*

*Specific Comments:*

*(1) Page 1942, section on Lag Time. During the TexAQS campaign, the authors observed an increase in lag time within their inlet tubing as the inlet filter became increasingly clogged. Is there any evidence for loss of ozone on the dirty filter (or perhaps a dampening of the ozone fluctuations?). I would be more concerned with this aspect of the contamination build-up on the inlet filter than with the changing lag time – which they show has only a relatively small (+/- 6%) effect on their fluxes.*

Authors' Response: As mentioned in the section 'Lag Time', during STRATUS-06 we observed a gradual loss of the instrument sensitivity during calibration runs. This effect was found to be due to accumulation of contaminants in the line. Subsequent experiments with decreasing sampling line purge rates revealed that an increasing portion of the ozone signal was lost as the flow rate decreased. Lower sampling line purge rates will have two effects, i.e. a decrease in the face velocity of the sample air being pulled through the inlet filter, and an increase in the length of the transport time of the sample air to the analyzer. We have not yet carefully investigated the influence of the sample line purge rate on the ozone power spectrum as most of our experiments are run at a constant, well-controlled sampling rate. The few data analyses conducted to date on

data from varying sampling line purge rates (lag times) have not shown evidence of a dampening of the ozone fluctuations.

*(2) Page 1950. The authors make the statement (in two different places) that an increase in the mean ozone flux leads to a decrease in the deposition velocity. This may only be in the semantics or definition of what an "increase" is – but intuition would suggest "an increase in the mean ozone flux" would be a flux of larger magnitude (for deposition - a larger negative flux with respect to the atmosphere). This would mean a larger deposition velocity (Vd(z) = - Flux/Concentration). I would also note that nowhere in this paper is the deposition velocity defined and it should also be noted that the Vd is defined at the measurement height (Vd is a function of height).*

Authors' Response: The ambiguity resides indeed in the semantics. An increase in the mean ozone flux corresponds to a flux of smaller magnitude (as ozone fluxes are negative), thus a smaller deposition velocity (decrease). The definition of deposition velocity (Vd(z) = - Flux/Concentration) has been added to the revised manuscript version.

*(3) Flux corrections for water vapor fluctuations are always problematic, especially in oceanic measurements, and I commend the authors for their detailed approach to this problem, but a few more aspects need to be mentioned:*

*a. From the description on page 1950, the authors use the fast H2O vapor measurements from the open path hygrometer to apply point-to-point density corrections of the ozone density for water vapor. However, this assumes that the lag time for H2O vapor and ozone in their inlet line is the same. That is not always the case – it is often observed that lag times for H2O are often 0.1-0.2 sec delayed from other scalars such as CO2. While this is likely a relatively small effect, it may be worth varying the H2O lag time by a few samples to quantitate this possible effect. Otherwise, the density correction can also be applied to the calculated covariance directly (not correcting each ozone density measurement individually) using the water vapor flux (see Webb et al., 1980 reference).*

Authors' Response: This is in interesting point. It is regrettable that the reviewer did not provide more specific details under which sampling conditions the 0.1-0.2 s delay was observed. Ibrom et al. (2007) found significant differences in lag time between $CO_2$ and water vapor. The phase effects in the tubing may be different from one closed-path system to another. The delay in the water vapor signal is expected to depend on a number or experimental variables, such as the length of the sampling tubing, tubing material, flow rate, degree of turbulent flow in the sample line, and overall residence time in the tubing. We have not evaluated the $H_2O$ lag explicitly, and we do not have an estimate if and by how much the water vapor signal would be delayed for our conditions. However, the Webb correction also was applied using the water vapor flux and yielded practically the same results as point-to-point density corrections. This shows that in our case decoupling between $H_2O$ vapor and ozone had negligible effect.

This issue has been added to the revised manuscript version.

Reference:
Ibrom, A., Dellwik, E., Larsen, S.E., Pilegaard, K., 2007: On the use of the Webb–Pearman–Leuning theory for closed-path eddy correlation measurements. Tellus 59, 937–946.

*b. The addition of the Nafion dryer appears to be a nice way to reduce the water vapor corrections to the flux; however, there is no mention of whether there is a loss of ozone in the dryer or a dampening of the ozone fluctuations (which are the basis of the flux calculation). Ozone power spectra with and without the dryer may be a good addition to the Supplement (along with the shown water vapor spectra) and some mention of the ozone loss (or lack thereof) in the dryer.*

Authors' Response: There is very little loss of ozone in the Nafion dryer under the conditions we apply in our system. Tests have shown a less than 2% change in the ozone sensitivity from use of the dryer. Since the instrument is regularly calibrated with the Nafion dryer in line, there is no need to accurately quantify the change in ozone sensitivity. We have not explicitly investigated potential losses in the high frequency range of the ozone spectrum. However, we plan to investigate this question in future deployments. This issue has been added to the revised version.

*(4) Figure 14. A better representation of the variance spectrum may be obtained by multiplying the spectral density (y-axis) by frequency. This allows the reader to clearly see the falloff curve at high frequencies typical of atmospheric turbulence and the frequency where white noise becomes important (indicated by a slope of +1).*

Authors' Response: The plot has been changed as suggested by the reviewer. We are now showing the normalized power spectrum, with two lines added that show the slope of +1 and the white noise level at $2.3\times10^{-2}$ ppbv$^2$ Hz$^{-1}$.

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Anonymous Referee #2

*General Comments: This paper presents the first open ocean ozone eddy correlation (EC) flux measurements. This is a very important step in understanding the controls on open ocean gas transfer. There is a great need for direct flux measurements of a range of trace gases that are influenced by different chemical, biological, and physical processes. The technique and data analysis are presented clearly and thoroughly. This paper should be published with minor corrections.*

*Specific Comments:*

*Pg. 1934, Abstract – Perhaps it would be nice to see the range of deposition velocities or fluxes measured using this technique in the abstract.*

Authors' Response: A sentence summarizing the range of deposition velocities has been added to the abstract.

*Pg. 1935, line 6 – It is stated that EC is the preferred method for the measurement of gas fluxes but there is a paucity of references to previously reported open ocean flux measurements.*

Authors' Response: EC is the preferred method for the measurement of gas fluxes, but the lack of references is on direct observations of open oceanic ozone fluxes. Some other gas fluxes, i.e. $CO_2$ and DMS have been successfully measured by EC from ship-borne platforms. This point has been clarified in the revised paper and references have been added.

Reference examples for oceanic DMS flux measurements:

Blomquist, B. W., C. W. Fairall, B. J. Huebert, D. J. Kieber, and G. R. Westby, 2006, DMS sea-air transfer velocity: Direct measurements by eddy covariance and parameterization based on the NOAA/COARE gas transfer model, Geophys. Res. Lett., **33**, L07601, doi:10.1029/2006GL025735.

Huebert, B. J., B. W. Blomquist, J. E. Hare, C. W. Fairall, J. E. Johnson, and T. S. Bates, 2004: Measurement of the sea-air DMS flux and transfer velocity using eddy correlation, Geophys. Res. Lett., **31**, L23113, doi:10.1029/2004GL021567.

Blomquist, B. W., B. J. Huebert and C. W. Fairall, 2009: Determining the sea-air flux of dimethylsulfide by eddy correlation using mass spectrometry, Atmos. Meas. Tech. Discuss., **2**, 1973-2025

Reference examples for oceanic $CO_2$ flux measurements:

McGillis, W. R., J. B. Edson, J. E. Hare, and C. W. Fairall, 2001: Direct covariance air-sea $CO_2$ fluxes, J. Geophys. Res., 106(C8), 16,729–16,746, doi:10.1029/2000JC000506.

McGillis, W. R., et al., 2004: Air-sea $CO_2$ exchange in the equatorial Pacific, J. Geophys. Res., 109, C08S02, doi:10.1029/2003JC002256.

*Pg. 1937, line 23 – The sampling lines were treated prior to use. Is this to avoid ozone absorption on the walls? Does this treatment happen once before installation? Would this treatment be ok for a sampling period longer than those presented here? Would there be any background ozone blanks to worry about with this treatment? Are there any considerations of blanks in the line at all (maybe this is trivial for the measurements)?*

Authors' Response: Ozone is a reactive gas and readily reacts with many organic materials. There are few materials that have been found to be unreactive with ozone. Teflon is one of them. Nonetheless, it is not untypical to observe losses of ozone in new, un-conditioned tubing. Similarly, ozone recovery can be diminished when sample air is pulled through contaminated ("dirty") tubing. We have found that these losses can be avoided by conditioning the tubing first, which is done by purging it for several hours with air enriched with ozone (200-300 ppb). After the tubing has been properly passivated, ozone at ambient levels typically passes through it quantitatively, i.e. with losses < 1-2 %. As ozone reacts away quickly with most materials, it cannot be stored for extended periods. Therefore, memory effects or blanks are typically not a concern with this type of sampling tubing and ozone measurement system. The sentence explaining that the sampling lines were treated prior to use has been re-written.

*Pg. 1938, line 14 – How often were calibrations performed? How were concentrations calculated (by interpolation, or by daily calibrations, or by taking the mean of all the calibrations)? The calibrations were very precise but there were some differences (e.g. DOY 206, what happened there?), which may contribute some uncertainty (scatter) in the flux numbers.*

Authors' Response: Calibrations schedules varied during the different cruises, but were performed regularly, i.e. every 5 days on average. Concentrations were calculated by interpolation between bracketing calibration results for most of the cruises, or by using the mean response factor (such as for GOMECC07). These points were added in the revised paper. The calibration result for DOY206 was an outlier (due to an error in the LabView code used for this measurement). Figure S-4 was corrected and DOY206 was excluded from the shown data.

*Pg. 1940, line 14-18 – Regarding motion correction, just wondering if the ozone detector feels the effect of the ship's motion?*

Authors' Response: The ozone chemiluminescence detector does not appear to respond to the ship's motion. We derived this conclusion from the fact that there is no detectable spike at the frequency of the ship's rolling frequency (~ 0.25 Hz) in the raw ozone spectrum or flux cospectrum. This has been clarified in the revised paper.

*Pg. 1942, line 3 – There is miswording in this sentence, "…transport through the sample though the…".*

Authors' Response: The sentence has been corrected.

*Pg. 1944, line 2 – How often underway would these "puff tests" be performed? There could be slight changes in the tubing delay for other reasons, like pressure waves or pump characteristics, which may change the delay slightly. In Figure 7, when the cross correlation method is compared to the puff method, how close in time are the two measurements made? I am getting at the fact that each 10 minute data set could have a slightly different delay but you can't do a puff test for all the measurements. However, because changes in delay are stated to only have a 6% effect, these are more academic questions than practical ones.*

Authors' Response: Puff tests were performed once a day on average, usually at the beginning of the day. The "puff tests" were performed within the first 10-min bin of the hour and were compared with the 10-min cross-correlation lag time results during that same hour. This has been clarified in the revised paper.

*Pg. 1945, line 1 – Since the puff tests did not show any significant change in the delay time before and after the filter was changed, do the authors still believe that the filter was the cause of the initial change in delay detected by cross correlation? What is the authors' best guess as to why the delay did not change after subsequent filter changes? It is possible that I am missing something here.*

Authors' Response: During the TexAQS 2006 cruise filters were changed after several days, whereas in the GOMECC 2007 filters were changed daily. With the more regular filter changes there was not enough time for particulate matter to accumulate on the filter, which in return led to more constant lag time results. Consequently, while the linear velocity inside the sampling line was more varyable during TexAQS2006, it was constant during GOMECC 2007. This issue has been clarified in the revised paper.

*Pg. 1948, line 22-23 – Do the authors also assume that the low frequency portion of the spectrum is the same for both scalars or is this determined before the high frequency correction? The low frequency end of the cospectra could have some large features that could be very different for ozone than for temperature. It seems that non-stationarity of ozone is examined but is the low frequency end of the temperate cospectrum also considered?*

Authors' Response: For this analysis of the lowpass filter effect of the sampling line, the low frequency portion of the spectra and cospectra are assumed to be the same, on average. For both scalars and we assume the mathematical form (8) is a reasonable approximation. The results compare closely with a different derivation that was used by Horst (1997).

Horst, T. W.: A simple formula for attenuation of eddy fluxes measured with first-order-response scalar sensors, Bound.-Lay. Meteorol., 82, 219–233, 1997.

*Pg. 1949, line 2 and Fig. 9 – I am not sure why the authors chose 0.4 Hz as the cutoff. It appears that the cutoff is 0.3 Hz based on the lines drawn on the plot. This would change their response time to 0.5 s.*

Authors' Response: We determined the fit functions for the best fit lines, and these resulted in a cutoff frequency of 0.4 Hz. This has been clarified in the revised paper.

*Pg. 1951, line 17 – The text reads Eq. 11 but I think it should say Eq. 12.*

Authors' Response: No, Eq. 11 is the correct equation referred to here.

*Pg. 1952, lines 2-12 – Did this filter account for all low frequency features in the 10 min cospectra?*

Authors' Response: Low frequency features in the cospectra are not used explicitly as a filter criterion. Clearly, a significant linear trend will cause some distortion of the low –frequency region. The variance criterion would be sensitive to spectral features regardless of the band. A feature in the variance spectrum may or may not show up in the cospectrum, so this is not a perfect filter. We did not apply an ogive type analysis that would have removed inadequate low frequency features. This has been clarified in the revised manuscript.

*Pg. 1952, line 23 - How was 8 km determined to be open ocean?*

Authors' Response: During the TexAQS 2006 cruise, the ship was sampling along the shore, and the distance to the shore was approximately 8 km. The term 'open ocean' is misused as one should look at the ocean bathymetry as well as other parameters to call it 'open ocean'. The word 'offshore' has been used in the revised paper instead.

*Results – It would be nice to see some plots of F vs. U or F vs. atmospheric ozone concentration. A lot of text here was devoted to the deposition velocity, but since this paper is focusing on flux measurements some flux plots would be nice to see. Also, plots of wind direction or back trajectories would help to illustrate if the concentrations and fluxes were influenced more by land processes or by oceanic process.*

The objective of this manuscript is to present this new ocean ozone flux technique. These further analyses and interpretations will be included in a new manuscript that is currently in preparation.

*Pg. 1954, line 26 – The division sign in the equation is under the square root sign.*

Authors' Response: This error has been corrected.

*References – There is a reference (and citation) to Storch et al or to von Storch. This is a typo. Also, one reference is missing for Lenschow et al.(1982).*

Authors' Response: These references have been edited.

*Figure 1 is bit confusing to follow. It may be helpful if the colored lines were defined in the caption or in a legend.*

Authors' Response: This figure has been revised.

*Figure 3 – The caption contains mistakes. At the end of the sentence describing the STRATUS cruise there is "(magenta)" after it had been defined as red (which appears correct). The last line says the other cruise track is the light colored track but I believe that should say magenta.*

Authors' Response: This error was corrected.

*Fig. 12 – The caption is confusing; there may be a wording problem there. The text regarding this figure is much clearer than the caption. Consider revising the caption to match the text.*

Authors' Response: The figure and caption have been corrected.

*Supplemental material, pg. 7, .line 66 – What is "man of counts"? I guess I don't understand this terminology.*

Authors' Response: The sentence has been corrected to "mean of counts"

*Supplemental material, pg. 7, line 73-75 – The sentence starting with "The other experiment shown…" is a bit awkward. I had trouble understanding it at first. You may want to consider revising.*

Authors' Response: The sentence has been corrected.

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*This paper represents a wonderful technical tour de force for measurement of reactive trace gases to ocean surfaces using the eddy covariance technique and the authors should be congratulated on achieving such a difficult measurement.*

*Could I suggest the authors might like to refer to the work published recently in GRL, Whitehead et al. (2009). In this work ozone eddy covariance flux measurements are presented for an extensive tidal plane at the French coast. Whitehead et al. report ozone deposition velocities to sea water of Vd = 0.0302 cm s-1 +/- 0.0095 cm s-1. This compares very favorably with the*

*authors reported open ocean values from the TexAQS-2006 cruise of Vd=0.036 ±0.003 cm s- 1, which I suggest is remarkably good agreement.*

*The much higher values quoted closer to land (Vd=0.24 cm s-1) by the authors are interesting and require further investigation but are within ranges reported previously for some locations. One might speculate on surface processes enhancing Vd closer to coastal sites in some cases.*

*REFERENCE J. D. Whitehead, G. B. McFiggans, M. W. Gallagher, & M.J. Flynn. Direct linkage between tidally driven coastal ozone deposition fluxes, particle emission fluxes and subsequent CCN formation, GEOPHYSICAL RESEARCH LETTERS, VOL. 36, L04806, doi:10.1029/2008GL035969, 2009.*

Indeed, this nice publication by Whitehead et al. adds valuable discussion to our research, and reference to this work has been added in our revised manuscript.