Author Comment with regard to:

"Air-Sea Fluxes of Oxygenated Volatile Organic Compounds Across the Atlantic Ocean" by M. Yang et al.

May 6, 2014

Many thanks for the constructive *comments and suggestions from Anonymous Referee #2*. Again we are glad to hear that the referee found our contribution valuable. Below are our replies to the specific comments, which are in *italic*.

Anonymous Referee #2

General Comments:
Yang et al. have used PTR-MS to perform eddy covariance (EC) measurements of three atmospherically important oxygenated volatile organic compounds (OVOCs), acetone, acetaldehyde, and methanol. These are among the first EC measurements of these compounds, especially with PTR-MS instrumentation. Certainly, this manuscript is an important contribution to the field and merits publication in ACP. There are some minor revisions needed before publication. Please see specific comments below.

Specific Comments:
Overall manuscript – what is your sign convention? Why do you include the contaminated funnel data instead of removing it and mentioning the contamination as the reason for the removal?

Perhaps this was not written clearly in our manuscript. Data obviously contaminated by the plastic funnel are not included in our quantitative analysis of flux and concentrations. The contaminated data are shown in Fig. 2 and 3 to illustrate the resultant artifacts. (We don't think the reviewer meant this, but in terms of the sign convention of the flux, a positive flux indicates sea-to-air emission.)

Pg 8023, lines 1-8 – How sure are the authors that 500 m depth are appropriate for the precision discussion? It seems that the ocean cycling of these compounds is not exactly pinned down. Why not use replicate standard measurements to determine the precision? Perhaps it is not obvious why these measurements determine the limit of detection and the authors can more clearly explain their logic here.

For the determination of precision and limit of detection, we measured eight replicating subsamples from the same bottle of source water (~ 8 L) taken from 500 m depth at one station. Deep seawater was used as it usually resulted in the lowest OVOC signals (i.e. lower than surface seawater and lower than milliQ water). We did not, as the referee seemed to be implying, estimate precision based on 500 m waters at different stations.

Pg 8028, line 25 until Pg 8029 – It seems that the authors neglect the roll of the oceanic sinks. Perhaps there is greater consumption at 500 m and the depth profile is reflecting *that instead of the production in the photic zone. Maybe previous authors are wrong about the extent of the photochemical source or perhaps the sinks mar the visibility of the signal. Not much is known about the full biogeochemical cycle of these compounds.*

Thanks for the comment. While a greater consumption of these compounds at depth would also explain the lower concentrations observed at 500 m, works from Dixon et al. (2012, 2013) suggest that microbial oxidations of these compounds are generally slower at depth than near the surface.

Pg 8030, lines 1 - 11 – The authors do not have an extensive comparison with previous work here. How does their calculation fit into atmospheric budget of acetone? Would the budget be balanced with their value(s)? How does it compare with known photo-chemistry in the atmosphere? What about the comparison with the Jacob budget or with Marandino et al (the values here are very different than their reported values)?

Thanks for the suggestion. A more extensive comparison has been added now. Briefly, our globally averaged net acetone fluxes are close in magnitude to the estimates from Jacob et al. 2002 and Fischer et al. 2012. The eddy covariance acetone flux from Marandino et al. 2005 was always into the ocean; from that they estimated a much larger oceanic sink of acetone, which is comparable to our gross acetone deposition (i.e. no ocean emission). If they had used their bulk air/sea concentrations (which show both deposition and emission) to estimate the global air-sea flux, they likely would have arrived at a much smaller sink on average.
Given the large range in the atmospheric inventory of acetone (3.8~7.2 Tg, as summarized by Fischer et al. 2012) and uncertainties in the other source/sink terms, it is not obvious to say which air-sea estimate best fits the atmospheric budget.

App B – The authors' hypothesis about acetaldehyde concentrations in the catalytic converter could be tested with standard additions – did they attempt this and if so what happened? If not, why not? I do not understand why air equilibrated with water was not then passed through the catalytic converter (instead of bypassing the equilibrator)?

In a lab test, we had water laden with acetaldehyde passing through the membrane, and routed the existing gas through the catalytic converter and into the PTR-MS. However, the catalytic converter did not remove much acetaldehyde even after ten minutes of flushing. We think the catalyst works inefficiently in this case because the carrier gas is nitrogen (i.e. little oxygen for combustion), and the gas existing the membrane is very moist. For air sampling, the difference in acetaldehyde background between air cleaned by the catalyst and pure nitrogen scaled to approximately half of the total acetaldehyde concentration.

Pg 8035, line 26 - typo controlled should be control

Thanks. This has been corrected.

Figure 3 – why is the spectrum of potentially contaminated data used for this figure? Can't the authors compare with a better flux run?

We could find a better cospectrum for methanol, certainly. For acetone and acetaldehyde, the largest delta C (air-sea concentration gradient) occurred in the Northern Hemisphere, where unfortunately our measurements of those compounds were contaminated by the funnel. While contamination was not an issue in the Southern Hemisphere, there was also hardly any delta C (or flux) there to measure. Here we just wanted to show the cospectra of all three OVOCs concurrently.

Figure 6b – it would be easier to see the equilibrium values if there was a line indicating it

This line has been added.

Figure 12 – latitude seems to have influence on the correlation, have the authors tried to separate and look at the different relationships (could also be instructive for figure 11)? If certain latitudes have better correlation than others, it is possible that other concurrently measured data can shed some light on the reasons.

We did indeed look at this, but the number of twice-a-day seawater data points becomes more limited in specific latitude bands, weakening the statistics. We do see significant correlations (95% confidence) between the seawater OVOC concentrations in the Tropical Atlantic (15 °N to 7 °S, $n = 13$): $r = 0.65$ (methanol vs. acetone), 0.82 (methanol vs. acetaldehyde), and 0.80 (acetone vs. acetaldehyde), as well as in the South Subtropical Convergence (30 °S to 47 °S, $n = 20$): $r = 0.51$ (methanol vs. acetone), 0.56 (methanol vs. acetaldehyde), and 0.75 (acetone vs. acetaldehyde). However, in general the seawater OVOC concentrations are not significantly correlated with available environmental variables (e.g. Chla, CDOM, SST, O_2).
Separation into different latitude bands might not be as useful for examining atmospheric concentrations, since they are heavily influenced by horizontal transport.