Author Comment with regard to:

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

Apr 4, 2014

Many thanks for the thoughtful *comments and suggestions from Anonymous Referee #1*. We are glad to hear that the referee found our contribution valuable. In order to present the measurement uncertainties more clearly, we have added a table summarizing our main results (fluxes) as well as the associated errors. Below are our replies to the specific comments, which are in *italic*.

Anonymous Referee #1

Acetone, acetaldehyde, and methanol concentrations were measured in air and seawater during the Atlantic Meridional Transect cruise in 2012 from the UK to Chile (49N to 39S). The AMT cruise was also equipped to measure fluxes of these species across the air-sea interface via the Eddie-Covariance (EC) technique utilizing a PTR-MS instrument. These flux measurements are compared with estimates of air-sea exchange using film models as well as previously published data. A somewhat identical experiment along the same track also occurred in 2009 but did not include direct flux measurements. These OVOC are important components of the atmosphere and a quantitative understanding of their oceanic source-sink relationship remains poorly understood. In that sense the manuscript adds valuable information and should be published.

The paper adds little that is fundamentally new knowledge but direct flux measurements are novel. Papers previously published by these authors (Beale et al., 2013; Yang et al., 2013b) also cover much of the same ground.

We would like to state that concurrent measurements of atmospheric and seawater OVOC concentrations are very rare. Beale et al. (2013) used atmospheric concentrations from a chemical transport model to predict air-sea OVOC fluxes. Our directly measured (e.g. EC) and predicted (based on in-situ concentrations) fluxes over the basin-wide coverage of the AMT are unique, and should help constrain future modeling estimates.

There are many measurement issues (interferences & detection limits) that are discussed here and there but hard to fully understand. There is little insight offered when large disagreement between EC flux and film models is observed (e. g. acetaldehyde). The paper should be shortened and reorganized to make it easier to read and understand. Here are some suggestions:

- Introduction is somewhat randomly organized with limited references and discusses many numbers from the literature that are hard to keep track of. Suggest creating a table that summarizes these data from literature and discuss briefly. In fact such an approach is used by your co-author in Beale et al (2013; Table 3) that contains much of the information being discussed here.

We have decided that global values of air-sea transport are not the focus of this paper. Extrapolations of our measurements from one cruise to the global oceans will certainly lead to significant errors. Thus we will simplify the introduction section, present the range of previous global estimates of air-sea transport, and refer to the summary from Beale et al. (2013) when appropriate.

The verbiage in the last paragraph about PTR-MS can be handled via citations as this is a commonly used instrument much discussed already by your group and others.

Thanks for the suggestion. This has been changed.

- A key issue is the PTR-MS detection sensitivity and role of interferences. 2-min average detection limits for acetone, acetaldehyde and methanol of 0.02, 0.02, and 0.05 ppb are provided (Page 8021-Line 27). However the EC data used is much higher resolution. What are the detection limit for 1-s or 10-s resolution?

At high frequencies, instrument noise contributes significantly to the variability of the signal. The detection limit for air concentration depends not only on total sampling frequency, but also on the dwell time of the PTR-MS at the m/z of interest. At a dwell time of 100 ms each at m/z of 59, 45, and 33 and a total sampling frequency of ~2.1 Hz, the noise (1 sigma) of raw data is about 0.1, 0.1, 0.2 ppb for acetone, acetaldehyde, and methanol, respectively. At 10-s resolution, the noise is reduced to 0.03, 0.04, and 0.05 ppb. The detection limit is considered to be three times the noise. This is now added to the manuscript.

It could be that the entire analysis of acetaldehyde is faulty for lack of a suitable measurement sensitivity on top of unstable standards. Could this be the main reason why EC flux and film model estimate disagree so much?

The detection limit for EC acetaldehyde flux is about 4 μmoles m^{-2} d^{-1} hourly and 2 μmoles m^{-2} d^{-1} for the latitudinal average (~6 hour). As shown in Table 1 below, the predicted flux is small and very close to the EC flux detection limit. Considering the uncertainties in EC flux and propagated errors in predicted flux, the directly measured and predicted fluxes are not inconsistent.

Was there any ozone interference for acetaldehyde as has been previously reported by others? Was O3 measured? Suggest that you discuss the issue of "sensitivity and interferences" for your molecules of interest in a single place and not have it scattered all over.

Thanks for the question. O3 was measured on this cruise (U. York) and does not demonstrate any relationship with atmospheric acetaldehyde. Previous reports of O3 interference (e.g. Northway et al. 2004; Apel et al 2008) suggest heterogeneous acetaldehyde formation in the tubing. For our EC acetaldehyde flux to match better with flux predicted using the two-layer model, one possibility would be a negative bias in the measured atmospheric acetaldehyde concentration (i.e. if the actual atmospheric acetaldehyde concentration were higher than measured). Thus O3-related acetaldehyde formation in the inlet does not seem to be an explanation for this discrepancy.

Thanks for the suggestion with regard to the paper structure. We have now moved the section of flux uncertainties to Appendix, along with other discussions of measurement uncertainties.

- Much is made of the difference between the use of H and H for acetaldehyde (Page 8031-8032 & Fig 8). This should be stated in one sentence in the text. It has been known for 30 years that the correct thing to use here is H*. Unnecessary use of H mainly causes confusion but adds little new information.*

We have shortened this section. Indeed the discussion on H and H* for compounds subject to aqueous reactions is not new within certain scientific communities (e.g. air-sea gas exchange). However, we still think it is worthwhile to present this issue in detail within the much larger atmosphere/ocean biogeochemistry community.

Our EC measurements illustrate that the true acetaldehyde flux is unlikely to be much higher (e.g. if chemical enhancement were large), otherwise it would have been clearly detected with EC.

- The fact that the experiment was done in 2012 only appears once in the abstract. Add dates and lat-long info in Page 8019 (top para). Also add year in Fig 1.
-Page 8017-Line 7: Singh et al. (2003) - Page 8046-Line 6: Singh, H.

Thanks for the suggestion. These have been changed accordingly.

Table 1. Summary of fluxes (*μmoles m^{-2} d^{-1}*) and associated uncertainties in parenthesis

	EC Flux	Predicted Net Flux	Bulk Deposition	Bulk Emission
50N~40N				
Acetone	-4.8 (3.5)	-7.8 (3.3)	-11.1 (4.4)	3.3 (1.2)
Acetaldehyde	0.8 (3.1)	3.9 (2.0)	-2.7 (1.0)	6.6 (2.3)
Methanol	-12.3 (3.9)	-10.5 (2.9)	-12.8 (2.9)	2.3 (1.0)
39N~3N				
Acetone	3.3 (3.2)	3.0 (3.2)	-8.8 (3.2)	11.8 (4.2)
Acetaldehyde	0.9 (2.4)	4.0 (1.5)	-2.5 (0.9)	6.5 (2.4)
Methanol	-12.7 (3.1)	-9.2 (2.6)	-12.3 (2.7)	3.1 (1.4)
2N~47S				
Acetone	-0.5 (2.3)	1.0 (1.1)	-3.4 (1.2)	4.4 (1.0)
Acetaldehyde	0.4 (2.1)	2.4 (1.0)	-1.5 (0.5)	3.9 (1.4)
Methanol	-8.0 (2.6)	-4.3 (1.4)	-6.5 (1.5)	2.2 (1.0)

Uncertainty in EC flux according to Blomquist et al. (2010).

Uncertainty in predicted/bulk fluxes propagated from the following uncertainties (~95% confidence level): 20% for airside and waterside transfer velocities; 20% for solubility; 20, 20, 10% for atmospheric concentrations of acetone, acetaldehyde, and methanol, respectively; 10, 10, 30% for seawater concentrations of these compounds.