Author Comments with regard to:

“Vertical fluxes and atmospheric cycling of methanol, acetaldehyde, and acetone in a coastal environment” by M. Yang et al.

May 24, 2013

Much appreciation for the thorough and constructive *comments and suggestions from Anonymous Referee #1*. We agree with the reviewer that the more valuable aspect of the paper is the development and characterization of the method. Given the scarcity of direct flux measurements of OVOCs in coastal regions, we think the biogeochemistry presented is still interesting in its own right. However, the interpretations of observed results are complicated by the non-ideal measurement location and inhomogeneous footprint. Below are our replies to the specific comments, which are in *italic*.

The authors describe how a PTR-MS has been applied to measure fluxes of methanol, acetaldehyde and acetone using eddy correlation from their laboratory roof. This appears to be predominantly a method description paper for a technique that will subsequently be used at sea. The authors have done a thorough job of describing how their fluxes were calculated and the limitations of this approach. There are clearly a great many assumptions necessary to arrive at a flux which leads to a high overall uncertainty. The approach and the data processing are well described. A crude photochemical model is invoked at the end to compare the fluxes and concentrations measured, the differences being generally interpreted in terms of an oceanic source or sink. This last section is very weak, the conclusions drawn on the role of the ocean in atmospheric cycling being heavily dependent on the assumptions within the “model”.

In order to interpret the results in terms of the oceanic effect (as implied by coastal I the title) it would be a major improvement to the paper if the OVOC fluxes presented could be compared to DMS fluxes which could be regarded as definitively oceanic. As the authors state on line 73, when multiple VOCs are measured simultaneously “commonality and difference in the sources and sinks may be inferred.” The authors show that on occasions DMS was measured, why are the fluxes not directly compared? This would immediately show the DMS/OVOC relationship and deliver new insights on these compounds.

Excellent suggestion. This was indeed our intention. Unfortunately we could not clearly detect DMS flux, likely because the expected DMS emission (on the order of a few μmoles m^{-2} d^{-1}) is below the flux detection limit of our system (on the order of 10 μmoles m^{-2} d^{-1}). To quantify DMS flux, a more sensitive and less noisy instrument (e.g. an atmospheric pressure chemical ionization mass spectrometer) would be necessary.

As the paper stands, there is a thorough method section, a crude model, OVOC results that appear not to be consistent with previous ocean based findings (see points below), but may have been influenced by terrestrial indirect sources, direct sources, advection, *horizontal turbulent transport. Besides the method description we have therefore learned little definitive.*

1) Title- This paper is not about the "atmospheric cycling"of the OVOCs it is a method paper with a brief consistency test. Would it not be more appropriate to title this work "Development of a method for OVOC vertical flux measurement by eddy correlation with PTR-MS for the ocean." A discussion of the instrument's suitability for this could then be added.

Thanks for the suggestion. We have changed the title to "Measurements of OVOC Fluxes by Eddy Covariance using a Proton-Transfer Reaction Mass Spectrometer – Method Development at a Coastal Site."

2) Abstract – states methanol does not show a diel cycle, yet the data from figure 2 shows that this is clearly the case for westerly winds.

Changed sentence to "Methanol mixing ratio and flux do not demonstrate consistent diel variability…"

3) The authors refer throughout to "concentrations" in the text but report mixing ratios. Correct throughout.

Suggestion accepted.

4) Line 14. Are the "values" referred to the fluxes of the mixing ratios, be specific.

Replaced "values" with mixing ratios and fluxes"

5) Line 29. Why are these molecules important for "climate"? Presumably the authors mean indirectly over their influence on ozone. The reference Tie et al. 2003 could be helpful here.

Thanks for the reference. We have removed "are important for atmospheric chemistry and climate" from the first sentence, as they are described below in subsequent paragraphs.

6) Line 33. An important missing reference is the paper of Galbally and Kirstine 2002. They describe that growth at night leads to nocturnal emission of methanol from terrestrial vegetation. This behavior was, however, not seen here.

Thanks for the reference, which we have added. Nocturnal emission of methanol could have occurred, but emissions during the day appeared to be much greater.

7) Line 37. Add "such as the oxidation of methane."

Added.

8) Line 42 Add "tropospheric" before ozone.
9) Line 42. radical should be radicals
10) Line Remove comma after dry
11) Lines 55-58. Be specific about direct emissions and indirect photochemical sources, it is not clear in the text.

Suggestions accepted.

12) Line 156. The two funnel construction is not clear to me, please rephrase.

Rephrased to "To keep out rain droplets, the gas inlet was constructed with two opposing funnels with mouths held together, sandwiching a coarse mesh."

13) The humidity dependence of the PTR-MS sensitivity to methanol and acetaldehyde is reasonably significant. Is this also addressed in the determination of mixing ratio?

For methanol, the ambient mixing ratio was derived from the ratio of the ambient signal (m/z 33) to the internal isotopic standard (m/z 36). Any humidity dependence in the PTR-MS is presumably similar for m/z 33 and 36, and thus should not affect the measured mixing ratio. The acetaldehyde mixing ratio was computed directly from the PTR-MS equation (1) and could be subject to humidity effects. Though in our setup, the water dimer (related to humidity) signal represented only ~5% of the water monomer (source ion) signal, suggesting that changes in humidity should not significantly affect the ionization chemistry in the PTR-MS.

14) While I don't think significant acetaldehyde will be generated in the inlet, I disagree with the statement on line 309 that acetaldehyde produced in this way should not depend on vertical wind velocity. This is because ozone is strongly deposited to the ground with the result that clear gradients in ozone exist over the first 100m.

Thanks for the suggestion. We have removed this sentence.

15) Line 317. It would be an interesting addition to the paper to see how the heavy rain affected the OVOC mixing ratios.

We completely agree that the effect of heavy rain on OVOC mixing ratios is of interest. However, we felt that our rain gauge measurement, which was taken every 5 minutes, was not frequent enough to fully capture the precipitation rate and allow a quantitative assessment on the effect on OVOCs.

16) Line 325 "possibly related to anthropogenic activity" is a very weak statement. What evidence is there ? Is there something in this direction, if so what. If there is nothing in particularly different I would recommend removing this speculation.

We made this speculation because the commercial ferry port and naval boatyard are located in that direction.

17) 332 Be quantitative, give sigma values for methanol and acetone for comparison.
18) Line 339. Why "should" methanol flux be several times larger than the acetone flux if mixing ratios are determined by vertical transport, explain. Also it would be helpful to cross reference the section where this is shown later.

Suggestions accepted. A larger flux is expected with the greater fluctuation in mixing ratio based on $F = \overline{w'x'}$.

19) Line 341. The simple explanation for the high methanol at low wind speeds (PBL was likely very shallow) is not very credible. In Sinha et al ACP 2006 a stronger ocean uptake of methanol was seen by night than by day.

While a greater oceanic uptake of methanol at night is possible, it likely wasn't the cause for the one order of magnitude increase in methanol concentration in the early morning (notice the log scale).

20) Line 348. Be specific are you referring to air or seawater measurements?

We were referring to atmospheric mixing ratio.

21) Line 357. Can we really consider nighttime OVOC mixing ratios as baselines as it has been shown by Sinha et al. that clear diel production/uptake cycles exist in the ocean for these species?

Diel production/uptake cycles no doubt exist, but are mostly likely lower in magnitude than terrestrial fluxes.

22) Line 415. How can the observation of a negative flux "confirm" the expected logarithmic profile?

Good point. We just meant to say that the transport of stress is downwards.

23) Line 457-8. Retain the passive. "Compared" and insert "to" before determine. 24) Line 529 Insert "a" before nocturnal
25) Line 542 "Stationarity" spelling.

Corrected.

26) Does the random flux sampling error really represent the total uncertainty in the measurement? Given the large number of assumptions and diverse data treatments I guess not. Please state the overall uncertainty in the measurement either in the error bars or the figure caption so that the reader may judge how to interpret this data. This is an important part of assessing the suitability of this 3 OVOC method for ocean work

The random flux sampling error represents the total uncertainty in the flux measurement from the perspective of instrument sensitivity/noise and natural variability. In an environment where natural variability in atmospheric mixing ratio is lower (expected for the ocean), the flux error will be reduced correspondingly. The suitability of the system for ocean work is in part reflected in the noise contribution to flux error.

27) Line 639. "suggests a pollution source". Why not a loss? Why not a biogenic emission which is presumably not classified as pollution. I think all that can be said here is that the methanol sources and sinks seem to be independent of those of acetaldehyde and acetone.

Thanks for the suggestion. We have rephrased the sentence as such.

28) Line 656. The large positive fluxes for methanol are not expected for an area under ocean influence. Quite the opposite in fact. Here would be a good place to contrast these finding with those of Sinha et al 2006 ACP who consistently found methanol uptake to seawater. It would be interesting to compare the pros and cons of the EC flux approach to the mesocosm and to the seawater/air concentration approach somewhere in the discussion.

Indeed. We think the discrepancy is due to large terrestrial signals within the flux footprint overwhelming the air-sea exchange. It would be difficult to quantitatively compare the EC approach with mesocosm without making side-by-side measurements.

29) Line 688 Insert "the" before acetaldehyde
30) Line 730 sea should be Sea

Corrected.

31) Lines 757. So methanol is clearly dominated by the terrestrial emissions. Presumably acetone and acetaldehyde are similarly heavily influenced if not dominated. With this in mind, and the flux print shown later, is the reference to ocean effects at all justified ?

The ocean undoubtedly influenced the mixing ratios and concentrations we measured. Though it is difficult to partition the contributions from land/water.

32) It would be interesting to have some sort of percent efficiency for this measurement method. i.e. From what fraction of the total measurement time could significant fluxes be measured and generated. How would this change if the method is applied at sea ? Would the lower mixing ratios over the open ocean allow all three species to be measured simultaneously?

The fraction of total flux measurement passing the quality control criteria has been discussed in Section 4.4. The applicability of the instrument for measurement at sea may further be gauged by comparing the expected air-sea flux with the instrumental noise (described in Section 4.3). The first author has taken this EC system to an open ocean cruise at the end of 2012. The results from that cruise will be published elsewhere.

33) Line 761 and onward. Marandino in fact reported large fluxes of acetone to the ocean. Fischer et al disagreed with this being the norm, and pointed to the air measurements being anomalously high, see the paper atmospheric budget section in the Fischer paper.

Thanks for the reference. We meant to say that the predicted deposition of acetone is consistent in sign with flux measurement by Marandino et al. and modeled output from Fisher et al.

34) Line769 in situ to in-situ (and elsewhere)
35) Line 772 reactions to reaction

Corrected.

36) Line 778. Acetone is efficiently produced from the oxidation of monoterpenes. How does this, presumably important production term, affect the budget calculation? The woods on Edgecombe must emit a lot of these species directly, and produce precursors that oxidize to these species later. Likewise, can ozone reactions with alkenes at night not produce acetaldehyde ?
37) A table summarizing the reactions and assumed yields included in the estimate would be helpful.

The simple atmospheric chemistry calculations were made as sanity checks for our flux measurements. Much more detailed reactions are already described in global models (e.g. Millet et al 2008, 2010; Jacob et al. 2002) and probably don't worth repeating here (especially since the paper is already long). Given the low ozone mixing ratio in the region, nighttime reaction with alkenes probably wasn't a large source of acetaldehyde. Lacking in-situ measurements of monoterpenes (beyond the mass scan range of the PTR-MS), we could not speculate on the production of acetone from this precursor.

38) Lines743 and on in this paragraph. It should be noted that Marandino et al. 2004 show that fluxes calculated from air and seawater (5m depth) measurements were not consistent with the directly measured fluxes of acetone made by EC.

Comment noted.

39) Line 780 "ay" to at
40) 808 – "increases in PBL column concentrations". As far I can make out you have not made PBL column measurements. The results are compared simply to the mixing ratios in a boundary layer that is assumed to be homogeneous.

Corrected