

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 28, 2013

We appreciate very much the detailed and helpful *comments and suggestions from Anonymous Referee #2*. Below are our replies to the specific comments, which are kept in *italic*.

*This paper describes the measurement and interpretation of vertical fluxes and atmospheric concentrations of three reactive oxygenated volatile organic compounds (oVOCs) on the south coast of the UK. The measurement technique (PTRMS), derivation of fluxes, their uncertainties, and their interpretation with respect to published flux estimates are all described in detail, and fluxes are interpreted alongside atmospheric abundances. Atmospheric budgets of these compounds (methanol, acetaldehyde and acetone) – particularly the latter two - remain somewhat uncertain, and this paper provides some useful insight into their behaviour in a coastal maritime environment. The paper is well-written and structured appropriately. The subject matter and results are appropriate to ACP, and I recommend that the paper is accepted for publication following modifications to address the following points.*

*Scientific points to address:*

*Page 8103 – Description of oVOC lifetimes. Atmospheric lifetimes are quoted for specific loss routes (e.g. for acetaldehyde, separate lifetimes against photolysis, OH loss and nitrate radical loss are given), however in the context of this study it would be useful to quote estimates for the overall atmospheric lifetime of each species (i.e. against all losses, including deposition). To infer this from the given information one would need to employ a simple atmospheric model.*

Thanks for the suggestion. The overall atmospheric lifetimes of methanol, acetaldehyde, and acetone globally are estimated to be 4.7 days (Millet et al. 2008), 0.8 days (Millet et al. 2010), and 14 days (Fischer et al. 2012).

*Page 8105, line 25 onwards. Shouldn't the roughness sublayer be defined above local ground, rather than sea-level? In this case, the PML roof is inside the roughness sublayer as defined (i.e. 15 m is inside the estimated 30 m layer). Please clarify this point.*

Good question. In this case, the PML roof is probably above, rather than within, the roughness sublayer because the ground in the upwind region slopes fairly steeply down to the waterfront (~30 m drop in elevation over a horizontal distance of ~200 m). The height of the roughness elements was thus gauged relative to sea level, instead of the local ground of the PML building.

*Page 8106, line 22 onwards: definition of flux footprint. How has it been determined that the flux footprint extends to 1 km upwind of the PML location?*

We have added a cross reference to Section 5.2 here.

*Page 8112, line 1 onwards – Discussion of propanal interference. Is there a good case for assuming that propanal only has an anthropogenic source?*

There could be other sources of propanal as well, which could only be quantified with a separate method (e.g. GC-MS) or a mass spectrometer with a higher mass resolution (e.g. time-of-flight versions).

*Page 8113, lines 5-6: Comparison to nighttime concentrations of acetaldehyde observed by Zhou and Mopper and Lewis et al. Please provide a range for the observed concentrations from these studies to help gain a quantitative comparison with your observations.*

Zhou and Mopper (1993) reported typical acetaldehyde mixing ratios of 0.2~0.6 ppb for marine air at night. From Lewis et al. (2005) at Mace Head, the acetaldehyde mixing ratio was about 0.1~0.5 ppb For W/SW (clean marine) winds.

*Page 8125, lines 2-8: Fraction of terrestrial emissions contributed by plant decay to the oVOC sources estimated by the Millet et al. studies and Jacob et al., (2002). These estimates are for the global budgets? i.e. they are determined by the balance between global plant decay and all the other terrestrial sources on a global scale. These fractions are therefore not applicable to your local flux observations, unless there happen to be the same fractions of the different sources located inside your flux footprint (i.e. you are not sampling the whole globe).*

We agree. The fraction  $\frac{1}{4}$  here was simply a guess of the nighttime OVOC emission from terrestrial plants relative to the daytime. Because our flux footprint included marine and terrestrial regions, we expected a greater marine contribution to measured flux when the terrestrial emissions are weaker (i.e. at night). The actual day/night difference in plant emissions may well be different.

*Section 5.2, discussion of flux and concentration footprints. Potentially, for the longerlived species the “concentration footprint” – which I assume means here the locations upwind from PML which can influence the observed oVOC abundances – are huge. This is particularly the case for acetone which has a lifetime of approximately 20 days. In this case, source locations throughout the northern hemisphere can potentially contribute to its observed atmospheric abundance. For such long-lived species, the atmospheric abundance would likely be determined more by advection and changes in origin of air than by local fluxes, unless the local fluxes are large enough to mask variability driven by advection. For acetaldehyde, its short atmospheric lifetime means that this is more likely controlled by local sources (both surface fluxes and local chemical production). A clearer discussion of this point, and how it relates to the observed*

*comparability of fluxes and concentrations for the different oVOCs would be enlightening for the reader in interpretation of the results. i.e. does it appear local fluxes are large enough to control acetone variability? Do the observations of concentration and flux for acetaldehyde support the idea that local processes dominate its atmospheric variability?*

Thanks for the suggestion. For a gas with a long lifetime, the upwind region that can influence the measured concentration is indeed huge. We tried to illustrate the different interplays between concentration and flux of the 3 OVOCs (e.g. the end of the abstract; the end of Section 5.4), but seems that the point was not explained clearly enough. Perhaps it is more intuitive to present in mixing ratio units. The average daytime fluxes of 200, 20, 40  $\mu\text{moles m}^{-2} \text{d}^{-1}$  for methanol, acetaldehyde, and acetone equate to increases of  $\sim 2, 0.2, 0.4$  ppb over 12 hours given a 1 km thick PBL, suggesting that local emissions contributed significantly to the observed variability of all three OVOCs during the day. At night, the measured fluxes of acetaldehyde and acetone were reduced to  $\sim 0.06, \text{ and } 0.1$  ppb over 12 hours. Compared to their “baseline” (mean nighttime and  $1 \sigma$ ) mixing ratios of 0.13 (0.02), 0.39 (0.08) ppb, local emission was more important for the budget of acetaldehyde than acetone

*Page 8127, Line 15: Small oceanic acetone deposition flux estimated by Fischer et al., (2012). Again, are you referring here to the small net global flux determined by this study, or their estimate in the UK coastal region? While the net global deposition flux was shown by this study to be small, it was a result of a balance between larger oceanic emission and deposition fluxes in different regions.*

We were referring to predicted influx in the higher latitudes of the North Atlantic (Fig. 2 from Fischer et al. 2012).

*Section 5.4 – estimates of photochemistry, production and loss rates. Have estimates of deposition loss rates been included in these calculations? If not, they could be estimated simply based on assumed PBL height and deposition velocities?*

Dry deposition over land has not been included here, partly because this occurs in only a third of the flux footprint region. We can crudely approximate the deposition velocity of the three OVOCs to be the same as the airside transfer velocity of methanol (since methanol has minimal waterside resistance as a result of its high solubility), at  $3100 \text{ cm hr}^{-1}$ . With mixing ratios of 0.46, 0.13, 0.39 ppb, the dry deposition fluxes of methanol, acetaldehyde, and acetone are about -14, -4, -12  $\mu\text{moles m}^{-2} \text{d}^{-1}$ , or -0.3, -0.1, -0.2 ppb  $\text{d}^{-1}$ .

*Page 8130, lines 6-8: “The small air-to-sea flux of acetone predicted is consistent with only some of the observations.” Which observations? Does this refer to observations of atmospheric abundance? If so, is this due to the long lifetime of acetone (as discussed above in relation to Section 5.2.*

We meant that the small air-to-sea flux of acetone predicted is consistent with only some of the observed fluxes at night.

*Editorial corrections*

*Page 8110, line 9: Omit the word “though” at end of sentence. This is overly conversational in style.*

*Section 3.4 and Section 5.1 titles. I recommend not using the word “trend” here. This implies a long-term increase or decrease over time. Better to use something like: “General behaviour of oVOC concentrations”, and likewise for fluxes section.*

*Page 8129, line 10: “a few oVOCs”. Why not say “three oVOCs”?*

*All equations throughout text: Please ensure all symbols are fully declared / defined.*

*This seems to not always be the case. See e.g. Equation 4.*

Suggestions accepted. Thank you.