

Dear Prof. Rinne, dear Janne,

we thank the reviewers for their comments, which helped to improve our paper. Below we provide a point-by-point reply to the reviewer comments (in bold letters headed by **Reply:...**), if necessary referring to page and line numbers of the revised paper. The corresponding changes in the manuscript are highlighted in yellow color. We believe that we adequately addressed the reviewer comments and hope that the paper is now acceptable for ACP.

Georg Wohlfahrt, on behalf of the co-authors

Interactive comment on “An ecosystem-scale perspective of the net land methanol flux: synthesis of micrometeorological flux measurements” by G. Wohlfahrt et al.
Anonymous Referee #1
Received and published: 26 March 2015

The authors present a comprehensive synthesis of methanol flux measurements at ecosystem scale which seems particularly interesting in the context of GPP and ecosystem respiration. Ecosystem scale measurements are critical to understanding complexity of sources, fates and sinks of atmospheric methanol. One of the emphases is on the emerging observations of methanol deposition and on characterization of controls behind the bidirectional exchange of methanol. This kind of synthesis/compilation papers is increasingly needed for taking a bigger-picture perspective, something which individual contributions on their own could not fully achieve. Overall, the story aligns nicely with the scope of ACP and will be a useful reference of atmospheric methanol ecosystem perspective. Below are just a few ideas for further discussions and relatively minor suggestions.

General

1) Globally plants are thought to be primary source of methanol and the relationships with GPP are typically clear for vegetative sites (e.g. Figure 5). Bearing in mind the challenges behind methanol measurements (e.g. the use of right materials in the sampling line, characterizing instrumental backgrounds, etc.), the compiled ecosystem flux dataset (altogether from 28 measurement sites) is impressive and it is encouraging to see the consistency of the net land methanol budgets with grand mean ecosystem flux measurements, even though currently most represented in measurements are temperate climates. The question is how to achieve the temporal and spatial representativeness in all different kinds of ecosystems including (and maybe focusing on) the tropics where the densest biomass is located. Consequently, another question is if we can constrain the overall uncertainty from environments which have never been sampled from? If relying on scaling from GPP data to infer methanol flux, how can we be certain that the part of unexplained variance is not disproportionately substantial in other sites in terms of possibly completely different magnitudes of methanol fluxes

uncoupled from GPP?

Reply: Achieving temporal representativeness requires that the community moves away from campaign-style to year-round and multi-annual measurements. We believe that this is already partially the case (3 out of the 8 study sites in this analysis had multi-year data) and also that this analysis shows the potential of seasonal/multi-year measurements for better understanding the temporal variability of the ecosystem-atmosphere exchange. The need for longer-term measurements is addressed on p. 2593 l. 18-21 of the ACPD paper.

In terms of spatial representativeness, site selection presently is entirely bottom-up and thus lacks the degree of representativeness, which would be required at global scale. Improving on this is likely to require a co-ordinated effort by the community and thus appropriate international funding. The need for studies in presently under-sampled regions is addressed on p. 2593 l. 13-17 of the ACPD paper.

Constraining the uncertainty of fluxes which have never been measured, in our opinion, falls into the category of “known unknowns”. Statistically speaking, our sample of study sites is known not to be representative of the population and thus we cannot answer this question. The uncertainties associated with this sampling bias are addressed on p. 2587 l. 2-5 of the ACPD paper.

2) I think that “future direction” element of the paper could be further enhanced. It is clear in the text that it makes sense to consider deposition and make use of micromet measurements but how can we address the enormous variability of fluxes during stress, different management practices, phenological/seasonal cycles, and massive herbivore infestations in the future global estimates? Perhaps the solution could be more routine long-term ecosystem tower networks (e.g. FLUXNET) which could include methanol measurements, and the constraints from mobile platforms and remote sensing?

Reply: The need for multi-year and more spatially representative flux measurements is discussed already on p. 2593 l. 13-21 of the ACPD paper. Following the reviewer comment we have added further discussion on the need for multi-disciplinary and multi-scale measurements to the conclusion section (p. 15 l. 26-31 of revised manuscript).

3) The paper suggests that controls behind biosphere-atmosphere methanol exchange seem to be largely site-specific. Thus, not only spatial representativeness of sites is needed, but also long-term character to characterize seasonal variations. Ecosystem scale measurements are excellent to characterize the net fluxes, but are they alone sufficient to understand the controls? While focusing on the EC fluxes why not also to combine with the full array of available tools including remote sensing, and look at scales from molecular through leaf, branch, tree, ecosystem, regional, to global?

Reply: Ecosystem-scale measurements alone are clearly not sufficient to move forward, as our study has shown that more detailed measurements are needed to understand the net exchange of methanol at the ecosystem scale. We have expanded the conclusion section to emphasise this issue (p. 15 l. 26-31 of revised manuscript).

4) Because methanol is a relatively non-specific volatile tracer in the atmosphere having numerous different sources and sinks, modeling methanol bidirectional exchange must necessarily be challenging. It is thus quite impressive that MEGAN seems to be

doing a reasonably good job for modeling vegetative methanol but there could certainly be sources it cannot capture. The latest MEGAN version description (Guenther et al., 2012) suggested deposition estimate which I guess can be one approach when we simply do not have measurements or information on controls. One other question is how we can represent stress in the model and how to deal with the compound which can be both stress related and stress unrelated? Should methanol be classed as a special complex case of a BVOC or maybe we need to step back and look holistically using interdisciplinary approaches to understand atmospheric methanol better and then come up with the holistic (perhaps chemometric) modeling approach, embracing all sources, sinks and controls (see comment below)?

Reply: We agree with the reviewer that improving on the rough approximation of the current version of MEGAN will be challenging. We expect that algorithms will be needed to represent both the stress and non-stress components of methanol emissions, as well as other sources and sinks. Methanol is not the only BVOC to be generated by more than one process but the large flux and the different controlling process warrant treating methanol differently than other compounds.

5) Are we missing any critical methanol sources? For example, large methanol emissions can be triggered by herbivores (e.g. von Dahl et al., 2006). These emissions are not just a result of wounding of a leaf but are the sustained stress-elicited responses as a result of defense mechanisms. Every year an unimaginable number of caterpillars molt into butterflies devouring portion of foliage. Has anyone looked at their life cycles that typically coincide in spring when the vegetation is growing? What is the role of up to 10 million epiphytic microbes per cm² of foliar surface (Lindow and Brandl, 2003) for methanol emission/uptake?

Reply: Extreme events are indeed an issue which is poorly represented in ecosystem-scale data (but see e.g. Bamberger et al. 2011) and thus poorly constrained in models. Performing multi-year measurements increases the likelihood of observing extreme events, such as insect attacks. We have expanded the conclusion section to emphasise this point (p. 15 l. 17-22 of revised manuscript). The need to better understand the role of microbes inhabiting plants and soils is already discussed on p. 2592 l. 14-19 of the ACPD paper.

6) In terms of methanol deposition, seems like the biggest problem is that we are lacking the measurements around the globe and as authors nicely point out the deposition largely depends on specific site. Deposition of methanol in a situation when anthropogenic methanol (e.g. from a landfill) is advected and deposited onto vegetation/soil

can be different from modeling deposition of methanol emitted by elongating conifers and taken up by soil microbes within the canopy. Could it be worthwhile to return to laboratory for dedicated fumigation experiments to understand and characterize stomatal and non-stomatal uptakes of methanol?

Reply: We agree in that for some of the processes emerging at ecosystem scale there is the need to go back to the laboratory for conducting targeted experiments under controlled conditions in order to disentangle the processes involved. However, there is also the need for detailed studies in the field in order to make laboratory study results transferable to real-world conditions. We have added a short paragraph to the paper outlining this perspective (p. 14 l. 15-21 of revised manuscript).

7) Given low Henry's Law constants, I wonder if it would be interesting to look more closely at how rain frequency, fog, surface wetness affects global net estimates of methanol exchange?

Reply: Definitely – doing so will require better data on surface wetness in order to be able to address condensation and drying after wetting, processes which are not captured by rain gauge data – a corresponding paragraph has been added to the paper (p. 14 l. 18-21 of revised manuscript).

Specific

8) In terms of the take-home message from this excellent synthesis (last sentence of the abstract), I agree that modeling separately deposition could be opposing the errors and this is important to mention but how do these errors compare to errors in overall uncertainty of global estimates (should not be mentioned?).

Reply: Global budgets are closed to be consistent with atmospheric measurements – the variability in atmospheric inventories is thus typically small between studies (e.g. 3.4-4 Tg; Jacob et al. 2005). These similar atmospheric inventories are achieved with widely diverging sources (122-350 Tg/y) and sinks (50-270 Tg/y), however (Jacob et al. 2005). This issue is dealt in more detail throughout the main text of the paper and for the abstract just mentioned briefly.

9) Introduction first paragraph: Could also add that methanol is often the most abundant in various places (example references).

Reply: done as suggested (including reference to Seco et al. 2011)

10) Introduction: second paragraph. When talking about primary and secondary sources, is it not relevant to include emissions from dairies, for regional atmospheres at least?

Reply: Added a reference emphasising the role of dairy farming for regional methanol budgets (Gentner et al. 2014)

11) P2583 L21 “little effort has been made . . . to standardize measurement protocols”. Why not to make this effort here? This paper looks like a great opportunity to standardize or make the first step to standardizing these protocols for future methanol EC measurements which hopefully will be done more routinely in the future.

Reply: Standardizing measurements is a totally different paper (likely in a different journal, e.g. AMT) with an entirely technical focus and thus out of scope of the present study.

12) I like the idea of summarizing methodologies in a table so I found table S1 particularly useful. The setups of different PTR instruments indeed seem impressively consistent. It would also be nice to include if the correction for isotopic $^{17}\text{O}^{16}\text{O}^+$ oxygen was done or not in each PTR-MS study and what was the relative percentage of O_2^+ relative to primary ions.

Reply: Generally the methanol flux calculated from the covariance between vertical wind and m/z 33 is not impacted due to internal background (e.g. the isotopes O^{18}O^+ , O_2H^+ and DNOH^+) as demonstrated by Müller et al. (AMT, 2010), because it would only contribute random noise to the signal. All reported methanol concentrations were background corrected by bypassing air through a catalytical converter and subtracting the residual from ambient measurements.

Technical

13) P2582 L26 "so-called" may be unnecessary.

Reply: "so-called" was removed

References

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., & Wang, X. (2012). The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2. 1): an extended and updated framework for modeling biogenic emissions.

Lindow, S. E., & Brandl, M. T. (2003). Microbiology of the phyllosphere. *Applied and environmental microbiology*, 69(4), 1875-1883.

Von Dahl, Caroline C., Michael Hävecker, Robert Schlögl, and Ian T. Baldwin. "Caterpillar - elicited methanol emission: a new signal in plant-herbivore interactions?." *The Plant Journal* 46, no. 6 (2006): 948-960.

Interactive comment on “An ecosystem-scale perspective of the net land methanol flux: synthesis of micrometeorological flux measurements” by G. Wohlfahrt et al.
Anonymous Referee #2
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Review: An ecosystem scale perspective of the net land methanol flux, authors Wohlfahrt, et al.. This study reviews the literature to find independent controlling variables for methanol emission and deposition by examining eddy covariance measurements at various sites. The most important variables for emission are noted to be PAR

and evapotranspiration, whereby methanol production in leaves is released through stomata. Deposition is more related to relative humidity and surface turbulence, implying that methanol is absorbed onto wet surfaces. These controlling variables have been recognized previously, as is cited. Although it is mentioned, no discussion is included on microbial production or consumption of methanol; the authors' omissions suggest that they consider this insignificant. Some comments on this may be helpful.

Reply: We mention the role of microbes on several occasions in the ACPD paper (p. 2581, l. 22, p. 2586, l. 17, p. 2592, l. 16), in doing so cite several references on this topic and discuss the need to better understand microbial methanol exchange in particular with regard to deposition of methanol during periods of surface wetness.

The discussion rightly indicates that current models, which treat emissions and deposition separately, have difficulty in assimilating eddy covariance data. While the summary of data from various experiments and the determination of the important variables controlling emission and deposition is useful, no attempt is made to outline how this may be accomplished. This is unfortunate, since several of the contributors may be well-placed to offer some ideas. Perhaps this may be included in a revised manuscript.

Reply: As indicated by the reviewer, the existing observations make it clear that we need a modeling approach that integrates both emission and deposition. The field observations described in this study are insufficient for developing this approach. Additional studies of these processes under controlled conditions are required for this (see reply above). The observational database described in this study can then be used to evaluate potential model approaches.