

Interactive comment on “Annual cycle of volatile organic compound exchange between a boreal pine forest and the atmosphere” by P. Rantala et al.

Anonymous Referee #2

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Rantala et al show impressively long-term VOC flux observations and interesting analysis from a forested site in Finland using PTR-MS. The surface layer profile method is used for estimation of the fluxes. The study is novel as there are very few long-term data on VOC fluxes which are critical for understanding the processes and improving accuracies of biogenic models. This is one reason why the paper could be very useful for the community. Overall, the scope of the study is appropriate for Biogeosciences and I would just have a few mostly minor comments/suggestions which hopefully can be addressed before the paper is published.

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General

1) Algorithm evaluation. The observations after gap-filling are used to estimate fluxes which are presented either as 5 day medians or monthly binned medians. The data are used among others to optimize emission algorithms for isoprene (+MBO), emission+deposition algorithms for methanol, and hybrid models are advocated for simulating monoterpene fluxes. The hybrid algorithm in principle should account for both de novo emissions and storage-pool emissions of monoterpenes. Despite the significant effort to describe the algorithms, it is quite surprising that they are not directly compared quantitatively to the measurement data, so it is difficult to evaluate how well the proposed algorithms perform (e.g. scatter plots of model vs observation could be useful).

2) Vertical profiles. The authors would be in a good position to discuss the below-canopy and above-canopy processes for the masses of interest but the set of graphs is not informative in this regard. For example, simple seasonally or monthly averaged 3D color maps (e.g. time of day vs height colored by concentration) would clearly show the diurnal dynamics of VOCs in the function of height.

3) Average vs median. It seems that the paper mostly relies on median values which is surprising because the environmental datasets often obey skewed lognormal distribution. As a result median and mean fluxes differ among reported in the literature (Kalogridis et al., 2014, Table 4). It would be highly recommended to include arithmetic (and/or geometric) means as well or a summary statistics for the long-term data. This is important because the monthly bin at the intersection of season may overlap with periods of high and low emissions leading to binomial distribution when median might be completely unrepresentative of average emissions.

4) Clarity. The method sections contain much inspiring and creative thinking, but there are places which are either unclear or the information is missing which may cause

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confusion for a reader who is not familiar specifically with this particular flux derivation method. The reader has to refer to the cited paper but the smooth introduction as to why this method is more relevant (e.g. to eddy covariance) would be appropriate in the introduction. Another question is whether the two methods give similar or different results and what would be the relative error?

5) Comprehensiveness. The results and discussions are almost exclusively focused on terpenes and methanol which is surprising because 14 masses showed significant fluxes. Despite the multiyear measurements, no wintertime data are shown for any year. This is unfortunate but maybe results from the high 4-sigma threshold? Would it make sense to include the data (e.g. differently colored) for 3-sigma?

6) Selectivity. The discussion of the results is often speculative as there are doubts about identities of m/z (e.g. confusion with hexanol). The dataset would have been much more convincing if GC-MS or PTR-ToF data (even used occasionally) could shed light on validation of the masses. Alternatively, in some cases correlations between different masses could exclude/confirm certain cases (see comment #7 below). Furthermore, in many places the authors use terminology that puts an equal sign between m/z , mass and compound. Table 1 is just an example where the authors probably meant “masses” but instead they say they measured “compounds”.

Specific

7) A few recommendations for excluding interferences: m/z 42 is attributed to acetonitrile which exhibits deposition (e.g. P9555 L24-25), but the signal at m/z 42 can be affected by alkanes even at typically used low relative ratios of O_2^+ (Dunne et al., 2014). The question is if the observed deposition is acetonitrile from biomass burning or alkanes (e.g. from advected distant pollution source). Because the main n -alkane fragments in PTR-MS would be expected at m/z 43, 57, 71, 85, 99 etc. (e.g. Erickson

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et al., 2014) the lack of correlations between these masses could be informative about this interference or their lack. Attribution of identity to m/z 85 is particularly uncertain as PTR-ToF usually sees three different peaks (e.g. Park et al., 2013 Table S2). One of these identities could be consistent with hexanol fragment (but not hexenol). In terms of m/z 155, cineol+linalool would make sense unless the authors are convinced it is cineol only. As to pinonaldehyde, m/z 169 dehydrates easily on m/z 151 (e.g. Wisthaler et al., 2001) so it would be recommended to replace m/z 169 with m/z 151 in the future measurements.

8) Multiple places. “MBO/Isoprene” is confusing because it is not a ratio. It is suggested to change to “isoprene+MBO”.

9) P9548 L16. It would be helpful to include a few more details to the method section. For example, was the inlet air for the ZA catalyst (cabin air? Outside air? Air from each tower levels?). Was the zero air regularly checked for efficiency? Did you observe any patterns for VOCs suggesting incomplete removal? Addressing these questions should add to the transparency. Further, the authors could consider adding some information about SEM optimizations (was only one type of SEM used consistently over the years? Was the long-term stability in primary ion count rates relatively constant over the years?).

10) Since this is not mentioned in the methods, I wonder if O_2^+ fraction (17O16O) was subtracted from m/z 33 or not and if it could have affected the reported fluxes for methanol (e.g. deposition could be the result of the loss of water vapor anticorrelated with m/z 32?).

11) Section 3.3 In terms of deposition parameterization, the authors correctly admit that the constant R_w value is only an assumption. Why did the authors not consider rearranging Eq. 14 to yield the actual R_c (e.g. for the periods when there was a clear net deposition?) (e.g. Misztal et al., 2011).

12) Methanol sources. The paper interestingly points to microbial emissions from mi-

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crobial plant decomposition in fall. The authors should also realize that there are millions of epiphytic bacteria per cm² living on live leaf surfaces (e.g. Lindow and Brandl, 2003). For example, some ubiquitous phyllospheric *Pseudomonas* spp. are capable of utilizing methanol (e.g. Hirano and Upper, 2000). The leaf wetness would therefore not be inconsistent with the possibility of microbial uptake.

13) P9550 L8-9 "Finally, we disregarded 2.5% of the lowest and highest values from every month as outliers". This is surprising why the data had to be altered in this way as well as why exactly 2.5% . How many points were removed? Could this affect suppressing true episodic events (e.g. due to stress)? Was this procedure performed instead of or in addition to the comprehensive quality control on the data?

14) Table 2 different number of significant figures and sometimes the numbers are identical for different compounds and season (poor precision?). Also, the authors could consider separating the data into total (night+day) and midday (e.g. 10:00-14:00 LT).

Technical

15) P9548 L4-L5 "samples were transported" can be confusing.

16) P9564 L25-26 remove "be"

17) The use of "e.g." is often inappropriate. It is acceptable within parentheses or between the commas, otherwise use "for example".

Additional references:

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