

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

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We thank the referee for the review and very good suggestions which improved the manuscript. The referee comments below are bolded whereas our responses are written in normal text.

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

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(+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).

This is a good suggestion. We plotted scatter plots (calculated vs. measured values) for methanol, isoprene+MBO and monoterpenes, and attached the figures into the manuscript.

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.

This is also an excellent idea. We added two figures related to concentration profiles that give more information about the sources (and sinks) of monoterpenes and methanol.

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

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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.

We have mostly used medians in Figures to present typical (daily, monthly etc) values. The Table 2 do represent arithmetic averages as this can be used to estimate total net emission or deposition (in daily, monthly etc time scale), It is clear that these differ from each other for non-symmetric distributions, but as the purpose of Figures and the Table is different, we prefer to use these parameters.

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 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?

We expanded the description of the flux measurement techniques trying to make it more understandable for the reader. We have also justified the choice of the flux measurement method more explicitly (chapter 2.2).

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

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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?

We agree with the referee that it would have been interesting to study some additional compounds in more detail. However, we wanted to concentrate on methanol and terpenoids as they are the most important compounds at the site. Moreover, we think that the paper would be too long if additional compounds were studied more carefully.

Unfortunately, we do not have much wintertime (January and February) data at all as either the PTR-MS or the anemometer was working improperly during those periods (see Fig. 1). Altogether, the number of data points was less than 30 from both months.

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"

Unfortunately, we did not run GC-MS or PTR-TOF-MS parallel with our flux measurements. There exists some measurements of terpenoid concentrations by GC-MS conducted at the site (Hakola et al., 2009; 2012). Thus we have used the commonly known identifications for masses. In the cases of m/z 69 we have actually used the correspondence to annual cycle to shed on the more exact identification (isoprene vs. MBO).

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Hexenol was a typo and was supposed to be hexanol.

We have clarified the usage of different terms. However, in the caption of the Table 1 we state "The compound names and the formulas listed below in third and fourth column, respectively, are educated estimates for the measured masses", thus not putting an equal sign to mass and compound.

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 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 *ci-neol* 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

Good suggestions, we will consider of replacing m/z 169 with m/z 151 as the PTR-MS should be more sensitive at m/z 151.

"Hexenol" was a typo and it was replaced by "hexanol". We also added linalool to Table 1. We admit that the identity of m/z 85 is uncertain, and we will mention this in Table 2.

Measured m/z 42 signal did correlate quite well with measured signals of alkane frag-

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ments. Therefore, we added speculation into the manuscript (chapter 3.1) whether the observed acetonitrile deposition was real or not.

Multiple places. "MBO/Isoprene" is confusing because it is not a ratio. It is suggested to change to "isoprene+MBO".

Changed.

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?).

We describe the PTR-MS measurements in more detail in the manuscript.

Samples for the zero air generator were taken outside of the measurement cabin close to the ground, and the stability of the generator was followed continuously. We found that the generator had some problems at m/z 93 but this did not affect on the flux calculations as the same zero air signal was subtracted from each concentration level.

The primary ion signal m/z 19 (measured at m/z 21) had some fluctuations over the years being approximately around $10 - 30 \times 10^6$ cps. SEM was always optimized before a calibration, and we used same SEM-model (MasCom MC-217) over all years.

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Since this is not mentioned in the methods, I wonder if O₂⁺ 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?).

The O₂⁺ fraction was subtracted from *m/z* 33. This was done by multiplying measured *m/z* 32 signal with the ¹⁷O¹⁶O/O₂ ratio (we used a constant ratio 0.00076). Thus the oxygen isotope effect should not affect the fluxes.

We will mention in the manuscript that the oxygen isotope was subtracted from *m/z* 33.

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).

We agree that this would be more independent method to determine *R_w*, However, it might be difficult to conclude whether the net deposition is clear or not. In addition, subtracting the possible methanol emissions from the flux values may bring another challenge.

Nevertheless, we tried this approach with a dataset from June-August. Methanol flux data was filtered using the threshold value $RH_0 = 75\%$. We used also a temperature and PAR filter with parameters $T < 15\text{ }^\circ\text{C}$ and $PPFD < 50\ \mu\text{mol m}^{-2}\text{s}^{-1}$. Finally, we also disregarded 10% of the highest and lowest values. With these values, median value for *R_w* was $127\ \text{sm}^{-1}$. This is pretty close to the estimate that we got with the revised flux values.

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Methanol sources. The paper interestingly points to microbial emissions from microbial 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

This is a good point and consistent with our discussion (chapter 3.3).

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?

The procedure was always performed after the other quality control, such as friction velocity filtering. Totally, 5–25 data points were disregarded from each month in the procedure.

We noticed that there were some clear outliers in the case of many flux compounds, although the other quality control was done carefully. Therefore, we ended up doing such a quantile filtering. We chose the 2.5% limit because then only few (up to 12-13) largest values were disregarded. We think that no real phenomena, such as stress related emissions, were sorted out in the process. However, if there are some stress related that are filtered out they would be difficult to analyse anyway due to their rarity and sporadic appearance. Furthermore, the very high deposition fluxes should be unphysical due to the diffusion limitation.

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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).

Precisions were weak in most cases as there are several sources of uncertainties and errors that may cause a systematic/random uncertainty of about 10% (section 3.1).

However, to be more consistent, we decided to express the values in Table 2 with two significant numbers but with maximum of one decimal. The data in Table 2 is separated to three categories: total (night+day), night (2–8 am) and day (11 am–5 pm).

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

We changed the sentence "samples were transported..." to "samples were drawn..."

16) P9564 L25-26 remove "be"

Removed.

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

We replaced inappropriate "e.g." by "for example"

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