

## ***Interactive comment on “Boreal forest soil is a significant and diverse source of volatile organic compounds” by Mari Mäki et al.***

### **Anonymous Referee #1**

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This manuscript is mainly focused on observations of belowground VOC concentrations at different soil depths and comparison with aboveground VOC exchange measurements by means of dynamic soil enclosures. The method of probing belowground soil gas concentrations has been applied for a bunch of other trace gases but not yet for VOC, which is innovative and thus the most appealing aspect of this manuscript.

The authors state that the observed belowground VOC concentrations in general were not directly coupled with forest floor VOC fluxes measured by means of dynamic enclosures applying VOC-free air as purging gas. In my opinion, this may have different reasons: (#1) for the enclosure VOC exchange measurements, zero air have been applied as purging gas. This way, an artificial concentration gradient is established that forces trace gas emission and omits any deposition or bi-directional exchange to be

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observed. Hence the above ground exchange measurements are not representative and cannot be transferred to real world conditions (or reflect observed belowground concentrations). On the other hand (#2), the authors did not simultaneously measure the aboveground ambient air VOC concentrations. Only based on the latter, one could infer any fluxes (or even directions: positive or negative) between soil and the atmosphere and estimate whether soil is a source or sink for VOC. The authors state that belowground and aboveground concentration (the latter from an earlier campaign) were “similar in magnitude”. In this case, one would assume that both emission and uptake is possible (the authors may also refer to, e.g., Gut et al. (2002) for a theoretical background of calculations necessary for this kind of soil trace gas measurements). But most importantly (#3), I have concerns about the belowground measurement procedure or representativeness of respective VOC concentrations. The question is how the belowground VOC concentrations were derived/calculated? I understand that the authors were running their sampling system in a closed loop, having a “perfect” sink for VOC at the side of the Tenax adsorption tube, i.e., the air flow downstream of the adsorption tube will be depleted of VOC. On the other side of the sampling system (at the inlet of the collector) this VOC-depleted air creates an artificial gradient that forces VOC from soil-air to penetrate through the collector membrane. This happens very soon after the sample pump starts, as the VOC that have been accumulated during the 15 min sample breaks are transferred to and trapped by the adsorption tubes within a time span of about 1-2 minutes (sample flow of 100-150 ml, and collector volume of 150 ml in 2009-2011; no numbers given for the volume in 2016). In the residual time of the (4x) 15 min sampling period the authors applied an artificial VOC concentration gradient by flushing the collectors with VOC-free air. That means that the longer the sample interval the more VOC will be accumulated in the adsorption tube. If taking the total sample volume (6-9 l) into account to calculate the VOC concentration this will not represent the VOC concentrations prevailing in the soil air. Rather, this is a measure of how much VOC can penetrate through the collector membrane when an artificial VOC gradient (with zero VOC in the collector) is applied. Of course the VOC penetration rate

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will, among others, depend on the soil VOC concentrations, but will by no means be representative of (or equilibrated with) the soil-air VOC absolute concentrations (compare Fig. 2). In fact, if the calculation is accounting for the total sampling volume, the derived concentrations will be much lower (with the concentrations inside the collector being lower as soon as the pump is on). Else: with very large sampling volumes of 6-9 liters one can assume breakthrough in the adsorption tubes to occur to some extent by some of the VOCs, which make things even more complicated.

What the authors measure is, to the most of their sampling procedure, the VOC transmission rate of their collector wall/membrane. This issue of the method/calculation of belowground concentration is especially critical for the sesquiterpenes, which are indeed expected to have relatively long equilibration times or lower Teflon diffusion rates, respectively. Else: even though a major fraction of this manuscript is reporting on sesquiterpenes, these compounds were not tested for collector permeability. As stated by the authors, the collector permeation rate can be assumed to be much lower than for the other compounds, as the penetration rate is, among others, dependent on size. Differences in transmission rates in Teflon can easily span several orders of magnitude, please see, e.g.: [https://www.chemours.com/KIV/zh\\_CN/assets/downloads/Chemours\\_Teflon\\_FEP\\_Film\\_Tech\\_Bulletin\\_K26942.pdf](https://www.chemours.com/KIV/zh_CN/assets/downloads/Chemours_Teflon_FEP_Film_Tech_Bulletin_K26942.pdf)

The authors either should have used an online VOC analytical device with high temporal resolution to detect the short high concentration peak directly after they had started the sampling pump. Only this small volume of air (if at all) can reflect the soil-air concentrations, assuming that the collector air volume has reached equilibrium during the 15 min sampling breaks. Or they should have used an online VOC analyzer within a close loop sampling system, which does not interfere with (adsorb) VOCs. Please correct me if I am wrong.

Due to the issues #1-3, an interpretation of the results of the manuscript is indeed difficult to achieve, and any conclusions can only be of speculative nature. Concerning issue #1, one could state that using zero-air for purging the enclosures reveals a

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measure of the potential soil VOC emission capacity. And a direct comparison with the belowground exchange measurements doesn't make sense anyhow, due to multiple reasons.

Concerning issue #2, the authors give a range of VOC concentrations measured in ambient air above this forest in an earlier campaign; and state that those were "similar in magnitude" as the observed belowground concentrations. This could be a fair projection, but only in case issue #3 could be solved.

Concerning issue #3, one could state that the observed belowground concentrations (and vertical profiles) are a (very)lower-bound estimate, but this is very much dependent on the individual compounds (diffusion characteristics). Then the vertical VOC concentration differences between the different soil depth/horizons could at least be discussed, rather than any of the absolute VOC concentrations.

In general, the way of data presentation/structure in the manuscript is sometimes not easy to follow or not precise, and the interpretation of the correlation analysis is kind of vague or speculative. In view of the issues presented above, the decoupling of the belowground VOC concentrations from the forest floor fluxes and the scarceness of correlations/gradients (e.g. for sesquiterpenes and OVOC) is not surprising. Even though the authors try to pin down potential dependencies (soil temperature and water content) by displaying tabulated statistical data, the data evaluation did not give a conclusive picture. The correlation analysis sometimes gives encouraging numbers for some soil layer horizons, or individual pits of those, but not for some others or adjacent soil layers, which doesn't add confidence in respective interpretations. In a recent paper, the authors already concluded from dynamic (zero-air) enclosure measurements that belowground dynamics might not play a major role in isoprenoid exchange, but instead the litterfall is the most important factor triggering VOC emissions (Mäki et al., 2017); and with all the short-coming presented above this seems to be confirmed by the belowground vertical gradients of VOC concentration in this manuscript.

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Concerning all issues above, I suggest that the authors consider reassessing their conclusions in respect with the critical points presented above (and below) and resubmit a new version.

The M&M section needs to describe more details.

- Before describing the collector permeability test (in section 2.2), the authors should first introduce/describe the innovative type of collectors used (as they did later in section 2.3.).
- What does "wet collector" mean (page 4, line 6)? How did you wet it? Did you apply humidified air?
- What is the meaning of "The beaks length . . ." (page 4, line 11)?
- Is the "sampling system" (page 4, line 22) the same as the "collector"? Otherwise I don't get it. What do the authors mean with ". . . with the pits" at the end of the same sentence? Connect the tubes with the pits? The term "within the pits" make more sense to me. Please clarify.
- "For aboveground sampling" (page 4, line 28:) can be misinterpreted, as you didn't do any aboveground measurements. I suggest to merge this and the follow-up sentence in a concise way.
- Permeability test: which concentrations did you use for the test (in the Fig. 2 it says "arbitrary units")? Were the concentrations inside the collector the same as outside ("at constant level"), as Fig. 2 lets assume?
- What is meant by "The possibility of creating a flux collectors that did not originate from the actual measured horizon" (page 5, line 4)?
- What is meant by "were closed between the samplings" (page 5, line 5). Closed in between the consecutive sampling intervals of one sample procedure (closed for 15 min during sampling brakes)? Or did the authors close the tubes when they finished

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one complete sampling cycle?

- I got lost understanding the different pits versus investigated soil horizon designations (2 versus 4 in the different campaigns) versus soil depth (5 in table 2). From Table A1, I understand that the two soil depths (organic and mineral) investigated in 2008-2011 refer to horizons H & B in 2016. On page 8, line 22, the authors state “mineral soil (A- and B-horizons)”. I suggest to shortly describe which layers of the 2018-2011 measurements refer to which in 2016 in the M&M section. What do negative numbers of soil depth mean in Table A1?

- The total sampling volume was 6-9 liters of air. Did the authors test any VOC breakthrough? 9 liters is much more than normally applied.

- Omit “0 cm being the surface of organic layer, not mineral soil” (page 5, line 17). What do the negative soil depth numbers in Table A1 mean? May be I didn’t get the above.

- What is meant by “. . . installed in the vertical face interfacing with the undisturbed soil . . .” (page 5, line 27)?

- Page 6, line 4: in case that VOC-free air was used to flush the enclosures (as in Mäki et al. 2017) you should mention this here; as in this way, an artificial concentration gradient is produced that enhances trace gas emission and omits any deposition or bi-directional exchange rates to be observed.

- Please give a some more details of the enclosure system applied (instead of only citing your previous paper). Also state the basic calculation formulas here.

Other minor issues:

- Page 1, line 16: omit “the” in “during the two measurement campaigns”

- Page 8, line 3: the authors state that “Belowground VOC concentrations were dominated by monoterpenes and sesquiterpenes, but the monoterpene concentrations were mainly decoupled from forest floor monoterpene fluxes.” Obviously also the SQT

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and OVOC were “decoupled”.

- Page 8, line 5: what is meant by “Belowground VOC concentrations in the vertical soil horizons”. Suggest: “Belowground vertical gradients of VOC concentrations”.

- Page 8, line 15: what is meant by “. . . when each soil horizon was tested separately”?

- Page 8, line 21: “Total monoterpene concentrations in organic soil were highest in late summer and in December”: Comparing late summer (28.07., 24.8., 21.9.) with fall (1.10., 14.10., 26.10., 8.11., 2.12.), this is hard to tell. It is sometimes hard to follow what the authors exactly mean when discussing data in spring, early/late summer, autumn in the different chapters of the main text. Did they really plot means in Fig. 5, or media (error bars are not evenly distributed to the positive/negative direction)?

- Page 8, line 25: “Total sesquiterpene concentrations in mineral soil were clearly highest in spring, in early June, in late summer, and in October (Fig. 5).” Early June is still spring time. I can’t see this general trend at all in Fig. 5c.

- Page 8, line 31: “There was no difference in VOC fluxes between measurement pits.” I am not sure whether I got this right. It’s hard to believe that all fluxes of all VOC (classes) were similar, due to the inhomogeneity of the forest floor mentioned.

- Page 9, line 3-4: I suggest: "In contrast to our hypothesis, the below ground vertical concentration profiles were not coupled to observed soil surface fluxes rates, ..."

- Page 9, line 5: “individual pits” is redundant.

- Page 9, line 12: “Confirming our third hypothesis that soil temperature and water content can be used to explain belowground VOC synthesis.” Due to a lack of correlation with all other VOC classes versus soil horizons, I would not state that these results are confirming the third hypothesis. May be you can state that these individual correlations are in line with the hypothesis, but then you also have to mention that all other correlations fail to do so. Else: this sentence is missing its subject.

- Page 9, line 23: “The organic soil showed seasonal variation in 2011 and 2016 ... (Fig. 6)”. As Fig. 6 only shows summer data: how can the authors claim that there are “seasonal variations?” Or did they mean inter-annual variations, or inter-campaign variations?

- Page 9, line 25: “Monoterpenes constituted almost 90% of the total VOC concentration, sesquiterpenes accounted for less than 10% between 2008 and 2011 (Table 5).” How does this VOC composition compare to (expected) ambient air data (in lack of own data, please give a general statement)?

- Section 3.4 (“Inter-annual variation”): the discussion on seasonal pattern is sometimes redundant (see section 3.1 and 3.2), but with different phrasings, e.g.: “Monoterpene concentrations in 2016 were highest in organic soil in summer, in October and in December, whereas seasonal variation was relatively small in mineral soil (in section 3.4).” versus “Total monoterpene concentrations in organic soil were highest in late summer and in December ... (section 3.2)”.

- Page 12, line 19: “Belowground isoprenoid concentrations varied seasonally, and the highest concentrations were measured during summer and early autumn in 2009 and 2011, whereas high belowground concentrations monoterpene concentrations were measured in late summer, in October, and in December in 2016.”. I think the authors should not compare the total isoprenoids (ISO, MT, SQT) in 2009-2011) with only the MT in 2006. What about the other isoprenoids (SQT, isoprene) and what about the OVOC in general?

- Page 13, line 27: “led to”

- Fig. 2: the x-axis has no units given

- Fig. 5: it seems that the x-axis has equi-distant steps for the different sample dates. I propose to use an absolute numeric time line (the sampling/breaks were not evenly distributed over time).

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- Figure A2: any idea why the water content of A horizon (lying between the H and B horizon) is so much higher than all the others? Indeed, the soil water content can be quite inhomogeneous (e.g., by water channeling etc.). If only measured by one single sensor per soil depth, these measurements are not necessarily representative.

References:

Gut et al. (2002): NO emission from an Amazonian rain forest soil: Continuous measurements of NO flux and soil concentration. *J. Geophys. Res.*, 107 (D20), 8057, doi:10.1029/2001JD000521.

Mäki et al. (2017): Contribution of understorey vegetation and soil processes to boreal forest isoprenoid exchange. *Biogeosciences*, 14 (5), 1055-1073, doi:10.5194/bg-14-1055-2017, 2017.

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