

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

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

The manuscript bg-2018-22 describes 2 new setups to measure seasonal and depth dynamics of volatile organic compounds in a haplic podzol in a boreal forest (SMEAR II site, Finland). The manuscript compares results measured with 2 methods and concludes about seasonality, which might be just caused by the differences in the methods. Additionally, the manuscript is written rather descriptive and general with a focus on atmospheric chemistry rather than biogeosciences. As it is, the manuscript might be better for publication in AMT or ACP. Instead of comparing the concentrations within

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the soil profile to the flux from the surface into the atmosphere, I would like to read more about possible biogeochemical processes involved in the production of the individual compounds based on literature.

I will point out some additional references and ideas to change the focus more towards biogeosciences. In general the measurement of soil VOCs measured in depth profiles measured via TD-tubes and analysis by GC-MS is very challenging and unique, thus, I recommend the manuscript for publication. I just have problems to conclude about seasonality if 2 different methods have been applied and no pressure was measured. I recommend to focus rather in the dynamics within the soil depth profile rather than on the seasonality. More detailed comments for a revision are addressed below.

First of all, I have a problem with the term storages. It suggests that e.g. in plants isoprenoids are stored and released based on physico-chemical processes. While this might certainly be true for the top litter layer, there is strong evidence that microbes in soil can actively produce mono- and sesquiterpenes (e.g. Schulz and Dickschat 2007, Yamada et al., 2015) within their metabolism. Page 1, line 27: It is not really the high organic carbon content which results high VOC emissions from organic horizons, but rather the highest abundance and activity of autotrophic and heterotrophic microbes in that layer.

Page 2, line 1-16: This is a general intro for the relevance of VOCs in atmospheric chemistry. Given the focus of the manuscript on VOC dynamics within a soil profile, I would recommend to start here with the role of VOCs as infochemicals (Insam and Seewald, 2010 and Schulz and Dickschat, 2007). As stated already on page 11 line 31 ff., the VOCs produced in the soil profile differ from the VOCs released into the atmosphere. Thus they are not necessarily transported all the way up into the atmosphere and thus their role within the soil should be focused.

Page 2, line 12 ff.: Diffusion also is dependent on soil moisture, not only soil temperature (see e.g. Skopp et al., 1990).

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Page 2, line 22 ff.: A major result of snow cover is that the soil is isolated from the cold air temperatures and is not freezing. Thus, I agree that microbial processes might still be ongoing. However, given the fact that microbial metabolism is strongly correlated to soil temperature, which should be quite soil in winter, I think an enrichment effect is more likely. The snow acts as a lid of a static chamber.

Page 4, line 21 ff.: In both setups polytetrafluoroethylene (PTFE) tubes, which were closed on one side by a sintering method, have been used. I have problems to understand how the first method, which was applied from 2008 until 2011 to suck air out of the sintered tube with a pump, reflect "diffusion of gases to occur"(line 21 ff.). According to my knowledge a pump creates a pressure difference from the inner tube to the surrounding soil. Thus, the soil air was sucked into the tube and does not reflect natural conditions where molecular diffusion occurs. This was improved in the second setup in 2016, where air was circulated through the same tubes and the assumption of molecular diffusion for that data are more likely to be valid. Without a pressure measurement as e.g. Gut et al. 1998, I have problems to follow the assumption of molecular diffusion for the first setup. PTFE tubes can be manufactured with different volume density and thus the mesh of stainless steel is also important to prevent that the soil is changing the inner volume of the PTFE tubing. Thus, the volume density should be included in the method description.

Page 8, line 9 ff.: Highest sesquiterpene and OVOC concentrations in the A horizon should be discussed with respect to the difference in particle density of O and A horizon material. This impacts the overall water filled pore space and thus might explain your result. In general, it is expected to observe highest concentrations in the O horizon. Another point which is missing in the discussion is the potential of utilizing sesquiterpenes and OVOCs as microbial signaling in the A horizon.

Page 8, line 18 ff.: low oxygen availability does not necessarily results low aerobic microbial activity. Anaerobic microbes will be still active.

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Page 9, line 3 ff.: I don't understand why the hypothesis surface VOC fluxes and belowground VOC concentrations are similar was formulated? Wouldn't exactly the opposite be true? The surface VOC flux is dependent on the turbulent eddy diffusion coefficient, whereas the belowground VOC concentrations are dependent on the molecular diffusion coefficient. Since they are several orders of magnitude different, I would not expect that surface VOC fluxes and belowground VOC concentrations should follow the same trend/pattern.

Page 9, line 18 ff.: I have problems to follow interannual variability if 2 different methods have been applied.

Page 10, line 11 ff.: It is a kind of recapitulation to summarize results and discussion in 2 sentences. I would remove both and rather move them into the conclusion.

Page 10, line 16 ff.: I agree, but in the discussion section I want to read also why the monoterpene concentrations are highest in the organic horizon (not soil)? The pores in the organic layer are much larger than in the mineral soil. Thus, fungi, which need to grow hyphae from one particle to another are rather slow. Thus it is not surprising that on the other hand bacteria were found in e.g. Timonen et al. 2017 to be high abundant in the humus. It is known that bacteria can easily colonize particles in the organic horizon since most are mobile. Thus, you could interpret the production of e.g. 3-carene and camphene from fungi as active inhibition of the swarming and swimming motility of bacteria. Such findings have been published already (Schmidt et al., 2015). These findings suggest that the production of terpenoids is rather connected to microbial activity than on microbial abundance. I am sure that you can find much more correlations of your data to microbial processes.

Page 11, line 20 ff.: Just for curiosity, can you comment on the speciation into  $\alpha$ -,  $\beta$ -,  $\gamma$ - sesquiterpenes?

Page 11, line 31 ff.: I did not yet found the commonly reported functions of belowground VOCs (e.g. defense communication and signaling).

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Page 13, line 29 ff.: I don't the reference for climate change fits for your manuscript. I am not an expert for snow cover, but as far as I know snow isolates the soil surface. Thus, if the snow in the future will not be present anymore, I would assume that the surface temperature of the soil should be colder.

Page 14, line 1: The sentence ...more research is needed I find too general. I think your manuscript shows some nice trends about VOCs in the soil depth profile which could be combined with existing literature to microbial processes. I can agree to ...more research is needed to combine soil VOCs to microbial processes.

Page 14, line 4: I find the conclusions rather short and just analyzing the temperature and moisture dynamics not very informative. I recommend discussing and concluding about microbial processes within the soil profile. Also you measured CO<sub>2</sub>, but did not really talk about the correlation.

Minor comments: It is confusing to read about the thicknesses (page 3 line 24 ff.) which are not reflected in the horizon borders in Table 1. Also I am missing the E horizon, which might explain the differences.

Fig. 1: The scheme is rather a fast draft. I got especially lost following arrows which are not connected to a tube. Maybe for the non-expert reader it would be worth to include in the figure caption that the sintered version of the PTFE tube means that it is closed on one side? Also a lid of the glas bottle would help.

Fig. 2: Maybe I did not get it, but the arbitrary signals for dry and wet indicate a moisture effect. In case you used cps, it might be worth to think about a different way to plot the data to correct for that effect or mention it in the method section?

Fig. 3: The collectors in a) were installed in 5 and 17 cm, which are not the interface of the horizons. I suggest to focus on 2016 only and include the surface tube for flux measurement in b) plus a depth y-axis in cm. It is confusing to use the term "organic soil" and "mineral soil" while you speak about H-, A-, B-, and C-horizons.

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Fig. 4: There seems to be a problem either of the graphic or my printer for some error bars. I would like to read what processes cause the large differences of a-pinene, 3-carene, linalool and limonene in the soil profile. It is also worth to think about a classification into different relationships of VOC concentration with depth (e.g. exponential vs. linear, etc.). The carbon content and microbial biomass should decrease exponentially with depth. Thus, if VOC concentrations follow a different pattern, e.g. a-gurjunene, a-humulene and b-himachalene it could indicate that their production is not linked to the storage in plant litter, but rather likely to microbes which are most abundant/active in a specific layer of soil (A-horizon).

Fig. 5: a) It is hard to explain the elevated isoprene around 01.10 for the A horizon. Wouldnt it make sense to finally conclude that predominantly there is no difference in isoprene concentration and flux except this single event?

Tab. 3: I recommend to plot CO<sub>2</sub> versus Sesquiterpene concentration and CO<sub>2</sub> versus Monoterpene concentration and discuss the contribution of autotrophs (CO<sub>2</sub> consumers) and heterotrophs (CO<sub>2</sub> producers), respectively.

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