Dear Reviewers and the Editor,

We would like to express our appreciation for taking your time to evaluate this manuscript. We have considered the suggestions with great care and rand for your good and constructive comments which have improved the manuscript in many places. We have revised the manuscript based on the suggestions. Below we will respond to the reviewer's feedback (reviewer's suggestions numbered in black font and our response below each comment in blue font).

Reviewer's suggestions:

Reviewer #1: 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 stablished that force trace gas emission and omits any deposition or bi-directional exchange to be observed. Hence the above ground exchange measurements are not representative and cannot be transferred to real world conditions (or reflect observed belowground concentrations).

We welcome the referee comments on the measurement methods as they improve opportunities to develop our measurement systems in the future. We have done changes in the text in order to clarify the method and believe it is now much clearer.

1) The enclosure measurements have originally been developed for inert gases and significantly larger fluxes (e.g. for CO_2 or CH_4). Also with reactive trace gases and small fluxes, the methods have been already applied in several papers before this manuscript. VOC flux measurements are commonly performed by using VOC-free air as a purging gas (e.g., Hakola et al 2006, Aalto et al., 2014, Aaltonen et al., 2011, 2013, Hellen et al., 2006, Mäki et al., 2017). Employment of dynamic chambers to measure trace gas fluxes is a reliable method, since flushing of the chamber headspace helps to avoid pressure and gas concentration changes inside the soil. Frequently, MnO2-scrubber and active carbon filters are being used between the supply air pump and the chamber to filter the air that is pumped into the chamber headspace. With concentrations that are often close to detection limits of the instruments, the most important requirements for the replacement air is a stable concentration with a steady flow rate. Employment of dynamic chambers to measure trace gas fluxes is considered as a reliable method, since flushing of the chamber headspace helps to avoid pressure and gas concentration changes inside the soil, and the artificial concentration gradient can be mainly avoided by sufficient flushing the chamber before the sampling period to achieve a steady-state VOC concentration inside the closed chamber. The fluxes are determined from concentration change during the chamber closure and calculated using mass balance equations, which eliminates the effect of an artificial concentration gradient. The dynamic enclosure method was previously tested in field conditions using standard gas with known VOC concentrations and quadrupole-PTR-MS (Kolari et al., 2012). The chamber system underestimates the artificially generated VOC emission rates at varying degree: for isoprene, monoterpene and many oxygenated VOCs the underestimation is 5-30%. The most uncertainties originate from adsorption of VOCs to moist or reactive surfaces, which are unavoidable when the enclosure contains living plant material.

Due to the reasons listed above, we believe that the dynamic enclosure measurements as implemented here are as accurate and representative as one can reasonably have, when the number of sampling points and the spatial placement is not unlimited and when the dynamics of field conditions are causing random noise to the measurements. We added description of the uncertainties and the reference Kolari et al., 2009 to the manuscript on Page 7, lines 8-12.

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).

We thank the referee for being thorough in reading the text. Here, the aboveground concentration has been used wrongly as a synonym for emissions, which is obviously not the case. The aboveground ambient air VOC concentrations can be obtained from the enclosure measurements before the closing of the chamber. We calculated that the ambient air concentrations were 0.3 to 17 per cent of the monoterpene concentrations in the O-horizon and the results are presented on Page 11, lines 11-14.

We acknowledge that for many VOCs both emission and uptake is possible, and indeed have also seen in our data that this is the case especially for water soluble compounds like methanol or acetone (see e.g. Aaltonen et al., 2013).

We referred to Gut et al., (2002) as a theoretical background on Page 5, line 26.

Aaltonen H., Aalto J., Kolari P., Pihlatie M., Pumpanen J., Kulmala M., Nikinmaa E., Vesala T., and Bäck J.: Continuous VOC flux measurements on boreal forest floor. Plant and Soil, 369, 241–256, doi:10.1007/s11104-012-1553-4, 2013.

Gut, A., van Dijk, S. M., Scheibe, M., Rummel, U., Welling, M., Ammann, C., Meixner, F. X., Kirkman, G. A., Andreae, M. O., and Lehmann, B. E.: NO emission from an Amazonian rain forest soil: Continuous measurements of NO flux and soil concentration, J. Geophys. Res.-Atmos., 107, 8057, doi:10.1029/2001JD000521, 2002.

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).

The VOC concentrations (C, µg m^{-3}) for the different soil horizons were calculated with Eq. (2):

$$C = m \Big/ \frac{V}{1000000} \qquad (2)$$

where m is the mass of sample (ng) and V is sampled volume (ml), divided by 1000000 to calculate the unit conversion from ml to m^3. V was calculated using Eq. (3):

$$V = F * t \quad (3)$$

where t is the sampling time (min) and F is the flow rate of the sampling (F, ml min^{-1}).

Soil is by nature very heterogenous measurement environment, and the spatial and temporal representativeness can naturally be questioned as always in soil measurements. We designed the sampling schedule so that both the temporal and spatial variation should be sufficiently covered with the 5-8 soil pits: 18 sampling events between November 2008 and October of 2011 (3 pits); and 13 sampling events in 2016 (5 pits). The measurement and analysis is tedious and time consuming, and therefore more samples could not be taken, unfortunately.

The measurement procedure was designed (and tested) in particular to avoid creating artificial gradients of VOCs in the soil and to avoid the possibility for sucking VOCs from a larger 'footprint' to the sample, and thus the sampling duration was optimized to 15 min with a break in between the samplings. The 15-min break between individual samplings was used to stabilize VOC concentration between the gas collector and surrounding soil air. The permeability test of the collector (Fig. 2) indicates that the collector itself should not create VOC vacuum by restricting the VOC flow.

3) 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 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 extend 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

The aim of this study was to measure the VOC concentration of certain soil volume within soil pores, not the VOC concentration of gas collector. We used the sample volume of 6–9 L to make sure that the amount sampled exceeded the detection limit of the TD-GC-MS for monoterpene and sesquiterpene quantification. On-line analysis techniques would be ideal for this kind of measurements, but PTR-quadrupole-MS is not capable to differentiate monoterpene species or measure sesquiterpenes even in single mass level reliably. Since sesquiterpenes occur in extremely

low concentrations and are highly reactive compounds, this means that they are very challenging to measure. Low flow rate was used to avoid/prevent the flow-through of VOCs in the adsorption tubes. 6-9 liters of sample air is required to achieve measurable concentrations of VOC from soil air. Usually 0.05-0.10 L min^{-1} flow rates are used in measuring VOCs with flow through chamber techniques (Aaltonen et al., 2011, Hellen et al., 2006, Mäki et al., 2017).

The gas collectors were made of polytetrafluoroethylene (PTFE) by sintering, with pore sizes of 5–10 μm. The pores in the collectors allow the diffusion of gases to occur, while water is unable to percolate into the collector. This was clarified on Page 4, line 31.

Breakthrough volumes of tubes have been tested and no breakthrough have been observed for the studied compounds even with higher (12 L) sampling volumes. This sentence was added on Page 6, lines 4-5.

We wrote in the manuscript: "All the VOC standard compounds permeate the collector easily and concentrations reach a constant level in order of minutes (maximum 7 minutes) also with the wetted collector (Fig. 3). α-Pinene was the heaviest compound in the calibration VOC gas mixture, and as expected, its diffusion through the wall of the collector was the slowest of the VOCs measured, with stabilization time 7 min. In contrast methanol peaked immediately after introducing the gas mixture into the glass bottle, but after that it stabilized quickly in 4 min. It was assumed therefore that stabilization of sesquiterpenes would take longer, since they are heavier than monoterpenes, thus the 15-min break time was chosen." Molecular weight of methanol is 32.04 g/mol and molecular weight of α-pinene is 136.23 g/mol, while it is 204.357 g/mol for α-gurjunene.

Teflon tubing was not permeating but only used for conducting the air flow to the sintered Teflon collector and consequently from the collector to the Tenax adsorbent.

Results from permeability tests of the PTFE collector were shown in Figure 2 on Page 23.

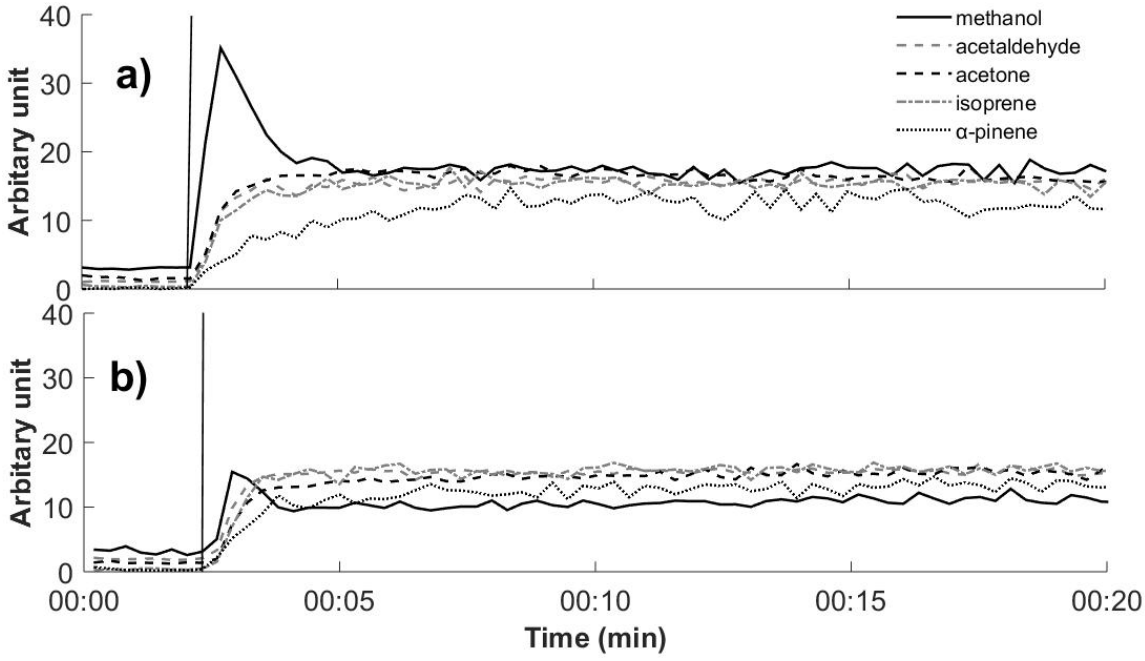

Figure 3: Results of the permeability tests of the PTFE collector with the five VOCs. A permeability test was used to monitor how fast VOCs permeate into the gas collector and to determine how fast VOC concentrations stabilize between the air inside and outside the collector. Panel a) shows the results with dry collector and panel b) with a wetted collector. Vertical line shows the time point when the introduction of the VOC standard began.

Aaltonen, H., Pumpanen, J., Pihlatie, M., Hakola, H., Hellén, H., Kulmala, L., Vesala, T., and Bäck, J.: Boreal pine forest floor biogenic volatile organic compound fluxes peak in early summer and autumn, Agricultural and Forest Meteorology, 151, 682–691, doi:10.1016/j.agrformet.2010.12.010, 2011.
Hellén, H., Hakola, H., Pystynen, K.H., Rinne, J. and Haapanala, S.: C2-C10 hydrocarbon emissions from a boreal wetland and forest floor. Biogeosciences, 3: 167–174, doi:10.5194/bg-3-167-2006, 2006.
Mäki, M., Heinonsalo, J., Hellén, H., and Bäck, J.: 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.

4) 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.

This would not be possible with online VOC analyzers (quadrupole-PTR-MS or PTR-TOF-MS), because they are unable to separate compounds with same molecular mass such as different monoterpenes or sesquiterpenes. Also detection limits especially for sesquiterpenes with quadrupole-PTR-MS are very high. We agree that the PTR-TOF could have been used for VOC concentration measurements, but the quantification accuracy of sesquiterpenes compared to real values is still unclear with this instrument. In order to cover the spatial variability in soil better, we wanted to install the collectors over a large area, and to measure them with PTR-MS would have required long tubes. The highly reactive sesquiterpenes can be transformed in long tubes through the chemical reactions before they will reach the detector. Further, online sampling of soil air is not as simple as sampling of ambient air, because soil water content can be high in the deeper soil horizons. We are anyway confident that the relative differences in the concentrations measured in different soil layers with this technique represent true differences in the actual concentrations between the layers.

One value of this experiment was that we were able to detect over 50 different VOCs from soil air. This was possible by using the TD-GC-MS, but would not have been possible with quadrupole-PTR-MS, because it is unable to separate compounds with same molecular mass such as different monoterpenes or sesquiterpenes.

5) 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 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.

We thank the referee for comprehensive criticism. In our responses to issues 1-3, we have tried to clarify and sharpen the methodological concerns the referee raises. It could indeed be said that all emission measurements are in fact emission 'potentials', however this terminology has already been reserved to the Guenther emission model concept where emissions are normalized to standard temperature and irradiance levels, so it may be even more confusing to use the word in a different context.

We agree with the Reviewer that the vertical VOC concentration differences between the different soil horizons could be discussed next to the absolute VOC concentrations. We have now phrased the comparisons between soil horizons in several places (Page 9, lines 27-30 and Page 10, lines 1-4) as the relative differences.

We agree that due to the multiple cross-correlating drivers, a conclusive and convincing statement of concentrations of all compounds and their relations to environment is difficult to obtain, especially in a field campaign as here. However, we still believe that our data is measured in a solid manner, analyzed with up-to-date methods and brings about novel understanding on the possible role of soil processes in VOC production. This is - as far as we know - the first quantitative analysis of this topic. We added this statement to the end of the conclusions on Page 16, line 32.

We also added following sentences to the manuscript on Page 6, lines 7-10: Especially for sesquiterpenes, which are expected to have low diffusion rates, concentrations are lower-end estimates. During the sampling sesquiterpenes are not expected to be diffusing fast enough through the walls of the tubes and most of the mass is actually collected during the 1-2 minutes of the sampling.

Limits of the methods have now been discussed in the manuscript and results have been discussed more by the differences in the concentrations and not by the absolute values.

6) 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. 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.

We have rewritten the conclusions on Page 16, lines 28-32: Soil vertical layer VOC concentrations were analysed and compared with simultaneous chamber flux measurements in field conditions in a Boreal coniferous forest. We detected more than 50 different VOCs, mostly mono- and sesquiterpenes, and belowground concentrations of VOCs differed between soil layers during the second campaign. Sources of the forest soil VOCs probably differ depending on the compound and soil layer. Dominating monoterpenes concentrations are comparable to the air concentrations above a coniferous forest. This is - as far as we know - the first quantitative analysis of this topic.

7) 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.).

The collector permeability test was moved after the gas collector description on Page 5, lines 10-26.

8) What does "wet collector" mean (page 4, line 6)? How did you wet it? Did you apply humidified air?

Before permeability measurements with the wetted collector, it was wetted with ultrapure water. Also the gas flow was humidified. This was done in the test to mimic the moist conditions inside the soil where the collectors remained between measurements. This description was added on Page 5, lines 17-18.

9) What is the meaning of “The break length…” (page 4, line 11)?

The 15-min break between individual samplings was used to stabilize VOC concentration between the gas collector and surrounding soil air. This was clarified on Page 5, lines 33-34.

10) 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.

‘Sampling system’ is the whole measurement system, where gas collectors (gas permeable PTFE-tubes) are connected to stainless steel tubes from which the VOC samples were taken. The misspelling on Page 5, line 1 was corrected.

11) “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.

These two sentences were rewritten on Page 5, lines 6-9.

12) 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?

The units are arbitrary, since the instrument was not calibrated for the test. As only concentration differences were measured, the calibration was not required. At the end of the individual tests, the VOC concentrations outside the collector was also measured and observed to be equal with concentrations inside.

13) What is meant by “The possibility of creating a flux collectors that did not originate from the actual measured horizon” (page 5, line 4)?

We mean that if the VOC sampling flow would be very high, it would suck VOCs from the surrounding soil horizons. With small flow rate, we minimize this risk and sample VOCs from the gas collector, which is placed in the middle of certain soil horizon. The misspelling was corrected on Page 5, line 30.

14) 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 one complete sampling cycle?

We agree that this part was very unclearly written and we made corrections on Page 5, lines 32-33.

15) 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?

Details were clarified on Page 6, lines 23-24, and in the Table A1 on Page 31.

16) 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.

The total sample volume of 6–9 L was used to exceed the detection limit of the TD-GC-MS. One value of this experiment was that we were able to detect over 50 different VOCs from soil air. We think that smaller sample volume would have been sufficient for monoterpene quantification. We used higher sample volume, because we wanted to measure sesquiterpene concentrations as well. Breakthrough volumes of studied compounds were tested and no breakthrough was observed even with the sampling volume of 12 L (Page 6, lines 5-6).

17) 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.

Correction was made on Page 6, line 13-15. Details were clarified in the Table A1 on Page 31.

18) What is meant by ": : : installed in the vertical face interfacing with the undisturbed soil: : :." (page 5, line 27)?

The sentence was rewritten on Page 6, line 25.

19) 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.

We added the following sentence on Page 7, line 5: "We flushed the chamber headspace for 30 minutes to equilibrate the measurement system." See also our response to Q1.

20) 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.

We added the following details on Page 7, lines 5-8, and Page 7, lines 12-18. "We flushed the chamber headspace for 30 minutes to equilibrate the measurement system. During the chamber enclosure, we continuously pushed (1 l min^{-1}) filtered (active carbon trap and MnO2-coated copper net) ambient air into the chamber headspace and sampled the incoming and outgoing air for 1.5–2 hours through two Tenax TA-Carboback-B adsorbent tubes (flow rate 0.1-0.15 l min^{-1})." We also added the equation for the flux calculations.

21) Other minor issues: Page 1, line 16: omit "the" in "during the two measurement campaigns"

The word was removed on Page 1, line 16.

22) 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 and OVOC were “decoupled”.

We made a clarification on Page 11, lines 2-3.

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

This title was corrected based on the suggestion (Page 9, lines 24-25).

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

We rewrote the sentence on Page 10, lines 8-9. Our aim was to say that there were no differences in VOC concentrations between the soil pits for O-, A-, B-, or C-horizon.

25) 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)?

In the Fig. 5 on Pages 26 and 27, we plotted the mean isoprene, monoterpene, and sesquiterpene fluxes and concentrations for the O- and A-horizon. Error bars of monoterpenes and sesquiterpenes are not evenly distributed to the positive/negative direction, because the values are presented in log scale on the y-axis. Details were clarified on Page 10, lines 15-22.

26) 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.

The sentence was rewritten on Page 10, lines 19-20: “Total sesquiterpene concentrations in the A-horizon were highest in spring (22.4. and 17.5.), in late summer (24.8.), and in October (1.10.)”.

27) 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.

The sentence was rewritten on Page 10, lines 25-26. This sentence was meant to present that there were no statistically significant differences in VOC fluxes between measurement pits within the different VOC groups. Typical feature for VOC emissions is that the flux rate variation is very high.

28) 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, ..."

This sentence was rewritten based on the Reviewer’s suggestion (Page 10, lines 29-30).

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

The sentence was rewritten based on the Reviewer’s comment (Page 10, line 32).

30) 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.

We think that this is a very good suggestion from the Reviewer. Our observation was rewritten on Page 11, lines 19-22.

31) 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?

Figure 6 showed seasonal variation from spring (May) and summer (July) in 2011 and 2016. The statement was clarified on the Page 12, lines 1-2. We agree with the Reviewer that you can also see inter-campaign variation between the campaigns one (2009-2011) and two (2016).

32) 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)?

Most of the sesquiterpenes, especially ß-caryophyllene which is the main sesquiterpene emitted by Scots pine, are so reactive towards ozone that they cannot be measured in the ambient air. Lifetime of B-caryophyllene in the air at the site is less than 2 minutes, while for monoterpenes lifetimes are few hours. Therefore VOC composition is not directly comparable to the emission composition. High sesquiterpene emissions have been measured at the site both from Norway spruce and Scots Pine shoots in summer (Hakola et al., 2017, Hakola et al. 2006), but due to high reactivity ambient air concentrations of sesquiterpenes have been mainly below detection limits, while monoterpenes have been detected in the ambient air even during winter (Hakola et al. 2012).

Hakola H., Hellén H., Rinne J., Hemmilä M., and Kulmala M., 2012. In situ chromatographic measurements of volatile organic compounds in a Boreal Forest. Atmospheric Chemistry and Physics, 12, 11665-11678.
Hakola, H., Tarvainen, V., Praplan, A. P., Jaars, K., Hemmilä, M., Kulmala, M., Bäck, J., and Hellén, H. Terpenoid and carbonyl emissions from Norway spruce in Finland during the growing season. Atmospheric Chemistry and Physics, 17, 3357–3370, 2017, doi:10.5194/acp-17-3357-2017.

33) 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)”.

The sentence on Page 12, lines 11-12 was removed.

34) 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?

Corrections were made on Page 15, lines 7-10. We did not quantify OVOC concentrations in 2008-2011.

35) Page 13, line 27: “led to”

We rewrote the sentence on Page 16, line 14.

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

We added the units for the x-axis (Page 24).

37) 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).

We agree with the Reviewer that this suggestion will make the Figure 5 more realistic. We have modified the Figure 5 (Pages 26 and 27). We have also removed the data from the B- and C-horizon to make the trends more visible.

38) 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.

The Figure A2b shows that soil water content is not highest in the A-horizon (black line with circle markers), but instead in the C-horizon (gray line with circle markers). Soil water content is highest in the C-horizon, because rainfall will percolate through the soil profile into the C-horizon. The measurement sensors are close to groundwater in the C-horizon. Soil volumetric water content in the O-, A-, and B-horizon are means of five measurement pits and volumetric water content in the C-horizon is mean of four measurement pits at the SMEAR II station. This clarification was added into the M&M section (Page, 7, lines 26-28). We agree with the Reviewer that soil water content can vary strongly between sensors immediately after rain events, but we strongly believe that these continuous soil water content measurements are representative for actual soil water content in the long run.

We have changed the coloring of the lines to make our point more clear (Fig A1 and A2, Pages 35-36).

Reviewer #2: 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 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 bellow. 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.

We have tried to emphasize this aspect throughout the manuscript. We agree on the scientific evidence that VOCs are produced by microbial metabolism and we wrote corrections into the text by using the suggested references on Page 1, lines 27-28. On Page 1, line 27, our aim was to point out that easily available carbon enhances microbial metabolism, which can lead to higher VOC production, but we clarified this on Page 1, lines 28-29 and Page 2, lines 1-2 based on the feedback: Organic soil layers can be a substantial source of VOCs due to the high abundance and activity of autotrophic and heterotrophic microbes. They drive decomposition processes where easily available carbon is utilised for microbial metabolism and VOCs may be produced either actively as secondary metabolites or as by-products in the decomposition process.

The measurement method itself was actually the same in both campaigns. Samples were collected by circulating air in the gas collectors and through Tenax TA–Carbopack-B adsorbent tubes at flow rates that ranged 100–150 ml min^{-1} using portable pumps and impermeable PTFE tubing. Gas collectors were placed into the different measurement pits in the campaigns one (2008-2011) and two (2016) and gas collector type was also different between campaigns. This probably will have some effect on VOC concentrations. For this reason, the main focus is in the second campaign (2016).

Schulz, S, and Dickschat, J.S. Bacterial volatiles: the smell of small organisms. Natural product reports, 24, p.814–842, 2007.
Yamanaka, K., Reynolds, K. A., Kersten, R. D., Ryan, K. S., Gonzalez, D. J., Nizet, V., Dorrestein, P. C., and Moore, B. S. Terpene synthases are widely distributed in bacteria. Proceedings of the National Academy of Sciences of the United States of America, 111, 1957–1962, doi:10.1073/pnas.1422108112, 2015.

2) 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 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.

Our aim in this chapter was to connect soil processes to atmospheric chemistry and to the climate change, but we agree that this part could be shorter. We change the focus of this chapter to soil VOCs dynamics on Page 2, lines 3-24.

Insam, H., and Seewald, M.: Volatile organic compounds (VOCs) in soils. Biology and Fertility of Soils, 46:199–213, doi:10.1007/s00374-010-0442-3, 2010.
Schulz, S, and Dickschat, J. S. Bacterial volatiles: the smell of small organisms. Natural product reports, 24, p.814–842, 2007.

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

We completely agree with the Reviewer and the sentence was rewritten on Page 2, lines 15-18.

4) 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.

We agree with the Reviewer that one the main reasons for VOC concentrations to be so high inside snow bed is the lid effect of snow. We rewrote the sentence on Page 2, lines 32-33.

5) 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.

The measurement method was actually the same in both setups. Samples were collected by circulating air in the gas collectors and through Tenax TA–Carbopack-B adsorbent tubes at flow rates that ranged 100–150 ml min^{-1} using portable pumps and impermeable PTFE tubing. Volume density of the PTFE tubes is not critical, because tube surface is impermeable. The PTFE tubes are used to transport gas sample from the gas collector into the Tenax TA–Carbopack-B adsorbent tube.

6) 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.

We added microbial signaling on Page 13, lines 20-25.

Soil properties also explain high monoterpene concentrations in the O-horizon. Soil porosity is higher in the O-horizon compared to the A-horizon, which means that gas diffusion is faster in the O-horizon compared to the A-horizon. The effect of rain filling soil pores and transporting VOCs towards deeper soil layers is likely stronger in the O-horizon. This was also added on Page 13, lines 1-4.

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

We agree with the Reviewer and we rewrote the sentence on Page 10, lines 12-13.

8) 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.

The Reviewer makes an excellent point that it is not straightforward to compare belowground concentrations and surface fluxes, because the production processes, transport mechanisms and temperature and moisture conditions are different. We thought that we could find similar seasonal pattern in belowground VOC concentrations and surface fluxes, but after the Reviewer's feedback, we decided to rewrite the hypothesis on Page 3, lines 18-20.

In the chamber headspace, we have a fan to homogenize the chamber air volume, but we don't have natural turbulent mixing, which regulates diffusion gradient between soil air and the below-canopy atmosphere. This can cause small error to the measurement system, although we continuously push VOC free air into the chamber headspace.

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

We agree that it is difficult to make comparisons between the campaigns one and two, when VOC concentrations measurements were done using two different measurement set-ups and we added this statement on Page 15, lines 11-13.

10) 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.

We rewrote the conclusions based on the suggestions on Page 16, lines 28-32.

11) 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.

This was an excellent advice. However, we did not determine microbial populations from the soil horizons. For this reason, it is difficult to make conclusions about interactions between bacteria and fungi, which would be supported by scientific evidence. We followed the Reviewer's suggestions and found that both fluxes and concentrations of the monoterpenes and sesquiterpenes correlate with the CO_2 flux in autumn, which supports our conclusion that VOC production was driven by microbial activity (heterotrophic production). We compared correlation between the total monoterpene and sesquiterpene fluxes (µg m^{-2} h^{-1}) and the chamber temperature (°C), and the CO_2 fluxes (µg m^{-2} h^{-1}) from the soil surface in spring, summer, and autumn in 2016 (Appendix Table A6, Page 37). We added a short description to the Material and Methods on Page 9, lines 7-9 and results on Page 11, lines 3-8. We also rewrote the discussion on Page 12, lines 26-28, based on these results.

We also compared correlation between the total monoterpene and sesquiterpene concentrations from the O- and the A-horizons and the CO_2 fluxes (µg m^{-2} h^{-1}) from the soil surface in spring, summer, and autumn in 2016 (Appendix Table A7, Page 38). We added this to the Material and Methods on Page 9, lines 9-11 and to the Results on Page 11, lines 8-10.

12) Page 11, line 20 ff.: Just for curiosity, can you comment on the speciation into α-, ß-, γ-sesquiterpenes?

We specified the sesquiterpenes without pure standards on Page 14, lines 1-2. Quantification of these sesquiterpenes is described on Page 8, lines 10-13: Calibration solutions for the sesquiterpenes, contained only longicyclene, isolongifolene, β-caryophyllene, α-humulene, α-gurjunene and β-farnesene. In 2016, other sesquiterpenes found in the samples were tentatively identified by their mass spectra and retention indices and quantified as β-caryophyllene, isolongifolene, or longicyclene.

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

We added a new sentence on Page 13, line 22-24, based on the suggestion.

14) 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.

We agree with the Reviewer that soil surface temperature would probably be colder without an isolating snow cover. Our aim with this sentence was to point out that VOC emissions from boreal soils could be increased, if there is no snow cover that hinders VOC diffusion in the atmosphere, because microbial activity also occurs in low temperatures. If air temperatures will increase and snow melts earlier, it could also increase VOC emissions from organic soil though microbial decomposition and metabolism in spring, when coming radiation warms a dark soil surface. We see that this part of the manuscript was written unclearly and we rewrote the sentence on Page 16, lines 15-19.

15) 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.

We rewrote the sentence on Page 16, lines 25-26.

16) 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 CO2, but did not really talk about the correlation.

We modified the conclusions on Page 16, lines 28-32.

17) 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.

This sentence was removed from the manuscript (Page 4, lines 3-4). The E-horizon is part of the A-horizon. Physical or chemical properties of the measurement pits have not been determined for the E-horizon. We agree, that it would have been useful information, when comparing VOC concentrations from the different measurement pits.

18) 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.

We modified the Figure 2 on Page 24.

19) 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?

Figure 3 on Page 24 shows results of the PTFE collector tests with the five VOCs. A permeability test was performed to monitor how fast VOCs permeate from the soil into the collector and to determine how fast VOC concentrations stabilize between the air inside and outside the collector. This was clarified on Page 24, lines 6-8. All the VOC standard compounds permeate the collector easily and concentrations reach a constant level in order of minutes (maximum 7 minutes) also with the wetted collector.

20) 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.

We rewrote the sentences by deleting confusing parts on Page 6, lines 14-15. We also edited the Figure 1b on Page 23.

21) 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).

We checked the error bars and they are correct in the Figure 4 (Pages 25-26). Please note that the error bars don't present standard deviation, but standard error of the individual measurements. The values are presented in log scale on the y-axis.

We agree that there is hardly any discussion on which processes were behind the individual monoterpenes. We added some discussion on Page 12, lines 23-24, and Page 13, lines 20-22. We did not find clear distinction between linear and exponential relationships between soil conditions and VOC concentrations for the different soil horizons.

22) Fig. 5: a) It is hard to explain the elevated isoprene around 01.10 for the A horizon. Wouldn't it make sense to finally conclude that predominantly there is no difference in isoprene concentration and flux except this single event?

We completely agree and this clarification was added on Page 10, line 22.

23) Tab. 3: I recommend to plot CO_2 versus Sesquiterpene concentration and CO2 versus Monoterpene concentration and discuss the contribution of autotrophs (CO2 consumers) and heterotrophs (CO_2 producers), respectively.

This was an excellent advice. We followed the Reviewer's suggestions and found that both fluxes and concentrations of the monoterpenes and sesquiterpenes correlate with the CO_2 flux in autumn, which supports our conclusion that VOC production was driven by microbial activity (heterotrophic consumption). We compared correlation between the total monoterpene and sesquiterpene fluxes (µg m^{-2} h^{-1}) and the chamber temperature (°C), and the CO_2 fluxes (µg m^{-2} h^{-1}) from the soil surface in spring, summer, and autumn in 2016 (Appendix Table A6, Page 37). We added a short description to the Material and Methods on Page 9, lines 7-9 and results on Page 11, lines 3-8. We also rewrote the discussion on Page 12, lines 26-28, based on these results.

We also compared correlation between the total monoterpene and sesquiterpene concentrations from the O- and the A-horizons and the CO_2 fluxes (µg m^{-2} h^{-1}) from the soil surface in spring, summer, and autumn in 2016 (Appendix Table A7, Page 38). We added this to the Material and Methods on Page 9, lines 9-11 and to the Results on Page 11, lines 8-10.

Boreal forest soil is a significant and diverse source of volatile organic compounds

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Keywords: volatile organic compounds, boreal forest, organic soil horizon

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Abstract. Vegetation emissions of volatile organic compounds (VOCs) are intensively studied world-wide because oxidation products of VOCs contribute to atmospheric processes, but the quantities by which different species of VOCs are produced by soil, or how effectively belowground VOCs are released into the atmosphere from soil remains largely unknown. This is the first published study that measures belowground VOC concentrations at different depths in a podzol combined with simultaneous soil surface flux measurements in a boreal coniferous forest. More than 50 VOCs, dominated by monoterpenes and sesquiterpenes, were detected in the air space in the soil during ~~the~~ two measurement campaigns. Organic forest soil was a significant monoterpene source as it contained fresh isoprenoid-rich litter, and the concentrations of monoterpenes were comparable to the VOC concentrations in the air above the coniferous forest. Belowground monoterpene concentrations were largely decoupled from forest floor monoterpene fluxes; thus, it seems that production processes and storages of VOCs partly differ from those VOCs that are simultaneously emitted from the soil surface. Relatively high isoprenoid concentrations were measured under snow cover, which indicates that snow and ice cover hinders gas diffusion and causes belowground accumulation of VOCs when the activity of vegetation is very low.

1 Introduction

Soil and understorey vegetation emit VOCs and these emissions are released from the diverse storages and processes (Hayward et al., 2001; Smolander et al., 2006; Leff and Fierer, 2008; Bäck et al., 2010; Aaltonen et al., 2011; Faubert et al, 2012, and Mäki et al., 2017). These studies reported that VOCs are produced by understorey vegetation, roots, decomposition processes, soil microbes, and vegetative litter concentrated in the organic soil layer. Microbes produce mono- and sesquiterpenes actively in their metabolism (Schulz and Dickschat 2007, Yamada et al., 2015). Organic soil layers can be a substantial source of VOCs due to the high abundance and activity of autotrophic and heterotrophic microbes. They drive decomposition processes where

easily available carbon is utilised for microbial metabolism and VOCs may be produced either actively as secondary metabolites or as by-products in the decomposition process.

VOCs have a crucial role in soils as infochemicals (Insam and Seewald, 2010, Schulz and Dickschat, 2007) by transmitting messages between soil organisms. Soil temperature and humidity influence many physical and biological processes related to VOC formation in soils (Asensio et al., 2007, Aaltonen et al., 2013). In soils, warming climate can affect VOC synthesis by mediating decomposition processes, whereby microbial enzyme activity is regulated by soil water content and temperature (Davidson and Janssens, 2006). ~~VOC exchange from the boreal forest floor varies from several per cent to tens of per cent of the boreal forest VOC exchange depending on the season (Aaltonen et al., 2013) and VOCs such as isoprene, monoterpenes, and especially sesquiterpenes have a precursor potential for secondary organic aerosol (SOA) formation. An SOA is formed in the atmosphere from condensed oxidation products of VOCs, and SOA particles contribute to cloud formation and affect the Earth's radiation budget by scattering and absorbing solar radiation (Arneth et al., 2010, Virtanen et al., 2010, Mahowald, 2011). This outcome is opposite to the effect of greenhouse gases, which is warming the climate. Warming can change vegetation cover and almost double VOC emissions from subarctic and arctic plants (Faubert et al., 2010, Kramshøj et al., 2016). Warming can also affect VOC synthesis in soils by mediating decomposition processes, whereby microbial enzyme activity is regulated by soil temperature and water content (Davidson and Janssens, 2006).~~ Soil water content impacts upon the transport and diffusion of organic compounds (Skopp et al., 1990, Zhong et al., 2014) and VOC emissions from vegetation (Svendsen et al., 2016), whereas temperature affects gas volatilization and diffusion ~~are mainly regulated by temperature~~. Soil water content also affects the decomposition of soil organic matter i.e. biological processes (Davidson and Janssens, 2006). Soil temperature and water content should be measured in parallel with belowground VOC concentrations and soil surface flux measurements to study how effectively VOCs from soils are released into the atmosphere from very complex structured podzol soils. Warming can also change vegetation cover and affect belowground VOC production of plants (Faubert et al., 2010, Kramshøj et al., 2016), which can almost double VOC emissions from subarctic and arctic plants. Soil VOC production contributes atmospheric chemistry, because isoprene, monoterpenes, and especially sesquiterpenes have a precursor potential for secondary organic aerosol (SOA) formation.

The VOCs in soils have also been suggested to have an effect on biological interactions, although the quantities and functions of compounds in soils are largely unknown (Tholl et al., 2006). VOCs can promote plant growth, control the nitrogen cycle, affect microbial metabolism and transmit long-distance communication between different decomposers (Insam and Seewald, 2010, Asensio et al., 2012, Peñuelas et al., 2014, Tahir et al., 2017). A deeper understanding on the dynamics of soil processes and the roles of different soil components to VOC formation is needed (Asensio et al., 2007, Leff and Fierer, 2008; Gray et al., 2010). The wintertime dynamics of soil VOC production is especially interesting, as activity of the vegetation during the snow cover period is low, but the concentrations in soil and inside the snowpack can be quite high (Aaltonen et al., 2012). This is probably due to snow and ice cover that hinders diffusion of VOCs produced by microbial metabolism in snow bed, especially close to soil surface~~, which is probably due to microbial decomposition activity~~.

Studies on belowground concentrations of VOCs are scarce (Lin et al., 2007), especially those in which measurements are made in situ. Earlier studies (Smolander et al., 2006; Pihlatie et al., 2007; Pumpanen et al., 2008; Leff and Fierer, 2008; Asensio et al., 2008; Gray et al., 2010) measured greenhouse gases such as CO_2 and CH_4 belowground routinely or presented results on soil VOC content, obtained by laboratory measurements from soil cores. There is, however, no available established and well-evaluated method for measuring VOCs belowground; it is also clear that these experiments have significant limitations compared to measuring VOC exchange in undisturbed forest soil. Laboratory experiments allow the manipulation of environmental conditions, but cause severe disturbances to natural soil processes that may include the regulation and release of VOCs from damaged roots and interfere with the balance between the roots and soil microbial components. We have developed a method to collect VOC samples in situ from collectors installed belowground and which equilibrates with VOC concentrations and fluxes of the surrounding soil.

Belowground VOC concentration measurements were conducted on organic and mineral soils in a boreal coniferous forest during two measurement campaigns from November 2008 to end of 2011 and from April to December of 2016. Belowground VOC concentrations were also compared with VOC fluxes in and from the forest floor in 2016. The overall aim of this study was to identify and quantify the VOC compounds that originate from the boreal podzolized forest soil at different depths, in addition to studying the association of VOC concentrations with VOC emissions from the boreal soil surface. We used the following hypotheses in our study: (1) Organic soil and the top mineral soil (the A-horizon) produce a major part of the VOC emissions as organic soil contains isoprenoid-rich litter, and fine roots and root-associated microbes are concentrated in the top horizon of the mineral soil. (2) The seasonal dynamic ~~and the production processes~~ of belowground VOC concentrations are different ~~similar~~ to those that contribute to VOC fluxes from the soil surface, because the production processes, transport mechanisms and temperature and moisture conditions are different. (3) Soil temperature and water content significantly affect VOC production belowground. (4) Belowground VOC concentrations differ between years.

2 Material and methods

2.1 Measurement site

The campaigns were performed in the southern boreal forest at the SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations) station (61°51'N, 24°17'E, 180 m a.s.l) (Hari and Kulmala, 2005). The forest is a 56-yr old (in 2017) Scots pine stand (*Pinus sylvestris* L.) with mean ~18 m stand height and a tree density ~1170 ha^{-1} (Ilvesniemi et al., 2009). Below-canopy vegetation includes tree seedlings such as *Sorbus aucuparia*, *Betula pendula* and *Picea abies* (Mäki et al., 2017) and the dominating vascular plants in ground vegetation are *Vaccinium myrtillus* L., *Vaccinum vitis-idea* L., *Deschampsia flexuosa* (L.) Trin., and *Calluna vulgaris* (L.) Hull. (Ilvesniemi et al., 2009; Aaltonen et al., 2011). In addition, the soil is 33–60% covered by mosses such as *Pleurozium schreberi, Dicranum sp.*, and *Hylocomium splendens* (Aaltonen et al., 2011). The soil above the homogeneous bedrock is Haplic podzol (FAO-UNESCO, 1990) formed in a glacial till, with a depth range of 0.5–0.7 m (Hari and Kulmala, 2005). The total C storage of the soil is 7 kg m^{-2} (Ilvesniemi et al., 2009) and it has been formed

during the last 7000 years. Frequent forest fires have an influence on soil C recovery and turnover time (Köster et al., 2014) and the last occasion the SMEAR II forest site was burned was in 1962 when the cutting residues were slash burned on site. ~~The vertical thickness of the organic soil is 6.0 cm, and that of A- and B-horizon 2.0 cm and 16 cm, respectively in 2016 (Mäki et al., 2017).~~ The mean C content was highest in the organic soil layer (356 mg g^{-1}), much lower in the A-horizon (32 mg g^{-1}) and lowest in the B (24 mg g^{-1}) and in the C-horizons (5 mg g^{-1}), when the plots were established in 1995 (Pumpanen et al., 2008). The average N content is also highest in organic soil (13 mg g^{-1}) and decreases towards the deeper soil horizons (~1 mg g^{-1}) (Table 1). The total surface area of the roots <2mm is 3.5 m^2 m^{-2} in the organic soil, 1.8 m^2 m^{-2} in the A-horizon and 0.8 m^2 m^{-2} in the B-horizon (Ilvesniemi and Liu, 2001). A Swedish study reported that total tree fine-root biomass from organic soil down to 30 cm in mineral soil is 227 g m^{-2} in Scots pine stands (Hansson et al., 2013).

~~**2.2 Permeability test for the gas collector**~~

~~A permeability test was performed to monitor how fast VOCs permeate from the soil into the collector and to determine how fast VOC concentrations stabilize between the air inside and outside the collector. The effect of soil moisture was also evaluated by a permeability test. These results were used as a background to facilitate taking decisions about measurement and stabilization times. The permeability of the gas collectors for VOCs was determined in laboratory conditions before the installation in the field. The determinations was made for both dry and wet collectors by using a gas mixture contained known concentrations of nine compounds (methanol, acetonitrile, acetaldehyde, acetone, isoprene, methyl vinyl ketone, 2-butanone, hexanal, and α-pinene) and proton transfer reaction-mass spectrometer (PTR-MS, Ionicon LTD, Austria) for on-line analysis (Fig. 1). The PTR-MS enabled fast response monitoring of the diffusion of VOC mixture. The field conditions did not allow the implementation of the PTR-MS for continuous VOC measurements, thus only an adsorbent tube collection method was used. The break length was designed so that the stabilisation time of VOC concentration between the collector inside and outside air was clearly shorter than the 15-min break. All the VOC standard compounds permeate the collector easily and concentrations reach a constant level in order of minutes (maximum 7 minutes) also with the wetted collector (Fig. 2). α-Pinene was the heaviest compound in the VOC gas mixture, and consequently its diffusion through the wall of the collector was the slowest of the VOCs measured. In contrast methanol peaked immediately after introducing the gas mixture into the glass bottle, but after that it stabilised quickly. It can be assumed therefore that stabilization of sesquiterpenes would take longer, since they are heavier than monoterpenes, thus the 15-min break time was chosen.~~

2.~~3~~ 2 VOC concentration measurements in the soil profile

During the first campaign from 2008 to 2011, samples were collected from cylindrical hydrophobic gas collectors (4 cm in diameter, 12 cm long) that had been installed into the soil pits (setup 1, Fig. ~~3a~~1a). The gas collectors were made of polytetrafluoroethylene (PTFE) by sintering, with pore sizes of 5–10 µm. The pores in the collectors allow the diffusion of gases to occur, while water is unable to percolate into the collector. The sampling system consisted of a gas permeable PTFE-tube (International Polymer Engineering, Arizona, USA) connected to stainless steel tubes from both ends with air-tight

connections using Swagelok connectors (Swagelok, Straight fitting, Union 10) within the pits (setup 2, Fig. ~~3a~~1a). A mesh made of stainless steel was installed around the PTFE-tube to protect the PTFE tube from physical damage from contact with the soil.

During the second campaign in 2016, samples were collected using PTFE tubes (International Polymer Engineering, Arizona, USA) that had been installed into the soil pits (setup 2, Fig. ~~3b~~1b), where the porosity enabled the diffusion of the VOC and air gases into the tubes. ~~For aboveground sampling, t~~Two PTFE sampling tubes (8 mm internal diameter) were installed inside stainless steel tubes (10 mm internal diameter) ~~and connected to the gas collector. The PTFE tubes were installed inside the stainless steel tubing~~ to prevent possible diffusion of VOCs through the PTFE and to protect the tubing against physical damage. PTFE sampling tubes were further connected to the gas collector.

A permeability test was performed to monitor how fast VOCs permeate from the soil into the collector and to determine how fast VOC concentrations stabilize between the air inside and outside the collector. The effect of soil moisture was also evaluated by a permeability test. These results were used as a background to facilitate taking decisions about measurement and stabilization times. The permeability of the gas collectors for VOCs was determined in laboratory conditions before the installation in the field. The determinations was made for both dry and wet collectors by using a gas mixture contained known concentrations of nine compounds (methanol, acetonitrile, acetaldehyde, acetone, isoprene, methyl vinyl ketone, 2-butanone, hexanal, and α-pinene) and proton transfer reaction-mass spectrometer (PTR-MS, Ionicon LTD, Austria) for on-line analysis (Fig. 2). Before permeability measurements with the wetted collector, it was wetted with ultrapure water. Also the gas flow was humidified. The PTR-MS enabled fast response monitoring of the diffusion of VOC mixture. The field conditions did not allow the implementation of the PTR-MS for continuous VOC measurements, thus only an adsorbent tube collection method was used. The 15-min break between individual samplings was used to stabilize VOC concentration between the gas collector and surrounding soil air. All the VOC standard compounds permeate the collector easily and concentrations reach a constant level in order of minutes (maximum 7 minutes) also with the wetted collector (Fig. 3). α-Pinene was the heaviest compound in the VOC gas mixture, and consequently its diffusion through the wall of the collector was the slowest of the VOCs measured. In contrast methanol peaked immediately after introducing the gas mixture into the glass bottle, but after that it stabilised quickly. It can be assumed therefore that stabilization of sesquiterpenes would take longer, since they are heavier than monoterpenes, thus the 15-min break time was chosen.

Soil trace gas measurements were performed earlier by Gut et al. (2002). In our study, s~~S~~amples were collected by circulating air in the gas collectors and through Tenax TA–Carbopack-B adsorbent tubes at flow rates that ranged 100–150 ml min^{-1} using portable pumps and impermeable PTFE tubing. Air was aspirated from the collector and pumped through the adsorbent tube then returned back to the collector. The possibility of creating a flux ~~collectors~~ that did not originate from the actual measured horizon was minimized by using a relatively small flow rate and circulating the gaseous mixture back to the collectors. The aboveground ends of the PTFE tubes were closed after we finished ~~between~~ the sampling of certain soil horizon~~s~~. Each sampling consisted of four 15-min pumping periods, with 15-min time intervals between them, which enabled the VOC concentrations to equilibrate fully between the collectors and into the soil around them. The permeability test revealed

that all compounds in the VOC standard permeated into the collector easily and concentration in the collector reached a constant rate in the order of minutes (maximum 7 minutes) for both the dry and with the wetted collectors (Fig. ~~2~~3). The total amount of VOCs in the air volume inside the collector (~0.15 L) alone would not have been sufficient for analysis as this volume of sample was below the detection limit. The sampling times were prolonged to 60 min (a total of 1 h 45 min with breaks), which resulted in a total sample volume of 6–9 L. Breakthrough volumes of tubes have been tested and no breakthrough have been observed for the studied compounds even with higher (12 L) sampling volumes. These measurements were designed so that they would cause a minimal disturbance to the soil profile: the pits were carefully prepared and soil layers kept apart so that they could be placed back into the pit as close to the original intact soil profile as possible. Especially for sesquiterpenes, which are expected to have low diffusion rates, concentrations are lower-end estimates. During the sampling sesquiterpenes are not expected to be diffusing fast enough through the walls of the tubes and most of the mass is actually collected during the 1-2 minutes of the sampling.

2.~~3~~2.1 Measurement setup for VOC concentration profile of the first campaign, 2008 to 2011

The collectors were permanently installed in the three permanent soil pits at two depths, 5 and 17 cm below the soil surface ~~(0 cm being the surface of organic layer, not mineral soil)~~ in May 2008 (Fig. ~~3a~~1a). The upper collectors were installed at the O-horizon ~~humus layer mineral soil interface~~, the lower collectors completely embedded in the B-~~mineral soil~~ horizon (Fig. ~~3a~~1a). The measurements were performed during the snow free seasons that started on November 2008 and ended on October of 2011; a total of 18 samplings events (Table A2) that provided 104 individual samples. The long-term annual mean precipitation and the annual mean temperature at the SMEAR II station are 711 mm and 3.5°C, respectively (Pirinen et al., 2012). During the sampling period, the year 2009 was clearly drier than normal (mean annual precipitation 565.5 mm), and the years 2008 and 2011 were warmer than normal (mean annual 5.8°C for 2008 and 6.1°C for 2011).

2.~~3~~2.2 Measurement setup for VOC concentration profile of the second campaign, 2016

The gas collectors were installed in four different soil horizons (O-horizon, A-horizon, B-horizon, and C-horizon) in five soil pits permanently in 2011 (Fig. ~~3b~~1b, Table 2, and Table A1). The gas collectors in the O- and B-horizon refer to the measurements performed from the O- and B-horizon between 2008 and 2011. The pits were carefully excavated and the soil horizons O-, A-, B and C- were kept separate. The collectors were installed horizontally towards ~~in the vertical face interfacing with~~ the undisturbed soil in the excavated pits to minimize the excavation disturbance effect. After the installation, the soil layers were carefully placed back in the original order and compacted to the original volume of the soil. The measurements started on 21th of April 2016 and ended on 2nd of December of 2016; a total of 13 sampling events (Table A2). The mean temperature was 5.9°C. There was some snow on the ground in November and permanent snow cover in December, but no snow remained in April, when measurements commenced.

2.~~4~~3 VOC and CO_2 flux measurements and supporting data

Soil collars for VOC and CO_2 flux measurements were placed next (20–50 cm) in the five VOC measurement pits (Table 2). Soil collars were placed in March, 2016, and the measurements were started in April, 2016. Isoprenoid and oxygenated VOC fluxes were measured using a dynamic enclosure chamber technique as described by Mäki et al. (2017). The headspace (height 40 cm, chamber volume 10 L) was a glass chamber placed for measurements on permanently installed soil collars (height 7 cm, diameter 21.7 cm). We flushed the chamber headspace for 30 minutes to equilibrate the measurement system. During the chamber enclosure, we continuously pushed (1 l min^{-1}) filtered (active carbon trap and MnO2-coated copper net) ambient air into the chamber headspace and sampled the incoming and outgoing air for 1.5–2 hours through two Tenax TA-Carboback-B adsorbent tubes (flow rate 0.1-0.15 l min^{-1}). The dynamic enclosure method was previously tested in field conditions using standard gas with known VOC concentrations and quadrupole-PTR-MS (Kolari et al., 2012). The chamber system underestimates the artificially generated VOC emission rates at varying degree: for isoprene, monoterpene and many oxygenated VOCs the underestimation is 5-30%. The most uncertainties originate from adsorption of VOCs to moist or reactive surfaces, which are unavoidable when the enclosure contains living plant material. We estimated the flux rate (E, µg m^{-2} h^{-1}) of each VOC for soil area (area inside to collar, m^2) and time (h) using Eq. (1):

$$E = (C_{out} - C_{in})\frac{F_{chamber}}{1000}\frac{60}{A}, \quad (1)$$

where C_{in} is the ingoing air concentration (µg m^{-3}) and C_{out} is the outgoing air concentration (µg m^{-3}), $F_{chamber}$ (m^3 min^{-1}) is the filtered air that was pushed into the chamber headspace, and A (m^2) is the soil surface area covered by the soil collar.

The fluxes of CO_2 were determined using a dark static chamber technique (diameter 20 cm and height 30 cm) whereby a concentration of CO_2 the closed chamber headspace was measured for 5 minutes using a GMP343 CO_2 probe (Vaisala Oyj, Vantaa, Finland) and the CO_2 efflux was calculated by linear fitting against time and CO_2 concentration in the chamber headspace (Pumpanen et al., 2015). The SMEAR II data from Avaa (https://avaa.tdata.fi/web/smart) was used as an ancillary dataset (Hari and Kulmala, 2005). This dataset also included soil temperatures and soil water content for each soil horizon from the same measurement pits, where VOC concentrations were measured in 2016. Soil temperature was measured by thermistors (Philips KTY81-110, Philips semiconductor, Eindhoven, the Netherlands) and soil water content with TDR method (TDR 100, Campbell Scientific Inc., Logan, USA). Soil volumetric water content in the O-, A-, and B-horizon are means of five measurement pits and volumetric water content in the C-horizon is mean of four measurement pits at the SMEAR II station. Precipitation was measured by an FD12P weather sensor (Vaisala Oyj, Helsinki, Finland). The understory vegetation cover of the different species were visually estimated for each soil VOC/CO_2-collar (Table 2).

2.~~5~~ 4 Analytical methods

The adsorbent tubes were analyzed in the laboratory, using a thermodesorption instrument (Perkin-Elmer TurboMatrix 650; PerkinElmer, Waltham, MA, USA) attached to a gas-chromatograph (Perkin-Elmer Clarus 600) with a mass-selective detector

(Perkin-Elmer Clarus 600T) (Aaltonen et al., 2011, Mäki et al., 2017). The sample tubes were desorbed at 300°C for 5 min, cryofocused in a Tenax cold trap (-30°C) prior to injecting the compounds into the column by rapidly heating the cold trap (40°C min^{-1}) to 300°C. The mass detector used enabled simultaneous full scan and singular ion monitoring. Four-point calibration standards in methanol solutions were used, except for the isoprene measurements for which we used one gaseous calibration standard (National Physical Laboratory). The standards were injected into the sampling tubes and the methanol was flushed away for 10 minutes before the analysis. The analytical variability was determined using replicate standard analysis. The detection limits varied from 0.0002 to 0.057 µg m^{-3} in concentration measurements and from 0.0005 to 1.477 µg m^{-2} h^{-1} in flux measurements (Appendix Table A3). The VOC concentrations of isoprene, monoterpenes, sesquiterpenes and different oxygenated VOCs (C_4-C_{15} alcohols, carbonyls and acetates, methyl-2/3-furoates and α-pinene oxide) were analyzed. Calibration solutions for the sesquiterpenes, contained only longicyclene, isolongifolene, β-caryophyllene, α-humulene, α-gurjunene and β-farnesene. In 2016, other sesquiterpenes found in the samples were tentatively identified by their mass spectra and retention indices and quantified as β-caryophyllene, isolongifolene, or longicyclene. One of the sesquiterpenes could not be tentatively identified and was therefore denoted as SQT1.

2.~~6~~ 5 Calculations and statistical analyses

~~The VOC flux rate (µg m^{-2} h^{-1}) calculations were performed using equations described by Mäki et al. (2017).~~ The VOC concentrations (C, µg m^{-3}) for the different soil horizons were calculated with Eq. (~~1~~2):

$$C = m \Big/ \frac{V}{1000000} \qquad (\text{~~1~~2})$$

where *m* is the mass of sample (ng) and *V* is sampled volume (ml), divided by 1000000 to calculate the unit conversion from ml to m^3. *V* was calculated using Eq. (~~2~~3):

$$V = F * t \qquad (\text{~~2~~3})$$

where t is the sampling time (min) and F is the flow rate of the sampling (F, ml min^{-1}).

Data analyses were performed with MATLAB software (version 2015a, MathWorks, Natick, MA, USA). The Kolmogorov-Smirnov and Shapiro-Wilkin tests were used to test the normality of the individual VOC concentrations for the different soil horizons (O-horizon n = 52, A-horizon n = 65, B-horizon n = 65, and C-horizon n = 65). The Kolmogorov-Smirnov and Shapiro-Wilkin tests were also used for the total fluxes of monoterpene, sesquiterpene, oxygenated VOC fluxes, chamber temperature (°C) and soil water content for each measurement pit (N = 6–13). The non-parametric Kruskal-Wallis test (n = 65, df = 1, significance level of $p<0.100$ (°), $p<0.050$, $p<0.010$, $p<0.001$) was used to determine whether the VOC concentrations of the soil horizons were statistically different from each other (Appendix Table A4). The non-parametric

Kruskal-Wallis test (n = 13, df = 1) was used for comparing the following flux parameters between the different soil pits: CO_2, total monoterpene, total sesquiterpene, total oxygenated VOCs. The Kruskal-Wallis test was also used to compare chamber temperature, soil temperature and soil water content between the soil pits (Table 3). Pearson correlation coefficients were calculated for the following parameters: correlations between the monoterpene and sesquiterpene fluxes and concentrations within the different pits (n = 5–13, Appendix Table A5). The Pearson correlation coefficients (n = 34–65, Table 4) were also calculated for the following parameters: correlations between the monoterpene and sesquiterpene concentrations and between the soil temperature and water content within the different soil horizons. The Pearson correlation coefficients (n = 12–19, Appendix Table A6) were also calculated to compare the monoterpene and sesquiterpene fluxes to the chamber temperature and to the CO_2 fluxes in spring, summer, and autumn. The Pearson correlation coefficients (n = 8–17, Appendix Table A7) were also used to compare the monoterpene and sesquiterpene concentrations in the O- and A-horizon to the CO_2 fluxes in spring, summer, and autumn. The monthly mean monoterpene concentrations were compared for the O-horizon and the B-horizon in summertime between years using the non-parametric Kruskal-Wallis test to determine if belowground VOC production differed strongly between years (n = 3–10) or between the different measurement pits and gas collectors (n = 17–24) used in campaigns one (2008–2011) and two (2016). The detection limit (µg m^{-2} h^{-1}) of the VOC flux quantification (Appendix Table A3) was calculated for each VOC compound and for all 13 samplings based on the equations that can be found in the publication by Mäki et al. (2017). The detection limit (µg m^{-3}) of the VOC concentration quantification (Appendix Table A3) for the soil horizon measurements was calculated using the signal-to-noise ratio data obtained from the VOC quantification.

3 Results

Over 50 different VOCs were detected in the soil air during the two measurement campaigns with high annual variation in the belowground VOC concentrations. Belowground VOC concentrations were dominated by monoterpenes and sesquiterpenes, but the monoterpene and sesquiterpene concentrations were mainly decoupled from forest floor monoterpene fluxes.

3.1 Belowground vertical gradients of VOC concentrations ~~Belowground VOC concentrations in the vertical soil horizons~~ in 2016

Belowground VOC concentrations in the different soil horizons were compared (Fig. 4). Our hypothesis, that the concentrations in the topsoil were highest, was only partly confirmed. The total monoterpene concentrations in the A-horizon were 23 per cent of the total monoterpene concentrations measured from the O-horizon (Appendix Table A4). In the B- and C-horizon, the total monoterpene concentrations were 34 and 3 per cent of the values measured from the O-horizon (Appendix Table A4). The median of the total monoterpene concentrations was highest in the organic soil (36 µg m^{-3}), lower in the A-horizon (10 µg m^{-3}, $p<0.1$) and significantly smaller in the lower horizons (B-horizon 4 µg m^{-3}, $p<0.001$ and C-horizon 4 µg m^{-3}, $p<0.001$) (Appendix Table A4). However, total sesquiterpene and total oxygenated VOC (OVOC) concentration means

were highest in the A-horizon (15 and 10 µg m^{-3}, respectively) (Appendix Table A4). The total sesquiterpene and OVOC concentrations in the O-horizon were 16 and 54 per cent of the total sesquiterpene and OVOC concentrations measured from the A-horizon (Appendix Table A4). In the B-horizon, the total sesquiterpene and OVOC concentrations were 28 and 40 per cent of the values measured from the A-horizon (Appendix Table A4). The spatial and temporal variation in belowground VOC concentrations was remarkable, and statistically significant differences between soil horizons could not be observed for the total sesquiterpenes or for the total oxygenated VOCs. Sesquiterpenes and OVOCs are two very diverse groups of chemical compounds in which some compounds occurred in the highest concentrations in organic soil and other compounds in the A-horizon (Fig. 4, Appendix Table A4). There were no differences in ~~individual~~ VOC concentrations between the soil pits ~~when each soil horizon was tested separately~~ (data not shown). Soil water content was high in the C-horizon, which led to the high humidity in the adsorbent tubes and consequently in some samples (pits 4 and 5) could not be analyzed using the thermal desorption-gas chromatography–mass spectrometry method. ~~However, i~~It can be assumed that concentrations would have been relatively low as low oxygen availability slows down aerobic microbial activity (Davidson and Janssens, 2006)~~.~~, although anaerobic microbial activity likely occurs.

3.2 Belowground VOC concentrations and VOC fluxes from the soil surface in 2016

Total monoterpene concentrations in organic soil were highest in late summer (28.7. and 24.8.) and in December (1.12.) when the soils were under snow cover (Fig. 5). Monoterpene concentrations in mineral soil (A-~~ and B~~-horizon~~s~~) were generally higher in spring and summer (22.4-24.8) and decreased towards autumn except in December (1.12.F), when concentrations suddenly increased (Fig. 5). In general, there seemed to be a clear trend that belowground concentrations were exceptionally high in December under snow cover. Total sesquiterpene concentrations in the A-horizon~~mineral soil~~ were ~~clearly~~ highest in spring (22.4. and 17.5.), ~~in early June,~~ in late summer (24.8.), and in October (1.10.) (Fig. 5). There was no clear seasonal variation in the organic soil, except in October and in December when the concentrations suddenly increased in the whole soil profile (Fig. 5). There was no difference in isoprene concentrations and fluxes except in early October (1.10) (Fig. 5).

Total monoterpene fluxes were highest in October and lowest in late summer, whereas total sesquiterpene fluxes were highest in spring, in late summer and in October. Total monoterpene flux varied between 19.7–61.9 µg m^{-2} h^{-1}, sesquiterpene flux between 0.7–11.2 µg m^{-2} h^{-1}, and oxygenated VOC flux between 0.6–5.1 µg m^{-2} h^{-1} in 2016 (Table 3). There ~~was~~ were no statistically significant differences in VOC fluxes between measurement pits within the different VOC groups. The CO_2 flux was lower (0.03–0.08 mg m^{-2} s^{-1}) when understorey vegetation cover was high (45–63%) and CO_2 flux increased (0.13–0.21 mg m^{-2} s^{-1}) when the understorey vegetation cover was low (10–35%) (Table 3).

The belowground vertical concentration profiles were not coupled to observed soil surface fluxes rates~~Belowground monoterpene and sesquiterpene concentrations in vertical soil horizons were decoupled from forest floor monoterpene and sesquiterpene fluxes~~, when the whole data were combined ~~contrary to our hypothesis~~. In the individual pits, the monoterpene flux ~~in the individual pits~~ correlated with the organic soil concentration in pit four (R^2=0.78, $p<0.05$) and with the A-horizon in pit five (R^2=0.83, $p<0.050$) (Appendix Table A5). The sesquiterpene flux also correlated with

concentrations of the organic soil (R^2=0.62, p<0.050) and of the A-horizon (R^2=0.72, p<0.010) in pit three (Appendix Table A5). ~~However, S~~sesquiterpene ~~concentrations and forest floor fluxes had similar seasonal variation (Fig. 5)~~and OVOCs concentrations were decoupled from soil surface fluxes (Fig. 5). The monoterpene flux correlated with the chamber temperature from summer (R^2=0.43, p<0.05) to autumn (R^2=0.62, p<0.01) and with the CO_2 flux in autumn (R^2=0.79, p<0.001) (Appendix Table A6). The sesquiterpene flux also correlated with the chamber temperature in spring (R^2=0.52, p<0.05) and autumn (R^2=0.47, p<0.05) and with the CO_2 flux from summer (R^2=0.57, p<0.05) to autumn (R^2=0.63, p<0.01) (Appendix Table A6). There was no correlation between the monoterpene and sesquiterpene fluxes and the soil water content (data not shown). The monoterpene concentration in the A-horizon correlated with the CO_2 flux in autumn (R^2=0.76, p<0.01) (Appendix Table A7). There was also a correlation between the sesquiterpene concentration in the O-horizon and the CO_2 flux in autumn (R^2=0.68, p<0.05) (Appendix Table A7).

The belowground vertical monoterpene concentrations were also uncoupled to the ambient air concentrations measured about 30cm from the soil surface using the proton-transfer reaction mass-spectrometer (quadrupole-PTR-MS) from August to November in 2016 (Fig. 6). The ambient air concentrations were 0.3 to 17 per cent of the monoterpene concentrations in the O-horizon.

3.3 Soil temperature and water content impact on VOC concentrations, 2008–2011 and 2016

There was a moderate correlation between the monoterpene concentration and soil temperature in the organic soil (R^2=0.35 p<0.010) and on the B-horizon (R^2=0.46, p<0.001) and between the sesquiterpene concentration and soil temperature in the organic soil (R^2=0.29, p<0.050) from 2008 to 2011 (Table 4). These correlations are in line with our third hypothesis that soil temperature and water content can be used to explain belowground VOC synthesis. However, monoterpene and sesquiterpene concentrations mainly fail to correlate with soil temperature in 2016. ~~Confirming our third hypothesis that soil temperature and water content can be used to explain belowground VOC synthesis~~. Relatively low correlation between the monoterpene concentration and soil temperature (R^2=0.33 p<0.010) and of the sesquiterpene concentration and soil water content (R^2=0.23 p<0.050) was also found in the A-horizon in 2016 (Table 4). The correlation between the monoterpene concentration and soil water content was always negative, but not significant. In general, soil water content and temperature variation remained at normal levels during the measurement years, compared to the values reported for the same site in the literature (Kolari et al., 2009).

3.4 Inter-annual variation of soil VOC concentrations from 2008 to 2011 and in 2016

We took measurements to establish whether the belowground VOC concentrations differ between years as podzol soil is heterogenic and measurements were conducted from the different soil pits during both measurement campaigns. Statistically higher (p<0.050) summertime concentrations for monoterpenes were measured in the organic soil in 2016 in comparison to the values obtained in the first campaign between 2009 and 2011 (Fig. 7). There was no significant difference in the B-horizon

between the measurement campaigns. The organic soil showed similar trend ~~seasonal variation~~ in 2011 and 2016, when monoterpene concentrations increased together with soil temperature from spring (May) to summer (July) (Fig. 7).

Monoterpenes constituted almost 90% of the total VOC concentration, sesquiterpenes accounted for less than 10% between 2008 and 2011 (Table 5). Monoterpenes were observed in every single sampling, but sesquiterpenes were absent in the months of April, May, June, and November in 2009. Low concentrations of isoprene and oxygenated VOCs were also observed. The mean annual monoterpene concentrations in 2008- 2011 varied between 1.7 μg m^{-3} and 6.3 μg m^{-3} in organic soil and between 1.4 μg m^{-3} and 4.4 μg m^{-3} in mineral soil during the first campaign (Table 5). Similar to 2016, monoterpene concentrations in 2008- 2011 were almost consistently higher in the collectors that were located in the organic layer, but the differences between the organic and the mineral soil were small (Table 5). Monoterpene concentrations in 2009- 2011 were generally highest in summer/early autumn in organic soil, whereas the concentrations in mineral soil tended to peak slightly later (data not shown). ~~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.~~ The mean sesquiterpene concentration in the organic layer in 2008-2011 was 0.3 μg m^{-3} and 0.8 μg m^{-3} in mineral soil, but the concentrations were basically similar in both profiles (Table 5). The belowground concentrations of isoprene were low, only 0.03 and 0.01 μg m^{-3} in organic and mineral layers in the 2008- 2011 period and they were also less than 0.06 μg m^{-3} in 2016, except for October 2016 when isoprene concentration suddenly increased in the top of the mineral soil. Statistically significant differences between the organic and the mineral soil were not obtained for the 2008- 2011 period for any major compound or compound group and the spatial variation in belowground isoprenoid concentrations between the three measurement pits was substantial.

4 Discussion

4.1 VOC concentrations reflect the biological and physico-chemical properties of soil horizons

Our results clearly show that monoterpene concentrations are highest in organic soil. Podzol soil surface is formed by fresh vegetative litter that contains easily decomposable glucose, starch and cellulose, and very slow-decomposable organic matter (Beyer et al., 1996; Prescott et al., 2000; 2010). The concentrations of α-pinene, camphene, ß-pinene, myrcene, and limonene were highest the O-horizon. Monoterpene concentrations and emissions from the organic layer are probably driven by the monoterpene rich litter, in which the decomposition processes are regulated by litter quantity and quality, climate and soil microbial populations (Prescott, 2000). Both fluxes and concentrations of the monoterpenes and sesquiterpenes correlate with the CO_2 flux in autumn, which supports our conclusion that VOC production was driven by microbial activity (heterotrophic consumption). The decomposing litter has been assumed to be the main source for VOCs in the forest floor (Hayward et al., 2001; Leff and Fierer, 2008; Mäki et al., 2017). It is evident that both decomposers and the decomposing material affect the formation of VOCs, and also that VOCs released through the decomposition processes are probably very dependent on the litter type (Gray et al., 2010). Microbes are most active in organic soil, which contains easily available carbon for their metabolism (Makkonen and Helmisaari, 1998; Leff and Fierer, 2008; Pumpanen et al., 2008). Organic carbon and nitrogen

availability is typically higher in organic soil than in mineral soil (Parmelee et al., 1993; Deluca and Boisvenue, 2012). Soil properties also explain high monoterpene concentrations in the O-horizon. Soil porosity is higher in the O-horizon compared to the A-horizon, which means that gas diffusion is faster in the O-horizon compared to the A-horizon. The effect of rain filling soil pores and transporting VOCs towards deeper soil layers is likely stronger in the O-horizon.

Microbial community composition is determined by the carbon nitrogen ratio (C:N) ratio, pH and tree cover (Högberg et al., 2007), whereas high organic carbon and oxygen availability enhances the decomposition processes. A low pH favours fungi as the main decomposers over bacteria in boreal coniferous forest soils (Alexander 1977). However, sequencing revealed that the dominating groups of bacteria in humus are Acidobacteria, Proteobacteria, and Actinobacteria (Timonen et al., 2017). The individual sources of VOCs are very difficult to determine under field measurement conditions, but laboratory experiments show the capability of soil fungi to produce and emit numerous volatile compounds (Bäck et al., 2010; Müller et al., 2013). Roots of trees and perennial shrubs are also an important belowground VOC source (Smolander et al., 2006; Lin et al., 2007) and their uneven coverage also causes spatial variation among the concentration measurements. Detectable isoprene concentrations belowground were surprising because isoprene is known to be produced in photosynthetic tissues, and production is strongly light dependent without storages in plant cells (Monson et al., 1989, Delwiche et al., 1993, Sharkey and Singsaas, 1995). However, laboratory measurements reported indicate that isoprene can also be produced by fungi (Bäck et al., 2010) and by needle litter during decomposition (Gray et al., 2010).

~~We detected higher monoterpene concentrations in organic soil compared to the B and C horizons, which could be explained by low biological activity as quantities of roots and organic carbon content for microbial metabolism decrease with depth.~~ H~~owever, h~~igh monoterpene and sesquiterpene concentrations were also detected in the A-horizon~~top horizon of mineral soil~~, which contains the bulk of roots and most of the root-associated microbes. Our results indicated that sesquiterpene production (bornylacetate, α-gurjunene, α-humulene, and ß-himachalene) is not linked to the storage in plant litter, but rather to roots and the root-associated microbes which are most abundant/active in the A-horizon. VOCs are widely used in soils as defence and communication infochemicals between soil organisms (Insam and Seewald, 2010 and Schulz and Dickschat, 2007, Peñuelas et al., 2014). The carbon content and microbial biomass was expected to decrease exponentially with depth, which likely explains why VOC concentrations were lowest in the B- and C-horizon. The VOCs in mineral soil may be related to the living roots or decaying root-litter. Monoterpene emissions from the root-soil interface can be quantitatively and qualitatively different from those emitted by dead roots (Lin et al., 2007), which can cause variation to the VOC concentrations between the soil horizons. Sesquiterpene concentrations were quite homogeneous between soil horizons, which indicates that sources for sesquiterpenes are more stable and possibly also relatively independent of environmental factors. Sesquiterpenes measured under laboratory conditions are produced by endophytes (Bäck et al., 2010), decomposers (Rösecke et al., 2000, Bäck et al., 2010, Weikl et al., 2016) and ectomycorrhizal fungi (Ditengou et al., 2015). The low volatility and high reactivity of sesquiterpenes can result in much higher concentrations near the sources than average concentrations in the soil horizon. Quantified sesquiterpene concentrations can be underestimated since organic soil is highly porous media and sesquiterpenes as highly reactive compounds can be converted into other compounds by chemical reactions with soil air

oxidants. A lack of pure standards also increased the uncertainty of certain sesquiterpene (SQT1, α-buinesene, γ-muurolene, α-bisabolene, β-himachalene, α-muurolene, Δ-cadinene) analyses.

Our results show moderate correlation between isoprenoid concentrations and soil temperature, which was expected as biological and physico-chemical processes such as diffusion and volatility are directly influenced by temperature (Peñuelas and Staudt, 2010). Moreover, enzyme activity of microbial metabolism that lead to the VOC production (Mancuso et al., 2015) are strongly affected by temperature. The results also showed negative correlations between soil water content and the monoterpene concentrations, although the correlation was not significant. Diffusion of gases can be effectively prevented by water, which blocks the microspores in the soil in wet weather or poorly drained soils. In sandy soils, water movement downward from organic soil horizon is usually efficient and this can also transport water soluble OVOCs (verbenone, 1-butanol, isopropanol, 2-butanone, 1-hexanol and cis-3-hexenyl acetate, and slightly water-soluble methyl-12-furoate, 1-penten-3-ol, 1-pentanol, butyl acetate, trans-3-hexen-1-ol, trans-2-hexen-1-ol, and α-pinene oxide) into the mineral soil and reduce the differences in VOC concentrations between the organic and mineral soil horizons.

The soil concentrations were mostly decoupled from forest floor VOC fluxes, which indicates that belowground sources are different from those that release VOCs from the soil surface. Most of the measured fluxes at the forest floor level probably originates from understorey vegetation and decomposing organic layer, humus (Hewitt and Street, 1992; Aaltonen et al., 2011; Faubert et al., 2012; Rinnan et al., 2014). The forest floor vegetation also absorbs VOCs on the moist leaf surfaces, which creates a bidirectional flux especially under moist conditions (Aaltonen et al., 2013). However, the time lag between concentrations deeper in the soil and the flux measured above the humus layer make it difficult to compare the concentrations with the fluxes. Temperature and moisture conditions are also probably different between belowground and soil surface, which suggests that effect of physico-chemical processes is different. There was some correlation between isoprenoid concentration and fluxes, when individual soil pits were compared. The total uncertainty at the 10 μg m^{-2} h^{-1} emission level with the used quantification method was found to be relatively low, 14–44% for monoterpenes and 14–20% for sesquiterpenes (Mäki et al., 2017).

Spatial variation in isoprenoid concentrations was substantial, even though the forest at the site was fairly homogenous. Similarly, very high spatial variation in forest floor VOC fluxes at the SMEAR II stand was reported by Aaltonen et al. (2011, 2013). This reflects the spatial heterogeneity in soil structure and soil processes, and which occurred in many other measurements, and underlines the importance of having a sufficient number of parallel sampling points. Despite the high spatial variability between the pits no significant differences in individual isoprenoid concentrations were found between each soil pit which were compared among soil horizons.

4.2 Seasonal and inter-annual variation

The three-year measurements of the 2009- 2011 period indicated noteworthy concentrations of isoprenoids in the belowground horizons that were similar in magnitude to reported aboveground concentrations. The following aboveground concentration ranges were obtained: α-pinene (0.2–6.3 μg m^{-3}), Δ-3-carene (0.1–2.5 μg m^{-3}), β-pinene (0.04–0.3 μg m^{-3}), and camphene

(0.02–0.3 µg m^{-3}) in the same boreal coniferous forest by Hakola et al., (2009). Soil VOC concentrations are not directly comparable with air concentrations as the soil air volume is concentrated only into soil pores. Belowground monoterpene~~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. The annual variability was also mostly covered, since measurements were executed in spring, summer and autumn in 2009, 2011, and also in 2016. The seasonal variation in monoterpene concentrations was more distinctive than in sesquiterpenes. With sesquiterpenes basically no seasonal trend was observable except in the year 2009, when emissions were highest in the O-horizon in August and in the B-horizon in September and in the year 2016 in October and in December, when the concentrations suddenly increased in the whole soil profile. There was no clear seasonal variation for isoprene. However, the variation in the belowground isoprenoid concentrations was less clear than what has been observed in isoprenoid fluxes sampled from the forest floor (Aaltonen et al., 2011, 2013; Mäki et al., 2017). It is difficult to make comparisons between the campaigns one and two, when VOC concentrations measurements were done using two different measurement set-ups. The timing of the high concentrations also differs from the peaks in forest floor VOC fluxes that were observed in earlier studies. Soil VOC concentrations were highest as early as in mid and late summer, whereas forest floor fluxes do not start to increase before the end of the summer (Aaltonen et al., 2011). High soil water content in spring hinders the diffusion process and could also cause isoprenoid accumulation in the soil. Isoprene was not consistently observed and its highest concentrations were always obtained during autumn, not during the season of active shoot growth. VOC concentration measurements were conducted in the different gas collectors during the first measurement 2008- 2011 and the second (2016) measurement campaigns. The experimental variables that changed in this study were structure, installation and the length of the recovery time between installation and measurements. Changes in any of these variables can impact upon the VOC concentrations between the two campaign periods. The recovery period between installation and first sampling was as short as six months in 2008, but by 2009 it was 11 months. The recovery period was as long as five years by the time the second campaign was implemented.

During the second campaign, the measurements indicated noteworthy concentrations of isoprenoids belowground throughout the year. Soil concentrations and forest floor fluxes of sesquiterpenes were relatively high during spring, which was contrary to the findings of two earlier studies that reported the branch measurements of sesquiterpene emissions mainly occurred in midsummer (Tarvainen et al., 2005; Hakola et al., 2006). Sesquiterpenes in soil can originate from vegetation and decomposition processes with decaying substrates. Belowground monoterpene concentrations varied seasonally and had high concentrations in late summer, in October, and in December. High concentrations in October are in agreement with observations of the timing of isoprenoid fluxes from the forest floor reported in other studies (Hellén et al., 2006; Aaltonen et al., 2011, 2013; Mäki et al., 2017). Our results indicate that isoprenoid production is not limited only to the maximum litter production period in autumn, but that the organic soil is a relatively active VOC production source during the whole snow free period. Decomposition processes slowly release isoprenoids from needle storages (Kainulainen and Holopainen, 2002) and vegetation drops small amounts of litter the year-round, thus litter is a continuous and renewable VOC

source on the soil surface. The low seasonal variation in monoterpene concentrations in deeper mineral soils compared to organic soil and top mineral soil may be related to differences in source abundance between vertical soil horizons. The VOCs can also be captured in soils through adsorption on clay minerals (Deng et al., 2017), which indicates that VOCs are not released into the atmosphere.

We also measured the soil isoprenoid concentrations on one occasion during the snow cover period in this study. It is likely that the relatively high concentrations of VOCs we found in that sample taken from organic soil in wintertime are related to physical characteristics of the snowpack. The snowpack would expected to have icy layers and low temperatures; characteristics that would render it to be relatively impermeable and thus hinder the diffusion of VOCs. Such a reduction in diffusion would result in the accumulation of VOCs at the snow-soil interface and also within the surface layers of soil itself. Aaltonen et al. (2012) measured both monoterpene (0.4–6.2 µg m^{-3}) and sesquiterpene (0.08–1.0 µg m^{-3}) concentrations inside the snowpack, and showed that the concentrations were generally higher close to the soil surface and lower just next the snowpack air interface. We found that the wintertime monoterpene concentrations in the organic layer were high, and were in the same order of magnitude as those reported inside snowpack during winters (Aaltonen et al., 2012). Microbial activity can led to~~ad~~ VOC production in the snowpack close to the soil surface (Liptzin et al., 2015).

It could be argued that the period of snow cover is diminishing due climate warming. ~~, which could mean that~~ VOC emissions from boreal soils could be increased without snow cover that hinders VOC diffusion in the atmosphere, because microbial activity also occurs in low temperatures. If air temperatures will increase and snow melts earlier, it could also increase VOC production and emissions from organic soil though microbial decomposition and metabolism, when radiation warms a dark soil surface. ~~VOC emissions would increase overall and also as a result of elevated temperatures.~~ Alternatively, activity might be reduced because of waterlogging in warmer wetter winters, which could make snow cover less permeable (Aaltonen et al., 2012). The water-soluble VOCs can also be sequestered by wet snow. Instead VOCs would probably be released into the atmosphere in spring, when the snow melts. Chamber flux measurements showed that some VOCs are released through the soil surface and snowpack into the atmosphere in December during continuous snow cover, which indicates that soil and snowpack is also a VOC source during wintertime. So far, there is a very small number of other studies that have measured VOC fluxes during wintertime and more research is needed ~~on~~ to combine soil VOCs to microbial processes~~how soil contributes to the atmospheric processes in winter time~~.

5 Conclusions

Soil vertical layer VOC concentrations were analysed and compared with simultaneous chamber flux measurements in field conditions in a Boreal coniferous forest. We detected more than 50 different VOCs, mostly mono- and sesquiterpenes, and belowground concentrations of VOCs differed between soil layers during the second campaign**.** Sources of the forest soil VOCs probably differ depending on the compound and soil layer. Dominating monoterpenes concentrations are comparable to the air concentrations above a coniferous forest. This is - as far as we know - the first quantitative analysis of this topic.

~~Our unique measurement setup demonstrates that boreal forest soil is a significant and diverse VOC source, in which dominating monoterpenes concentrations are comparable to the air concentrations above a coniferous forest. Soil is a potential VOC source during winter time and this phenomenon merits further study and our measurement setup would be a potentially useful tool for investigating that. These measurements revealed high belowground isoprenoid concentrations, thus, the next step is to study the formation processes of VOCs by using a laboratory approach. It would also be important to determine in the laboratory, how strongly production processes of VOCs are regulated by temperature and water content, and also study how the warming climate will impact upon VOC fluxes from the boreal forest floor.~~

Data availability. Mäki, Mari (2017), "Data for the manuscript", Mendeley Data, v1. DOI: 10.17632/dn2rj3yf9p.1

Author contributions. Manuscript preparation and analyzing results (M.M. and H.A.). All authors contributed to the experimental planning, the discussion of the results and the writing on the manuscript.

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Figures and Tables

Table 1: Soil characteristics of the measurement site. The depth of lower horizon border (cm), volume weight (g cm^{-3}), particle size of clay (%), silt (%), and sand (%), N-content (mg g^{-1}), C-content (mg g^{-1}), and pH value (in $CaCl_2$) of the measurement pits for the different soil horizons at the SMEAR II station in 1995. Values are means of measurement pits 1, 4, and 5.

Horizon	Depth of lower horizon border	Volume weight (g cm^{-3})	Rocks (% of weight)	Particle size (% of weight) clay	silt	sand
O	0.00					
A	6.54	0.75	28.61	5.65	13.72	52.02
B	26.83	0.86	27.68	6.72	13.01	52.60

C	71.14	1.27	36.25	6.91	12.56	44.28

Horizon	N-content (mg g^{-1})	C-content (mg g^{-1})	pH in $CaCl_2$
O	13.46	355.68	3.39
A	1.02	32.23	3.53
B	1.07	23.51	4.36
C	0.13	4.15	4.49

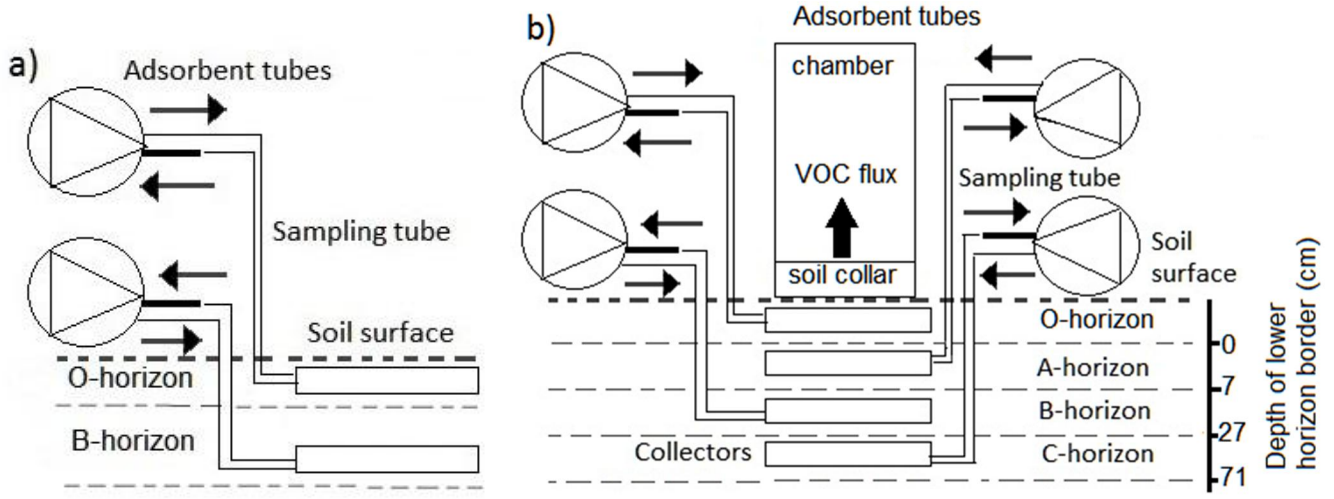


Figure 1: Measurement set-up for soil VOC concentration profiles a) in 2008- 2011 and b) in 2016.

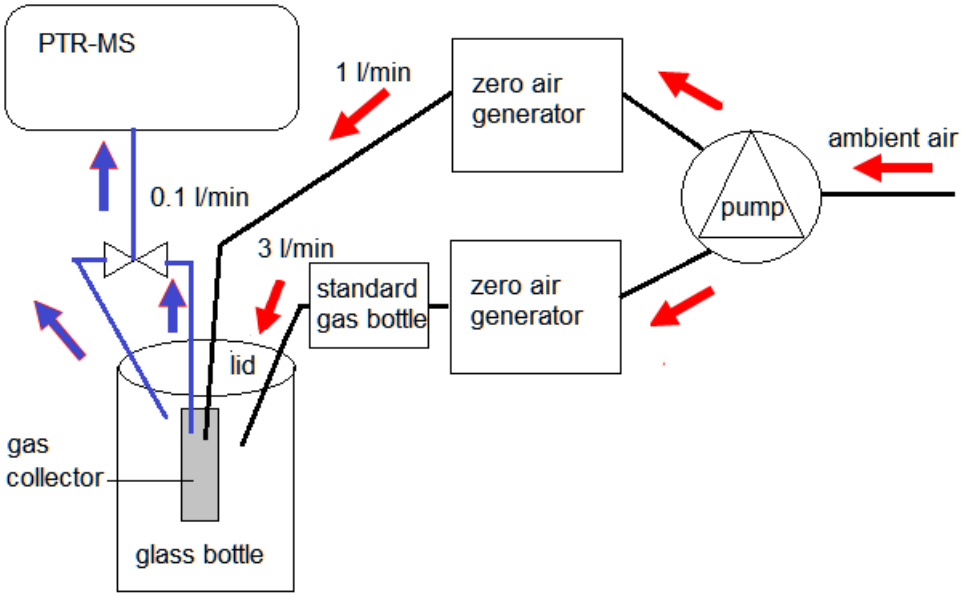


Figure ~~1~~2: Set-up for the permeability tests of the sintered gas collectors. The sintered gas collector means that PTFE tube is closed on one side.

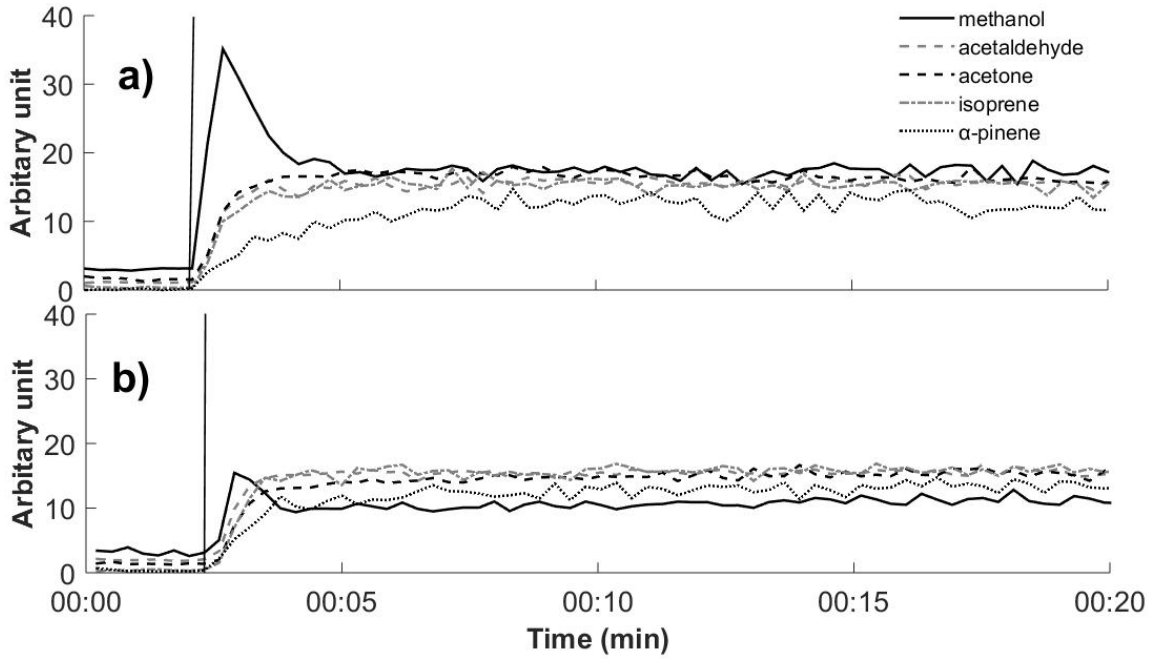
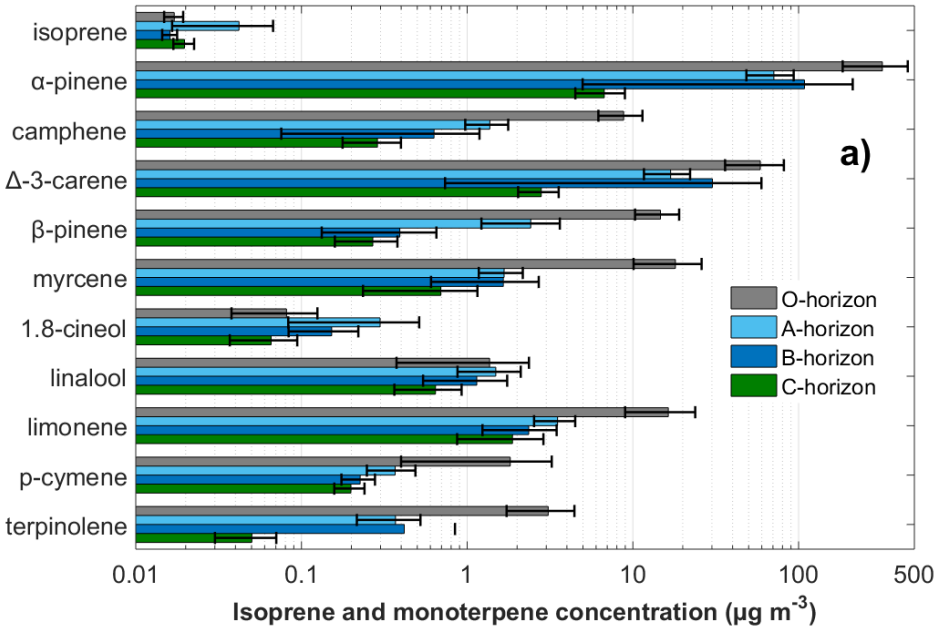


Figure ~~2~~3: Results of the permeability tests of the PTFE collector with the five VOCs. A permeability test was used to monitor how fast VOCs permeate into the gas collector and to determine how fast VOC concentrations stabilize between the air inside and outside the collector. Panel a) shows the results with dry collector and panel b) with a wetted collector. Vertical line shows the time point when the introduction of the VOC standard began.

Table 2: Soil depth (cm) and soil surface coverages (%) of ericoid shrubs, mosses, grasses, and non-vegetative surface on the different measurement pits in 2016.

Pit	Soil depth (cm)	Ericoid shrubs (%)	Mosses (%)	Grasses (%)	Non-vegetative surface (%)
1	50	25	10	¾	65
2	60	5	¾	5	90
3	80	25	20	¾	55
4	130	15	30	18	37
5	160	7	2	8	83



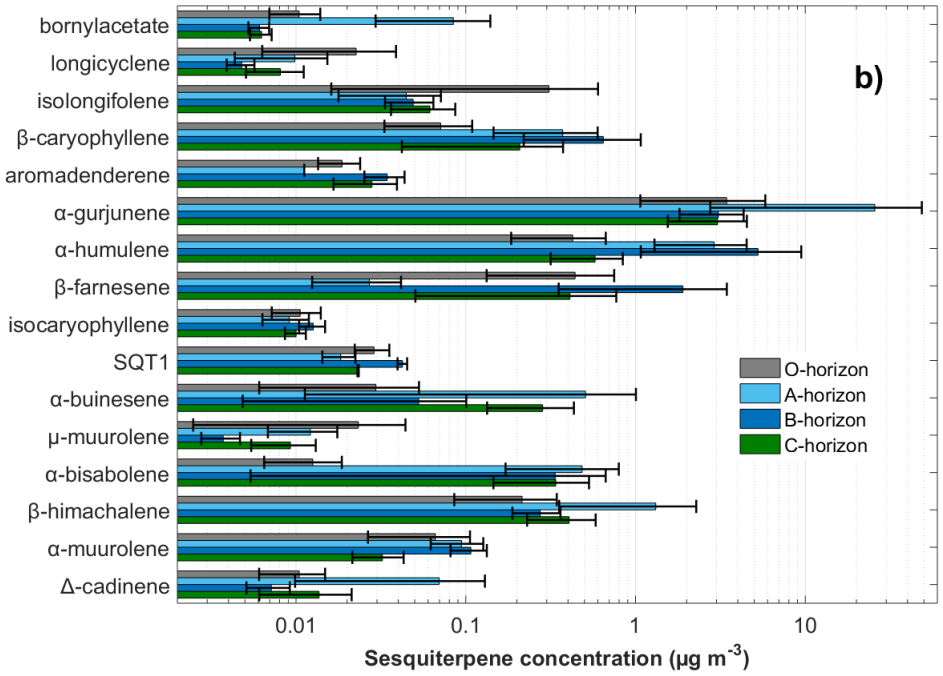
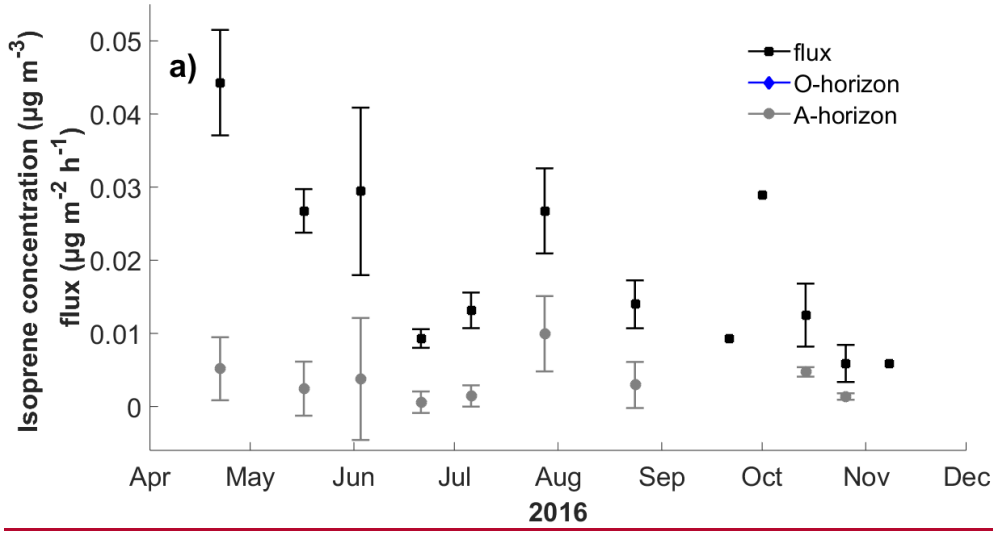


Figure 4: Isoprene and individual monoterpene (a) and sesquiterpene (b) concentrations (μg m^{-3}) from the different soil horizons (O (N=52), A (N=65), B (N=65), and C (N=65)) in 2016. Concentrations are means and error bars are standard error of the whole data for each soil horizon. SQT1 was not identified.

5



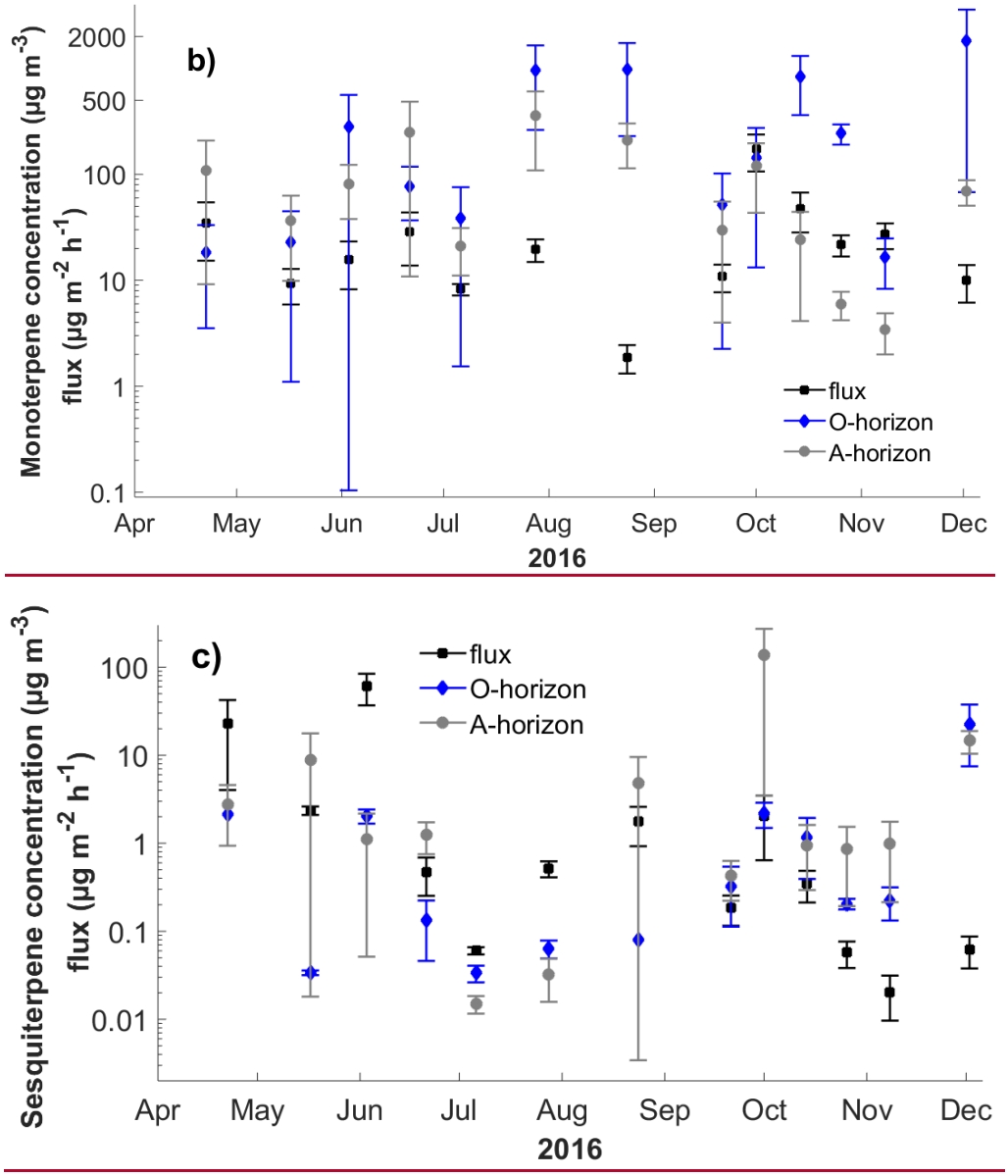


Figure 5: The mean a) isoprene, b) monoterpene, and c) sesquiterpene fluxes (µg m^{-2} h^{-1}) from the forest floor and concentration (µg m^{-3}) from the O- and A-horizon ~~each soil horizon~~ from April to December in 2016. Error bars are standard error of the four (O-horizon) or five (A-~~, B-, and C-~~horizon) gas collectors.

Table 3: The soil depth (cm), the mean monoterpene, sesquiterpene, oxygenated VOCs (C4–C15 alcohols, carbonyls and acetates, methyl-2/3-furoates and α-pinene oxide) and CO_2 fluxes above the soil surface (µg m^{-2} h^{-1}), chamber temperature (°C), soil temperature (°C, A-horizon), and soil water content (m^3 m^{-3}, A-horizon) from the measurement pits. Values are means (S.E.) of the whole dataset in 2016 (N= 6–13). The effect of soil horizon on fluxes and environmental conditions was tested with the Kruskal-Wallis test ($p<0.050$). Significant differences between the pits are indicated with different letters (Kruskal-Wallis test; $p<0.050$).

Pit	Soil depth cm	Monoterpenes µg m^{-2} h^{-1}	Sesquiterpenes µg m^{-2} h^{-1}	OVOC µg m^{-2} h^{-1}	CO_2 flux µg m^{-2} h^{-1}	Chamber temperature C°	Soil temperature C°	Soil water content m^3 m^{-3}
1	50	49.05[a] (30.30)	4.56[a] (2.80)	5.12[a] (3.72)	0.15[a] (0.02)	10.82[a] (2.28)	8.29[a] (1.27)	0.14[a] (0.01)
2	60	19.71[a] (7.25)	6.34[a] (5.50)	1.84[a] (0.67)	0.13[ac] (0.04)	11.08[a] (1.99)	8.67[a] (1.54)	0.12[a] (0.09)
3	80	20.73[a] (4.80)	11.16[a] (10.91)	0.59[a] (0.14)	0.03[b] (0.02)	9.33[a] (2.77)	8.39[a] (1.32)	0.34[b] (0.06)
4	130	26.09[a] (8.72)	8.08[a] (7.63)	0.61[a] (0.26)	0.08[c] (0.01)	10.45[a] (3.04)	7.72[a] (1.51)	0.30[b] (0.02)
5	160	61.90[a] (36.95)	0.67[a] (0.25)	0.96[a] (0.33)	0.21[a] (0.07)	12.24[a] (2.40)	6.58[a] (1.20)	0.78[c] (0.12)

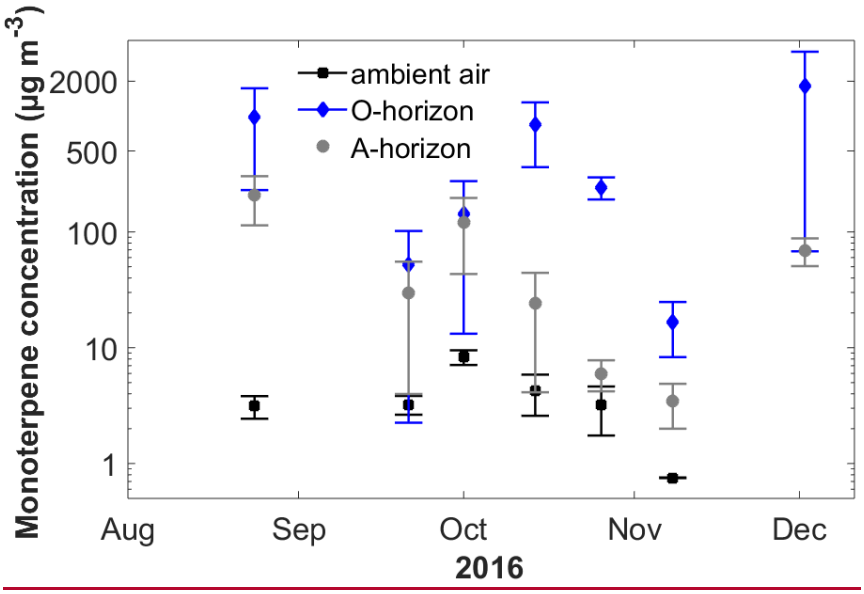


Figure 6: The mean monoterpene concentration (µg m^{-3}) from the O- and A-horizon and from the ambient air from August to December in 2016. Error bars are standard error of the four (O-horizon) or five (A-horizon) gas collectors. Error bars of ambient air measurements are based on two measurement locations at the SMEAR II station.

Table 4: Pearson correlation between the total monoterpene and sesquiterpene concentrations and soil temperature (°C) and water content (m^3 m^{-3}) from the O- and the B-horizon in 2008–2011 and from the different soil horizons in 2016. The significance level of p<0.100 (o), p<0.050 (*), p<0.010 (**), p<0.001 (***)) was used. VOC concentrations were measured from the different gas collectors in 2008–2011 and in 2016 (Fig. 1a and 1b).

Year	Horizon	Correlation coefficient	N	P value	Correlation coefficient	N	P value

	Soil temperature C°	Monoterpene concentration µg m^{-3}			Sesquiterpene concentration µg m^{-3}		
2008–2011	O	**0.35**	49	0.007**	**0.29**	34	0.049*
2008–2011	B	**0.46**	51	0.0004***	0.16	36	0.17
2016	O	-0.01	52	0.52	-0.32	52	0.97
2016	A	**0.33**	65	0.005**	0.02	65	0.44
2016	B	-0.21	65	0.98	-0.27	65	0.98
2016	C	-0.17	65	0.89	-0.32	65	0.99
	Soil water content m^3 m^{-3}	Monoterpene concentration µg m^{-3}			Sesquiterpene concentration µg m^{-3}		
2008–2011	O	-0.13	49	0.81	-0.30	34	0.96
2008–2011	B	-0.35	51	0.99	-0.43	36	0.99
2016	O	-0.01	52	0.53	-0.11	52	0.75
2016	A	-0.09	65	0.76	**0.23**	65	0.04*
2016	B	-0.09	65	0.75	0.03	65	0.42
2016	C	-0.09	65	0.74	**0.19**	65	0.098º

Table 5: Annual mean isoprenoid concentrations (S.E., µg m^{-3}) in soil. Note that the year 2008 consists of only one sampling in November. BDL means below detection limit of the VOC quantification.

µg m^{-3}	2008 1 sampling		2009 9 samplings		2010 3 samplings		2011 4 samplings	
	5 cm	17cm	5 cm	17cm	5 cm	17cm	5 cm	17cm
isoprene	0.01	$4x10^{-3}$	0.02 (0.01)	0.01 ($2x10^{-3}$)	0.06 (0.01)	0.03 ($3x10^{-3}$)	0.02 (0.02)	0.01 ($2x10^{-3}$)
methyl butenol	$4x10^{-3}$	$3x10^{-3}$	0.01 (0.01)	$3x10^{-3}$ ($1x10^{-3}$)	0.01 ($3x10^{-3}$)	0.02 (0.01)	0.01 ($2x10^{-3}$)	$4x10^{-3}$($1x10^{-3}$)
Monoterpenes								
α-pinene	0.63	0.60	1.88 (0.92)	2.35 (0.99)	1.37 (0.72)	1.61 (1.13)	2.88 (0.80)	1.80 (0.54)
camphene	0.02	0.02	0.07 (0.02)	0.11 (0.06)	0.06 (0.03)	0.04 (0.02)	0.04 (0.01)	0.04 (0.02)
ß-pinene	0.04	0.04	0.35 (0.24)	0.26 (0.10)	0.07 (0.03)	0.43 (0.35)	0.14 (0.04)	0.11 (0.05)
Δ-3-carene	0.84	0.67	2.56 (0.79)	1.42 (0.35)	1.34 (0.77)	1.07 (0.70)	2.92 (0.92)	2.14 (0.61)
p-cymene	0.06	0.04	0.07 (0.02)	0.06 (0.01)	0.09 (0.03)	0.03 (0.01)	0.06 (0.02)	0.04 (0.01)
1,8-cineol	BDL	BDL	BDL	BDL	0.02 ($3x10^{-3}$)	0.01 ($1x10^{-3}$)	$3x10^{-3}$ ($1x10^{-3}$)	$3x10^{-3}$ ($1x10^{-3}$)
limonene	0.07	0.05	0.20 (0.05)	0.16 (0.06)	0.21 (0.05)	0.11 (0.03)	0.25 (0.08)	0.18 (0.05)
terpinolene	BDL	$4x10^{-3}$	0.12 (0.07)	0.12 (0.03)	0.19 (0.13)	0.10 (0.07)	0.04 (0.01)	0.03 (0.01)
linalool	BDL	BDL	$3x10^{-3}$	0.04 (0.02)	0.11	0.01	0.01 (0.01)	$3x10^{-3}$
myrcene	BDL	BDL	BDL	BDL	BDL	BDL	0.01 ($1x10^{-3}$)	0.01 ($2x10^{-3}$)
nopinone	BDL	BDL	0.01 ($5x10^{-3}$)	0.02 (0.01)	0.02 ($3x10^{-3}$)	0.01 ($2x10^{-3}$)	$4x10^{-3}$ ($1x10^{-3}$)	$4x10^{-3}$ ($2x10^{-3}$)
bornylacetate	BDL	0.001	0.05 (0.02)	0.21 (0.10)	0.02 (0.01)	0.01 ($2x10^{-3}$)	0.01 (0.01)	$3x10^{-3}$ ($1x10^{-4}$)

Total monoterpenes	1.66	1.43	4.85 (1.83)	4.30 (1.44)	3.18 (1.60)	3.18 (2.14)	6.34 (1.84)	4.35 (1.27)
Sesquiterpenes								
longicyclene	BDL	BDL	0.05 (0.02)	0.16 (0.06)	0.11 (0.05)	0.01 ($2x10^{-3}$)	0.01($1x10^{-3}$)	0.01 ($2x10^{-3}$)
iso-longifolene	$3x10^{-3}$	$4x10^{-3}$	0.04 (0.01)	0.17 (0.07)	0.02 (0.01)	0.01 ($2x10^{-3}$)	$4x10^{-3}$ ($1x10^{-3}$)	$3x10^{-3}$ ($1x10^{-3}$)
ß-caryophyllene	BDL	BDL	0.07 (0.02)	0.21 (0.08)	0.08 (0.05)	0.05 (0.01)	0.03 (0.01)	0.02 (0.01)
aromadendrene	BDL	BDL	0.06 (0.02)	0.26 (0.11)	0.04 (0.02)	0.01 (0.01)	0.06 (0.04)	0.08
α-humulene	BDL	BDL	0.06 (0.02)	0.21 (0.10)	0.02 (0.002)	0.01 (0.01)	$1x10^{-3}$ ($3x10^{-4}$)	0.01 (0.01)
ß-farnesene	BDL	BDL	0.09 (0.03)	0.38 (0.11)	0.03 (0.003)	0.01 ($2x10^{-3}$)	0.01 ($2x10^{-3}$)	0.01 ($2x10^{-3}$)
Total sesquiterpenes	0.03	$4x10^{-3}$	0.28 (0.08)	1.03 (0.36)	0.22 (0.08)	0.07 (0.02)	0.06 (0.02)	0.04 (0.01)

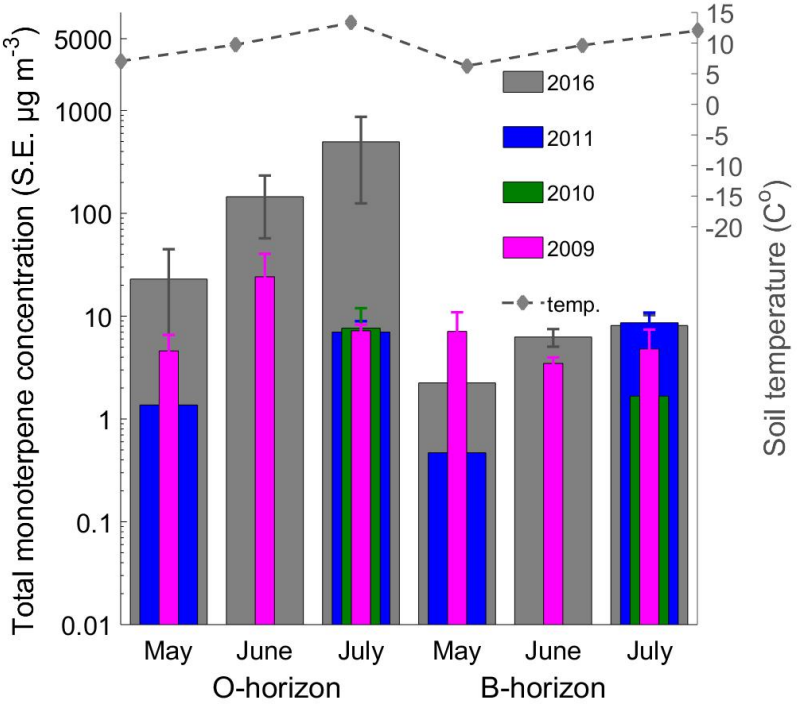


Figure 7: The monthly mean monoterpene concentration (µg m^{-3}) and soil temperature (C°) for the O-horizon and the B-horizon during the summer months in 2009- 2011 and in 2016. Error bars are standard error of the three gas collectors in 2009, 2010, and 2011, and four (O-horizon) or five (B-horizon) gas collectors in 2016.

Appendix

Table A1: Measurement depths (cm) of the different soil horizons (O, A, B, and C) from eight measurement pits. The campaign measurements were made from three soil pits in 2008- 2011 (0 cm being the surface of O-horizon) and from five pits in 2016 (0 cm being the surface of mineral soil).

2008–2011					
Pit 1		**Pit 2**		**Pit 3**	
Horizon	Depth	Horizon	Depth	Horizon	Depth
O	-5	H	-5	O	-5
B	-17	B	-17	B	-17

2016									
Pit 1		**Pit 2**		**Pit 3**		**Pit 4**		**Pit 5**	
Horizon	Depth	Horizon	Depth	Horizon	Depth	Horizon	Depth	Horizon	Depth
O	-2			O	-3	O	-3	O	-2
A	2	A	1	A	7	A	3	A	5
B	9	B1	13	B	29	B1	15	B1	20
		B2	35			B2	27	B2	33
C	23	C	63	C	62	C1 C2	50 97	C	57

Table A2: Measurement months for VOC concentrations measurements in 2008- 2011 period and for VOC concentration and chamber flux measurements in 2016.

Year	Measurement months	Sampling times
2008	November	1
2009	April, May, June, July, October, November, and December	1
	September	2
2010	July, August, and November	1
2011	May, June, August, and October	1
2016	April, May, June, November, and December	1
	July, August, September, and October	2

Table A3: The detection limit of measured VOCs in concentration (µg m^{-3}) and flux measurements (µg m^{-2} h^{-1}). Compounds marked with (†) are only tentatively identified and quantified.

Compound	Concentration 2008–2011	Concentration 2016	Flux	Compound	Concentration 2016	Flux

isoprene	$5x10^{-3}$	$5x10^{-3}$	0.01	**OVOCs**		
2-methyl-3-buten-2-ol	$2x10^{-3}$			geraniol	$4x10^{-3}$	0.12
Monoterpenes				methyl-12-furoate	$1x10^{-3}$	0.01
α-pinene	$1x10^{-3}$	0.03	0.18	α-bisabolol	0.01	0.04
camphene	$1x10^{-3}$	0.02	0.01	verbenone	0.01	0.02
Δ-3-carene	$2x10^{-3}$	0.06	0.06	nuciferol	$2x10^{-4}$	0.01
ß-pinene	$2x10^{-3}$	0.01	0.01	methy-3-furoate	0.01	0.02
myrcene	$2x10^{-3}$	0.01	0.01	1-butanol	0.06	0.18
1,8-cineol	$3x10^{-3}$	0.01	0.01	isopropanol	$2x10^{-3}$	0.01
linalool	0.01	0.01	0.32	2-butanone	0.02	0.04
limonene	$2x10^{-3}$	$5x10^{-3}$	0.10	1-penten-3-ol	$2x10^{-3}$	$5x10^{-3}$
p-cymene	$1x10^{-3}$	0.02	0.02	1-pentanol	0.01	0.01
terpinolene	0.01	$2x10^{-3}$	$2x10^{-3}$	2-methyl-2-buten-1-ol	$1x10^{-3}$	$2x10^{-3}$
Sesquiterpenes				butyl acetate	$1x10^{-3}$	$5x10^{-3}$
bornylacetate	$3x10^{-3}$	$2x10^{-3}$	$4x10^{-3}$	cis-3-hexen-1-ol	0.01	0.02
longicyclene	$1x10^{-3}$	$1x10^{-3}$	$2x10^{-3}$	trans-3-hexen-1-ol	0.01	0.01
isolongifolene	$1x10^{-3}$	$2x10^{-3}$	$5x10^{-3}$	trans-2-hexen-1-ol	$2x10^{-3}$	$4x10^{-3}$
ß-caryophyllene	0.01	0.01	0.01	1-hexanol	$1x10^{-3}$	0.01
aromadendrene†	$3x10^{-3}$	0.01	$5x10^{-3}$	cis-2-hexen-1-ol	0.01	0.02
α-gurjunene		0.01	1.48	1-octen-3-ol	$2x10^{-3}$	0.03
α-humulene	$4x10^{-3}$	$2x10^{-3}$	0.09	6-methyl-5-heptene-2-one	$5x10^{-3}$	0.03
ß-farnesene	$2x10^{-3}$	0.02	0.02	cis-3-hexenyl acetate	0.03	0.06
isocaryophyllene†		$4x10^{-3}$	0.01	hexyl acetate	0.01	0.012
SQT1†		0.01	0.02	trans-2-Hexenyl acetate	$3x10^{-3}$	0.005
α-buinesene†		$1x10^{-3}$	0.02	α-pinenepxide	0.01	0.01
γ-muurolene†		$2x10^{-3}$	$1x10^{-3}$			
α-bisabolene†		$3x10^{-4}$	$1x10^{-3}$			
β-himachalene†		$1x10^{-3}$	$3x10^{-3}$			
α-muurolene†		$1x10^{-3}$	0.01			
Δ-cadinene			0.15			

Table A4: Isoprene, monoterpenes, sesquiterpenes and oxygenated VOC concentrations, means (S.E. µg m^{-3}) of the different soil horizons (O (N=52), A (N=65), B (N=65), and C (N=65)) in 2016. Concentrations are means (S.E.) and <u>medians</u> of the whole data (BDL = below the detection limit of the VOC quantification). The effect of soil horizon on concentrations was tested with the Kruskal-Wallis test ($p<0.050$). Significant differences in concentrations between the horizons are indicated with different letters (Kruskal-Wallis test; $p<0.050$). Compounds marked with (†) are only tentatively identified and quantified.

Concentration	O	A	B	C
isoprene	0.02^{a} ($2x10^{-3}$) $\underline{0.01}$	0.04^{a} (0.03) $\underline{0.01}$	0.02^{a} ($2x10^{-3}$) $\underline{0.01}$	0.02^{a} ($3x10^{-3}$) $\underline{0.01}$
α-pinene	320.4^{a} (135.8) $\underline{28.0}$	71.0^{a} (22.5) $\underline{5.0}$	108.6^{b} (103.6) $\underline{1.6}$	6.7^{b} (2.2) $\underline{1.5}$
camphene	8.8^{a} (2.6) $\underline{0.7}$	1.4^{a} (0.4) $\underline{0.1}$	0.6^{b} (0.6) $\underline{0.03}$	0.3^{b} (0.1) $\underline{0.01}$
Δ-3-carene	58.8^{ac} (22.8) $\underline{4.3}$	16.9^{a} (5.2) $\underline{2.6}$	30.2^{bc} (29.5) $\underline{1.2}$	2.8^{b} (0.8) $\underline{1.3}$
ß-pinene	14.7^{a} (4.4) $\underline{1.2}$	2.4^{b} (1.2) $\underline{0.2}$	0.4^{c} (0.3) $\underline{0.1}$	0.3^{c} (0.1) $\underline{0.1}$
myrcene	18.1^{a} (8.0) $\underline{1.9}$	1.7^{b} (0.5) $\underline{0.1}$	1.7^{c} (1.0) $\underline{0.05}$	0.7^{c} (0.5) $\underline{0.04}$
1,8-cineol	0.08^{a} (0.04) $\underline{0.02}$	0.3^{a} (0.2) $\underline{0.04}$	0.2^{a} (0.1) $\underline{0.02}$	0.1^{a} (0.03) $\underline{0.01}$
linalool	1.4^{a} (1.0) $\underline{0.1}$	1.5^{a} (0.6) $\underline{0.1}$	1.1^{a} (0.6) $\underline{0.1}$	0.6^{a} (0.3) $\underline{0.1}$
limonene	16.4^{ab} (7.4) $\underline{0.7}$	3.5^{a} (1.0) $\underline{1.0}$	2.4^{ab} (1.1) $\underline{0.6}$	1.9^{b} (1.0) $\underline{0.4}$
p-cymene	1.8^{a} (1.4) $\underline{0.1}$	0.4^{ab} (0.1) $\underline{0.1}$	0.2^{ab} (0.1) $\underline{0.1}$	0.2^{b} (0.04) $\underline{0.1}$
terpinolene	3.1^{a} (1.4) $\underline{0.2}$	0.4^{ab} (0.2) $\underline{0.03}$	0.4^{bc} (0.4) $\underline{0.02}$	0.05^{c} (0.02) $\underline{0.01}$
Sum of monoterpenes	**422.2^{a} (157.9) $\underline{35.6}$**	**96.0^{a} (28.8) $\underline{9.7}$**	**144.6^{b} (133.7) $\underline{4.2}$**	**12.8^{b} (3.7) $\underline{4.1}$**
bornylacetate	0.01^{a} (0.01) $\underline{0.01}$	0.1^{a} (0.1) $\underline{0.01}$	0.01^{a} ($1x10^{-3}$) $4x10^{-3}$	0.01^{a} ($1x10^{-3}$) $\underline{4x10^{-3}}$
longicyclene	0.02^{a} (0.02) $\underline{0.01}$	0.01^{a} ($5x10^{-3}$) $3x10^{-3}$	$5x10^{-3a}$ ($1x10^{-3}$) $3x10^{-3}$	0.01^{a} ($3x10^{-3}$) $\underline{2x10^{-3}}$
isolongifolene	0.3^{a} (0.3) $\underline{0.01}$	0.04^{a} (0.03) $\underline{0.02}$	0.05^{a} (0.02) $\underline{0.03}$	0.1^{a} (0.03) $\underline{0.05}$
ß-caryophyllene	0.1^{a} (0.1) $\underline{0.02}$	0.4^{a} (0.2) $\underline{0.02}$	0.6^{a} (0.4) $\underline{0.02}$	0.2^{a} (0.2) $\underline{0.03}$
aromadendrene†	0.02^{a} ($5x10^{-3}$) $\underline{0.02}$	0.01^{a} $\underline{0.01}$	0.03^{a} (0.01) $\underline{0.03}$	0.03^{a} (0.01) $\underline{0.01}$
α-gurjunene	3.4^{a} (2.4) $\underline{0.1}$	25.7^{a} (22.9) $\underline{0.2}$	3.1^{a} (1.3) $\underline{0.2}$	3.0^{a} (1.5) $\underline{0.1}$
α-humulene	0.4^{a} (0.2) $\underline{5x10^{-3}}$	2.9^{a} (1.6) $\underline{0.3}$	5.3^{a} (4.2) $\underline{0.3}$	0.6^{a} (0.3) $\underline{0.01}$
ß-farnesene	0.4^{a} (0.3) $\underline{0.1}$	0.03^{a} (0.01) $\underline{0.03}$	1.9^{a} (1.5) $\underline{0.03}$	0.4^{a} (0.4)
isocaryophyllene†	0.01^{a} ($3x10^{-3}$) $\underline{0.01}$	0.01^{a} ($3x10^{-3}$) $\underline{0.01}$	$3x10^{-3a}$ ($2x10^{-3}$) $\underline{0.01}$	0.01^{a} ($1x10^{-3}$)
SQT1†	0.03^{a} (0.01) $\underline{0.03}$	0.02^{a} ($4x10^{-3}$) $\underline{0.02}$	0.04^{a} ($3x10^{-3}$) $\underline{0.04}$	0.02^{a} $\underline{0.02}$
α-buinesene†	0.03^{a} (0.02) $\underline{0.01}$	0.5^{a} (0.5) $\underline{0.02}$	0.1^{a} (0.05) $\underline{4x10^{-3}}$	0.3^{a} (0.1) $\underline{0.2}$
γ-muurolene†	0.02^{ab} (0.02) $\underline{0.02}$	0.01^{a} (0.01) $\underline{0.01}$	$4x10^{-3b}$ ($1x10^{-3}$) $\underline{3x10^{-3}}$	0.01^{ab} ($4x10^{-3}$) $\underline{5x10^{-3}}$
α-bisabolene†	0.01^{a} (0.01) $\underline{0.01}$	0.5^{a} (0.3) $\underline{0.02}$	0.3^{a} (0.3) $\underline{0.01}$	0.3^{a} (0.2) $\underline{0.2}$
β-himachalene†	0.2^{a} (0.1) $\underline{0.02}$	1.3^{a} (1.0) $\underline{0.3}$	0.3^{a} (0.1) $\underline{0.2}$	0.4^{a} (0.2) $\underline{0.2}$
α-muurolene†	0.07^{a} (0.04) $\underline{0.01}$	0.1^{a} (0.03) $\underline{0.05}$	0.1^{a} (0.03) $\underline{0.1}$	0.03^{a} (0.01) $\underline{0.02}$
Δ-cadinene†	0.01^{a} ($4x10^{-3}$) $\underline{2x10^{-3}}$	0.1^{a} (0.1) $\underline{0.01}$	0.01^{a} ($2x10^{-3}$) $3x10^{-3}$	0.01^{a} (0.01) $4x10^{-3}$
Sum of sesquiterpenes	**2.4^{a} (1.4) $\underline{0.2}$**	**15.1^{a} (12.1) $\underline{0.2}$**	**4.3^{a} (2.0) $\underline{0.3}$**	**2.1^{a} (0.9) $\underline{0.2}$**
geraniol	0.1^{a} (0.1) $\underline{0.02}$	2.3^{a} (2.3) $\underline{0.01}$	0.1^{a} (0.03) $\underline{0.01}$	0.2^{a} (0.1) $\underline{0.01}$

methyl-2-furoate	$5x10^{-3a}$ ($1x10^{-3}$) $4x10^{-3}$	0.1^{a} (0.1) $3x10^{-3}$	$5x10^{-3a}$ ($1x10^{-3}$) $3x10^{-3}$	$4x10^{-3a}$ ($1x10^{-3}$) $4x10^{-3}$
α-bisabolol	0.01^{a} 0.01	0.1^{a} (0.03) 0.04	0.03^{a} (0.01) 0.02	0.03^{a} (0.01) 0.02
verbenone	2.6^{a} (1.7) 0.2	0.1^{ab} (0.1) 0.1	0.03^{ab} 0.03	0.02^{b} ($3x10^{-3}$) 0.02
nuciferol	0.02^{a} (0.01) 0.02	0.03^{a} (0.01) 0.02	0.02^{a} ($4x10^{-3}$) 0.01	0.02^{a} ($4x10^{-3}$) 0.01
methy-3-furoate	BDL	BDL	0.02^{a} 0.02	BDL
1-butanol	1.9^{a} (1.0) 0.3	9.0^{a} (6.8) 0.4	2.3^{a} (1.0) 0.4	1.7^{a} (0.6) 0.5
isopropanol	0.01^{a} ($1x10^{-3}$) 0.01	0.01^{a} ($2x10^{-3}$) 0.01	0.02^{a} (0.01) 0.01	0.02^{a} (0.01) 0.01
1-butanone	0.2^{a} (0.1) 0.03	0.7^{a} (0.5) 0.03	0.1^{a} (0.1) 0.04	0.2^{a} (0.1) 0.03
penten-3-ol	0.5^{a} (0.2) 0.4	1.2^{a} (0.8) 0.02	0.3^{a} (0.1) 0.1	0.2^{a} (0.1) 0.1
1-pentanol	0.2^{a} (0.07) 0.03	0.6^{b} (0.3) 0.1	0.1^{ab} (0.02) 0.04	0.1^{a} (0.03) 0.03
2-methyl-2-buten-1-ol	0.04^{a} (0.03) 0.01	0.1^{a} (0.02) 0.03	0.01^{a} ($3x10^{-3}$) 0.01	0.02^{a} (0.01) 0.01
butyl acetate	0.01^{a} ($2x10^{-3}$) 0.01	0.1^{a} (0.04) 0.01	0.01^{a} ($2x10^{-3}$) 0.01	0.01^{a} ($2x10^{-3}$) 0.01
cis-3-hexen-1-ol	BDL	BDL	BDL	BDL
trans-3-hexen-1-ol	BDL	0.02^{a} 0.02	1.8^{a} (1.8) 1.8	0.01^{a} (0.01) 0.01
trans-2-hexen-1-ol	0.4^{a} (0.3) 0.01	0.1^{a} (0.02) 0.01	0.4^{a} (0.3) 0.01	0.2^{a} (0.1) 0.03
1-hexanol	0.02^{a} ($5x10^{-3}$) 0.01	0.04^{a} (0.03) 0.01	0.1^{a} (0.1) 0.01	0.02^{a} ($4x10^{-3}$) 0.01
cis-2-hexen-1-ol	0.01^{a} ($1x10^{-3}$) 0.01	0.03^{a} (0.02) 0.01	0.02^{a} (0.01) 0.01	0.1^{a} (0.04) 0.02
1-octen-3-ol	0.2^{ab} (0.1) 0.03	1.4^{a} (1.3) 0.03	1.3^{ab} (1.3) 0.03	0.25^{b} (0.1) 0.02
6-methyl-5-heptene-2-one	2.5^{a} (1.4) 0.1	0.5^{a} (0.2) 0.1	0.2^{b} (0.1) 0.04	0.2^{b} (0.1) 0.03
cis-3-hexenyl acetate	1.2^{a} (0.8) 0.1	1.2^{a} (0.7) 0.1	1.0^{a} (0.5) 0.1	1.9^{a} (0.8) 0.1
hexyl acetate	0.03^{a} (0.01) 0.04	1.1^{a} (1.1) 0.03	0.05^{a} (0.02) 0.03	0.02^{a} ($4x10^{-3}$) 0.02
trans-2-hexenyl acetate	0.3^{a} (0.3) 0.02	0.02^{a} (0.01) $4x10^{-3}$	0.4^{a} (0.3) $5x10^{-3}$	0.2^{a} (0.2) $5x10^{-3}$
α-pineneoxide	1.0^{a} (0.7) 0.2	1.3^{a} (0.6) 0.1	0.4^{a} (0.2) 0.1	0.04^{a} (0.03) 0.04
Sum of OVOCs	**5.4^{a} (2.5) 1.2**	**10.0^{a} (6.7) 0.8**	**4.0^{a} (1.9) 0.5**	**2.8^{a} (1.1) 0.6**

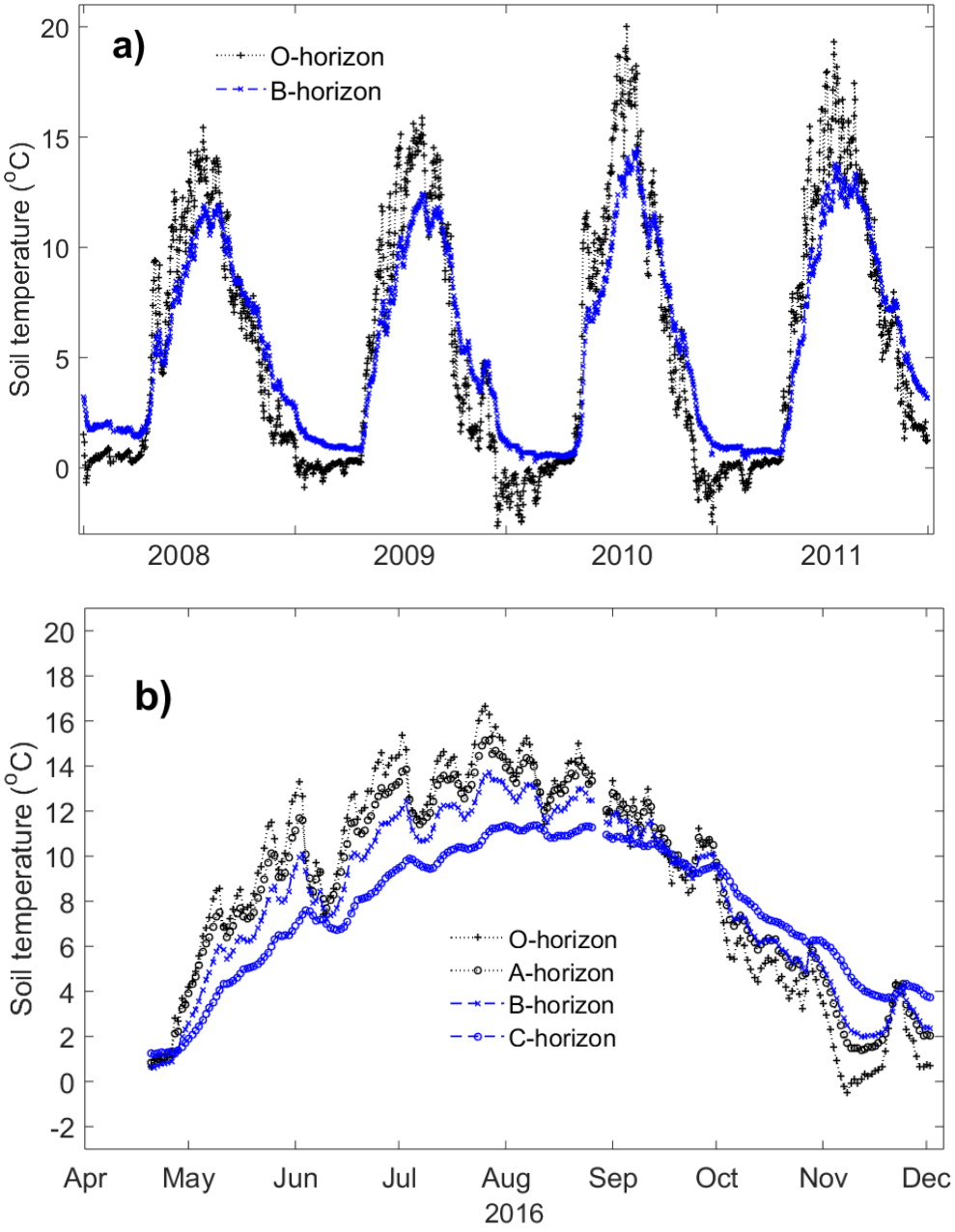


Figure A1: a) Soil temperature (C°) measured at the O-horizon (0–5 cm) and B-horizon (10–28 cm) over the 2008-2011 period and b) soil temperature measured at the different soil horizons in 2016.

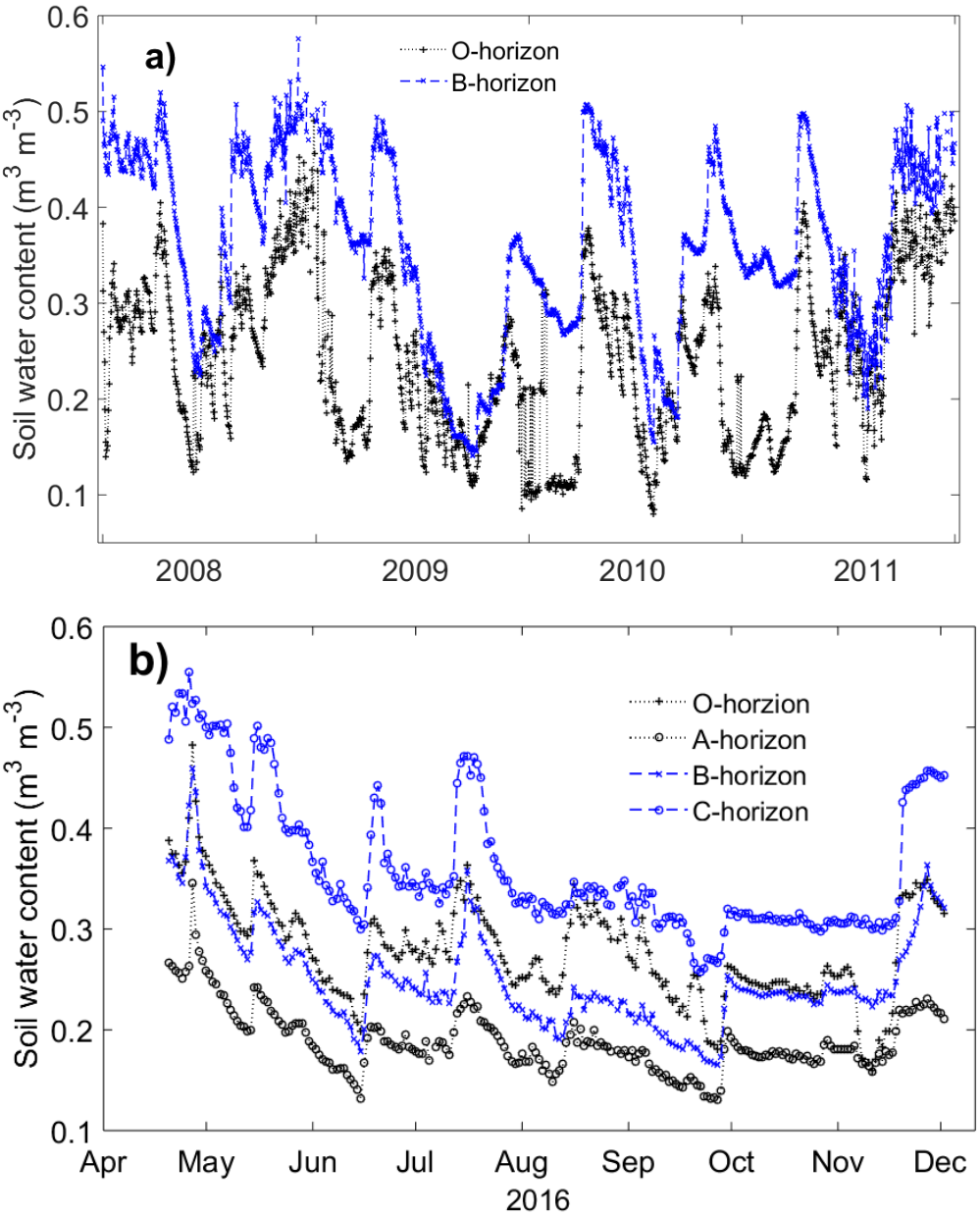


Figure A2: a) Soil water content ($m^3\ m^{-3}$) measured at the O-horizon (0–5 cm) and B-horizon (10–28 cm) in years 2008- 2011 and b) soil water content ($m^3\ m^{-3}$) measured at the different soil horizons in 2016. High wintertime variation is explained the change from liquid water to solid phase by freezing as TDR measurement method is highly sensitive for freezing.

Table A5: Pearson correlations between the total monoterpene and sesquiterpene fluxes (µg m^{-2} h^{-1}) and concentrations (µg m^{-3}) in the O- and the A-horizons in the different measurement pits in 2016. The significance level of p<0.100 (o), p<0.050 (*), p<0.010 (**), p<0.001 (***)) was used.

Concentration (µg m^{-3})		**Monoterpene flux (µg m^{-2} h^{-1})**			**Sesquiterpene flux (µg m^{-2} h^{-1})**		
Pit	Horizon	Correlation	N	P value	Correlation	N	P value
1	O	-0.19	11	0.70	0.02	11	0.47
1	A	-0.27	11	0.78	-0.09	11	0.61
2	A	0.20	11	0.29	**0.46**	12	0.07º
3	O	-0.39	13	0.91	**0.62**	9	0.04*
3	A	-0.55	12	0.97	**0.72**	10	0.01**
4	O	**0.78**	7	0.020*	-0.43	7	0.83
4	A	-0.34	9	0.81	-0.16	10	0.67
5	O	-0.10	6	0.57	0.01	5	0.99
5	A	**0.83**	6	0.020*	0.54	5	0.17

Table A6. Pearson correlation between the total monoterpene and sesquiterpene fluxes (µg m^{-2} h^{-1}) and chamber temperature (°C), and CO_2 fluxes (µg m^{-2} h^{-1}) from the soil surface in spring, summer, and autumn in 2016. The significance level of p<0.100 (o), p<0.050 (*), p<0.010 (**), p<0.001 (***)) was used. VOC fluxes were measured from the different measurement pits in 2016.

Period	**Correlation coefficient**	**N**	**P value**	**Correlation coefficient**	**N**	**P value**
Chamber temperature (C°)	Monoterpene flux (µg m^{-2} h^{-1})			Sesquiterpene flux (µg m^{-2} h^{-1})		
April-June	-0.12	16	0.67	**0.52**	**14**	**0.02***
July-September	**0.43**	**19**	**0.03***	0.24	19	0.16
October-December	**0.62**	**18**	**0.003****	**0.47**	**17**	**0.03***
CO_2 flux (µg m^{-2} h^{-1})	Monoterpene flux (µg m^{-2} h^{-1})			Sesquiterpene flux (µg m^{-2} h^{-1})		
April-June	0.30	13	0.16	-0.42	12	0.91
July-September	-0.42	15	0.94	**0.57**	**15**	**0.01***
October-December	**0.79**	**13**	**0.0007*****	**0.63**	**13**	**0.01***

Table A7. Pearson correlation between the CO_2 flux and the total monoterpene and sesquiterpene concentrations from the O- and the A-horizon in spring, summer, and autumn in 2016. The significance level of p<0.1 (o), p<0.05 (*), p<0.01 (**), p<0.001 (***)) was used.

CO_2 flux		Monoterpene concentration			Sesquiterpene concentration		
Period	Horizon	Correlation	N	P value	Correlation	N	P value
April-June	O	0.36	8	0.19	-0.16	8	0.65
July-September	O	-0.03	12	0.54	-0.15	10	0.66
October-December	O	0.14	9	0.36	**0.68**	**9**	**0.02***
April-June	A	0.35	13	0.12	-0.25	13	0.80
July-September	A	0.20	17	0.22	**0.50**	**14**	**0.04***
October-December	A	**0.76**	**12**	**0.002****	-0.12	10	0.63