

We would like to express our gratitude for the Reviewers and Editor Marianne Glasius for taking your valuable time to evaluate this manuscript. We thank Alex Guenther for considering this manuscript as generally interesting to readers of Biogeosciences and we thank both Reviewers for the relevant and constructive suggestions which have guided us to make improvements to the manuscript. We have carefully considered the suggestions and revised the manuscript based on the feedback. In the following text we will respond to the reviewer's suggestions (reviewer's suggestions numbered in black font and our response below each comment in green).

Reviewer's suggestions:

1) Reviewer #1: This manuscript describes a field study characterizing VOC emissions from a boreal forest floor. The study provides valuable new observations and insights. A novel aspect of the study is their approach to segregate roots from the rest of the system. The paper is well-written and this is an important topic of general interest to readers of Biogeosciences. I recommend the paper be published after the authors address the following points:

General: The text indicates that these emissions are an important component of forest emissions (for example, Page 2, line 35, Page 14, line 8, Conclusions section) but the authors have not really made the case for this. They do show that these emissions become relatively more important in spring and fall but they are still small so the importance is not clear. In order to conclude that this is important, and should be the focus of future studies, the authors should provide some quantitative evidence that these low level emissions are significant with respect to their impact on atmospheric composition. This would also enhance the impact of this manuscript. Perhaps this could be done with a simple 1D modeling study or even referencing past studies that have already been conducted at this well studied site.

Previous analyses from the same site show that the magnitude of soil and understory monoterpene emissions in pine forest is rather variable in time, but that in maximum it can make up to 10-15% of the ecosystem scale emissions (Aaltonen et al., 2013). While Aaltonen et al., only report the emissions of monoterpenes, we also emphasize that the forest floor VOC exchange is relevant since the current knowledge of sesquiterpene exchange from the boreal forest floor is very limited.

“Sesquiterpene emissions can be significantly higher than the currently measured flux rates since they are difficult to detect and quantify due to the low volatility and high reactivity (Guenther et al., 2013). Sesquiterpenes are important in the atmospheric processes since they have high precursor potential for secondary organic aerosol (SOA) formation (Guenther et al., 2011).” Page 15, lines 13-17:

The large soil source for reactive compounds may also explain the missing OH sink in the canopy layer (Sinha et al., 2010, Nölscher et al., 2012).

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.

Guenther, A.: Biological and chemical diversity of biogenic volatile organic fluxes into the atmosphere. *ISRN Atmospheric Sciences*, Volume 2013, doi:10.1155/2013/786290, 2013.

Guenther, A., Kulmala, M., Turnipseed, A., Rinne, J., Suni, T., and Reissell, A.: Integrated land ecosystem-atmosphere processes study (iLEAPS) assessment of global observational networks.

Boreal Environment Research, vol. 16, no. 4, pp. 321–336, 2011.

Nölscher, A. C., Williams, J., Sinha, V., Custer, T., Song, W., Johnson, A. M., Axinte, R., Bozem, H., Fischer, H., Pouvesle, N., Phillips, G., Crowley, J. N., Rantala, P., Rinne, J., Kulmala, M., Gonzales, D., Valverde-Canossa, J., Vogel, A., Hoffmann, T., Ouwersloot, H. G., Vilà-Guerau de Arellano, J., and Lelieveld, J.: Summertime total OH reactivity measurements from boreal forest during HUMPPA-COPEC 2010. *Atmospheric chemistry and Physics* 12, no. 17: 8257-8270, 2012.

Sinha, V., Williams, J., Lelieveld, J., Ruuskanen, T.M., Kajos, M.K., Patokoski, J., Hellen, H., Hakola, H., Mogensen, D., Boy, M. and Rinne, J.: OH reactivity measurements within a boreal forest: evidence for unknown reactive emissions. *Environmental science & technology*, 44(17), pp.6614-6620, 2010.

2) Reviewer #1: Specific: Page 2, line 33: While this statement is generally correct, it should be noted there is a wide range of solubility and reactivity for different terpenoid compounds.

We strongly agree that terpenoids are a large group of compounds with different chemical properties, including atmospheric lifetime and solubility, and we have clarified this (Page 3, lines 1-4):

“Isoprenoids are very diverse group of chemical species (Guenther, 2013). Daytime lifetimes of BVOCs in the ambient air varies from minutes (sesquiterpenes) to hours (isoprene, monoterpenes) (Rinne et al., 2007, Bouvier-Brown, 2009; Guenther, 2013, Peräkylä et al., 2014).”

In Section 4.4 we have discussed this issue by introducing lifetime of different isoprenoids. Page 15, lines 17-19: “Sesquiterpene flux rates are probably underestimated more than isoprene and monoterpene flux rates, since daytime lifetime (OH and O₃) is 1.3 min for β -caryophyllene, 27 min for isoprene, 29 min for Δ^3 -carene, and 41 min for α -pinene (Rinne et al., 2007).”

Guenther, A.: Biological and chemical diversity of biogenic volatile organic fluxes into the atmosphere. *ISRN Atmospheric Sciences*, Volume 2013, doi:10.1155/2013/786290, 2013.

Bouvier-Brown, N. C., Goldstein, A. H., Gilman, J. B., Kuster, W. C., and de Gouw, J. A.: In-situ ambient quantification of monoterpenes, sesquiterpenes and related oxygenated compounds during BEARPEX 2007: implications for gas- and particle-phase chemistry. *Atmospheric Chemistry and Physics*, vol. 9, no. 15, pp. 5505–5518, 2009.

Peräkylä, O., Vogt, M., Tikkanen, O. P., Laurila, T., Kajos, M. K., Rantala, P. A., Patokoski, J., Aalto, J., Yli-Juuti, T., Ehn, M., Sipilä, M., Paasonen, P., Rissanen, M., Nieminen, T., Taipale, R., Keronen, P., Lappalainen, H. K., Ruuskanen, T. M., Rinne, J., Kerminen, V.M., Kulmala, M., Bäck, J., Petäjä, T.: Monoterpenes' oxidation capacity and rate over a boreal forest: temporal variation and connection to growth of newly formed particles. *Boreal Environment Research*, 19, 293-293, 2014.

Rinne, J., Taipale, R., Markkanen, T., Ruuskanen, T. M., Hellén, H., Kajos, M. K., Vesala, T., and Kulmala, M.: Hydrocarbon fluxes above a Scots pine forest canopy: measurements and modeling. *Atmospheric Chemistry and Physics*, 7(12), 3361–3372, doi:10.5194/acp-7-3361-2007, 2007.

3) Reviewer #1: Page 3, line 3: Clarify whether you mean that it changes the flux measured with an enclosure or the actual flux

The sentence has been clarified on Page 3, lines 8-11: “Large biomass or coverage of understory vegetation can also decrease the total measured VOC flux from soil because transpiration can induce the formation of water film on the leaf and chamber inner surfaces, which can enhance isoprenoid absorption.”

4) Reviewer #1: Page 4, line 24: The third point is an objective but not a hypothesis

We have rewritten this sentence more precisely (Page 4, lines 31-33): “A statistical model including prevailing temperature, seasonality, trenching treatments, understory vegetation cover, above-canopy PAR, soil water content, and soil temperature can be used to estimate isoprenoid fluxes.”

5) Reviewer #1: Page 5, line 1: what is the tree cover fraction at this site?

The stem basal area of all the trees was added on Page 5, lines 8-9.

6) Reviewer #1: Section 2.2: Some analytical details should be given including the precision and accuracy of the flux measurements and whether there were any replicate samples to test the reproducibility of the tubes. How was the methanol flushed away? Were tests done to ensure that none of the VOC standards were removed in the process?

We have presented total uncertainty for the emissions on Page 15, lines 22-24, and calculations and results of total uncertainty, precision and systematic errors for the emissions on Pages 38 and 39 (Appendix, Table A2).

“Methanol was flushed away using nitrogen (N₂) flow of 80 ml min⁻¹ through the Tenax TA-Carboack-B adsorbent tubes for 10 minutes.” This description and more analytical details have now been added on Page 6, lines 28-36. Flow and time for nitrogen flushing have been optimized and no losses have been detected within 10 minutes flushing with the flow of ~80 ml/min for any of the studied compounds. Breakthrough volumes are much higher, in the order of hours with this flow.

7) Reviewer #1: Section 2.3: the detection limit should also consider the detection limit of the VOC quantification.

We fully agree that the term ‘the detection limit of the VOC quantification’ is better in this context. We have added this term into the Sections 2.2 (Page 7, line 1) and 2.3 (Page 7, line 14), and into Table 3 (Page 30).

8) Reviewer #1: Section 3.2: It is a bit difficult to follow the text in this section. I am not sure what is meant by the second sentence. Also, it is stated that understory vegetation is a monoterpene sink but then goes on to indicate that there was no difference when vegetation was present as long as there were fungi. If the presence of the fungi is the typical situation then this suggests that the vegetation is not a sink.

The second sentence was rewritten on Page 9, line 35.

The sum of the monoterpene fluxes was higher from bare soil than from soil with vegetation cover, where the ingrowth of mycorrhizal fungi was allowed, but the difference was not statistically significant due to the high variation of the emissions. The dominating compound was α -pinene. Different mycorrhizal fungal species produce different amounts of α -pinene (Bäck et al., 2010). One explanation for this would be that the experimental plots included mycorrhizal fungal species which

produce high amounts of α -pinene and this would decrease flux differences between bare soil and soil with vegetation cover, when the ingrowth of mycorrhizal fungi was allowed.

9) Reviewer #1: Section 3.3: The title of this section suggests this will focus on soil sources but instead it discusses vegetation which was the focus of the previous section.

We agree with the Reviewer, and for this reason the sections 3.2 and 3.3 were combined into one section (Pages 9-10).

10) Reviewer #1: Page 10. Line 4: rewrite the sentence to clarify what was observed in October. Was it high isoprene or high temperature/PAR?

We agree that this sentence is unclear and reader has to interpret the message. We have rewritten the sentence and it has been added on Page 10, lines 29-30: "Isoprene fluxes were highest in June and July when temperature and PAR was high (Fig. 3), but interestingly high isoprene fluxes were also observed in October, when temperature and PAR was low."

11) Reviewer #1: Page 13, line 6 to 11: An alternative hypothesis is that the VOC are consumed by microbes living on the leaves. It seems to me that this just as likely as the possibility that they are absorbed on the cuticle.

Several studies have been published which support our conclusion that hydrocarbons can be adsorbed on lipophilic layer on plant leaves (Brown et al., 1998, Welke et al., 1998, Binnie et al., 2002, Joensuu et al., 2016). We think that this is a very interesting suggestion from the reviewer and we have discussed it carefully. This alternative conclusion was added on Page 13, line 35.

Binnie, J., Cape, J. N., Mackie, N., and Leith, I. D.: Exchange of organic solvents between the atmosphere and grass – the use of open top chambers, *Sci. Total Environ.*, 285, 53–67, 2002.

Brown, R. H. A., Cape, J. N., and Farmer, J. G.: Partitioning of chlorinated solvents between pine needles and air, *Chemosphere*, 36, 1799–1680, 1998.

Farré-Armengol, G., Filella, I., Llusia, J., and Peñuelas, J.: Bidirectional Interaction between Phyllospheric Microbiotas and Plant Volatile Emissions. *Trends in Plant Science*, 21(10), 854–860, 2016.

Joensuu, J., Altimir, N., Hakola, H., Rostás, M., Raivonen, M., Vestenius, M., Aaltonen, H., Riederer, M., and Bäck J. Role of needle surface waxes in dynamic exchange of mono- and sesquiterpenes. - *Atmospheric Chemistry and Physics Discussions* doi:10.5194/acp-2015–1024, 2016.

Welke, B., Ettliger, K., and Riederer, M.: Sorption of volatile organic chemicals in plant surfaces, *Environ. Sci. Technol.*, 32, 1099–1104, 1998.

12) Reviewer #1: Page 14, line 7: define/quantify what you mean by "decent"

This sentence was rewritten more carefully on Page 14, lines 34-35.

13) Reviewer #1: Page 14, line 8: What is meant by "unsolved"

The sentence was rephrased (Page 15, lines 34-36 and Page 15, lines 1-3):

“The mixed effects linear models explained considerable part (43%) of variation in monoterpene emissions although more improvement should be achieved in the future. Possible reasons behind the emissions not explained by the model are oxygen and nutrient availability (Rinnan et al., 2011, the fertilization effect of *Salix phylicifolia* on the β -selinene flux), quality and quantity of the organic matter, soil composition, and microbial community structure, which were not determined in our study.”

14) Reviewer #1: Page 14, line 30: How does this overcome the issue of measuring net exchange? The fast response instrument will still be measuring net exchange.

This paragraph was changed so that with PTR-MS it is possible to follow fast changes in the emission, but we chose to use TD-GC-MS which enables the speciation of different compounds (Page 15, lines 27-32).

15) Reviewer 2#: The manuscript presents an interesting study of the influence of understory on boreal forest isoprenoid fluxes, including an approach enabling investigation of separate factors such as vegetation vs. bare soil and in-growth of microbes and fungi. Generally, the manuscript, including figures and tables, presents the results in a clear and straightforward way. I have listed my specific comments below.

16) Reviewer #2: Abstract. Most sentences start with "we" or "our". Please try to vary this. In line 17 "Our results show that" can be removed.

We rephrased the sentences (Page 2, lines 4-21) as suggested.

17) Reviewer #2: Page 2 lines 27-32: This is a very long sentence with a lot of information. Please rephrase.

This very long sentence was rewritten (Page 2 lines 29-33) in the following way:

“The boreal forest floor, including tree roots, understorey vegetation (grasses, shrubs, mosses, lichens, and other vegetation) and the organic soil layer (different stages of decomposing litter, a variety of decomposing and other microorganisms) emits isoprenoids. According to the earlier studies, the boreal forest floor emits monoterpenes (Aaltonen et al., 2011, $5 \mu\text{g m}^{-2} \text{h}^{-1}$ and Hellén et al., 2006, $0\text{--}373 \mu\text{g m}^{-2} \text{h}^{-1}$), isoprene (Aaltonen et al., 2011, $0.050 \mu\text{g m}^{-2} \text{h}^{-1}$ and Hellén et al., 2006, $0\text{--}1.9$) and sesquiterpenes (Aaltonen et al., 2011, $0.045 \mu\text{g m}^{-2} \text{h}^{-1}$ and Hellén et al., 2006 $0\text{--}0.8 \mu\text{g m}^{-2} \text{h}^{-1}$: β -caryophyllene).”

18) Reviewer #2: Page 3 Line 9: "Photosynthesized carbon through the roots was shown to currently contribute 54% of soil respiration". Please clarify what you mean here.

We agree that this sentence should be written more carefully. The sentence was rephrased on Page 3 (lines 15-16) by writing that “Photosynthesized carbon allocated belowground was shown to contribute 54% of soil respiration”.

19) Reviewer #2: P3 L12: "The main monoterpene sources are suggested to degrade litter" Do you mean "to be degraded litter"?

The expression “degrade litter” was rewritten to “degraded litter” (Page 3, line 19).

20) Reviewer #2: P3L21-22: rephrase to "from primary metabolism and energy generation of decomposers".

Corrected as suggested (Page 3, line 28).

21) Reviewer #2: P4 L15-16: Do you mean fluxes from soil?

We agree that the reference to the soil fluxes was not clear enough so the sentence was rephrased according to the reviewer's suggestion by writing on Page 4 (lines 22-23) that "high isoprenoid fluxes from soils are also measured after rain events (Greenberg et al., 2012)".

22) Reviewer #2: P6 L24: Remove "&". Please state details of the GC-MS method including at least column and temperature program.

"&" was removed by describing a mass selective detector in the following way "Perkin Elmer Clarus 600T, Waltham, USA" (Page 6, line 29). More details of the GC-MS method and temperature program was added (Page 6, line 32-33).

23) Reviewer #2: P8 L19: Information about where the measurements were situated should be moved to experimental section. How far away were these measurements from the study area?

All the measurements (flux measurements and environmental data) were executed at the SMEAR II stand. The sentence "Ambient air temperature and PAR were measured at the SMEAR II stand" on Page 8 (line 24) was situated to the Trenching experiment –section on Page 5 (lines 33-37) in the following way.

"All plots at the SMEAR II stand were equipped with a 0.5m long tube, where soil water content was measured using the capacity probe (PR2, Delta-T Devices) every second week. Soil temperature sensors were placed in the soil surface layer on each plot (depth 4 cm), and data were logged every fourth hour from May to October in 2012–2015. Photosynthetically active radiation (PAR) was measured also measured at the SMEAR II stand from a wavelength range of 400–700 nm using an LI-190SZ quantum sensor (Li-Cor, Biosciences, Lincoln, NE) at heights of 18.0 m (above canopy) and 0.6 m (below canopy)."

24) Reviewer #2: P8 L27: I suggest to explain the abbreviations for the study areas the first time they appear in the text.

The reviewer makes an excellent point that the abbreviations should be explained in this section.

The sentence was rewritten (Page 9, lines 14-17):

"Chamber and soil temperature did not differ between treatments, except during July and August (period 4), when soil temperature was higher in Control- (13.5 °C), where the ingrowth of roots and mycorrhizal fungi was allowed without understorey vegetation cover, than in Control+ (12.6 °C) with understorey vegetation cover. Soil water content was higher in Control+ (0.13 m³ m⁻³) than in Control- (0.10 m³ m⁻³) and higher in Tr1- (0.19 m³ m⁻³, only decomposer activity was allowed without understorey vegetation cover) compared to Control+ and Control- in September and early October (period 5) (data not shown)."

25) Reviewer #2: P8 section 3.1: It would be useful for the reader if you spend some time in the first section to give an overview of the data set such as ranges of fluxes, before discussing correlations. This could include moving some text from 3.2 to 3.1.

We wrote a new section where we give an overview about which compounds were measured and which were the dominating compounds. We will also give flux range of isoprene, monoterpenes and sesquiterpenes for the whole data (Page 8, lines 29-35 and Page 9, lines 1-3).

26) Reviewer #2: P9 L6: discovered -> observed.

The more accurate expression “observed” was used (Page 9, line 29).

27) Reviewer #2: P9 L13: "Instead" does not seem like the right word here.

We have rephrased the sentence according to reviewer’s suggestions (Page 10, line 2).

28) Reviewer #2: P9 L13-19: Please try to keep sentences about the same group of compounds together, to improve readability.

We very much agree with the reviewer and the order of the sentences were reorganized in the following way (Page 8, lines 31-35 and Page 9, lines 1-3) : “Monoterpene flux range was 0.40–221.0 $\mu\text{g m}^{-2} \text{h}^{-1}$ (data not shown). The most dominating compounds were α -pinene, camphene, β -pinene, and Δ^3 -carene, covering 84–94% of the flux spectra (Table 3). The exception was Tr1+, where isoprene covered 20% of the spectrum (Table 3). Sesquiterpene flux range was 0.01–10.9 $\mu\text{g m}^{-2} \text{h}^{-1}$ (data not shown). Sesquiterpene fluxes from various sources were equally low (0.35–0.73 $\mu\text{g m}^{-2} \text{h}^{-1}$), and the most abundant sesquiterpenes emitted were β -caryophyllene and aromadendrene (Table 3). Isoprene fluxes from the different sources were also low (0.98–4.91 $\mu\text{g m}^{-2} \text{h}^{-1}$) (Table 3) and flux range was 0.005–99.8 $\mu\text{g m}^{-2} \text{h}^{-1}$ (data not shown).”

29) Reviewer #2: P11 L5-10: This can be removed since this is clear from the previous sections.

We believe that it is reader-friendly to shortly summarize the background and aims of the study before going deeper into the interpretation of the results. However, if needed we can also delete this introductory chapter from the discussion.

30) Reviewer #2: P11 L35: significant -> considerable (unless the authors did a statistical test of this).

Litterfall contribution to decomposition processes was not analyzed using a statistical test and for this reason word “considerable” was used (Page 12, line 27) as the reviewer wisely suggested.

31) Reviewer #2: P12 L7: Remove "references".

The word "references" was removed (Page 12, line 34).

32) Reviewer #2: P13 L8: "absorbed" should be changed to "adsorbed".

The misspelling was corrected (Page 13, line 32).

33) Reviewer #2: P14L19: "disappear" is not the right word here. Use "be removed" or similar instead.

The sentence was rephrased by writing “which means that they can be removed through chemical reactions” (Page 15 line 11).

34) Reviewer #2: P15 L1-2: Could the fan affect the removal rate/deposition of VOC in your chamber?

No significant losses were detected for studied compounds in the recovery tests, where fan was used.

Contribution of understorey vegetation and soil processes to boreal forest isoprenoid exchange

Mari Mäki¹, Jussi Heinosalo², Heidi Hellén³, Jaana Bäck¹

5 ¹Department of Forest Sciences, P.O. Box 27, FI-00014 University of Helsinki, Finland.

²Department of Food and Environmental Sciences, P.O. Box 66, FI-00014 University of Helsinki, Finland.

³Finnish Meteorological Institute, P.O. Box 503, FI-00101 Helsinki, Finland.

10 Keywords: BVOCs, boreal soil, microbial activity, mycorrhizal fungi, vegetation, trenching

Correspondence to: Mari Mäki (mari.maki@helsinki.fi)

15

20

25

30

Abstract. Boreal forest floor emits biogenic volatile organic compounds (BVOCs) from the understorey vegetation and the heterogeneous soil matrix, where the interactions of soil organisms and soil chemistry are complex. Earlier studies have focused on determining the net exchange of VOCs from the forest floor. ~~This Our~~ study takes one step forward, with the aim of separately determining whether the photosynthesized carbon allocation to soil affects the isoprenoid production by different soil organisms, i.e. decomposers, mycorrhizal fungi, and roots. In each treatment, photosynthesized carbon allocation through roots for decomposers and mycorrhizal fungi was controlled by either preventing root ingrowth (50 μ m mesh size) or the ingrowth of roots and fungi (1 μ m mesh) into the soil volume, which is called the trenching approach. ~~We measured isoprenoid~~ Isoprenoid fluxes were measured using dynamic (steady-state flow-through) chambers from the different treatments. This study ~~We also~~ aimed to analyze how important the understorey vegetation is as a VOC sink. Finally, ~~we constructed~~ a statistical model was constructed based on prevailing temperature, seasonality, trenching treatments, understorey vegetation cover, above canopy photosynthetically active radiation (PAR), soil water content, and soil temperature to estimate isoprenoid fluxes. The final model included parameters with a statistically significant effect on the isoprenoid fluxes. ~~The Our~~ results show that the boreal forest floor emits monoterpenes, sesquiterpenes, and isoprene. Monoterpenes were the most common group of emitted isoprenoids, and the average flux from the non-trenched forest floor was 23 $\mu\text{g m}^{-2} \text{h}^{-1}$. ~~The Our~~ results also show that different biological factors, including litterfall, carbon availability, biological activity in the soil, and physico-chemical processes, such as volatilization and absorption to the surfaces, are important at various times of the year. ~~This study also~~ We also discovered that understorey vegetation is a strong sink of monoterpenes. ~~The Our~~ statistical model, based on prevailing temperature, seasonality, vegetation effect, and the interaction of these parameters, explained 43% of the monoterpene fluxes, and 34–46% of individual α -pinene, camphene, β -pinene and Δ^3 -carene fluxes.

1 Introduction

Vegetation in coniferous forests is a primary and well-quantified source of biogenic volatile organic compounds (BVOCs) on the shoot level (Rinne et al., 2000; Hakola et al., 2003; Kim et al., 2005; Bäck et al., 2012, Aalto et al., 2014). The boreal forest floor, including tree roots, understorey vegetation (grasses, shrubs, mosses, lichens, and other vegetation) and the organic soil layer (different stages of decomposing litter, a variety of decomposing and other microorganisms) emits isoprenoids. According to the earlier studies, the boreal forest floor emits monoterpenes (Aaltonen et al., 2011, 5 $\mu\text{g m}^{-2} \text{h}^{-1}$ and Hellén et al., 2006, 0–373 $\mu\text{g m}^{-2} \text{h}^{-1}$), isoprene (Aaltonen et al., 2011, 0.050 $\mu\text{g m}^{-2} \text{h}^{-1}$ and Hellén et al., 2006, 0–1.9) and sesquiterpenes (Aaltonen et al., 2011, 0.045 $\mu\text{g m}^{-2} \text{h}^{-1}$ and Hellén et al., 2006 0–0.8 $\mu\text{g m}^{-2} \text{h}^{-1}$: β -caryophyllene). ~~(monoterpenes: Aaltonen et al., 2011, 5 $\mu\text{g m}^{-2} \text{h}^{-1}$ and Hellén et al., 2006, 0–373 $\mu\text{g m}^{-2} \text{h}^{-1}$, isoprene and sesquiterpenes: Aaltonen et al., 2011, 0.050 and 0.045 $\mu\text{g m}^{-2} \text{h}^{-1}$; Hellén et al., 2006, 0–1.9 and 0–0.8 $\mu\text{g m}^{-2} \text{h}^{-1}$ β -caryophyllene).~~ Isoprenoids are a lipophilic group of volatile organic compounds (VOCs) emitted in trace amounts. Isoprenoids are poorly water-soluble and highly

reactive in the atmosphere. Isoprenoids are very diverse group of chemical species (Guenther, 2013).
Daytime reactivity lifetimes of isoprene, and monoterpenes and sesquiterpenes in the ambient air
are varies from hours to minutes (Rinne et al., 2007, and daytime reactivity of sesquiterpenes varies
from hours to minutes Bouvier-Brown, 2009, Guenther, 2013, Peräkylä et al., 2014).

5 Forest floor was discovered to be a significant monoterpene source during spring and
fall, when photosynthesis is low (Hellén et al., 2006; Aaltonen et al., 2011, 2013). On the forest floor,
understorey vegetation emits monoterpenes (Aaltonen et al., 2011, Faubert et al., 2012) and
photosynthesized energy regulates isoprene syntheses (Ghirardo et al., 2011). Large biomass or
coverage of understorey vegetation can also decrease the total measured soil-VOC flux from soil
10 because transpiration can induce the formation of water film on the leaf and chamber inner surfaces,
which can enhance isoprenoid absorption (Aaltonen et al., 2013). Trees allocate 40–73% of the
photosynthesized carbon for root metabolism, growth and root-associated microbes (Grayston et al.,
1997), and the largest portion of photosynthesized carbon is consumed in the root-induced respiration
of microbes. The belowground carbon allocation of labelled C¹³ from canopy photosynthesis can be
15 500% higher in August than June (Högberg et al., 2010). Photosynthesized carbon allocated
belowground through the roots was shown to currently contribute 54% of soil respiration (Högberg et
al., 2001), but 47% of the carbon allocated to roots and mycorrhizal fungi can also be released to the
soil microbial metabolism after root death (Fogel and Hunt, 1983). The main monoterpene sources are
suggested to degraded litter (Aaltonen et al., 2011; Faiola et al., 2014), while emitted VOCs strongly
20 depend on litter type (Ramirez et al., 2010) and tree roots (Lin et al., 2007; Aaltonen et al., 2011, 2013),
especially damaged ones (Hayward et al., 2001). Forest management can affect the soil isoprenoid
fluxes. Clear-cut logging reduced soil VOC fluxes compared to non-disturbed forest soil (Paavolainen
et al., 1998), but high monoterpene fluxes are also reported from stumps after a clear-cut (Haapanala et
al., 2012). Mycorrhizal fungi also emit oxidized VOCs and small amounts of isoprenoids in a species-
25 specific manner (Bäck et al., 2010). The microbial decomposition of organic matter produces VOCs in
soil (Insam and Seewald, 2010; Greenberg et al., 2012). VOCs are often synthesized as side products
(aerobic carbon metabolism, fermentation, amino acid degradation, terpenoid biosynthesis and sulfur
reduction) from primary metabolism and energy generation of decomposers ~~during decomposers~~
~~primary metabolism and energy generation~~ (Peñuelas et al., 2014).

30 In addition to being released from living or decaying plant material and microorganisms,
isoprenoids affect soil processes in multiple ways. Sesquiterpene signalling of mycorrhizal fungi was
discovered to enhance root surface area for nutrient uptake and carbon availability for fungi as root
exudates (Ditengou et al., 2015). VOCs can induce or reduce microbial activity (Asensio et al., 2012),
control the population density of soil organisms (Wenke et al., 2010), and stimulate plant growth as
35 fungal metabolites (Hung et al., 2012). Isoprenoids can inhibit nitrification and mineralization activity
by being toxic for some microbes (Smolander et al., 2012), and some bacterial volatiles can have an
antagonistic effect on plant pathogens (Kai et al., 2006) or can inhibit or stimulate the growth of soil

fungal species (Mackie and Wheatley, 1999). Soil can also be a sink for isoprenoids (Insam and Seewald, 2010, Peñuelas et al., 2014), as some decomposers will also use VOCs as a carbon source (Greenberg et al., 2012). Soil enzymes can release substrates for metabolic VOC production (Mancuso et al., 2015), but isoprenoids can also inhibit enzyme activity in boreal forest soil (Adamczyk et al., 2015).

Soil VOC production processes have not been fully identified in field conditions, despite results showing that they may correspond to tens of percents of the boreal ecosystem flux (Aaltonen et al., 2013). Microbial VOC production depends on microbial community structure (Bäck et al., 2010), microbial biomass (Wieder et al., 2013), oxygen and nutrient availability (Insam and Seewald, 2010), the physiological state of decomposers (Insam and Seewald, 2010), and substrate quality (Stotzky and Schenk, 1976). Freezing–thawing and drying–wetting events increase isoprenoid fluxes, as they contribute to organic matter degradation (Asensio et al., 2007, 2008; Insam and Seewald, 2010; Aaltonen et al., 2013). Temperature affects VOC production (Asensio et al., 2007), indirectly through the temperature dependence of enzyme production and activity in VOC synthesis (Peñuelas and Staudt, 2010), and directly through volatilization, which is a function of temperature (Guenther et al., 1993). Enclosure techniques are a widely used method to measure soil gas fluxes (Pumpanen et al., 2004), and the enclosure temperature was shown to explain isoprenoid fluxes in stronger way than soil temperature (Hayward et al., 2001, Aaltonen et al., 2013). Increasing temperature and decreasing soil water content contributed higher monoterpene volatilization from soil into the atmosphere (van Roon et al., 2005). Soil water content can also determine which microbial groups are most active (Veres et al., 2014). The flux rate depends on the compound. Monoterpenes are released from storage structures when temperature-dependent vapor pressure changes (Schurgers et al., 2009). High isoprenoid fluxes from soils are also measured after rain events (Greenberg et al., 2012).

This experiment was designed to determine whether carbon allocation to soil via roots affects soil isoprenoid fluxes through root metabolism and microbial activity, when the trenching approach was assumed to change the microbial communities between the different treatments. The aim was to identify isoprenoid sources, quantify isoprenoid fluxes and estimate the parameters regulating the isoprenoid fluxes based on the following hypotheses: (1) Presence of roots and mycorrhizal fungi enhances the amount of structurally non-bound (labile, e.g. fast turnover rate) carbon in the soil, which will increase isoprenoid fluxes. (2) Understorey vegetation is a sink of isoprenoids, as isoprenoids can be adsorbed on leaf surfaces. (3) A statistical model including prevailing temperature, seasonality, trenching treatments, understorey vegetation cover, above-canopy PAR, soil water content, and soil temperature can be used to estimate isoprenoid fluxes.

2 Material and methods

2.1 Trenching experiment

Measurements were executed in the southern boreal forest at the SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations) station (61°51'N, 24°17'E, 180 m above sea level) (Hari and Kulmala, 2005). The forest is a 55yr old Scots pine stand (*Pinus sylvestris*), where *Sorbus aucuparia*, *Betula pendula* and *Picea abies* grow below-canopy. Soil above the bedrock is Haplic podzol and soil depth is approximately 0.5–0.7 m. The average thickness of the soil horizons from the SMEAR II stand is 6.0 cm (organic layer), 2.0 cm (E-horizon) and 16 cm (B-horizon). The stand was established by sowing after prescribed burning in 1962. Current canopy height is ca. 17 m and one-side leaf area index (LAI) is 2.0–2.5 m² m⁻² (Aalto et al., 2014). The stem basal area of all the trees was 24.3 m² ha⁻¹ (Ilvesniemi et al., 2009). The understorey vegetation is formed by shrubs, such as *Vaccinium vitis-idaea*, *Vaccinium myrtillus*, and *Calluna vulgaris*, mosses, such as *Pleurozium schreberi*, *Dicranum polysetum*, *Dicranum scorparium*, and *Hylocomium splendens* and grasses such as *Deschampsia flexuosa* and *Melampyrum sylvaticum*. Soil surface coverages of the different vascular and moss species on the experimental plots were determined using the eye estimation method in July 2015. Measurements were conducted on three replicate experimental sites (1, 2, and 3) at the station. Site 1 is directed towards the east, site 2 towards the south-east and site 3 towards the south-east. The distance between replicate sites was 50–100 m. The experimental sites are described in more detail in Table 1.

The experimental setup was established in 2012 to study the effect of carbon allocation by tree roots and mycorrhizal fungi into soil. Each replicate site includes 20 experimental plots with different below- and aboveground treatments, which were implemented to regulate the carbon flow from trees and the understorey vegetation to soil microbes through roots and mycorrhizal fungi. Thirty-six of the experimental plots were measured in our study (Table 2). All the experimental plots were trenched by digging around a square volume (0.9 x 0.9 m) of soil until reaching the bedrock, or to a depth of up to 40 cm, and cutting roots between the experimental plot and the surrounding ground. Soil C input by plant allocation was controlled by comparing the soil, where the ingrowth of roots and mycorrhizal fungi and decomposer mobility was allowed (Control, 18 plots) to experimental plots where the ingrowth of tree roots and fungi was inhibited by placing isolating mesh (1 µm) around the soil volume (code Tr1, 12 plots). The treatment Tr50 (mesh size 50µm, six plots) allowed access for microbes and mycorrhizal fungi, but prevented the ingrowth of tree roots (Table 2). Both meshes allowed water and nutrient exchange. As the understorey vegetation also allocates part of the photosynthetically produced C into the soil, the effect of the understorey vegetation was monitored by comparing plots with different vegetation: either the understorey vegetation was growing normally (marker +, 21 plots), or vegetation was removed by cutting (marker -, 15 plots) (Table 2).

All plots at the SMEAR II stand were equipped with a 0.5m long tube, where soil water content was measured using the capacity probe (PR2, Delta-T Devices) every second week. Soil temperature sensors were placed in the soil surface layer on each plot (depth 4 cm), and data were logged every fourth hour from May to October in 2012–2015. Photosynthetically active radiation (PAR) was measured at the SMEAR II stand from a wavelength range of 400–700 nm using an LI-190SZ quantum

sensor (Li-Cor, Biosciences, Lincoln, NE) at heights of 18.0 m (above canopy) and 0.6 m (below canopy). The monthly total litterfall (needles, bark, twigs, and cones) and fraction of needles in the litterfall was determined once a month at the SMEAR II stand from April to October using 21 litter collectors (diameter 0.48 m).

5

2.2 Measurement methods

The flux of isoprenoids from each plot was measured 5–6 times between 15th of April and 23rd of October, 2015. To analyze the seasonality of the isoprenoid fluxes, the results were pooled into six periods: 1) 15th–24th of April, 2) 30th of April–10th of May, 3) 21st of May–24th of June, 4) 21st of July to 21st of August, 5) 31st of August – 9th of October, and 6) 19th – 23rd of October. The sequence of measurements was randomly arranged, to avoid any systematic errors in flux measurements between plots. The exact timing and sequence of the measurements are presented in the Appendix (Table A1).

Isoprenoid concentrations in the chamber headspace (height 40 cm, chamber volume 10 l) were measured with two dynamic (steady-state flow-through) glass chambers. The chambers were placed on permanent soil collars (height 7 cm, diameter 21.7 cm), which were placed on each plot in 2012. Incoming and outgoing air was sampled for 1.5–2 hours using sampling flow (0.1 l min⁻¹) through two Tenax TA-Carboback-B adsorbent tubes, and the flux was calculated from the difference between ingoing and outgoing air (see Eq1). Filtered (active carbon trap and MnO₂-coated copper net) ambient air was continuously pumped (1 l min⁻¹) into the chamber, and the chamber air volume was flushed for 0.5 hours before sampling to stabilize the system. Chamber temperature was measured using a thermometer (Fluke 54II, Fluke, WA, USA) from 20–30 cm above ground. Hemiterpenes (isoprene and 2-methyl butenol), monoterpenes (α -pinene, camphene, β -pinene, myrcene, Δ 3-carene, p-cymene, limonene, and terpinolene, while oxygen containing 1.8-cineol and linalool are typically categorized for monoterpenes) and sesquiterpenes (longicyclene, iso-longifolene, β -caryophyllene, aromadendrene and α -humulene) were measured from the adsorbent tubes.

Tenax TA-Carboback-B adsorbent tubes were kept in cold (5 °C) and analyzed the week after sampling using a thermodesorption instrument (Perkin Elmer TurboMatrix 650, Waltham, USA) connected to a gas-chromatograph (Perkin-Elmer Clarus 600, Waltham, USA) with DB-5MS (60m, 0.25mm, 1 μ m) column and a mass selective detector (Perkin-Elmer Clarus 600&T, Waltham, USA). The sample tubes were thermally desorbed for 5 min (300 °C), cryo-focused in a Tenax cold trap operating at -30 °C, and injected into the column using rapid heating (300 °C) (Aaltonen et al., 2011). The column was first heated from 50°C to 150°C at the rate of 4°C min⁻¹ and then at the rate of 8°C min⁻¹ up to 250°C, where it was kept for 5 min. Total time of the analysis was 42.50 min. Six standards in methanol solutions were used for calibration by injecting (5 μ l) into the sample tubes. Methanol was flushed away using nitrogen (N₂) flow of 80 ml min⁻¹ through the Tenax TA-Carboback-B adsorbent tubes for 10 minutes, after which the methanol was flushed away (10 min). The uncertainty of analysis

35

was 5-10 % depending on the compound. The analytical detection limit of the VOC quantification was 0.005–2.431 $\mu\text{g m}^{-2} \text{h}^{-1}$ for the different isoprenoids.

2.3 Flux calculations and statistical analyses

- 5 The flux rates (E , $\mu\text{g m}^{-2} \text{h}^{-1}$) of the different compounds were calculated for soil area (area inside to collar, m^2) and time (h) using Eq. (1):

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

- 10 where C_{in} is the concentration of ingoing air sample ($\mu\text{g m}^{-3}$) and C_{out} is the concentration of outgoing air sample ($\mu\text{g m}^{-3}$), $F_{chamber}$ ($\text{m}^3 \text{min}^{-1}$) is the flow rate of air pumped into the chamber, and A (m^2) is the soil surface area inside the collar.

- 15 The detection limit (DL) of the VOC quantification was calculated for every compound and for every measurement week using Eq (2):

$$DL = \left(k_{mean} \left(3 \sqrt{\frac{\sum(m_{in} - \bar{m}_{in})^2}{n-1}} \right) \right) \frac{F_{chamber\ mean}}{1000} \frac{60}{A}, \quad (2)$$

- 20 where k_{mean} is the mean sampled air volume (m^3), c_{in} is the compound mass of ingoing air sample ($\mu\text{g m}^{-3}$), $F_{chamber\ mean}$ ($\text{m}^3 \text{min}^{-1}$) is the mean flow rate of air pumped into chamber, A (m^2) is the soil surface area inside the collar. Data were analyzed using MATLAB software (version 2015a, MathWorks, Natick, MA, USA), and statistical analyses were conducted using SPSS software (version 23, IBM SPSS Statistics; Chicago, IL, USA). R Language and Environment for Statistical Computing program (version 3.2.4; R Core Team, 2016) was used to construct the mixed effects linear models. A random
- 25 permuted block design was used in our study with block sizes 3 (Tr50+ and Tr50-), 6 (Control-, Tr1+, Tr1-), and 11 (Control+). The normality of sum monoterpene flux (sum of ten monoterpenes), α -pinene flux, chamber temperature, soil temperature, and soil volumetric water content were tested during six periods using the Kolmogorov-Smirnov and Shapiro-Wilkin tests (degree of freedom: 60=Control+, 28=Control-, 17=Tr50+, 6 =Tr50-, 28=Tr1+, and 24=Tr1-). We also tested whether the annual total
- 30 fluxes of different compounds from the trenching treatments were normally distributed. If the data were non-normally distributed, the non-parametric Kruskal-Wallis test (degree of freedom=1) at the significance level of <0.05 was used to determine whether the treatments were statistically different (Table 3 and 4).

The effect of period, vegetation effect, trenching treatment, chamber temperature, above canopy PAR, soil water content, soil CO₂ flux, and soil temperature for total monoterpene, total sesquiterpene, and individual isoprenoid fluxes were tested using the mixed effects linear models. For example, total monoterpene fluxes (M) were modelled by the mixed effects linear model:

5

$$M = B_0 + B_s + B_v + B_c C + B_{sv} + B_{sc} C + B_{vc} C + B_{svc} C + \epsilon, \quad (3)$$

where B_0 denotes a fixed intercept parameter, B_s are denoting fixed unknown parameters associated with season variable, B_v are denoting fixed unknown parameters associated with vegetation effect variable, B_c are denoting fixed unknown slope parameter related to chamber temperature C , B_{sv} are denoting fixed parameters for interaction of period and vegetation, B_{sc} are denoting fixed slope parameters for interaction of season and chamber temperature, B_{vc} are denoting fixed slope parameters for interaction of vegetation and chamber temperature, B_{svc} are denoting fixed parameters for three way interaction of period, vegetation, and chamber temperature. In the model (3), the error term ϵ is assumed to have a form:

15

$$\epsilon = \alpha_l + \alpha_p + u, \quad (4)$$

where α_l are denoting random parameters related trenching plot, α_p are denoting random parameters related to the measurement site (1, 2, and 3), and u is unobservable random error term. Random effects parameters and random error term are assumed to follow normal distributions $\alpha_l \sim N(0, \sigma_l^2)$, $\alpha_p \sim N(0, \sigma_p^2)$, and $u \sim N(0, \sigma_u^2)$, respectively.

20

Similar type of mixed models with different variable combinations (factor variables are period, vegetation effect, trenching treatment, and numerical variables are chamber temperature, above canopy PAR, soil water content, soil CO₂ flux, and soil temperature) were used to model total sesquiterpene fluxes and individual isoprenoid fluxes (Table 5 and Table 6).

25

3 Results

Hemiterpenes (isoprene), monoterpenes (α -pinene, camphene, β -pinene, myrcene, Δ^3 -carene, p-cymene, limonene, and terpinolene) and sesquiterpenes (longicyclene, β -caryophyllene, aromadendrene and α -humulene) were measured from the different treatments. Monoterpene flux range was 0.40–221.0 $\mu\text{g m}^{-2} \text{h}^{-1}$ (data not shown). The most dominating compounds were α -pinene, camphene, β -pinene, and Δ^3 -carene, covering 84–94% of the flux spectra (Table 3). The exception was Tr1+, where isoprene covered 20% of the spectrum (Table 3). Sesquiterpene flux range was 0.01–10.9 $\mu\text{g m}^{-2} \text{h}^{-1}$ (data not shown). Sesquiterpene fluxes from various sources were equally low (0.35–0.73 $\mu\text{g m}^{-2} \text{h}^{-1}$), and the

30

35

most abundant sesquiterpenes emitted were β -caryophyllene and aromadendrene (Table 3). Isoprene fluxes from the different sources were also low (0.98–4.91 $\mu\text{g m}^{-2} \text{h}^{-1}$) (Table 3) and flux range was 0.005–99.8 $\mu\text{g m}^{-2} \text{h}^{-1}$ (data not shown).

5 3.1 Correlations of temperature, soil moisture, and PAR with VOC measurements

At the experimental sites, soil water content and chamber and soil temperature were measured to observe their influence on the fluxes. ~~Ambient air temperature and PAR were measured at the SMEAR H-stand.~~ Daily temperature followed PAR (Fig. 1a). Chamber, soil and ambient temperatures followed very similar patterns. The median difference between chamber and soil temperature was 3.6 °C, and the median difference between chamber and ambient temperature was 0.9 °C. Water content was 0.06–0.45 $\text{m}^3 \text{m}^{-3}$ in the mineral soil (Fig. 1c), and it was higher from April to end of July and very low from August to the end of October. During the measurements PAR was 10–1440 $\mu\text{mol m}^{-2} \text{s}^{-1}$ above the canopy and 1–410 $\mu\text{mol m}^{-2} \text{s}^{-1}$ below the canopy (Fig. 1b). Chamber and soil temperature did not differ between treatments, except during July and August (period 4), when soil temperature was higher in Control- (13.5 °C), where the ingrowth of roots and mycorrhizal fungi was allowed without understorey vegetation cover, than in Control+ (12.6 °C) with understorey vegetation cover. Soil water content was higher in Control+ (0.13 $\text{m}^3 \text{m}^{-3}$) than in Control- (0.10 $\text{m}^3 \text{m}^{-3}$) and higher in Tr1- (0.19 $\text{m}^3 \text{m}^{-3}$, only decomposer mobility activity was allowed without understorey vegetation cover) compared to Control+ and Control- in September and early October (period 5) (data not shown).

Temperature dependence of monoterpene and sesquiterpene fluxes were determined by combining all the measurements. Sesquiterpene fluxes showed exponential correlation with chamber temperature ($R^2=0.26$, $p<0.001$, Fig. 2a). Monoterpene fluxes did not correlate with chamber temperature ($R^2=0.03$, $p>0.05$, Fig. 2b).

Monoterpene fluxes from the Tr50-plots (ingrowth of decomposers and mycorrhizal fungi) were higher when chamber temperatures were lower ($R^2=0.91$, $p<0.01$), but in all other treatments the effects were not significant ($p>0.05$) (Appendix Fig. A2).

We also analyzed the effects of soil water content and temperature, chamber temperature, PAR, and soil CO_2 flux on monoterpene and sesquiterpene fluxes from all the treatments. Although we ~~observed~~ discovered some statistically significant differences, the R^2 values were very small, varying from 0.00 to 0.08 (Appendix Fig. A1).

3.2 Different VOC sources in soil ~~The effect of understorey vegetation~~

Understorey vegetation was a monoterpene sink, since isoprenoid fluxes measured on bare soil were higher than when isoprenoid fluxes were measured on bare soil or on soil with vegetation cover in different treatments. The sum of the monoterpene fluxes ~~were~~ was highest from the bare soil, ~~when~~

where the soil was non-trenched (Control-) or ~~when where roots and mycorrhizal hyphae were excluded~~ and decomposers were the only ~~source-active microbes~~ (Tr1-). ~~On the contrary~~ **Instead**, the sum of the monoterpene fluxes did not differ between bare soil and soil with vegetation cover, ~~when~~ **then** the ingrowth of mycorrhizal fungi was allowed (Tr50) (Table 3). ~~The most dominating compounds were α -pinene, camphene, β -pinene, and Δ^3 -carene, covering 84–94% of the flux spectra (Table 3). The exception was Tr1+, where isoprene covered 20% of the spectrum (Table 3). Sesquiterpene fluxes from various sources were equally low (0.35 – $0.73 \mu\text{g m}^{-2} \text{h}^{-1}$). The most dominating compounds were α -pinene, camphene, β -pinene, and Δ^2 -carene, covering 84–94% of the flux spectra (Table 3). The exception was Tr1+, where isoprene covered 20% of the spectrum (Table 3). The most abundant sesquiterpenes emitted were β -caryophyllene and aromadendrene (Table 3).~~

3.3 Different VOC sources in soil

Isoprenoid fluxes were compared between the treatments in the six periods. The mean total monoterpene flux from the treatments was 2.0 – $78.0 \mu\text{g m}^{-2} \text{h}^{-1}$ and the mean total α -pinene flux was 0.6 – $60.2 \mu\text{g m}^{-2} \text{h}^{-1}$ (Table 4), with high temporal variation. However, the presence of vegetation and decomposer activity clearly affected the fluxes in July–August (period 4) and October (period 6) (Table 4). In July–August, the presence of vegetation (Control+) significantly decreased the total monoterpene and α -pinene fluxes compared to both Control- and Tr1- (Control-: $p_{\text{monoterpenes}}=0.015$ and $p_{\alpha\text{-pinene}}=0.011$; Tr1-: $p_{\text{monoterpenes}}=0.027$ and $p_{\alpha\text{-pinene}}=0.035$). In October, the decomposer-only treatment (Tr1-) had significantly higher fluxes than Control+ ($p_{\text{monoterpenes}}=0.027$ and $p_{\alpha\text{-pinene}}=0.027$) and Tr1+ ($p_{\text{monoterpenes}}=0.034$ and $p_{\alpha\text{-pinene}}=0.034$).

3.4.3 Seasonality of VOC fluxes

Seasonal variations of monoterpene, sesquiterpene, and isoprene fluxes were determined from non-trenched soil with vegetation (Control+). Monoterpene, sesquiterpene, and isoprene fluxes varied between 0 – $149 \mu\text{g m}^{-2} \text{h}^{-1}$, 0 – $4 \mu\text{g m}^{-2} \text{h}^{-1}$, and 0 – $29 \mu\text{g m}^{-2} \text{h}^{-1}$, respectively (Fig. 3). Monoterpene fluxes were highest in October and lowest in mid-April, but as shown in Fig. A2, they poorly correlated with soil temperature. Soil temperature was close to 0°C in early October and between 1°C and 5°C in mid-April (Fig. 3). Sesquiterpene fluxes were highest in summer. Isoprene fluxes were highest in June and July when temperature and PAR was high (Fig. 3), but interestingly **high isoprene fluxes were also observed in October, when temperature and PAR was low.**

Average total monoterpene fluxes were highest from non-trenched and bare soil in September–October (period 5), and from bare soil with decomposers in October (period 6) (Table 4). As shown in Fig. 4, the flux rates correlate with total litterfall and the fraction of needles in the litterfall. As shown in Fig. 3, the effect of litterfall on monoterpene flux rates occurs after a short delay in October. Monthly

total litterfall (8.7–114.2 g m⁻²) and the total amount of needles in the litterfall (1.6–99.7 g m⁻²) varied at the SMEAR II stand from April to October 2015 (Fig. 4). Monthly total and needle litterfall were 75–92% and 84–98% higher in September, and 58–87% and 66–97% higher in October, respectively, compared to the spring and summer months (p<0.001), but total litterfall was also high in July (Fig. 4).

5

3.5.4 Mixed effects model results

Mixed effects linear models were used to determine, which parameters are best in estimating the flux rates of monoterpenes and sesquiterpenes from boreal forest soil. The best fit was obtained with a combination of several biological and abiotic parameters. The presence of vegetation cover, measurement timing (period) and chamber temperature explained 43% of the individual monoterpene fluxes (p<0.05), whereas measurement timing (period) and chamber temperature explained 29% of the individual sesquiterpene fluxes (p<0.01) (Table 5). The effect of the trenching treatment, PAR, soil water content, soil temperature, and soil CO₂ flux were also tested, but their effects were non-significant (p>0.05).

10

15

Mixed effects linear models were also used to determine, which parameters are best in estimating the flux rates of different individual isoprenoids. When the model included chamber temperature, vegetation effect, seasonality (period), and the interaction of these parameters, it explained 34–46% of the individual α -pinene, camphene, b-pinene, and Δ 3-carene fluxes (Table 6). When the model included seasonality, chamber temperature, soil water content, and the interaction of these, it was able to explain 40% of the variation within the longicyclene fluxes (Table 6). Chamber temperature, seasonality, and the interaction of these, explained 35% of the variation within the α -humulene fluxes. Seasonality, soil temperature, soil water content, and the interaction of these were able to estimate 35% of the variation within the isoprene fluxes (Table 6).

20

25

4 Discussion

Identifying the sources of isoprenoid fluxes from forest understorey vegetation and soil in field conditions is challenging, as most measurement techniques only yield net exchange (including all sources and sinks). The only way to dissect various processes is to manipulate the system, which was done here during the trenching treatment and vegetation removal. With the presented trenching experiment, where soil biological processes could be separated into different components, it was possible to separately analyze the fluxes originating from the decomposer, mycorrhizal fungal, tree roots, and understorey vegetation individually for the first time. First, we tested whether the photosynthesized carbon allocation to the soil affects the isoprenoid production of different soil organisms (decomposers, mycorrhizal fungi, and roots). Second, we analyzed how important the vegetation is as a sink. Third, we aimed to construct a statistical model including prevailing temperature,

30

35

seasonality, trenching treatments, understorey vegetation cover, above-canopy PAR, soil water content, and soil temperature to estimate isoprenoid fluxes.

4.1 Seasonality and carbon source impacts on emission rates and spectra

5 Our results show that the seasonality of emissions is largely correlated to litterfall, especially for monoterpenes, and our results confirm the emission spectrum and temporal variation of isoprenoids from the boreal forest understorey and soil layer found by Hellén et al., (2006) and Aaltonen et al., (2011; 2013). Earlier studies have also suggested that litter and decomposers are important isoprenoid sources (Hayward et al., 2001; Asensio et al., 2007, 2008; Isidorov et al., 2010, Insam and Seewald, 10 2010, Aaltonen et al., 2013, Greenberg et al., 2012, Faiola et al., 2014). Monoterpenes can be produced simultaneously by MEP pathway in plastids and by MVK pathway in cytoplasm, and at least some fungi and bacteria are capable of activating the MEP pathway (Rohmer et al., 1993; 1996; Eisenreich et al., 1998; Walter et al., 2000; Banerjee and Sharkey, 2014). Soil can also absorb 80% of litter-produced VOCs (Ramirez et al., 2010), when soil and litter samples from a *Pinus taeda* stand on a 15 loamy sand soil (pH 3.6, 50% of the water holding capacity) were studied in a laboratory.

The litterfall amount reflects the stand density and dominating tree species of the forest canopy, and indirectly the size of forest carbon storage. VOC release from the fresh litter appears important, as the highest isoprenoid fluxes were measured in October, correlating with litterfall (especially needle) production. Decomposition releases isoprenoids from needle storages (Aaltonen et al., 2011), and litter 20 emissions are regulated by microbial activity i.e. soil respiration, microbial biomass, carbon availability, temperature, and rain events (Leff and Fierer, 2008; Greenberg et al., 2012). Old litter can also be an important isoprenoid source during the following year, as the degradation of Scots pine litter is a slow process (Kainulainen and Holopainen, 2002). Decomposition can continue in soil under snow cover, and isoprenoids are released after snowmelt (Aaltonen et al., 2011). Isoprenoids can also be released 25 after non-enzymatic, thermo-chemical reactions (Greenberg et al., 2012), and soil processes can be efficient isoprenoid sources also during wintertime (Aaltonen et al., 2012). Litterfall contribution to decomposition processes is generally considerable ~~significant~~, as the decomposition of fresh litter requires less energy than the decomposition of non-labile organic compounds. The quantity of carbon and its decomposability also decreases with litter age (Greenberg et al., 2012).

30 Contrary to our hypothesis, belowground carbon availability did not clearly affect emissions, as only minor differences were observed between the trenching treatments. This is a significant finding and indicates that despite microbial communities most probably being very different in various trenching treatments, community changes do not significantly affect the net VOC flux from soils. We propose that the reason for this is that VOCs used for microbial signalling (e.g. ~~references~~, Wenke et al., 2010; Ditengou et al., 2015) are produced in low concentrations and therefore they cannot be seen 35 in the soil net VOC flux. One theory for this would be that the presence of tree roots and plant-derived

carbon flow favours microbes that are able to use VOCs as an energy source (Greenberg et al., 2012). However, we were unable to investigate either the microbial community structure or their VOC signalling in our study. As a conclusion, we may say that soil VOC fluxes are likely regulated by other processes than those directly dependent on plant-derived C flow into soil via roots.

5 In addition to litterfall, seasonal temperature variations also had an effect, especially on the sesquiterpene emissions. This was expected, as temperature can regulate isoprenoid emissions through physical processes (volatility and diffusion) and the enzyme activity of VOC synthesis (Peñuelas and Staudt, 2010). The traditional approach for modelling isoprenoid emissions is to use the so-called Guenther algorithm (Guenther et al., 1991; 1993; 1995), which calculates individual plant- or
10 ecosystem-scale emissions rates according to prevailing temperature. The global emission model MEGAN (Model of Emissions of Gases and Aerosols from Nature) was developed based on the Guenther algorithm, and the model includes plant functional type, long-term temperature response, leaf age, and soil water content (Guenther et al., 2006; 2012). Often this is a good approximation for forest ecosystem- or global-scale inventories of biogenic VOC emissions (Grote and Niinemets, 2008; 15 Sindelarova et al., 2014; Chatani et al., 2015). However, the effects of temperature on emissions from soil are not straightforward, as the soil biological activity is very different between spring and autumn, although air or soil temperatures may be very similar. This was clearly seen in our results. Sesquiterpenes are known to be signalling compounds between the roots and ectomycorrhizal fungi (Ditengou et al., 2015), and this signalling could be stronger during active periods of the tree. 20 Sesquiterpene flux rates were small in our study, possibly as they can react in the topsoil, or on leaf surfaces before they are released into the chamber headspace. Sesquiterpene volatilization also requires a higher temperature than the volatilization of monoterpenes, and the adsorption of sesquiterpenes on leaf and chamber surfaces is more likely than monoterpene adsorption. Other effects of carbon availability on isoprenoid fluxes were not confirmed.

25 **4.2 Effect of understorey vegetation on VOC fluxes**

The most important contributing factor to net flux from the forest floor during the entire growing period seems to be the vegetation cover, which was discovered to be a sink for isoprenoids. The difference in total monoterpene fluxes between the vegetated and bare soil plots was largest in July–August (soil
30 with decomposers only, 8.5-fold) and in mid-October (non-trenched soil, 3.5-fold), and the average flux difference between the two treatments was 2.8-fold. Isoprenoids, especially monoterpenes, were likely ~~absorbed~~adsorbed on the leaf surfaces. Leaf surfaces are covered by a lipophilic cuticle layer that offers protection against environmental stress (cold, UV light, drought etc.) (Pollard et al., 2008). Monoterpenes, as lipophilic and volatile compounds, can be absorbed on the lipophilic cuticle layer
35 (Joensuu et al., 2016). Microbes living on plant surfaces can also modify VOC emissions by

metabolizing plant emitted VOCs (Farré-Armengol et al., 2016). The lowest isoprenoid fluxes were previously measured from soil with dense understorey vegetation cover (Aaltonen et al., 2013), which supports our conclusion.

The *Vaccinium spp.* -dominated understorey vegetation in Scots pine forests also synthesize monoterpenes (Faubert et al., 2012). Janson et al., (1999) and Aaltonen et al., (2011) reported isoprenoid emissions from a forest floor covered with shrubs, such as *Vaccinium myrtillus*, mosses, such as *Pleurozium schreberi* and *Hylocomium splendens*, and grasses such as *Melampyrum sylvaticum*. Kesselmeier et al., (1999) reported that *Pleurozium schreberi* emits aldehydes. Temperate grassland species have been observed to emit isoprenoids (He et al., 2005), along with Mediterranean plant species (Owen et al., 2001), crop species, and tree species (Karl et al., 2009; Laothawornkitkul et al., 2009) such as *Betula nana*, *Salix sp.*, *Cassiope tetragona*, *Populus tremula* (Hakola et al., 1998; Rinnan et al., 2011). Hewitt and Street (1992) and Rinnan et al., (2014) discovered that *Deschampsia sp.* does not emit isoprene or monoterpenes. Subarctic heath emits isoprenoids (Faubert et al., 2012). Mosses are important to consider in the forest floor VOC exchange, as they emit isoprene (Hanson et al., 1999) and produce up to 40% of the gross photosynthetic production of the understorey vegetation at the SMEAR stand (Kolari et al., 2006).

4.3 Testing the factors involved in VOC flux from the forest floor

This experimental setup was designed to determine whether carbon allocation to soil via the roots affects soil isoprenoid fluxes through root metabolism and microbial activity, and whether radiation-driven photosynthesized carbon availability for roots and microbes regulates isoprenoid fluxes. According to our statistical model, belowground carbon availability does not significantly affect the boreal forest soil isoprenoid exchange.

Our measurement setup enables us to test contributing factors for isoprenoid emissions by constructing a statistical model. Different statistical models were tested, but only the parameters with a statistically significant effect were included, and the best model with the highest explanatory power was chosen. The best model included seasonality, vegetation effect, prevailing temperature, and the interaction of these parameters was able to explain 29–43% of the variation within monoterpene and sesquiterpene fluxes, which means that a significant portion of the variation was solved. We were also able to construct a model explaining 46% of the individual α -pinene fluxes based on vegetation effect, seasonality, prevailing temperature, and the interaction of these parameters. This indicates that separate models should always be built for different compound groups (monoterpenes and sesquiterpenes) with different physical and chemical properties.

The mixed effects linear models explained considerable part (43%) of variation in monoterpene emissions. ~~We were able to estimate the flux rates with decent explanation power,~~ although more improvement should be achieved in the future. Possible reasons behind the ~~unsolved~~

emissions ~~rates not explained by the model~~ are oxygen and nutrient availability (Rinnan et al., 2011, the fertilization effect of *Salix phylicifolia* on the β -selinene flux), quality and quantity of the organic matter, soil composition, and microbial community structure, which were not determined in our study. It is also possible that some tested parameters were non-linear, and for this reason were unsuitable parameters into the mixed effects linear model. A process-based model should be built in the future, as it would increase our understanding of the forest floor isoprenoid exchange by including dependencies of the different environmental parameters and soil processes.

4.4 Error sources in the measurements

Isoprenoids are difficult to measure under field conditions, as they are emitted in trace amounts and are highly reactive, which means that they can ~~be removed~~~~disappear~~ through chemical reactions before they have been sampled or analyzed. ~~Sesquiterpenes, with very small emission rates, low volatility, and high reactivity, are especially difficult to detect and quantify (Guenther et al., 2013). Sesquiterpene emissions can be significantly higher than the currently measured flux rates since they are difficult to detect and quantify due to the low volatility and high reactivity (Guenther et al., 2013). Sesquiterpenes are important in the atmospheric processes since they have high precursor potential for secondary organic aerosol (SOA) formation (Guenther et al., 2011).~~ Sesquiterpene flux rates are probably underestimated more than isoprene and monoterpene flux rates, since daytime ~~reactivity-lifetime~~ (OH and O₃) in the atmosphere is 1.3 min for β -caryophyllene, 27 min for isoprene, 29 min for Δ^3 -carene, and 41 min for α -pinene (Rinne et al., 2007), although the majority of oxidants are filtered before the chamber headspace. The difference in emission rates between treatments can be smaller than the random errors in the measured fluxes, produced by the sampling and analysis system. Total uncertainty for the emissions at the level 10 $\mu\text{g m}^{-2} \text{h}^{-1}$, which was median emission rate of α -pinene, was 14–44% for monoterpenes (except for camphene: 60%) and 14–20% for sesquiterpenes (Appendix, Table A2).

As the sampling time should to be considerably long (here: 1.5–2 hours) to exceed the detection limit of the TD-GC-MS, this means that the results are cumulative emissions over the sampling time. With fast-response analytical methods such as Proton-transfer reaction Mass spectrometry (PTR-MS) fast changes in the emissions could be followed. The chamber method combined with adsorbent sampling thus measures the net exchange with simultaneous sources and sinks, and this can only be overcome with fast response analytical methods such as Proton transfer reaction Mass spectrometry (PTR-MS). However, the speciation to different compounds is only possible with a TD-GC-MS, which is why we chose to use this method.

Temperatures inside the enclosure typically increase during the measurements, especially if the enclosure time is long and the chamber is in direct sunlight. This can cause overestimations in the flux rates, when increasing temperature affects the volatility and diffusion rate of the compounds (Niinemets et al., 2011). Luckily, in our study, the median difference of enclosure

temperature and ambient air was small (0.9 °C) for the entire data set, probably since we used a fan inside the chamber and the purge flow rate was approximately 1 lpm. Further, temperatures close to the soil surface are rather stable due to the lack of direct sunlight under the closed canopy.

Many isoprenoids are released in large amounts from cut surfaces or due to the rough handling of measured plants. The trenching and cutting of vegetation was performed three years prior to these measurements. Since the distance from our measurement collar to the closest trench was 30 cm, we assume that the effect of root cutting is very small. Mechanical removal (cutting) of vegetation could cause some local effects and random variation to the plots where the vegetation was removed, but since the need for repeated cutting in the third year was rather small, and it was mostly performed in spring, we believe that it did not significantly affect the fluxes later on. Soil surfaces in the cut treatments were still partly covered by mosses (16–20%), as it is impossible to remove a very thin moss cover without disturbing the organic soil. This may influence the observed differences between bare soil and soil with vegetation, as mosses are known to emit isoprene (Hanson et al., 1999). A minor trend was observed where the highest isoprene emissions occurred when the fraction of mosses made up over 55% of the soil surface coverage.

Soil is a highly heterogenic matrix, where soil depth, nutrient status, root density, and water content can vary based on vegetation cover, shading and soil composition (porosity, texture, and stoniness). High spatial and temporal variation can make differences between the treatments more difficult to detect.

5 Conclusions

Our results show that belowground carbon availability does not play a major role in isoprenoid exchange, but instead the litterfall, i.e. carbon from above, is important. Our results emphasize that the net sink effect of understorey vegetation should be included for modelling forest VOC exchange. These results add to our knowledge concerning forest floor VOC fluxes for modelling stand-level VOC exchange. The accurate quantification of soil VOC fluxes can improve air chemistry models, where the difference in the hydroxyl radical (OH) reactivity sink between the measurements and air chemistry models is most likely due to the unknown VOC sources (Mogensen et al., 2011). OH is the most important oxidant for atmospheric VOCs, and more accurate quantification of the OH reactivity sink is needed to enhance our understanding of the atmospheric capacity to oxidize gas-phase organic trace gases for secondary organic aerosol formation (SOA).

Author contribution. Manuscript preparation and analyzing results (M.M.). All authors contributed to project planning, experimental design, the discussion of the results and commenting on the manuscript.

Acknowledgements. This research was funded by the Academy of Finland Center of Excellence programme (grant no 272041) and by the Jenny and Antti Wihuri Foundation. The research was also supported by the Academy research fellow projects (Academy of Finland, projects 275608, 263858, and 292699). We also thank Eeva-Stiina Tuittila and Aino Korrensalo for the understory vegetation survey on the experimental plots, Jarkko Isotalo for the guidance on the statistical analysis and the staff of the SMEAR II station and Hyytiälä Forestry Field station.

Disclaimer: The authors declare that the work is original contribution not submitted elsewhere, and there are no competing financial interests.

10 **References**

Aalto, J., Kolari, P., Hari, P., Kerminen, V. M., Schiestl-Aalto, P., Aaltonen, H., Levula, J., Siivola, E., Kulmala, M., and Bäck, J.: New foliage growth is a significant, unaccounted source for volatiles in boreal evergreen forests. *Biogeosciences*, 11(5), 1331–1344, doi:10.5194/bg-11-1331-2014, 2014.

15 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, *Agr. Forest Meteorol.*, 151, 682–691, doi:10.1016/j.agrformet.2010.12.010, 2011.

Aaltonen, H., Pumpanen, J., Hakola, H., Vesala, T., Rasmus, S., and Bäck, J.: Snowpack concentrations and estimated fluxes of volatile organic compounds in a boreal forest, *Biogeosciences*, 9(6), 2033–2044, doi:10.5194/bg-9-2033-2012, 2012.

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.

Adamczyk, S., Adamczyk, B., Kitunen, V., and Smolander, A.: Monoterpenes and higher terpenes may inhibit enzyme activities in boreal forest soil. *Soil Biology and Biochemistry*, 87, 59–66, doi:10.1016/j.soilbio.2015.04.006, 2015.

30 Andersson-Sköld, Y., and Simpson, D.: Secondary organic aerosol formation in northern Europe: A model study. *Journal of Geophysical Research: Atmospheres* (1984–2012), 106(D7), 7357–7374, 2001.

Asensio, D., Peñuelas, J., Filella, I., and Llusià, J.: On-line screening of soil VOCs exchange responses to moisture, temperature and root presence. *Plant and Soil*, 291(1-2), 249–261, doi:10.1007/s11104-006-9190-4, 2007.

- Asensio, D., Peñuelas, J., Prieto, P., Estiarte, M., Filella, I., and Llusà, J.: Interannual and seasonal changes in the soil exchange rates of monoterpenes and other VOCs in a Mediterranean shrubland. *European journal of soil science*, 59(5), 878–891, doi:10.1111/j.1365-2389.2008.01057.x, 2008.
- 5 Asensio, D., Yuste, J. C., Mattana, S., Ribas, À., Llusà, J., and Peñuelas, J.: Litter VOCs induce changes in soil microbial biomass C and N and largely increase soil CO₂ efflux. *Plant and soil*, 360(1-2), 163–174, doi:10.1007/s11104-012-1220-9, 2012.
- Averill, Colin, Benjamin L. Turner, and Adrien C. Finzi: Mycorrhiza-mediated competition between plants and decomposers drives soil carbon storage, *Nature* 505.7484, 543–545, doi:10.1038/nature12901, 2014.
- 10 Banerjee, A., and Sharkey, T. D.: Methylerythritol 4-phosphate (MEP) pathway metabolic regulation. *Natural product reports*, 31(8), 1043-1055, doi: 10.1039/C3NP70124G, 2014.
- 15 [Bouvier-Brown, N. C., Goldstein, A. H., Gilman, J. B., Kuster, W. C., and de Gouw, J. A.: In-situ ambient quantification of monoterpenes, sesquiterpenes and related oxygenated compounds during BEARPEX 2007: implications for gas- and particle-phase chemistry. *Atmospheric Chemistry and Physics*, vol. 9, no. 15, pp. 5505–5518, 2009.](#)
- 20 Bäck, J., Aaltonen, H., Hellén, H., Kajos, M. K., Patokoski, J., Taipale, R., Pumpanen, J., and Heinonsalo, J. Variable fluxes of microbial volatile organic compounds (MVOCs) from root-associated fungi isolated from Scots pine. *Atmospheric Environment*, 44(30), 3651–3659, doi:10.1016/j.atmosenv.2010.06.042, 2010.
- 25 Bäck, J., Aalto, J., Henriksson, M., Hakola, H., He, Q., and Boy, M. Chemodiversity of a Scots pine stand and implications for terpene air concentrations. *Biogeosciences*, 9(2), 689–702, doi:10.5194/bg-9-689-2012, 2012.
- Chatani, S., Matsunaga, S. N., and Nakatsuka, S. Estimate of biogenic VOC emissions in Japan and their effects on photochemical formation of ambient ozone and secondary organic aerosol. *Atmospheric Environment*, 120, 38–50, doi:10.1016/j.atmosenv.2015.08.086, 2015.
- 30 Croft, K. P., Juttner, F., and Slusarenko, A. J. Volatile products of the lipoxygenase pathway evolved from *Phaseolus vulgaris* (L.) leaves inoculated with *Pseudomonas syringae* pv *phaseolicola*. *Plant Physiology*, 101(1), 13–24, 1993.
- 35 Dicke, M., Agrawal, A. A., and Bruin, J. Plants talk, but are they deaf? *Trends in plant science*, 8(9), 403–405, doi:10.1016/S1360-1385(03)00183-3, 2003.
- 40 Ditengou, F. A., Müller, A., Rosenkranz, M., Felten, J., Lasok, H., van Doorn, M. M., Legue, V., Palme, K., Schnitzler, J.-P., and Polle, A. Volatile signalling by sesquiterpenes from ectomycorrhizal fungi reprogrammes root architecture. *Nature communications*, 6:6279, doi:10.1038/ncomms7279, 2015.

Eisenreich, W., Schwarz, M., Cartayrade, A., Arigoni, D., Zenk, M. H., and Bacher, A.: The deoxyxylulose phosphate pathway of terpenoid biosynthesis in plants and microorganisms. *Chemistry & biology*, 5(9), R221-R233, 1998.

5 Effmert U., Kaldéras J., Warnke R., and Piechulla B.: Volatile mediated interactions between bacteria and fungi in the soil. *Journal of Chemical Ecology* 38, 665–703, doi:10.1007/s10886-012-0135-5, 2012.

Faubert, P., Tiiva, P., Michelsen, A., Rinnan, Å., Ro-Poulsen, H., and Rinnan, R.: The shift in plant species composition in a subarctic mountain birch forest floor due to climate change would modify the biogenic volatile organic compound emission profile. *Plant and Soil*, 352(1-2), 199–215, doi:10.1007/s11104-011-0989-2, 2012.

Faiola, C. L., VanderSchelden, G. S., Wen, M., Elloy, F. C., Cobos, D. R., Watts, R. J., Jobson, B. T., and VanReken, T. M.: SOA Formation Potential of Fluxes from Soil and Leaf Litter, *Environ. Sci. Technol.*, 48, 938–946, doi: 10.1021/es4040045, 2014.

15 [Farré-Armengol, G., Filella, I., Llusia, J., and Peñuelas, J.: Bidirectional Interaction between Phyllospheric Microbiotas and Plant Volatile Emissions. *Trends in Plant Science*, 21\(10\), 854–860, 2016.](#)

20 Fogel, R., and Hunt, G.: Contribution of mycorrhizae and soil fungi to nutrient cycling in a Douglas-fir ecosystem. *Canadian Journal of Forest Research*, 13(2), 219–232, 1983.

Forney, C. F., Javorek, S. K., Jordan, M. A., and Vander Kloet, S. P.: Floral volatile composition of four species of *Vaccinium*. This article is part of a Special Issue entitled “A tribute to Sam Vander Kloet FLS: Pure and applied research from blueberries to heathland ecology”. *Botany*, 90(5), 365–371, doi:10.1139/B2012-008, 2012.

25 Ghirardo, A., Gutknecht, J., Zimmer, I., Brüggemann, N., and Schnitzler, J. P.: Biogenic volatile organic compound and respiratory CO₂ fluxes after ¹³C-labeling: online tracing of C translocation dynamics in poplar plants. *PLoS One*, 6(2), e17393, doi:10.1371/journal.pone.0017393, 2011.

30 Grayston, S. J., Vaughan, D., and Jones, D.: Rhizosphere carbon flow in trees, in comparison with annual plants: the importance of root exudation and its impact on microbial activity and nutrient availability. *Applied soil ecology*, 5(1), 29–56, doi:10.1016/S0929-1393(96)00126-6, 1997.

35 Greenberg J.P., Asensio D., Turnipseed A., Guenther A.B., Karl T., and Gochis D.: Contribution of leaf and needle litter to whole ecosystem BVOC fluxes. *Atmospheric Environment* 59, 302–311, doi:10.1016/j.atmosenv.2012.04.038, 2012.

40 Grote, R., and Niinemets, Ü.: Modeling volatile isoprenoid emissions—a story with split ends. *Plant Biology*, 10(1), 8–28, doi:10.1055/s-2007-964975, 2008.

Guenther, A. B., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability: observations with eucalyptus and emission rate algorithm development. *Journal of Geophysical Research: Atmospheres*, 96(D6), 10799–10808, doi:10.1029/91JD00960, 1991.

5 Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses. *Journal of Geophysical Research: Atmospheres* (1984–2012), 98(D7), 12609–12617, doi:10.1029/93JD00527, 1993.

10 Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley P., Klinger L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions. *Journal of Geophysical Research: Atmospheres*, 100(D5), 8873-8892, doi:10.1029/94JD02950, 1995.

15 Guenther, A. Seasonal and spatial variations in natural volatile organic compound fluxes. *Ecological applications*, 7(1), 34–45, doi:10.2307/2269405, 1997.

20 Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Journal metrics. Atmos. Chem. Phys*, 6, 3181-3210, doi:10.5194/acp-6-3181-2006, 2006.

25 Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2. 1): an extended and updated framework for modeling biogenic emissions, *Geoscientific Model development* 5:1417–1492, doi:10.5194/gmd-5-1471-2012, 2012.

30 Guenther, A.: Biological and chemical diversity of biogenic volatile organic fluxes into the atmosphere. *ISRN Atmospheric Sciences*, Volume 2013, doi:10.1155/2013/786290, 2013.

35 Haapanala, S., Hakola, H., Hellén, H., Vestenius, M., Levula, J., and Rinne, J. Is forest management a significant source of monoterpenes into the boreal atmosphere?. *Biogeosciences*, 9(4), 1291–1300, doi:10.5194/bg-9-1291-2012, 2012.

40 Hakola, H., Rinne, J., and Laurila, T.: The hydrocarbon emission rates of tea-leafed willow (*Salix phylicifolia*), silver birch (*Betula pendula*) and European aspen (*Populus tremula*). *Atmos. Environ.* 32, 1825–1833, doi:10.1016/S1352-2310(97)00482-2, 1998.

45 Hakola, H., Tarvainen, V., Laurila, T., Hiltunen, V., Hellén, H., and Keronen, P.: Seasonal variation of VOC concentrations above a boreal coniferous forest. *Atmospheric Environment*, 37(12), 1623–1634, doi:10.1016/S1352-2310(03)00014-1, 2003.

- Hanson, D. T., Swanson, S., Graham, L. E., and Sharkey, T. D.: Evolutionary significance of isoprene emission from mosses. *American Journal of Botany*, 86(5), 634–639, 1999.
- Hari, P., and Kulmala, M.: Station for Measuring Ecosystem–Atmosphere Relations (SMEAR II). *Boreal Environment Research* 10: 315–322.
- Hayward, S., Muncey, R. J., James, A. E., Halsall, C. J., and Hewitt, C. N.: Monoterpene fluxes from soil in a Sitka spruce forest. *Atmospheric Environment*, 35(24), 4081–4087, doi:10.1016/S1352-2310(01)00213-8, 2001.
- He, N.P., Han, X.G., and Pan, Q.M.: Variations in the volatile organic compound emission potential of plant functional groups in the temperate grassland vegetation of inner Mongolia. *China. J. Integr. Plant Biol.* 47, 13–19, 2005.
- Hellén, H., Hakola, H., Pystynen, K. H., Rinne, J., and Haapanala, S.: C 2-C 10 hydrocarbon fluxes from a boreal wetland and forest floor. *Biogeosciences*, 3(2), 167–174, doi:10.5194/bg-3-167- 2006, 2006.
- Helmisaari, H. S., Derome, J., Nöjd, P., and Kukkola, M.: Fine root biomass in relation to site and stand characteristics in Norway spruce and Scots pine stands. *Tree Physiology*, 27(10), 1493–1504, 2007.
- Hewitt, C. N., and Street, R. A.: A qualitative assessment of the emission of non-methane hydrocarbon compounds from the biosphere to the atmosphere in the UK: present knowledge and uncertainties. *Atmospheric Environment. Part A. General Topics*, 26(17), 3069–3077, doi:10.1016/0960-1686(92)90463-U, 1992.
- Hung, R., Lee, S., and Bennett, J. W.: *Arabidopsis thaliana* as a model system for testing the effect of Trichoderma volatile organic compounds. *Fungal Ecology*, 6(1), 19–26, doi:10.1016/j.funeco.2012.09.005, 2013.
- Högberg, P., Nordgren, A., Buchmann, N., Taylor, A. F., Ekblad, A., Högberg, M. N., Nyberg G., Ottosson-Löfvenius, M., and Read, D. J.: Large-scale forest girdling shows that current photosynthesis drives soil respiration. *Nature*, 411(6839), 789–792, doi:10.1038/35081058, 2001.
- Högberg, M. N., Briones, M. J., Keel, S. G., Metcalfe, D. B., Campbell, C., Midwood, A. J., Thornton, V. H., Linder, S., Näsholm, T., and Högberg, P.: Quantification of effects of season and nitrogen supply on tree below-ground carbon transfer to ectomycorrhizal fungi and other soil organisms in a boreal pine forest. *New Phytologist*, 187(2), 485–493, doi:10.1111/J.1469-8137.2010.03274.X, 2010.
- [Ilvesniemi, H., Levula, J., Ojansuu, R., Kolari, P., Kulmala, L., Pumpanen, J., Launiainen, S., Vesala, T., and Nikinmaa, E.: Long-term measurements of the carbon balance of a boreal Scots pine dominated forest ecosystem. *Boreal Environ. Res.* 14, 731–753, 2009.](#)

- Insam, H., and Seewald, M. S.: Volatile organic compounds (VOCs) in soils. *Biology and fertility of soils*, 46(3), 199–213, doi:10.1007/s00374-010-0442-3, 2010.
- IPCC AR5, Climate change 2013: The physical science basis, in Contribution of Working Group I (WGI) to the Fifth Assessment Report (AR5) of the Intergovernmental Panel on Climate Change (IPCC), 2013.
- Isidorov, V., and Jdanova, M.: Volatile organic compounds from leaves litter. *Chemosphere*, 48(9), 975–979, 2002.
- Isidorov, V. A., Smolewska, M., Purzyńska-Pugacewicz, A., and Tyszkiewicz, Z. Chemical composition of volatile and extractive compounds of pine and spruce leaf litter in the initial stages of decomposition. *Biogeosciences*, 7(9), 2785–2794, doi:10.5194/bg-7-2785-2010, 2010.
- Joensuu, J., Altimir, N., Hakola, H., Rostás, M., Raivonen, M., Vestenius, M., Aaltonen, H., Riederer, M., and Bäck J. Role of needle surface waxes in dynamic exchange of mono- and sesquiterpenes. - *Atmospheric Chemistry and Physics Discussions* doi:10.5194/acp-2015-1024, 2016.
- Junker, R.R., and Tholl, D. Volatile organic compound mediated interactions at the plant-microbe interface. *Journal of Chemical Ecology* 39, 810–825, doi:10.1007/s10886-013-0325-9, 2013.
- Kai, M., Effmert U., Berg G, and Piechulla, B.: Volatiles of bacterial antagonists inhibit mycelial growth of the plant pathogen *Rhizotonia solani*. *Arch Microbiol* 187:351–360, doi:10.1007/s00203-006-0199-0, 2007.
- Kainulainen, P., and Holopainen, J. K.: Concentrations of secondary compounds in Scots pine needles at different stages of decomposition. *Soil Biology and Biochemistry*, 34(1), 37–42, doi:10.1016/S0038-0717(01)00147-X, 2002.
- Kanerva, S., Kitunen, V., Loponen, J., and Smolander, A.: Phenolic compounds and terpenes in soil organic horizon layers under silver birch, Norway spruce and Scots pine. *Biology and Fertility of Soils*, 44(4), 547–556, doi:10.1007/s00374-007-0234-6, 2008.
- Karl, G. A.: A new European plant-specific emission inventory of biogenic volatile organic compounds for use in atmospheric transport models. *Biogeosciences*, 6, 1059–1087, doi:10.5194/bg-6-1059-2009, 2009.
- Kaufman, Y., Tanre, D., and Boucher, O.: A satellite view of aerosols in the climate system, *Nature*, 419, 215–223, doi:10.1038/nature01091, 2002.
- Kesselmeier, J., Wilske, B., Muth, S., Bode, K., and Wolf, A.: Exchange of oxygenated volatile organic compounds between boreal lichens and the atmosphere. LAURILA T, LINDFORS V. Biogenic VOC emissions

and photochemistry in the boreal regions of Europe. CEC Air Pollution Research Report. Luxembourg: Official Publication of the European Commission, 70, 57–71, 1999.

5 Kim, J. C., Kim, K. J., Kim, D. S., and Han, J. S.: Seasonal variations of monoterpene fluxes from coniferous trees of different ages in Korea. *Chemosphere*, 59(11), 1685–1696, doi:10.1016/j.chemosphere.2004.10.048, 2005.

10 Kleinheinz, G. T., Bagley, S. T., John, W. S., Rughani, J. R., and McGinnis, G. D.: Characterization of alpha-pinene-degrading microorganisms and application to a bench-scale biofiltration system for VOC degradation. *Archives of environmental contamination and toxicology*, 37(2), 151–157, 1999.

Korhonen, J. F. J., Pihlatie, M., Pumpanen, J., Aaltonen, H., Hari, P., Levula, J., A. J. Kieloaho, E. Nikinmaa, T. Vesala, and Ilvesniemi, H.: Nitrogen balance of a boreal Scots pine forest. *Biogeosciences*, 10(2), 1083–1095, doi:10.5194/bg-10-1083-2013, 2013.

15 Kolari, P., Pumpanen, J., Kulmala, L., Ilvesniemi, H., Nikinmaa, E., Grönholm, T., and Hari, P.: Forest floor vegetation plays an important role in photosynthetic production of boreal forests. *Forest Ecology and Management*, 221(1), 241–248, doi:10.1016/j.foreco.2005.10.021, 2006.

20 Kolari, P., Bäck, J., Taipale, R., Ruuskanen, T. M., Kajos, M. K., Rinne, J., Kulmala, M., and Hari, P. Evaluation of accuracy in measurements of VOC fluxes with dynamic chamber system. *Atmospheric Environment*, 62, 344–351, doi:10.1016/j.atmosenv.2012.08.054, 2012.

25 Kulmala M., Hameri K., Aalto P. P., Mäkelä J. M., Pirjola L., Nilsson E. D., Buzorius G., Rannik U., Maso M., Seidl W., Hoffman T., Janson R., Hansson H.-C., Viisanen Y., Laaksonen A., O’Dowd C.: Overview of the international project on biogenic aerosol formation in the Boreal forest (BIOFOR). *Tellus*, 53B, 324–343, 2001.

30 Kulmala, M., Suni, T., Lehtinen, K.E.J., Dal Maso, M., Boy, M., Reissell, A., Rannik, Ü., Aalto, P.P., Keronen, P., Hakola, H., Bäck, J., Hoffmann, T., Vesala, T., Hari, P.: A new feedback mechanism linking forests, aerosols, and climate. *Atmos. Chem. Phys.* 4, 557–562, doi:10.5194/acp-4-557-2004, 2004.

35 Kulmala, M., Nieminen, T., Nikandrova, A., Lehtipalo, K., Manninen, H. E., Kajos, M. K., Kolari, P., Lauri, A., Petäjä, T., Krejci, R., Hansson, H.-C., Swietlicki, E., Lindroth, A., Christensen, T. R., Arneth, A., Hari, P., Bäck, J., Vesala, T., and Kerminen, V.-M.: CO₂-induced terrestrial feedback mechanism: From carbon sink to aerosol source and back, *Boreal Environ. Res.*, 19, suppl. B, 122–131, 2014.

Laothawornkitkul, J., Taylor, J. E., Paul, N. D., and Hewitt, C. N.: Biogenic volatile organic compounds in the Earth system. *New Phytologist*, 183(1), 27–51, doi: 10.1111/j.1469-8137.2009.02859.x, 2009.

- Leff, J. W., and Fierer, N.: Volatile organic compound (VOC) emissions from soil and litter samples. *Soil Biology and Biochemistry*, 40(7), 1629–1636, doi:10.1016/j.soilbio.2008.01.018, 2008.
- Lin, C., Owen, S.M., Peñuelas, J.: Volatile organic compounds in the roots and rhizosphere of *Pinus* spp. *Soil Biol. Biochem.* 39, 951–960, doi:10.1016/j.soilbio.2006.11.007, 2007.
- Lundell, R., Saarinen, T., Åström, H., and Hänninen, H.: The boreal dwarf shrub *Vaccinium vitis-idaea* retains its capacity for photosynthesis through the winter. *Botany*, 86(5), 491–500, doi:10.1139/B08-022, 2008.
- Mackie, A. E., and Wheatley, R. E.: Effects and incidence of volatile organic compound interactions between soil bacterial and fungal isolates. *Soil Biology and Biochemistry*, 31(3), 375–385, doi:10.1016/S0038-0717(98)00140-0, 1999.
- Mancuso, S., Taiti, C., Bazihizina, N., Costa, C., Menesatti, P., Giagnoni, L., Arenella, M., Nannipieri P., and Renella, G.: Soil volatile analysis by proton transfer reaction-time of flight mass spectrometry (PTR-TOF-MS). *Applied Soil Ecology*, 86, 182–191, doi:10.1016/j.apsoil.2014.10.018, 2015.
- Melin, E., and Krupa, S.: Studies on ectomycorrhizae of pine II. Growth inhibition of mycorrhizal fungi by volatile organic constituents of *Pinus silvestris* (Scots Pine) roots. *Physiologia Plantarum*, 25(3), 337–340, doi:10.1111/j.1399-3054.1971.tb01451.x, 1971.
- Mogensen, D., Smolander, S., Sogachev, A., Zhou, L., Sinha, V., Guenther, A., Williams, J., Nieminen T., Kajos, M. K., Rinne, J., Kulmala, M., and Boy, M.: Modelling atmospheric OH-reactivity in a boreal forest ecosystem. *Atmospheric Chemistry and Physics*, 11(18), 9709–9719, doi:10.5194/acp-11-9709-2011, 2011.
- Myhre, G., Samset, B. H., Schulz, M., Balkanski, Y., Bauer, S., Berntsen, T. K., Bian, H., Bellouin, N., Chin, M., Diehl, T., Easter, R. C., Feichter, J., Ghan, S. J., Hauglustaine, D., Iversen, T., Kinne, S., Kirkevåg, A., Lamarque, J.-F., Lin, G., Liu, X., Lund, M. T., Luo, G., Ma, X., van Noije, T., Penner, J. E., Rasch, P. J., Ruiz, A., Seland, Ø., Skeie, R. B., Stier, P., Takemura, T., Tsigaridis, K., Wang, P., Wang, Z., Xu, L., Yu, H., Yu, F., Yoon, J.-H., Zhang, K., Zhang, H., and Zhou, C.: Radiative forcing of the direct aerosol effect from AeroCom Phase II simulations, *Atmos. Chem. Phys.*, 13, 1853–1877, doi:10.5194/acp-13-1853-2013, 2013.
- Niinemets, Ü., Kuhn, U., Harley, P. C., Staudt, M., Arneth, A., Cescatti, A., Ciccioli, P., Copolovice, L., Geron, C., Guenther A., Kesselmeier, J., Lerdau, M. T., Monson R. K., and Peñuelas, J.: Estimations of isoprenoid emission capacity from enclosure studies: measurements, data processing, quality and standardized measurement protocols. *Biogeosciences*, 8(8), 2209–2246, doi:10.5194/bg-8-2209-2011, 2011.
- Nölscher, A. C., Williams, J., Sinha, V., Custer, T., Song, W., Johnson, A. M., Axinte, R., Bozem, H., Fischer, H., Pouvesle, N., Phillips, G., Crowley, J. N., Rantala, P., Rinne, J., Kulmala, M., Gonzales, D., Valverde-Canossa, J., Vogel, A., Hoffmann, T., Ouwensloot, H. G., Vilà-Guerau de Arellano, J., and Lelieveld, J.:

Summertime total OH reactivity measurements from boreal forest during HUMPPA-COPEC 2010. *Atmospheric chemistry and Physics* 12, no. 17: 8257-8270, 2012.

5 Olofsson, M., Ek-Olausson, B., Jensen, N.O., Langer, S., and Ljungström, E.: The flux of isoprene from a willow coppice plantation and the effect on local air quality. *Atmos. Environ.* 39, 2061–2070, doi:10.1016/j.atmosenv.2004.12.015, 2005.

Owen, S. M., Boissard, C., and Hewitt, C. N.: Volatile organic compounds (VOCs) emitted from 40 Mediterranean plant species: VOC speciation and extrapolation to habitat scale. *Atmospheric Environment*, 35(32), 5393–5409, 10 doi:10.1016/S1352-2310(01)00302-8, 2001.

Paavolainen, L., Kitunen, V., and Smolander, A.: Inhibition of nitrification in forest soil by monoterpenes. *Plant and Soil*, 205(2), 147–154, doi: 10.1023/A:1004335419358, 1998.

15 Pakeman, R. J., Beaton, J. K., Thoss, V., Lennon, J. J., Campbell, C. D., White, D., and Iason, G. R.: The extended phenotype of Scots pine (*Pinus sylvestris*) structures the understorey assemblage. *Ecography* 29:451–457, 2006.

Peñuelas, J., and Staudt, M.: BVOCs and global change. *Trends in plant science*, 15(3), 133–144, doi:10.1016/j.tplants.2009.12.005, 2010.

20 Peñuelas, J., Asensio, D., Tholl, D., Wenke, K., Rosenkranz, M., Piechulla, B., and Schnitzler, J. P.: Biogenic volatile emissions from the soil. *Plant, cell & environment*, 37(8), 1866–1891, doi:10.1111/pce.12340, 2014.

25 [Peräkylä, O., Vogt, M., Tikkanen, O. P., Laurila, T., Kajos, M. K., Rantala, P. A., Patokoski, J., Aalto, J., Yli-Juuti, T., Ehn, M., Sipilä, M., Paasonen, P., Rissanen, M., Nieminen, T., Taipale, R., Keronen, P., Lappalainen, H. K., Ruuskanen, T. M., Rinne, J. Kerminen, V.M., Kulmala, M., Bäck, J., Petäjä, T.: Monoterpenes' oxidation capacity and rate over a boreal forest: temporal variation and connection to growth of newly formed particles. *Boreal Environment Research*, 19, 293-293, 2014.](#)

30 Pollard, M., Beisson, F., Li, Y., and Ohlrogge, J. B.: Building lipid barriers: biosynthesis of cutin and suberin. *Trends in plant science*, 13(5), 236–246, doi:10.1016/j.tplants.2008.03.003, 2008.

Possell, M., and Loreto, F.: The role of volatile organic compounds in plant resistance to abiotic stresses: responses and mechanisms. In *Biology, controls and models of tree volatile organic compound fluxes*. Springer Netherlands, 35 209–235, doi:10.1007/978-94-007-6606-8, 2013.

Pumpanen, J., Kolari, P., Ilvesniemi, H., Minkkinen, K., Vesala, T., Niinistö, S., Lohila, A., Larmola, T., Moreto, M., Pihlatie, M., Janssen, I., Yüester, J. C., Grunzweig, J. M., Reth, S., Subke, J.-A., Savage, K., Kutsch, W., Østreg G., Ziegler, W., Anthoni, P., Lindroth A., and Hari, P.: Comparison of different chamber techniques for

measuring soil CO₂ efflux. *Agricultural and Forest Meteorology*, 123(3), 159–176, doi:10.1016/j.agrformet.2003.12.001, 2004.

5 Ramirez, K. S., Lauber, C. L., and Fierer, N.: Microbial consumption and production of volatile organic compounds at the soil-litter interface. *Biogeochemistry*, 99(1-3), 97–107, doi:10.1007/S10533-009-9393-X, 2010.

Rinnan, R., Rinnan, Å., Faubert, P., Tiiva, P., Holopainen, J. K., and Michelsen, A.: Few long-term effects of simulated climate change on volatile organic compound emissions and leaf chemistry of three subarctic dwarf shrubs, *Environmental and Experimental Botany* 72, 377–386, doi:10.1016/j.envexpbot.2010.11.006, 2011.

10 Rinnan, R., Gierth, D., Bilde, M., Rosenørn, T., & Michelsen, A.: Off-season biogenic volatile organic compound emissions from heath mesocosms: responses to vegetation cutting. *The Microbial Regulation of Global Biogeochemical Cycles*, 160, doi:10.3389/fmicb.2013.00224, 2014.

15 Rinne, J., Tuovinen, J. P., Laurila, T., Hakola, H., Aurela, M., & Hypén, H.: Measurements of hydrocarbon fluxes by a gradient method above a northern boreal forest. *Agricultural and Forest Meteorology*, 102(1), 25–37, doi:10.1016/S0168-1923(00)00088-5, 2000.

20 Rinne, J., Taipale, R., Markkanen, T., Ruuskanen, T. M., Hellén, H., Kajos, M. K., Vesala, T., and Kulmala, M.: Hydrocarbon fluxes above a Scots pine forest canopy: measurements and modeling. *Atmospheric Chemistry and Physics*, 7(12), 3361–3372, doi:10.5194/acp-7-3361-2007, 2007.

Rohmer, M., Knani, M., Simonin, P., Sutter, B., and Sahm, H.: Isoprenoid biosynthesis in bacteria: a novel pathway for the early steps leading to isopentenyl diphosphate. *Biochemical Journal*, 295(2), 517–524, 1993.

25 Rohmer, M., Seemann, M., Horbach, S., Bringer-Meyer, S., and Sahm, H.: Glyceraldehyde 3-phosphate and pyruvate as precursors of isoprenic units in an alternative non-mevalonate pathway for terpenoid biosynthesis. *Journal of the American Chemical Society*, 118(11), 2564–2566, 1996.

30 Schurgers, G., Arneth, A., Holzinger, R., and Goldstein, A. H.: Process-based modelling of biogenic monoterpene fluxes combining production and release from storage. *Atmospheric chemistry and physics*, 9(10), 3409–3423, doi:10.5194/acp-9-3409-2009, 2009.

35 Sindelarova, K., Granier, C., Bouarar, I., Guenther, A., Tilmes, S., Stavrou, T., Muller J.-F., Kuhn, U., Stefani, P., and Knorr, W.: Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years. *Atmospheric Chemistry and Physics*, 14(17), 9317–9341, doi:10.5194/acp-14-9317-2014, 2014.

40 [Sinha V., Williams J., Lelieveld J., Ruuskanen T., Kajos M., Patokoski J., Hellén H., Hakola H., Mogensen D., Boy M., Rinne J., Kulmala M.: OH Reactivity Measurements within a Boreal Forest: Evidence for Unknown Reactive Emissions. *Environmental Science and Technology*. 44 \(17\), 6614–6620, doi:10.1021/es101780b, 2010.](#)

- Stotzky, G., Schenck, S., and Papavizas, G. C.: Volatile organic compounds and microorganisms. *CRC critical reviews in microbiology*, 4(4), 333–382, doi:10.3109/10408417609102303, 1976.
- 5 Taipale, R., Ruuskanen, T. M., Rinne, J., Kajos, M. K., Hakola, H., Pohja, T., and Kulmala, M.: Technical Note: Quantitative long-term measurements of VOC concentrations by PTR-MS—measurement, calibration, and volume mixing ratio calculation methods. *Atmospheric Chemistry and Physics*, 8(22), 6681–6698, doi:10.5194/acp-8-6681-2008, 2008.
- 10 Tarvainen, V., Hakola, H., Hellén, H., Bäck, J., Hari, P., & Kulmala, M.: Temperature and light dependence of the VOC fluxes of Scots pine. *Atmospheric Chemistry and Physics*, 5(4), 989–998, doi:10.5194/acpd-4-6691-2004, 2005.
- 15 Van Roon, A., Parsons, J. R., Krap, L., and Govers, H. A.: Fate and transport of monoterpenes through soils. Part II: calculation of the effect of soil temperature, water saturation and organic carbon content. *Chemosphere*, 61(1), 129–138, doi:10.1016/j.chemosphere.2005.02.082, 2005.
- 20 Veres, P. R., Behrendt, T., Klapthor, A., Meixner, F. X., and Williams, J.: Volatile Organic Compound fluxes from soil: using Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS) for the real time observation of microbial processes. *Biogeosciences Discussions*, 11(8), 12009–12038, doi:10.5194/bgd-11-12009-2014, 2014.
- 25 Walter, M. H., Fester, T., and Strack, D.: Arbuscular mycorrhizal fungi induce the non-mevalonate methylerythritol phosphate pathway of isoprenoid biosynthesis correlated with accumulation of the ‘yellow pigment’ and other apocarotenoids. *The Plant Journal*, 21(6), 571–578, doi: 10.1046/j.1365-313x.2000.00708.x, 2000.
- Wieder, W. R., Bonan, G. B., & Allison, S. D.: Global soil carbon projections are improved by modelling microbial processes. *Nature Climate Change*, 3(10), 909–912, doi:10.1038/NCLIMATE1951, 2013.

Tables and Figures

Table 1. Soil depth (cm) and soil surface coverages (%) of mosses, ericoid shrubs, grasses, and tree seedlings on the soil-vegetation interface (+) and on bare soil, where vegetation was removed by cutting (-) on all experimental plots at three experimental sites (1, 2, and 3) in 2015. The standard error of the mean is given next to the mean.

Site	Vegetation	Soil depth	Mosses	Ericoid shrubs	Grasses	Tree seedlings
1	+	41.1 (5.4)	67.8 (9.7)	35.4 (9.1)	8.4 (5.5)	0.2 (0.2)
	-	45.3 (3.3)	20.1 (6.5)	0.2 (0.1)	0.0 (0.0)	0.0 (0.0)
2	+	34.1 (4.3)	69.9 (9.9)	30.4 (6.4)	17.5 (12.4)	0.1 (0.1)
	-	46.4 (5.5)	17.1 (2.4)	0.0 (0.0)	0.1 (0.0)	0.0 (0.0)
3	+	41.8 (7.4)	67.7 (8.7)	24.1 (6.6)	8.7 (5.7)	0.4 (0.3)
	-	43.7 (3.8)	16.1 (7.5)	2.4 (2.1)	0.1 (0.0)	0.0 (0.0)

Table 2. Number (N) of measured experimental plots on the different trenching treatments (Control: soil was non-trenched, Tr50: the ingrowth of mycorrhizal fungi was allowed, and Tr1: decomposers were the only source) with vegetation (+) and those with bare soil (-) and the total number of plots.

Treatment	N	Treatment	N	Treatment	N
Control+	12	Tr50+	3	Tr1+	6
Control-	6	Tr50-	3	Tr1-	6
		Total	36		

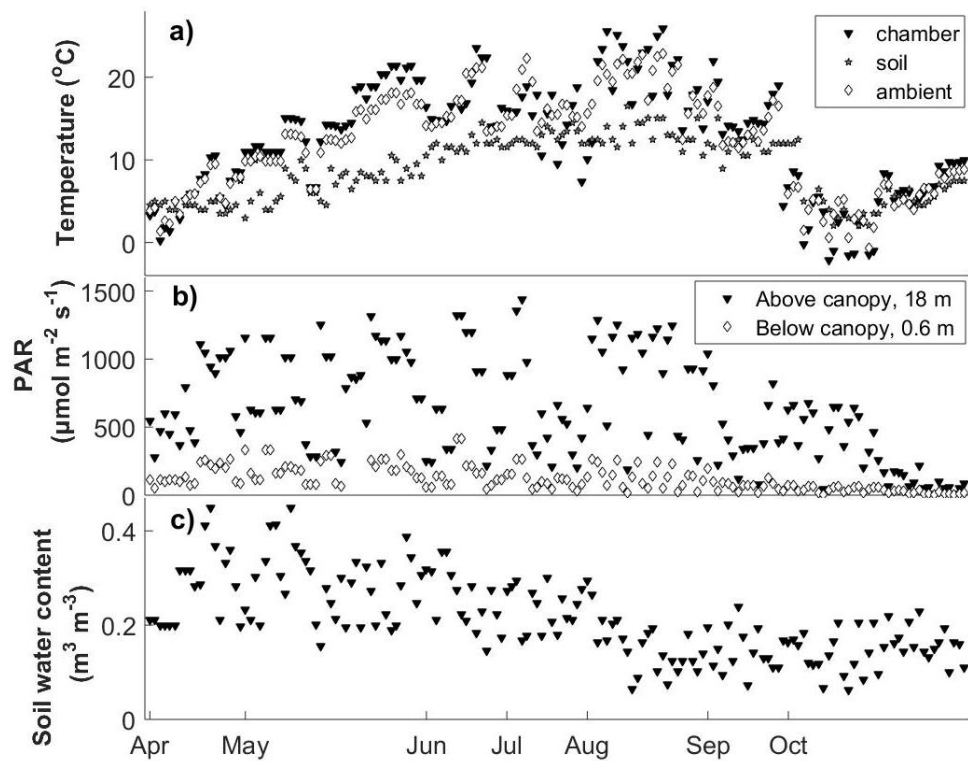
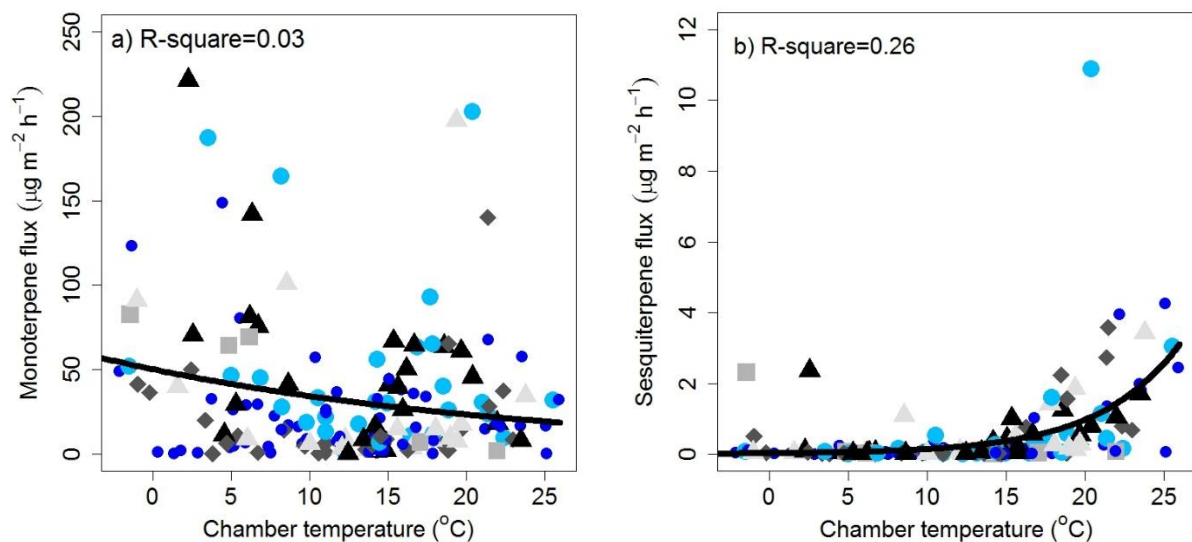


Figure 1. Environmental parameters during the measurements from 15th of April to 23th of October 2015.

- 5 a) Chamber, soil, and ambient temperature ($^{\circ}\text{C}$). b) Photosynthetically active radiation (PAR, $\mu\text{mol m}^{-2} \text{s}^{-1}$) above and below the canopy. c) Soil water content ($\text{m}^3 \text{m}^{-3}$).



- 10 **Figure 2.** Relationship between monoterpene (a, $R^2=0.03$, $p\text{-value}<0.01$) and sesquiterpene (b, $R^2=0.26$, $p\text{-value}>0.05$) fluxes ($\mu\text{g m}^{-2} \text{h}^{-1}$) and chamber temperature, presented as combined data from the different treatments (Control: soil was non-trenched, Tr50: the ingrowth of mycorrhizal fungi was

allowed, and Tr1: decomposers were the only source) with vegetation (+) and those with bare soil (-). The treatments (Control+=small blue circle, Control-=solid blue circle, Tr50+=filled gray triangle point-up, Tr50-=filled gray square, Tr1+=filled gray diamond, and Tr1-=filled black triangle point-up) were measured during periods 1–6, 2015.

5

Table 3. Isoprenoid fluxes ($\mu\text{g m}^{-2} \text{h}^{-1}$) from the different trenching treatments (Control+ (N=60), Control- (N=28), Tr1+ (N=28), Tr1- (N=24), Tr50+ (N=17) and Tr50- (N=6)) during periods 1–6, 2015. Fluxes are means (S.E.) of the whole data set. BDL = below detection limit of the VOC quantification. The effect of vegetation on fluxes between the plots with vegetation (+) and those with bare soil (-) was tested with the Kruskal-Wallis test ($p < 0.05$). Values were marked in bold if they differed between vegetation treatments. Significant differences in flux rates between the trenching treatments are indicated with different letters (Kruskal-Wallis test; $p < 0.05$).

Flux	Control+	Control-	Tr50+	Tr50-	Tr1+	Tr1-
isoprene	1.60 ^a (0.56)	0.98 ^a (0.33)	4.43 ^a (2.78)	1.24 ^a (0.93)	4.91 ^a (3.55)	4.10 ^a (2.27)
Monoterpenes						
α -pinene	14.68^a (2.57)	31.35^b (6.93)	21.98 ^{ac} (8.41)	26.35 ^{ab} (11.15)	11.53^a (3.42)	36.18^{bc} (8.09)
camphene	1.70^{ac} (0.23)	4.34^b (1.05)	2.87 ^{ab} (0.87)	3.08 ^{abc} (0.87)	1.39^c (0.39)	3.07^b (0.55)
β -pinene	0.30^a (0.06)	0.70^b (0.18)	0.46 ^{ab} (0.21)	0.44 ^{ab} (0.24)	0.25 ^a (0.08)	0.53 ^{ab} (0.14)
myrcene	0.09^a (0.02)	0.21^b (0.06)	0.19 ^{ab} (0.10)	0.18 ^{ab} (0.09)	0.14 ^{ab} (0.04)	0.23 ^b (0.06)
Δ 3-carene	5.41^a (0.79)	10.97^b (2.17)	7.32 ^{ac} (2.87)	7.83 ^{ab} (3.09)	5.25^a (1.64)	8.57^{bc} (1.44)
p-cymene	0.19^{ad} (0.07)	0.29^b (0.05)	0.16 ^{ac} (0.06)	0.13 ^{abc} (0.04)	0.13^c (0.05)	0.23^{bd} (0.04)
limonene	0.29^a (0.05)	0.49^b (0.09)	0.34 ^{ac} (0.15)	0.23 ^{ab} (0.10)	0.27^a (0.09)	0.44^{bc} (0.07)
terpinolene	0.05^a (0.01)	0.09^b (0.03)	0.09 ^{ab} (0.04)	0.07 ^{ab} (0.03)	0.05^a (0.02)	0.09^b (0.02)
Sum of the monoterpenes	22.87^a	48.62^b	33.59 ^{ac}	38.43 ^{ab}	19.18^a	49.49^{bc}
Sesquiterpenes						
longicyclene	0.01 ^a (0.002)	0.01 ^a (0.002)	0.01 ^a (0.004)	BDL	0.01 ^a (0.002)	0.01 ^a (0.002)
β -caryophyllene	0.24 ^a (0.073)	0.51 ^a (0.273)	0.39 ^a (0.150)	0.34 ^a (0.317)	0.38 ^a (0.140)	0.34 ^a (0.106)
aromadendrene	0.07 ^a (0.026)	0.16 ^a (0.093)	0.10 ^a (0.052)	BDL	0.06 ^a (0.023)	0.07 ^a (0.023)
α -humulene	0.03 ^a (0.010)	0.06 ^a (0.027)	0.05 ^a (0.022)	0.06 ^a (0.062)	0.05 ^a (0.021)	0.03 ^a (0.010)
Sum of the sesquiterpenes	0.35 ^a	0.73 ^a	0.55 ^a	0.42 ^a	0.50 ^a	0.45 ^a

Table 4. Mean (S.E.) total monoterpene and α -pinene fluxes ($\mu\text{g m}^{-2} \text{h}^{-1}$) from different treatments (Control+, Control-, Tr50+, Tr50-, Tr1+ and Tr1-) during periods 1 to 6, 2015. The periods are 1) 15th–24th of April, 2) 30th of April to 10th of May, 3) 21st of May to 24th of June, 4) 21st of July to 21st of August, 5) 31st of August to 9th of October and 6) 19th–23rd of October. Values were denoted different letters (a, b, and c) if they differed between treatments within the certain time period (Kruskal-Wallis test; $p < 0.05$).

Period	Control+	Control-	Tr50+	Tr50-	Tr1+	Tr1-
Monoterpenes						
1	13.0 (5.8)	30.5 (2.7)	-	-	10.2 (9.8)	-
2	17.9 (5.5)	16.6 (6.2)	37.5 (31.7)	5.4 (-)	5.1 (1.8)	18.1 (11.8)
3	21.4 (6.9)	52.4 (25.9)	58.4 (46.5)	-	34.4 (21.8)	39.9 (10.2)
4	13.8 ^a (3.4)	48.0 ^b (11.9)	15.4 (9.6)	2.0 (-)	18.6 (10.2)	39.5 ^b (11.8)

5	44.8 (12.8)	78.0 (31.7)	32.7 (15.7)	51.3 (22.8)	24.5 (8.4)	67.1 (33.4)
6	19.3 ^a (3.8)	36.9 (9.0)	7.6 (1.5)	69.2 (-)	8.6 ^b (2.9)	73.5 ^c (25.4)
α-pinene						
1	7.0 (3.1)	16.8 (1.0)	-	-	7.9 (7.6)	-
2	10.7 (3.5)	6.7 (2.8)	20.4 (19.4)	0.6 (-)	2.1 (0.9)	11.5 (7.6)
3	13.0 (4.3)	31.7 (16.6)	38.3 (31.1)	-	21.1 (13.5)	25.3 (7.3)
4	7.6 ^a (2.2)	30.9 ^b (8.9)	9.2 (6.8)	0.8 (-)	7.9 ^a (4.3)	28.2 ^b (9.6)
5	31.8 (9.4)	55.1 (22.9)	24.3 (12.2)	35.7 (16.4)	17.7 (6.4)	50.0 (25.6)
6	13.2 ^a (2.6)	26.5 (6.9)	5.3 (1.0)	49.6 (-)	5.4 ^a (1.7)	60.2 ^b (22.8)

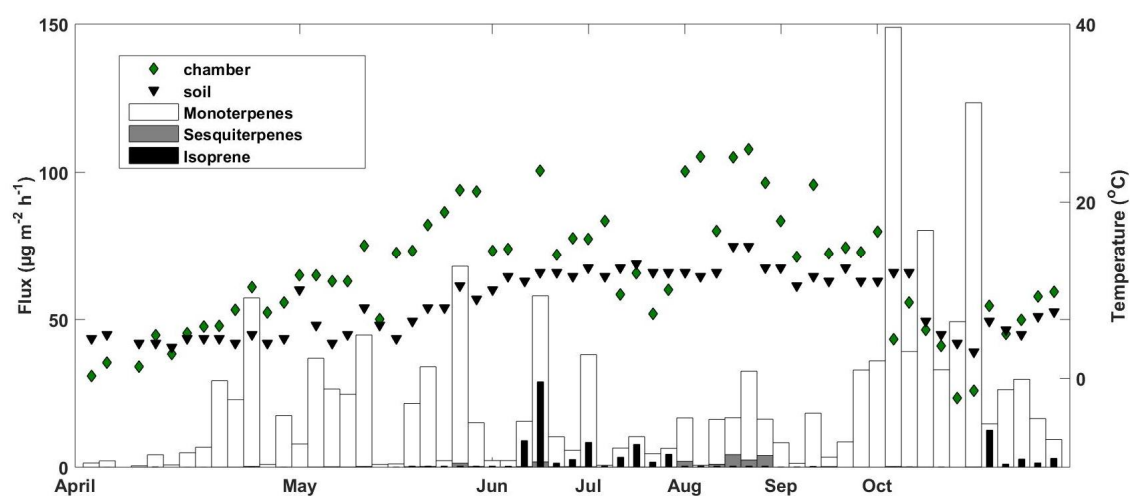


Figure 3. Monoterpene, sesquiterpene, and isoprene fluxes ($\mu\text{g m}^{-2} \text{h}^{-1}$), and chamber and soil temperatures ($^{\circ}\text{C}$) from a non-trenched forest floor (Control+) during April–October 2015.

5

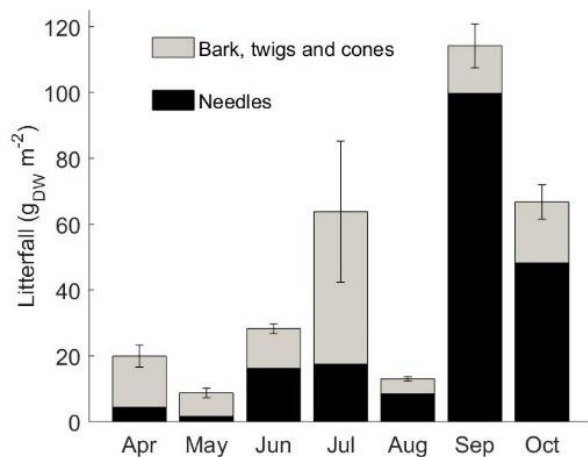


Figure 4. Monthly litterfall of bark, twigs, and cones (grey, g (DW) m^{-2}), and the fraction of needles in litterfall (black, g (DW) m^{-2}) at the SMEAR II stand from April to October 2015. Error bars indicate the standard error of monthly total litterfall from 21 litter collectors.

10

Table 5. Results from the mixed effects linear models, testing the factors impacting monoterpene and sesquiterpene fluxes from boreal forest soil (N [all treatments] = 163, N [plot] = 36, N [site] = 3). Tested effects: period (1–6), vegetation (+/-), chamber temperature (chamber temp), soil temperature (soil temp), PAR, soil water content (soil wt), and the interactions of these. Random effects were related to trenching plot number and trenching site. Pseudo-R-squared was calculated based on Nakagawa and Schielzeth, (2013), and Johnson et al., (2014).

MONOTERPENES			
<u>Fixed effects:</u>	Chisq value	p-value	Pseudo-R-squared
factor (period)	16.762	0.004975 **	0.43
factor (vegetation)	12.52	0.0004026 ***	
chamber temp	7.7944	0.005241 **	
period*vegetation	6.9411	0.2251	
period*chamber temp	27.771	4.035e-05 ***	
vegetation*chamber temp	4.5996	0.03198 *	
period*vegetation*chamber temp	5.3451	0.3752	
SESQUITERPENES			
<u>Fixed effects:</u>	Chisq value	p-value	Pseudo-R-squared
factor (period)	7.0716	0.2154	0.29
chamber temp	6.8436	0.008896 **	
period*chamber temp	22.44	0.0004318 ***	

Table 6. Results from the mixed effects linear models, testing the factors impacting isoprenoid fluxes from boreal forest soil (N [all treatments] = 163, N [plot] = 36, N [site] = 3). Tested effects: period (1-6), vegetation (+/-), chamber temperature (chamber temp), soil temperature (soil temp), PAR, soil water content (soil wt), and the interactions of these. Random effects were related to trenching plot number and trenching site. Pseudo-R-squared was calculated based on Nakagawa and Schielzeth, (2013), and Johnson et al., (2014).

Fixed effects:	Chisq value	p-value	Pseudo-R-squared	Chisq value	p-value	Pseudo-R-squared
MONOTERPENES						
-			α-pinene		camphene	
factor (period)	20.206	0.001143 **	0.46	10.281	0.06764	0.44
factor (vegetation)	13.086	0.0002975 ***		11.928	0.000553 ***	
chamber temp	11.28	0.0007833 ***		0.8389	0.3597	
period*vegetation	8.7498	0.1195		1.1673	0.948	
period*chamber temp	25.809	9.717e-05 ***		28.527	2.87e-05 ***	
vegetation*chamber temp	5.4705	0.01934 *		1.0471	0.3062	
period*vegetation*chamber temp		0.3903		11.508	0.04219 *	
-			b-pinene		Δ3-carene	
factor (period)	25.781	9.841e-05 ***	0.39	9.6409	0.08607	0.34
factor (vegetation)	7.8661	0.005037 **		7.169	0.007417 **	
chamber temp	6.6896	0.009697 **		1.7575	0.1849	
period*vegetation	7.0668	0.2157		5.0279	0.4125	
period*chamber temp	21.477	0.000658 ***		27.831	3.927e-05 ***	
vegetation*chamber temp	3.2511	0.07138		2.6246	0.1052	
period*vegetation*chamber temp	6.391	0.27		3.0477	0.6926	
-			limonene			
factor (period)	11.947	0.03552 *	0.38			
PAR	5.407	0.02006 *				
chamber temp	0.2088	0.6477				
period*PAR	12.302	0.03087 *				
period*chamber temp	5.542	0.3534				
PAR*chamber temp	5.9393	0.01481 *				
period*PAR*chamber temp	8.4248	0.1343				
SESQUITERPENES						
-			longicyclene			
factor (period)	13.364	0.0202 *	0.40			
soil wt	4.2641	0.03893 *				
chamber temp	8.8191	0.002981 **				
period*soil wt	0.8172	0.9759				
period*chamber temp	21.212	0.0007388 ***				
soil wt*chamber temp	5.403	0.0201 *				
period*soil wt*chamber temp	9.9874	0.07559				
-			α-humulene		β-caryophyllene	
factor (period)	11.38	0.04434 *	0.35	5.9382	0.3123	0.31
chamber temp	3.5212	0.06059		6.0838	0.01364 *	
period*chamber temp	22.849	0.0003608 ***		21.981	0.0005279 ***	
ISOPRENE						
factor (period)	5.5947	0.3477	0.35			
soil wt	1.077	0.2994				
soil temp	5.4103	0.02002 *				

period*soil wt	10.32	0.06665
period*soil temp	25.991	8.958e-05 ***
soil wt*soil temp	0.1811	0.6705
period*soil wt*soil temp	15.851	0.007282 **

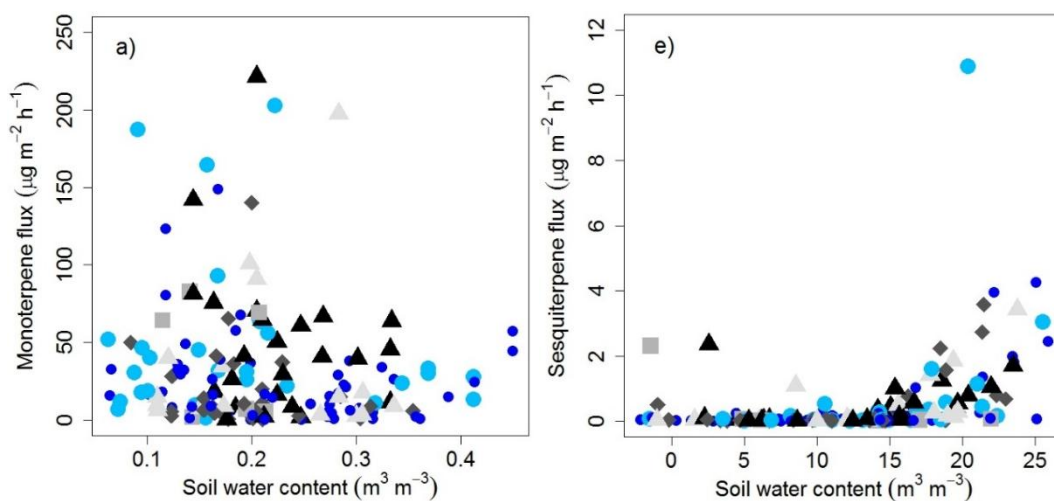
Appendix

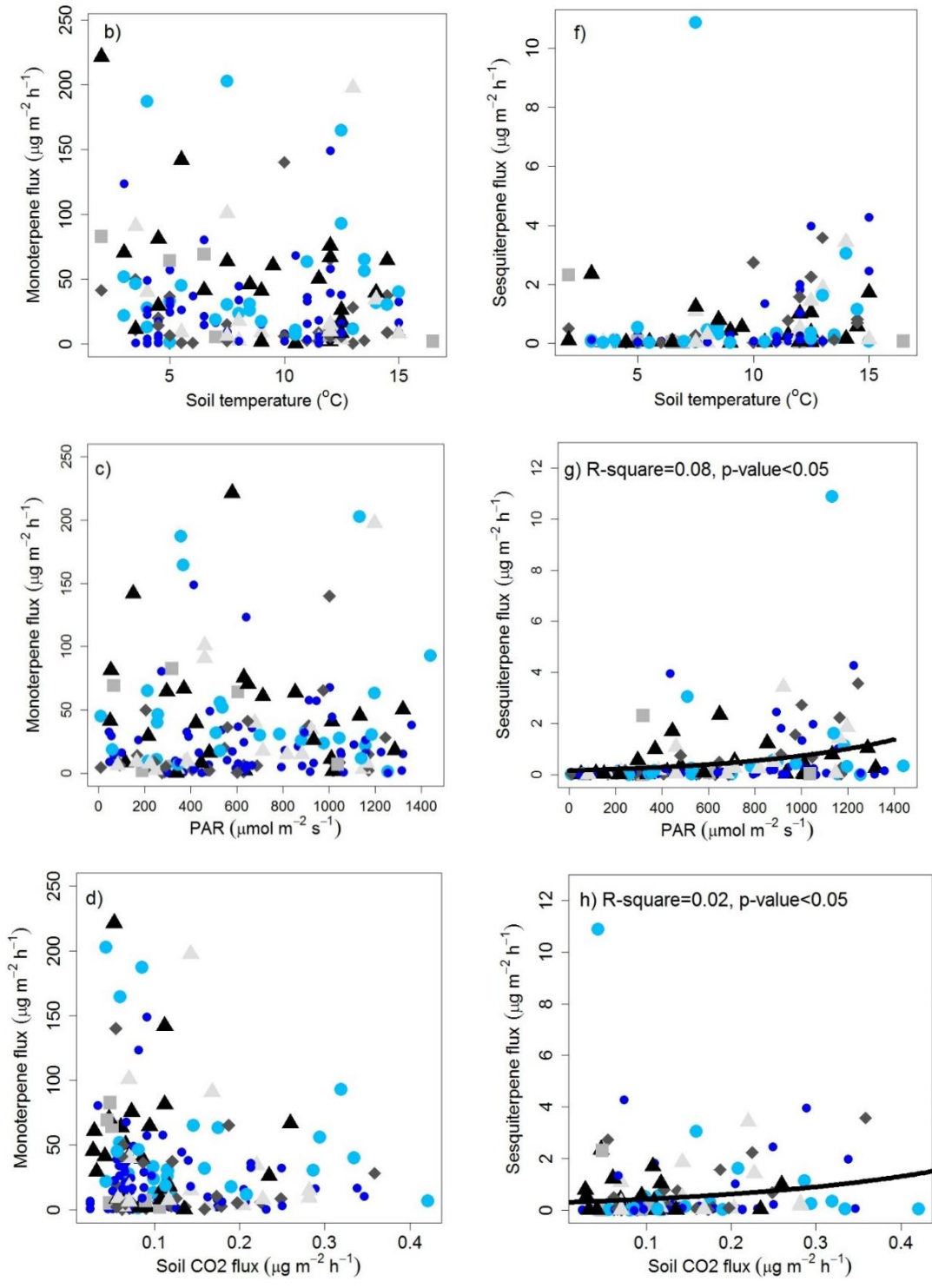
Table A1. Chamber measurements from the different trenching treatments (Control+, Control-, Tr1+, Tr1-, Tr50+, Tr50-) from 15th of April to 23th of October 2015.

Time	Trt	Plot	Time	Trt	Plot	Time	Trt	Plot
15 th April 1 PM	Tr1+	2	23 rd May 4 PM	Tr50+	19	31 st August 1 PM	Control+	37
15 th April 3 PM	Tr1+	1	22 nd June 10 AM	Control-	52	31 st August 4 PM	Control-	43
16 th April 10 AM	Control+	38	22 nd June 10 AM	Tr1+	14	1 st September 8 AM	Control+	39
16 th April 1 PM	Control+	38	22 nd June 12 AM	Tr1-	18	1 st September 11 AM	Tr50-	11
17 th April 9 AM	Control+	38	22 nd June 1 PM	Control+	46	1 st September 1 PM	Control+	38
17 th April 1 PM	Control+	38	22 nd June 3 PM	Control+	48	1 st September 4 PM	Tr50+	7
23 rd April 10 AM	Control+	53	22 nd June 3 PM	Tr50+	19	2 nd September 9 AM	Control-	44
23 rd April 12 PM	Control+	53	23 rd June 9 AM	Control+	53	2 nd September 11 AM	Control+	40
23 rd April 2 PM	Control+	53	23 rd June 10 AM	Tr1-	29	2 nd September 2 PM	Tr1+	2
24 th April 3 PM	Control+	37	23 rd June 12 PM	Control-	59	2 nd September 4 PM	Tr1-	6
25 th April 9 AM	Control+	56	23 rd June 12 PM	Tr50+	31	3 rd September 9 AM	Tr1-	17
25 th April 10 AM	Control-	51	23 rd June 3 P M	Control+	55	3 rd September 11 AM	Control-	51
25 th April 12 PM	Control+	48	23 rd June 3 PM	Tr1+	25	3 rd September 1 PM	Control+	45
25 th April 1 PM	Control-	52	24 th June 8 AM	Control-	60	3 rd September 4 PM	Tr1+	13
30 th April 9 AM	Tr1+	1	24 th June 8 AM	Control+	54	4 th September 9 AM	Control+	47
30 th April 9 AM	Tr1-	5	24 th June 11 AM	Tr1-	30	4 th September 11 AM	Control+	47
30 th April 11 AM	Control+	39	24 th June 11 AM	Tr1+	26	4 th September 1 PM	Tr50+	19
30 th April 2 PM	Control+	37	24 th June 1 PM	Control+	56	4 th September 3 PM	Tr50+	19
30 th April 3 PM	Tr50+	7	24 th June 2 PM	Tr50+	31	5 th October 8 AM	Control+	48
2 nd May 9 AM	Control-	44	21 st July 9 AM	Control+	39	5 th October 10 AM	Tr1-	18
2 nd May 11 AM	Tr1+	2	21 st July 12 PM	Control-	43	5 th October 12 PM	Control+	46
2 nd May 2 PM	Control+	40	21 st July 2 PM	Tr1+	1	5 th October 2 PM	Control-	52
2 nd May 2 PM	Control+	38	21 st July 5 PM	Tr1-	5	6 th October 8 AM	Tr1+	14
3 rd May 9 AM	Control+	47	21 st July 9 AM	Control+	37	6 th October 10 AM	Tr50+	19
3 rd May 9 AM	Control-	51	22 nd July 12 PM	Tr1+	2	6 th October 12 PM	Tr50-	23
3 rd May 12 PM	Control+	45	22 nd July 2 PM	Tr1-	6	6 th October 2 PM	Control+	53
3 rd May 12 PM	Tr1+	13	22 nd July 5 PM	Control-	44	6 th October 4 PM	Control+	55
8 th May 9 AM	Tr1-	18	23 rd July 8 AM	Control+	38	7 th October 8 AM	Control+	56
8 th May 9 AM	Control+	48	23 rd July 11 AM	Control+	40	7 th October 10 AM	Tr1+	25
8 th May 12 PM	Control-	52	23 rd July 1 PM	Control-	51	7 th October 12 PM	Tr1-	29
8 th May 12 PM	Tr1+	14	23 rd July 4 PM	Tr1-	17	7 th October 2 PM	Control-	59
8 th May 2 PM	Tr50+	19	23 rd July 6 PM	Tr1+	13	8 th October 8 AM	Control-	60

9 th May 12 PM	Control+	53	24 th July 6 AM	Control+	47	8 th October 10 AM	Control+	54
9 th May 12 PM	Tr1+	26	24 th July 9 AM	Control+	45	8 th October 12 PM	Tr1-	30
10 th May 8 AM	Control-	60	24 th July 11 AM	Tr50+	19	8 th October 3 PM	Tr1+	26
10 th May 11 AM	Control+	56	17 th August 10 AM	Tr1-	18	9 th October 8 AM	Tr50-	35
10 th May 11 AM	Tr1-	30	17 th August 12 PM	Control+	48	9 th October 9 AM	Tr50+	31
10 th May 1 PM	Tr50-	35	17 th August 3 PM	Control-	52	19 th October 7 PM	Control-	43
10 th May 2 PM	Tr50+	31	18 th August 9 AM	Tr1+	14	19 th October 12 PM	Tr1+	1
21 st May 10 AM	Control-	43	18 th August 11 AM	Control+	46	19 th October 2 PM	Control+	39
21 st May 10 AM	Control+	37	18 th August 2 PM	Tr50+	19	20 th October 8 AM	Control+	37
21 st May 1PM	Tr1-	5	18 th August 5 PM	Tr50-	23	20 th October 10 AM	Tr50+	7
21 st May 1 PM	Control-	43	19 th August 9 AM	Control+	55	20 th October 1 PM	Tr1-	5
21 st May 4 PM	Control+	39	19 th August 11 AM	Control-	59	20 th October 3 PM	Tr50-	11
22 nd May 9 AM	Control+	40	19 th August 2 PM	Tr1+	25	21 st October 8 AM	Tr1+	2
22 nd May 9 AM	Tr1+	2	19 th August 4 PM	Tr1-	29	21 st October 10 AM	Tr1-	6
22 nd May 11 AM	Tr-	6	20 th August 9 AM	Tr50+	31	21 st October 12 PM	Tr1-	5
22 nd May 12 PM	Control-	44	20 th August 12 AM	Control+	53	21 st October 1 PM	Control+	38
22 nd May 2 PM	Control+	38	20 th August 2 PM	Control+	56	21 st October 3 PM	Control-	44
22 nd May 2 PM	Tr1+	1	21 st August 9 AM	Control-	60	22 nd October 8 AM	Tr1-	17
23 rd May 10 AM	Tr1+	13	21 st August 11 AM	Tr1+	26	22 nd October 10 AM	Control+	45
23 rd May 1 PM	Control+	45	21 st August 4 PM	Control+	54	22 nd October 12 PM	Control-	51
23 rd May 1 PM	Control-	51	31 st August 8 AM	Tr1+	1	22 nd October 3 PM	Tr1+	13
23 rd May 3 PM	Tr1-	17	31 st August 10 AM	Tr1-	5	23 rd October 8 AM	Control+	47
						23 rd October 10 AM	Tr50+	19

5





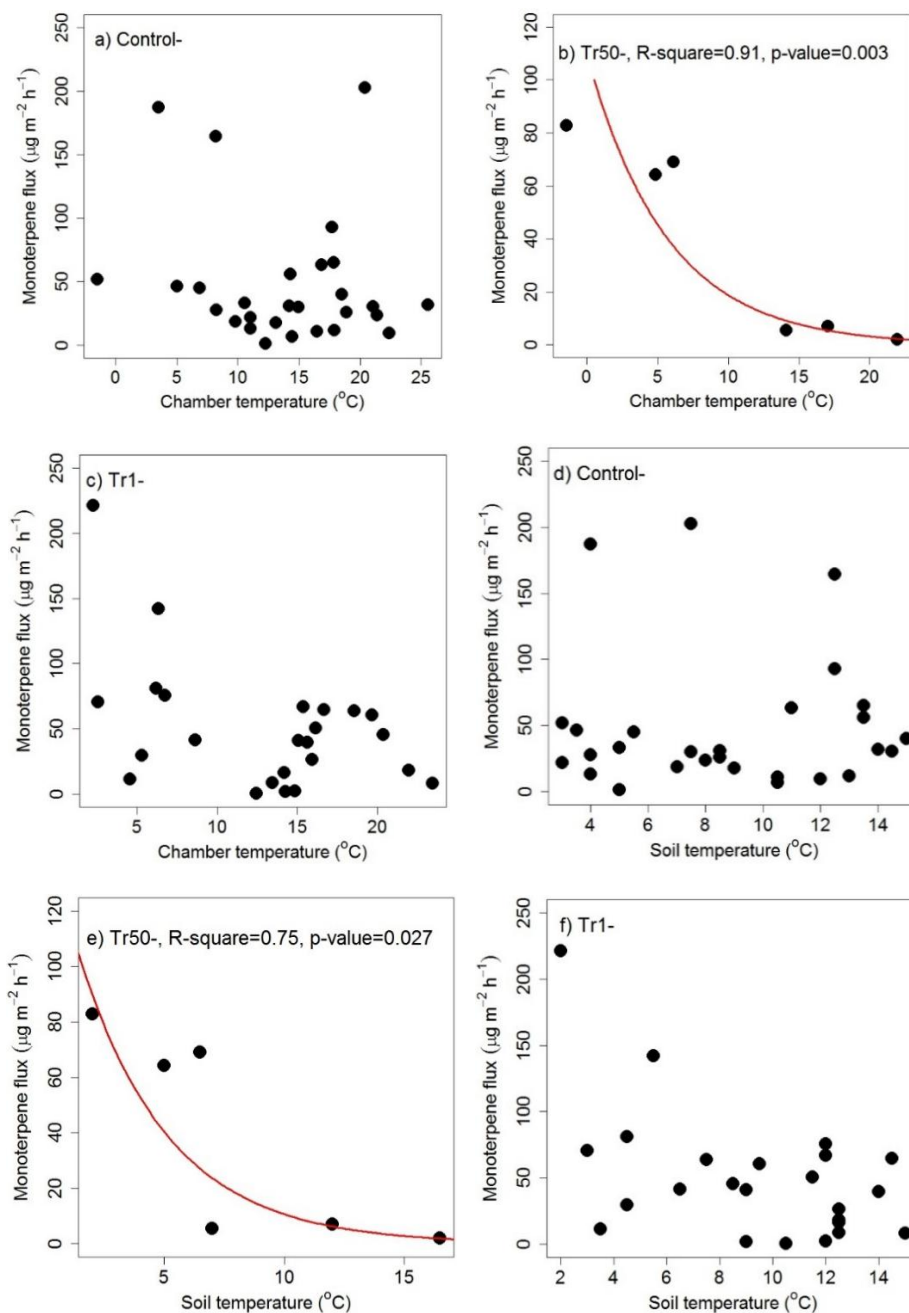
5

10

Figure A1. Relationships between monoterpene (a–d) and sesquiterpene flux (e–h) ($\mu\text{g m}^{-2} \text{h}^{-1}$) and soil water content ($\text{m}^3 \text{m}^{-3}$), soil temperature ($^{\circ}\text{C}$), above-canopy PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$), and soil CO₂ flux ($\mu\text{g m}^{-2} \text{h}^{-1}$). The presented data were combined from all treatments (Control: soil was non-trenched, Tr50: the ingrowth of mycorrhizal fungi was allowed, and Tr1: decomposers were the only source) with vegetation (+) and those with bare soil (-). The treatments (Control+=small blue circle, Control-=solid blue circle, Tr50+=filled gray triangle point-up, Tr50-=filled gray square, Tr1+=filled gray diamond,

and Tr1- (filled black triangle point-up) were measured from April to October 2015. The regression coefficient and p-value are indicated where the regression was significant.

5



10 **Figure A2.** Relationships between monoterpene flux ($\mu\text{g m}^{-2} \text{h}^{-1}$) and chamber temperature ($^{\circ}\text{C}$) on Control- (bare soil was non-trenched), Tr50- (bare soil where ingrowth of mycorrhizal fungi was allowed) and Tr1- (bare soil where decomposers were the only source) plots (a, b and c) and soil temperature ($^{\circ}\text{C}$) on Control-, Tr50- and Tr1- plots (d, e and f). The presented data were combined from all the periods, 2015. The regression coefficient and p-value are indicated where the regression was significant.

15

Total uncertainty of the emissions (U_{tot}) was calculated directly from precision (U_{prec}) and systematic errors (U_{sys}):

$$U_{tot}^2 = U_{prec}^2 + U_{sys}^2 \quad (1)$$

The precision (U_{prec}) was calculated using Eq (2):

$$U_{prec} = \frac{1}{3}DL + RSD \times \chi \quad (2)$$

where DL is the detection limit of the VOC quantification ($\mu\text{g m}^{-2} \text{h}^{-1}$), RSD is relative standard deviation between the parallel samples taken from the chamber enclosures and χ is the median emission rate of α -pinene: $10 \mu\text{g m}^{-2} \text{h}^{-1}$) at the SMEAR II site during periods 1 to 6, 2015 (Table A2). For lower emission rates uncertainties are expected to be higher.

The systematic error includes uncertainty of the standard preparation ($U_{stdprep}$, 5%) estimated for the equipment that was used, uncertainty of the sample volume (U_{vol} , 3%) that was obtained for the uncertainty of the mass flow controllers, errors due to variation in ingoing air concentration (U_{in}) was calculated using Eq (3) based on 4 replicates of the ingoing air and 8 of the outgoing air during the chamber closure (Table A2).

$$U_{sys}^2 = U_{stdprep}^2 + U_{vol}^2 + U_{in}^2 \quad (3)$$

Systematic error was higher than error of the precision (see Table A2). This was mainly due to variations in ingoing air.

Recovery of different compounds was tested by injecting known amounts of studied compounds into ingoing air and recovery was measured from the outgoing air. Results are shown in Table A2.

Table A2. Relative standard deviation between the parallel samples taken from the chamber enclosures (RSD, %), the detection limit of the VOC quantification (DL, $\mu\text{g m}^{-2} \text{h}^{-1}$), and errors due to variation in ingoing air concentration (U_{in} , %), and based on these values, precision (U_{prec} , %), systematic error (U_{sys} , %) and total uncertainty (U_{tot} , %) of the emissions were calculated for the emissions at the level $10 \mu\text{g m}^{-2} \text{h}^{-1}$, which was mean emission rate of α -pinene

	RSD	DL	U_{in}	U_{prec}	U_{sys}	U_{tot}
-						

<u>Monoterpenes</u>	-	-	-	-	-	-
<u>α-pinene</u>	<u>8 %</u>	<u>0.84</u>	<u>32 %</u>	<u>11 %</u>	<u>33 %</u>	<u>35 %</u>
<u>camphene</u>	<u>8 %</u>	<u>0.18</u>	<u>59 %</u>	<u>8 %</u>	<u>29 %</u>	<u>60 %</u>
<u>β-pinene</u>	<u>7 %</u>	<u>0.01</u>	<u>17 %</u>	<u>7 %</u>	<u>27 %</u>	<u>20 %</u>
<u>myrcene</u>	<u>7 %</u>	<u>0.01</u>	<u>10 %</u>	<u>7 %</u>	<u>27 %</u>	<u>14 %</u>
<u>Δ^3-carene</u>	<u>10 %</u>	<u>0.53</u>	<u>42 %</u>	<u>12 %</u>	<u>34 %</u>	<u>44 %</u>
<u>p-cymene</u>	<u>11 %</u>	<u>0.04</u>	<u>26 %</u>	<u>11 %</u>	<u>33 %</u>	<u>29 %</u>
<u>limonene</u>	<u>11 %</u>	<u>0.08</u>	<u>17 %</u>	<u>11 %</u>	<u>34 %</u>	<u>22 %</u>
<u>terpinolene</u>	<u>12 %</u>	<u>0.002</u>	<u>7 %</u>	<u>12 %</u>	<u>34 %</u>	<u>15 %</u>
<u>Sesquiterpenes</u>	-	-	-	-	-	-
<u>longicyclene</u>	<u>10 %</u>	<u>0.004</u>	<u>8 %</u>	<u>10 %</u>	<u>32 %</u>	<u>14 %</u>
<u>β-caryophyllene</u>	<u>12 %</u>	<u>0.022</u>	<u>15 %</u>	<u>12 %</u>	<u>34 %</u>	<u>20 %</u>
<u>α-humulene</u>	<u>10 %</u>	<u>0.004</u>	<u>15 %</u>	<u>10 %</u>	<u>32 %</u>	<u>19 %</u>