Agricultural and Forest Meteorology 308-309 (2021) 108584

Contents lists available at ScienceDirect

Agricultural and Forest Meteorology

journal homepage: www.elsevier.com/locate/agrformet

Age-related response of forest floor biogenic volatile organic compound fluxes to boreal forest succession after wildfires

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ARTICLE INFO

Keywords:
Forest floor BVOC fluxes
Wildfire
Forest succession
Ground vegetation changes
Scots pine forests

ABSTRACT

The amplification of global warming in the Northern regions results in a higher probability of wildfires in boreal forests. On the forest floor, wildfires have long-term effects on vegetation composition as well as soil and its microbial communities. A large variety of biogenic volatile organic compounds (BVOCs) such as isoprene, monoterpenes, sesquiterpenes have been observed to be emitted from soil and understory vegetation of boreal forest floor. Ultimately, the fire-induced changes in the forest floor affect its BVOC fluxes, and the recovery of the forest floor determines the quantity and quality of BVOC fluxes. However, the effects of wildfires on forest floor BVOC fluxes are rarely studied. Here we conducted a study of the impacts of post-fire succession on forest floor BVOC fluxes along a 158-year fire chronosequence in boreal Scots pine stands near the northern timberline in north-eastern Finland throughout a growing season. We determined the forest floor BVOC fluxes and investigated how the environmental and ground vegetation characteristics, soil respiration rates, and soil microbial and fungal biomass are associated with the BVOC fluxes during the post-fire succession. The forest floor was a source of diverse BVOCs. Monoterpenes (MTs) were the largest group of emitted BVOCs. We observed forest age-related differences in the forest floor BVOC fluxes along the fire chronosequence. The forest floor BVOC fluxes decreased with the reduction in ground vegetation coverage resulted from wildfire, and the decreased fluxes were also connected to a decrease in microbial activity as a result of the loss of plant roots and soil organic matter. The increase in BVOC fluxes was associated with the recovery of aboveground plant coverage and soils. Our results suggested taking into consideration the implications of BVOC flux variations on the atmospheric chemistry and climate feedbacks.

1. Introduction

Boreal forest ecosystems are the second largest forest area after tropical forest ecosystems, with about 12.1 $\times$ 10^6 km^2 (Potter et al., 1996). Among that, the forest area in Finland covers about 0.203 $\times$ 10^6 km^2 (Vaahtera et al., 2018). Forest fire is one of the principal natural disturbances affecting forest dynamics and biodiversity, and terrestrial carbon stocks in boreal forest ecosystems (Kelly et al., 2013; Seidl et al., 2017). Boreal forests have a higher risk of fires in the future due to global warming (Moritz et al., 2012) that will be strongest in the higher latitudes (Collins et al., 2013). An increasing frequency of warm and dry periods is particularly facilitating fire activity in boreal forests (e.g. Kelly et al., 2013; Seidl et al., 2017). Therefore, the danger of forest fires will most likely increase in Finland, too (Lehtonen et al., 2016).

Biogenic volatile organic compounds (BVOCs) released from soil and ground vegetation of boreal forest floor are considered as a significant BVOC source to the atmosphere (Aaltonen et al., 2011, 2013; Hellén et al., 2006; Mäki et al., 2019; Wang et al., 2018). The vascular plant species and mosses, the most dominating ground species in the boreal forest floor, have been identified as BVOC emission sources (Hanson et al., 1999; Mäki et al., 2019; Wang et al., 2018; Zhang-Turpeinen et al., 2020). A large variety of BVOCs are also emitted from soil, that may

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https://doi.org/10.1016/j.agrformet.2021.108584
Received 5 March 2021; Received in revised form 28 July 2021; Accepted 1 August 2021
Available online 11 August 2021

originate from plant roots, decomposing litter, soil organic matter (SOM), and soil microorganisms (Asensio et al., 2008; Bäck et al., 2010; Hayward et al., 2001; Leff and Fierer, 2008). The forest floor BVOC emissions are strongly associated with plants' above-ground processes and living roots (Bäck et al., 2010). Also, microbes are important in the decomposition of plant litter and release gases and volatiles (Leff and Fierer, 2008). The most commonly emitted BVOC species consist of isoprene, monoterpenes (MTs) and sesquiterpenes (SQTs), as well as other BVOCs with alcohols, ketones, aldehydes, acids, and various carbohydrates (Kesselmeier and Staudt, 1999; Llusià et al., 2002; Peñuelas and Staudt, 2010; Rinne et al., 2009).

In forest ecosystems, wildfires destructively affect aboveground ecosystem components such as trees, ground vegetation, litter and belowground components, including plant roots and soil microbial communities (Bond and Van Wilgen, 1996; Cairney and Bastias, 2007; Nearly et al., 1999). Fire effects are likely to vary with fire intensity and temperature (Nearly et al., 1999). During recovery from wildfire, the forest floor is first covered with soot and charred surfaces and later with different plant species corresponding to the stage of succession (Amiro et al., 2006; Köster et al., 2015a, 2017; Kurz and Apps, 1999; Randerson et al., 2006; Zhang-Turpeinen et al., 2020). SOM is increasing during the first post-fire years due to inputs of litter from dying trees, but the recovery of microbial activity and litter decomposition rate is slow, and it may take decades for the microbial activity to recover to pre-fire levels (Köster et al., 2016). In post-fire succession, the indirect and interacting effects of fires on biogeochemical cycles, energy balance, and hydrology continue over many decades (Kelly et al., 2013). Thus, these alterations to the forest floor ecosystem by wildfires are likely linked to BVOC fluxes, as these are closely associated with the metabolism of plants and soil microorganisms (Insam and Seewald, 2010; Peñuelas et al., 2014). Therefore, the successional stage of the burnt forest floor is important in determining the sources and amounts of BVOC fluxes (Zhang-Turpeinen et al., 2020). The same applies to CO_2 and CH_4 fluxes (Köster et al., 2015a). Previous studies suggest an interconnection between BVOC fluxes and CO_2 and CH_4 fluxes. For example, monoterpenes released by tree roots into soils may inhibit atmospheric CH_4 oxidation by forest soils (Amaral and Knowles, 1998; Maurer et al., 2008), and microbes can mineralize monoterpenes and increase soil CO_2 production (Maurer et al., 2008). Moreover, there was a negative relationship between isoprene emissions and CO_2 produced in ecosystem respiration due to bacterial uptake of isoprene in thawed permafrost soil (Kramshøj et al., 2016).

The duration of the effects of fire on boreal forest floor CO_2 and CH_4 fluxes is still under debate. Some field studies have indicated that the impacts can last for more than a decade while other studies found only a short-term influence of fire on CO_2 and CH_4 fluxes in the boreal forest floor (Dore et al., 2008; Köster et al., 2015b; Kulmala et al., 2014; Montes-Helu et al., 2009; Sullivan et al., 2011). The intensity of the fire, soil-specific conditions, and post-fire succession are important in influencing the duration of the effect of forest fire on greenhouse gas fluxes, and also, on BVOC fluxes. For example, Köster et al (2014) observed that it takes several decades for the soil C balance to recover to the pre-fire status due to profound changes in the fungal abundance of the soil after the fire.

BVOCs facilitate climate change by acting as precursors of tropospheric ozone (O_3) and by lengthening the lifetime of methane (CH_4) through a series of photochemical reactions in the atmosphere (Finlayson-Pitts and Pitts, 1986). BVOC oxidation products are associated with the formation of secondary organic aerosols (SOA) by condensing onto the aerosol surface (Jimenez et al., 2009). Therefore, BVOC emissions indirectly influence the formation of cloud condensation nuclei (CCN) which increases the scattering and reflectance of solar radiation and cloud formation and leads to enhanced albedo (Paasonen et al., 2013). Thus, BVOCs can affect both air quality and global temperatures. As an indirect consequence of wildfires to the forest floor, the compositions and quantities of different BVOCs affect atmospheric chemical reactions, and the impact of changes in BVOC emissions on climate change have been suggested to be varying during the post-fire forest succession (Ciccioli et al., 2014; Zhang-Turpeinen et al., 2020).

Fires also have an impact on the land surface albedo (Ciccioli et al., 2014) which changes the microclimatic conditions on the soil surface. Direct solar radiation is more intensive and surface soil temperatures higher under open canopy shortly after a fire compared to the closed canopy in old forests (McMillan and Goulden, 2008; Weisse and Goldman, 2017). The changes in soil surface have a large impact on BVOC fluxes from the forest floor, as the BVOC emissions are affected by light and temperature conditions (Laothawornkitkul et al., 2009). Also, soil moisture conditions are affected by the fire with consequences on BVOC emissions because of the volatility and solubility of BVOCs to water (Kramshøj et al., 2019; Tang et al., 2019). Moreover, changes in aerobic and anaerobic microbial decomposition processes lead to the production of different types of BVOCs (Aaltonen et al., 2013; Kramshøj et al., 2018).

To date, researchers have investigated the forest floor BVOC emission trends (e.g. Aaltonen et al., 2011, 2013), the sinks and sources of BVOCs (e.g. Mäki et al., 2017), and the response of BVOC emissions to climate (e.g. Wang et al., 2018). However, the effects of wildfires on forest floor BVOC fluxes are poorly known. The forest floor BVOC fluxes have been mostly investigated in low and mid-latitudes, while studies conducted in high latitude forests close to the northern timberline are rare. In 2016, we carried out one study of forest floor BVOC fluxes in Central Siberian Larch forests that have been exposed to wildfires (Zhang-Turpeinen et al., 2020). We observed that fire-induced permafrost thawing as such did not affect the BVOC fluxes significantly but the forest age-related changes in ground vegetation and the amount of decomposing litter in the soil induced changes in the composition and amount of BVOC fluxes. The climate in our previous study was continental with extremely cold winters and warm and dry summers (Zhang-Turpeinen et al., 2020) and the main tree species was a deciduous tree - Siberian larch. A large part of boreal forest is located on non-permafrost areas and covered by coniferous trees with different litter quality and litterfall patterns which most likely results in differences in BVOC fluxes. There is a lack of knowledge on the age-related changes in forest floor BVOC fluxes in non-permafrost soils. In addition, seasonal variation with peaks in early summer and autumn BVOC emissions from boreal forest floor has been revealed in previous studies (e.g. Aaltonen et al., 2011). However, the effect of forest stand age on the seasonal variation in BVOC fluxes is poorly known. This study aimed to examine changes in the BVOC fluxes from forest floor along a 158-year fire chronosequence in natural boreal Scots pine (*Pinus sylvestris* L.) stands in northern Finland near the northern timberline throughout a growing season. We determined the seasonal variation in the type and quantity of post-fire BVOC fluxes from the forest floor. We investigated how the environmental and ground vegetation characteristics, soil respiration rates, and soil microbial and fungal biomass are associated with BVOC fluxes. We hypothesized that the post-fire succession of forest floor affects the BVOC fluxes and their seasonal patterns. We expected that the reduction in living tree biomass and ground vegetation coverage by wildfire decreases the forest floor BVOC fluxes, and the decrease in these fluxes may be also connected to a decrease in microbial and fungal biomass as a result of the loss of tree roots and SOM (Hanson et al., 2000). We assumed that the response of BVOC fluxes to post-fire succession is associated with the recovery of aboveground plant coverage and soil. We also hypothesized that the increase in ground vegetation coverage during the growing season affects the seasonal pattern of forest floor BVOC fluxes. We expect that our study will bring new quantitative information on the changes in BVOC fluxes following forest fires and during the post-fire forest succession, which may also be useful for atmospheric chemistry modelers.

2. Materials and methods

2.1. Site description and experimental design

The study was conducted in four forest areas across fire chronosequences in boreal Scots pine forests in north-eastern Finland. The forests had been exposed to a wildfire last time in (i) 2014, (ii) 1969, (iii) 1951, and (iv) 1859. From here on, we refer to the area burnt in 2014 as "3-year-old area" (3), the area burnt in 1969 as "48-year-old area" (48), the area burnt in 1951 as "66-year-old area" (66), and the area burnt in 1895 as "158-year-old area" (158). The 3-year-old forest area is in Lokka (67° 55' N, 27° 56' E), and the three older forest age classes are located in Värriö Strict Nature Reserve (67° 46' N, 29° 35' E) in Finnish Lapland (Fig. 1a).

The study was conducted between mid-June and mid-August, 2017. The average length of the growing season of our study sites is four months, from June to September (Palviainen et al., 2017; Pohjonen et al., 2008). The areas are snow-covered from late October until mid-May. The nearby stations for weather observation by the Finnish meteorological institute (FMI) are in Värriö (67° 75' N, 29° 61' E) and Lokka (67° 82' N, 27° 75' E). During the growing season, the daily average temperature in Värriö was 9.8 °C and in Lokka 10.3 °C, based on a 30-year observation 1981-2010 (Pirinen et al., 2012). Between June and August 2017, the daily air temperature was 10.7 °C in Värriö and 10.9 °C in Lokka, the mean of daily precipitation was 1.8 mm in Värriö and 1.6 mm in Lokka. For more detailed information on the daily air temperature and precipitation of Värriö and Lokka from June to August 2017, see Fig. S1. The soil texture in the study areas is sandy till and classified as haplic podzol. For detailed soil characteristics in the Värriö area, see Köster et al. (2014). The soil in both areas has no underlying permafrost.

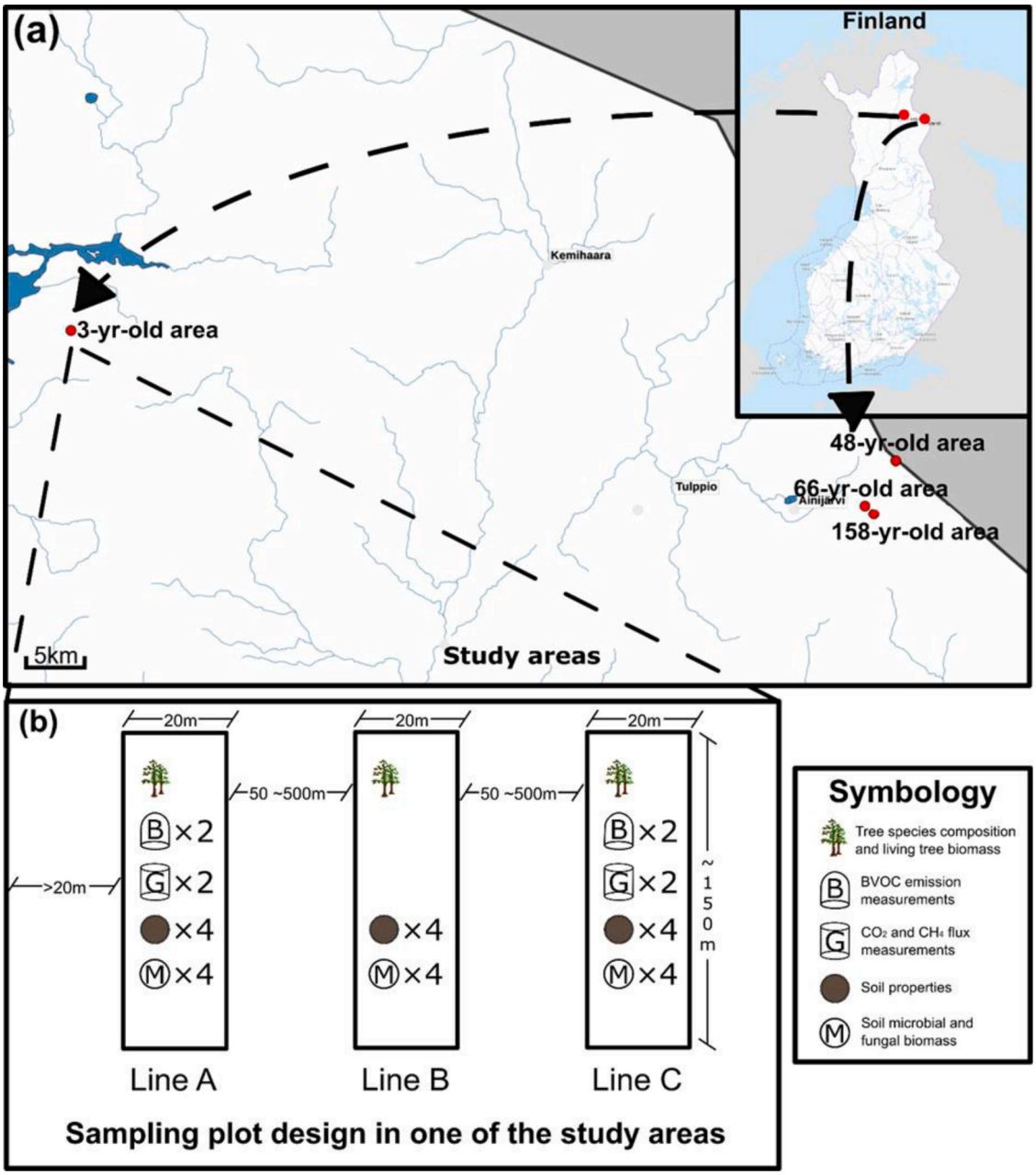

Fig. 1. Diagram of study area locations and sampling line design. (a) Location of the study areas in Finnish Lapland in the current study. (b) Schematic illustration of the sampling plots and the sampling replication in sampling lines of one of the study areas. The symbols show samplings and measurements in each forest age class. Note that the symbols in the sampling lines do not represent the exact location of the samplings.

None of the forest areas was exposed to completely stand-replacing fire. Some trees in the oldest area were older than 158 years, and many trees survived in the younger areas (Table 1). However, in all four areas, forest floor vegetation and the organic layer on top of the soil were exposed to fire. The vascular vegetation in the areas consisted mainly of *Vaccinium myrtillus* L., *Vaccinium vitis-idaea* L., *Empetrum nigrum* L., and *Calluna vulgaris* L.. Mosses were dominated by *Hylocomium splendens* (Hedw.) Schimp. and *Dicranum* sp., and lichens by *Cladina* sp. (Köster et al., 2014; Palviainen et al., 2017).

2.2. Tree biomass measurements, soil sampling, and soil pysical and chemical analyses

In each age class, we established three 150-m-long sample lines as replicates that were spatially separated by 200–500 m from each other in Värriö and 50 m in Lokka. All lines were at least 20 m away from the border of the fire area, to avoid edge effects (Fig. 1b). In total, we had 12 sampling lines for the current study. The lines were set up in terrain with topography as flat as possible to minimize the effect of topographic variation and slope aspect on the results. The tree species composition and living tree biomass were determined by measuring stem diameters and tree heights from one circular sample plot (400 m^2 in size) set up on each line described in Köster et al. (2014).

Scots pine (*Pinus sylvestris*) was the most dominant tree species contributing to total tree biomass, followed by downy birch (*Betula pubescens* Ehrh). To estimate the tree biomass of pine, we used allometric equations in Repola (2009). The equation in Repola (2008) was used for estimating the tree biomass of birch. For details of the stand characteristics, see Table 1.

Soil samples for physical and chemical analyses were taken in mid-August. We took four soil cores with a steel cylinder (0.06 m in diameter and length) from the litter and humus layer and the mineral soil at each sampling line. All samples were stored at -20 °C for later analysis. We measured soil pH, soil gravimetric water content, organic matter (OM), as well as microbial and fungal biomass. Before the analysis, soil samples were homogenized by sieving them through a 4 mm mesh, and thereafter visible roots were removed. Soil pH was measured in a mixture of soil: milli-Q-H_2O slurry (10:25 v/v) with a pH meter (pH340, WTW, Germany). Gravimetric soil water content (amount of water in one gram of dried soil; GWC) was determined by drying the humus samples 24 h at 65 °C and mineral soil samples at 105 °C. Soil organic matter (SOM) content was determined from the loss of ignition by burning dried and ground soil samples in an oven for 2 h at 550 °C (Nabertherm Laboratory Furnace B 170). After burning, the remaining ash contained the mineral part of the soil, thus the weight loss in the ignition represents the soil OM content (Maljanen et al., 2013).

Soil microbial C was estimated using the chloroform fumigation extraction (CFE) method (Beck et al., 1997). Ergosterol analysis was done for estimating soil fungal biomass (Frostegård and Bååth, 1996; Köster et al., 2014). Ergosterol content is well correlated with fungal biomass (Köster et al., 2014; Volker et al., 2000) because ergosterol is present only in fungi and can be found in their cell membranes (Bermingham et al., 1995; Frostegård and Bååth, 1996). The soil properties and soil microbial and fungal biomass of the study areas are presented in Table 1.

2.3. BVOC measurements and the environmental conditions

BVOC fluxes were measured three times during the growing season in 2017. Forest floor BVOC fluxes were measured on two sampling lines in each area (Lines A and C in Fig. 1b).

BVOC sampling chambers consisted of a metallic collar (diameter of 22 cm) and chamber frame (height of 27 cm) made of aluminium. Disposable transparent polyethylene terephthalate film bags (45 × 55cm, Rainbow, Finland) pre-cleaned at 120°C for 1 hour (Stewart-Jones and Poppy, 2006) were placed over the chamber frame and collar to form a dome-shaped chamber (Zhang-Turpeinen et al., 2020) approximately 6 L in headspace volume.

The BVOC fluxes were measured by using a dynamic headspace technique (Tholl et al., 2006; Tiiva et al., 2009) with a conventional push-pull system. Before collecting the BVOCs, we first flushed the chamber with filtered and ozone-scrubbed (by active carbon trap and MnO_2 scrubber / coated copper net) air at a flow rate of 205 ml min^{-1} for 30 min. Before BVOC measurements, the collar was gently placed on selected spots that contained ground vegetation species that are representative for this area. The spots were on relatively flat ground to ensure an airtight enclosure of the chamber. Our BVOC collection system allowed measurements with two chambers simultaneously. To ensure independent flux measurements on two locations at the same time we placed the chambers 10 - 15 m apart from each other on both sides of the sampling line. Thus, each age class had four, and the whole fire chronosequence 16 BVOC chamber measurement locations. The BVOC measurements were carried out with vegetation inside the chambers and the vegetation was kept intact in the measurement locations until the last BVOC measurement campaign in August.

Adsorbent tubes (Tenax TA, 100mg and Carbopack B, 100mg, mesh 60/80; Markes International Ltd, Llantrisant, UK) were used for the collection of BVOC samples. Battery operated pumps pulled the headspace air at the flow rate of 200 ml min^{-1} through the adsorbent tube for 30 min (i.e. 6 L sample). During the flushing and sampling, the chamber air was mixed with a small fan (Zhang-Turpeinen et al., 2020). The adsorbent tubes were tightly closed with screwed brass caps after sample

Table 1
Stand characteristics, and soil physico-chemical characteristics of the four study areas. Mean (S.E.) (n=3) of soil gravimetric water content, soil pH and soil organic matter (OM) in the humus layer and mineral layer of soil, and soil microbial and fungal biomass in OM from study areas were analyzed from soil samples collected in August 2017.

Forest area	Year of last fire	Tree species composition (%)	Living tree biomass (kg m^{-2})	Soil gravimetric water content (%) (humus layer/mineral layer)	Soil pH (humus layer/ mineral layer)	OM (%) (humus layer/ mineral layer)	Microbial biomass (mg TOC^+/g OM)	Fungal biomass (μg ergosterol /g OM)
3-yr-old	2014	100 P	0.9	63.5^{a}/2.7^{a}	4.1^{a}/4.5	60^{a}/4.1	$5.65\ (0.41)^{a}$	$216.87\ (15.63)^{a}$
48-yr-old	1969	100 P	2.8	37.1^{bc}/14.4^{ab}	3.7^{a}/4.4	33^{a}/4.3	$9.57\ (0.90)^{b}$	$306.08\ (13.60)^{ab}$
66-yr-old	1951	95 P, 5 B	3.2	32.1^{b}/18.6^{bc}	3.9^{ab}/4.5	16^{b}/5.0	$4.11\ (0.34)^{ac}$	$428.53\ (45.66)^{b}$
158-yr-old	1859	96 P, 4 B	6.5	45.4^{c}/23.2^{c}	3.6^{b}/4.2	30^{ab}/3.4	$3.76\ (0.41)^{c}$	$297.14\ (18.26)^{a}$
P-value				<0.05/<0.05*	<0.05/0.83	<0.05*/ 0.23*	<0.05	<0.05*

Asterisks indicate the most dominant tree species: Pinus sylvestris (P); and Betula pubescens (B). Underline values are originating from Köster et al. (2014). +TOC: Total organic carbon. P-values from one-way ANOVA or Kruskal-Wallis test (*). Different letters show significant (P<0.05) difference between the forest areas. The absence of letters indicates the difference was not significant.

collection and kept in cold before analysis.

During the BVOC sampling, air temperature and humidity in the chamber headspace approximately 0.2 m above the ground were measured using a thermohygrometer (Testo 605-H1-Mini Thermohygrometer, Testo Ltd., Alton Hampshire, UK). Forest floor vegetation coverages (%) in the BVOC sampling plots were estimated visually (Mäki et al., 2017) and the coverage was classified into five groups: vascular plants, mosses, lichens, litter, and bare soil. Soil temperature and soil volumetric water content (VWC) were measured from the surrounding area of the BVOC measuring plots when collecting the BVOCs. Soil temperature was measured with a portable probe (P 300w, Dostmann Electronic GmbH, Germany) and soil VWC with a soil moisture sensor (ThetaProbe ML2x, Delta-T Devices Ltd, Cambridge, UK). Photosynthetically active radiation (PAR) was measured with Delta-T Quantum sensor (Delta-T Devices Ltd, Cambridge, UK) during the sampling. To maintain the PAR inside the chamber similar across different measurements and to make the conditions inside the chamber comparable, in sunny conditions the chambers were sheltered with a piece of polypropylene fabric that reduced PAR by up to 50%.

Besides the 16 BVOC measurements in the study areas, eight blank measurements were conducted in all of the four forest age classes. Blank measurements were aimed to exclude BVOCs originating from the used materials or/and analysis system and those existing in the ambient air in case the filters did not work properly. To do so, the BVOC sampling frame and collar were put into a polyethylene terephthalate film bag to isolate them from the ground vegetation and soil. The amounts of BVOCs detected from blank measurements were subtracted from those of actual measurements. All BVOC measurements and blank measurements were done in the daytime.

2.4. Analysis of BVOCs

The BVOCs sampled into absorbent tubes were analysed using a thermodesorption instrument (ATD400; Perkin Elmer, Wellesley, MA, USA) connected to a gas chromatography-mass spectrometer (GC-MS) (Hewlett – Packard 6890, MSD 5973; Hewlett – Packard, Palo Alto, CA, USA). The samples were thermally desorbed at 325°C for 3 min and cryofocused at -30°C. Compounds were separated in an HP-5 capillary column (60 m × 0.25 mm, film thickness 0.25μm) using helium as a carrier gas. The oven temperature was first kept at 40°C for 6 min, and then heated to 125°C with a rate of 5°C min^{-1}, and finally, the temperature was raised to 260°C with a rate of 10°C min^{-1}.

The compounds were identified and quantified using 72 standard compounds (26 of which were terpenoids) and Wiley library. Commercial standard mixtures or self-made mixtures from pure compounds in methanol were injected into adsorbent tubes using a calibration solution loading rig (Markes International Ltd, Llantrisant, UK) and N_2 as a carrier gas. The detected compounds, which were not included in the standard compound mixtures, were identified according to the mass spectra in the Wiley data library (identification quality > 90%) and quantified based on the similar chemical structure of the compounds (e.g., α-pinene for monoterpenes, 1,8-cineole for oxygenated monoterpenes, longifolene for sesquiterpenes). The quantification of detected compounds was based on total ion counts (TIC). The chromatograms were determined using the Enhanced ChemStation software (G1701EA Revision E.02.01 19 April 2017; Agilent Technologies, Santa Clara, CA, USA) followed by extracting and sorting the information with an in-house function. The BVOC masses were expressed as μg.

To calculate the BVOC concentrations and fluxes we have used the equations presented in Zhang-Turpeinen et al. (2020). The concentration of each BVOC detected in an adsorbent tube was calculated with equation 1:

$$BVOC\ concentration\left[\mu gL^{-1}\right] = \frac{\left(BVOC\ mass_{(Forestfloor)}[\mu g] - BVOC\ mass_{(Blank)}[\mu g]\right)}{\left(Samplingtime[\min] \times Air\ flow\ through\ ATD\ tube\left[L\min^{-1}\right]\right)} \quad (1)$$

where BVOC mass $_{\text{Forest floor}}$ represents the mass of each compound detected from the forest floor BVOC measurements. BVOC mass $_{\text{Blank}}$ represents the average BVOC mass in the blank measurements, which was calculated from the two blank measurements in each age class area and in each sampling time. The sampling time was 30 mins and the air-flow through the ATD tube was 0.2 L min^{-1}.

The BVOC fluxes of every compound were calculated using equation 2:

$$BVOC\ flux\left[\mu gBVOC\ m^{-2}\ ground\ area\ hour^{-1}\right] = \frac{\left(BVOC\ concentration\left[\mu gL^{-1}\right] \times Air\ flow_{in}\left[L\min^{-1}\right]\right)}{\left(Surface\ area\ of\ collar[m^2] \times 60[\min]\right)} \quad (2)$$

where Air flow $_{\text{in}}$ represents the air flow rate pumped into the BVOC chamber, which was 0.205 L min^{-1}.

In addition to actual BVOC fluxes, the fluxes were standardized and presented as emission potentials at the temperature of 30°C and the PAR of 1000 μmol m^{-2} s^{-1} according to algorithms by Guenther et al. (1993). Standardization was done to reduce variation in BVOC fluxes due to varying environmental conditions between the three sampling times in June, July, and August 2017. The empirical coefficients, for converting BVOC fluxes to BVOC emission potentials, were based on the values given by Guenther et al. (2012). The algorithm has been examined by Hayward et al. (2001), who considered it is reasonable and applicable for forest floor flux studies, and the algorithm has been widely used in previous studies (such as, van Meeningen et al., 2017; Wang et al., 2018; Zhang-Turpeinen et al., 2020). The detected compounds were divided into four groups and calculated as isoprene, total monoterpenes (MTs), total sesquiterpenes (SQTs), and total other BVOCs.

2.5. Forest floor CO_2 and CH_4 fluxes

To characterize the biological activity in the soil during the BVOC collection, we measured carbon dioxide (CO_2) and methane (CH_4) fluxes between the forest floor and the atmosphere, at the same sampling lines we used for BVOC flux measurements (Fig. 1b). There were two flux measurements conducted in each of those lines. Therefore, the number of CO_2 and CH_4 flux measurements was the same as in the BVOC flux measurements.

A portable chamber method was used for measuring the CO_2 and CH_4 fluxes (Pumpanen et al., 2004). A cylindrical chamber (diameter 22 cm and height 24 cm) that was made of Plexiglas and covered with aluminium foil to prevent photosynthesis of the ground vegetation was placed on the pre-installed soil collar during the flux measurements. A small fan (2.5 cm in diameter) was used for circulating the air inside the chamber headspace. The chamber was equipped with an outlet tube and a 3-way stopcock valve (BD Connecta TM Stop-cock, Becton Dickinson, NJ, USA) for air sampling. Polyvinyl chloride (PVC) collars were placed on the forest floor before the measurements and sealed with sand to avoid the leakage of air from the collar. Vegetation inside the collar was not damaged or removed during the measurements.

Air from the chamber headspace was collected into glass vials (12 ml Soda glass Labco Exetainer®, Labco Limited, UK) using a 50 ml

polypropylene syringe (BD Plastipak 60, BOC Ohmeda, Helsingborg, Sweden). Air samples were taken at 0, 1, 3, 5, 10, and 20 min after closing the chamber. The gas samples were analysed by an Agilent Gas Chromatograph model 7890B (GC, Agilent Technologies, USA) equipped with a Gilson GX-271 autosampler (Gilson Inc., Middleton, WI, USA). The GC was equipped with a Thermal Conductivity Detector (TCD) to determine CO_2 concentrations and with a Flame Ionization Detector (FID) for measuring the CH_4 concentrations. Two certified standards for calibration, with a CO_2 concentration of 400 and 3990 ppm and CH_4 concentration of 2 and 15 ppm were used. Helium was used as a carrier gas and synthetic air and hydrogen were used as the flame gases, and N_2 was used as the make-up gas for the FID. The oven temperature was 60 ℃, and the detector temperature was 300℃. The CO_2 and CH_4 fluxes were calculated by fitting a linear regression to time and concentration change inside the chamber headspace (Pihlatie et al., 2013). The readouts from GC of all time points (at 0, 1, 3, 5, 10 and 20 min) were included in the CH_4 flux calculation. In the CO_2 flux calculation, the first four time points (at 0, 1, 3 and 5 min) were used for determining the CO_2 flux because the CO_2 concentration inside the chamber saturates faster than the CH_4. The possible outliers in the chamber concentrations were discarded based on the standard deviation of individual data points from the slope of the linear regression line (as in Köster et al., 2015).

2.6. Statistical analyses

In statistical analysis, the number of sampling lines (n =3) was set as a statistical unit for soil physical and chemical measurements in each age

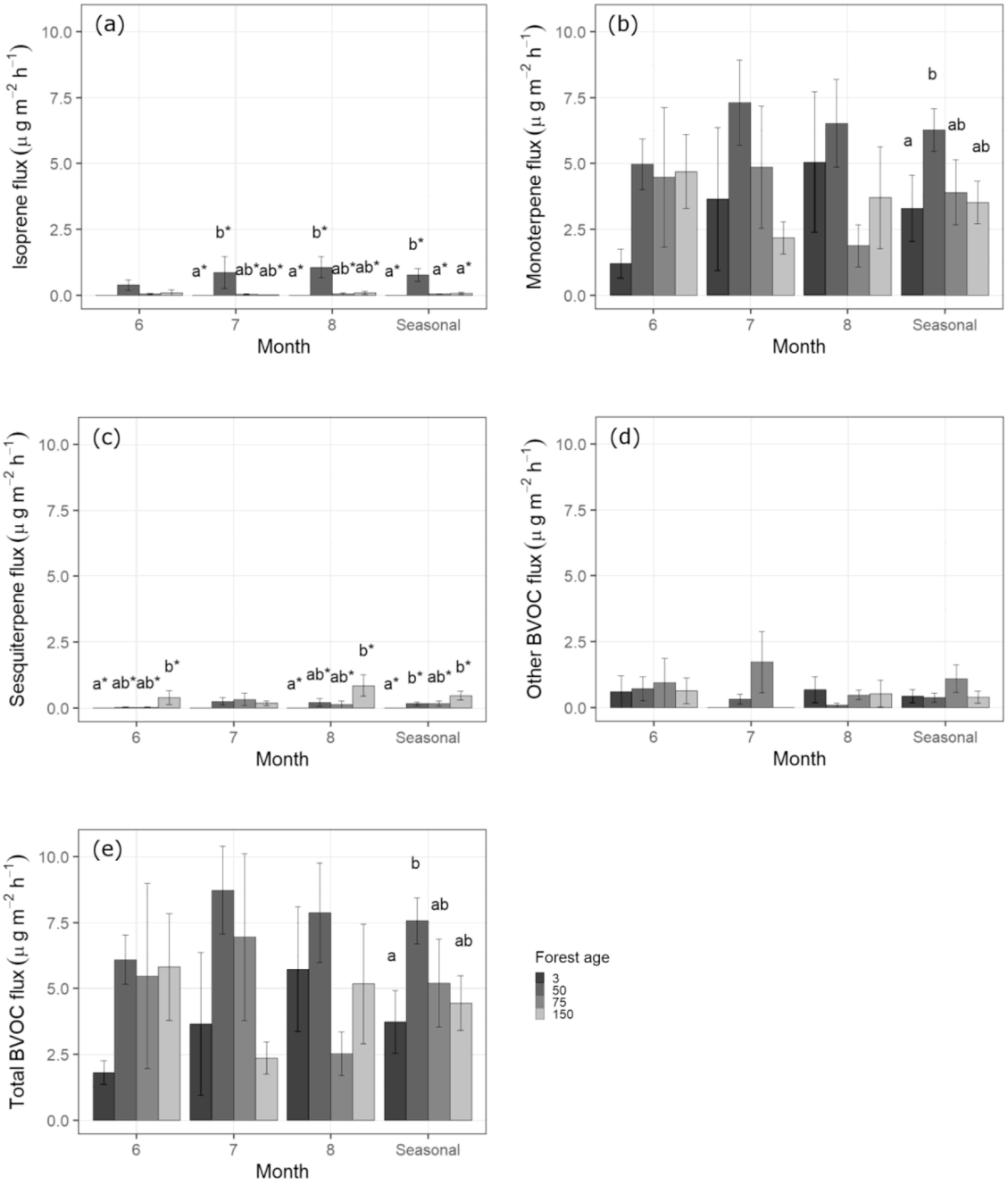

Fig. 2. Month and seasonal means (± S.E.) (n=4) of actual BVOC emission from the study areas in four different forest age classes during the growing season 2017. a) Isoprene, b) Monoterpenes, c) Sesquiterpenes, d) Other BVOCs, e) Total BVOCs. Significant differences ($P<0.05$) between forest age classes analyzed by one-way ANOVA or Kruskal-Wallis test (*) are shown. The absence of letters indicates the difference was not significant.

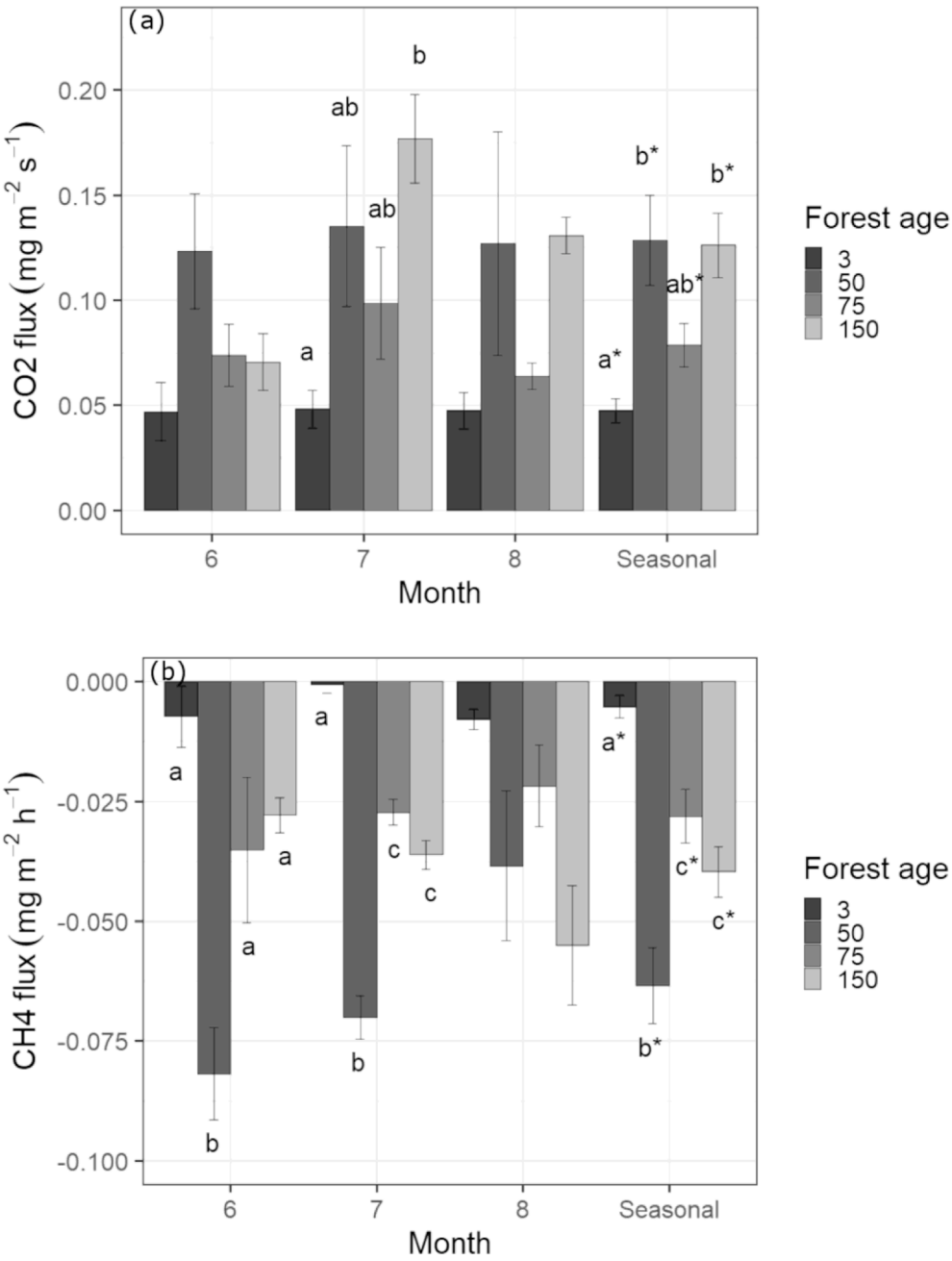

Fig. 3. Month and seasonal means (± S.E.) (n=4) of (a) Carbon dioxide fluxes (mg m^{-2} s^{-1}) and (b) methane fluxes (mg m^{-2} s^{-1}) for June, July, August and the season of 2017 from the four forest areas of different ages. Significant differences ($P<0.05$) between forest age classes analyzed by one-way ANOVA or Kruskal-Wallis test (*) are shown. The absence of letters indicates the difference was not significant.

class. The BVOC, CO_2 and CH_4 fluxes were measured from four collars in each age class. Therefore, the number of replicates for gas flux measurements (Fig. 2 & 3), environmental characteristics (Table 2), and ground vegetation coverage (Table 3) was four (n = 4) in each age class.

To discover the effect of environmental factors, CO_2 and CH_4 fluxes, and ground vegetation on BVOC flux, partial least squares regression (PLSR) analysis was applied. In PLSR analysis, the BVOC emission potential values from the three measurement campaigns (Table S2) were treated as the dependent variables, while the soil moisture and air humidity, ground vegetation coverage (Table 3) over the BVOC measuring plots, and forest floor CO_2 and CH_4 fluxes (Table S3) were the independent variables. For consistency, in the PLSR analysis, the negative CH_4 fluxes were converted to positive, which indicates CH_4 oxidation (uptake). Cross-validated one-component PLSR models were used separately for each BVOC group. The PLS analyses were conducted using SIMCA 15.0.0 (Umetrics, Umeå, Sweden).

The main effects of forest age and sampling campaign (season) and their interacting effects on each environmental and vegetation variables were tested using Linear Mixed Model (LMM). In LMM, forest age and sampling campaign were treated as fixed effect factors, and the line and/or plot as random effect factors. The random effect factor took into account the data dependency on line (parallel measurements from the same line) and plot (the same plot was measured several times). The LMM was used only when the residuals of the model had a normal distribution. The normality of all variables included in LMM and residuals from LMM was tested using the Shapiro-Wilk test. In cases of non-normality distribution, logarithmic transformation (log 10(x+1)) was applied to fulfill the assumptions of LMM or one-way ANOVA when

Table 2
Environmental characteristics in the study areas measured during BVOC samplings along the growing season of 2017: means (S.E.) (n=4) of ambient photosynthetically active radiation (PAR), soil temperature, soil moisture, air temperature, air humidity, chamber temperature, and chamber humidity.

		3-year-old area	48-year-old area	66-year-old area	158-year-old area	P-value
Ambient photosynthetically active radiation (PAR)	June ^{AB}	379.1 (89.6)	160.5 (2.5)	442.1 (98.5)	1108.1 (264.2)	A: 0.21
	July ^{A}	240.1 (31.0)	762.3 (208.1)	653.9 (202.1)	381.8 (63.6)	S: <0.05
	August ^{B}	704.2 (264.0)	1191.4 (43.0)	675.7 (253.9)	655.6 (217.7)	
Soil Temperature (°C)		3-year-old area ^{a}	48-year-old area ^{ab}	66-year-old area ^{b}	158-year-old area ^{b}	P-value
	June ^{A}	9.7 (0.1)	9.7 (1.3)	7.2 (0.6)	7.5 (0.6)	
	July ^{B}	12.7 (0.1)	12.3 (0.9)	12.2 (0.9)	11.7 (0.1)	A: <0.05
	August ^{B}	13.5 (0.1)	11.0 (0.6)	10.6 (0.4)	10.6 (0.2)	S: <0.05
Soil Moisture (%)		3-year-old area ^{a}	48-year-old area ^{b}	66-year-old area ^{c}	158-year-old area ^{c}	P-value
	June	39.0 (1.2)	16.5 (1.2)	24.3 (2.7)	24.5 (1.3)	A: <0.05
	July	48.0 (4.2)	17.3 (1.1)	24.7 (2.2)	29.1 (0.4)	S: 0.20
	August	38.4 (8.3)	17.6 (1.3)	25.7 (1.9)	24.0 (0.4)	
Air Temperature (°C)		3-year-old area ^{a}	48-year-old area ^{b}	66-year-old area ^{c}	158-year-old area ^{bc}	P-value
	June ^{A}	7.6 (0.3)	17.1 (0.5)	20.7 (0.5)	23.5 (0.5)	
	July ^{B}	12.8 (0.3)	24.5 (0.7)	22.3 (0.8)	17.6 (0.5)	A: <0.05
	August ^{C}	16.5 (0.4)	22.4 (0.7)	14.8 (1.0)	20.0 (0.2)	S: <0.05
Air Humidity (%)		3-year-old area ^{a}	48-year-old area ^{b}	66-year-old area ^{c}	158-year-old area ^{b}	P-value
	June ^{A}	68.6 (0.6)	52.8 (1.6)	33.1 (3.9)	22.9 (0.5)	
	July ^{B}	69.1 (0.9)	37.9 (2.4)	34.6 (1.0)	66.9 (2.6)	A: <0.05
	August ^{B}	62.6 (1.2)	40.5 (2.4)	44.5 (2.7)	45.2 (1.4)	S: <0.05
Chamber Temperature (°C)		3-year-old area ^{a}	48-year-old area ^{b}	66-year-old area ^{bc}	158-year-old area ^{c}	P-value
	June ^{A}	10.5 (0.5)	18.6 (0.5)	24.7 (1.0)	25.9 (2.0)	
	July ^{B}	14.5 (0.6)	32.4 (1.6)	26.0 (0.9)	25.9 (2.1)	A: <0.05
	August ^{A}	19.1 (2.5)	23.7 (1.5)	17.4 (1.0)	27.1 (2.2)	S: <0.05
Chamber Humidity (%)		3-year-old area ^{a}	48-year-old area ^{b}	66-year-old area ^{b}	158-year-old area ^{b}	P-value
	June ^{A}	76.1 (1.4)	75.3 (2.8)	41.6 (4.5)	33.8 (1.8)	A: <0.05
	July ^{B}	80.6 (2.8)	51.5 (6.6)	64.0 (6.1)	74.3 (5.2)	S: <0.05
	August ^{B}	73.5 (6.1)	68.7 (5.6)	76.0 (4.8)	66.3 (4.2)	

P-values for the main effect of forest age class (A) and season (S) from LMM ANOVA are shown (interactions were not significant). Different UPPERCASE subscript letters show significant (P<0.05) differences between sampling campaigns during the season and the different lowercase subscript letters between the forest ages. The absence of letters indicates the difference was not significant.

needed.

MT and total BVOC fluxes were tested by LMM which showed that line or plot (the factors potentially causing dependency) did not have a significant impact on the model (P>0.2). The other flux data did not fulfill the criteria for using LMM even after logarithmic transformation. For consistency, all the flux data were tested by one-way ANOVA (with Tukey HSD or Dunnett's T3 test for pairwise comparisons) to study the differences between the forest age classes or sampling campaigns, assuming the parallel flux measurements were independent. The homogeneity of variances was tested using Levene's test. In case the data remained non-normally distributed after logarithmic transformation, the non-parametric Kruskal-Wallis test with Bonferroni pairwise comparison tests at the significance level of <0.05 was used to determine differences between age classes and sampling campaigns. The effects of age class or sampling campaign on all variables were also tested separately for data split by sampling campaign or forest age class. The soil samples for microbial and fungal biomass and soil properties had been only sampled once in August, and therefore, the effects of age class on the soil microbial and fungal biomass were tested by either one-way ANOVA or Kruskal-Wallis test. Statistical analyses were conducted using SPSS software (version 25, IBM SPSS Statistics; Chicago, IL, USA).

3. Results

3.1. Soil properties, environmental and ground vegetation variables

The average soil gravimetric water content at the study areas ranged from 32.1% to 63.5% in the humus layer and from 2.7% to 23.2% in the mineral layer. The 3-yr-old area had the highest water content in the humus layer, but the lowest water content in the mineral layer. The 158-yr-old area had significantly higher soil water content in the humus layer than the 66-yr-old area, but the water content in the mineral layer was the highest among the study areas (Table 1). Soil pH of the humus layer was the highest in the 3-yr-old area and lowest in the 158-yr-old area. The 66-yr-old area had significantly lower soil organic matter content in the humus layer than the other three areas (Table 1). Soil microbial biomass was significantly higher in the 48-yr-old area than in the other three forest areas (Table 1). The lowest soil microbial biomass was determined in the 158-yr-old area. The highest soil microbial biomass in the 48-yr-old area was more than 3 times that in the 158-yr-old area (Table 1). Fungal biomass, indicated by ergosterol content, was significantly lower in the 3- and 158-yr-old areas than in the other areas. The highest amount of fungal biomass was observed in the 66-yr-old area (Table 1).

In general, the trends of air temperature in Lokka and Värriö were rather similar from mid-June till late August, while in Värriö the air temperature was slightly higher during a few days at the beginning of June (Fig. S1). During the measurement days, the 3-yr-old area had significantly lower air temperature than the other areas, and the air temperature in the 66-yr-old area was higher than in the 48-yr-old area (Table 2). Chamber temperatures followed the air temperatures during the measurement days (Table 2). Soil temperatures were significantly lower in the 66- and 158-yr-old areas than in the 3-yr-old area. The soil temperatures were higher in July and August than in June (Table 2). The 48-yr-old area had the lowest soil moisture, while the soil in the 3-yr-old area was the moistest among the forest age classes (Table 2). The air humidity and chamber humidity of the 3-yr-old area were the highest among the study areas. PAR varied and fluctuated widely between different forest age classes during and between the measurement campaigns (Table 2).

As the last forest fire occurred only 3 years ago, the 3-yr-old area had no moss and a very low amount of vascular plants and lichens, but the

Table 3
Means (S.E.) (n=4) of ground vegetation coverage[+] of the four forest age areas determined three times during the measurement campaigns, in June, July and August of 2017.

Vascular Plants (cm^2)		3-year-old area [a]	48-year-old area [b]	66-year-old area [ab]	158-year-old area [b]	P-value
	June [A]	11.4 (4.7)	85.5 (23.1)	31.4 (4.5)	55.1 (12.2)	A: <0.05*
	July [AB]	23.8 (2.9)	123.5 (29.5)	118.8 (52.8)	209.1 (54.3)	S: <0.05*
	August [B]	38.0 (7.8)	128.3 (46.2)	126.4 (53.2)	204.3 (39.8)	
Moss (cm^2)		3-year-old area [a]	48-year-old area [b]	66-year-old area [bc]	158-year-old area [c]	P-value
	June	0.0 (0.0)	190.1 (69.0)	256.6 (49.4)	327.9 (16.2)	A: <0.05
	July	0.0 (0.0)	173.0 (82.7)	269.0 (58.7)	354.5 (7.5)	S: 0.86
	August	0.0 (0.0)	163.5 (68.2)	242.3 (64.2)	342.1 (7.8)	
Lichen (cm^2)		3-year-old area [a]	48-year-old area [b]	66-year-old area [b]	158-year-old area [b]	P-value
	June	0.0 (0.0)	78.9 (48.3)	95.0 (70.6)	18.1 (4.5)	A: <0.05
	July	4.8 (2.9)	79.8 (42.4)	82.7 (68.0)	38.0 (19.0)	S: 0.68
	August	0.0 (0.0)	76.0 (47.0)	85.5 (66.9)	25.7 (10.8)	
Litter (cm^2)		3-year-old area [a]	48-year-old area [b]	66-year-old area [bc]	158-year-old area [c]	P-value
	June	266.1 (32.0)	147.3 (32.3)	71.3 (19.6)	65.6 (12.2)	A: <0.05
	July	247.1 (20.5)	123.5 (29.5)	71.3 (34.2)	52.3 (9.1)	S: 0.36
	August	209.1 (20.5)	114.0 (32.0)	74.1 (26.7)	42.8 (5.7)	
Bare Soil (cm^2)		3-year-old area [a]	48-year-old area [b]	66-year-old area [b]	158-year-old area [b]	P-value
	June	139.7 (42.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	A: <0.05*
	July	142.5 (19.8)	14.3 (9.1)	0.0 (0.0)	0.0 (0.0)	S: 0.70*
	August	180.6 (18.2)	14.3 (9.1)	0.0 (0.0)	0.0 (0.0)	

[+] Ground vegetation coverage indicates the vegetation included within the BVOC measuring collars. P-values for the main effect of forest age class (A) and season (S) from LMM ANOVA are shown (interactions were not significant) and P-values marked with * are from the Kruskal-Wallis test. Different UPPERCASE subscript letters show significant ($P<0.05$) differences between sampling campaigns during the season and the different lowercase subscript letters between the forest ages. The absence of letters indicates the difference was not significant.

litter and bare soil coverages in this area were significantly higher than in the older forest age classes (Table 3). The coverages of vascular plants, mosses, and lichens were significantly higher in the three older forest areas than in the 3-yr-old area (Table 3). In the 158-yr-old area, there was no visible bare soil, the smallest amount of litter, but the largest amount of moss coverage (Table 3). The vascular plant coverage of the 158-yr-old area was more than 5 times higher than that of the 3-yr-old area. Additionally, the coverage of vascular plants was significantly higher in the late summer than in the early growing season (Table 3).

3.2. BVOC fluxes in the boreal forest floor

The proportions of each BVOC compound group (isoprene, monoterpenes, sesquiterpenes and other BVOCs) varied between the different forest age classes throughout the growing season (Fig. S2). In general, monoterpenes (MTs) were the largest group of compounds contributing to the total BVOC emission profile in all forest age classes and all sampling campaigns.

In the 3-yr-old area, isoprene was not detectable during the growing season (Figs 2a & S2, Table S1). The seasonal mean isoprene fluxes of the 48-yr-old area were significantly higher (0.8 ± 0.2 μg m^{-2} h^{-1}) than those in the 66-and 158-yr-old areas, where the fluxes varied between 0.01 – 0.1 μg m^{-2} h^{-1} (Fig. 2a & Table S1). Furthermore, isoprene, as a single compound, accounted for ca. 10% of the seasonal mean total BVOC fluxes in the 48-yr-old area. The MT fluxes in the 3-yr-old area varied from 0.05 to 12.8 μg m^{-2} h^{-1} during the growing season (Fig. 2b). In July, the entire BVOC emission profile of the 3-yr-old area consisted of MTs (Fig. S2 & Table S1). Among the forest age classes, the 48-yr-old area had the highest MT fluxes in each sampling campaign and as a seasonal mean. The seasonal mean MT fluxes in this area were 1.9 times higher than those of the 3-yr-old area (Fig. 2b &Table S1) and the difference between these two areas was significant. The SQT fluxes were below the detection limit in the 3-yr-old area. The seasonal mean SQT fluxes in the 158-yr-old area were 2 times higher than those in the 48- and 66-yr-old areas (Fig. 2c & Table S1). The other BVOC fluxes were not significantly affected by forest age (Fig. 2d & Table S1). The trend of total BVOC fluxes in areas of different ages approximately followed that of MTs, as MTs were the most dominant compound group in the BVOC fluxes (Fig. 2b, 2e & Table S1). Additionally, there was no statistically significant difference between the sampling campaigns (seasonal changes) in the fluxes of any of the BVOC groups (Table S1).

The detected compounds consisted of isoprene, 13 monoterpenes (MTs), 20 sesquiterpenes (SQTs) and 23 other BVOCs (see Table S1 for individual compounds). Most of these compounds were emitted at low rates and detected only from few measurements (Table S1). In general, the MTs α-pinene, camphene and Δ-3-Carene were detected from all forest age classes and sampling campaigns, and limonene and tricyclene were the dominating compounds in most cases (Table S1). The most emitted MT in the studied areas was α-pinene with emission rates varying from 0.02 to 7.2 μg m^{-2} h^{-1} (Table S1). Some of the MTs were only detected in the 48-year-old area, while the 3-yr-old area had the lowest number of detected MTs. The 158-yr-old area had the most diverse SQT profile (Table S1). The most emitted SQT was α-copaene, and its emission rates varied between 0-0.36 μg m^{-2} h^{-1}. The diversity of other BVOCs was similar in the forest areas where the fire had occurred more than 50 years ago. However, in the most recently burnt forest area, many of the other BVOCs were emitted only in June (Table S1). The fluxes of each compound emitted during each sampling campaign and the seasonal means can be found in Table S1.

The emission potentials for all BVOC groups are shown in Supplementary Table S2. The significant forest age effect remained for the standardized isoprene and SQT emission rates. The forest age effects were consistent with the actual BVOC emission rates. For the MTs, other BVOCs, and total BVOCs the effect of forest age was not significant. In each BVOC compound group, the emission potentials had no statistically significant difference between sampling campaigns (Table S2).

3.3. Forest floor CO_2 and CH_4 fluxes (oxidations)

During the entire growing season, the forest floor was a source of CO_2 (Fig. 3a). Forest age after a wildfire affected the CO_2 fluxes (Fig. 3a & Table S3). The forest floor CO_2 fluxes were lowest in the 3-yr-old area throughout the growing season (Fig. 3a & Table S3). The seasonal mean CO_2 fluxes in the 48- and 158-yr-old areas were more than 2 times higher than the fluxes in the area burnt 3 years ago (Fig. 3a), and there were statistically significant differences between these older age classes and the most recently burned area (Table S3). There were no significant differences in soil CO_2 fluxes between sampling campaigns (Fig. 3a & Table S3).

The forest floor was a sink of CH_4 (Fig. 3b). The highest CH_4 oxidation was measured in the 48-yr-old area and the lowest in the most recently burnt area (Fig. 3b & Table S3). All older areas were statistically

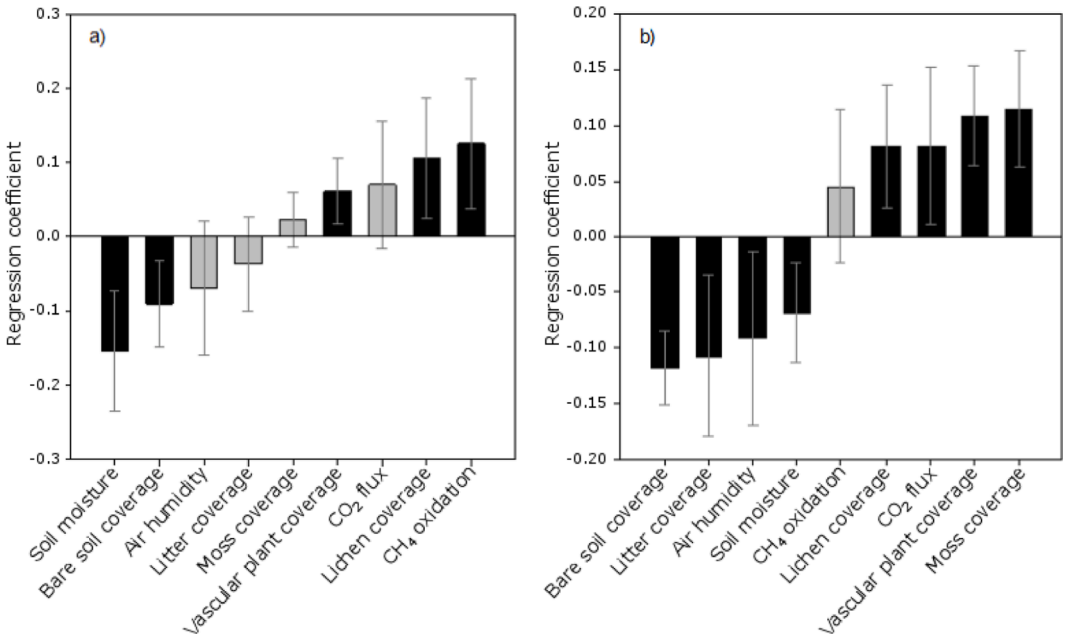

Fig. 4. Regression coefficients of a partial least squares regression (PLSR) analysis for the covariance between environmental factors, forest floor CO_2 flux and CH_4 oxidation, vegetation coverage and (a) isoprene and (b) total SQTs emission potentials. A positive regression coefficient indicates positive relationship and a negative one indicates negative relationship. The error bars show the confidence intervals of the regression coefficients. Significant factors (error bars are not crossing the x coordinate) are shown in black.

different from the 3-yr-old area. During the growing season, the CH_4 fluxes of each forest age class varied, but the sampling campaigns in different months did not affect the CH_4 fluxes (Table S3).

3.4. Linking the explanatory variables and BVOC emissions

PLSR analysis assessed how environmental and vegetation variables, forest floor CO_2 flux and CH_4 oxidation affect the BVOC emission potentials. The isoprene emission potentials correlated positively with the forest floor CH_4 oxidation, the coverage of vascular plants and lichens (Fig. 4a). In contrast, the coverage of bare soil, and soil moisture had a negative correlation with isoprene emission potentials (Fig. 4a). The emission potentials of SQTs were negatively correlated with the coverage of litter and bare soil, soil moisture, and air humidity, but positively correlated with forest floor CO_2 flux, CH_4 oxidation, the coverage of lichens, vascular plants and mosses (Fig. 4b). PLSR analyses for the emission potentials of total MTs and other BVOCs did not show any correlation to the environmental and vegetation characteristics, and CO_2 flux and CH_4 oxidation (see Fig. S3).

4. Discussion

4.1. Age-related differences in BVOC fluxes and forest floor CO_2 fluxes

Our results emphasize that there were fire-induced forest age-related differences in the forest floor BVOC fluxes. The composition of BVOC fluxes in the most recently burned forest was distinctly different from the older forest stands. The isoprene, MT and SQT fluxes and their total sum were lowest in the area where wildfire occurred 3 years ago, and significantly different from those in the 48-yr-old area. The BVOC fluxes decreased after wildfire probably in response to a decrease in the amount of ground vegetation and a disturbed soil ecosystem, thus supporting one of the main hypotheses. The 3-yr-old area was largely covered by litter and bare soil throughout the growing season. Many previous studies have suggested that decomposing litter and soil can be important sources for considerable amounts of isoprene, MTs, SQTs, and other BVOCs (Aaltonen et al., 2013; Bäck et al., 2010; Greenberg et al., 2012; Hellén et al., 2006; Isidorov et al., 2016; Kivimäenpää et al., 2018; Leff and Fierer, 2008). According to the PLSR results, the coverage of bare soil was negatively correlated with isoprene and SQT fluxes, and the SQT fluxes also had a negative correlation with the litter coverage. These correlations were most likely because the isoprene and SQT fluxes in the 3-yr-old area were always below the detection limit. The lower air temperatures in the 3-yr-old area may have affected the BVOC fluxes from the forest floor. Also, the soil was wettest in the 3-yr-old area; the BVOC produced in the soil may be deposited or dissolved in soil water and hardly volatilize (Tang et al., 2019). In addition to the absent ground vegetation, the SOM quality decreased as the fire burned the easily decomposable litter and left the recalcitrant SOM which was more difficult to decompose by the saprophytic microorganisms (Köster et al., 2014; Pietikäinen et al., 2000). The undetectable isoprene and SQT fluxes from the forest floor could be associated with the low post-fire microbial activity in the soil (Asensio et al., 2007; Köster et al., 2016; Leff and Fierer, 2008) as the area was also characterised with the lowest CO_2 fluxes (Gray et al., 2015; Kanerva et al., 2008). Microbes drive many of the soil processes, and the recovery of microbial and fungal biomass in boreal forests is related to the recovery of SOM and ground vegetation (Cairney and Bastias, 2007). The potential impact of soil microbes on BVOC fluxes might be more significant in the recovered areas where the ground vegetation coverage, microbial biomass, and CO_2 fluxes were higher.

The burn-down impact of wildfire on forest floor BVOC fluxes may be transient, but the influences of post-fire succession may last for several decades because of the close link between the BVOC fluxes, forest floor vegetation and soil. The previous study of Köster et al. (2014) conducted in Värriö suggested that the effects of wildfire on soil carbon last for several decades. The BVOC fluxes were highest in the 48-yr-old area in our study suggesting that the forest floor, including ground vegetation, SOM and soil microbial communities in the 48-yr-old area had recovered from wildfire resulting in an increase in BVOC fluxes. The higher coverage and diversity of vegetation probably affected the BVOC compound diversity and the amount of fluxes in the older forest areas. The seasonal mean of isoprene fluxes in the 48-yr-old area was the highest among the study areas, and our PLSR results revealed a positive

relationship between high isoprene fluxes and abundant vascular plants and lichens. The dwarf shrubs, *V. myrtillus* L., *V. vitis-idaea* L., *E. nigrum* L., and *C. vulgaris* L., that were the dominant ground vegetation in our study areas, are isoprene, MTs and SQTs emitters (Aaltonen et al., 2011; Faubert et al., 2012; Hanson et al., 1999; Schollert et al., 2014; Tiiva et al., 2009). Diverse terpenoids are produced as secondary metabolites of lichens (Goga et al., 2020). The positive relationship between BVOC fluxes, especially those of MTs and SQTs, and the abundance of forest floor mosses was also reported by Aaltonen et al. (2011), Svendsen et al. (2016), Zhang-Turpeinen et al. (2020). Additionally, the highest microbial biomass and activity associated with the highest CO_2 fluxes in the 48-yr-old area most likely also contributed significantly to BVOC fluxes in that area (Bäck et al., 2010; Gray et al., 2010; Leff and Fierer, 2008). From our results, the forest floor SQT fluxes were indicated to positively correlate with CO_2 fluxes. The fluxes of other BVOCs, for example, toluene, benzene and its derivates, and propanal are not light or temperature-dependent, and they have been earlier demonstrated to be emitted from soil and litter (Gray et al., 2010; Leff and Fierer, 2008; Schollert et al., 2014).

None of the studied forest areas was exposed to stand-replacing fire and some trees survived the disturbance (Köster et al., 2014). Thus, we assumed some pine roots were growing in the ground where we set up measurement collars. Methanotrophic bacteria play significant roles in methane oxidation in soils and associate with plant root tissues and the rhizosphere (Hanson and Hanson, 1996). Higher CH_4 oxidation rates observed in the older forest areas were probably resulted from increasing root biomass and soil microbial biomass along with the recovery of ground vegetation. The changes in CH_4 oxidation rates were also associated with soil moisture and temperature changes (Köster et al., 2015). On the other hand, our PLSR results revealed that the isoprene fluxes and CH_4 oxidation rates were positively correlated, indicating that root and the rhizosphere together with soil microorganisms also contribute to the BVOC fluxes (Peñuelas et al., 2014; Walker et al., 2003). In previous studies, MT and SQT have been reported as the most emitted BVOCs from pine roots (Leff and Fierer, 2008; Lin et al., 2007; Peñuelas et al., 2014). However, the contribution of BVOCs emitted from roots to the BVOC fluxes along the forest succession is difficult to separate from other sources with in situ measurements (Tang et al., 2019).

We determined relatively high BVOC fluxes from the 66- and 158-yr-old forest areas. However, the fluxes were lower than those in the 48-yr-old area despite the continued increase in the coverage of forest floor vegetation. This can be partly explained by the dense forest floor vegetation coverage, such as the very abundant moss coverages in the 66- and 158-yr-old areas which increases the moist plant surface. It can reduce the BVOC fluxes by adsorbing compounds to the water film formed on the plant surface (Aaltonen et al., 2013). Soil moisture was significantly higher in the 66- and 158-yr-old areas than that in the 48-yr-old area which decreases the diffusivity of gases between soil and the atmosphere (Pumpanen et al., 2003). In boreal forests, the dense moss layer not only retains higher soil moisture but also results in colder temperatures which reduce the biological activity in the soil and thus affects the cycling of carbon compounds within soil and vegetation systems (Gornall et al., 2007). This may be reflected in BVOC fluxes too. During the measurements, water vapour accumulating inside the chambers due to the dense vegetation, soil and ambient condition resulted in the higher relative humidity (RH) in chmabers then in the ambient air. Mäki et al. (2019) observed that, at 20 – 25 °C chamber temperature, MT fluxes were decreased by about 20% in a chamber with RH of over 75% compared to fluxes with RH under 75%. In our chambers, the RH was mostly under 75%, and therefore the effect of RH on chamber measurements in our study was likely smaller. In general, the measurements of low molecular weight oxygenated BVOCs such as methanol, acetaldehyde, and acetone originating from litter decomposition and/or soil fungi may be easily affected by high RH in the chamber (Aaltonen et al., 2013; Mäki et al., 2019) while terprenes have low water-solubility (Martins et al., 2017). The low molecular weight oxygenated compounds were not detectable with the BVOC sampling method of our current study (Aaltonen et al., 2013). Consequently, the BVOC fluxes we observed were not as sensitive to the possible artifacts related to the accumulation of moisture inside the chamber.

We previously conducted a study on BVOC emissions along a fire chronosequence in larch forests located in Central Siberia (Zhang-Turpeinen et al., 2020). The isoprene, MTs, SQTs, and other BVOCs fluxes in the larch forests were substantially higher than those in our current study. Compared to other common boreal trees such as Norway spruce and Scots pine, larch was shown to emit more MTs and SQTs (Ghirardo et al., 2010). Larch trees are deciduous species and shed all their needles every autumn (Abaimov, 2010), while Scots pine is an evergreen tree that sheds only the oldest needle generation every autumn. The dominating tree species and their litterfall were probably one of the most important factors causing the large differences in forest floor BVOC fluxes between the larch forests in Siberia (Zhang-Turpeinen et al., 2020) and the Scots pine forest in Finnish Lapland in this study. The study areas in Siberia had experienced stand-replacing (high intensity) wildfires, while the fires were of low intensity in the forest areas of the current study. Fire intensity is considered to be one of the most important fire characteristics and it determines the pattern of ground vegetation succession, microbial biomass recovery, and soil processes (Köster et al., 2014; Ruokolainen and Salo, 2009). Therefore, fire intensity may also indirectly be reflected to differences in forest floor BVOC fluxes between this study and our previous study. Similarly to the current study, age-related differences in terms of BVOC emissions and soil microbial decomposition were shown in the Siberian larch forest chronosequence, and slightly lower BVOC emissions were reported in the oldest (>100-yr-old) forest areas than in the 23-yr-old area. In the oldest forests, dense lichen coverage may obstruct BVOC fluxes by adsorbing BVOCs emitted from the soil (Zhang-Turpeinen et al., 2020).

4.2. Seasonal variation of BVOC emissions at the forest floor

Interestingly, the seasonal variation in BVOC fluxes was not as drastic as the significant differences observed between forest age classes. One possible explanation is that forest age is a long-term factor affecting BVOC emissions and linked to comprehensive conditions in the forest floor during the succession of a forest. Seasonal variations in BVOC emissions are linked to the seasonality in plant BVOC synthesis, environmental conditions, litter decomposition, and soil microbial activity (Aaltonen et al., 2011, 2013; American Chemical Society, 1992; Hellén et al., 2006; Hellén et al., 2020; Mäki et al., 2017, 2019). Many previous studies have reported seasonality in the BVOC fluxes from the forest floor, such as the MT fluxes peaking in spring and fall (Aaltonen et al., 2011, 2013; Hayward et al., 2001; Hellén et al., 2006; Mäki et al., 2017, 2019). Our study did not include sampling right after snowmelt or autumnal litterfall which are known to affect seasonal peaks in forest floor BVOC emissions (Aaltonen et al., 2011).

4.3. Implication in atmospheric chemistry

Currently, about 1% of the total boreal forest area is burned annually (Köster et al., 2014), and as a consequence of the warming climate, the burned boreal forest areas will be continuously increasing. Similar to the fires occurring in current study areas, the fires occurring in Eurasian boreal forests tend to be non-stand-replacing and burn closer to the ground (Rogers et al., 2015). Given an increase in the area of burnt forests resulted from the climate change-induced increase in forest wildfires, the differences in BVOC fluxes and emission profiles at the 3- and 48-yr-old areas should arise attention to the possible changes in boreal forest floor BVOC emissions, because they might affect atmospheric chemistry in different ways and cause opposite feedbacks to climate warming. For instance, highly reactive compounds such as isoprene and SQTs (Monson and Baldocchi, 2013; Shu and Atkinson,

1995) were not observed in our measurements in the recently burnt forest areas. The lack of those emissions reduces SOA formation through BVOC oxidation processes and further reduces the indirect cooling effect of BVOCs by changing Earth's radiation budgets (Kourtchev et al., 2016; Monson and Baldocchi, 2013; Virtanen et al., 2010). On the other hand, the older forest areas had higher MT fluxes from the forest floor, particularly the MT fluxes were highest in the 48-yr-old area. A large amount of MT emissions can be a significant OH sink, which affects the oxidation of OH radicals in the atmosphere (Monson and Baldocchi, 2013). In the boreal forest, large BVOC emissions from forests are tightly coupled to increased cloud formation and amplify the cooling feedbacks of BVOC fluxes (Kulmala et al., 2014). Due to the large age-related differences in boreal forest floor BVOC fluxes, the variations of BVOC flux during the successional recovery from wildfire should be included in atmospheric-chemical reaction models.

5. Conclusions

The forest floor was a source of BVOCs to the atmosphere throughout the fire chronosequence. Our study conducted with field observations and focusing on long-term effects of wildfire provided evidence on the age-related differences in forest floor BVOC fluxes along forest succession. The age-related differences in the BVOC fluxes suggest that the recovering vegetation was the most important factor determining the quality and quantity of forest floor BVOC fluxes. The recovery of soil microbial composition and activity were probably also determining the net BVOC fluxes. Our results did not show a seasonal variation in the BVOC fluxes, and one explanation could be that the peak emission periods in early spring and late autumn were not included in our sampling campaigns. To better understand the importance of potential BVOC emitting sources in different forest age classes, we suggest to carry out experiments for studying the effect of C allocation on BVOC fluxes. An increasing wildfire frequency under the global warming scheme is likely to change the age class distribution of the forest areas with consequences on BVOC and other greenhouse gas fluxes. Rapid and intensive increase in BVOC fluxes could affect atmospheric chemistry and radiation budget during the few decades after a wildfire.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Huizhong Zhang-Turpeinen reports financial support was provided by Finnish Cultural Foundation. Jukka Pumpanen reports administrative support, article publishing charges, equipment, drugs, or supplies, and travel were provided by University of Eastern Finland. Jukka Pumpanen reports administrative support, article publishing charges, equipment, drugs, or supplies, and travel were provided by Academy of Finland. Minna Kivimaenpaa reports financial support was provided by Academy of Finland. Kajar Koster reports financial support was provided by Academy of Finland. Jukka Pumpanen reports administrative support, equipment, drugs, or supplies, and travel were provided by Academy of Finland Centre of Excellence.

Acknowledgments

The authors would like to thank the personnel at Värriö Field Station for field assistance and logical support. We are grateful to Åsmund Rinnan for programming the in-house function used in the BVOC analyses, Timo Oksanen for construction the equipment and Pasi Yli-Pirilä for assistance in the GC-MS analyses. This study is financially supported by strategic funding of the University of Eastern Finland (project number: 931675), project funding of the Academy of Finland (project number: 286685, 294600 and 278424). H. Zhang-Turpeinen gratefully acknowledges the financial support of the Finnish Cultural Foundation. The authors would also like to thank the Academy of Finland Centre of Excellence (project No. 307331). All the authors of this paper received no financial interest concerning the study.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.agrformet.2021.108584.

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