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Volatile organic compound fluxes from northern forest soils

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Academic dissertation

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Emissions of biogenic volatile organic compounds (BVOCs) cool down the global climate via their impacts on aerosol and cloud formation. Climate change will likely have a major impact on BVOC fluxes from the biosphere, including soils, due to temperature-driven plant biosynthesis of volatile organic compounds (VOCs), compound volatility and microbial activity. Soils are a poorly quantified source of VOCs, where the diversity of driving factors creates high spatial and temporal variability in soil VOC fluxes.

The aim of this study was to analyse the magnitude and variability of forest floor VOC fluxes, to determine the role of the boreal forest floor in the forest stand BVOC exchange and to estimate plant ecophysiological and microbiological processes, which drive forest floor VOC exchange. Forest floor VOC exchange was determined using a steady-state flow-through chamber technique coupled with mass spectrometry in the boreal and hemiboreal climates.

We revealed that the boreal forest floor contributes significantly to forest stand fluxes, but its importance varies between seasons. The forest floor accounted only a few per cent of the total forest stand fluxes of monoterpenes in summer, while in spring and autumn it could be up to 90%. The forest floor VOC exchange was stable between years, while fluxes had clear seasonal dynamic. Monoterpenes and oxygenated VOCs originated from fresh litter, microbial activity, and ground vegetation VOC biosynthesis. Air inside soil layers was found to contain diverse compounds. Forest floor VOC fluxes varied strongly depending on climate and tree species.

Atmospheric chemistry may be strongly affected by soils during periods when plant-related BVOC biosynthesis and fluxes are low. In the future, we need continuous and simultaneous VOC exchange measurements from forest floors and forest stands in various ecosystems and climate zones. The global budget for soil VOC emissions should also be defined based on existing studies.

Keywords: forest floor, VOC, litter, vegetation, temperature, flux

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LIST OF ORGINAL SCIENTIFIC ARTICLES

This thesis includes a summary and four scientific articles, two of which have been published, one that has been accepted and one that has been submitted. The articles are referred to in the text using their Roman numerals:

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II. Mäki, M., Krasnov, D., J., Hellén, H., Noe, S. M., and Bäck, J. Stand type affects forest floor fluxes of volatile organic compounds in hemiboreal and boreal climates. Accepted for publication in Plant and Soil.
III. Mäki, M., Heinonsalo, J., Hellén, H., and Bäck, J. (2017) Contribution of understorey vegetation and soil processes to boreal forest isoprenoid exchange. Biogeosciences 14: 1055–1073. https://doi.org/10.5194/bg-14-1055-2017
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The articles were printed in the thesis with acceptance from Frontiers Media (study **I**), Copernicus Publications (study **III**) and Springer (study **IV**). Studies **II** and **IV** are the authors' manuscripts submitted to Plant and Soil.

Author contribution:

The summary was written by Mari Mäki. Mari Mäki was responsible for data analysis and writing papers **I**, **II, III** and **IV.** The experimental planning and writing of all manuscript were done in collaboration with all co-authors.

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ABBREVIATIONS AND TERMS

Amu	Atomic mass unit
BVOC	Biogenic volatile organic compound
Chamber	An enclosed headspace that is used to measure gas exchange between soil and the atmosphere
CNN	Cloud condensation nuclei
Concentration	Mass of compound per unit volume of mixture
FEP	Fluorinated ethylene-propylene
Flux	Continuous flow of a compound
Forest floor	Soil and ground vegetation
GC	Gas-chromatograph
Soil horizon	Horizontal soil layer that differs from layers above and below
Isoprene	C_5H_8 hydrocarbon
Isoprenoid	One or more C_5H_8 hydrocarbon units
Monoterpene	$C_{10}H_{16}$ hydrocarbon
MS	Mass spectrometer
NIST	The National Institute of Standards and Technology
oVOC	Oxygenated VOC
PAR	Photosynthetically active radiation
PTFE	Polytetrafluoroethylene
PTR-MS	Proton-transfer reaction mass-spectrometer
RCP	Representative Concentration Pathway
Sesquiterpene	$C_{15}H_{24}$ hydrocarbon
SOA	Secondary organic aerosol
TD	Thermodesorption
TD-GC-MS	Thermal desorption-gas chromatograph-mass spectrometer
Ground vegetation	Soil surface covered with mosses, grasses, tree seedlings and ericoid shrubs, height 0–50 cm from the soil surface
VOC	Volatile organic compound

1. INTRODUCTION

1.1. VOC exchange between ecosystems and the atmosphere

The biosphere is the main producer of biogenic volatile organic compounds (BVOCs), a diverse cocktail of compounds with varying chemical properties and reactivity. Global atmospheric chemistry is affected by volatile organic compounds (VOCs) that are emitted by multiple plant species and soils from tropical forests to Arctic and boreal forests (Rinne et al., 2000; 2007; Karl et al., 2009; Laothawornkitkul et al., 2009; Rinnan et al., 2011; Bourtsoukidis et al., 2018). Oxidation products of VOCs, oxidized by OH radicals, O_3 and NO_3 radicals, may form secondary organic aerosols (SOAs) (Ziemann and Atkinson, 2012). SOAs may act as cloud condensation nuclei (CCN), which may change the earth's radiation budget by affecting cloud formation and properties such as lifetime and albedo (Kazil et al., 2010). Higher cloud albedo and SOA concentrations increase the proportion of reflected radiation compared to total radiation (Kulmala et al., 2004, 2014; Ezhova et al., 2018), which may boost plant photosynthesis (Gu et al., 2002). Higher temperature and plant photosynthesis may delay global warming by increasing carbon uptake and BVOC production in boreal forests (Kulmala et al., 2014). A cooling feedback mechanism is expected to affect the regional boreal climate (Paasonen et al., 2013). Monoterpenes cover 11 per cent of global emissions and their oxidation products affect the global SOA yield (Sindelarova et al., 2014; Jokinen et al., 2015).

In boreal and hemiboreal coniferous forests, BVOC emissions are dominated by monoterpenes. Boreal and hemiboreal tree shoots (*Alnus* spp., *Pinus* spp., *Picea* spp., *Betula* spp., *Acer* spp., *Salix* spp., *Quercus* spp., *Sorbus* spp., *Tilia* spp., *Juniperus* spp. and *Populus* spp.) produce and release isoprene, monoterpenes, sequiterpenes and oxygenated VOCs (Hakola et al., 1998; Karl et al., 2009; Laothawornkitkul et al., 2009; Aalto et al., 2014; Hakola et al., 2017). Shoot BVOC emissions are well quantified compared to soil VOC fluxes. In particular, the contribution of soil and ground vegetation to forest stand fluxes remains unknown.

The global mean surface temperature is estimated to increase 0.3–4.8°C under Representative Concentration Pathway (RCP) scenarios by 2100 (IPCC Fifth Assessment Report, 2014) due to climate change. Warming has direct and indirect effects on BVOC emissions from plants, which may change global VOC emissions. Plant BVOC biosynthesis and compound volatility are strongly affected by temperature (Guenther et al., 1993, Kesselmeier and Staudt, 1999). Temperature accelerates isoprene emission capacity in leaves (Sharkey et al., 1999). Temperature may also affect biosynthesis and storage pools of isoprenoids in leaves (Faubert et al., 2010c). Warming will also extend the growing season length and increases plant biomass, which may increase the total VOC budget from terrestrial ecosystems.

Warming may move hemiboreal (Hickler et al., 2012; Noe et al., 2016), temperate and boreal climate zones further north (Lathiere et al., 2005). This may increase total BVOC fluxes in the Northern Hemisphere due to wider forest cover and temperate ecosystems, which are the second highest producer of global BVOC emissions after tropical forests (Guenther et al., 2013). Warming may also favour broadleaf trees over coniferous trees. This may have major impact on regional air chemistry, because many broadleaf trees emit isoprene (Karl et al., 2009) with a lower precursor potential for SOA formation compared to monoterpenes released by conifers such as *Pinus* spp. and *Picea* spp. (Hakola et al., 2006; 2017). Forest effects on climate may be defined by considering the albedo effect of vegetation and the soil surface, the carbon uptake and storage in soil, and the growing biomass and SOA and cloud formation potential as BVOC emissions.

The biosphere contains isoprene-, monoterpenes- and sesquiterpenes and oxygenated VOCs-emitting plants (Karl et al., 2009). Biosynthesis of isoprenoids in plants takes place in chloroplasts via a mevalonate-independent pathway and in cytoplasm via a mevalonate pathway (Rohmer et al., 1996; Lichtenthaler et al., 1997; Banerjee and Sharkey, 2014). Plants continuously emit BVOCs, but the emissions are induced by abiotic (heat, drought and high light or ozone exposure) and biotic stresses such as herbivores (Loreto et al., 2010, Niinemets et al., 2013). For example herbivore attacks on corn seedling roots was found to accelerate sesquiterpene fluxes from shoots (Rasmann et al., 2005). Shoot BVOC emissions also transmit signals between plants, because BVOC signal from one plant activates defence mechanisms against herbivores in neighbouring plants (Baldwin et al., 2006).

Ground vegetation plays a role in global BVOC emissions, because monoterpenes and sesquiterpenes are released by Arctic vegetation types, Mediterranean and grassland plants and boreal ground vegetation (Owen et al., 2001; He et al., 2005; Aaltonen et al., 2011, Faubert et al., 2012; Schollert et al., 2014). Ground vegetation contribution to forest stand fluxes may change in the warming climate. Warming may increase the abundance or biomass of deciduous shrubs (Tape et al, 2006; Rinnan et al., 2008), which may change soil surface albedo, soil nutrient levels and gross primary production of ground vegetation, which may further increase the amount of litter, which is a significant VOC source (Hayward et al., 2001). Warming may also increase temperatures on dark surfaces such as evergreen leaves and soil more than ambient temperatures, which may change BVOC emissions from ground vegetation.

Soils are a simultaneous source, sink and storage of VOCs. VOCs are produced, consumed or transformed by physicochemical processes, such as oxidation and volatilization, by biological processes including microbial uptake, production and decomposition, and by plant biosynthesis in the leaves and roots. Roots produce BVOCs to interact with other soil organisms and to strengthen their resilience to pathogens and herbivores, while root exudates also stimulate microbial production or the uptake of VOCs (Rasmann et al., 2005; Kai et al., 2007; Peñuelas et al., 2014). Plant-derived BVOCs may also affect soil organic matter decomposition (Adamczyk et al., 2018). VOCs are released by decomposers as metabolic side products in aerobic carbon metabolism, fermentation, amino acid degradation, isoprenoid biosynthesis and sulphur reduction (Peñuelas et al., 2014) or are metabolized to transmit signals from ectomycorrhizal fungi to plant root (Ditengou et al., 2015). Within microbial groups, VOCs are capable of reducing enzyme activity, nitrification and mineralization, affecting the population dynamics of soil organisms, boosting the growth of fungal communities or roots and acting as a carbon source for microbes (Mackie and Wheatley, 1999; Wenke et al., 2010; Asensio et al., 2012; Smolander et al., 2012; Hung et al., 2013; Peñuelas et al., 2014; Adamczyk et al., 2015). Microbial VOC production may also be used as a proxy to describe microbial activity and changes in microbial communities (McNeal and Herbert, 2009). Microbial activity is boosted by tree litter, which contains easily-available carbon sources and stored VOC. Stored BVOCs are released from coniferous and broadleaf litter during biotic and abiotic processes (Hayward et al., 2001; Isidorov and Jdanova, 2002; Isidorov et al., 2010; Gray et al., 2010; Greenberg et al., 2012). Abiotic processes impact soil VOC dynamics by adsorbing VOCs on clay particles and in decaying litter through thawing-freezing and drying-wetting cycles (Asensio et al., 2007; 2008; Insam and Seewald, 2010; Deng et al., 2017), which may become more common if the warming climate increases weather extremes.

Due to lack of knowledge on forest floor VOC exchange, below-canopy emissions are not included into global emission models. There is a major knowledge gap concerning how much VOCs the forest floor emits during different seasons and which environmental factors and biological processes regulate VOC fluxes in various ecosystems. In the boreal atmosphere, ecosystem fluxes are affected by soils especially in early spring and autumn, when soils release a high VOC load and BVOC fluxes from the shoots are low. The boreal forest floor contributed to forest stand VOC exchange by a few per cent to tens of per cents (Aaltonen et al., 2013). In boreal ecosystems, the BVOC spectrum is affected by tree cover, which is typically dominated by only a few species. For example in Finland, only three species (*Pinus sylvestris*, *Picea abies* and *Betula pendula*) strongly dominate the total forest cover. Boreal canopies release at least 25 different BVOCs (Schallhart et al., 2018). Soils may be a highly diverse VOC source and storage, because ground vegetation and soil organisms are formed by multiple species with individual emission potentials making below-canopy chemistry highly complex. Above- and below-canopy chemistry of hydroxyl and nitrate radicals and ozone forming SOAs is strongly driven by monoterpenes and sesquiterpenes in boreal forests (Peräkylä et al., 2014, Mogensen et al., 2015, Hellén et al., 2018). Air chemistry models and measurements of ozone concentrations and hydroxyl radical reactivities include significant differences (Mogensen et al., 2011; Wolfe et al., 2011; Rannik et al., 2012; Zhou et al., 2017a), which indicates that current VOC flux estimates are biased. These biased estimates could be improved by including currently missing soil VOC fluxes into the models that predict ozone concentrations and hydroxyl radical reactivites in boreal forest air.

Sesquiterpenes may have an important role in regional atmospheric chemistry due to a high SOA production potential (Guenther et al., 2011) and therefore their fluxes should be quantified from soils in various ecosystems. Sesquiterpenes were shown to be the main contributor to the below-canopy production of oxidation products during summer in a boreal forest (Hellén et al., 2018), while monoterpenes mainly drive oxidation chemistry above the canopy (Peräkylä et al., 2014) due to their lower oxidation capacity compared to sesquiterpenes. Sesquiterpene contribution to atmospheric chemistry may be even higher than believed so far, as highly reactive sesquiterpenes are challenging to measure, which may cause biases in concentration and flux measurements.

1.2. Forest floor VOC fluxes in various ecosystems

Accurate estimations of atmospheric precursors, such as BVOCs, are required to forecast global aerosol-climate-biosphere feedbacks (Kourtchev et al., 2016). Global BVOC emissions are often modelled using MEGAN (Model of Emissions of Gases and Aerosols from Nature), which estimates VOC emissions according to plant functional type, vegetation temperature response, leaf age and soil moisture (Guenther et al., 2006; 2012). Soil moisture impacts tree growth and VOC biosynthesis, while also affecting soil VOC fluxes depending on climate zone and ecosystem type. Tropical and temperate ecosystems are the main producers of global BVOC emissions (Guenther et al., 2013). Boreal ecosystem emissions contribute less to global BVOC emissions (Guenther et al., 2013), but these emissions have a major effect on air chemistry in the Northern Hemisphere. Land-use changes affect global BVOC emissions in the Southern Hemisphere, as tropical forests emit more BVOCs than croplands (Lathiere et al., 2006). Land-use change may also affect soil VOC fluxes, because emission potentials vary between species (Karl et al., 2009), and soil carbon

and nitrogen cycling and losses due to land-use changes (Murty et al., 2002; Dalal et al., 2013) affect microbial communities.

Broadleaf and coniferous trees are estimated to cover approximately 80% and 5% of global BVOC emissions, respectively (Guenther, 2013). In forest ecosystems, tree cover determines quantity and quality of litter and root exudates, which are substrates for microbial decomposition, and therefore also may indicate differences in BVOC production rates e.g. between broadleaf and conifer forests. Microbial decomposition activity, biomass and population composition regulate VOC production in the soil and litter of cultivated fields, grasslands and forests (Stahl and Parkin, 1996; Leff and Fierer, 2008). Decomposition of broadleaf litter is typically faster than the decomposition of coniferous litter at least in early stages (Prescott et al., 2000; 2004), meaning that the temporal dynamic of VOC release from litter likely differs between leaves and needles. Litter VOC emissions have been highlighted by several studies (Hayward et al., 2001; Isidorov and Jdanova, 2002; Isidorov et al., 2016; Leff and Fierer, 2008; Gray et al., 2010; Svendsen et al., 2018). These studies show that decomposing litter is a major stock and source of VOCs. Litter-released VOCs may be 15-fold compared to VOCs released by mineral soil in various ecosystems (Leff and Fierer, 2008), and monoterpene emissions from decomposition of Scots pine (*Pinus sylvestris*) litter were from five to nearly ten times higher compared to decomposition of Norway spruce (*Picea abies*) litter within the first 77 days (Isidorov et al., 2010). Isidorov and Jdanova (2002) determined the leaf litter of broadleaves, such as Eurasian aspen (*Populus tremula*), silver birch (*Betula pendula*) and *Salix* spp., to be a diverse BVOC source, releasing hydrocarbons, isoprenoids, aldehydes, ketones, alcohols, esters, and sulphur- and chlorine-containing compounds.

Soil VOC release has been quantified from various ecosystems, from boreal forest soils, Arctic and subarctic soils, temperate grasslands, agricultural fields and tropical soils (Hellén et al., 2006; Asensio et al., 2007a; Karl et al., 2009; Faubert et al., 2010c; Aaltonen et al., 2011; 2013; Kramshøj et al., 2016; Bourtsoukidis et al., 2018). Wetland VOC emissions have also been quantified in cold ecosystems (Janson et al., 1999; Hellén et al., 2006; Tiiva et al., 2007). Soil VOC fluxes are affected by growing season length, soil depth, microbial community, soil properties, such as clay content, and carbon and nitrogen availability. Soil composition plays a role, because natural adsorbents, such as clay minerals or humic acids (Insam and Seewald, 2010), may hinder VOC release from soils and bind water tightly into soil pores.

Forest floor VOC fluxes are also affected by microclimate such as light availability, soil moisture and temperature. Temperature increase stimulates BVOC emissions from Arctic and subarctic vegetation (Faubert et al., 2010c; Lindwall et al., 2015; Kramshøj et al., 2016) and from boreal mineral and wetland soils (Hellén et al., 2006; Aaltonen et al., 2011). In a subarctic wetland, biogenic volatile organic compound (BVOC) emissions were driven by temperature (Holst et al., 2010). A study by Faubert et al. (2010c) is an extreme example of how temperature affects BVOC fluxes, as monoterpene and sesquiterpene emissions from the subarctic tundra doubled in their study with only a 1.9–2.5°C temperature increase. This is likely due to high temperature sensitivity of isoprenoid emissions from subarctic plants (Faubert et al., 2010c). Warming may have a lesser effect on soil VOC exchange in the boreal forest floor, because plants are able to cool their leaves though evaporation under shading canopy and soil moisture changes are lower.

Soil VOC fluxes are likely driven by environmental parameters that limits ecosystem production. Temperature is one such environmental parameter in colder climates, while soil moisture is an important parameter in warmer climates, such as in Mediterranean forest soils, where both soil moisture and temperature appear to play a role in soil VOC emissions (Asensio et al., 2007a, 2007b). Soil moisture increase promoted sesquiterpene emissions from the tropical forest soils (Bourtsoukidis et al., 2018). Soil moisture regulates belowground gas diffusion, vegetation BVOC emissions and organic matter decomposition (Skopp et al., 1990; Davidson and Janssens, 2006; Zhong et al., 2014; Svendsen et al., 2016), by regulating oxygen availability in soil pores for roots and aerobic microbes. High soil moisture may also increase microbial VOC synthesis, because VOC production is higher and more diverse in anaerobic than aerobic conditions (Seewald et al., 2010). Microbial VOC synthesis is likely driven by temperature-dependent enzyme activity (Davidson and Janssens, 2006), but enzyme activities and microbial community structure are also affected by soil moisture (Brockett et al., 2012).

1.3. Forest floor VOC exchange and climate change

The warming climate is expected to extend the growing season length, increase the global mean surface temperature and change the temporal and spatial distribution of global precipitation (IPCC Fifth Assessment Report, 2014). Warming may cause direct and indirect effects on VOC fluxes from the forest floor and increase or decrease soil VOC fluxes, depending on the climate zone, ecosystem and season. Warming may directly increase BVOC synthesis in plants and BVOC evaporation from leaves (Guenther et al., 1993, Kesselmeier and Staudt, 1999, Fig. 1A). Warming may cause direct and indirect effects on BVOC fluxes from subarctic plants, because warming may stimulate BVOC synthesis, but changes in plant coverage and vegetation composition may also occur (Valolahti et al., 2015). Higher vegetation biomass may increase BVOC fluxes from roots and vegetation (Fig. 2A). Warming may

increase the biomass production of well-adapted species, and these species will likely displace poorly adapted species, which may increase or decrease BVOC production (Fig. 2A). If climate warming favours deciduous shrubs (Tape et al, 2006; Rinnan et al., 2008), the soil surface albedo and temperature in early spring after snowmelt will be altered. Highest monoterpene fluxes from the boreal forest floor were measured in early spring after snowmelt (Hellén et al., 2006). A shorter snow cover period may increase frost damages in plants (Sakai and Larcher, 1987; Blume-Werry et al., 2016) and decrease microbial activity due to lower soil temperatures, which may also affect forest floor VOC exchange (Fig. 2D).

Warming with higher vegetation cover was found to increase fine root biomass, and dissolved organic carbon and total carbon levels in a subarctic heath ecosystem (Rinnan et al., 2008). Higher carbon availability may increase microbial VOC synthesis or uptake. Temperature increase accelerates microbial activity (Davidson and Janssens, 2006), which may directly increase microbial VOC synthesis and uptake (ref, Fig. 1B). A low boundary layer depth in the night-time may lead to a higher night-time temperature increase compared to the daytime in the warming climate (Davy and Esau, 2016). Night-time warming may boost VOC fluxes from decomposition, where enzymatic activity is strongly affected by temperature (Davidson and Janssens, 2006).

Increased vegetation biomass may also cause priming effect in soil. Priming effect means that additional organic matter accelerates decomposition processes in soil (Bingeman 1953). Priming effect may significantly boost carbon, nitrogen and nutrient availability in soil (Kuzyakova et al., 2000). Priming effect may increase carbon allocation from roots to microbes, which may promote microbial VOC synthesis and uptake (Fig. 2C). Soil VOC fluxes may increase (Peñuelas and Staudt, 2010) if changing vegetation cover increases litter quantity in soil (Cornelissen et al., 2007) (Fig. 2B). Warming may increase gross primary production of vegetation, which may also increase litter quantity (Fig. 2B), although Faubert et al. (2010c) found the effect of litter addition to VOC emissions from the subarctic tundra to be small. If tree cover changes in the Northern Hemisphere, it will also influence the quality and quantity of litter, which is a substrate for microbial activity and a significant VOC source (Isidorov and Jdanova, 2002; Greenberg et al., 2012) (Fig. 2F). Microbial VOC production may be transformed by changing vegetation type (Gray et al., 2010). Tree cover changes may also impact ground vegetation cover by affecting light availability, nutrient levels and water use, which may affect soil VOC fluxes.

The warming climate is expected to change precipitation patters, which may have direct effect on soil VOC fluxes by increasing deposition of water soluble VOCs and by hindering gas diffusion and VOC evaporation from the soil surface (Fig. 1C). Soil VOC fluxes were also found to be boosted by rewetting events (Rossabi et al., 2018), which means that VOC fluxes could also be increased by heavy rain periods. The expected increase in high rainfall events in the Northern Hemisphere may also have indirect effect on soil VOC fluxes by reallocating organic matter and VOCs in the soil profile (Fig. 2E). High soil moisture may affect root functions and aerobic processes by limiting oxygen availability. Increased high rain events or drought periods may affect plant VOC biosynthesis through stress mechanisms. For example, BVOC fluxes from the high Arctic were highly dependent on plant cover affected by soil moisture (Svendsen et al., 2016). The climate change effect on forest floor VOC exchange is difficult to predict, because the forest floor contains a high diversity of VOC sources with various temperature and soil moisture responses. The climate change effect on forest floor VOC exchange likely depends on season, climate zone and ecosystem type.

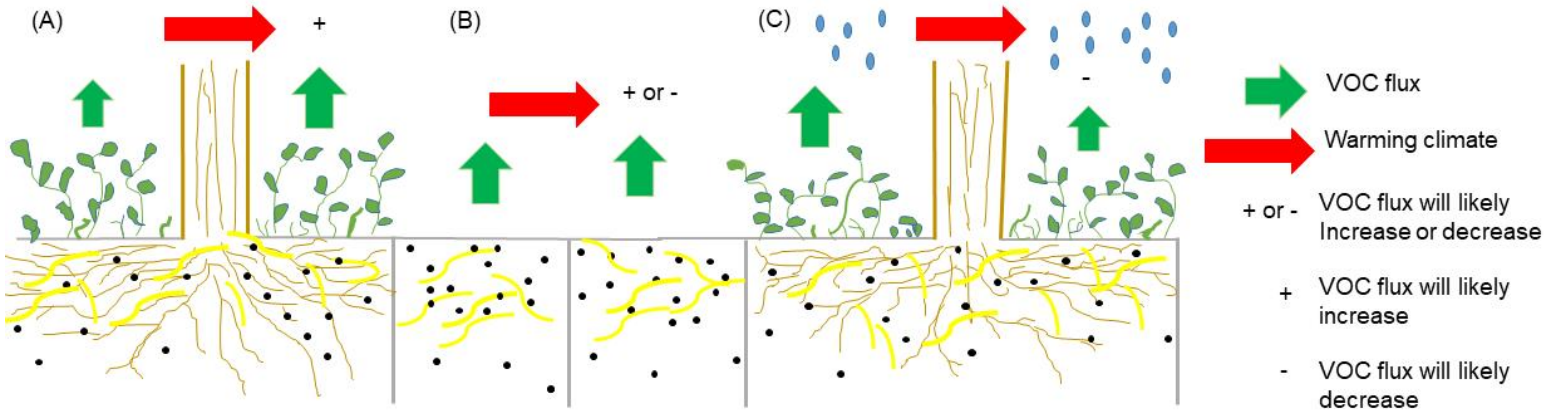

Figure 1. The possible direct effects (+ or - = total VOC flux will increase or decrease, + = total VOC flux will likely increase and - = total VOC flux will likely decrease) of the warming climate (red arrow) on total VOC fluxes (green arrow) from northern soils. (A) Higher temperature increases VOC biosynthesis of plants and VOC release from leaves. (B) Higher temperature increases microbial activity = VOC synthesis and uptake of microbes. (C) Heavy rain increases soil moisture and hiders gas diffusion in soil and VOC evaporation from the soil surface.

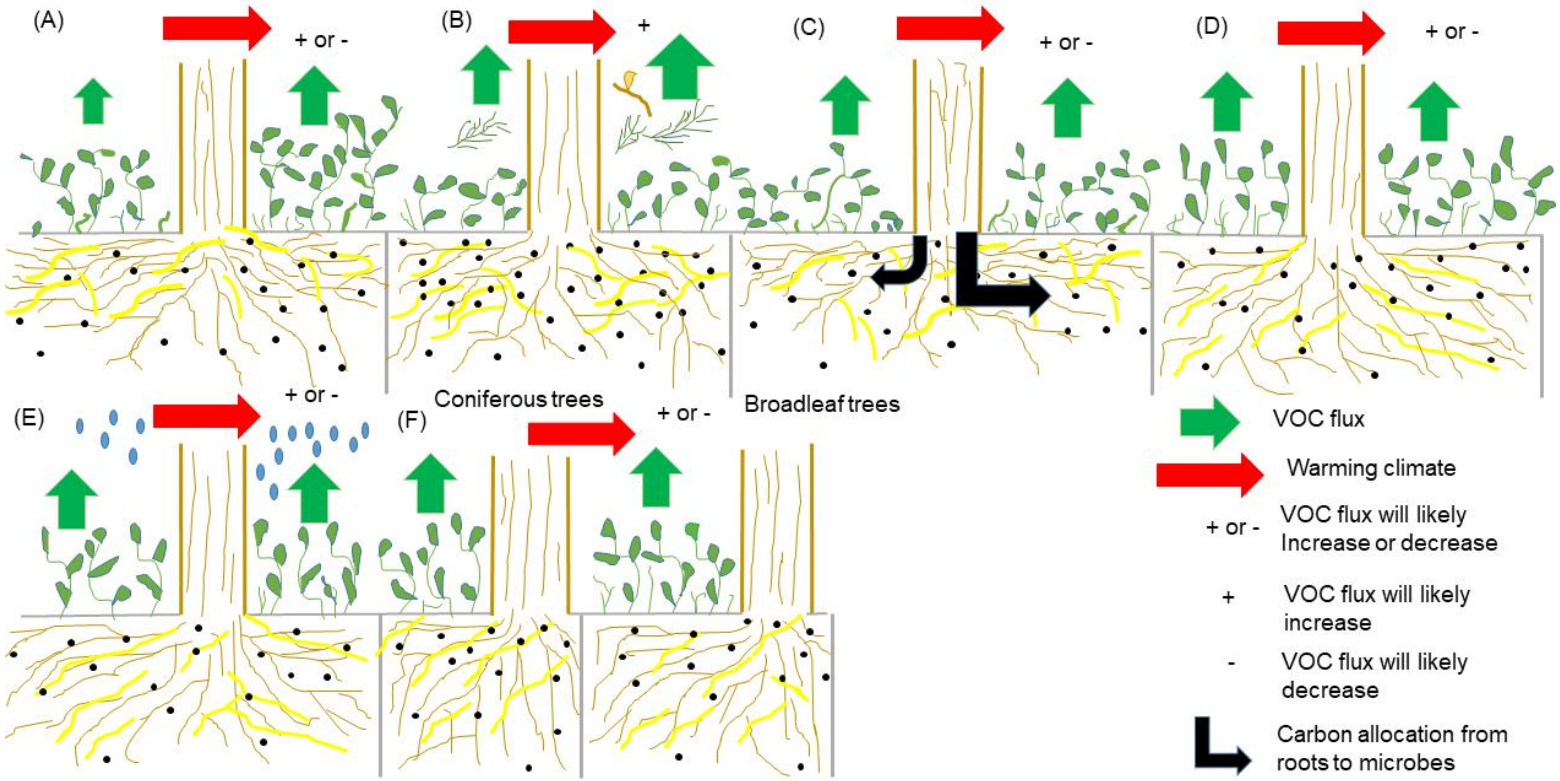

Figure 2. The possible indirect effects (+ or - = total VOC flux will increase or decrease, + = total VOC flux will likely increase and - = total VOC flux will likely decrease) of the warming climate (red arrow) on total VOC fluxes (green arrow) from northern soils. (A) Higher vegetation biomass will increase VOC biosynthesis, but also adsorption and deposition of VOCs on leaf surfaces. (B) Higher vegetation growth may increase amount of litter, which is a significant VOC source. (C) Warming may increase carbon allocation from roots to microbes as root exudates and this labile carbon may further promote microbial activity and decomposition of recalcitrant organic matter (priming effect), which may further increase microbial VOC synthesis and uptake. (D) Shorter snow cover period may increase frost damages in plants and decrease soil temperatures for microbial activity. (E) Heavy rain may reallocate organic matter and VOCs in soil towards the bedrock. (F) Changing forest cover impacts litter quality and quantity, which likely affects VOC fluxes from the forest floor.

1.4. Aim and objectives

The aim of this study was to analyse the magnitude and variability of VOC exchange between northern forest soils and atmosphere, and to analyse the importance of plant ecophysiological and microbiological processes related to this exchange. To do this, we measured the VOC exchange of a boreal forest floor over snow-free periods during eight years, compared that to the ground-level VOC exchange in a more southern, hemiboreal stand and finally experimentally scrutinized the VOC sources from various layers of soil and in conditions where the carbon source to soil microbes was limited. The objectives were:

1. To estimate the inter-annual, seasonal and diurnal dynamics of VOC fluxes from the boreal forest floor (studies **I**, **II**, **III** and **IV**).
2. To determine the contribution of the boreal forest floor to forest stand VOC fluxes (study **I**).
3. To assess how tree species and climate affect VOC fluxes from boreal and hemiboreal forest soils (study **II**).
4. To determine the biological and physico-chemical processes and environmental parameters that drive VOC exchange from the boreal forest floor (studies **I**, **II**, **III** and **IV**).

2. MATERIAL AND METHODS

2.1. Experimental sites

2.1.1. Boreal Pinus sylvestris and Picea abies stands

VOC exchange measurements were performed at four measurement sites (Fig. 3A–3C). The first measurement site (studies **I–IV**) is a nearly sixty-year-old boreal *Pinus sylvestris* stand, located at the SMEAR II station, on Haplic podzol soil (61°51'N, 24°17'E, 180 m above sea level). The canopy consists of *Pinus sylvestris* (75%), *Picea abies* (15%) and broadleaf trees (10%) such as silver birch (*Betula pendula*) and rowan (*Sorbus aucuparia*). The ground is covered by ericoid shrubs (lingonberry (*Vaccinium vitis-idaea)*, European blueberry (*Vaccinium myrtillus*) and common heather (*Calluna vulgaris*)), mosses (red-stemmed feather moss (*Pleurozium schreberi*), waxyleaf moss (*Dicranum polysetum*), broom fork-moss (*Dicranum scorparium*) and splendid feather moss (*Hylocomium splendens*)) and grasses (wavy hair-grass (*Deschampsia flexuosa*) and small cow-wheat (*Melampyrum sylvaticum*)) (Fig. 4A–4B). The cumulative litter production was 223.7 g_{DW} m^{-2} from May to October in 2017 and 224.7 g_{DW} m^{-2} from May to August in 2018 at the site one. Soil depth is 50–160 cm. The second site (study **II**) is a boreal *Picea abies* stand on Haplic podzol soil located right next to the *Pinus sylvestris* stand. The ground vegetation is dominated by ericoid shrubs (*V. vitis-idaea* and *V. myrtillus*) and mosses (*Pleurozium schreberi*, *Dicranum polysetum*, *Dicranum scorparium* and *H. splendens*) (Fig. 3). The mean annual temperature is 2.9 °C and annual precipitation is 697 mm at the SMEAR II station (Ilvesniemi et al., 2010).

2.1.2. Hemiboreal Pinus sylvestris and Picea abies stands

The last two measurement sites are located at the SMEAR Estonia station (58 °25'N, 27°46'E, 36 m above sea level) (Noe et al., 2016) (Fig. 3C). The third site is a hemiboreal mixed stand where the canopy is formed by *Pinus sylvestris* with smaller coverages of *Picea abies*, *B. pendula* and downy birch (*Betula pubescens*) (study **II**). The scanty ground vegetation consists of *V. myrtillus* and mosses such as *Sphagnum* spp. (Fig. 4C–4D). The cumulative litter production was 347.1 g_{DW} m^{-2} from May to October in 2017 and 225.6 g_{DW} m^{-2} from May to August in 2018. The fourth site is a hemiboreal *Picea abies* stand, where ground vegetation is dominated by mosses such as *Sphagnum* spp. (study **II**). The cumulative litter production was 154.7 g_{DW} m^{-2} from May to October in 2017 and 182.8 g_{DW} m^{-2} from May to August in 2018. Sites three and four are located on Haplic Gleysol soil. Soil hydraulic conductivity is low, because clay content is high (Noe et al. 2011). The mean annual temperature is 4–6 °C and annual precipitation is 500–750 mm at the SMEAR Estonia station (Noe et al., 2012).

Figure 3. Boreal Scots pine (*Pinus sylvestris,* top left (A)) and Norway spruce (*Picea abies*, top right (B)) stands at the SMEAR II station, hemiboreal mixed and *Picea abies* stands (bottom left, (C)) at the SMEAR Estonia station and a satellite map that shows location of SMEAR II station (red circle) and location of SMEAR Estonia station (blue star) (bottom right, (D)). VOC exchange measurements in studies **I**, **III** and **IV** were performed at the SMEAR II station and measurements in study **II** were performed at both stations.

Figure 4. Soil collars with ground vegetation in a boreal Scots pine (*Pinus sylvestris*, top left (A)) and a Norway spruce (*Picea abies*, top right (B)) stand at the SMEAR II station and in a hemiboreal mixed (bottom left (C)) and a *Picea abies* (bottom right (D)) stand at the SMEAR Estonia station.

2.2. Methods

VOC exchange measurements were performed using dynamic (steady-state flow-through) chambers, where chamber headspace is continuously flushed to hinder pressure and gas concentration changes in the soil beneath the chamber. Chambers were placed on permanent soil collars made from stainless steel. The VOC flux is estimated from gas concentration changes within the closed chamber with mass balance equations (Jensen et al., 1996, Hari et al., 1999). The VOC exchange measurements are introduced in Table 1.

Table 1. The VOC exchange measurements including instrument and chamber type, measurement timing, experimental set-up, and measured masses (atomic mass units, amu) or dominating monoterpenes and sesquiterpenes performed in the studies **I**, **II**, **III**, and **IV**.

Paper	Instrument	Measured compounds/masses (amu)	Timing	Experimental set-up	VOC source or sink
I	quadrupole-PTR-MS	Methanol (33), acetaldehyde (45), acetone (59), isoprene (69), benzene (79), monoterpene fragment (81), methyl butenol (87), toluene (93), hexenal (99), hexanal (101), and monoterpenes (137), and methyl salicylate (153)	2010−2017	three soil collars with automated chamber	soil and ground vegetation
II	TD-GC-MS	isoprene, monoterpenes especially α-pinene, camphene, β-pinene, and Δ3-carene and sesquiterpenes especially β-caryophyllene, α-gurjunene, and α-humulene	2017−2018	six soil collars with manual chamber for each four stands	soil and ground vegetation
III	TD-GC-MS	isoprene, monoterpenes especially α-pinene, camphene, β-pinene, and Δ3-carene and sesquiterpenes especially β-caryophyllene	2015	manual chamber measurements from six different treatments: vegetation and non-trenched soil (n=12), bare and non-trenched soil (n=6), vegetation and soil, where the ingrowth of mycorrhizal fungi was allowed (n=3), bare soil, where the ingrowth of mycorrhizal fungi was allowed (n=3), vegetation and soil, where decomposers were the only source (n=6) and bare soil, where decomposers were the only source (n=6).	ground vegetation, roots, mycorrhizal fungi and decomposers
IV	TD-GC-MS	isoprene, monoterpenes especially α-pinene, camphene, β-pinene, and Δ3-carene and sesquiterpenes especially β-caryophyllene, α-gurjunene, and α-humulene	2016	five soil collars with manual chamber	soil and ground vegetation

VOC fluxes from the boreal forest floor were continuously measured using three automated dynamic (steady-state flow-through) chambers (Fig. 5D) coupled with a quadrupole-proton-transfer reaction mass-spectrometer (quadrupole-PTR-MS; Ionicon Analytik, Innsbruck, Austria, de Gouw and Warneke, 2007) at the SMEAR II station between 2010 and 2017 (study **I**). Flux measurements were performed each year from April or May to September or October. Summer was defined to begin, when daily mean temperature was over 10°C, and autumn started, when daily mean temperature was below 10°C. Flux data were lacking between mid-June and October in 2012, between September and October in 2014, and between April and mid-August in 2016. VOC fluxes were also determined using manual (steady-state flow-through) chambers in studies **II**–**IV**. VOC fluxes from boreal and hemiboreal forest floors were compared in 2017 and 2018 (study **II**, Fig. 5C). Various measurement techniques were utilized to determine the VOC fluxes from forest floor and belowground VOC concentrations (Fig. 5A–5D). The effect of photosynthesized carbon allocation through roots and mycorrhizal fungi for soil VOC fluxes were studied in the trenching experiment by preventing root ingrowth (50 µm mesh size) or the ingrowth of roots and fungi (1 µm mesh) into the soil volume (study **III**, Fig. 5A). The effect of ground vegetation was also studied by comparing plots without vegetation to normal vegetation plots (study **III**). Simultaneous soil VOC fluxes and belowground VOC concentrations from the O-, A-, B- and C-horizons were compared in 2016. VOC concentrations from the O- and B-horizons were also determined between 2008 and 2011 (study **IV**).

Figure 5. Trenching experiment plot where manual chamber measurements (top left (A), study **III**), and belowground VOC concentration and soil surface flux measurements (top right (B), study **IV**) were performed. VOC exchange measurements from the forest floor were performed using a manual chamber (bottom left (C), studies **II–IV**) and an automated chamber connected to the quadrupole-PTR-MS (bottom right (D), study **I**) at the SMEAR II station in Finland.

2.2.1. Chamber measurements

2.2.1.1. Automated chambers

Chamber frames were made of aluminium and chambers were covered with a transparent fluorinated ethylene-propylene (FEP) film (0.05 mm). The masses of 33 (methanol), 45 (acetaldehyde), 59 (acetone), 69 (isoprene), 79 (benzene), 81 (monoterpene fragment), 87 (methyl butanol), 93 (toluene), 99 (hexenal), 101 (hexanal), 137 (monoterpenes) and 153 (methyl salicylate) were measured. These masses were chosen, because the earlier study by Aaltonen et al., (2013) showed that forest floor VOC fluxes were dominated by these masses, and because the PTR-MS is able to quantify these masses without major fragmentation during the H3O+/VOC reactions. Forest floor VOC exchange (study **I**) was estimated based on the VOC concentration change (C) during chamber closure, which was calculated using mass balance equation 1 (Hari et al., 1999):

$$V\frac{dC}{dt} = E + F\,(C_i - C) \qquad (1)$$

, where V is the chamber headspace volume (m^{-3}), E is the emission rate (µg m^{-2} h^{-1}), F is the flow rate of replacement air (m^{-3} min^{-1}), C_i is the VOC concentration of the replacement air (µg m^{-3}) and C is the VOC concentration of the chamber (µg m^{-3}) calculated using equation 2 (Hari et al., 1999).

$$C(\mathrm{t}) = C_0 + \left(\frac{C_i - C_0}{V} + \frac{E}{F}\right)\left(1 - e^{-\frac{Ft}{V}}\right) \qquad (2)$$

, where C_0 is the VOC concentration (µg m^{-3}) at the time when the chamber was closed. Emission rate E (µg m^{-2} h^{-1}) was estimated as a slope of a linear curve fitted based on equation 1 in the measured concentration change during the first 400 seconds after the chamber was closed.

2.2.1.2. Manual chambers

VOC fluxes were measured using the steady-state flow-through chambers made from glass and the analyses were performed afterwards in a laboratory (studies **II–IV**) (Fig. 4). These campaign-based measurements were performed from April 2015 to July 2018 at the SMEAR II station and from May 2017 to July 2018 at the SMEAR Estonia Station. The VOCs were sampled for 40–120 minutes into Tenax TA–Carbopack-B adsorbent tubes and the fluxes were calculated based on the VOC concentration difference between ingoing and outgoing air. VOC fluxes of isoprene and individual monoterpenes, sesquiterpenes and oxygenated VOCs were analysed in the laboratory using a thermal desorption-gas chromatography-mass spectrometer (TD-GC-MS). The flux rate (E, µg m^{-2} h^{-1}) of each VOC from the manual chamber measurements was calculated based on equation 3:

$$E = (C_{out} - C_{in})\frac{F_c}{1000}\frac{60}{A} \qquad (3)$$

, where C_{in} is the VOC concentration of ingoing air (µg m^{-3}), C_{out} is the VOC concentration of outgoing air (µg m^{-3}), F_c is the air flow rate of replacement air (l min^{-1}) and A is the soil surface area (m^2).

2.2.2. VOC concentration measurements in soils

To define whether the whole boreal forest soil is a VOC storage and potential source, we also performed VOC concentration measurements from the different soil horizons in two different measurement campaigns between 2008–

2011 and 2016 (study **IV**). VOC concentrations were measured from the O- and B-horizons during the first measurement campaign and from the O-, A-, B- and C-horizons during the second campaign. VOCs were sampled by sucking air from the gas collectors through a Tenax TA–Carbopack-B adsorbent tube and then returning the air to the collector.

2.2.3. Analytical methods

The individual VOC concentrations of the Tenax TA–Carbopack-B adsorbent tubes were quantified using a thermodesorption instrument (Perkin-Elmer TurboMatrix 650; PerkinElmer, Waltham, MA, USA) attached to the gas chromatograph (Perkin-Elmer Clarus 600) and to the mass-selective detector (Perkin-Elmer Clarus 600T) (TD-GC-MS, studies **II–IV**). The concentrations of isoprene, monoterpenes (α-pinene, camphene, β-pinene, Δ-3-carene, linalool, limonene, p-cymene), sesquiterpenes (longicyclene, isolongifolene, β-caryophyllene, α-humulene, α-gurjunene, β-farnesene, SQT1, α-buinesene, γ-muurolene, α-bisabolene, β-himachalene, α-muurolene and Δ-cadinene) and different oxygenated VOCs (C_4-C_{15} alcohols, carbonyls and acetates, methyl-2/3-furoates and α-pinene oxide) were quantified. The sample tube was analysed using 5-min thermal desorption (300 °C), cryofocusing in the cold trap (-30 °C) and finally by injecting the gas sample into a gas chromatograph column using rapid heating (300 °C). To calibrate the measured VOC masses, we used four to six different concentrations of the standard mixtures in methanol solutions by injecting (5 μL) into the sample tubes. The gas chromatograph was used to separate various VOCs (e.g. monoterpenes and sesquiterpenes with same molecular mass) and the mass spectrometer was used as a detector to confirm the identification of various compounds and to reach high accuracy and low detection limits. The compounds were identified by comparing their retention times and the mass spectras to the authentic standards. Certain sesquiterpenes were tentatively identified by comparing them to the NIST (the National Institute of Standards and Technology) mass spectral library and by retention time indexes.

3. RESULTS AND DISCUSSION

3.1. Temporal dynamics of forest floor VOC fluxes

3.1.1. Interannual dynamics

In these measurements, the yearly total VOC exchange from the boreal forest floor was relatively constant (study **I**, Fig. 5). The forest floor fluxes were dominated by monoterpenes and oxygenated VOCs such as methanol, acetone and acetaldehyde (study **I**). The yearly monoterpene fluxes were slightly higher during years when the annual temperature sum was higher and annual precipitation lower (study **I**). A similar effect on methanol, acetone and acetaldehyde was not observed (study **I**). Similar to this thesis, total BVOC emissions rates from subarctic heath were also comparable between two growing seasons (10.9 μg m^{-2} h^{-1} in 2006 and 14.6 μg m^{-2} h^{-1} in 2007) (Faubert et al., 2010c), while the mean monoterpene fluxes were higher from subarctic heath in 2007 (9.8 μg m^{-2} h^{-1}) compared to 2006 (1.5 μg m^{-2} h^{-1}) due to higher mean temperature (11.0 and 9.6 °C) (Faubert et al., 2010c). Monoterpene exchange rates from Mediterranean shrubland also varied between the two measurement years due to contrasting precipitation (Asensio et al., 2008). Though the boreal forest floor appears to be a relatively constant VOC source, atmospheric monoterpene concentrations showed high inter-annual variation at our measurement site between 2000 and 2007 (Hakola et al., 2009). Atmospheric concentration measurements were performed above a canopy and later in the canopy, because the mean canopy height of Scots pine stand increased 2.1 m from 2010 to 2007 (Hakola et al., 2009).

3.1.2. Seasonal dynamics

The cumulative forest floor VOC exchange was stable between years, while fluxes had clear seasonal dynamics (study **I**). The seasonal dynamic of forest floor exchange depends on the compound, i.e. monoterpenes or oxygenated VOCs (studies **I**–**IV**). The forest floor was the highest monoterpene source in spring (May–June, max 59 μg m^{-2} h^{-1}) and autumn (September–October, max 86 μg m^{-2} h^{-1}) compared to summer (study **I**). Fluxes were likely driven by litter decomposition and VOC synthesis of plants and microbes (studies **I**, **III** and **IV**, Fig. 6). Study **I** provides evidence that forest floor monoterpene fluxes are released by both plant ecophysiological and microbiological processes. High monoterpene fluxes in spring were also observed in previous studies at our boreal forest site, where monoterpene fluxes above the boreal forest peaked during snowmelt (Schallhart et al., 2018). Monoterpene fluxes measured from the forest floor peaked also

after snowmelt (373 µg m^{-2} h^{-1}, Hellén et al., 2006). High monoterpene fluxes observed from the forest floor in autumn (studies **I** and **III**) were also supported by previous studies, where monoterpene fluxes from the boreal forest floor peaked in October (Janson 1993; Aaltonen et al., 2011; Wang et al., 2018) due to decomposing litter that releases monoterpenes from needle storages (Kainulainen and Holopainen, 2002). A seasonal dynamics in soil monoterpene exchange has also been observed in warm ecosystems (Asensio et al., 2007; 2008).

The similarity in seasonal dynamics of the forest floor and forest stand oxygenated VOC fluxes indicated that vegetation played a significant role also in the forest floor fluxes (study **I**). Methanol fluxes were highest in spring and summer (max 24 and 79 µg m^{-2} h^{-1}, Fig. 7) during maximum growth indicating that vegetation growth is a significant methanol source (study **I**). Plant ecophysiological processes i.e. VOC biosynthesis seems to be the highest source of oxygenated VOC fluxes in the forest floor (study I). Methanol is released in pectin demethylation in plants (Fall et al., 2003). The forest floor also emitted methanol in autumn (study **I**), likely from decomposing litter and microbial metabolism (Bäck et al., 2010; Gray et al., 2010; Greenberg et al., 2012). High acetone and acetaldehyde fluxes observed above a hardwood forest in autumn were also speculated to be released by leaf senescing and decaying biomass (Karl et al., 2003).

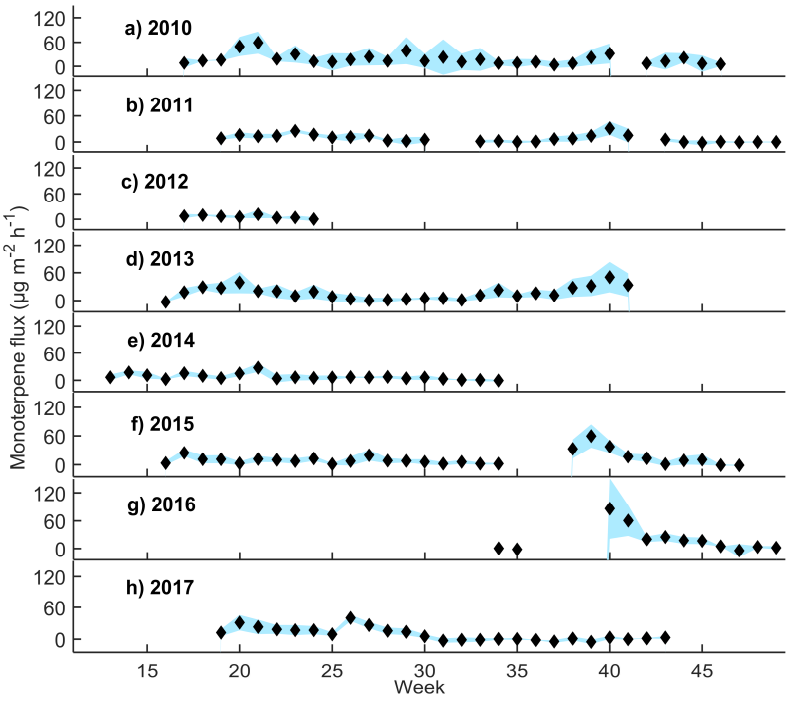

Figure 6. Weekly mean monoterpene fluxes (diamonds, µg m^{-2} h^{-1}) and standard deviation (blue areas, n = 3) from the boreal forest floor between 2010 and 2017 measured using the quadrupole-PTR-MS (study **I**) (modified based on Mäki et al., 2019).

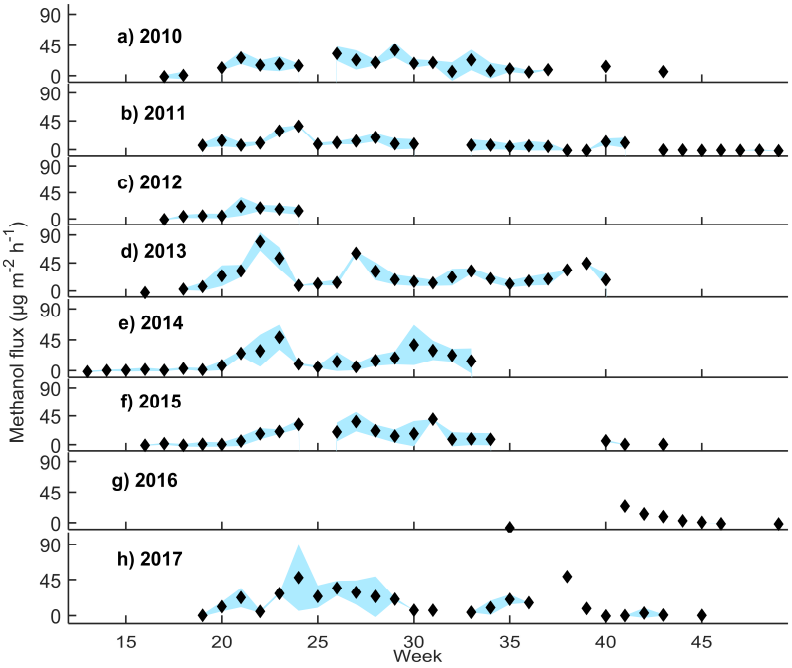

Figure 7. Weekly mean methanol fluxes (diamonds, µg m^{-2} h^{-1}) and standard deviation (blue areas, n = 3) during the daytime (9am to 8pm) from the boreal forest floor between 2010 and 2017 measured using quadrupole-PTR-MS (study **I**) (modified based on Mäki et al., 2019).

3.1.3. Diurnal dynamics

Forest floor vegetation was a net source of oxygenated VOCs such as methanol, acetone and acetaldehyde in the daytime and especially during growing season (study **I**), similar as oxygenated VOC fluxes from *Pinus sylvestris* shoots (Aalto et al., 2014). The forest floor monoterpene fluxes were also the highest during daytime from spring to autumn (study **I**). A similar trend was observed in previous studies at our measurement site, where the forest floor was mainly a daytime source (Aaltonen et al., 2013). Forest floor vegetation was a net sink of oxygenated VOCs in the nighttime, when water-soluble VOCs were dissolved in moist surfaces on leaves (study **I**). Similar to the boreal forest floor (study **I**), the bare temperate cropland was a daytime source and night-time sink for methanol in spring (Bachy et al., 2018). However, the forest floor was also a night-time source of monoterpenes (study **I**). Atmospheric chemistry may be affected by soils during night-time and early morning, when tree emissions are low.

3.2. Effect of soil fluxes on VOC budgets

The forest floor contributed significantly to the forest stand monoterpene fluxes (study I), indicating that the in-canopy air chemistry may be affected by soil processes. The 8-yr dataset shows that in summer the soil contribution to monoterpene fluxes was only a few per cent, while in spring and autumn it could be up to 90%. This approach does not include oxidation, which occurs when compounds are transported from the forest floor to the above canopy atmosphere, and for this reason, these results should be taken as order of magnitude estimates rather than exact values determining the proportion of forest floor-emitted VOCs. For example, acetone and acetaldehyde are produced in the forest atmosphere through VOC oxidation. Study **I** is supported by previous results, where forest floor fluxes from the forest stand fluxes ranged from a few per cent to tens of per cents (Aaltonen et al., 2013), or 20% to 40% of the canopy flux rates (Janson, 1993). Another study estimated soil VOC fluxes in the various ecosystems to be one to two orders of magnitude lower than vegetation fluxes (Peñuelas et al., 2014), e.g. a Sitka spruce (*Picea sitchensis*) forest, where forest floor fluxes were under 3% of the forest stand fluxes (Hayward et al., 2001). Litter-released VOCs were found to cover under 1% of above-canopy fluxes (Greenberg et al., 2012), but the litter contribution was likely underestimated, because this comparison was made based on summer measurements without considering the seasonal dynamic of litter-released VOCs. Mochizuki et al. (2015) found high α-pinene concentrations above the forest floor (2 m) in July which were interpreted to be released by litter and roots in a Japanese larch (*Larix kaempferi*) stand. BVOC emissions are globally highest from tropical forests

(Guenther, 2013), where the role of soils is also significant, as highly reactive sesquiterpene fluxes from soils were in same magnitude as modelled canopy fluxes during the dry season in the Amazon (Bourtsoukidis et al., 2018). Based on these studies, it is clear that simultaneous and continuous above- and below-canopy flux measurements for VOCs are required to determine the importance of soils to global atmospheric processes.

Oxygenated VOC fluxes were dominated by methanol (study **I**). The boreal forest floor released large proportion of the total forest stand fluxes in spring and early summer, because shoot fluxes were low and forest stand fluxes relatively high (study **I**). Methanol, with relatively high mixing ratios, has implications to tropospheric chemistry by affecting global budgets of hydroxyl radicals and ozone (Jacob et al., 2005), while the contribution to SOA formation is small due to high volatility of methanol and its oxidation products. Soil VOC production may also affect tree emissions, because water-soluble methanol produced in the roots may be emitted through the stomata (Folkers et al., 2008).

3.3. Spatial variation of soil VOC fluxes

Spatial variation is typically high in soil, because soil depth, root density and biomass, nutrient availability, carbon content, temperature and water content differ depending on vegetation cover, litter quality and quantity, shading and soil composition (porosity, texture and rockiness). We observed that temporal variation of forest floor VOC exchange was estimated relatively well using only three automated chambers (study **I**). The spatial variation of VOC fluxes was significant due to varying vegetation cover and prevailing temperature (study **I**). The differences between soil collars within one studied forest stand were small and non-systematic in our other studies, when we investigated the effects of tree species and climate (study **II**) or compared simultaneous belowground VOC concentrations and soil surface fluxes (study **IV**). Based on these studies, temporal variation is apparently the most significant source of flux rate variability within one measurement site. When we scale up forest floor VOC exchange for a certain climate zone, both spatial and temporal variation appear to play a major role in forest floor VOC exchange. When we compared the climate zones, spatial variation at a regional scale is caused by both ecosystem characteristics and climate features.

Forest management practises may also play a major role in forest floor VOC exchange, because high VOC fluxes were observed from the stumps and fresh logging residues from the clear-cut area (Haapanala et al., 2012). These VOC fluxes are likely decreased if logging residues and stumps are gathered away from the site for bioenergy production.

3.4. Plant ecophysiological processes affect forest floor VOC exchange

By comparing VOC fluxes from coniferous forest floor in boreal and hemiboreal climates, we analysed the long-term effects of climate change on forest floor emissions (study **II**). We found that the forest floor monoterpene and sesquiterpene fluxes differ a lot depending on stand biomass, tree species and climate (study **II**). The seasonal dynamic of forest floor VOC exchange was independent from tree species and climate, as total monoterpene and sesquiterpene fluxes were highest in spring and summer on all studied forest stands (study **II**). Monoterpene fluxes from the hemiboreal mixed forest floor also peaked in October (study **II**), which was in line with our results from the boreal *Pinus sylvestris* forest floor in studies **I** and **III**. In this thesis, the total monoterpene fluxes were highest in the hemiboreal mixed forest floor, likely due to the highest litter quantity compared to other forest stands and higher temperatures in hemiboreal than boreal climate, which likely increased VOC release from the forest floor, although the difference compared to the boreal *Pinus sylvestris* forest floor was not statistically significant (study **II**). Global warming may increase BVOC emissions from the Northern Hemisphere, as some boreal forests will turn into hemiboreal forests that emit more BVOCs (Noe et al., 2011; 2012; Bourtsoukidis et al., 2014) and as vegetation zones move towards the north (Lathiere et al., 2005). Study **II** provides evidence that monoterpene fluxes from the forest floor could also increase, if the warming climate increases tree biomass in boreal forests, leading to increased litter production.

In this thesis, we observed that forest floor VOC fluxes are affected by tree species and litter quality, as shown by the higher monoterpene fluxes from the mixed and *Pinus sylvestris* forest floor than the *Picea abies* forest floor in hemiboreal and boreal climates (study **II**, Fig. 8). Similar total mean isoprenoid flux rates (28.9–81.5 $\mu g\ m^{-2}\ h^{-1}$) were also measured from the *Pinus sylvestris* forest floor in the hemiboreal (Estonia coast) and boreal climates (northern Finland) (Kivimäenpää et al., 2018). Our results were supported by a previous study, where the monoterpene emission rate from decomposition of *Pinus sylvestris* litter was from five to nearly ten times higher than from decomposition of *Picea abies* litter within the first 77 days (Isidorov et al., 2010). The rhizosphere may also explain differences in flux rates between mixed and *Picea abies* forest floors in our study **II**, because *Pinus* spp. roots are a major VOC source (Lin et al., 2007). Monoterpene concentrations of soil atmosphere were highest on the *Pinus sylvestris* stand, lower on the *Picea abies* stand and lowest on the *B. pendula* stand (Smolander et al., 2006).

In the future it would be important to compare the effect of climate and tree species on forest floor VOC fluxes using higher number of studied stands. By studying larger variety of different stands, it would be possible to generalize these

results to the whole climate zone. The effect of tree species on forest floor VOC fluxes may also be influenced by varying soil moisture conditions within boreal and hemiboreal stands. Soil type was the same between *Pinus sylvestris* and *Picea abies* stands within boreal (Haplic Podzol) and hemiboreal (Haplic Gleysol) climates, so the differences in forest floor VOC fluxes between *Pinus sylvestris* and *Picea abies* stands within the certain climate zone cannot be explained by soil type.

Coniferous litter is a higher monoterpene source than broadleaf litter, because total monoterpene fluxes from decomposing *Pinus* spp. litter were significantly higher (7.8–15.7 μmol g_{DW}^{-1}) than from *Populus* spp. and *Quercus* spp. litter (0.1–0.3 μmol g_{DW}^{-1}) (Isidorovand Jdanova, 2002). Coniferous needles contain monoterpene storage structures (Kainulainen and Holopainen, 2002) and monoterpenes are emitted after synthesis or later from storages (Laothawornkitkul et al., 2009). Broadleaf trees are mainly isoprene emitters (synthesis: Karl et al., 2009) and monoterpene storages in leaves are likely small, although small amount of monoterpenes may be stored in lipid and liquid phases of leaves without specific storage structures (Grote et al., 2008). Estimating how much the broadleaf forest floor releases VOCs is important in the future, as certain boreal coniferous forests are expected to shift to broadleaf forests in the warming climate. VOC synthesis or uptake of microbes could be higher in broadleaf forest soils compared to coniferous forest soils, because decomposition of broadleaf litter is faster than the decomposition of coniferous litter, especially in early stages of decomposition (Prescott et al., 2000; 2004). Microbial community structures also differ between *Pinus sylvestris*, *Picea abies* and *Betula pendula* stands (Priha et al., 2001).

We observed that monoterpenes are likely released, deposited and consumed simultaneously in the forest floor (study **I**). VOC fluxes are bidirectional and both emissions and deposition of monoterpenes, sesquiterpenes and oxygenated VOCs were observed above a temperate grassland (Bamberger et al., 2011). In study **II**, dense ground vegetation cover likely increased the monoterpene flux rates on our boreal *Pinus sylvestris* stand compared to the boreal *Picea abies* stand with lower vegetation cover. Dense ground vegetation on the boreal *Pinus sylvestris* stand was dominated by *Vaccinium spp*. and mosses, which release isoprene, monoterpenes, sesquiterpenes and oxygenated VOCs (Hanson et al., 1999; Hellén et al., 2006; Aaltonen et al., 2011; Faubert et al., 2012). Forest floor VOC exchange was also bidirectional, because ground vegetation may be a monoterpene sink (study **III**), when monoterpenes are adsorbed on the lipophilic cuticle layer (Joensuu et al., 2016). Microbial uptake of plant-emitted BVOCs on leaf surfaces (Farré-Armengol et al., 2016) or microbial degradation of VOCs in soil (Albers et al., 2018) may also decrease VOC emissions from the forest floor. In fact, the forest floor was a stronger monoterpene source when ground vegetation cover was low at our measurement site (Aaltonen et al., 2013). Forest floor vegetation was also a net sink of water-soluble VOCs such as methanol, acetone and acetaldehyde during the nighttime, when compounds were dissolved in moist surfaces on leaves (study **I**). Soil may also be a potential VOC sink (Asensio et al., 2007) for litter-emitted VOCs (Ramirez et al., 2010). Studies **I**–**IV** show that compound volatilization, deposition of water-soluble VOCs and adsorption of lipophilic monoterpenes on leaf surfaces are the main physico-chemical processes, which drive VOC exchange from the boreal forest floor.

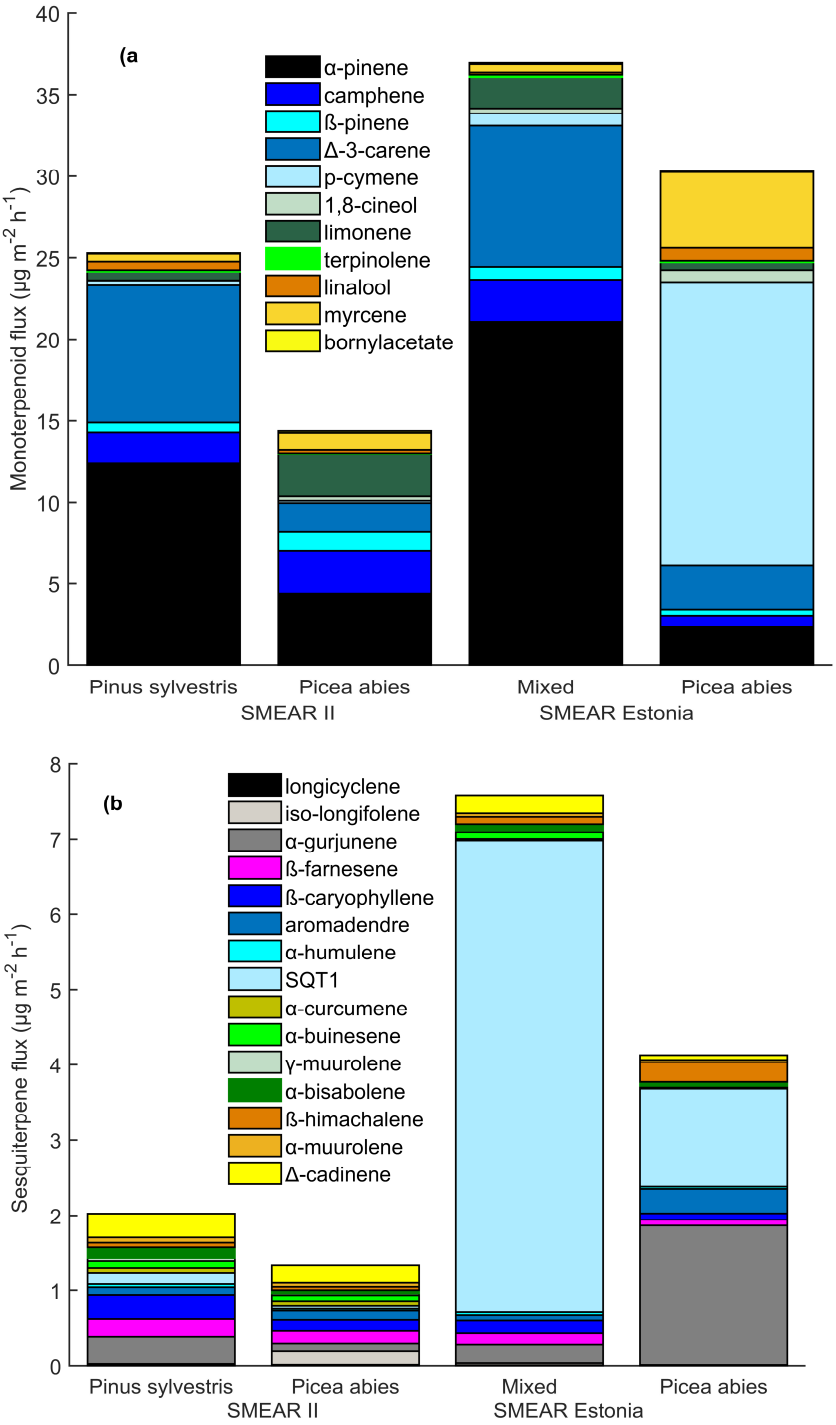

Figure 8. Individual mean monoterpenoid and sesquiterpene fluxes (µg m^{-2} h^{-1}) from *Pinus sylvestris* and *Picea abies* forest floors in boreal (SMEAR II) and from mixed and *Picea abies* forest floors in hemiboreal (SMEAR Estonia) climates in 2017–2018 (study **II**).

3.5. Microbiological processes affect forest floor VOC exchange

In this thesis, we studied the effect of photosynthesized carbon allocation through roots and mycorrhizal fungi on soil monoterpene and sesquiterpene fluxes in the trenching experiment in a boreal *Pinus sylvestris* stand (study **III**). We found that soil carbon allocation of the rhizosphere is not a dominating mechanism affecting soil VOC production, but instead the decomposing litter and decomposers themselves were suggested to be the highest monoterpene sources (study **III**). Monoterpene and sesquiterpene fluxes from the bare soil with decomposers and litter were similar to fluxes from the bare soil containing roots, mycorrhizal fungi, decomposers and litter (Fig. 8 and Fig. 9, study **III**). Monoterpenes are also released by roots (Hayward et al., 2001), but it is possible that microbial degradation of VOCs (Albers et al., 2018) in rhizosphere decreases forest floor VOC fluxes from treatments where roots are present. Living roots and litter were likely the main VOC sources instead of vegetation from the boreal forest floor according to Janson (1993).

In this thesis, the highest monoterpene fluxes were observed in October from bare soil with decomposers and litter (73 μg m^{-2} h^{-1}) (study **III**). Wang et al. (2018) detected also highest total monoterpene fluxes (10.2 μg m^{-2} h^{-1}) from the boreal forest floor dominated by *Picea abies* and *Pinus sylvestris* in October in Sweden during maximum litter production, when the temperature was under 10 °C (Wang et al., 2018). High monoterpene fluxes were also measured earlier from a boreal *Pinus sylvestris* forest floor in October in Sweden (Janson 1993). Total mean monoterpene fluxes from the boreal forest floor in study **III** (control plots: 23 μg m^{-2} h^{-1}) were in the same magnitude compared to total monoterpene fluxes from subarctic heath (1.5–9.8 μg m^{-2} h^{-1}, Faubert et al., 2010c), from low and high Arctic heath (0.01–7 μg m^{-2} h^{-1}, Lindwall et al., 2015), and from the *Pinus sylvestris* forest floor (Janson 1993: 5–580 μg m^{-2} h^{-1}, Hellen et al., 2006: 0–373, Aaltonen et al., 2011: 5 μg m^{-2} h^{-1} and Aaltonen et al., 2013: 4–40 μg m^{-2} h^{-1}). Relatively high total VOC fluxes were observed in the low Arctic from *Salix* spp. and *Betula* spp. heath (140–205 μg m^{-2} h^{-1}) (Lindwall et al., 2015). Fluxes of isoprene, monoterpenes, sesquiterpenes and other reactive VOCs were explained by photosynthetically active radiation and temperature, while other VOCs, dominated by methyl-butane, were also emitted during night-time (Lindwall et al., 2015).

Based on this thesis, it is clear that northern soils are a significant and highly varying source of sesquiterpenes. In this thesis, total mean sesquiterpene fluxes from boreal forest floors were estimated using campaign-based measurements over a four-year period (studies **II**, **III** and **IV**). Sesquiterpene fluxes were higher from the boreal forest floor (Fig. 9: study **III**: 0.3–0.7 μg m^{-2} h^{-1}, study **II**: 0.5–1.3 μg m^{-2} h^{-1}, and study **IV**: 0.7–11.2 μg m^{-2} h^{-1}) than in an earlier study from the same forest (0.05 μg m^{-2} h^{-1}, Aaltonen et al., 2011), likely because the number of quantified sesquiterpenes was higher in studies **II** and **IV**. Sesquiterpene fluxes from boreal and Arctic soils have been observed in various studies (Table 2), but quantification of VOC synthesis from individual sources remains mostly unknown. Supporting this thesis, total sesquiterpene fluxes in other studies were mainly in the same magnitude: 2.7–3.4 μg m^{-2} h^{-1} from subarctic heath (Faubert et al., 2010c), 4 μg m^{-2} h^{-1} from subarctic heath with evergreen and deciduous dwarf shrubs (Rinnan et al., 2013), 0.15 μg m^{-2} h^{-1} from high Arctic *Cassiope*-heath (Lindwall et al., 2015), 7 μg m^{-2} h^{-1} from low Arctic *Betula*-heath (Lindwall et al., 2015), 1 μg m^{-2} h^{-1} from low arctic *Salix*-heath (Lindwall et al., 2015) and 0.004–0.2 μg m^{-2} h^{-1} from a boreal forest floor (Wang et al., 2015).

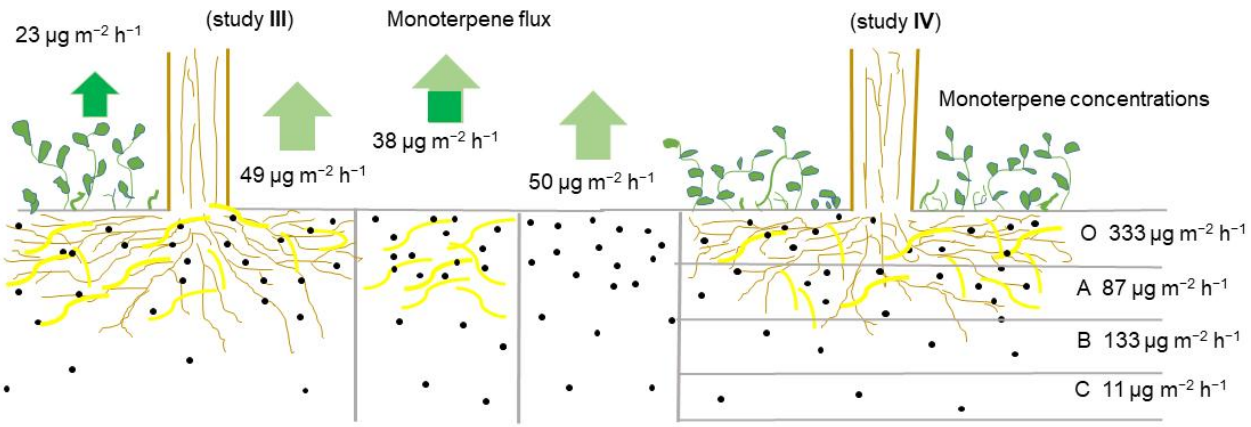

Figure 9. Contribution of various soil compartments, such as ground vegetation, roots, mycorrhizal fungi and decomposers, to soil monoterpene fluxes (study **III**), and monoterpene concentrations of the different soil horizons in boreal soils (study **IV**). Significant differences in flux rates between the treatments are indicated with different arrow colours

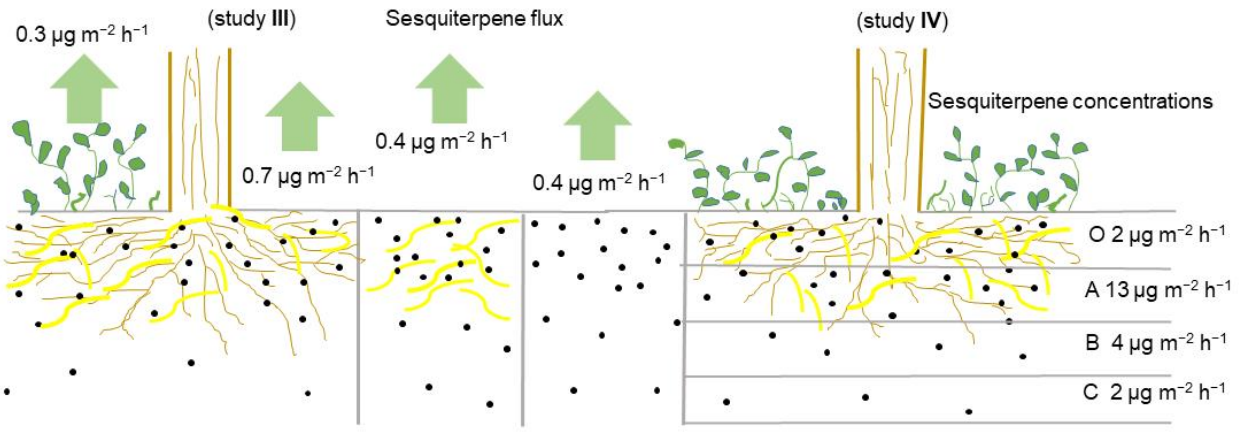

Figure 10. Contribution of various soil compartments, such as ground vegetation, roots, mycorrhizal fungi and decomposers, to soil sesquiterpene fluxes (study **III**), and sesquiterpene concentrations of the different soil horizons in boreal soils (study **IV**).

In this thesis, VOC concentrations were measured from the different soil horizons in a boreal *Pinus sylvestris* stand (study **IV**). Monoterpene concentrations were highest in the O-horizon, with lots of organic carbon that accelerates microbial decomposition, and sesquiterpene concentrations in the A-horizon, with roots and associated microbes (Fig. 9 and Fig. 10). These horizons mainly contributed to the soil surface fluxes (study **IV**). VOCs are metabolized by autotrophic and heterotrophic microbes (Schulz and Dickschat, 2007; Yamada et al., 2015) and released by *Pinus* spp. roots (Lin et al., 2007), which are likely most active and abundant in the O- and in the A-horizons. Sesquiterpenes observed in the A-horizon in boreal soil (study **IV**) were likely produced in interaction between the roots and ectomycorrhizal fungi (Ditengou et al., 2015). Fungal species isolated from *Pinus sylvestris* roots were observed to release sesquiterpenes (Bäck et al., 2010). Study **IV** is supported by an earlier study, where monoterpene emission potentials were higher from undisturbed soil compared to soil where the uppermost horizon was removed in a *Picea sitchensis* stand (Hayward et al., 2001). Similar to study **IV**, sesquiterpene production of soil microorganisms was higher in the O- and A-horizons compared to the B-horizon also in Amazonian soils (Bourtsoukidis et al., 2018). We should note, that belowground interaction does not always lead to higher VOC concentrations, as in Schenkel et al. (2018), where *Fusarium* spp. enhanced root length (Arabidopsis) by reducing soil VOCs concentrations. The interactions between organisms transmitted by VOCs are concurrently at least as diverse in the soil as in tree canopies (Wenke et al., 2010).

Table 2. Isoprene, monoterpenes, sesquiterpenes and total VOC emissions for different sources from field (F) and laboratory studies (L) (modified based on Peñuelas et al., 2014) concerning various climate (Köppen-Geiger climate classification) and global ecological zones (The Global Forest Resources Assessment of FAO, 2000).

VOC source	Climate zone	Vegetation zone	VOC group	Emission rate	Unit	T (°C)	Measurement technique	Study	Reference
high Arctic *Cassiope*-heath	polar	boreal	Total VOCs	9	μg m^{-2} h^{-1}	16.3	TD-GC-MS [a]	F	Lindwall et al., 2015
high Arctic *Cassiope*-heath	polar	boreal	Isoprene	0.3	μg m^{-2} h^{-1}	16.3	TD-GC-MS [a]	F	Lindwall et al., 2015
high Arctic *Cassiope*-heath	polar	boreal	Monoterpenes	**7**	μg m^{-2} h^{-1}	16.3	TD-GC-MS [a]	F	Lindwall et al., 2015
high Arctic *Cassiope*-heath	polar	boreal	Sesquiterpenes	0.15	μg m^{-2} h^{-1}	16.3	TD-GC-MS [a]	F	Lindwall et al., 2015
high Arctic *Salix*-heath	polar	boreal	Total VOCs	43	μg m^{-2} h^{-1}	17.8	TD-GC-MS [a]	F	Lindwall et al., 2015
high Arctic *Salix*-heath	polar	boreal	Isoprene	40	μg m^{-2} h^{-1}	17.8	TD-GC-MS [a]	F	Lindwall et al., 2015
high Arctic *Salix*-heath	polar	boreal	Monoterpenes	0.01	μg m^{-2} h^{-1}	17.8	TD-GC-MS [a]	F	Lindwall et al., 2015
high Arctic *Salix*-heath	polar	boreal	Sesquiterpenes	0	μg m^{-2} h^{-1}	17.8	TD-GC-MS [a]	F	Lindwall et al., 2015
soil with mixed heath (evergreen and deciduous dwarf shrubs)	cold	boreal	Sesquiterpenes	4	μg m^{-2} h^{-1}	13.6	TD-GC-MS [a]	F	Rinnan et al., 2013
soil with mixed heath (evergreen and deciduous dwarf shrubs)	cold	boreal	Total VOCs	10	μg m^{-2} h^{-1}	13.6	TD-GC-MS [a]	F	Rinnan et al., 2013
soil with heath (*Deschampsia flexuosa*)	cold	temperate	Monoterpenes	0.05	μg m^{-2} h^{-1}	18.0	TD-GC-MS [a]	F	Rinnan et al., 2013
soil with heath (*Deschampsia flexuosa*)	cold	temperate	Total VOCs	3	μg m^{-2} h^{-1}	18.0	TD-GC-MS [a]	F	Rinnan et al., 2013
subarctic heath and soil	cold	boreal	Monoterpenes	1.5−9.8	μg m^{-2} h^{-1}	9.6−11.0	TD-GC-MS [a]	F	Faubert et al., 2010c
subarctic heath and soil	cold	boreal	Sesquiterpenes	2.7−3.4	μg m^{-2} h^{-1}	9.6−11.0	TD-GC-MS [a]	F	Faubert et al., 2010c
subarctic heath and soil	cold	boreal	Total VOCs	10.9−14.6	μg m^{-2} h^{-1}	9.6−11.0	TD-GC-MS [a]	F	Faubert et al., 2010c
peatland (*Sphagnum fuscum*, sedges and dwarf shrubs)	cold	boreal	Monoterpenes	76.0	ng g_{DW}^{-1} h−1	25.1	TD-GC-MS [a]	F	Faubert et al., 2010b

peatland (*Sphagnum fuscum*, sedges and dwarf shrubs)	cold	boreal	Sesquiterpenes	2.4	ng g_{DW}^{-1} h−1	25.1	TD-GC-MS [a]	F	Faubert et al., 2010b
peatland (*Sphagnum fuscum*, sedges and dwarf shrubs)	cold	boreal	Total VOCs	85	ng g_{DW}^{-1} h−1	25.1	TD-GC-MS [a]	F	Faubert et al., 2010b
subarctic peatland	cold	boreal	Monoterpenes	0.3−0.5	µg m^{-2} h^{-1}	11.9 & 23.5	TD-GC-MS [a]	F	Faubert et al., 2012
subarctic peatland	cold	boreal	Total BVOCs	1.1−1.8	µg m^{-2} h^{-1}	11.9 & 23.5	TD-GC-MS [a]	F	Faubert et al., 2012
Pinus spp. litter biotic production	cold and arid	temperate	Monoterpenes	8−14	µmol g_{DW}^{-1} h^{-1}	22	PTR-MS [a]	L	Gray et al., 2010
Pinus spp. litter abiotic production	cold and arid	temperate	Monoterpenes	8−16	µmol g_{DW}^{-1} h^{-1}	22	PTR-MS [a]	L	Gray et al., 2010
Pinus spp. litter biotic production	cold and arid	temperate	Isoprene	0.2−1.4	µmol g_{DW}^{-1} h^{-1}	22	PTR-MS [a]	L	Gray et al., 2010
Pinus spp. litter abiotic production	cold and arid	temperate	Isoprene	1.1−1.5	µmol g_{DW}^{-1} h^{-1}	22	PTR-MS [a]	L	Gray et al., 2010
low Arctic *Betula*-heath	cold	boreal	Total VOCs	140	µg m^{-2} h^{-1}	12.3	TD-GC-MS [a]	F	Lindwall et al., 2015
low Arctic *Betula*-heath	cold	boreal	Isoprene	8	µg m^{-2} h^{-1}	12.3	TD-GC-MS [a]	F	Lindwall et al., 2015
low Arctic *Betula*-heath	cold	boreal	Monoterpenes	1	µg m^{-2} h^{-1}	12.3	TD-GC-MS [a]	F	Lindwall et al., 2015
low Arctic *Betula*-heath	cold	boreal	Sesquiterpenes	7	µg m^{-2} h^{-1}	12.3	TD-GC-MS [a]	F	Lindwall et al., 2015
low Arctic Salix-heath	cold	boreal	Total VOCs	205	µg m^{-2} h^{-1}	12.7	TD-GC-MS [a]	F	Lindwall et al., 2015
low Arctic *Salix*-heath	cold	boreal	Isoprene	75	µg m^{-2} h^{-1}	12.7	TD-GC-MS [a]	F	Lindwall et al., 2015
low Arctic *Salix*-heath	cold	boreal	Monoterpenes	1	µg m^{-2} h^{-1}	12.7	TD-GC-MS [a]	F	Lindwall et al., 2015
low Arctic *Salix*-heath	cold	boreal	Sesquiterpenes	1	µg m^{-2} h^{-1}	12.7	TD-GC-MS [a]	F	Lindwall et al., 2015
Decomposing fungi	cold	boreal	Monoterpenes	0.1−2.7	µg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010
Ectomycorrhizal fungi	cold	boreal	Monoterpenes	0.0−0.8	µg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010

Endophytic fungi	cold	boreal	Monoterpenes	0.0−0.02	μg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010
Decomposing fungi	cold	boreal	Isoprene	0.9−1.4	μg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010
Ectomycorrhizal fungi	cold	boreal	Isoprene	0.0−2.7	μg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010
Endophytic fungi	cold	boreal	Isoprene	0.3−0.4	μg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010
Pinus sylvestris litter	cold	boreal	Monoterpenes	0.2−7.5	μg g_{DW}^{-1} h^{-1}	20	TD-GC-MS [d]	L	Isidorov et al., 2010
Picea abies litter	cold	boreal	Monoterpenes	0.5−1.5	μg g_{DW}^{-1} h^{-1}	20	TD-GC-MS [d]	L	Isidorov et al., 2011
Pinus sylvestris forest floor	cold	boreal	Monoterpenes	4−40	μg m^{-2} h^{-1}	9.8–10.7	PTR-MS [a]	F	Aaltonen et al., 2013
Pinus sylvestris forest floor	cold	boreal	Isoprene	0.3	μg m^{-2} h^{-1}	9.8–10.7	PTR-MS [a]	F	Aaltonen et al., 2013
Pinus sylvestris forest floor	cold	boreal	Monoterpenes	23	μg m^{-2} h^{-1}	11.9	TD-GC-MS [a]	F	study **III**
Pinus sylvestris forest floor	cold	boreal	Sesquiterpenes	0.4	μg m^{-2} h^{-1}	11.9	TD-GC-MS [a]	F	study **III**
Pinus sylvestris soil with roots and vegetation removed	cold	boreal	Monoterpenes	49	μg m^{-2} h^{-1}	14.0	TD-GC-MS [a]	F	study **III**
Pinus sylvestris soil with roots and vegetation removed	cold	boreal	Sesquiterpenes	0.7	μg m^{-2} h^{-1}	14.0	TD-GC-MS [a]	F	study **III**
Pinus sylvestris forest floor with mycorrhizal fungi and decomposers	cold	boreal	Monoterpenes	34	μg m^{-2} h^{-1}	13.7	TD-GC-MS [a]	F	study **III**
Pinus sylvestris forest floor with mycorrhizal fungi and decomposers	cold	boreal	Sesquiterpenes	0.6	μg m^{-2} h^{-1}	13.7	TD-GC-MS [a]	F	study **III**
Pinus sylvestris soil with mycorrhizal fungi and decomposers and vegetation removed	cold	boreal	Monoterpenes	38	μg m^{-2} h^{-1}	10.4	TD-GC-MS [a]	F	study **III**
Pinus sylvestris soil with mycorrhizal fungi and decomposers and vegetation removed	cold	boreal	Sesquiterpenes	0.4	μg m^{-2} h^{-1}	10.4	TD-GC-MS [a]	F	study **III**

Pinus sylvestris forest floor with decomposers	cold	boreal	Monoterpenes	19	μg m^{-2} h^{-1}	12.4	TD-GC-MS [a]	F	study **III**
Pinus sylvestris forest floor with decomposers	cold	boreal	Sesquiterpenes	0.5	μg m^{-2} h^{-1}	12.4	TD-GC-MS [a]	F	study **III**
Pinus sylvestris soil with decomposers and vegetation removed	cold	boreal	Monoterpenes	49	μg m^{-2} h^{-1}	12.9	TD-GC-MS [a]	F	study **III**
Pinus sylvestris soil with decomposers and vegetation removed	cold	boreal	Sesquiterpenes	0.4	μg m^{-2} h^{-1}	12.9	TD-GC-MS [a]	F	study **III**
Pinus sylvestris forest floor	cold	boreal	Monoterpenes	7.2−19.1	μg m^{-2} h^{-1}	7.3−10.5	PTR-MS [a]	F	study **I**
Pinus sylvestris forest floor	cold	boreal	Monoterpenes	0−373	μg m^{-2} h^{-1}		TD-GC-MS [b]	F	Hellén et al., 2006
Wetland dominated by *Sphagnum* spp. mosses	cold	boreal	Isoprene	224	μg m^{-2} h^{-1}	30	TD-GC-MS [b]	F	Hellén et al., 2006
Pinus sylvestris forest floor	cold	boreal	Monoterpenes	5−580	μg m^{-2} h^{-1}	20	GC-ITD [b]	F	Janson 1993
Pinus sylvestris forest floor	cold	boreal	Monoterpenes	5	μg m^{-2} h^{-1}	8.5	TD-GC-MS [a]	F	Aaltonen et al., 2011
Pinus sylvestris forest floor	cold	boreal	Sesquiterpenes	0.04	μg m^{-2} h^{-1}	8.5	TD-GC-MS [a]	F	Aaltonen et al., 2011
Pinus sylvestris forest floor	cold	boreal	Isoprene	0.05	μg m^{-2} h^{-1}	8.5	TD-GC-MS [a]	F	Aaltonen et al., 2011
Pinus sylvestris and *Picea abies* forest floors	cold	boreal	Monoterpenes	3.2−10.2	μg m^{-2} h^{-1}	1.9−24.0	TD-GC-MS [a]	F	Wang et al., 2018
Pinus sylvestris and *Picea abies* forest floors	cold	boreal	Sesquiterpenes	0.004−0.2	μg m^{-2} h^{-1}	1.9−24.0	TD-GC-MS [a]	F	Wang et al., 2018
Pinus sylvestris and *Picea abies* forest floors	cold	boreal	Isoprene	0.003−0.05	μg m^{-2} h^{-1}	1.9−24.0	TD-GC-MS [a]	F	Wang et al., 2018
Pinus sylvestris and *Picea abies* forest floors	cold	boreal	Total VOCs	3.3−10.3	μg m^{-2} h^{-1}	1.9−24.0	TD-GC-MS [a]	F	Wang et al., 2018
Pinus sylvestris forest floor	cold	boreal	Monoterpenes	23	μg m^{-2} h^{-1}	14.7	TD-GC-MS [a]	F	study **II**
Pinus sylvestris forest floor	cold	boreal	Sesquiterpenes	0.9	μg m^{-2} h^{-1}	14.7	TD-GC-MS [a]	F	study **II**
Picea abies forest floor	cold	boreal	Monoterpenes	11	μg m^{-2} h^{-1}	13.5	TD-GC-MS [a]	F	study **II**
Picea abies forest floor	cold	boreal	Sesquiterpenes	0.5	μg m^{-2} h^{-1}	13.5	TD-GC-MS [a]	F	study **II**

Pinus sylvestris forest floor	cold	temperate	Monoterpenes	32	μg m^{-2} h^{-1}	15.1	TD-GC-MS [a]	F	study **II**
Pinus sylvestris forest floor	cold	temperate	Sesquiterpenes	1.3	μg m^{-2} h^{-1}	15.1	TD-GC-MS [a]	F	study **II**
Picea abies forest floor	cold	temperate	Monoterpenes	9	μg m^{-2} h^{-1}	12.9	TD-GC-MS [a]	F	study **II**
Picea abies forest floor	cold	temperate	Sesquiterpenes	0.6	μg m^{-2} h^{-1}	12.9	TD-GC-MS [a]	F	study **II**
Pinus sylvestris forest floor	cold	boreal	Monoterpenes	19.7−61.9	μg m^{-2} h^{-1}	9.3−12.2	TD-GC-MS [a]	F	study **IV**
Pinus sylvestris forest floor	cold	boreal	Sesquiterpenes	0.7−11.2	μg m^{-2} h^{-1}	9.3−12.2	TD-GC-MS [a]	F	study **IV**
Picea sitchensis forest soil	temperate	temperate	Monoterpenes	34	μg m^{-2} h^{-1}	30	TD-GC-MS [a]	F	Hayward et al., 2001

[a] dynamic enclosure

[b] static chamber

[c] headspace from pure fungal culture

[d] solid-phase microextraction (SPME)

Table 3. Oxygenated VOC emissions for the different sources in field (F) and laboratory studies (L) (modified based on Peñuelas et al., 2014) concerning various climate (Köppen-Geiger climate classification) and vegetation zones.

VOC source	Climate zone	Vegetation zone	VOC group	Emission rate	Unit	T (ºC)	Measurement technique	Study	Reference
Pinus spp. litter biotic production	cold and arid	temperate	Methanol	294−1218	μmol g_{DW}^{-1} h^{-1}	22	PTR-MS [a]	L	Gray et al., 2010
Pinus spp. litter abiotic production	cold and arid	temperate	Methanol	66−86	μmol g_{DW}^{-1} h^{-1}	22	PTR-MS [a]	L	Gray et al., 2010
Pinus spp. litter biotic production	cold and arid	temperate	Acetaldehyde	0.1−1.1	μmol g_{DW}^{-1} h^{-1}	22	PTR-MS [a]	L	Gray et al., 2010
Pinus spp. litter abiotic production	cold and arid	temperate	Acetaldehyde	18−38	μmol g_{DW}^{-1} h^{-1}	22	PTR-MS [a]	L	Gray et al., 2010
Pinus spp. litter biotic production	cold and arid	temperate	Propanal/Acetone	4−22	μmol g_{DW}^{-1} h^{-1}	22	PTR-MS [a]	L	Gray et al., 2010
Pinus spp. litter abiotic production	cold and arid	temperate	Propanal/Acetone	10−14	μmol g_{DW}^{-1} h^{-1}	22	PTR-MS [a]	L	Gray et al., 2010

Pinus sylvestris forest floor	cold	boreal	Methanol	-0.6−7	μg m^{-2} h^{-1}	9.8–10.7	PTR-MS [a]	F	Aaltonen et al., 2013
Pinus sylvestris forest floor	cold	boreal	Acetone	-0.8−2.2	μg m^{-2} h^{-1}	9.8–10.7	PTR-MS [a]	F	Aaltonen et al., 2013
Pinus sylvestris forest floor	cold	boreal	Acetaldehyde	0.8−2.2	μg m^{-2} h^{-1}	9.8–10.7	PTR-MS [a]	F	Aaltonen et al., 2013
Pinus sylvestris forest floor	cold	boreal	Methanol	-0.9−3.3	μg m^{-2} h^{-1}	7.3−10.5	PTR-MS [a]	F	study **I**
Pinus sylvestris forest floor	cold	boreal	Acetone	-0.2−1.6	μg m^{-2} h^{-1}	7.3−10.5	PTR-MS [a]	F	study **I**
Pinus sylvestris forest floor	cold	boreal	Acetaldehyde	0.7−1.9	μg m^{-2} h^{-1}	7.3−10.5	PTR-MS [a]	F	study **I**
Pinus sylvestris forest floor	cold	boreal	oxygenated VOCs	0.6−5.1	μg m^{-2} h^{-1}	9.3−12.2	TD-GC-MS [a]	F	study **IV**
Decomposing fungi	cold	boreal	Methanol	0.7−1.2	μg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010
Ectomycorrhizal fungi	cold	boreal	Methanol	-34−2.3	μg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010
Endophytic fungi	cold	boreal	Methanol	23−113	μg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010
Decomposing fungi	cold	boreal	Acetone	17−781	μg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010
Ectomycorrhizal fungi	cold	boreal	Acetone	4943−574	μg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010
Endophytic fungi	cold	boreal	Acetone	-5.1 − -2.4	μg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010
Decomposing fungi	cold	boreal	Acetaldehyde	7.2−7.3	μg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010
Ectomycorrhizal fungi	cold	boreal	Acetaldehyde	4.7−1.5	μg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010
Endophytic fungi	cold	boreal	Acetaldehyde	23−113	μg g_{DW}^{-1} h^{-1}	20	PTR-MS [c]	L	Bäck et al., 2010

[a] dynamic enclosure

[b] static chamber

[c] headspace from pure fungal culture

3.6. Environmental parameters that drive VOC exchange from the boreal forest floor

Studies **I**–**IV** provide evidence that temperature, soil moisture and relative humidity are the environmental parameters that mainly drive VOC fluxes from the boreal and hemiboreal forest floor. In this thesis, sesquiterpene fluxes from the boreal forest floor correlated exponentially with temperature (studies **II** and **III**, Fig. 11). The very clear exponential temperature dependence of ambient air concentrations was also observed on-site (Hellén et al., 2018) and in previous studies where sesquiterpene fluxes from various plant species were strongly driven by temperature (Hansen and Seufert, 1999; Duhl et al., 2008; Kramshøj et al., 2016). Temperature promotes compound volatility, plant VOC biosynthesis (Guenther et al., 1993), VOC quantity and diversity in soil (Raza et al., 2017) and microbial enzyme activities of metabolic pathways that release VOCs (Mancuso et al., 2015). Warming may also have a major indirect impact on BVOC emissions in the Arctic due to changing vegetation composition (Valolahti et al., 2015). On a global scale, higher sesquiterpene emissions in the warming climate may affect ecological interactions and climate feedback mechanisms (Faubert et al., 2010c; Peñuelas and Staudt, 2010).

When all the measurements in this thesis from all four years and from all collars were combined, monoterpene fluxes from boreal forest floor were less affected by temperature than sesquiterpene fluxes (Fig. 11, studies **II**, **III** and **IV**). Temperature dependence of forest floor VOC exchange reflects temperature responses of various microbiological and plant ecophysiological processes present in the forest floor. It seems that sesquiterpenes are produced by partly different processes than monoterpenes. The temperature response and activity of certain VOC sources also depends on the season. In study **I**, the boreal forest floor was a higher monoterpene source in autumn than spring due to decomposing litter, despite that temperatures (0−15 °C) in spring and autumn were quite similar. We assumed the difference would be mainly due to the decrease in pool sizes from autumn with fresh litter to spring with more decomposed litter, rather than temperature. Another reason is that plant BVOC release is a complex mixture of direct, temperature-dependent release from storage and indirect, less temperature dependent processes related to BVOC synthesis or other physiological processes. Monoterpenes and sesquiterpenes may be emitted directly from plants after VOC biosynthesis or later from storages in resin ducts and glandular trichomes (Laothawornkitkul et al., 2009). Plants store BVOCs, because BVOC synthesis is a carbon-expensive process and because they prepare to release more BVOCs during abiotic and biotic stresses (Loreto et al., 2010, Niinemets et al., 2013).

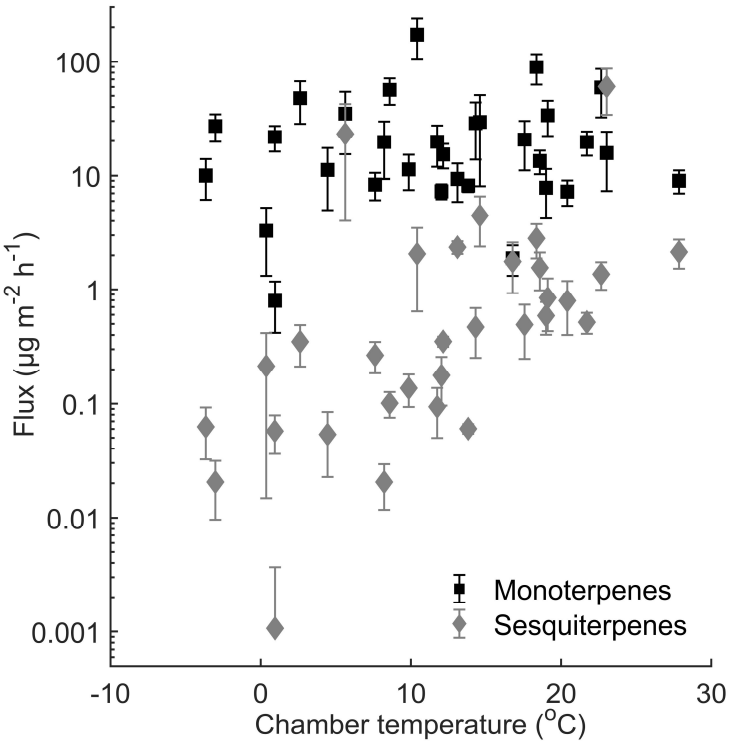

Figure 11. The relationship of total mean monoterpene (R^2=0.00, p<0.001***) and sesquiterpene (R^2=0.07, p=0.088) fluxes (µg m^{-2} h^{-1}) and chamber temperature (°C) from a *Pinus sylvestris* stand in Finland between April 2015 and July 2018. The fluxes are shown on logarithmic scale. Error bars are standard errors of the soil collars (2015:2–9 collars, 2016: 5 collars, and 2017–2018: 5–6 collars) (studies **II**, **III** and **IV**).

Roots may also release high quantities of monoterpenes from storage structures (Hayward et al., 2001), but is unclear whether these fluxes are driven by temperature. Litter is also a significant monoterpene source and these emissions typically follow temperature exponentially (Greenberg et al., 2012), as monoterpenes are released from needle storage pools during decomposition, where microbial enzyme activity is temperature dependent (Davidson and Janssens, 2006). Microbial VOC synthesis (Schulz and Dickschat, 2007; Yamada et al., 2015), which is enzymatically catalysed, is also likely driven by temperature. Finally, there is a temperature difference between the chamber headspace and the soil, as in study **III**, where the median difference between chamber and soil temperature was 3.6 °C. This may cause an error in measurements, as various VOC sources may respond differently to different temperatures. This distinction may be even higher in spring, when the soil is frozen and radiation heats evergreen leaves and the chamber headspace.

When we studied each chamber individually, forest floor fluxes of monoterpenes and oxygenated VOCs correlated with temperature (study **I**). Temperature, relative humidity and interaction of the measurement chamber with relative humidity and temperature explained 79–88% of the variation of forest floor fluxes of monoterpenes (Fig. 12), methanol, acetone and acetaldehyde using the mixed effects linear model (study **I**). A simple modelling approach appears to be able to estimate the VOC fluxes of a certain soil patch using temperature and relative humidity (study **I**). Relative humidity had a significant decreasing effect on forest floor monoterpene and methanol fluxes and for this reason, it was included in the model (study **I**). High VOC fluxes from the forest floor were underestimated by this model and these fluxes are likely driven by other environmental parameters or biological and physicochemical processes such as VOC release from fresh litter. An earlier study Aaltonen et al. (2013) observed the deposition of oxygenated VOCs on leaf surfaces and chamber walls when relative humidity increased within the chamber. Soil deposition is a significant phenomenon, as it is estimated to cover 42% of the total dry deposition of methanol in boreal stand (Zhou et al., 2017b). Prevailing temperature within the chamber is more similar to leaf temperature than to ambient temperature (Pape et al., 2009), which may also illustrate why VOC fluxes were well explained by the mixed effects linear model. Greenberg et al. (2012) also modelled VOC fluxes from the litter based on temperature, moisture content and labile carbon content of the litter.

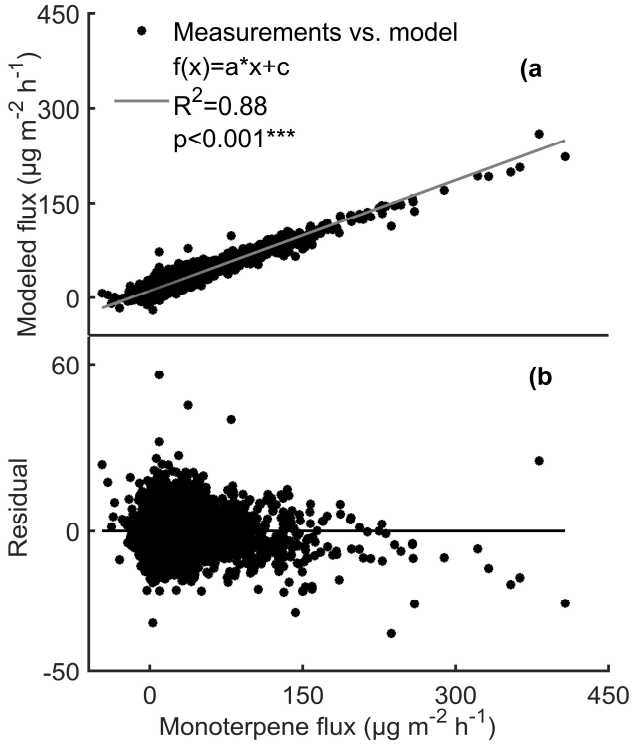

Figure 12. Comparison between measured monoterpene fluxes (µg m^{-2} h^{-1}) (a) from the forest floor and fluxes calculated using the mixed effects linear model with linear fit and (b) residuals (study **I**). The model is based on the flux data measured from all three chambers between 2010 and 2017 (modified based on Mäki et al., 2019). Grey line: measured flux = modeled flux.

Despite the complex temperature dependence of monoterpene fluxes from the forest floor in this thesis (studies **I–IV**), several warming experiments indicate that soil VOC fluxes will increase under the warming climate. Separate long-term trends from immediate temperature responses are important when discussing temperature dependences of VOC fluxes. Monoterpene fluxes were explained by chamber temperature, light and litter abundance in a temperate heath ecosystem after six-year-long elevated carbon dioxide levels, a longer summer drought and night-time warming (Davy and Esau, 2016). The 8–9 years long warming treatment with litter addition, increased isoprene, monoterpene and sesquiterpene emissions from a wet dwarf shrub heath (Tiiva et al., 2008; Faubert et al., 2010c; Michelsen et al., 2012). In subarctic tundra, monoterpene and sesquiterpene fluxes increased 85% and 130% in 2006 and 120% and 250% in 2007, when the prevailing temperature was increased by 1.9 and 2.5 °C (Faubert et al., 2010c). Based on a 15-year-long experiment of warming climate manipulation, microbial community structure was changed in a subarctic heath ecosystem (Rinnan et al., 2007), which may change microbial synthesis and uptake of VOCs.

This thesis emphasizes also the importance of tree species on soil VOC exchange and suggests that the global soil VOC emissions budget should be calculated by considering tree cover (study **II**) similarly to MEGAN, which estimates global BVOC emissions using plant functional type, vegetation temperature response, leaf age and soil moisture (Guenther et al., 2006; 2012). According to MEGAN estimates, global emissions from terrestrial vegetation are 89 TgC yr^{-1} for monoterpenes and 36 TgC yr^{-1} for sesquiterpenes (Acosta Navarro et al., 2014). Plant BVOC emissions have been estimated using prevailing light and temperature (Gunther et al., 1995, 2006). Monoterpene fluxes from *Pinus sylvestris* trees were well explained by only temperature (Tarvainen et al., 2005). VOC flux rates from the forest floor or from the forest stand are controlled by several factors, which lead to large quantitative, qualitative, temporal and spatial variation in flux rates (Peñuelas and Llusià, 2001). The challenging part is how to model the effect of spatial variation on forest floor VOC fluxes. Spatial variation is caused by varying microclimate, soil properties and vegetation cover, where phenology, growing strategy, root presence and resource use (water, nutrients and carbon dioxide) differ between species. Spatial variation of one stand may be captured with a high number of chambers coupled with the quadrupole-PTR-MS or proton transfer reaction-time of flight mass spectrometer (PTR-TOF-MS). It is equally important to cover spatial variation between stands using manual chambers, because the measurement system is easy to transport from one stand to another. For modelling purposes, it is also important to capture the inter-annual and seasonal variation of forest floor fluxes.

In this thesis, forest floor VOC exchange was not explained by soil moisture in the boreal climate (studies **I**−**IV**). The soil moisture effect on forest floor VOC exchange was less clear, because various VOC sources, which are present in the same soil volume, have different soil moisture optimum and they perform both direct and delayed responses to changing soil moisture. Soil moisture change may have a direct effect on forest floor VOC fluxes, because it regulates gas diffusion (Som et al., 2017a), microbial enzyme activities (Brockett et al., 2012), water availability of roots, volatilization of compounds from the soil surface and deposition of compounds on dry and moist surfaces (Cousins et al., 1999). Soil surface is covered by vegetation, where soil moisture may have an immediate effect on stomata conductance, as in studies by Nemecek-Marshall et al., (1995), Fall and Monson, (1992) and Filella et al., (2009), where stomata closure strongly affected oxygenated VOC exchange, but had only minor effect on isoprene exchange between leaf and the atmosphere. Soil moisture may also have a delayed effect on plant growth and further on plant VOC biosynthesis, as in a study by Lin et al. (2007), where BVOC emissions from stone pine (*Pinus pinea*) roots were changed by drought and in Svendsen et al. (2016), where BVOC emissions from high Arctic soil were strongly affected by plant cover and soil moisture.

Soil moisture varied more in the hemiboreal stands compared to the boreal stands. Increasing soil moisture decreased monoterpene fluxes from the hemiboreal forest floor (study **II**). This was likely, because the drying-wetting cycles may increase VOC biodegradation in soil (Cho et al. 2005). The soil moisture effect on monoterpene fluxes was likely visible also due to a fewer number of VOC sources present in the hemiboreal forest floor compared to the boreal forest floor (study **IV**). Ground vegetation cover was scanty in hemiboreal stands and soil processes likely drove the soil moisture effect on the fluxes. Study **IV** was supported by Som et al. (2017a), who found increasing soil moisture to inhibit VOC diffusion in soil and by Asensio et al. (2007), who reported high soil moisture to increase VOC uptake in Mediterranean soil. Soil moisture also regulates the activity of various microbial groups (Veres et al., 2014), which may affect soil VOC exchange. Seewald et al. (2010) found that VOC production was higher and more diverse in anaerobic than aerobic soils. High soil moisture may also increase VOC exchange. VOC bursts from litter were measured immediately after rain (Greenberg et al., 2012), indicating that wetting events have a major impact on soil VOC emissions (Rossabi et al., 2018) in certain ecosystems. Sesquiterpene fluxes from tropical soils released by microorganisms were also strongly stimulated by increasing soil moisture (Bourtsoukidis et al., 2018). Both microbial decomposition and biodegradation likely regulate VOC concentrations in soil and microbial community structure defines if soil is a net sink or source of VOCs (study **II**). It may also be difficult to detect clear patterns in a net VOC flux, which is a result of two processes to opposite direction. VOC synthesis may have a clear dependence with soil moisture simultaneously with VOC uptake or oxidation, but when the net flux is measured, these clear dependencies with soil moisture are not visible anymore.

3.7. Technical challenges when performing VOC exchange measurements

VOC exchange measurements from soils are challenging to perform (Faubert et al., 2010c; Aaltonen et al., 2011; 2013; Kolari et al., 2012). The VOC flux rates are small and isoprenoids are reactive or very reactive with hydroxyl and nitrate radicals and ozone with low ambient mixing ratios. Ambient mixing ratios are affected by light and turbulent mixing, and soil may emit VOCs also during night-time, when turbulent mixing is close to zero. Isoprenoid mixing ratios decreased with height below a forest canopy, indicating upward fluxes near the forest floor (Gordon et al., 2014). VOCs are highly diverse, with various physicochemical properties (size, reactivity and solubility) that impact the VOC dynamics in the soil, vegetation and atmosphere. Estimation of VOC production from individual soil processes is difficult, because various processes are present in the same soil volume. It is important to consider a variety of VOC sources present in the soil, because each VOC source has a unique emission potential, temperature and moisture response and seasonal dynamic. Microclimate (temperature, moisture and radiation) and vegetation cover also vary between chambers, which creates spatial variation in VOC flux rates. There is therefore plenty of room for methodological developments, and these issues should also be considered as thoroughly as possible when planning and designing experiments and measurement campaigns.

Temporal variation of forest floor VOC exchange was covered using an automated dynamic chamber coupled with the quadrupole-PTR-MS (study **I**). An automated dynamic chamber has been used in reactive trace gas measurements from grasslands (Pape et al., 2009). The dynamic chamber technique was field-tested using VOC standards and the quadrupole-PTR-MS (Kolari et al., 2012). The chamber technique caused 5–30% underestimates of VOC emission rates for isoprene, monoterpenes and oxygenated VOCs such as acetone, acetaldehyde and methanol (Kolari et al., 2012). Causing minimal disturbance for plant physiology and growth is important when conducting continuous measurements from the vegetation surface (Pape et al., 2009). Damaged roots and leaves emit VOC bursts that are much larger than emissions from healthy plant parts. Shoot chambers (Aalto et al., 2014) may eventually disturb shoot development and growth, while the disturbing effect for vegetation is small in the soil chambers, because they cover a larger vegetation surface instead of having direct contact with only one shoot. The PTR-MS has been widely used for BVOC flux measurements from various ecosystems (Seco et al., 2007). The main advantage of the quadrupole-PTR-MS is that a high sensitivity and short response time instrument is able to perform online measurements of VOC exchange from the forest floor, while calibration and identification of individual compounds was the main source of uncertainty. The quadrupole-PTR-MS was calibrated once or twice a month using VOC standards (Apel–Riemer Environmental, Inc., Broomfield, USA) based on Taipale et al. (2008).

Temperature may also increase in the chamber headspace, leading to overestimated flux rates, as the volatility and diffusion rate of the compounds is strongly temperature dependent (Niinemets et al., 2011). This problem may be minimized using a fan, by shading and by conducting a high enough air flow into the chamber headspace, and by only using a 15-minutes closure time in the on-line measurements with the quadrupole-PTR-MS. This problem is minimized further with automated chamber measurements, because we calculated the rate of change of concentrations during the first 400 seconds. In the future, chamber closure time should be minimized to five minutes. Flux and concentration measurements of water-soluble VOCs are somewhat biased, because these compounds are easily adsorbed on moist surfaces (vegetation, soil and chamber walls) or into water films on soil pores. For this reason, automated chamber data of water soluble VOCs were filtered with 75% relative humidity (study **I**). Kolari et al. (2012) recommended a threshold of 70% relative humidity in the chamber. Data coverage is typically low during night-time and from autumn to winter, because relative humidity in the chamber is continuously high. In the future, developing methods to capture soil VOC exchange during the night-time and in late autumn and winter during snow cover would be important. Despite the listed reasons, the dynamic chamber technique is the best existing method for soil VOC exchange measurements.

A manual dynamic chamber was used in studies **II**, **III** and **IV** to estimate forest floor VOC exchange in boreal and hemiboreal climates. The enclosure measurements for reactive trace gases have been used previously (Hakola et al., 2006; Aaltonen et al., 2011; 2013; Hellén et al., 2006). The flow-through chamber technique was tested for carbon dioxide and methane in earlier studies (Pumpanen et al., 2004). The high spatial coverage of the VOC flux measurements is the main advantage of the manual chamber measurements, as one chamber may be used to measure several soil collars. The TD-GC-MS is a highly sensitivity instrument with a long response time. The quadrupole-PTR-MS is used to measure the total monoterpene sum (mass 137), while the TD-GC-MS is able to separate compounds with the same molecular mass such as different monoterpenes and sesquiterpenes. The TD-GC-MS was calibrated using four to six VOC standards in a methanol solution that were injected into the Tenax TA Carbopack B adsorbent tubes and analysed with the samples. The total uncertainty of the VOC emissions at the 10$\mu g\ m^{-2}\ h^{-1}$ level, measured using manual chambers and analysed using the TD-GC-MS, varies depending on the compound, i.e. 14–44% for monoterpenes (60% for camphene) and 14–20% for sesquiterpenes (study **III**).

In this thesis, we measured the total monoterpene sum (mass 137) using the quadrupole-PTR-MS and the sum of ten different monoterpenes measured by the TD-GC-MS. Total mean monoterpene fluxes were found to agree relatively well between manual and automated dynamic chambers from April to August in 2015 (Fig. 13), even when the analytical

methods and soil collar locations differed at the SMEAR II station. The agreement between the different methods was lowest in October, which was likely explained by spatial variation, including different vegetation cover and especially varying litter biomass.

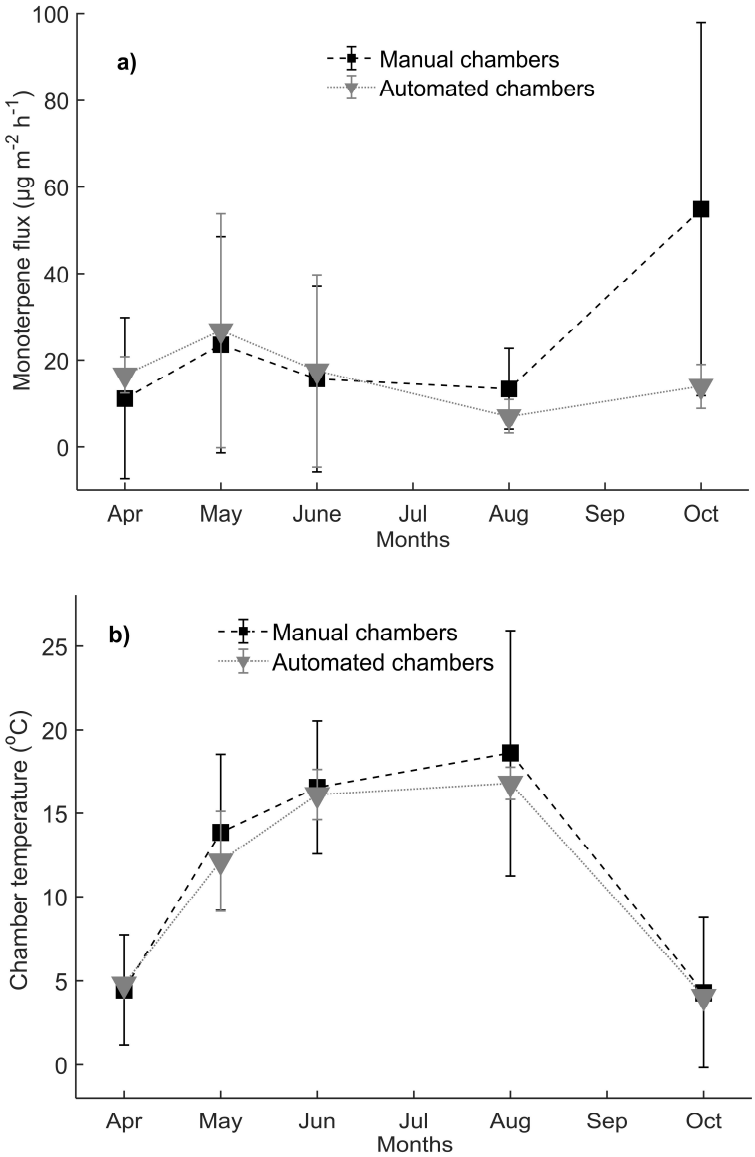

Figure 13. Monthly mean (a) monoterpene fluxes and (b) chamber temperature (°C) from a boreal forest floor measured using automated chambers (n = 3) connected to the quadrupole-PTR-MS and manual chamber measurements (n = 4–9) quantified using the TD-GC-MS in 2015. Monoterpene flux measurements using automated chambers were performed simultaneously with the manual chamber measurements. Error bars are the standard deviation of the chambers for each month.

Belowground VOC concentrations were quantified in study **IV**, to determine the belowground processes that release VOCs. A polytetrafluoroethylene (PTFE) membrane has been successfully used in measuring e.g. carbon dioxide gas concentrations in soil and water (Pumpanen et al., 2008; Cueva et al., 2015). In this study, we applied a similar membrane for soil VOC measurements. According to the permeability test, all the VOC standard compounds permeated the collector easily and reached a constant level in a few to seven minutes, also with the wetted collector (Fig. 14, study **IV**). Based on the seven-minute stabilization time of α-pinene, we speculated that sesquiterpene stabilization would take longer, and for this reason, we used a 15-minute stabilization time between individual VOC sampling cycles in the field.

The main advantage of our measurement procedure is that VOC concentrations were measured in situ compared to laboratory measurements, where soil processes are strongly disturbed, when soil cores or other soil samples are collected from the field and analysed in a laboratory. The weakness in VOC collection from soil samples is that root cutting is unavoidable (Smolander et al., 2006), however in the study we used pits which were done several months or years before the measurements, and thus the effect of disturbance should have been already rather small. VOC fluxes are likely biased by soil sampling, because root cutting may release high VOC emissions from damaged fine roots (Hayward et al., 2001) or accelerate decomposition processes, when root cutting increases labile carbon availability for microbes as root litter. Oxygen availability, temperature and soil moisture may also change in soil samples, when they are moved from natural conditions to the laboratory and shifting conditions may change microbial activity of soil samples. Spatial variation in the soil profile may cause random error in our VOC concentration measurements, because low volatility and highly reactivity sesquiterpenes may cause higher concentrations near the sources than mean concentrations in the soil horizon. Roots also contain monoterpene storages (Hayward et al., 2001) and uneven rhizosphere distribution between measurement pits will also cause spatial variation in the measurements.

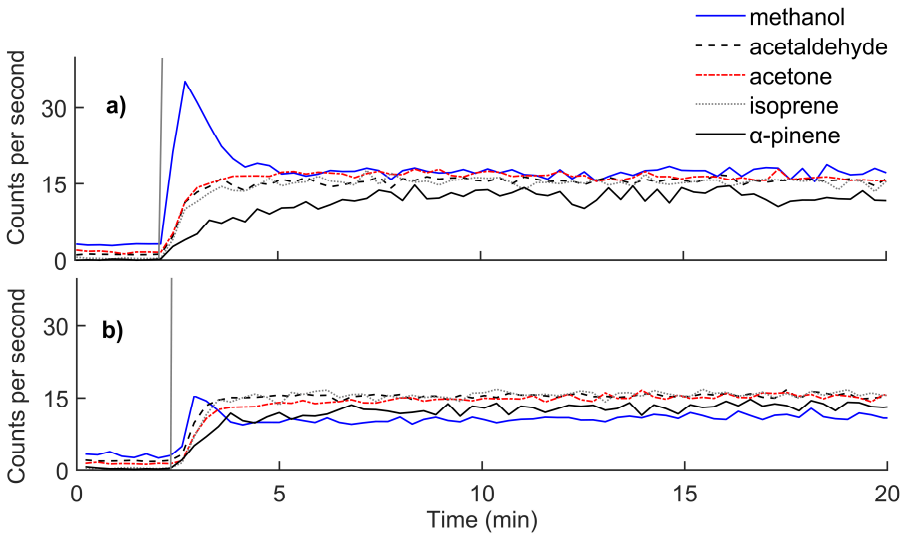

Figure 14. Results of the permeability tests of the a) dry and b) wet PTFE collector for isoprene, α-pinene and oxygenated VOCs, including methanol, acetaldehyde and acetone. Vertical line shows the time, when calibration gas was injected into the system (modified based on study **IV**).

4. CONCLUSIONS

Several studies have measured forest floor VOC fluxes from individual soil collars during short time periods, while spatial and temporal variation in soil VOC exchange remains unknown in many ecosystems. Only a few studies cover inter-annual variability of soil VOC exchange. Studies **I**–**IV** cover temporal variation between seasons and years using experimental set-ups and a continuous eight-year-long data set to define the magnitude and variability of VOC exchange between northern forest soils and atmosphere. We found that forest floor VOC exchange was stable between years (study **I**). The boreal forest floor was a major VOC source, as its contribution to the total boreal forest monoterpene fluxes was significant in spring and autumn (study **I**). The forest floor released large proportion of methanol to the total forest stand fluxes in spring and early summer (study **I**).

We concluded that temporal variation is the main source of flux rate variability from the forest floor within one studied stand (studies **I**–**IV).** We observed VOC source activity to be regulated by season (studies **I**–**IV)**. The seasonal dynamics of forest floor exchange were nearly opposite between monoterpenes and oxygenated VOCs (studies **I**–**IV**). Monoterpene fluxes peaked in spring and autumn. Sesquiterpenes and oxygenated VOC fluxes were highest in spring and summer (studies **I**–**IV**). Oxygenated VOC fluxes were mainly produced by plant ecophysiological processes (study **I**). Study **I** showed that forest floor monoterpene fluxes were released by both plant ecophysiological and microbiological processes. Boreal forest soil was found to be a significant VOC storage, and the O- and A-horizons appear to contribute mainly to soil surface VOC fluxes due to microbial metabolism, litter decomposition and root activity (study **IV**). Trees allocate photosynthesized carbon to roots and root-associated microbes, but the interaction of roots and mycorrhizal fungi using VOCs is not a main mechanism that leads to VOC fluxes from the forest floor (study **III**). Instead, forest floor VOC exchange is affected both by litter-driven microbial decomposition that releases VOCs and by the ground vegetation effect, where VOCs are released, but also adsorbed on leaf surfaces (study **III**) or dissolved in moist surfaces on leaves (study **I**). Studies **I** and **III** clearly show that forest floor VOC exchange is bidirectional. Studies **I**–**IV** provide evidence that compound volatilization, deposition and adsorption of lipophilic monoterpenes on leaf surfaces are the physico-chemical processes, which drive VOC exchange from the boreal forest floor.

The *Pinus sylvestris* forest floor was a higher monoterpene source compared to the *Picea abies* forest floor in boreal and hemiboreal climates due to decomposing *Pinus sylvestris* litter that releases more monoterpenes from needle storage pools than *Picea abies* litter (study **II**). Tree species affect forest floor VOC fluxes, and for this reason, the global soil VOC emission budget should be estimated by taking into account the vegetation cover. In the future it would be important to study forest floor VOC exchange from the different stands with varying stand age, tree species composition, forest management practises and soil type, because then it would be possible to generalize the results to the whole biome.

Studies **I**–**IV** show that temperature, soil moisture and relative humidity are the environmental parameters that mainly drive VOC fluxes from the forest floor. We found that VOC flux rates of individual chambers may be modelled well using the mixed effect linear model by considering the increasing effect of temperature and decreasing effect of relative humidity on VOC flux rates (study **I**). The boreal forest floor was also a temperature-driven sesquiterpene source (studies **II**–**IV**) that may contribute to atmospheric chemistry due to high reactivity and high SOA formation potential. These studies indicate that a global process-based model for soil VOC fluxes should be based on biological activity that is driven by temperature, soil moisture, soil composition, such as clay content and carbon and nitrogen availability, and litter quality and quantity.

Soil VOC exchange is a crucial research topic, because soils are the foundation of terrestrial ecosystems, where certain ecological interactions between species and organism groups, including plants, microorganisms and soil animals, are maintained using VOCs. The warming climate may change VOC dynamics in soils and affect soil VOC exchange in unpredictable ways. Long-term trends in soil VOC exchange are more difficult to detect and quantify compared to immediate temperature responses of flux rates, because they are often driven by multiple biological and physico-chemical processes. Long-term trends are an important research topic, because this knowledge is required to predict how much soils produce VOCs in the warming climate. Temperature affects soil VOC emissions in northern terrestrial ecosystems, while soil moisture has a stronger effect on VOC emissions in southern ecosystems, likely because temperature is a limiting factor for ecosystem productivity in the Northern Hemisphere and soil moisture in the Southern Hemisphere. It remains unclear how boreal ground vegetation cover will change in the warming climate and how this will affect VOC emissions. Spatial and temporal variation of soil VOC exchange is also poorly known compared to monoterpene emissions from vegetation, which are relatively well quantified in the Northern Hemisphere, while sesquiterpene emissions from vegetation are also poorly quantified.

Seasonal dynamics of forest floor fluxes (studies **I**–**IV**) indicate that VOC flux measurements should always cover seasonal and inter-annual variability. Continuous VOC exchange measurements should be performed in terrestrial ecosystems of various climate zones to define how much soils contribute to global VOC emissions and to predict how these emissions will change in the warming climate. Such knowledge is required to form a global soil VOC emission budget. It is also important to estimate spatial variation between stands using the measurement system, which is easy to transport from one stand to another. Soil VOC exchange should be measured simultaneously with ecosystem VOC

exchange, which would help estimate the impact of soil fluxes on atmospheric chemistry in various ecosystems. The below-canopy portion is missing from global VOC emission estimates, because of a major knowledge gap in how much the forest floor emits VOCs during different seasons and which environmental factors and biological processes regulate VOC fluxes from the forest floor. VOC exchange measurements require continuous development, as highly reactive VOCs are difficult to measure with low flux rates and small ambient mixing ratios. In soil VOC flux measurements, covering the whole snow-free period from spring to autumn is important, as VOC flux rates vary strongly between seasons. In experimental set-ups, it is crucial to measure soil VOC fluxes from the different treatments (trenching, vegetation removal, elevated carbon dioxide, fertilizers etc.) in similar temperature conditions, because temperature has a significant impact on VOC flux rates due to compound volatility.

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