

**Dissertationes Forestales 208**

Seasonal and spatial variation of VOC emissions from  
boreal Scots pine forest

Juho Aalto

Department of Forest Sciences  
Faculty of Agriculture and Forestry  
University of Helsinki

Academic dissertation

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*Author:* Juho Aalto

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*Thesis Supervisors:*

Prof. Jaana Bäck, Department of Forest Sciences, University of Helsinki, Finland  
Emer. Prof. Eero Nikinmaa, Department of Forest Sciences, University of Helsinki, Finland  
Doc. Taina Ruuskanen, Department of Physics, University of Helsinki, Finland  
Emer. Prof. Pertti Hari, Department of Forest Sciences, University of Helsinki, Finland

*Pre-examiners:*

Prof. Alex Guenther  
Department of Earth System Science, University of California, Irvine, USA  
Assistant Prof. Miikka Dal Maso  
Department of Physics, Tampere University of Technology, Finland

*Opponent:*

Dr. Carlo Calfapietra  
Institute of Agro-Environmental & Forest Biology (IBAF), National Research Council

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Boreal forests are the most significant source of volatile organic compounds (VOCs) in Northern Europe, emissions originating both from trees and forest floor. The VOCs are reactive trace gases that participate in chemical reactions in the atmosphere, thus affecting aerosol formation and climate.

The overall aim was to characterize the temporal and spatial variability of VOC emissions and explain the processes and phenomena affecting those. Extensive field measurements were used, including both gas chromatograph and mass spectrometer as VOC analyzers. A dynamic enclosure method was utilized in measuring VOC fluxes from the forest floor and emissions from Scots pine shoots.

The genetic background determines the blend of terpenoids emitted by Scots pine, thus having effects on the atmospheric composition. Forest floor and soil also has substantial effect on VOC fluxes on the ecosystem scale. In addition to the considerable spatial variation in VOC fluxes from the forest floor, there is variation of VOC emissions from Scots pine shoots; differences were associated with needle age, seasonality and growth processes. New foliage dominates the VOC emissions from Scots pine foliage during spring and early summer, when growth processes release significant amounts of VOCs, especially of monoterpenes. Scots pine shoots are a strong source of monoterpenes during the early stages of photosynthetic recovery; these periods last from a couple of days to about one week and are likely related to the protection of evergreen foliage against photo-oxidative stress.

The studies challenge the presumption of constant emission capacities, which is currently a common presumption in VOC emission inventories. Atmospheric concentrations of VOCs result from an output of the existing sources and their seasonal and spatial variation; this underlines the relevance and importance of details on large a scale. The findings provide new opportunities for developing VOC emissions models based on underlying physico-chemical processes.

**Keywords:** monoterpene, emission potential, dynamic enclosure, photosynthesis, chemodiversity, atmospheric chemistry

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## LIST OF ORIGINAL ARTICLES

The thesis is based on the following research articles, which are referred to in the text by their Roman numerals. The articles are reprinted with the kind permission of the publishers:

- I Bäck J., Aalto J., Henriksson M., Hakola H., He Q., Boy M. (2012). Chemodiversity of a Scots pine stand and implications for terpene air concentrations. *Biogeosciences* 9: 689-702.  
doi: 10.5194/bg-9-689-2012
- II Aaltonen H., Aalto J., Kolari P., Pihlatie M., Pumpanen J., Kulmala M., Nikinmaa E., Vesala T., Bäck J. (2013). Continuous VOC flux measurements on boreal forest floor. *Plant soil* 369: 241-256.  
doi: 10.1007/s11104-012-1553-4
- III Aalto J., Kolari P., Hari P., Kerminen V.-M., Schiestl-Aalto P., Aaltonen H., Levula J., Siivola E., Kulmala M., Bäck J. (2014). New foliage growth is a significant, unaccounted source for volatiles in boreal evergreen forests. *Biogeosciences* 11: 1331-1344.  
doi: 10.5194/bg-11-1331-2014
- IV Aalto J., Porcar-Castell A., Atherton J., Kolari P., Pohja T., Hari P., Nikinmaa E., Petäjä T., Bäck J. (2015). Onset of photosynthesis in spring speeds up monoterpene synthesis and leads to emission bursts. *Plant, Cell & Environment* 38: 2299-2312.  
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Author's contribution:

For compiling the summary, Juho Aalto alone was responsible. The author conducted collecting the field samples and participated in planning of the study, data interpretation and writing paper **I**. The author was responsible for the VOC measurements and data calculation and participated in commenting the manuscript of paper **II**. The author was responsible conducting the VOC emission rate and gas exchange measurements, and also conducted most of the data calculation, interpretation and writing the bulk of the text for papers **III** and **IV**.

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## INTRODUCTION

### Plant volatile organic compounds

Volatile organic compounds (VOCs), including wide variety of terpenoids, alcohols, aldehydes, alkenes, ketones and aromatic hydrocarbons with low boiling point, are present everywhere in the biosphere. Humans have long been able to recognize and even utilize some VOCs because of their characteristic scents. However, VOCs have been an object of study in continuously expanding scientific research since 1960s. The ability of terrestrial organisms to synthesize and release volatile organic compounds is commonplace. Human activities such as transport, energy production and the chemical industry are also sources of such emissions (Guenther et al. 1995). The biogenic sources of VOCs are dominated by plants: fruits and all the vegetative parts of the plants are typical sources of terrestrial terpenoids and other BVOCs (Biogenic VOCs), but in practice the plant leaves are the most significant source of BVOCs into the atmosphere (Guenther et al. 2012) and are therefore the most commonly studied subject in this field of research. Terpenoids are the most commonly studied group of VOCs and they are a diverse group of volatile organics sharing the basic structure of isoprene (1-n five-carbon isoprene subunits, C<sub>5</sub> isoprene, C<sub>10</sub> monoterpenes, C<sub>15</sub> sesquiterpenes etc.). The entire group of terpenoids includes thousands of different compounds and their enantiomers (Martin et al. 2002). Other common VOCs include short-chained alcohols, ketones and aldehydes, of which at least methanol, acetone and acetaldehyde are also emitted by forests (Rinne et al. 2007).

Volatile organic compounds have multiple roles in plants. Constitutively and inductively emitted VOCs are utilized as short-term and long-term defence towards biotic stress factors such as herbivores and pathogens (Yuan et al. 2009; Fineschi et al. 2013). Direct defence is based on the synthesis of compounds that are toxic or otherwise undesirable for the herbivores, whereas indirect defence is based on attracting the natural enemies of the pest insects (Yuan et al. 2009; Fineschi et al. 2013). Traditionally the defence against biotic stress agents and mechanical damage were thought to be the primary role of BVOCs, but since the 1990s it has been proposed they also have roles in counteracting abiotic stress factors such as extreme environmental conditions have been proposed (Niinemets 2009; Fineschi & Loreto 2012). Recently, Loreto & Fineschi (2015) suggested that the role of terpenoids is essential in running efficient photosynthesis and in overcoming short-term stress. It seems that in general the functions of VOCs are far more complex than was hitherto thought.

In addition to the functions for the sources of volatile organic compounds themselves, VOCs have effects on tropospheric chemistry because they contribute to the new particle formation and growth (Clayes et al. 2004; Kulmala et al. 2004; Tunved et al. 2006) as well as to the production and destruction of tropospheric ozone (Atkinson and Arey 2003). Non-methane VOCs and methane also compete for hydroxyl radical (OH) which extends the lifetime of methane (Kaplan et al. 2006). BVOCs also play a key role in production of Extremely Low-Volatility Organic Compounds (ELVOCs, Ehn et al. 2012; Ehn et al. 2014). These multiple impacts upon atmospheric composition clearly indicate that BVOCs interact with climate in many, as yet, poorly understood ways (Kulmala et al. 2004). A key property is that BVOCs decrease radiative forcing and thereby possibly slow down the climate

warming through increased cloud formation and through changes in precipitation patterns (Paasonen et al. 2013; Kulmala et al. 2014).

The atmospheric lifetime of a compound depends on its reactivity. Therefore, the atmospheric lifetimes of many terpenoids range from minutes to some hours (Rinne et al. 2007) though the lifetimes of oxygenated VOCs (OVOCs) are typically considerably longer. The current knowledge on seasonal variation in BVOC fluxes does not fully match what is known about the measured (Sinha et al. 2010; Nölscher et al. 2012) or modelled (Mogensen et al. 2011) OH-reactivity, which potentially is an indication of inaccurate estimates for BVOC emissions. Short-chained carbonyls also have an effect on the chemical composition of the upper troposphere because of their relatively long atmospheric lifetimes, which range from hours to several weeks or even months (Rinne et al. 2009).

Biogenic sources play a central role in the VOC budget over extensive areas, and this is especially the case in rural areas (Lindfors et al. 2000), where trees are considered as the main contributors to VOC emissions over one year. Biogenic sources also dominate atmospheric VOC production globally (Guenther et al. 1995). Current knowledge indicates that boreal forests are far less effective in producing VOCs than tropical forests: Despite the coverage of boreal areas exceeding that of the tropical forests, total VOC emissions from tropical forests are estimated to be almost an order of magnitude higher than those that originate from the boreal forests (Guenther et al. 2012). However, climate change is likely to bring about an increase in the importance of boreal forests as a source of volatiles because the activity of evergreen vegetation would be expected to increase when the cooler months become increasingly warmer and extend the growing season (Peñuelas & Staudt 2010).

Apart from inter-specific variation (Mentel et al. 2009) boreal tree species exhibit significant intra-species variation in the composition of emitted VOCs, especially for terpene emissions (Muona et al. 1986; Pohjola 1993; Hakola et al. 2001; Vuorinen et al. 2005; Tarvainen et al. 2005; Thoss et al. 2007). The physical or biochemical processes behind this variation remain unclear, but the variation is considered to be genetically determined property (Muona et al. 1986). This variation in emission composition may have important implications on the chemical reactions that take place in the atmosphere because of the differences in atmospheric lifetimes and reactivity properties of different terpenoids.

### **Environmental controls in VOC synthesis and emission**

Plants synthesize VOCs from photosynthesized carbon. The synthesis of volatile terpenoids is closely connected to the synthesis of primary metabolites including essential terpenoids such as gibberellic acid and carotenoids (Owen & Peñuelas 2005). However, VOCs are considered as secondary metabolites as they are not directly involved in the normal growth, development or reproduction of an organism unlike the essential terpenoids. Any metabolic process depends on the environmental conditions, substrate availability and physiological status of the organism. The synthesis of terpenoids in plants depends on temperature, solar radiation and carbon dioxide concentration acting as the short-term direct environmental controls (for review, see Niinemets et al. 2010a). The effects of these environmental conditions were first described as responses of primary metabolic processes; accordingly application of these principles to secondary metabolism is reasonable because as biochemical phenomena primary and secondary metabolism share common synthesis pathways and energy sources and are thus indivisible.



Terpenoids are produced via two different metabolic pathways. Isoprene (2-methyl-1,3-butadiene) and MBO (3-methyl-2-buten-1-ol) are both synthesized from dimethylallyl diphosphate (DMADP). DMADP and its isomer isopentenyl diphosphate (IDP) are, in turn, synthesized via the mevalonic acid (MVA) pathway in the cytosol or via the methylerythritol phosphate (MEP) pathway in chloroplasts. The precursor for isoprene and MBO (DMADP) is synthesized by the MEP pathway (Lichtenthaler et al. 1997; Ashour et al. 2010). Most monoterpenes as well as carotenoids are synthesized via the MEP pathway, whereas cytosolic MVA pathway synthesizes sesquiterpenes. Proteins that are coded by genes in the terpene synthase (Tps) family play a key role in terpenoid synthesis processes. Isoprene synthase (IspS) catalyzes the isoprene synthesis from DMADP (Ashour et al. 2010). The final precursor for monoterpenes is geranyl diphosphate, combined from IDP and DMADP produced by the MEP pathway. Monoterpene synthesis is catalyzed by several synthases (Ashour et al. 2010). Sesquiterpenes are synthesized from farnesyl diphosphate in the cytosolic MVA pathway by several sesquiterpene synthases (Ashour et al. 2010). Metabolite pool sizes and availability of energy tend to vary over time because of changes in environmental conditions, which affects the terpenoid synthesis (Li & Sharkey 2013a) in addition to the physical changes in reaction kinetics (Singsaas & Sharkey 1998). Metabolism relies upon enzymatic reactions, therefore these reactions have a temperature optimum, which in the case of terpenoid synthesis is relatively high, at about 40 °C, with nonlinear decreasing synthesis rates on both sides of the activity peak (Singsaas & Sharkey 2000). The energy source of all plant metabolism is photosynthesis. Li & Sharkey (2013a) discussed the evidence that the effect of light on isoprene synthesis is due to the influence of photosynthetic light reactions on the DMADP availability (Rosenstiel et al. 2002; Rasulov et al. 2009; Li & Sharkey 2013b) rather than any changes in IspS activation state (Sasaki et al. 2005). However, Monson (2013) stressed that DMADP analyses used as evidence for this statement are not unequivocal or trouble-free, hence the causal relationship between light and BVOC synthesis remain largely unclear. On the other hand, Guenther et al. (1993) implicated light in addition to temperature as a driving force for isoprene emissions, and Staudt et al. (2000) and Ghirardo et al. (2010) applied the approach to monoterpenes as well.

The evaporation of BVOCs from specialized storage structures is also controlled by temperature based on the compound volatility according to Henry's law (Copolovici & Niinemets 2005). The isoprene passes through two membrane systems (chloroplast and plasma membrane) because of its high volatility and it is released into the atmosphere without forming substantial storage or even a temporary buffer within the leaf. Lower volatility enables the storing of both mono- and sesquiterpenes in specialized storage structures such as resin ducts. Indeed, in the plants with option to store terpenoids, mono- and sesquiterpene emission from storage structures contribute 50–90 % of the total emissions whereas the rest originate directly from the synthesis (Ghirardo et al. 2010).

Although MEP and MVA pathways synthesize the essential and non-essential terpenoids, the syntheses of many other VOCs are the product of the main reaction or are synthesized as the by-products. Methanol emissions are primarily caused by the enzyme pectin methylesterase, which is most active in the cell wall of plant cells (Pelloux et al. 2007). Growing leaves emit considerably more methanol than mature leaves, and methanol potentially originates from cell wall formation (Hüve et al. 2007). The temperature dependency in the short-term regulation of methanol emissions is may be partially explained by the indirect and direct effects of temperature on growth processes including cell wall formation (Antonova & Stasova 1993). Stomatal conductance, in practice total gas phase conductance and methanol partial pressure difference, limits the methanol release from

substomatal cavity into the atmosphere (Harley et al. 2007). Harley et al. (2007) showed that methanol emissions tend to express light-dependency-like behaviour because stomatal aperture follows changes in photosynthetically active radiation to some extent. Acetone has multiple enzymatic and non-enzymatic sources in plant tissue (Warneke et al. 1999). Acetaldehyde emissions have been linked to the rapid light-dark transitions in leaves (Karl et al. 2002; Jardine et al. 2012) and to the oxidation of fatty acids, which causes emissions of green leaf volatiles as well (Graus et al. 2004). The further details concerning the emissions of acetaldehyde and green leaf volatiles (C6 and C9 aldehydes, alcohols and their esters, ul Hassan et al. 2015) are unclear but are probably linked to perturbations in the balance of carbon flows through primary and secondary pathways. This topic has been extensively reviewed by Monson (2013).

The overview of environmental controls for BVOC emissions from forests emphasizes the complexity and multidimensionality of the current knowledge. A large proportion of current knowledge on the effects of light and temperature on VOC emissions was obtained from studies that involved controlled laboratory conditions or short-term campaign measurements. These factors complicate the inference of the findings under field conditions or upscaling to regional and global scales. In addition to the instantaneous responses on environmental controls, pronounced seasonal changes in capacity to produce and release VOCs will affect the annual VOC emissions. These seasonal effects potentially have significant impacts on regional and global VOC emission estimates, therefore they are discussed here in conjunction with the methods used for obtaining those estimates.

### **The shortcomings of current BVOC emission models**

Estimates of biogenic volatile organic compound emissions are necessary inputs for constructing valid tropospheric chemistry and climate models because of the role BVOCs play in the atmosphere (Kaplan et al. 2006; Paasonen et al. 2013; Kulmala et al. 2014). These estimates can be obtained by using emission models that use emission algorithms (Guenther et al. 1991, 1993) combined with data on environmental driving variables, vegetation maps, land use patterns and/or some other data that represents types and amounts of BVOC sources.

The topic of VOC emission inventories has been reviewed by Rinne et al. (2009). The current emission models are supposed to describe BVOC emissions (especially terpenoid emissions) for inventory and modelling purposes, and have been mostly concentrated on estimating terpenoid emissions, although there are also some attempts to estimate the emissions of other VOCs. For example, in Finland several VOC emission estimates have been reported (Guenther et al. 1995; Simpson et al. 1999; Lindfors & Laurila 2000; Lindfors et al. 2000; Guenther et al. 2006; Tarvainen et al. 2007; Müller et al. 2008). The results of these inventories have usually been in the same order of magnitude as each other, but estimates have also shown remarkable variation, such as an order of magnitude differences in estimates on total isoprene emissions and more than 3-fold differences in estimates on total monoterpene emissions from Finland (Rinne et al. 2009).

Empirical emission algorithms are mathematical formulations of observed dependencies between environmental drivers and VOC emission rates, without the requirement to have fundamental basis on physico-chemical or biochemical theory. On the other hand, there are also emission algorithms that are primarily based on detailed description and theory of metabolic and other processes that generate VOC emissions (Zimmer et al. 2000; Bäck et al. 2005), but those models are not currently used in full-size emission inventory models at the

regional or global scale. The distribution into empirical and process-based models is a fine line, but the gradation of the utilization of process knowledge is considered to be a crucial factor in this sense.

The majority of the BVOC emissions originate from plant biomass and especially from the green leaves. It has been known for decades that isoprene emissions from vegetative parts of the plants follow light and temperature (Tingey et al. 1979; Tingey et al. 1980). Guenther et al. (1991, 1993) used the seminal work conducted by Tingey et al. and developed an isoprene emission algorithm based on the hypothetical light and temperature responses of isoprene synthesis. The mathematical formulation of these algorithms, referred to simply as G91 and G93 algorithms, mimic the light and temperature response of photosynthesis, using synthesis activity factors. These activity factors are related to the dependence of enzyme activity on temperature and the dependence of the electron transport rate on irradiation. The description of isoprene emissions included both synthesis activity factors but without any evaporation from pools, whereas monoterpenes were supposed to be emitted solely from the unconstrained pools (Tingey et al. 1980; Pierce & Waldruff 1991). This mathematical description is based on the dependence of saturation vapour pressure on temperature, although many tree species emit monoterpenes both from storage pools and directly from synthesis (Ghirardo et al. 2010). It is important to note that G-based algorithms namely G91, G93, G95 and the further phases of development (Guenther et al. 1999, 2006), have their roots in physiology: the photosynthesis is the source of carbon assimilates that are used in BVOC biosynthesis. However, the terpenoid biosynthesis processes that involve enzymatic reactions are largely ignored when the mathematical formulae describing the dependence of photosynthesis on environmental drivers is applied for modeling the terpenoid emissions.

The ‘G-based’ algorithms from the nineties (Guenther et al. 1991, 1993, 1995, 1999) are at the core of a global emission model given the acronym MEGAN (Model of Emissions of Gases and Aerosols from Nature, Guenther et al. 2006, 2012). In addition to the above-mentioned emission algorithms MEGAN includes a description of plant functional types. The latest version of MEGAN also includes long-term temperature response, leaf age and soil moisture algorithms when describing the responses of emissions to varying environmental conditions (Guenther et al. 2012). The G-based algorithms as a component of MEGAN are widely used in regional emission inventories (for review see Arneth et al. 2008; Grote & Niinemets 2008). A model given the acronym BEIS (Biogenic Emissions Inventory System, Pierce & Waldruff 1991) is also a ‘G-based’ emission model but its use is limited only to regional estimates. Despite the common foundation of BEIS and MEGAN there are considerable differences when the estimates produced by the two models are compared (Carlton & Baker 2011). These discrepancies probably arise from the differences in land-cover, emission capacity and canopy models.

The common feature of all existing BVOC emission inventory models is that they are based on the concept of constant emission capacities i.e. the capacity of the plant to produce and maintain VOC emissions under certain conditions. Alternatively the emission models use an arbitrarily defined scaling factor for reproducing the seasonal effects on emission capacities (Guenther et al. 2012). Seasonality has influences on emissions because the sensitivity of the tree to environmental driving factors, especially to temperature, is not constant over the year or growing season (Hakola et al. 2006; Holzke et al. 2006). The object of measurement (emissions) and the target of the determination (the emission potential) change over time, which complicates the determination of emission potentials especially with very limited amounts of data. Seasonality can also have an influence on the terpenoid emission potentials due to changes in inherent biological processes involved in biosynthesis of the compounds in addition to the instantaneous effects of light and temperature on

synthesis and/or evaporation from a pool (Niinemets et al. 2010a, b). Mathematical formulae that replicate the empirical seasonal phenomena have been developed by several authors (Keenan et al. 2009, Monson et al. 2012), but their focus was on deciduous trees, and evergreen plants such as Scots pine (*Pinus sylvestris* L.) were not assumed to exhibit any dependence of emission capacities upon the leaf developmental stage (Staudt et al. 2000). The VOC emissions from deciduous trees are more or less linked to the season when trees are in leaf (Lehning et al. 2001; Ciccioli et al. 2001; Grote 2007) although there may be distinct differences in emission capacities during the period with leaves (Hakola et al. 2001). Evergreens are in leaf all year round, and their emission dynamics must be linked to some other phenomena (Rinne et al. 2009), and these are probably partially caused by inherent, physiological factors (Grote & Niinemets 2008). Strong seasonal changes in temperature and irradiation characterize climatic conditions of the boreal area, which eventually has significant effects on metabolic processes such as photosynthesis (Rohde & Bhalerao 2007; Porcar-Castell 2011; Kolari et al. 2014) of boreal evergreens. The boreal evergreens in practice use the ability to regulate the state of photosynthetic machinery in such a way that a compromise between the risk of damages and the efficiency of carbon assimilation is pursued. When estimates of BVOC emissions are used as background information for atmospheric chemistry modelling, it is essential to produce emission data in such a way that the emission dynamics and their spatial distributions are taken into account. Thus, several aspects in BVOC emission models still require further improvements.

Any model or algorithm that is used for estimating or describing BVOC emissions is always bound to some given spatial and temporal scale in addition to being linked to fundamental presumptions used as the basis for the logic of the model. This constraint goes for measurements as well. Therefore any measurement is a compromise in relation to the temporal and spatial scales in addition to data quality and disposable resources. The spatial scale is typically chosen to present suitable functional unit such as leaf or canopy and then the results concerning that are upscaled to match the needs. The temporal scale is always an artificial factor to some extent because the processes involved in BVOC synthesis and emission take place within scale seconds or less. Because this would be an impractical temporal scale for most measurement and modeling purposes, instead a suitable operational temporal scale of minutes or hours is typically chosen. These limitations in measurement and modeling may lead to a situation with inadequate and unrepresentative data on phenomena coupled with high demand for producing estimates as background for further studies. Arneth et al. (2008) described this type of problem with estimates on regional and global estimates on terpenoid emissions. Regardless of how well the results of the different emission estimating methods match, it is obvious that there are omissions of key components of the models, especially for emission capacities.

In addition to the complexity of arboreal vegetation of boreal forests as VOC source, also forest floor and soil in combination form a multifaceted VOC source. Forest floor and soil include VOC fluxes from living plant roots, decomposition of organic matter, other microbial activity and ground vegetation (Gray et al. 2010; Insam & Seewald 2010; Veres et al. 2014). In addition to temperature, both ambient and soil temperature, the soil moisture likely has an effect on the processes producing and releasing VOCs (Veres et al. 2014) from the soil. This interaction arises from the dependency between soil moisture and microbial aerobic activity. In respect to the needs of comprehensive soil VOC flux modeling, the current information on driving forces of soil and forest floor VOC emissions and fluxes is scattered and incomplete (Asensio 2007, 2008; Insam & Seewald 2010). Detailed descriptions of VOC emissions from soil and forest floor are not implemented in currently used emission inventory

models such as MEGAN; instead an inexact method for estimating VOC emissions from soil is used (Guenther et al. 2012).

Whether one is primarily interested in the phenomenon itself or in developing empirical or process-based models, the first step is to observe all imaginable spatial and seasonal variation and dynamics of BVOC emissions, then try to find the characteristic patterns, related explanatory factors and causal relationships behind the variation. Continuous, long term (i.e. more than one year) field measurements of VOC emissions from boreal trees and soil are rarely conducted. Nevertheless, continuous measurements are essential when it comes to characterizing the phenomena that cause VOC synthesis and emissions. Moreover, long term emission data are essential when various models including emission models, atmospheric chemistry models etc. are to be developed and tested. The seasonal changes in VOC emissions are supposed to be driven by environmental conditions. Therefore, extensive measurements on both VOC emissions and environmental conditions are essential in studying seasonal and spatial variation on VOC emission dynamics. Any measurement method is a compromise between several factors, such as accuracy, spatial and temporal resolution and available resources. In practice, one of the key objectives of the studies presented in this thesis was to find out, how well the sources of VOCs can be observed, another major goal was to find how much information on the physico-chemical processes related to the sources can be obtained from measurements conducted under field conditions.

## Objectives

The studies presented in this thesis are hereafter referred to by their Roman numerals (**I-IV**). The overall motivation for the research done for this thesis was to explore the VOC sources of boreal Scots pine forest in order

- i. to reveal the spatial and seasonal variation in BVOC emissions up to stand scale,
- ii. to analyse the physiological mechanisms behind temporal variations in shoot scale emission rates to underpin a better description on dynamics of emissions, and
- iii. to contribute to better estimates on boundary layer chemistry in the boreal forest.

The extensive setup for long-term observation of BVOC emissions under field conditions was used to meet the specific objectives in the sub-studies, which are:

- to survey the intra-specific variation in composition of terpenoids emitted by Scots pine (**I**),
- to determine the seasonal changes and environmental drivers in VOC fluxes from boreal forest floor and soil (**II**),
- to describe the seasonal changes related to VOC emissions of Scots pine canopy and forest floor and analyze the physiological mechanism behind the annual rhythm (**II-IV**), and
- to characterize the spatial and temporal variation in VOC emissions from boreal forest (**I-IV**).

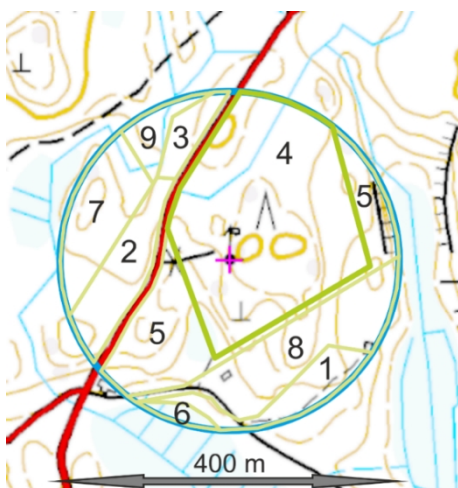
## METHODS

Study **I** was based on separate sampling and analysis of emission blends, whereas studies **II–IV** used an automated gas exchange measurement setup for online observation of emission rates and fluxes. The methods are outlined below; more detailed descriptions are found in the original articles **I–IV**.

### Study site

The studies were conducted at the SMEAR II measurement station (Station for Measuring Forest Ecosystem – Atmosphere Relations) in Hyytiälä, Southern Finland (61°N, 24°E, 180 m a.s.l.). The site is in a managed forest that is dominated by about 50-year old managed Scots pine with a closed canopy. The projected leaf area index is 2–2.5 m<sup>2</sup> m<sup>-2</sup> (Rautiainen et al. 2012) and the canopy reaches a height of 17 m, with a living canopy height of 8 m. A scaffolding tower provides access to the top of the canopy. Understorey is mainly composed of woody shrubs (*Vaccinium myrtillus*, *Vaccinium vitis-idaea* and *Calluna vulgaris*) and mosses (*Dicranum polysetum*, *Pleurozium schreberi*). The soil is mainly Haplic podzol with a thin humus layer and a low nitrogen level. More details about the site can be found in Hari & Kulmala (2005) and Ilvesniemi et al. (2009). The annual mean temperature at the site is 3.5 °C and mean annual precipitation 711 mm (Pirinen et al. 2012). In this thesis, winter refers to the months of December to February inclusive, spring from March to May inclusive, summer from June to August inclusive and autumn from September to November inclusive.

According to the stand history information the present stand was established by being sown with mixed seeds after prescribed burning in 1962. Therefore, the seeds may include various provenances, e.g. both from south and north. Scots pine predominate in most of the stands that are adjacent to the SMEAR II study stand. There are however also some stands that are dominated by Norway spruce (*Picea abies* L. Karsten) and a mixture of deciduous trees, mainly silver and downy birches (*Betula pendula* Roth and *Betula pubescens* Ehrh.) and trembling aspen (*Populus tremula* L.) within 200 m of the study site. The ages of the stands adjacent to SMEAR II study stand vary from 32 to approximately 90 years (Fig. 1 & Table 1). Scots pines at surrounding stands represent mainly local provenances.



**Figure 1.** The map of SMEAR II study stands and the stands adjacent to the study site, within 200 m radius around measurement mast, marked with a purple cross. The legend for the regeneration history of the stands 1-9 is presented in table 1.

### Chemotype screening (I)

Sample branches from 40 Scots pine trees were collected according to a systematic sampling protocol to analyze the chemotypic variation of the Scots pines around the SMEAR II station. The sample of 25 trees were located at the SMEAR II stand and 15 others at stands adjacent to the SMEAR II stand. The closest sampling trees were located at distance of 5 meters from the main tower of SMEAR II whereas the furthestmost sampled trees were at the distance of 185 m. The branches were collected from the upper part of the canopy of a southerly aspect. Samples included two most recent needle age classes of one shoot, which in this study occurred in 2008 and 2009, and sampling was conducted in August of 2009. The samples were stored in chilled (+4 °C) in dark plastic bags before collecting the emissions of the branch onto a Tenax TA adsorbent under standard laboratory conditions. Emission blends were analyzed and determined by a gas chromatograph-mass spectrometer (GC-MS) according the method described by Tarvainen et al. (2005). The instrumentation consisted of a thermodesorption instrument (Perkin-Elmer TurboMatrix 650 ATD) with a gas chromatograph-mass spectrometer (Perkin-Elmer Clarus 600) using HP-1 column (60 m, i.d. 0.25 mm). Authentic standards and NIST library were used to identifying the compounds. The detection limits varied between 10 and 200 ng m<sup>-3</sup> for most of the compounds.

The measured emissions were converted to relative abundance of different compounds. K-means clustering was conducted for the relative emission contents, in order to group the individual trees into 3–4 groups. The final approach was to use three groups: pinene, intermediate and carene trees based on the abundance of the most substantial compounds. A one-dimensional chemistry-transport model SOSA (Model to Simulate the concentrations of Organic vapours and Sulphuric Acid, described by Boy et al. 2011) was used for simulating the atmospheric relevance of chemodiversity.

**Table 1.** Regeneration history of the SMEAR II study stand and stands adjacent to the SMEAR II stand.

Stand number	Time of regeneration	Regeneration method	Species	Area ha (approx.) within 200 m of the SMEAR II mast
1	1920–1930	Natural	Mixture	0.2
2	1948	Natural	Scots pine	1.3
3	1957	Planting, saplings from Hyytiälä station	Scots pine	0.4
4 (SMEAR II)	1962	Sowing	Scots pine	5.6
5	1962	Planting, saplings from Hyytiälä station	Scots pine	1.5
6	1962–1966	Natural	Mixture	0.1
7	1962–1966	Natural	Scots pine	0.9
8	1973	Planting	Norway spruce-Scots pine mixture	2.3
9	1983	Natural, maybe also planting	Norway spruce/mixture	0.3

### Gas exchange measurement system (II–IV)

The automatic, dynamic gas-exchange measurement system (Fig. 2) consisted of cylindrical shoot enclosures (volumes 3.5 or 4.5 dm<sup>3</sup>, Fig. 3 b & c), box-type soil chambers (volume 80 dm<sup>3</sup>, Fig. 3 a), sampling tubing, and analyzers. The shoot enclosures were made of acrylic plastic and the internal surfaces were coated with transparent fluorinated ethylene propylene (FEP) film, whereas the soil chambers were constructed of aluminium frames and transparent FEP film coating. The enclosure remained mostly open and only closed intermittently for 3 minutes for sampling, typically four times during each three hour intervals. The duration of closure for the soil chambers was 14 minutes but there were only one closure per 3-hour cycle. The interior of the enclosures was in contact with ambient unfiltered air when the enclosure was open. During a closure episode, sample air was drawn from the enclosure into the gas analyzers along the sample tubes. Ambient air was simultaneously allowed to enter the enclosure through small holes in the chamber walls to compensate for the sample air-flow taken from the enclosure. The sample flow taken from the soil sampling chambers was compensated for by pumping ambient air into the chamber at a flow rate that was slightly higher than the sample flow rate in order to avoid a vacuum from being created inside the chamber. The ambient air used for this was typically somewhat drier than air inside the soil chamber before the closure took place. Air temperature inside the enclosure and photosynthetically active photon flux density (PPFD) were measured before and during the



closure and the values recorded at 5-s intervals. Carbon dioxide and water vapour concentrations during the closures were measured using infrared light absorption analyzers (URAS 4, Hartmann & Braun, Frankfurt am Main, Germany).

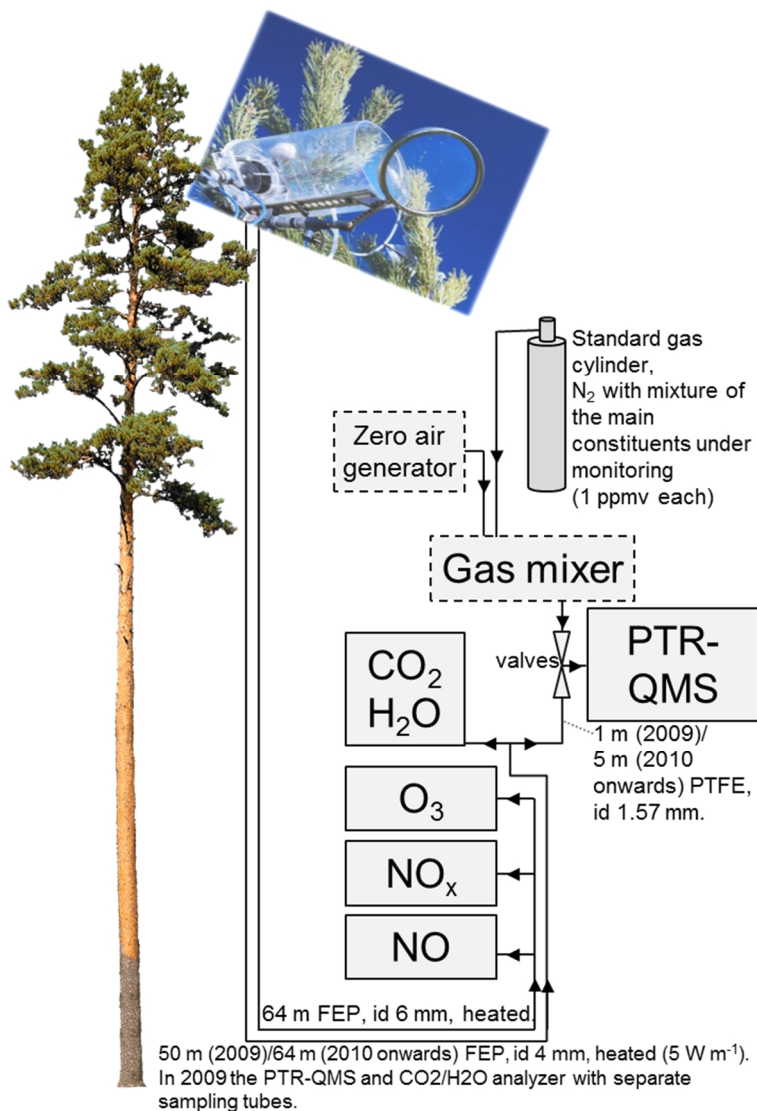
Shoot enclosure measurements for this thesis were conducted during years 2009–2013 inclusive, whereas soil chamber measurements were conducted in 2010 only (Table 2). The shoot enclosures (studies **III** and **IV**) were installed to unshaded top canopy branches at least one month before the measurements began to ensure that any damage to the shoot potentially caused during the installation would not affect the measured VOC emission rates to any great extent. All buds of the mature shoot and all auxiliary buds of the growing shoot were also gently removed about one month before the installation occurred, to avoid excessive numbers of shoots from growing inside the enclosure. One enclosure in study **III** had a mature shoot inside and another enclosure had only a terminal bud inside the enclosure (hereafter referred to as ‘growing shoot’). The growth of the growing shoot was recorded by using photographic measurements, with theoretical accuracy of 0.065 mm and practical repeatability of less than 1 mm.

### **Proton transfer reaction – quadrupole mass spectrometer as the online VOC emission detector (II–IV)**

The VOC sample ( $0.1 \text{ dm}^3 \text{ min}^{-1}$ ) for PTR-QMS (Photon transfer reaction – quadrupole mass spectrometer, Ionicon Analytik, Innsbruck, Austria) was taken from a sample tube that used flow rate  $1 \text{ dm}^3 \text{ min}^{-1}$ , which led the sample air from the enclosure towards the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  analyzers. A heated FEP-tubing of 64 m length (i.d. 4 mm) was used as a high flow sample tube from 2010 onwards, whereas in 2009 the sampling for PTR-QMS analyses were taken using a separate 50 m long heated FEP tubing. The sample for a high sensitivity PTR-QMS was drawn from the high flow sample tube through a polytetrafluoroethylene (PTFE) tube (i.d. 1.57 mm and length of 5 meters).

**Table 2.** The measurement periods of the four studies. Automated gas-exchange measurements at SMEAR II are continuous, but selecting material for papers **II–IV** was based on the study objectives.

	<b>Study I</b>	<b>Study II</b>	<b>Study III</b>	<b>Study IV</b>
2009	August		March–July	March–May
2010		May–December	March–October	March–May
2011			March–October	
2012				March–May
2013				March–May



**Figure 2.** Schematic figure of the main components of the gas exchange measurement system coupled with PTR-QMS. The specific gas analyzers are marked by the rectangles with solid borders, whereas the other instruments are marked using rectangles with a dashed border. The calibration system consists of a zero air generator, standard gas cylinder and gas mixing and the setup illustrated was used from summer 2011 onwards. In summer 2010 a commercial gas mixer (GCU, Ionicon) with matching functioning was used, and in 2009 as well as partly in 2010 and in 2011 the standard gas and the zero air flows were adjusted and mixed using pressure regulator and needle valves as expressed in Taipale et al. (2008). Data recorded with O<sub>3</sub>-, NO<sub>x</sub>- and NO -analyzers was not utilized in this thesis. The PTR-QMS analyzer was also used to measure the ambient VOC volume mixing ratios at several sampling heights between 4.2 and 67 m (the details not shown in the figure and data not used in this thesis).



**Figure 3.** Different enclosure types used in studies **II** (a, soil chamber) and **III–IV** (b & c, shoot enclosures). The volume of the soil chamber was 80 dm<sup>3</sup>. The volumes of the shoot enclosures were 4.5 dm<sup>3</sup> (b) or 3.5 dm<sup>3</sup> (c), depending if growth of the shoot inside the enclosure was allowed or not.

The operating procedures for PTR-QMS analyses (de Gouw & Warneke 2007) are explained in detail by Taipale et al. (2008). Briefly, PTR-QMS measures the total concentration of all compounds that have equal atomic mass with a resolution of 1 amu (atomic mass unit). The ionization protonates the target compound, which leads to an increase in atomic mass of the target compound of 1. The time resolution (interval between consecutive measurements) depends on the number of measured masses; in studies **II–IV** it was 9.5–12.5 s with an integration time of 1 s per mass. The three sections of the instrument are the ion source (producing H<sub>3</sub>O<sup>+</sup>-primary ions), the drift tube (taking care of the photon transfer reaction) and the quadrupole mass spectrometer (selecting and detecting the target ions). The PTR-QMS method is capable of detecting a wide variety of compounds; the compounds present in the standard gases and enclosure measurement are listed in table 3. The lower limit of detection was around 10–300 pptv (Taipale et al. 2008). The PTR-QMS

was operated with drift tube voltages 450–510 V and drift tube pressure 1.93–2.27 mbar. The primary ion signal ( $\text{H}_3\text{O}^+$ ) was most of the time above  $1 \times 10^7$  cps, typically  $1.5\text{--}2.5 \times 10^7$  cps. Whenever the primary ion signal decreased below  $1 \times 10^7$  cps, the parameters were adjusted to ensure sufficient primary ion signal. The contribution of  $\text{O}_2^+$  impurity ions (compared to the primary ion signal) was about 3% or lower most of the time.

Any background signal resulting offset on the signal of the target compound potentially causes systematic error. Such background signals were corrected by measuring the signal from the air that flows through the zero air generator (Parker ChromGas Zero Air Generator, model 3501, USA) obtaining the associated signal (background signal) and then subtracting the background signal from the measured volume mixing ratios. It is worth noting that the emission rate measurement by the enclosure method is not particularly sensitive to this type of fairly constant systematic error. The systematic bias in this method is by definition equal for all the absolute values and therefore it does not affect the differences between the absolute values, which are obtained by subtraction. Calibration of the PTR-QMS was conducted two to four times per month in order to correct the changes in the sensitivity over the mass range mainly caused by adjusting the voltage of the secondary electron multiplier. The standard gases contained ca. 1 ppmv of methanol, acetaldehyde, acetone, isoprene,  $\alpha$ -pinene and several other compounds (Apel-Riemer Environmental Inc., USA, and Ionimed GmbH, Austria, see table 3). The VOC concentrations in the standards gas cylinders tend to decrease over several years. Therefore, the standards gas containing cylinders were replaced every second or third year by a newly filled cylinder. When the VOC concentrations of the contents of the 2-3 year old standard gas cylinder were compared to the contents of a fresh standard gas cylinder, the difference in concentration to the original concentration was in general within 10%, but after some more years (4-6 year old standard gas) the detected concentrations of some VOCs decreased to as low as 50-70% of the original concentrations. The standard gas was diluted close to the atmospheric concentrations, about 5–20 ppbv using the zero air generator. The emission rate calculations were expressed as per dry needle mass, which were determined at the end of each measurement period.

The proton transfer ionization coupled with quadrupole mass spectrometer only distinguishes compounds based on their mass-to-charge ratio ( $m/z$ ), thus the same mass can include several different compounds or their fragments. For example the  $m/z$  of 69 includes both MBO (in fragmented form) and isoprene (de Gouw & Warneke 2007). Scots pine and many other pine species are known to emit considerable amounts of MBO (Zeidler & Lichtenthaler 2001; Tarvainen et al. 2005; Gray et al. 2006), but only negligible amounts of isoprene. It is therefore very likely that in this case the emission at  $m/z$  69 we obtained from Scots pine shoots was mostly composed of the MBO fragment. Isoprene fluxes from forest floor have been reported (Aaltonen et al. 2011); the fluxes detected at  $m/z$  69 from forest floor may contain both isoprene and MBO fragment.

**Table 3.** Information on standard gas composition and protonated masses measured using PTR-QMS in 2009–2013.

		Standard gas cylinder		
		a	b	c
Period of use		2009, Oct 2010–Jul 2011	March–Sep 2010	Jul 2011–2013
Manufacturer		Apel-Riemer Environmental	Ionimed	Apel-Riemer Environmental
m/z	Compounds in N <sub>2</sub>	Concentrations (ppmv) reported by manufacturer		
31	Formaldehyde	-	1.01	-
33*, <sup>x</sup>	Methanol	0.67	1.01	1.02 <sup>1</sup>
42	Acetonitrile	1.01	1.01	0.97
45*, <sup>x</sup>	Acetaldehyde	0.99	1.01	1.14
47	Ethanol	-	1.01	-
57	Acrolein	-	0.98	-
59*, <sup>x</sup>	Acetone	1.05	1.02	1.03
69*, <sup>x</sup>	Isoprene	1.02	0.99	0.96
71	Methyl vinyl ketone <sup>a,c</sup> or crotonaldehyde <sup>b</sup>	0.92	0.92	1.00
73	Methyl ethyl ketone	1.11	1.01	1.02
79*	Benzene	1.21	1.01	1.00
81*, <sup>x</sup>	Monoterpene fragment	-	-	-
83	Hexanal fragment	0.90	-	-
87 <sup>x</sup>	MBO	-	-	-
93 <sup>x</sup>	Toluene	1.16	1.02	0.96
99*	Hexenal	-	-	-
101*	Hexanal	1.15	-	0.84
107	o-xylene <sup>b</sup> or m-xylene+o-xylene <sup>a,c</sup>	2.08	1.03	1.91
113	Chlorobenzene	-	1.02	1.02
121	1,2,4-trimethylbenzene <sup>a</sup> or 1,3,5-trimethylbenzene <sup>c</sup>	1.04	-	0.96
129	Naphtalene	1.00	-	1.14 <sup>2</sup>
137*, <sup>x</sup>	α-pinene	0.93	0.93	0.97
153*	Methyl salicylate	-	-	-
148	1,2-dichlorobenzene	-	1.03	-
182	1,2,4-trichlorobenzene	0.91	1.01	0.93

In addition to the measured protonated masses above, m/z 21 (water isotopes) and m/z 39 (water cluster isotopes) were also included in the measurement due to volume mixing ratio calculation requirements.

\* = Mass included in enclosure measurements until summer 2012.

<sup>x</sup> = Mass included in enclosure measurements from autumn 2012 onwards.

- 1) Not used in volume mixing ratio calculation due to unstable results in calibration; instead the volume mixing ratios were corrected according to the relative transmission curve, see Taipale et al. 2008.
- 2) Not used in volume mixing ratio calculation due to unstable results in calibration.

a, b and c refer to the three cylinders containing the VOC standards in N<sub>2</sub> gas.

### Emission rate calculations (II–IV)

The VOC emission rate calculation and other gas-exchange calculations of the results measured using the dynamic, flow-through measurement system were based on the mass balance equation

$$V \frac{dc}{dt} = E + F(C_s - C) \quad (1)$$

where  $V$  is the volume of the enclosure,  $C$  is the concentration inside the enclosure,  $E$  is the source of trace gas or water vapour inside the enclosure (emission source),  $F$  is the volumetric flow rate through the enclosure and  $C_s$  is the concentration in the (ambient or supply) air entering the enclosure (Hari et al. 1999; Kolari et al. 2012). This approach is used if a steady-state concentration is not reached, and solving the equation to determine the concentration  $C$  as a function of time  $t$  since the beginning of the closure leads to the solution

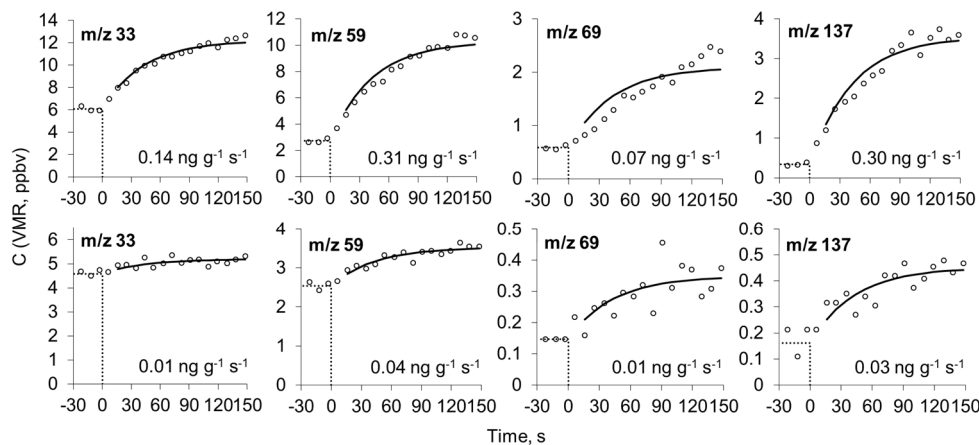
$$C(t) = C_0 + \left( \frac{C_s - C_0}{V} + \frac{E}{F} \right) \left( 1 - e^{-\frac{Ft}{V}} \right) \quad (2)$$

where  $C_0$  is the initial concentration measured in an open chamber (Kolari et al. 2012). Equation 2 is used applied when the concentration in the supply air ( $C_s$ ) is unequal to the ambient concentration before the closure (II); if those concentrations are equal the equation simplifies to the form used in studies III–IV:

$$C(t) = C_0 + \frac{E}{F} \left( 1 - e^{-\frac{Ft}{V}} \right) \quad (3)$$

Depending on whether the supply air is fed to the enclosure or not, equation 2 or 3 is fitted to the data by using the least-squares method, which determines the emission rate  $E$ . Figure 4 represents examples of the mass balance equation fits in moderate and low emission rate events for different compounds. In some cases the calculated initial emission rate may be slightly overestimated, in this particular case for  $m/z$  69 in the upper panel (fig. 4). This overestimation is probably because of an increase in temperature during the closure has a stimulating effect on the synthesis and therefore the emission rate increases during the closure.

VOC release from Scots pine shoot is hereafter referred to as ‘emission’, and from the soil and forest floor as ‘flux’. Negative sign indicates that the detected net flux is negative, and is caused by deposition, adsorption, absorption or any combination of these of VOCs. The scheme for calculating  $\text{CO}_2$  exchange rate of the Scots pine shoots and forest floor matches to that presented above for VOCs.



**Figure 4.** Examples of the mass balance equation fit in case of moderate emission rates measured around midday on 25.5.2013 (upper row) and low emission rates measured during the night on 25.5.2013 (lower row). The open circles represent the measured volume mixing ratios (VMR), and solid line represents the mass balance equation fitted utilizing the least sum of residual squares. The chamber is closed with  $t=0$ , expressed by a vertical dashed line. Three measurements in the beginning were conducted when the enclosure was open; the mean VMR observed during those measurements is expressed with horizontal dashed line. The corresponding emission rate is expressed in each sub-figure.

### Emission potential algorithms (IV)

An approach called the ‘hybrid algorithm’ was used in study **IV** in order to assess the changes in temperature and light dependencies of monoterpene emissions (Ghirardo et al. 2010). This algorithm is underexploited and yet it offers a handy tool for following seasonal changes of monoterpene emissions from plants. It is also noteworthy that this algorithm has strict constraints: the data must follow the dependencies that serve the basis for the hybrid algorithm; otherwise there is increased risk of unpredictable results. In uncontrolled field studies temperatures also depend to some extent on solar radiation, which may partially mask the effect of light on terpenoid synthesis.

In the hybrid algorithm the emission rate  $E$  is described as a function of two source terms, referred as *de novo* emissions ( $E_{\text{synth}}$ ) and pool emissions ( $E_{\text{pool}}$ ):

$$E = E_{\text{synth}} + E_{\text{pool}} = E_{0,\text{synth}} C_T C_L + E_{0,\text{pool}} \gamma \quad (4)$$

$E_{0,\text{synth}}$  and  $E_{0,\text{pool}}$  are the emission potentials of the two sources, *de novo* and pool emissions, respectively.  $C_T$  and  $C_L$  are unitless synthesis activity factors that describe the dependence of enzyme activity on temperature ( $C_T$ ) and the dependence of electron transport rate on light ( $C_L$ ), expressed as used by Guenther et al. (1991, 1993). Also the unitless temperature activity factor related to pool emissions,  $\gamma$ , is the same as used by Guenther et al. (1991, 1993), and describes the dependence of saturation vapour pressure on temperature:

$$E_{pool} = E_{0,pool} e^{\beta(T-T_0)} \quad (5)$$

Where  $E_{0,pool}$  is the standard emission potential under standard temperature  $T_0=30$  °C, logarithmic part refers to  $\gamma$ ,  $T$  is (leaf) temperature and  $\beta$  is an empirical parameter that describes the temperature dependence of the monoterpene evaporation from the monoterpene pools. The approach is based on the compound volatility as described by Copolovici & Niinemets (2005), and in case of many terpenoids  $\beta$  usually has the constant value of  $0.09$  °C<sup>-1</sup> (Guenther et al. 1993). This pool algorithm has also been widely used without the hybrid component because it is assumed that all emitted monoterpenes originate from pools (Guenther et al. 1993). In this work the pool algorithm (Eq. 5) is used, in addition to the use as a part of hybrid algorithm, to estimate how emission rates can be affected by the difference between the ambient and the enclosure temperature, and to estimate the bias of G93 approach compared to the measured mean emission rates; in these cases it is used independent, excluding the  $E_{0,synth}$  (Eq. 4).

The operational formulation of the hybrid formulation for emission rate is converted as follows (Ghirardo et al. 2010):

$$E = E_0 [f_{synth} C_T C_L + (1 - f_{synth}) \gamma] \quad (6)$$

Here  $f_{synth}$  (range from 0 to 1) is the *de novo* emission potential expressed as a fraction of the total emission potential, and  $E_0$  (ng g<sup>-1</sup> s<sup>-1</sup>) is the total monoterpene emission potential under standardized conditions. The variation of parameters  $E_0$  and  $f_{synth}$  were used for following the changes in emission potential. The underlying idea is that the emissions that follow light and temperature (as expressed in temperature and light dependent synthesis activity factors  $C_T$  and  $C_L$ ) originate directly from synthesis (*de novo* emission), and correspondingly, the emissions that follow temperature activity factor  $\gamma$  originate from storages (pool emission). The value for temperature dependence of evaporation from storage structures,  $\beta$ , was kept constant at  $0.09$  K<sup>-1</sup> (Guenther et al. 1993) in study **IV**.



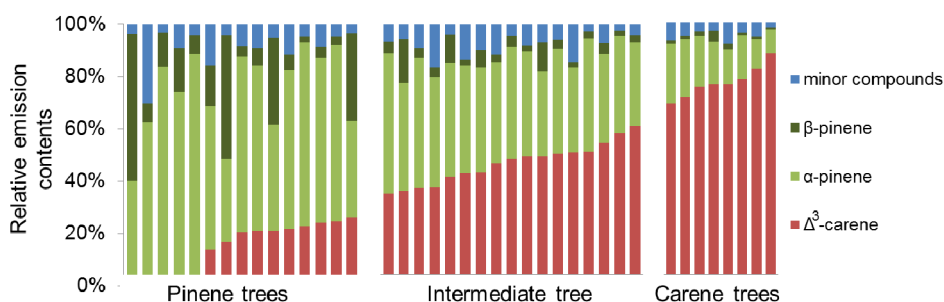
## RESULTS AND DISCUSSION

The long-term measurements in the studies **II–IV** revealed temporal variation in the VOC emission patterns of Scots pine whereas study **I** focused on the spatial variation in the emission blend. The main findings are introduced below; more detailed results are found in the original articles.

### Chemodiversity (I)

Clear chemotypic variation between individual Scots pines was detected in study **I**. The sample trees were classified as carene-, pinene- or intermediate trees based on the relative emission contents of  $\Delta^3$ -carene,  $\alpha$ -pinene and  $\beta$ -pinene. The intra-specific variation in the proportions of emitted  $\Delta^3$ -carene and  $\alpha$ -pinene ranged from 0% up to over 80% (Fig. 5). In general the sampled trees emitted  $\Delta^3$ -carene and  $\alpha$ -pinene in almost equal proportions, about 40% for both compounds. Hakola et al. (2006) and Tarvainen et al. (2005) have also reported that emissions of Scots pine individuals growing in one stand were either  $\Delta^3$ -carene or pinene (both  $\alpha$ -pinene and  $\beta$ -pinene) dominated.

Different emission blends from individual Scots pine trees are called chemotypes (Thoss et al. 2007). The re-analysis of the results measured by Tarvainen et al. (2005) suggests that the chemotypes are relatively stable over a growing season and also over a longer time frame, which is logical because the chemotypes are expected to be genetically determined (Muona et al. 1986). The evidence as to whether the chemotypes also affect the quantities of emitted monoterpenes is limited, but Yassaa et al. (2012) found some indication that the ‘pinene trees’ (trees emitting mainly pinenes) are stronger monoterpene sources than the ‘carene trees’ (trees emitting mainly  $\Delta^3$ -carene). The presumption that the chemotypes are genetically determined leads to the hypothesis that the emission blend of a stand is affected by the genetic constitution of its population.



**Figure 5.** Chemotypic variation among sample trees in paper **I**. The trees were clustered into three groups based on the relative abundance of carene and pinenes in total emissions.

Stand history had an effect on chemotypic diversity. For example,  $\Delta^3$ -carene was more abundant than  $\alpha$ -pinene in the emissions from the Scots pine of the SMEAR II stand, whereas these proportions were reversed for the trees on the surrounding stands. The SMEAR II stand is the only stand in the whole surrounding vicinity of Smear II station in which the forest regeneration was conducted by sowing (Fig. 1 & table 1). The quality standards for seeds used for direct sowing were very lax during the 1950s and 1960s, and the variation in seed quality will probably have resulted in the wider genetic constitution of the stand than for stands sown with seeds selected under more strict quality standards. During the 1950s, 1960s and 1970s the closest nursery was located at Hyytiälä forestry field station, less than one kilometer from the current SMEAR II study stand. Saplings for the plantings conducted at the surrounding study stands came from that nursery. The common practice in the mid-20<sup>th</sup> century was to collect the seeds for the nursery from only a couple of stands that were located relatively close to the nursery, and this would result in relatively narrow genetic variation amongst the saplings of particular nursery. However, natural regeneration may also result in relatively narrow genetic variation because the seeds originate from the trees growing at or adjacent to the regenerated stand. The genetic variation in stands established around the mid-20<sup>th</sup> century is therefore likely to be the highest for seed-sown stands and somewhat lower for naturally regenerated or planted stands. The high variation in relative emission contents recorded for the SMEAR II stand is in agreement with the hypothesis that different seed origins may represent different chemotypes (Muona et al. 1986, Pohjola et al. 1993). More support for this hypothesis is found when the wide variation in relative emission contents is compared with the low variation in the corresponding relative emission contents of the surrounding stands. The surrounding stands represent mainly local genetic origins, which could explain the lower variation found in their relative emission contents. The linkage between the genetic origins and chemotypes remains an open question until further studies concerning emission blends of known origins are carried out.

Muona et al. (1986) found that high carene-type trees are more common among southern stands than among northern stands. Pohjola (1993) has also reported that low  $\Delta^3$ -carene emitters are more common in northeastern areas of Finland than in southwestern areas. Muona et al. (1986) reported that for some unidentified reason there was no geographical pattern related to carene emissions amongst plustrees, which are high quality individual trees (high quality phenotype) that are selected for the forest tree breeding purposes. According to both Muona et al. (1986) and Pohjola (1993) the geographical variation in the incidence of high carene emitters is especially marked for natural stands and it presumably depends on ecological factors such as day length, length of the growing season, pollen production and gene flow from the south to the north. Muona et al. (1986) and Pohjola (1993) used 90% as a cut-off limit for high carene emitters, but in the study I no trees with such a high carene emissions were found. It is plausible that the lack of very high carene emitters is a consequence of the fact that very high carene emitters characterize southern or southwestern provenances. Nonetheless, this result is not in full agreement with the results of Muona et al. (1986) who were able to find some high carene emitters among northern Scots pine provenances. The fact that they were not able to find a connection between carene emissions and origin among plustrees may be a consequence of unidentified genetic coupling of high carene emissions and some visible character favoured in the selection of the plustrees. Muona et al. (1986) stated that favouring southern features does not explain the missing geographical variation in the carene emissions of plustrees. It is possible that high carene emission and some other feature that is not related to geographical location may be coupled.

Earlier SMEAR II measurements found that the above-canopy concentrations in the site had been dominated by  $\alpha$ -pinene, which in general is three times more abundant in ambient

air than the second most common compound,  $\Delta^3$ -carene (Hakola et al. 2009, sub-study I). On the other hand, branch scale measurements revealed that  $\Delta^3$ -carene was 4–5 times more abundant than  $\alpha$ -pinene (Tarvainen et al. 2007). Moreover,  $\Delta^3$ -carene is slightly more reactive than  $\alpha$ -pinene (Rinne et al. 2007) although the difference in atmospheric lifetimes is small, only 10% in daytime (Rinne et al. 2009). Wind directions or trajectories do not explain the difference between the measured branch scale emission and above-canopy concentrations. In general, the atmospheric VOC concentrations result from the output of the existing sources, which change according to their seasonal and spatial variation properties. The discoveries regarding the intra-specific chemotypic variation provide valuable background information for studying the atmospheric composition and chemistry of the troposphere.

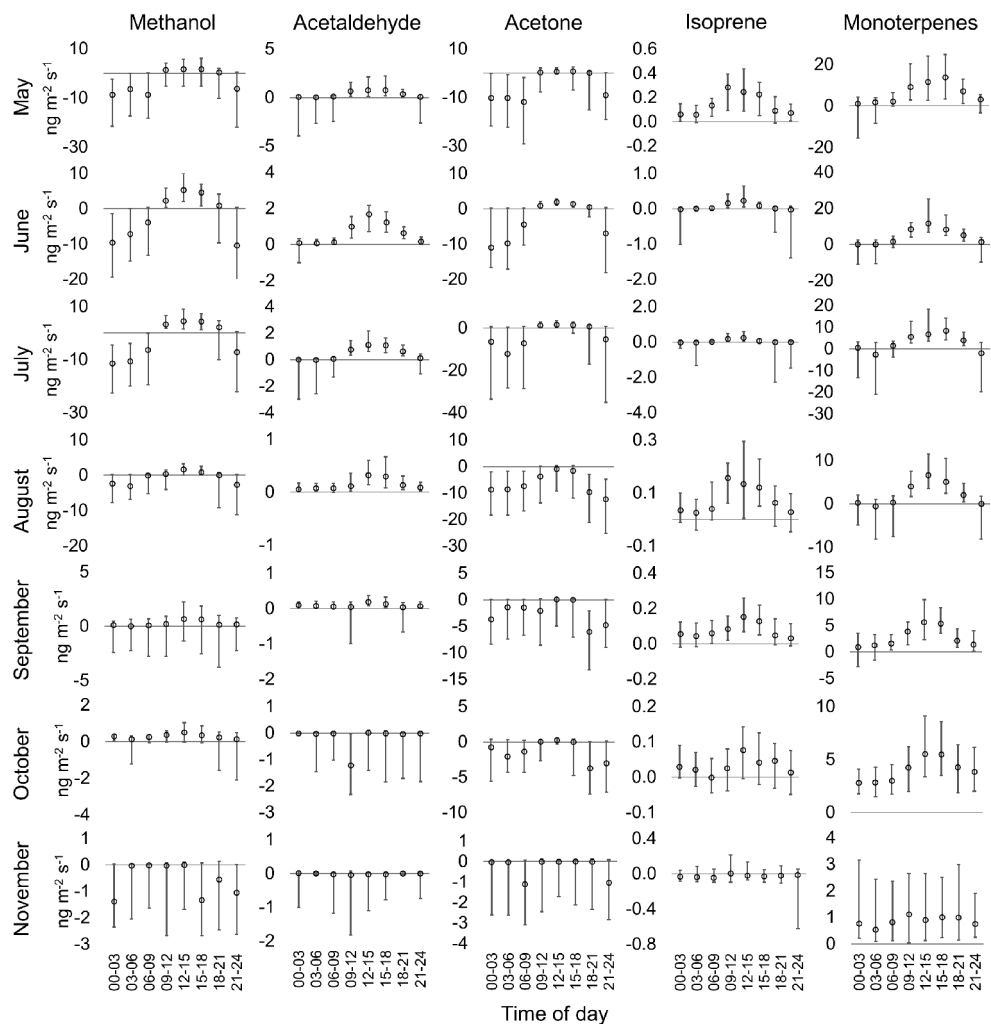
## VOC emissions from boreal forest floor and soil (II)

VOC fluxes from boreal forest floor exhibited a clear diurnal cyclical pattern and a seasonal variation. There was also remarkable spatial variation with lowest flux rates measured in chambers that enclosed the areas with the most dense vascular plant coverage. Monoterpene fluxes from the soil were clearly higher than the fluxes of other measured VOCs. Flux rates were following ambient temperature and light (positive correlation), whereas relative humidity had a reducing impact on measured fluxes. Negative flux rates were observed regularly. Hellén et al. (2006) and Aaltonen et al. (2011) had measured high VOC fluxes from the forest floor at the same site using manual sampling setup and GC-MS analysis. The annual pattern of VOC fluxes measured in study II matches rather well with those of earlier observations.

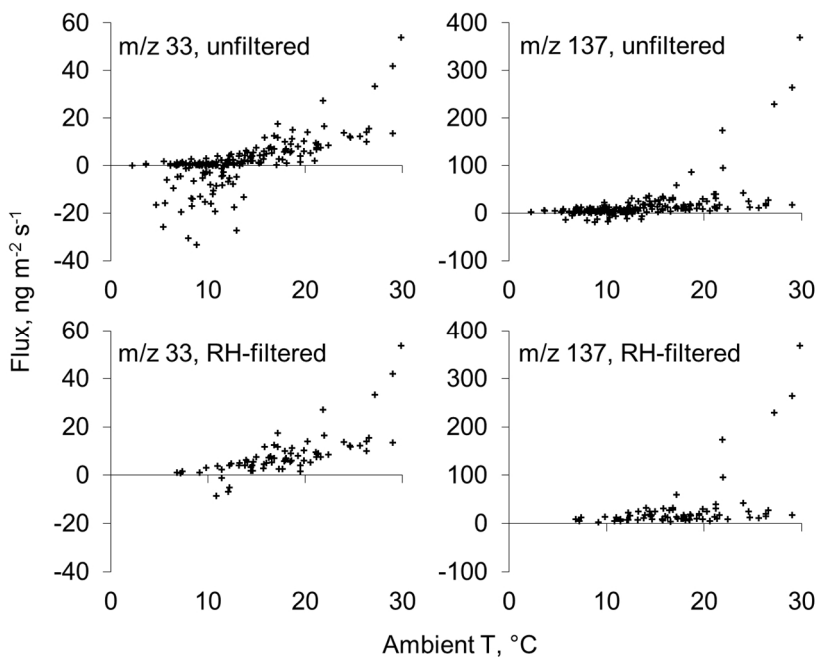
Several VOCs expressed observable diurnal pattern in the flux from the forest floor (Fig. 6). The diurnal patterns mostly followed the ambient temperatures for the within one-month periods. Over the measurement period from May to November, the highest median flux rates were measured during the early afternoons in summer and the lowest in nighttime during the autumn. Negative flux rates were common especially for OVOCs and in nighttime. The negative values dominated the measured OVOC fluxes in the autumn, whereas in case of monoterpenes the median flux rates were mostly positive throughout the entire measurement period.

The ambient temperature explained the VOC fluxes from soil better than soil temperature in study II. New biomass production at the forest floor may also partially explain the high monoterpene fluxes in spring (III). Apart from the ambient temperature, several factors such as soil temperature, relative humidity, soil water content, irradiation and CO<sub>2</sub> flux correlate with or act as an environmental driver for VOC fluxes from the forest floor (study II). This underlines the concept that soil should not be seen as a VOC source that is simply driven by the ambient temperature or any other single driving factor. Any single driver or straightforward combination of these drivers does not explain the variation of the VOC fluxes from the soil and the forest floor. The variation of VOC fluxes from these sources are instead probably the result of complex interactions of several simultaneous sources and processes, which are in turn controlled by different driving forces. The most obvious sources of VOCs found in study II, were the decomposition of needle litter, Scots pine roots and also probably the floor vegetation although the density of vascular plants had a reducing impact on the detected fluxes. The role of root associated soil fungi (Bäck et al. 2010) and microbial activity (Veres et al. 2014) can not be excluded. The complexity of soil and forest floor VOC fluxes can not be effectively studied without long-term field studies because the importance of different factors on VOC fluxes may change in time both intra-annually and inter-annually

(for example because of the large variation of soil water content that can occur from year to year).



**Figure 6.** Diurnal pattern of measured fluxes of methanol ( $m/z$  33), acetaldehyde ( $m/z$  45), acetone ( $m/z$  59), isoprene ( $m/z$  69) and monoterpene ( $m/z$  137) from the forest floor in May–November 2010 as a median of the results measured using three automated chambers. Circles represent the median fluxes and error bars the lower and upper quartiles. Note that there are variations in scales for flux rates for same compound between the months.



**Figure 7.** Relationship between ambient temperature inside a soil chamber before closure compared to the fluxes of methanol ( $m/z$  33) and monoterpenes ( $m/z$  137) from the boreal forest floor. The measurements represent one flux measurement chamber during June 2010. Upper figures are unfiltered data whereas results presented in lower figures are filtered according to relative humidity cut-off (points with  $RH > 70\%$  omitted).

Negative VOC fluxes from the boreal forest floor were relatively common. Rantala et al. (2015) reported considerable deposition of methanol occurs on the ecosystem scale, but in addition to natural deposition there is also likely to be experimental artifacts that are related to the measurement method per se. The inverse correlation between relative humidity and soil VOC fluxes was demonstrated in study II: when humidity before the closure exceeded 80% the mean of the measured flux was practically  $0 \text{ ng m}^{-2} \text{ s}^{-1}$ . This correlation is partly explained by the coincidence of low temperatures and high relative humidity. Alternatively, relative humidity by itself seems to cause decreases in fluxes (Fig. 7). This inhibitory phenomenon was most obvious in the case of methanol ( $m/z$  33), though it also occurred to a lesser extent with the other compounds measured. Altimir et al. (2006) and Kolari et al. (2012) studied the effect of moisture on measuring concentrations and fluxes of trace gases with a chamber method, and have pointed out that  $RH = 70\%$  is the limit for dry conditions without notable confounding effects of water, and wet conditions are characterized by the adsorption of trace gases by water films. The finding can be interpreted in terms of adsorption onto plant and internal chamber surfaces, absorption to water (due to moist surfaces) (Kolari et al. 2012) or deposition to forest floor, although it is worth noticing that deposition and adsorption are clearly overlapping phenomena. Evapotranspiration during the closure tends to lead to an increase in water vapour concentration inside the chamber, which makes it more

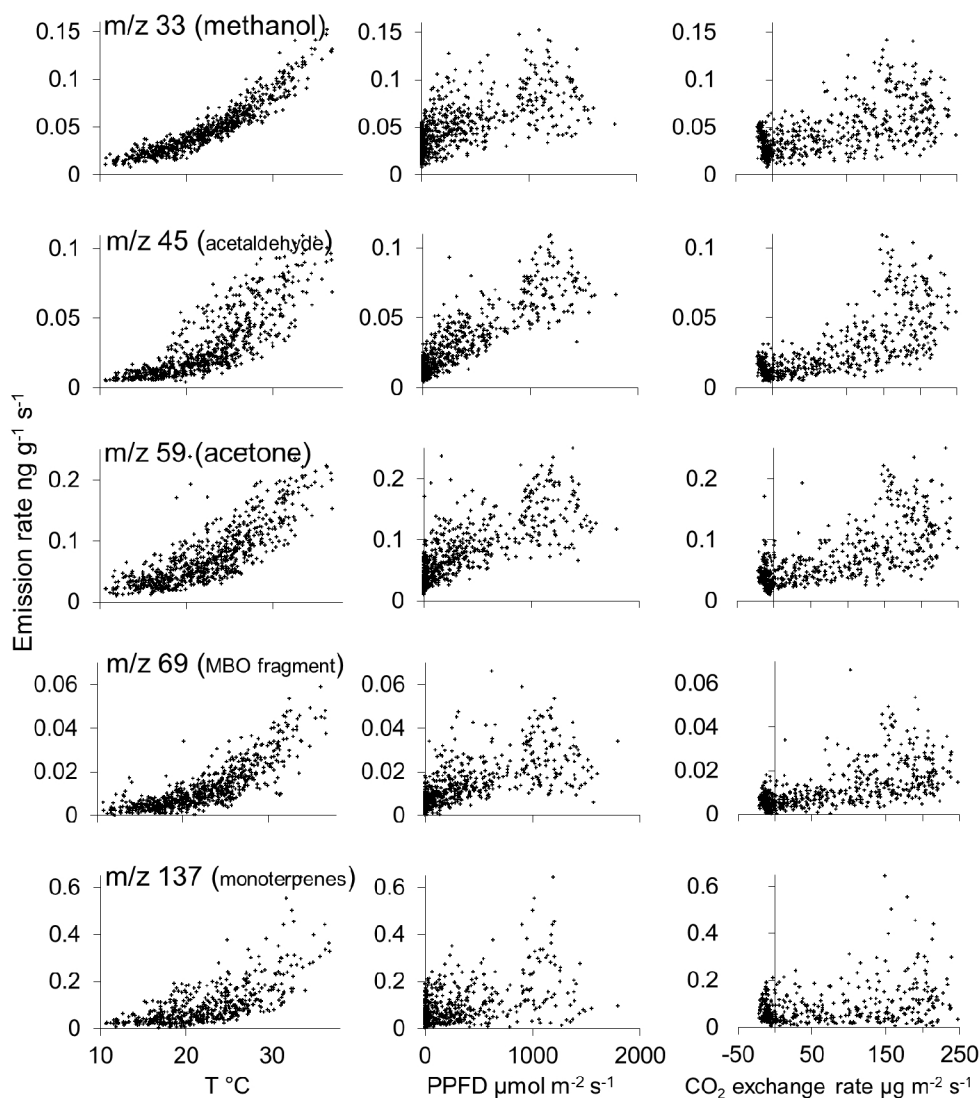
complicated to separate between the natural loss (deposition) and that caused by the measurement method.

### VOC emissions from Scots pine foliage (III and IV)

The seasonal pattern of VOC emission from Scots pine were discussed in studies **III** and **IV** with the focus on springtime and early summer. Scots pine shoots were a source of most of the studied compounds but in nighttime and during the cold seasons the emissions were close to zero and/or below the practical limit of detection. Scots pine shoots typically showed significant emissions in daytime and during the active seasons from mid-Spring to autumn. The clearest diurnal and annual variation was recorded for methanol, acetaldehyde, acetone, isoprene/MBO fragment and monoterpenes.

Temperature is the most important environmental factor that explains the measured VOC emission rates (Fig. 8). Irradiation and CO<sub>2</sub> exchange rate have a clear positive correlation with VOC emission rates. Such an association however may be partially confounded by the strong positive interrelationships between irradiation, temperature and CO<sub>2</sub> exchange themselves. The effect of temperature on VOC emissions matched well with the assumption on evaporation from pools (Tingey et al. 1980; Pierce & Waldruff 1991), traditionally described utilizing exponential relationship (Eq. 5). Interestingly, the emissions of compounds that did not originate from specialized storage structures, such as OVOCs, followed the temperature increase exponentially, and in most cases the dependency was even more manifest than that measured for the monoterpenes. The same pattern also held for irradiation and CO<sub>2</sub> exchange. The explanations of the OVOC emissions were generally more straightforward. For example, temperature alone could be used to explain the monoterpene emissions (Fig. 8). This indicates that the emissions of monoterpenes from Scots pine shoots probably involve a more complex set of processes than the emissions of other measured VOCs. One source of complexity is that the responses of VOC emissions to changes in environmental conditions are not constant over a whole year; fig. 8 represents only one month but the inclusion of longer time frames would probably show altered responses because of seasonal changes in capacity to maintain emissions.

An estimate of the contributions of growing vs. mature shoots to the total foliage VOC emission rates was needed, which was obtained by approximating the relative proportions of these shoot types using a model for needle and shoot growth (Schiestl-Aalto et al. 2013). The results showed that although the needles of the new shoots have a small biomass at the beginning of the growth period, their contribution in canopy scale emissions is large (study **III**). Buds were even found to be the dominating source of monoterpenes before the bud break, except during short periods of increased monoterpene emissions linked to photosynthesis recovery (study **IV**). The contribution of the buds for VOC emissions from the canopy was less for other compounds. Despite this the Scots pine buds are important sources of MBO and methanol in spring as well. The most intensive needle elongation period occurs in June, during which the growing shoots were strong sources of methanol, MBO and monoterpenes, and in summed together they contributed about 50% of the total emissions from Scots pine foliage. Only when the shoots and needles were fully-grown in early August, the contribution of the current year's shoots to the total emissions from the foliage is approximately equal with that of the mature shoots.



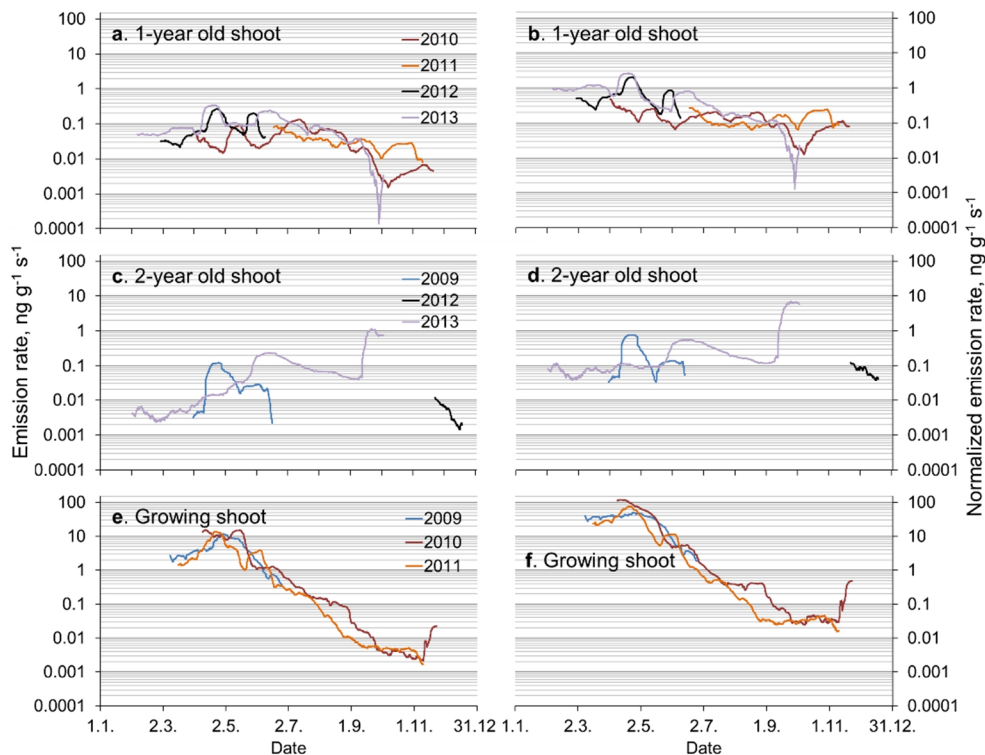
**Figure 8.** The comparison between the ambient temperature (measured inside the enclosure before the closure), photosynthetic photon flux density (PPFD, measured outside the enclosure), CO<sub>2</sub> exchange rate and emission rates of methanol, acetaldehyde, acetone, MBO and monoterpenes of a one year old Scots pine shoot during the month of July 2010.

Some primary metabolites such as carotenoids as well as gibberellins, the plant hormones that regulate various developmental processes, including cell division and shoot and needle elongation, are produced in close association with the synthesis of volatile terpenoids (Lichtenthaler 1999). Owen and Peñuelas (2005) suggested that volatile terpenoid emissions might occur alongside the factors that control the terpenoid pathway that produced the



primary metabolites. Thus, high levels of production of volatile terpenoids as a by-product of the synthesis of essential terpenoids would be expected if there is a considerable simultaneous imbalance between the demand and the supply for DMADP (Rosenstiel et al. 2004). Methanol, on the other hand, is a by-product from cell wall synthesis and it leaks out of the developing tissues due to demethylation of cell wall pectins in cell elongation (MacDonald & Fall 1993; Hüve et al. 2007), and is thus connected to the growth processes. The results obtained by studies **III** and **IV** imply that the reason for the extremely high monoterpene, MBO and methanol emission rates in spring was the high metabolic activity in the quiescent buds and growing shoots and needles, which resulted in *de novo* synthesis of metabolites, and boosted *de novo* synthesis in mature Scots pine shoots during critical stage of photosynthetic spring recovery. It seems that several biosynthetic pathways that produce VOCs are activated during the new biomass growth period although it is unclear if the physiological controls of these pathways are actually co-ordinated. The findings of study **IV** also suggest that the increases in monoterpene synthesis observed in spring serves as a protective functional role against photo-oxidative damage during critical period of photosynthetic spring recovery, possibly via preventing the excess sequestration of phosphates (DMADP and IDP) and allocates them to terpenoid synthesis (Peñuelas & Llusia 2004; Owen & Peñuelas 2005; Porcar-Castell et al. 2009; Loreto & Schnitzler 2010). On the other hand, the pool emission capacity in study **IV** was constant throughout the spring recovery period, which implied that the monoterpene emissions from pools of mature Scots pine needles were not going through seasonal adjustments in spring.

There is a clear seasonal pattern in the capacity to maintain emissions (Fig. 9). Scots pine foliage is a more active source of VOCs, especially monoterpenes, before mid-summer than after it. Mature and growing shoots exhibited pronounced emissions at that time: mature shoots transiently emitted copious quantities of monoterpenes early in the spring (study **IV**), whereas growing shoots were a strong source of various VOCs throughout the spring and early summer (study **III**). There are also distinct differences in monoterpene emission rates in addition to temperature normalized emission rates between growing, 1-year old and 2-year old Scots pine shoots. This was demonstrated by the comparison between the emission rates of growing and mature shoots (study **III**) and also by the finding that 1-year old shoots were more sensitive to boost the monoterpene synthesis in spring than 2-year old shoots (study **IV**). The standardized monoterpene emission rate of mature, 1-year old Scots pine shoots was typically  $0.1\text{--}1.0 \text{ ng g}^{-1} \text{ s}^{-1}$  at  $30 \text{ }^{\circ}\text{C}$ , with declining trend towards autumn. There was a minimum in temperature-normalized monoterpene emission rate (normalized emission rate  $0.001\text{--}0.1 \text{ ng g}^{-1} \text{ s}^{-1}$ ) in the mid-autumn but the summertime values were again reached by the beginning of November. No declining trend was observed during the summer for the 2-year-old Scots pine shoots. The 2-year old Scots pine shoots in spring were weaker sources of monoterpenes than the 1-year old shoots, but after midsummer the situation reversed. High temperature-normalized emission rates from a 2-year old shoot coincided with the needle senescence in autumn. The monoterpene emission rates of growing shoots in autumn were even lower than those of mature shoots, whereas before the bud break the normalized emission rates were extremely high. The emission rates of growing shoots declined through summer and stabilized when the needles have reached their full size.



**Figure 9.** Monoterpene emission rate and temperature normalized monoterpene emission rate ( $E_{0,pool}$  as in Eq. 5) of Scots pine shoots. The lines represent rolling averages over 300 measurement points. The normalization is conducted assuming exponential temperature response, with  $\beta=0.09$ , and the standard temperature is 30 °C (Eq. 5). Panels **a** and **b**: 1-year old Scots pine shoot, **c** and **d**: 2-year old shoot, and **e** and **f**: growing shoot.

Studies **III** and **IV** discussed some weaknesses of the current emission models. The present emission inventories are based on using emission algorithms together with temporally constant emission potentials (Guenther et al. 2012), which is a combination that lacks the description of inherent physiological processes of the plant that produced the seasonal variations in the synthesis and emission rates of terpenoids (Arneeth et al. 2008; Niinemets et al. 2010b). The different model estimates therefore have large uncertainties in total emission rates. The global monoterpene and isoprene emission estimates are usually obtained either by scaling-up the leaf-level responses to plant functional types and/or by using a dynamic vegetation model. Thus, the variations in emissions are coupled only to changes in the amount of emitting leaf biomass, whereas the variations in emission strength with leaf age of evergreen species are neglected (Guenther et al. 2012; Oderbolz et al. 2013; Monson et al. 2012). In addition to this, Guenther et al. (2012) take into account the ‘Leaf age emission activity factor’, but it lacks a defined physiological basis for the change in the activity factor. Niinemets et al. (2010a, b) have criticized the empirical emission algorithms because of missing physico-chemical controls and poor spatio-temporal resolution. The findings of study **III** suggest that the emission potential of growing shoots is all but constant. The five

years of continual shoot scale VOC emission measurement data discussed in this thesis indicate that the temperature normalized emission rate *per se* also reflects seasonal variations (Fig. 9). The long-term measurements with high time-resolution provide an insight into the dynamic processes, such as photosynthesis, monoterpene biosynthesis and emissions caused by senescence, which influence the monoterpene emission potential. Table 4 presents a ‘back of the envelope’ estimate of how a simple empirical description could serve as a basis for empirical models used in current emission models. This example would apply to a case in which both parameters of Eq. 5 are fitted to the data with constant values for each year, separately. The average match between the measured and modelled monoterpene emissions from 1-year old Scots pine shoot is perfect, but a closer look at the details reveals large discrepancies. Although the resulting errors in the modelled monoterpene emissions during midsummer are acceptable, within -13... .. 26%, in spring and autumn there are order-of-magnitude discrepancies between the measured and modelled estimates, which strongly suggests that the approach based on constant emission potentials has clear weaknesses in determining a seasonal component. It is noteworthy the success of the G93 pool algorithm is not symmetrical around midsummer (Table 4 and Fig. 9), and this feature suggests that the hybrid model would not solve the problem. Therefore seasonal adjustment is essential in modelling VOC emission capacities.

**Table 4.** Measured and modelled mean monoterpene emission rates of 1-year old Scots pine shoots in 2010–2013 (4 different shoots). The modelled emissions were obtained by fitting a temperature dependent G93 pool emission model (Eq. 5) to the data of each shoot separately, minimizing the sum of squares between the model estimate and measured values. Both  $E_{0,pool}$  and  $\beta$  were allowed to have unconstrained values. Values for  $\beta$  varied in range 0.05... ..0.10 K<sup>-1</sup>, whereas  $E_{0,pool}$  got values 0.14... ..0.27 ng g<sup>-1</sup> s<sup>-1</sup>. Difference between the modelled and measured values refers to over-/underestimation between the two estimates.

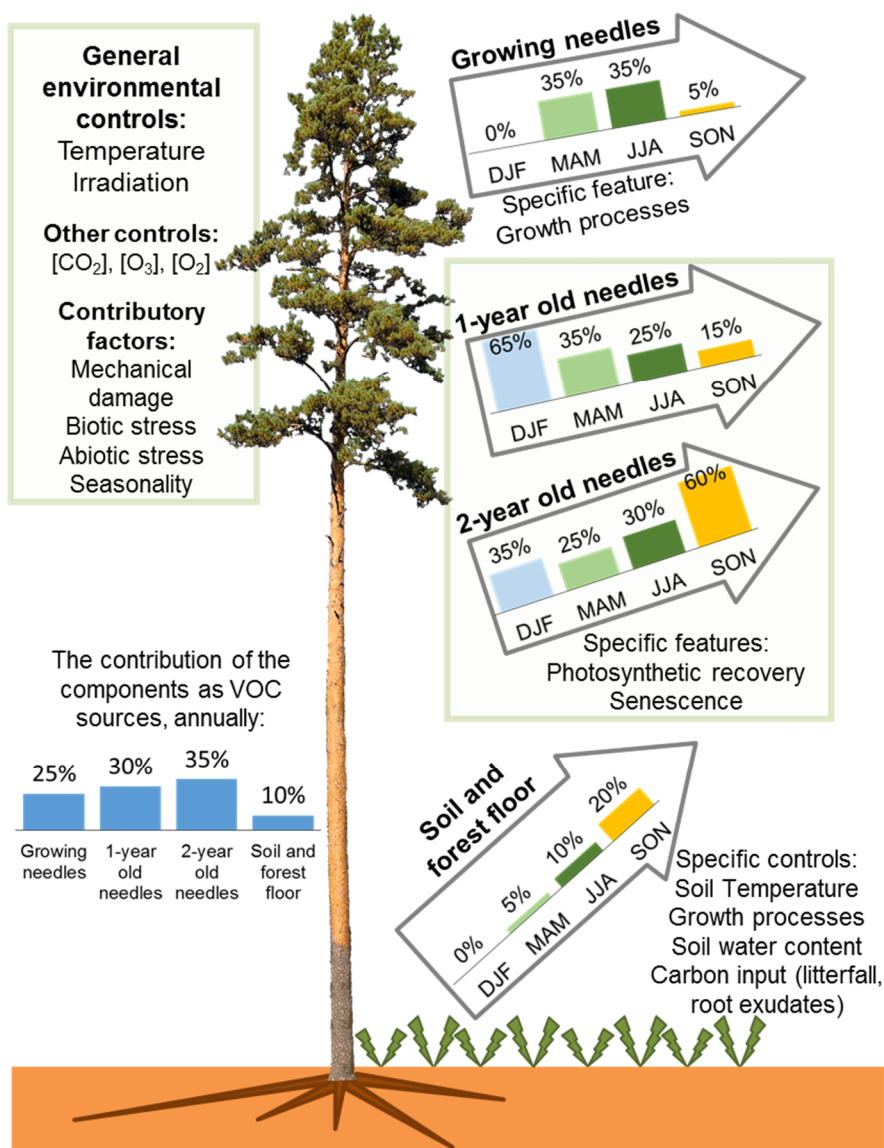
	Measured mean emission rate ng g <sup>-1</sup> s <sup>-1</sup>	Modelled (G93) mean emission rate ng g <sup>-1</sup> s <sup>-1</sup>	Difference between modelled and measured %
January	0.040	0.042	6
February	0.048	0.044	-7
March	0.045	0.053	16
April	0.105	0.041	-61
May	0.087	0.088	1
June	0.090	0.078	-13
July	0.068	0.085	26
August	0.043	0.064	47
September	0.019	0.048	155
October	0.012	0.029	142
November	0.008	0.010	25
December	0.001	0.005	312
<b>Over year</b>	<b>0.060</b>	<b>0.060</b>	<b>0</b>

There have been several attempts to estimate the regional or global terpenoid emissions, but the inventories of OVOC emissions are more rare (for a review see e.g. Rinne et al. 2009). One plausible reason for this is an incomplete knowledge about the processes that produce the OVOC emissions and how environmental conditions affect those processes. Although new foliage biomass growth was found to contribute to the OVOC emissions from Scots pine shoot (study **III**), the relationship between the environmental factors and the OVOC emissions seems to be clearly more straightforward than for monoterpenes (Fig. 8). Although there exists some degree of seasonal adjustment in OVOC emissions, modelling and the conducting of an inventory for the OVOC emissions is potentially less challenging than doing the equivalent for the terpenoids. On the other hand, Arneth et al. (2008) emphasized that the lack of knowledge may lead to the false perception that successful research had been carried out, and that there may still indeed be more unknown factors than known factors. This misperception was originally related to terpenoid emission modelling but the same reasoning goes for modelling OVOC emissions.

### **Characteristics of Scots pine forest as VOC source**

The annual cycle of perennial vegetation in all ecosystems includes both active and inactive periods, which involve profound changes in the physiological processes in plants over the whole year. The inactive rest period (dormancy) of boreal evergreens increases freezing tolerance, which is a prerequisite for sustained foliage retention. The dormancy release in spring leads to a quiescent phase without any visible clear signs of activity, and after that phase the new growth can start and the metabolism reaches the summertime state when conditions are favourable, which is typically during the late spring. Environmental cues activate the expression of genes that encode enzymatic pathways to synthesize new macromolecules for supporting growth during the quiescent phase (Heide 1993; Rohde & Bhalerao 2007; Sutinen et al. 2009).

Studies **III** and **IV** describe for the first time two previously unaccounted phenomena that act as sources for biogenic emissions from Scots pine shoots, both of which take place in spring or early summer. In addition to these two factors, soil is a significant source of VOCs, especially for monoterpenes in spring. The results of study **II** agree with those of Hellén et al. (2006) and Aaltonen et al. 2011, which showed that the monoterpene flux from boreal forest floor peaks in spring and early summer. Vanhatalo et al. (2015) reported that Scots pine stems emit considerable amounts of monoterpenes simultaneously with the recovery of sapflow during spring recovery. As a summary of these findings boreal Scots pine forest has multiple intensive VOC – especially terpenoid – emission sources which occur in springtime.



**Figure 10.** Schematic figure clarifying the complexity of the driving forces and contributing factors for VOC emissions, especially monoterpene synthesis and emission, after the findings of this study and Kesselmeier & Staudt 1999; Fall et al. 2001; Loreto et al. 2004; Bäck et al. 2010; Aaltonen et al. 2011; Bracho-Nunez et al. 2011; Bourtsoukidis et al. 2012; Copolovici et al. 2012; Possell & Loreto 2013. The percentages represent the relative importance of different needle age classes (shoots with needles of different age) of Scots pine and forest floor and soil as source of C in the form of VOCs into atmosphere based on amount of carbon released as major VOCs (sum of C in released methanol, acetaldehyde, acetone, isoprene/MBO, monoterpenes) from the study stand during the four seasons and annually. The contributions of the components add up to 100%; and other than the above mentioned VOC sources are ignored, although they may play substantial role on an ecosystem scale.

Traditionally the terpenoid emission models have been based on the finding that temperature and light are the major driving forces of diel changes in measured emission rates (Kesselmeier & Staudt 1999). Schematic figure (Fig. 10), however, illustrates the variety of potential driving forces and contributory factors besides temperature and light, and some of those affect only emissions from a certain section of a tree or impact only on synthesis or emission of specific compounds. Obviously the division into growing needles, mature needle age classes and soil/forest floor is inadequate if all the processes behind the emissions are fully discussed but the scheme primarily illustrates the diversity of driving forces and contributing factors in the scale of tree, canopy and ecosystem. Furthermore, the spatial and temporal variation in VOC emission discussed in this thesis complicate the full view on VOC emissions on any level from tissue to the global scale. Finally, many forms of spatial and temporal variation are driven or affected by the same driving forces and factors that regulate or contribute to the VOC emission and synthesis so it is inevitable that the phenomena listed in the schematic figure are strongly interlinked.

The emission estimates that are based on the empirical algorithms do not take into account the emissions that originate from growth processes (III), especially when the parameters for emission potentials are obtained using enclosure method. Guenther et al. (2012) have estimated that tropical forests globally emit the majority of terrestrial terpenoids and that emissions from boreal areas play a minor role. According to Arneeth et al. (2008) there are distinct differences between current emission estimates of terpenoids. New foliage growth in boreal forests takes place within 2–3 months around midsummer. The measured BVOC fluxes during this period of maximum foliage growth are at their highest (Rantala et al. 2015) and the main environmental factors of VOC synthesis and emission processes i.e. temperature and light, are favourable at that time. However, tropical forests do not undergo such extreme variation in thermal and light conditions throughout the year. The consequence of this enables either more even distributions of new foliar biomass production over the year, or several smaller episodic peak flushes (new foliage production periods) take place instead of only a single growing period. Study III demonstrated the effect on total emissions from the canopy by growing shoots with an estimation of the ‘concealed emissions’. This component is the proportion of canopy scale VOC emissions that are ignored when the emissions from growing shoots are not taken into account. The calculation of this result in study III revealed that 10–30% of the cumulative methanol, acetone and MBO emissions from a boreal forest over a normal growing period will be missed when the emissions from growing shoots are not taken into account. The effect of concealed emissions of monoterpenes is even more striking: roughly half of the canopy scale VOC emissions are ignored when the effect of growing shoots is not taken into consideration (III).

Shoot-scale VOC emissions from boreal Scots pine forest are low compared to the carbon assimilation of such forests. The simultaneous measurements of CO<sub>2</sub> exchange and VOC emission rates indicate that 1-year old Scots pine shoot generally releases only 0.05% of the assimilated C into the atmosphere as monoterpenes. Even during the monoterpene emission burst events that occur in spring, the fraction of lost C is generally less than 1%. Assuming that there is some synthesis costs for VOCs and accounting also the emissions of other VOCs than monoterpenes, the fraction of assimilated C used for VOCs syntheses and emissions may easily double. Nevertheless, the importance of VOCs regarding the total C exchange is low even on the shoot scale. The result does not change dramatically on the ecosystem scale: Applying the results by Rinne et al. (2007) or Rantala et al. (2015) together with the net ecosystem CO<sub>2</sub> exchange (SMEAR-database, <http://avaa.tdata.fi/smart/smear>, Junninen et al. (2009) show that on average less than 1% of the carbon annually sequestered by the

ecosystem (Kolari et al. 2009) is released into the atmosphere as monoterpenes; the fraction roughly doubles to 1.5% when methanol, acetaldehyde, acetone and isoprene are also included.

When applying all the monoterpene emission rates recorded 2009–2013 (studies **II–IV**) to the whole SMEAR II stand the contribution of growing shoots to the annual cumulative monoterpene emissions was found to be higher than the contribution of the shoots of other two needle age classes. The contribution of growing shoots to the emissions of other VOCs was lower than those of the other age classes. The 2-year old needles are quite potent sources of OVOCs, which suggests signs of incipient senescence. A comparison of the mean emission rates of different shoot age classes (Table 5) indicates that there is a need for more detailed, extensive enclosure measurements: especially when the aim is to provide information on the amounts of emitted compounds or emission capacities for modeling and/or emission inventory purposes. Choosing only single needle age class for study objects and attributing the results to the whole canopy or stand probably leads to biased results in upscaling. For example, using a mean emission rate of monoterpenes from a 1-year old shoot for the whole canopy would yield a 13% underestimation of total monoterpene emissions from the canopy on an annual basis. Given the great uncertainty in estimating VOC emissions for a specific landscape (Arneeth et al. 2008; Guenther 2013), a bias in the order of 10% on an annual basis would be generally acceptable. However, the varying dynamics and seasonal cycles of different VOC sources (soil and forest floor, stems, different needle age classes etc.) suggest that the bias of 10% would undergo a multifold increase, such as that increase that occurs in early summer when growing foliage is a strong source of monoterpenes.

The average contribution of soil and forest floor to the total emissions is no more than 10%. However, Aaltonen et al. (2011) reported that boreal soil and forest floor is a strong source of VOCs in spring and autumn, which was also confirmed in study **II**. When other sources of VOCs are quite weak such as in autumn, the contribution of soil and forest floor vegetation to total VOC emissions is somewhat higher than during the summer (Fig. 10). In autumn, about one-fifth of the VOCs emitted by the study stand originated from the forest floor (Fig. 10). In general, the agreement between the VOC fluxes presented in table 5 and the VOC fluxes measured above-canopy (Rinne et al. 2007; Rantala et al. 2015) is good.

**Table 5.** The mean VOC emission rates of Scots pine shoots measured at SMEAR II during period the 2009–2013. The unit of the emission rate is  $\text{ng m}^{-2} (\text{land area}) \text{ s}^{-1}$ ; the emission rates of Scots pine shoots are converted per land area assuming a total needle biomass  $5000 \text{ kg ha}^{-1}$  (Ilvesniemi et al. 2009).

	Methanol	Acetaldehyde	Acetone	Isoprene/ MBO frag.	Monoterpenes
<b>0-yr old needles</b>	1.3	0.4	2.1	0.5	7.0
<b>1-yr old needles</b>	1.8	1.5	3.9	0.9	5.4
<b>2-yr old needles</b>	3.1	2.0	4.7	0.6	6.2
<b>Soil and forest floor</b>	1.5	0.3	0.4	0.1	2.1

## The implications on atmospheric processes

The effect of chemodiversity on atmospheric chemistry was found to be remarkable (**I**). The inclusion of the data on chemotypes into the one-dimensional chemistry-transport model SOSA (Boy et al. 2011) including emission model MEGAN (Guenther et al. 2006) showed that depending on the month, there was 30–50 % difference in atmospheric monoterpene concentrations between the average pinene and carene type sources. This difference was not caused by changes in the emission rates, it was caused by the reactivities of the main emitted compounds (study **I**). The changes in the reactivities may have considerable impact on atmospheric chemistry at the boundary layer (Smolander et al. 2014), but it is largely ignored in the atmospheric studies. Furthermore, when the chemodiversity affects the magnitude of the emissions, the current knowledge on source strength may be significantly biased. For practical experimental reasons, the number of replicates in studying emission rates of different VOCs is often very limited, which may easily lead to biased results in determining the emissions rates for tree species. Moreover, the data will be especially biased when the results are extrapolated to the regional scale and used as a basis for studying the atmospheric reactivity, radical concentrations and aerosol formation processes.

Atmospheric new particle formation (NPF) and their growth are closely linked to the concentrations of their organic precursors such as terpenoids that originate from biosphere processes (Kulmala et al. 2013). The NPF events in a wide variety of environments peak in springtime (Dal Maso et al. 2005; Manninen et al. 2010). The biosphere in studies **II-IV** indicate there is a strong source of volatiles during the three to four spring and early summer months that coincide with frequent NPF events (Dal Maso et al. 2005; Manninen et al. 2010). The importance of the increased monoterpene emissions during spring may be even greater when the increase is concentrated in the most reactive, stress-induced compounds. Whether the springtime increase in monoterpene emissions affects the blend of emitted compounds or not is currently unclear, but the blend of emitted compounds potentially have substantial effects on chemical reactions in the atmosphere (Smolander et al. 2014). Dal Maso et al. (2009) hypothesized that emissions of more reactive compounds during the photosynthesis spring recovery would match the increase in frequency of NPF events in the spring. The information on the composition of emissions would also have the potential to explain the processes that produce ELVOCs (Ehn et al. 2012; Ehn et al. 2014). The findings of all the studies provide valuable information on the features of missing OH reactivity detected at the SMEAR II station (Sinha et al. 2010).

Climate change has brought about a lengthening of the growing season, which will most likely advance the timing of springtime processes related to bud-burst, soil thawing and photosynthetic recovery. However, the uncertainties in seasonal emission estimates related to those aforementioned events may consequently become even more important. The results of studies **III** and **IV** support the concept of a refined, mechanistic description for emission processes during the new foliage biomass growth and photosynthetic spring recovery. In addition to this, a more detailed description of the characteristic growth patterns for the different plant functional types should be incorporated into emission models. Including the effects of chemotypic variation on atmospheric monoterpene concentrations (**I**) and the pronounced VOC emissions from the soil and forest floor (**II**) would benefit the emission models in terms of accuracy and representativeness. This in turn calls for a new generation of emission models that is based on functions that accurately describe the key metabolic and other processes behind VOC synthesis and release, and testing them under field conditions with datasets of sufficiently high temporal resolution. The incorporation of the results presented in studies **III** and **IV** into the current empirical emission models would be



inconsistent, and instead a dynamic modelling approach would provide a more natural way to proceed and also yield more information on terpenoid emissions and controls over the biochemical processes. Such novel approaches, however, require high quality measurement data for testing such complex models; otherwise the complexity of the scheme could allow one to fit a model to data without gaining any further understanding on the processes. It is for this purpose that the VOC emission measurements conducted at SMEAR II would provide a first-class opportunity for a new approach.

### **Methodological considerations and suggestions**

The evaluation of methodology was one of the key objectives of this thesis. It was especially important to find out how well the sources of VOC emissions could be observed. Another key objective was to obtain information on the physico-chemical processes related to the VOC sources by using measurements conducted under field conditions. Here the uncertainty, the representativeness and the suggestions for further studies are discussed in detail.

Study I was focused on characterizing the spatial variation in the blend of terpenoids emitted by Scots pine. Although the sample size at about 0.5% of all Scots pines within the sampling area was relatively low, the results, especially the comparison between the chemodiversity of different provenances, suggest that the variation was adequately covered. This result is applicable to the vicinity of the SMEAR II station, but lacks applicability as a regional estimate of terpenoid blends of Scots pine, such as for the whole Finnish south boreal area. Therefore, repeating the same kind of sampling in several places around the south boreal region would offer more reliable and valuable information, but one worthwhile option would be to utilize the material available for forest tree breeding because it covers wide genetic variation. For example, the provenance trials or seed orchards would allow cost-effective methods for quantifying the chemotypic variation of different tree species and origins. This information, when combined with measured emission characteristics of different chemotypes and the coverage of plant functional types, would be expected to result in more accurate estimates of BVOC emissions. The current understanding is that chemotypes are constant, which indicates that no regular seasonal pattern in emission blend from individual trees occurs. This should obviously be confirmed with repetitive observations conducted with rather small ( $n \approx 10$ ) samples of trees.

Large discrepancies between the measured branch scale emissions and above-canopy concentration measurements (Tarvainen et al. 2007; Hakola et al. 2009) suggest that the measurements of emissions on the branch scale do not fully represent the sources of terpenoids for a stand, population or at the footprint level. Because the emission measurements are commonly made from one or only a few trees, the representativeness of these measurements for the stand-level air chemistry scale is therefore highly questionable, especially when the magnitude of emissions varies with chemotype. The chemotypic characterization conducted in study I has significant potential to reveal the sources of the discrepancy between branch scale emissions and the above-canopy concentrations of VOCs and is therefore a key to understanding the implications on air chemistry at the boundary layer. In study I data for the pinene trees were more common in the surrounding stands than for the SMEAR II stand. Extrapolating this result to a much larger area (typical transport distance for  $\alpha$ -pinene and  $\Delta^3$ -carene at a wind speed of  $5 \text{ m s}^{-1}$  is approximately 40 km, Rinne et al. 2009) would partially explain the earlier findings on the dominance of  $\alpha$ -pinene in contrast to  $\Delta^3$ -carene in atmospheric concentrations measured above SMEAR II canopy. On the other hand, Scots pines are not the only monoterpene source in SMEAR II; other sources

of monoterpenes include Norway spruce, birches and soil and forest floor, which should be added to complete the emission dataset for the stand. According to Lindfors et al. (2000) Norway spruce emits clearly more  $\alpha$ -pinene than  $\Delta^3$ -carene, which would offer a reasonable explanation for the detected blend of the compounds in the atmosphere. It is worth noting that the above-canopy measurements of monoterpene concentrations represent quite a large area; a 40 km radius around the measurement station covers a total area of 5000 km<sup>2</sup>.

Various types of errors are involved in measuring VOC emissions using PTR-QMS coupled with a dynamic gas exchange measurement system. Reactive trace gases tend to be adsorbed onto the chamber walls and the sample tubing and absorbed to the water films on chamber walls. The precision and accuracy of the dynamic enclosure setup used in this study was reliable in terms of the quantities of losses onto the chamber walls and sampling tubing (Kolari et al. 2012). High humidity also reduces the detected emission rates, but in cases of a shoot enclosure even the highest losses of monoterpenes were within tens of per cent. The setup underestimates the monoterpene emission rates in the range of 5–30%, depending on the environmental conditions, especially relative humidity (Kolari et al. 2012). In contrast, the losses of OVOC emissions may occasionally be considerably higher (Kolari et al. 2012). These losses caused by adsorption onto the chamber walls, materials and sampling tubes are probably partially canceled out by the effect of increased temperature during the closure on the emission rate (typically 2–4 K in daytime). Moreover, the temperature inside the shoot enclosure tends to be 0–2 K higher than the ambient temperature even when the enclosure is open. A typical association in the quantity of evaporation from storage structures ( $E_{\text{pool}}$ ) and temperature (Eq. 5) would yield an overestimation of the emission rate in the range of 0–20% when compared to the theoretical emission rate outside the chamber, depending on the temperature difference mentioned above. Inclusion of both the temperature difference mentioned above and the effect of temperature increase during the closure would increase the difference by roughly 0–10%. In general, the length of a closure of the shoot emission measurement setup should not exceed 2–4 minutes, which is a reasonable compromise between maximizing the accuracy, precision and minimizing the effect of changes in conditions inside the enclosure (Kolari et al. 2012). The time limit for the closure length of the soil chamber in our set up was not very low because the increase in temperature in the forest floor was minor due to shading. However, the increase in humidity inside the soil chamber observed correlates with the closure length.

Random error always occurs in all environmental measurement data. It cannot be avoided but it usually has not been discussed in detail in VOC emission studies. Typically the standard deviation, minimum and maximum values or confidence intervals are reported in studies that present VOC volume mixing ratios, which were measured by a PTR-QMS or matching setup, without taking into account that there can be large variations in environmental conditions and in environmental drivers (e.g. Ruuskanen et al. 2005; Aaltonen et al. 2011; Taipale et al. 2011). Substantial random error can be dealt with as long as the rate of change of the volume mixing ratio (increase or decrease) during the closure clearly exceeds the standard deviation in volume mixing ratio measurement (for example, see Fig. 4, m/z 69 in lower panel). The measurement of ambient concentrations of trace gases has the lower limit of detection at 10–300 pptv for most compounds, which can be limiting for many studies (Taipale et al. 2008). However, measuring emission rates by using the enclosure method has the potential to solve the extremely low emission rates when the ambient VOC concentrations are below the theoretical detection limit because measuring volume mixing ratio several times ( $\geq 15$ ) during closure and applying mass balance equation fitting has the potential to reduce the effect of random errors significantly (Fig. 4). Taipale et al. (2008) and Kajos et al. (2015) determined the limit of detection for concentration measurements by multiplying the standard deviation of the zero air measurement by a factor of 2 (Taipale et al.) or 3 (Kajos et al.). This approach

is valid for measuring atmospheric concentrations and hence it can be used for the concentrations before closing the enclosure and, which were for most of the time above the detection limits reported by Taipale et al. (2008). The emission rates were obtained for all cases regardless of whether the volume mixing ratios exceeded detection limits because otherwise there would have been a risk of systematic error towards higher values in average emission rates.

High relative humidity was found to affect the measured VOC fluxes from the forest floor and soil. The high solubility in water rendered the OVOCs to be particularly sensitive to both absorption and adsorption effects, but the same effect was also relevant for monoterpenes although the water solubility of those is lower. The losses are highest in the spring, when soil water content tends to be high, and in autumn, when relative humidity often exceeds the critical level, 70–80%. Comparison between the mean monoterpene flux measured using the three automated soil chambers ( $5.3 \text{ ng m}^{-2} \text{ s}^{-1}$ , time frame matching to Aaltonen et al. 2011) with that measured using five manual soil chambers with clearly longer closure ( $1.4 \text{ ng m}^{-2} \text{ s}^{-1}$ , Aaltonen et al. 2011) suggests that the longer the closure is, the lower are the detected fluxes, which could be due to the occurrence of enhanced adsorption, absorption and deposition or any combination of these. Even more important than the length of closure is the approach used: the contribution of the concentration change in the beginning of the closure in the dynamic enclosure method is high compared to the contribution of the concentration (change) in the end of the closure. In contrast, the contribution of the final concentration is essential in the flux calculation of the steady state measurement. Arguably the adsorption effect that is caused by the chamber itself and also by the enclosed plants have more significant effects on the detected final concentration than on the initial concentration change that occurred at the beginning of the closure. On the other hand, desorption of the molecules by the chamber and plant surfaces may further confound the detected signal. The relative humidity inside the soil chamber tends to increase significantly during the closure because the evapotranspiration continues: the mean increase was 10 percentage points. Isoprene is less sensitive for adsorbing onto wet surfaces than most other measured VOCs. Even a longer closure time with a manual chamber, which exposes the chamber interior to even higher air humidity will produce isoprene fluxes of the same level (Aaltonen et al. 2011) as those the automated chamber with notably shorter closure time. This similarity in result under different collection conditions indicates that isoprene is less sensitive to moisture effects. In summary, measuring VOC fluxes from the forest floor and from soil under field conditions tends to underestimate the fluxes because of the losses caused by the increase in adsorption due to the measurement method. In addition to absorption and adsorption, there occurs also a method-independent, natural sink for VOCs, caused by deposition (Rantala et al. 2015).

One option to manage the confounding effect of moisture on the measuring of VOC fluxes from forest floor would be to filter the data in relation to the recorded relative humidity, and, if needed for balance estimation, to fill the gaps caused by filtration using suitable method. Filtering using  $\text{RH}=70\%$  as a cut-off limit (Altimir et al. 2006; Kolari et al. 2012) clearly eliminates most of the measured negative VOC fluxes (Fig. 7). The filtering removes practically all measurements whose measurement is at risk of being confounded by conditions that favour absorption, adsorption or deposition, regardless of the fact that deposition may also take place under natural conditions. Nevertheless, there is a risk that the natural deposition is perturbed by the high humidity inside the chamber. Filtering and gapfilling data using exponential relation between ambient temperature and VOC flux measured during low relative humidity has the potential to be used as a method for reducing the underestimation of measured mean VOC fluxes from the soil. A minor bias may still exist because of missed deposition, however. The user of the data should be aware of the fact that

the chamber method for measuring soil VOC fluxes can significantly underestimate the fluxes, whereas the filtering described above may also remove or decrease the effect of some of the studied phenomena. Filtering and gapfilling should only be used as a method for calculating the mean fluxes over a long time-span i.e. it should not be used to explain the fluxes with transient responses to environmental drivers. It seems that air humidity, and perturbation from moisture in general, plays a central role in measuring VOC fluxes from soil and forest floor by using chamber methods. This suggests that the relative humidity should be taken into account regardless of technical issues related to moisture when measuring soil VOC emissions. Relative humidity should be considered alongside other important factors such as temperature, solar radiation and CO<sub>2</sub> fluxes when short term controls over VOC fluxes from soil and forest floor are to be studied. Further technical studies on the effect of moisture on the detected VOC fluxes are needed to improve the accuracy of the soil chamber method.

Most BVOC emission measurement studies so far have been either experiments (in laboratory or field conditions, including manipulation in environmental conditions) or otherwise based on short-term measurement data (without manipulating the environmental conditions). Few if any studies have involved longer-term measurements. The paucity of information of experiments and longer-term measurements have been partly addressed with the four studies presented in this thesis. Short-term studies have been an important source of information on VOC emissions from forests, but they have a fundamental limitation: the long-term effects or variation by definition cannot be detected by using short-term studies. Novel, unexpected findings reported in studies **III** and **IV**, which revealed enhanced emissions during new biomass growth and spring recovery, were obtained by using setups designed for long-term observation. Such types of processes are not typically detected under laboratory conditions or during short-term field studies because of the lack of the phenomena under study conditions (because of timing of the study or limitations caused by laboratory conditions etc.) or because of a conscious avoidance of dealing with dynamic phenomena due to the simplicity of a study design. The effective utilization of short-term studies requires that the objectives should be strictly focused and based on well-defined hypotheses. In contrast, both objectives and hypotheses are typically substantially broader and less fixed to certain presumptions in long-term studies. Ideally both short- and long-term approaches should benefit and complement each other: long-term observations enables discovering new phenomena and testing the hypotheses under field conditions, whereas short-term experiments and studies are an effective way to gain detailed information on crucial phenomena. In other words, long-term observation reveals something about everything, whereas short-term studies aim at explaining everything about something. The flip-side of recording continuous, long-term information on VOC emissions by using the enclosure method is that the spatial representativeness is often limited. This is also a shortcoming that holds for the measurements conducted in studies **II**, **III** and **IV**. There was chance to use three measurement chambers in study **II**, which revealed considerable spatial variation in VOC fluxes from the forest floor. Aaltonen et al. (2011) reported comparable spatial variations in VOC fluxes. This suggests that for reliable estimates on VOC emissions from soil and forest floor, only three measurement chambers is certainly too low, especially considering the small scale variations in soil properties and forest floor vegetation.

The first step to improve the representativeness of the shoot enclosure method would be to conduct measurements with shoots that representing different chemotypes. It is unclear, whether the chemotypes also affect the magnitude of terpenoid emission (study **I**). In practice this would mean a characterization of the VOC emissions rates and emission capacities of

different chemotypes. Here the sample size is a secondary factor; it is more important to centralize the measurements to 2–4 trees that represent the characterized chemotypes well, and to continue observing the VOC emissions from those trees for at least over one year, to ensure that annual variations are covered to a reasonable extent. VOC emissions of different shoots of the same individual, or different shoot representing different needle age classes may express significant differences (studies **III** and **IV**), which should also be observed by measuring the emissions of different kinds of shoots. Preferably this should be conducted simultaneously (as in study **III**) in order to minimize the effect of variation due to environmental conditions.

The temporal resolution of the automated VOC emission rate measurements was 15–30 min (24–48 closures per day) for the shoot enclosures, and 3 hours (8 closures per day) for the soil chambers. The time interval between the measurements was long enough to reach the minimum measurable ambient trace gas concentrations (Kolari et al. 2012). From the purely scientific perspective increasing the number of closures per day would offer better material for analysis, but there were also other ongoing measurements not directly connected with this PhD research that utilized the same measurement setup or gas analyzers and this had to be accommodated in the experimental setup. Fewer than 50 closures per day is certainly enough for characterizing the emissions and emission rates in general, but it may set considerable limitations for analysis when physico-chemical or biochemical processes are studied because many of the processes take place within considerably shorter time-scales than the interval of the closures in enclosure method. However, long-term measurements have the potential to decrease those limitations because many recurring regular phenomena such as that reported in study **IV** tend to be exposed when enough data have been recorded. In general, the dynamic enclosure method allows sufficient observation of VOC sources in field conditions, thus it provides adequate information on biological processes behind the VOC fluxes. One major advantage of the enclosure method is that the study object can be maintained under or near to natural conditions and fluctuations. On the other hand, this is also a shortcoming in some cases because of the lack of any control or normalization over environmental conditions. Finally, ecosystem scale measurements are needed to complete the range of observation types for determining VOC emissions because relying upon upscaling based on only the enclosure measurements is too inaccurate and compromises the data. The combination of precise, well-defined enclosure measurements complemented with highly representational recording of above-canopy fluxes with high would offer the most cost-effective way to obtain new information, in comparison to only one or other methods that exist. The SMEAR II station offers a unique opportunity to take such measurements, because to date it is the only site in the world where long-term, continuous observations on VOC emissions, fluxes and atmospheric concentrations in combination are conducted.

## CONCLUSIONS

The common denominator of the studies of this thesis is that there exists a wide variety of seasonal and spatial variation in the VOC emissions from boreal forests. There is a broad, inherited variation in the monoterpene emission blend of the Scots pine (I). Forest floor and soil sources contribute a maximum 10% annually to the ecosystem VOC fluxes, but the spatial variation in fluxes and the changes in seasonal contribution is significant (II). Scots pine buds are very active sources of monoterpenes in spring, before bud break. During the most intensive needle elongation period, which occurs after bud-break the growing pine shoots emit various VOCs, which partially originate from the growth processes (III). During the early stages of photosynthetic recovery in spring there is a clear peak in monoterpene emissions from Scots pine shoots (IV). The seasonal changes in the capacity to maintain VOC emissions, reported in studies III and IV, were clearly caused by physiological adjustment rather than by any independent, external factors such as biotic stress or changes in atmospheric composition. The common feature of the phenomena presented in this series of studies is that they have transitory or permanently high impacts on the quality or quantity of the VOCs fluxes from boreal Scots pine forest into the atmosphere, and hence have substantial importance in relation to atmospheric composition of trace gases. The studied seasonal and spatial variation potentially have important implications for the chemistry of the atmosphere as demonstrated in study I. Studies II–IV found and present novel processes that potentially have a large impact on ecosystem scale VOC fluxes especially during spring (III–IV) and autumn (II).

All studies raise several questions to be answered in further studies. Study I described the chemodiversity of a typical South-Finnish boreal Scots pine forest, but what about the chemodiversity among other origins and tree species? It was demonstrated in study II that measuring and analyzing VOC fluxes from the soil is challenging both because of technical issues caused by humidity-related surface reactions and because of the complexity of VOC production in the soil. The question that arises is: how to manage with the accuracy of chamber method, and how to model, empirically or otherwise, the complexity and spatial variations of emissions from soil? Studies III and IV discussed the high VOC emissions from Scots pine shoot during certain, rather limited periods. The findings of those two studies are to some extent inconsistent with the current approach, which emphasizes the presumptions of constant emission capacities and describe seasonal changes in emissions as a direct, transient response to environmental conditions. Repeating the studies under controlled laboratory conditions would be crucial to gain in-depth and precise understandings on processes that cause changes in the quantity of emissions. Investigating the effects described in studies III and IV with plant species other than Scots pine would entail the inclusion of those effects in emission models although there would probably be substantial challenges in covering the wide variety of emissions among different plant species, landscapes and biomes. The findings of this thesis in relation to the breadth of seasonal and spatial variation are limited. If the order of magnitude of variation in VOC emissions is so broad within only one study site, then it will probably be broader still when the extensive variations within the terrestrial ecosystems are taken into consideration. Nevertheless, when detailed information on the effects of new biomass growth and seasonal recovery processes becomes available, the major findings should be incorporated into current emission models. Moreover, the

development of process models for VOC emissions would also largely benefit from all such detailed information.

The study approach used in the research for this thesis, especially the utilization of very long-term and comprehensive field measurements provided a continual source of detailed information on phenomena and processes that take place under widely varying spatial and temporal scales. Short-term or simplistic study designs sets limitations on drawing conclusions or estimating global emissions. Spatial and temporal variations, including seasonality, offer a limitless field for VOC emission and flux research. Simplified approaches may be enough for estimating current BVOC emission to a reasonable extent, but if estimates or determinations of future BVOC emissions are the aim, then we must turn to in-depth, detailed but also holistic approaches and analyses. This thesis both points out severe deficiencies in current approaches and serves as a starting point for developing new, more comprehensive approaches to estimate BVOC emissions.

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