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Patrick Faubert

Responses of Non-Methane Biogenic Volatile Organic Compound Emissions to Climate Change in Boreal and Subarctic Ecosystems

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ABSTRACT

Non-methane biogenic volatile organic compound emissions (BVOCs) have important roles in the global atmospheric chemistry but their feedbacks to climate change are still unknown. This thesis reports one of the first estimates of BVOC emissions from boreal and subarctic ecosystems. Most importantly, this thesis assesses the BVOC emission responses to four effects of climate change in these ecosystems: 1) the direct effect of warming, and its indirect effects via 2) water table drawdown, 3) change in the vegetation composition, and 4) enhanced UV-B radiation. BVOC emissions were measured using a conventional chamber method in which the compounds were collected on adsorbent and later analyzed by gas chromatography-mass spectrometry. On a subarctic heath, warming by only 1.9-2.5°C doubled the monoterpene and sesquiterpene emissions. Such a high increase of BVOC emissions under a conservative warming cannot be predicted by the current models, which underlines the importance of a focus on BVOC emissions from the Subarctic under climate change. On a subarctic peatland, enhanced UV-B did not affect the BVOC emissions but the water table level exerted the major effect. The water table drawdown experimentally applied on boreal peatland microcosms decreased the emissions of monoterpenes and other VOCs (BVOCs with a lifetime > 1 d) for the hollows (wet microsites) and that of all BVOC groups for the lawns (moderately wet microsites). The warming treatment applied on the lawn microcosms decreased the isoprene emission. The removal of vascular plants in the hummock (dry microsites) microcosms decreased the emissions of monoterpenes while the emissions between the microcosms covered with *Sphagnum* moss and bare peat were not different. In conclusion, the results presented in this thesis indicate that climate change has complex effects on the BVOC emissions. These results make a significant contribution to improving the modeling of BVOC emissions for a better understanding of atmospheric chemistry and climate change effects in the boreal and subarctic regions.

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CAB Thesaurus: volatile compounds; organic compounds; isoprenoids; monoterpenes; sesquiterpenes; climatic change; global warming; ultraviolet radiation; water table; vegetation; tundra; *Sphagnum*; *Eriophorum*; peat; peatlands; bogs; net ecosystem exchange; carbon dioxide; methane; Northern Europe; Arctic regions

Yleinen suomalainen asiasanasto: haihtuvat orgaaniset yhdisteet; terpeenit; ilmastonmuutokset; lämpeneminen; ultraviolettisäteily; hiilidioksidi; ekosysteemit; kasvillisuus; turvemaat; suot; tundra; boreaalinen vyöhyke; subarktinen vyöhyke; Pohjois-Eurooppa

Je dédie cette thèse à mes grands-pères Gilles et Rémi, deux hommes inspirants dont les qualités ne cessent d'enrichir ma vie.

I dedicate this thesis to my grandfathers Gilles and Rémi, two inspiring men with qualities that have enriched my life.

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Kuopio, December 2010

Patrick Faubert

Abbreviations

Acetyl-Co-A	Acetyl coenzyme A
a.s.l.	Above sea level
ATD	Automatic thermal desorption
BVOC	Non-methane biogenic volatile organic compound
DEC	Disjunct eddy-covariance
DMAPP	Dimethylallyl pyrophosphate
DNA	Deoxyribonucleic acid
DW	Dry weight
FID	Flame ionization detector
FPP	Farnesylpyrophosphate
GC-MS	Gas chromatography – mass spectrometry
GPP	Geranylpyrophosphate
Hollow	In an ombrotrophic peatland, microsite with its vegetation surface below the water table level
Hummock	In an ombrotrophic peatland, microsite with its vegetation surface above the water table level
IPP	Isopentenyl pyrophosphate
Lawn	In an ombrotrophic peatland, microsite with its vegetation surface even with the water table level
LOX	Lipoxygenase
MEP	Methyl-erythritol pyrophosphate pathway
Minerotrophic peatland or fen	Peatland receiving nutrients both from precipitation and groundwater sources
MVA	Mevalonic acid pathway
NDVI	Normalized differential vegetation index
NEE	Net ecosystem CO_2 exchange
Oligotrophic peatland	Minerotrophic peatland with a nutrient poor status

Ombrotrophic peatland or bog	Peatland receiving nutrients uniquely from precipitation
ORVOC	Other reactive volatile organic compound
OTC	Open-top chamber
PAR	Photosynthetically active radiation
PC	Principal component
PCA	Principal component analysis
P_G	Gross photosynthesis
PPFD	Photosynthetic photon flux density
PTR-MS	Proton transfer reaction mass spectrometer
PVC	Polyvinyl chloride
REA	Relaxed eddy accumulation
R_{TOT}	Total respiration
SE	Standard error
SOA	Secondary organic aerosol
SOM	Soil organic matter
UV	Ultraviolet
UV-A	Ultraviolet A radiation
UV-B	Ultraviolet B radiation
VOC	Volatile organic compound

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on data presented in the following articles, referred to in the text by their chapter numbers.

Chapter 2 Faubert P, Tiiva P, Rinnan Å, Michelsen A, Holopainen JK and Rinnan R. 2010. Doubled volatile organic compound emissions from subarctic tundra under simulated climate warming. *New Phytologist* **187**: 199-208.

Chapter 3 Faubert P, Tiiva P, Rinnan Å, Räsänen J, Holopainen JK, Holopainen T, Kyrö E and Rinnan R. 2010. Non-methane biogenic volatile organic compound emissions from a subarctic peatland under enhanced UV-B radiation. *Ecosystems* 13: 860-873.

Chapter 4 Faubert P, Tiiva P, Rinnan Å, Räty S, Holopainen JK, Holopainen T and Rinnan R. 2010. Effect of vegetation removal and water table drawdown on the non-methane biogenic volatile organic compound emissions in boreal peatland microcosms. *Atmospheric Environment* 44: 4432-4439.

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AUTHORS' CONTRIBUTIONS

Chapter 2 Patrick Faubert contributed to the field work, data analysis and wrote the paper. Päivi Tiiva contributed to the field work, data analysis and writing. Åsmund Rinnan contributed to the methods in the data analysis and writing. Anders Michelsen conceived and designed the study, contributed to the field work and writing. Jarmo K. Holopainen contributed to the writing. Riikka Rinnan conceived and designed the study, contributed to the field work, data analysis and writing.

Chapter 3 Patrick Faubert contributed to the field work, data analysis and wrote the paper. Päivi Tiiva contributed to the field work, data analysis and writing. Åsmund Rinnan contributed to the methods in the data analysis and writing. Janne Räsänen contributed to the field work and data analysis. Jarmo K. Holopainen, Toini Holopainen and Esko Kyrö conceived and designed the study and contributed to the writing. Riikka Rinnan conceived and designed the study, contributed to the field work, data analysis and writing.

Chapter 4 Patrick Faubert designed the study, contributed to the field work, measurements in plant growth chambers, data analysis and wrote the paper. Päivi Tiiva designed the study, contributed to the field work, measurements in plant growth chambers, data analysis and writing. Åsmund Rinnan contributed to the methods in the data analysis and writing. Sanna Räty contributed to the measurements in plant growth chambers and data analysis. Jarmo K. Holopainen and Toini Holopainen contributed to the writing. Riikka Rinnan conceived and designed the study, contributed to data analysis and writing.

Chapter 5 Patrick Faubert designed the study, contributed to the field work, measurements in plant growth chambers, data analysis and wrote the paper. Päivi Tiiva designed the study, contributed to the field work, measurements in plant growth chambers, data analysis and writing. Tchamga A. Nakam contributed to the field work, measurements in plant growth chambers and data analysis. Jarmo K. Holopainen and Toini Holopainen contributed to the writing. Riikka Rinnan conceived and designed the study, contributed to data analysis and writing.

Contents

1. General Introduction

1.1 BACKGROUND

The Sun provides energy to the Earth's climate. One third of the solar energy that reaches the upper layer of the atmosphere is reflected back into space (Kiehl and Trenberth 1997). The two thirds remaining are absorbed by the Earth's surface and the atmosphere (Kiehl and Trenberth 1997). The solar energy received on Earth is in the form of short wavelengths. This energy is reflected back from the Earth's surface through long wavelengths in the form of infrared radiation as Earth's surface is much colder than the Sun. A part of the infrared radiation passes through the atmosphere and is released into space (defined as the atmospheric window) but most of it is re-emitted back to Earth by clouds and greenhouse gases (Kiehl and Trenberth 1997). This forms the greenhouse effect. The average air temperature on Earth is approximately 14°C (IPCC 2007) and without the greenhouse effect, this temperature would drop below the freezing point and life on Earth as we actually know would be much different. Water vapor is the most important gas responsible for the greenhouse effect followed by carbon dioxide (CO_2) and other important gases such as methane (CH_4), nitrous oxide (N_2O) and tropospheric ozone (O_3; Kiehl and Trenberth 1997; IPCC 2007). Most of these gases are naturally released by living organisms on Earth. For instance, water vapor is released by ocean and freshwater sources, and CO_2 from the respiration activity of all living organisms. Microbial activity also releases CO_2, CH_4 and N_2O. Tropospheric O_3 is produced following complex chemical reactions in the atmosphere which involve nitrogen oxides (NO_x) and volatile organic compounds (VOCs; Finlayson-Pitts and Pitts Jr. 1997). NO_x are mainly

produced by anthropogenic activities whereas VOCs can be both of anthropogenic and biogenic sources.

Human activity has increased the greenhouse effect since the beginning of the industrial era (ca. 1750 A.D.). The major greenhouse gases released by human activity are CO_2, CH_4, N_2O and halocarbons (IPCC 2007). Atmospheric concentrations of CO_2, CH_4 and N_2O have mainly increased following the burning of fossil fuels and the increase of agricultural activity with the use of fertilizers (IPCC 2007). Halocarbons include chlorofluorocarbons, which were previously used in the refrigeration systems. Atmospheric concentrations of halocarbons are diminishing as their productions have been regulated by the Montreal protocol. The increased greenhouse effect due to human activity has warmed the mean air temperature on Earth's surface during the last hundred years (between 1906 and 2005) by 0.74°C (IPCC 2007). Further increases in global air temperature are predicted for the next century (IPCC 2007) if no concrete action is taken to reverse the impact of human activity on the increased greenhouse effect.

Life in present form on Earth also depends on the protection that the stratospheric O_3 layer provides against solar ultraviolet-B (UV-B; wavelength of 280-320 nm) radiation. Since 1980, the stratospheric O_3 layer has been gradually depleted by substances such as halogen source gases and oxides of nitrogen mainly released by human activity (WMO 2007). The depletion of stratospheric O_3 has been more severe in the polar areas than at lower latitudes. For instance, one of the most extreme cases of O_3 depletion was discovered in the Antarctic in 1980 (WMO 2007). This severe O_3 depletion has been called an ozone hole due to its dramatic appearance from the satellite images. Since 1980, the O_3 depletion has increased over the Antarctic with some stabilization in the 1990s and 2000s, except in 2002 when another case of severe depletion was reported (WMO 2007).

In 1987, nations of the world began to commit to the Montreal protocol in which emissions of O_3 depleting substances were regulated. Nowadays, the stratospheric O_3 layer is still depleted by about 4% averaged over the globe and the depletion has remained severe over the poles, although the Montreal protocol has been respected and the emissions of O_3 depleting substances have been consistently reduced (WMO 2007). Complete recovery of the stratospheric O_3 layer is complex and will take several decades (WMO 2007).

This thesis discusses the effects of climate change on the non-methane biogenic volatile organic compound (BVOC) emissions from boreal and subarctic ecosystems. The responses of BVOC emissions to climate warming on a subarctic heath and boreal peatland are examined in detail. Moreover, the effect of enhanced UV-B radiation caused by stratospheric O_3 depletion on a subarctic peatland is investigated.

1.2 CLIMATE WARMING IN THE BOREAL AND SUBARCTIC REGIONS

Climate warming has been more severe in the boreal and subarctic regions than averaged over the globe. In the area north of 60°N, air temperature increases have been monitored during the last century and the annual mean temperature is projected to increase by 3.7°C by 2090, which is twice the average temperature increase projected over the globe (ACIA 2005). Models even predict that annual mean temperatures could increase by 7°C (ACIA 2005) in some regions of the Arctic.

Warmer temperatures in the boreal and subarctic regions increase the length of the growing season (Peñuelas and Filella 2001; Zhou et al. 2001), which has significant consequences on the ecosystem dynamics. In the Subarctic, longer growing seasons have already increased plant growth and the abundance of deciduous shrubs (Myneni et al. 1997; Tape et al. 2006). The

tree line of species such as the mountain birch (*Betula pubescens* ssp. *czerepanovii*) has already moved to higher altitudes (Truong et al. 2007) and to more northern latitudes (Callaghan et al. 2004). Thus, the increased plant growth and abundance of deciduous species in the subarctic region increase the leaf litter fall (Cornelissen et al. 2007), which is one of the indirect effects of climate warming in the high latitudes. Furthermore, increased litter fall has a fertilizing effect by increasing the amount of nutrients in the soil (Rinnan et al. 2007, 2008a).

Climate warming is expected to have an indirect effect on boreal peatlands by decreasing the water table level (Roulet et al. 1992). The predictions for the future precipitation patterns under climate change are not certain for the boreal and subarctic regions, although there is a tendency for an increase during the winter months (IPCC 2007; Strack et al. 2008). Nevertheless, if the atmospheric relative humidity remains constant, the warmer temperatures predicted under climate change are expected to increase the ecosystem evapotranspiration (Strack et al. 2008). The increased evapotranspiration is projected to induce water table drawdown that has been estimated between 14 and 22 cm, using a simple hydrological peatland model with a 3°C increase of air temperature and precipitation of 1 mm day^{-1} (Roulet et al. 1992).

Water table drawdown is expected to change the vegetation composition on boreal peatlands because it controls the microtopographic gradient through the distribution of vascular plants and mosses (Strack et al. 2008). For instance in ombrotrophic peatlands (nutrient poor), the microtopography consisting of hummocks, lawn and hollows is characterized by distinct vegetation communities. In the hummocks, water table drawdown is expected to decrease the cover of *Sphagnum* moss and increase the abundance of shrubs and lichens, while lawns would be invaded by sedges and the open water surface of hollows would be colonized by *Sphagnum* (Strack et al. 2006, 2008). On the landscape scale, water table drawdown would

also increase the abundance of trees, changing the ecological and biogeochemical functions of boreal peatlands (Strack et al. 2008).

1.3 UV-B RADIATION IN THE ARCTIC

The O_3 in the stratosphere has an important role in relation to the solar UV-B radiation reaching the Earth (WMO 2007). In contrast to the tropospheric O_3, which is considered as bad O_3, stratospheric O_3 is considered as good O_3 because it absorbs harmful solar UV-B radiation (WMO 2007). Thus, depletion of stratospheric O_3 leads to an increase in the flux of UV-B radiation to the Earth's surface and poses a potential problem for many life forms on Earth.

Stratospheric O_3 layer has been globally depleted by O_3 depleting substances produced by human activity (WMO 2007). The depletion of the stratospheric O_3 layer has been more severe in the Arctic than in lower latitudes. This has increased the amount of UV-B radiation reaching the ecosystems (ACIA 2005; WMO 2007). The emissions of O_3 depleting substances combined with the strong polar vortex during late winter and early spring depleted the total column O_3 by 7% in the Arctic for the period 1979-2000 (approx. -3% per decade; ACIA 2005).

Emissions of O_3 depleting substances have been reduced since the ratification of the Montreal protocol. However, the complete recovery of the stratospheric O_3 layer will still last for several decades, thus maintaining increased UV-B radiation levels in the Arctic (ACIA 2005; WMO 2007). The increased emissions of greenhouse gases are also partly responsible for the large O_3 losses over the Arctic and might partly delay the recovery of the O_3 layer (Shindell et al. 1998). Greenhouse gases warm the troposphere but cool the stratosphere radiatively (reviewed by Shindell et al. 1998), which creates conditions favorable for O_3 depletion over the Arctic (Shindell et al. 1998). The O_3 formation

depends on temperature (WMO 2007). Thus, a cooler stratosphere than normal prevents the formation of stratospheric O_3. The frequency of the sudden stratospheric warmings in the Northern Hemisphere, favorable for O_3 formation, is reduced by the temperature and wind changes induced by the increasing emissions of greenhouse gases in the troposphere (Shindell et al. 1998).

There is an indirect connection between climate change and enhanced UV-B radiation reaching the Earth's surface (WMO 2007). In the ongoing climate change, the stratosphere is expected to cool while the Earth's surface becomes warmer following the positive radiative forcing caused by increased emissions of greenhouse gases (WMO 2007).

Plants generally show mild changes in response to the photo-oxidation caused by enhanced UV-B radiation. In the polar regions, plants respond to enhanced UV-B radiation often by an increased production of UV-B absorbing compounds, DNA damage and a reduced growth depending on the species (Newsham and Robinson 2009). On a subarctic peatland in northern Finland (the site presented in chapter 3 of this thesis), enhanced UV-B radiation did not affect the physiology of the dominant sedge *Eriophorum russeolum* (Scharf 2006). However, Tiiva et al. (2007) reported that enhanced UV-B increased the isoprene emission from the peatland. Enhanced UV-B also had subtle effects on the CO_2 balance of this subarctic peatland after three years of exposure by slightly increasing the CO_2 uptake and decreasing the total respiration (Haapala et al. 2009), probably caused by reduced microbial respiration (Rinnan et al. 2008b). Rinnan et al. (2008b) suggested that enhanced UV-B radiation altered the peat bacterial community through changes in the plant photosynthate allocation and root exudation. In general, it has been hypothesized that changes in the natural amount of UV-B radiation indirectly affect soil microbial community through effects on plants root exudation (Avery et al. 2003, 2004; Rinnan et al. 2005a). In the Antarctic, Avery et al.

(2003) observed that reduced UV-B radiation altered the phenotypic profile of the rhizosphere microbial community by increasing their utilization of carbohydrate and carboxylic acid. In the Arctic, Johnson et al. (2002) showed that plant exposure to enhanced UV-B radiation altered the soil microbial community and the content of nitrogen held in the soil microbial biomass.

1.4 EMISSIONS OF NON-METHANE BIOGENIC VOLATILE ORGANIC COMPOUNDS (BVOCS)

1.4.1 Definition and function of BVOCs

The term biogenic volatile organic compounds (BVOCs) refers to hydrocarbons or "organic atmospheric trace gases other than carbon dioxide and monoxide" (Kesselmeier and Staudt 1999). On the global scale, 90% of the non-methane volatile organic compound emissions are of biogenic sources while the remaining 10% is of anthropogenic origin (Fuentes et al. 2000). BVOCs are released from all living organisms from bacteria to humans.

BVOCs were first studied by Sanadze (1956) who showed that isoprene was emitted from leaves of some plant species. The research group led by the pioneer Professor Sanadze discovered plant isoprene emission through experiments done in 1954 where the gas releases from leaves were studied in the context of allelopathy (reviewed by Sanadze 2004). The work of Went (1960) was the first to describe the importance of BVOC emissions in the physics and chemistry of the atmosphere. It was explained that the formation of blue haze originated from reactions of BVOC forming aerosols. Since the first studies on BVOC emissions in the 1960s, over 1000 articles have been published on the synthesis and function of BVOC emissions and the number of publications is increasing year after year (reviewed by Laothawornkitkul et al. 2009 and Dicke and Loreto 2010).

In this thesis, I will present studies of emissions of isoprene, monoterpenes, sesquiterpenes, other reactive volatile organic compounds (ORVOCs; compounds with a lifetime of less than one day as a result of reactions with the OH radicals, NO_3 and O_3; Guenther et al. 1995) and other volatile organic compounds (other VOCs; compounds with a lifetime of more than one day; Guenther et al. 1995). Figure 1 shows examples of molecular structures for each of these compound groups. The responses of BVOC emissions to the effects of climate change were assessed in experiments on some ecosystems of the boreal and subarctic regions.

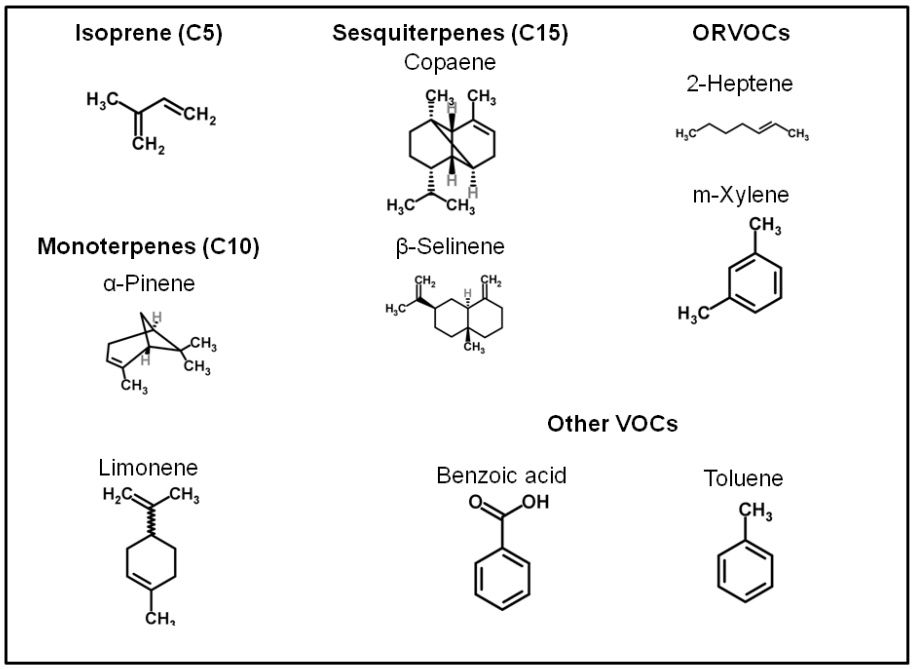

Figure 1. Examples of molecular structures of compounds measured in this thesis (Source: ChemSpider, http://www.chemspider.com/).

The annual global BVOC emissions range between 700-1000 × 10^{12} g C in which isoprene is the most emitted compound (Table 1; Laothawornkitkul et al. 2009). Monoterpenes are also emitted in large quantities as well as the ORVOCs and other VOCs.

Table 1: *Global BVOC emissions on Earth (adapted from Laothawornkitkul et al. 2009).*

BVOC group	**Estimated global annual emission (10^{12} g C)**	**Examples of compounds measured in this thesis**
Isoprene	412-601	
Monoterpenes	33-480	α-Pinene, β-myrcene, limonene
ORVOCs	~ 260	Sesquiterpenes, 2-heptene, xylenes
Other VOCs	~ 260	Toluene, benzoic acid, methylcyclopentane
Total BVOCs	700-1000	

Sources used by Laothawornkitkul et al. (2009) to compile these emissions: Guenther et al. (1995), Hewitt et al. (1997), Kirstine et al. (1998), Fall (1999), Fukui and Doskey (2000), Lathière et al. (2005), Arneth et al. (2008), Davison et al. (2008), BAI Data BVOC (http://bai.acd.ucar.edu/Data/BVOC/index.shtml, 2010)

BVOC emissions play important roles in the biological interactions between plants and animals. Plants release BVOCs to attract pollinators (Knudsen et al. 2006). In addition, BVOCs are also used by plants as repellents or feeding deterrents, which give a direct defense against herbivores (Dicke 1986; Holopainen and Gershenzon 2010). Plants attacked by herbivores also release BVOCs in indirect defense mechanisms where BVOCs attract the predators of the specific herbivores (Dicke et al. 1990; Turlings et al. 1990; Holopainen and Gershenzon 2010). Furthermore, BVOCs are also important in plant-to-plant communication. Damaged or infected plants release BVOCs as signals that are received by neighbors of the same or different species and prime against an eventual attack (Baldwin and Schultz 1983; Heil and Karban 2010).

Microorganisms living in the soil are also known to release and degrade BVOCs (Cleveland and Yavitt 1998; Asensio et al. 2007; Owen et al. 2007; Bäck et al. 2010; Insam and Seewald 2010; Seewald et al. 2010). Moreover, litter decomposition by microorganisms releases BVOCs (Isidorov and Jdanova 2002; Leff and Fierer 2008; Isidorov et al. 2010; Ramirez et al. 2010).

BVOC emissions have also been measured from peat cores (Beckmann and Lloyd 2001; Rinnan et al. 2005b).

BVOCs are also important in the chemistry of the atmosphere. The reactions between BVOCs and oxides of nitrogen form tropospheric O_3 (Chameides et al. 1988; Laothawornkitkul et al. 2009; Peñuelas and Staudt 2010), which is an important greenhouse gas and a pollutant in urban areas. BVOCs also compete with CH_4 for the hydroxyl (OH) radicals (Kaplan et al. 2006). Thus, BVOCs lengthen the lifetime of CH_4 by scavenging OH radicals. Atmospheric reactions between BVOCs, oxides of nitrogen and tropospheric O_3 also form secondary organic aerosols and the end product of the BVOC oxidation cycle is CO_2 (Fehsenfeld et al. 1992; Fuentes et al. 2000; Peñuelas and Staudt 2010). Thus, oxidative reactions of BVOCs in the atmosphere might have an impact on climate warming as BVOCs can increase the concentrations of three major greenhouse gases: CO_2, CH_4 and tropospheric O_3. However, the formation of secondary organic aerosols from BVOCs has a cooling effect on land surface (IPCC 2007). In contrast, in the specific conditions found over the Arctic Ocean, secondary organic aerosol warms the surface by an increased cloudiness causing a climatologically significant warming (Mauritsen et al. 2010). The interactions between BVOCs and greenhouse gases have unknown feedbacks on climate warming (IPCC 2007; Peñuelas and Staudt 2010).

1.4.2 Isoprene, the most emitted BVOC

Isoprene (C_5H_8, 2-methyl-1,3-butadiene) is part of the terpenoid (or isoprenoid) family (Kesselmeier and Staudt 1999) and is the most emitted BVOC by living organisms (Table 1). All terpenoids are synthesized from a common C_5 precursor, the isopentenyl pyrophosphate (IPP; Kesselmeier and Staudt 1999). IPP is converted to the isomer dimethylallyl pyrophosphate (DMAPP) that is the precursor for isoprene (Kesselmeier and Staudt 1999; Sharkey and Yeh 2001). Isoprene can be synthesized through two pathways that produce IPP

transformed to DMAPP: the mevalonic acid pathway (MVA) and methyl-erythritol pyrophosphate pathway (MEP). The MVA pathway takes place in the cytosol and uses acetyl-CoA to produce DMAPP that is converted to isoprene (Deneris et al. 1985; Kesselmeier and Staudt 1999; Sanadze 2004). The MEP pathway takes place in the chloroplast and uses pyruvate and glyceraldehyde-3-phosphate as substrates to produce DMAPP (Rohmer et al. 1993; Kesselmeier and Staudt 1999; Sharkey and Yeh 2001). DMAPP is converted to isoprene by the enzyme isoprene synthase (Silver and Fall 1991).

Isoprene is not stored in plant organs but from de novo synthesis (Sharkey and Yeh 2001), thus its emission is controlled by its synthesis (Sharkey 1991). Isoprene is released through stomata (Tingey et al. 1981) and a negligible amount is released through the cuticle, when stomata are closed (Jones and Rasmussen 1975; Monson and Fall 1989; Fall and Monson 1992). If stomata are closed, isoprene concentration increases in the leaf intercellular space up to a point where the diffusive gradient forces the release in order to maintain the equilibrium (Fall and Monson 1992). Thus, the emission rate is reestablished to the equilibrium in the intercellular space and follows the rate of isoprene synthesis (Fall and Monson 1992).

Isoprene emission from plants is light dependent (Guenther et al. 1993; Kesselmeier and Staudt 1999; Sanadze 2004). The light dependence of isoprene emission was first noticed by the research group of Professor Sanadze in the late 1950s when illuminated leaves were emitting isoprene in larger quantities than other hydrocarbons (reviewed by Sanadze 2004). Isoprene emission under light follows a similar pattern as photosynthesis. Isoprene emission increases linearly with light until it reaches a plateau in conditions of saturating light intensity (Guenther et al. 1993; Kesselmeier and Staudt 1999). Under high light intensity, isoprene emission can dissipate excess energy and has been shown to have a photoprotective role (Peñuelas and Munné-Bosch 2005). Isoprene emission reacts quickly to changes in light

intensity and the emission is immediately reduced when conditions turn to dark (Tingey et al. 1981; Monson et al. 1991).

Isoprene emission is also temperature dependent (Monson et al. 1992; Guenther et al. 1993; Harley et al. 1999). The dependence between isoprene emission and temperature is different from light dependence. Isoprene emission increases exponentially with temperatures between 15 and 35°C up to an optimum reached at 40-42°C (Harley et al. 1999). Above this temperature threshold, isoprene emission decreases due to the too high temperature that decreases the activity of the enzyme isoprene synthase (Monson et al. 1992). Elevated temperature increases the isoprene emission capacity of leaves (Sharkey et al. 1999; Pétron et al. 2001) in the medium term (days to months), where the increases of isoprene emission provide a protective role in plants subjected to warming. Isoprene emission has been shown to increase the thermotolerance of plants under elevated temperature and could protect the photosynthetic apparatus (Sharkey and Singsaas 1995; Sharkey and Yeh 2001; Velikova et al. 2006; Behnke et al. 2007). A suggested potential mechanism responsible for the protective role of isoprene under warming is the protection of the thylakoid membrane in the chloroplast where isoprene is synthesized (Sharkey and Yeh 2001; reviewed by Peñuelas et al. 2005b). Isoprene maintains photosynthetic capacity by preventing the denaturation of the membrane lipids under warming, thus increasing the membrane stability (Sharkey 2005; Velikova and Loreto 2005). Another potential protection mechanism is that isoprene scavenges the reactive oxygen species that are produced during heat stress (Loreto and Velikova 2001; Sharkey 2005; Velikova and Loreto 2005).

Isoprene emission may also have a protective role against the oxidative effects of tropospheric O_3 on plants. It has been suggested that isoprene can protect the cell membranes either by acting as an antioxidant, reacting with O_3 before it forms oxidative agents, or by quenching the peroxide formed by O_3

reactions inside the leaf, reducing the degradation of lipids in the membrane (Loreto and Velikova 2001).

Plant emission of isoprene is also sensitive to water conditions in the soil. Severe water deficit and stress caused by drought has been reported to decrease isoprene emission whereas a return to pre-stress conditions increases the emission to levels higher than the pre-stress values (Sharkey and Loreto 1993; Pegoraro et al. 2004; Peñuelas and Staudt 2010). Tiiva et al. (2009) showed that water table drawdown applied on boreal peatland microcosms decreases isoprene emission. It was hypothesized that oxic conditions in the peat soil due to lower water table could have favored the degradation of isoprene by microorganisms (Cleveland and Yavitt 1998; Tiiva et al. 2009).

1.4.3 Monoterpenes

Monoterpenes are part of the terpenoid family and are characterized by a C_{10} skeleton. Monoterpenes are synthesized in the plastids through the MVA and MEP pathways where an IPP unit is added to DMAPP, forming the monoterpene geranylpyrophosphate (GPP; reviewed by Kesselmeier and Staudt 1999; Laothawornkitkul et al. 2009). GPP is the starting unit from which other monoterpenes are formed. Monoterpenes can be stored in plant organs such as resin ducts or glands and leaf reservoirs in monoterpene storing species (Monson et al. 1995; Lerdau et al. 1997; Kesselmeier and Staudt 1999). However, Ghirardo et al. (2010) show that a significant part of monoterpene emissions from many species originates from de novo synthesis and not from storage deposits, similarly to isoprene emission.

Monoterpene emissions from monoterpene storing species are not typically light dependent, although some storing species show a light dependence (reviewed by Kesselmeier and Staudt 1999). Monoterpene emissions can also be directly light dependent in the non-storing species, which is observed in

leaves of many deciduous species such as oaks and poplars (Loreto and Schnitzler 2010).

All monoterpene emissions are temperature dependent (Guenther et al. 1993; Laothawornkitkul et al. 2009; Loreto and Schnitzler 2010). The relation between monoterpene emissions and temperature is exponential but the emissions decrease once the temperature reaches a threshold of 45°C (Tingey et al. 1980; Staudt and Bertin 1998; Kesselmeier and Staudt 1999). In the monoterpene storing species, elevated temperature increases the emissions from the storage organs by increasing the volatility and synthesis through increased enzymatic activity (Loreto and Schnitzler 2010). In the non-storing species, monoterpenes are pooled temporarily in the leaf mesophyll and released out following the concentration gradient affected by temperature (Loreto and Schnitzler 2010). In this case, stomatal conductance also interacts with temperature on the emission rate of monoterpenes (Loreto and Schnitzler 2010).

Water conditions in the soil can also affect monoterpene emissions from the emitting species. Severe water stress related to water table drawdown or drought decreases monoterpene emissions in most of the cases (Bertin and Staudt 1996; Lavoir et al. 2009; Niinemets 2010; Peñuelas and Staudt 2010). In contrast, mild water stress increases or does not affect monoterpene emissions (Staudt et al. 2008; Niinemets 2010; Peñuelas and Staudt 2010). In a boreal Scots pine forest, drought has been observed to increase monoterpene emissions (Lappalainen et al. 2009).

Monoterpenes are also emitted from diverse components in soil. Plant roots of some species have been identified as monoterpene emitters. For instance, the interactions between the roots of *Arabidopsis* and microorganisms release the monoterpene 1,8-cineole among other BVOCs (Steeghs et al. 2004). Litter and its decomposition by microorganisms is also a source of monoterpenes from soil. The microbial activity releases several

monoterpenes through the decomposition of litter from various deciduous and coniferous species (Isidorov and Jdanova 2002; Leff and Fierer 2008; Isidorov et al. 2010; Ramirez et al. 2010). Pure cultures of fungi isolated from roots of Scots pine release monoterpenes such as α-pinene, δ3-carene, limonene and linalool (Bäck et al. 2010). Monoterpene emissions from soil also depend on the aerobic conditions that can trigger a release or degradation by the microbial activity (Insam and Seewald 2010; Seewald et al. 2010).

1.4.4 Sesquiterpenes

Sesquiterpenes are terpenoids with a C_{15} skeleton and highly reactive, which makes them challenging to study (Duhl et al. 2008). They are synthesized via the same pathway as monoterpenes (i.e. MVA and MEP) where an IPP unit is added to GPP to form the sesquiterpene body farnesylpyrophosphate (FPP, reviewed by Kesselmeier and Staudt 1999; Laothawornkitkul et al. 2009). Similar to monoterpenes, sesquiterpenes are stored in plant organs, which is a factor controlling the emissions (reviewed by Duhl et al. 2008).

Emissions of semivolatile sesquiterpenes are strongly temperature dependent (Hansen and Seufert 1999; Duhl et al. 2008). Helmig et al. (2006) found that sesquiterpene temperature dependence was stronger than for monoterpenes in Loblolly pine trees in ambient temperatures over 30°C. Moreover, the ratio sesquiterpenes/monoterpenes increases with temperature for Pine trees of the contiguous United States (Helmig et al. 2007). Thus, sesquiterpene emissions become more important under warm temperatures. Sesquiterpene emissions have also been observed to be light dependent to some extent, depending on the compound emitted and plant species (reviewed by Duhl et al. 2008).

Sesquiterpene emissions are also affected by soil moisture conditions (reviewed by Duhl et al. 2008). For instance, Hansen and Seufert (1999) show that a severe drought stress decreases

β-caryophyllene emission, the most emitted sesquiterpene released from branches of a young orange tree. However, a mild drought stress did not affect the β-caryophyllene emission (Hansen and Seufert 1999). Sesquiterpene emissions can be decreased under severe water stress (Llusià and Peñuelas 1998) if the photosynthesis is decreased because their synthesis depends on a small carbon pool immediately fixed during photosynthesis (Niinemets 2010).

The activity of soil microorganisms, for example fungi, releases sesquiterpenes (reviewed by Insam and Seewald 2010). For instance, Bäck et al. (2010) measured sesquiterpene emissions from pure cultures of fungi isolated from Scots pine roots in a boreal forest. Leff and Fierer (2008) reported that litter decomposition in montane, hardwood and pine forests of United States releases caryophyllene.

1.4.5 ORVOCs and other VOCs

The ORVOCs are compounds that have a lifetime of less than one day due to their reactions with OH radicals, NO_3 and O_3 (Guenther et al. 1995). Common examples of ORVOCs are the green leaf volatiles released after a physical damage on a plant (Laothawornkitkul et al. 2009). Other examples of ORVOCs are the compounds acetaldehyde, formaldehyde and those in the hexenal family (Laothawornkitkul et al. 2009).

The other VOCs are less reactive than ORVOCs and have a lifetime of more than one day (Guenther et al. 1995). A common example of an "other VOC" emitted in the experiments of this thesis is toluene. Biogenic sources of toluene include the anoxic hypolimnion in a stratified lake (Jüttner and Henatsch 1986), and peat cores (Beckmann and Lloyd 2001; Rinnan et al. 2005b). However, the larger sources of toluene are most commonly anthropogenic (Jüttner and Henatsch 1986). Methanol is also another common example of an "other VOC" substantially emitted by plants (reviewed by Sharkey 1996), although it was not measured in this thesis. Holst et al. (2010) measured

emission of methanol from a subarctic mire in northern Sweden. Peñuelas et al. (2005a) and von Dahl et al. (2006) found that a large quantity of methanol was induced from plants wounded by caterpillars feeding. Methanol has a long atmospheric lifetime (Atkinson and Arey 2003) and its emission after wounding may play a role in long-distance signaling in plant-herbivore interactions (Peñuelas et al. 2005a; von Dahl et al. 2006).

The pathways by which ORVOCs and other VOCs are synthesized in plants are well studied but the bioregulation and function of these emissions are still not clearly known (Laothawornkitkul et al. 2009). ORVOCs and other VOCs are synthesized in different pathways than terpenoids (reviewed by Laothawornkitkul et al. 2009). For instance, green leaf volatiles are synthesized through the lipoxygenase (LOX) pathway (reviewed by Laothawornkitkul et al. 2009).

Temperature and light dependences have been reported for emissions of some ORVOCs and other VOCs (Kesselmeier et al. 1997; Staudt et al. 2000b). Kesselmeier et al. (1997) showed that the emissions of short chain acetic and formic acids from *Quercus ilex* and *Pinus pinea* were light and temperature dependent. The emissions of formic and acetic acids could be modeled by the light-temperature algorithm used for isoprene (Guenther et al. 1993; Kesselmeier et al. 1997). Staudt et al. (2000b) also showed a clear light dependence of formic and acetic acids emissions using the light algorithm of Guenther et al. (1993), while the response to temperature was more variable.

The activity of microorganisms in soil is responsible for the emissions of several ORVOCs and other VOCs (Insam and Seewald 2010). For instance, Bäck et al. (2010) measured emissions of the short chained ORVOC acetaldehyde and the other VOC acetone from pure cultures of fungi isolated from Scots pine roots. Beckmann and Lloyd (2001) and Rinnan et al.

(2005b) also measured emissions of several ORVOCs and other VOCs from peat cores.

1.5 BVOC EMISSIONS AND CARBON EXCHANGE

Carbon emitted as BVOCs can reach a significant proportion of the net and gross primary productivity in some ecosystems (Llusià and Peñuelas 2000; Kesselmeier et al. 2002; Kuhn et al. 2007; Tiiva et al. 2007; Bäckstrand et al. 2008). Therefore, it is important to consider this quantity of carbon released as BVOCs when assessing the carbon balance of an ecosystem. Kuhn et al. (2007) estimated that carbon emitted as isoprene and monoterpenes was as high as 6% of the net and gross primary productivity in an Amazonian rainforest, whereas Kesselmeier et al. (2002) reported proportions reaching 12% for tree species from the Mediterranean area and tropical rainforest in Amazonia. The proportion of carbon emitted as BVOCs from CO_2 uptake through photosynthesis can also vary between seasons as shown by Llusià and Peñuelas (2000) for monoterpene emissions from Mediterranean woody species. For these species, the carbon fixed by photosynthesis and reemitted as monoterpenes reached higher proportions in the summer (0.51% to 5.64%) than during other seasons (below 1%; Llusià and Peñuelas 2000).

Some studies reported significant proportions of carbon emitted as BVOCs relative to CO_2 uptake in boreal and subarctic ecosystems. Bäckstrand et al. (2008) estimated that 5% of the CO_2 uptake was reemitted in BVOCs in a subarctic peatland in northern Sweden. This proportion was lower in a subarctic peatland in northern Finland where isoprene emission was below 0.5% of CO_2 uptake, although a maximum of 10% was measured during unusually warm temperature (Tiiva et al. 2007); the carbon emitted as isoprene was also 6% of the carbon emitted as CH_4. On a subarctic heath, only 0.1% of the CO_2 uptake was emitted as isoprene (Tiiva et al. 2008).

Water table level affects the proportion of carbon emitted as BVOCs from boreal peatland vegetation. In an experiment with boreal peatland microcosms, a water table drawdown of 20 cm increased the proportion of carbon emitted as isoprene relative to CO_2 uptake from 0.1 to 3% (Tiiva et al. 2009). In contrast, water table drawdown did not affect the proportion of carbon emitted as isoprene relative to CH_4 emission, which was 2%, because both isoprene and CH_4 emission were similarly affected by water table drawdown (Tiiva et al. 2009).

1.6 BVOC EMISSIONS FROM BOREAL AND SUBARCTIC ECOSYSTEMS

Some ecosystems of the boreal and subarctic regions have been investigated for BVOC emissions but a lot of research is still needed to better cover these vast areas and increase the accuracy of the emission estimates. Table 2 shows that BVOC emissions from some peatlands, heaths and forests of the north have been measured for certain periods of time, although the ecosystems of the southern latitudes have been more extensively studied (Kesselmeier and Staudt 1999). Klinger et al. (1994) were among the first to report BVOC emissions from boreal peatlands and forests in the Hudson Bay lowland in Canada. Other research groups have been active in measuring the BVOC emissions from the boreal and subarctic zones in Sweden and Finland (Table 2). Most of these studies consist of observational measurements of the BVOC emissions with no experimental treatment applied in the field. However, the work done by Tiiva et al. (2007, 2008) investigated some effects of climate change such as warming and enhanced UV-B radiation on isoprene emission. Therefore, more experiments are warranted to study the impact of climate change on the emissions of BVOCs other than of isoprene from the boreal and subarctic ecosystems.

Table 2: *Summary of BVOC emissions from the boreal and subarctic ecosystems.*

Study	Area	Ecosystem	Method	Isoprene	Monoterpenes	Sesquiterpenes	Total BVOCs
BOREAL ZONE							
Peatlands							
Klinger et al. (1994)	Hudson Bay lowland	Fen	Static chamber	0.8-67.9 mg C m^{-2} h^{-1}	22.5-146.3 mg C m^{-2} h^{-1}	n. m.	n. m.
		Sphagnum Bog		17.9-104.2 mg C m^{-2} h^{-1}	0-54.6 mg C m^{-2} h^{-1}	n. m.	n. m.
Janson and De Serves (1998)	Finland, Sweden	*Sphagnum* fen	Static chamber	[a,b]624 µg C m^{-2} h^{-1}	n. m.	n. m.	n. m.
Janson et al. (1999)	Sweden	*Sphagnum* fen	Static chamber	[b]Jun: 55 µg C m^{-2} h^{-1} [b]Aug: 408 µg C m^{-2} h^{-1}	[b]Jun: 19 µg C m^{-2} h^{-1} [b]Aug: 90 µg C m^{-2} h^{-1}	n. m.	n. m.
Haapanala et al. (2006)	Southern Finland	*Sphagnum* fen	REA	[a,b]680 µg m^{-2} h^{-1}	n. m.	n. m.	n. m.
Forests							
Klinger et al. (1994)	Hudson Bay lowland	Bog forest	Static chamber	0-9.6 mg C m^{-2} h^{-1}	40-67.5 mg C m^{-2} h^{-1}	n. m.	n. m.
		Black spruce		6.3-150.4 mg C m^{-2} h^{-1}	192.9-293.3 mg C m^{-2} h^{-1}	n. m.	n. m.
Rinne et al. (2000)	Northern Finland	Mountain birch, Scots pine, Siberian spruce	Gradient method	[c]14 µg m^{-2} h^{-1}	[d]108-216 µg m^{-2} h^{-1}	n. m.	n. m.

Study	Area	Ecosystem	Method	Isoprene	Monoterpenes	Sesquiterpenes	Total BVOCs
Tarvainen et al. (2007)	Finland	Southern boreal	Modeling	[a]73 kg km^{-2} y^{-1}	[a]657 kg km^{-2} y^{-1}	[a]54 kg km^{-2} y^{-1}	n. m.
		Middle boreal		[a]56 kg km^{-2} y^{-1}	[a]567 kg km^{-2} y^{-1}	[a]46 kg km^{-2} y^{-1}	n. m.
		Northern boreal		[a]45 kg km^{-2} y^{-1}	[a]342 kg km^{-2} y^{-1}	[a]26 kg km^{-2} y^{-1}	n. m.
SUBARCTIC ZONE							
Peatlands							
Tiiva et al. (2007)	Northern Finland	Fen	Dynamic chamber	[a,e]53 µg m^{-2} h^{-1}	n. m.	n. m.	n. m.
Bäckstrand et al. (2008)	Northern Sweden	Mire	Automated static chambers	n. m.	n. m.	n. m.	[f]150 kg C
Tiiva et al. (2008)	Northern Sweden	Heath	Dynamic chamber	[e]36-58 µg m^{-2} h^{-1}	n. m.	n. m.	n. m.
Holst et al. (2010)	Northern Sweden	Mire	PTR-MS, DEC	[g]329 µg C m^{-2} h^{-1}	n. m.	n. m.	n. m.

n.m. not measured

[a]Standardized to 30°C and PPFD of 1000 µmol m^{-2} s^{-1}

[b]Mean

[c]Mean day time flux

[d]Total day time flux

[e]Mean for one growing season

[f]Growing season of 150 days

[g]Standardized to 20°C and PPFD of 1000 µmol m^{-2} s^{-1} for a period of 50 days (1 August to 19 September 2006)

1.7 DESCRIPTION OF THE METHOD FOR BVOC MEASUREMENTS

All BVOC emissions reported for the experiments done on field and in growth chambers were measured using a conventional chamber technique (Figures 2, 3) and gas chromatography-mass spectrometry (GC-MS) analyses. Briefly, the sampling technique was a conventional push-pull system used for measurement of BVOC emissions from the whole plant/soil system (Tholl et al. 2006; Ortega and Helmig 2008; Tiiva et al. 2007, 2008, 2009). Air sampling was done using a transparent polycarbonate chamber placed on a collar filled with water to air-tighten the chamber headspace. A small battery-operated pump pulled the air sample through an Automatic Thermal Desorption (ATD) steel tube filled with a combination of Tenax TA and Carbopack B adsorbents (100 mg of each, mesh 60/80). Air sampling for BVOCs lasted 30 minutes, during which an air volume of six liters was sampled. The outflow was set to 200 ml min^{-1} through the sample tube. In order to prevent air leakage from outside into the chamber, a slightly superior inflow was maintained by pumping air at a rate of 215 ml min^{-1} (Staudt et al. 2000a; Tiiva et al. 2009). The BVOC concentrations in the inflow air were considered to be negligible thanks to the purification system consisting of a charcoal filter to remove BVOCs and a MnO_2 scrubber to remove O_3 (Ortega and Helmig 2008). During the sampling period, the chamber air was circulated with a small fan and the photosynthetic photon flux density (PPFD), air temperature and humidity were measured.

The samples were analyzed by GC-MS and the BVOCs were identified according to the mass spectra in the Wiley data library, and quantified by pure standard compounds according to total ion counts. The emission rates were calculated by dividing the BVOC mass in the ATD tube by the air outflow rate and sampling time, and then multiplied by the chamber volume to obtain the absolute amount of BVOCs in the headspace (Tiiva

et al. 2007, 2008, 2009). The soil surface microtopography was taken into account when determining the chamber headspace volume by measuring the chamber height from grid points on the soil surface. The emission rate of BVOCs was finally divided by the surface area of the plot and given per hour.

This chamber method has some weaknesses (discussed in section 6.1) but was ideal and convenient for comparison of treatment effects in the well-replicated field experiments in remote locations or in plant growth chamber experiments.

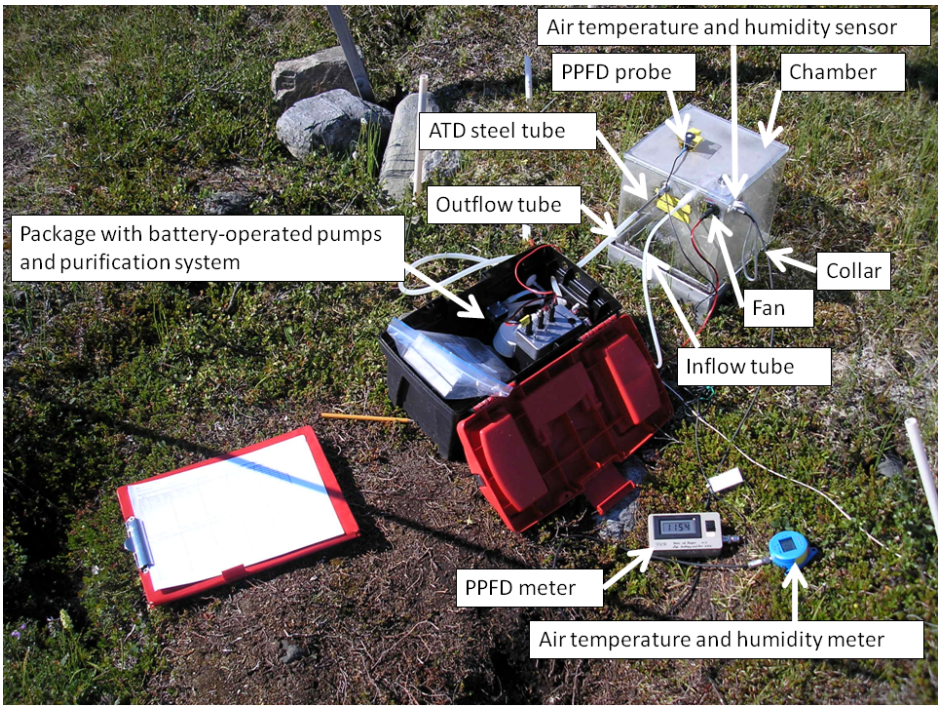

Figure 2. Photo of the chamber set-up and technique used to measure the BVOC emissions in the field experiments.

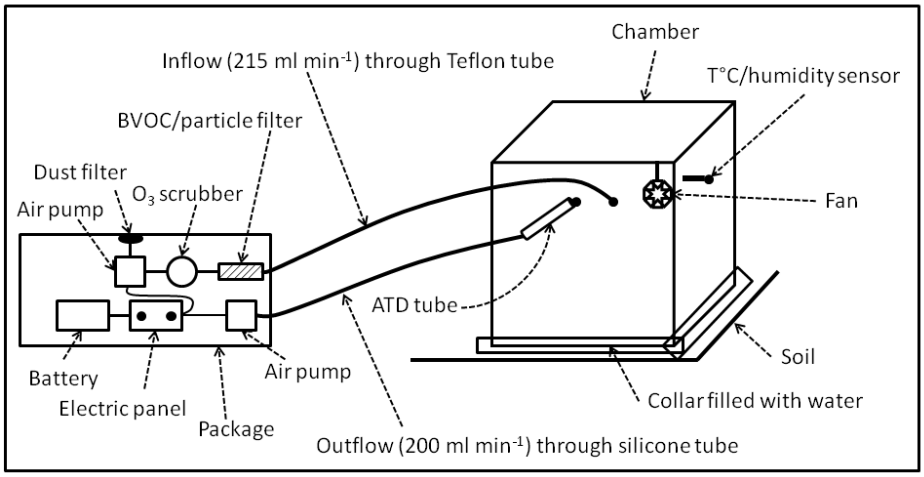

Figure 3. Annotated diagram of the chamber set-up and sampling line used to measure the BVOC emissions.

1.8 OBJECTIVES OF THE RESEARCH AND OVERVIEW OF THE EXPERIMENTS

The aim of this thesis was to assess the responses of BVOC emissions to climate change in boreal and subarctic ecosystems. Four effects of climate change were examined on the BVOC emissions:

1) the direct effect of warming, and its indirect effects via
2) water table drawdown
3) change in the vegetation composition
4) enhanced UV-B radiation

The hypotheses tested related to each of these objectives are shown in table 3. As shown in section 1.6 (Table 2), a number of studies have monitored BVOC emissions from boreal and subarctic ecosystems but few of them have examined the effects of climate change on the BVOC emissions besides the experiments done by Tiiva et al. (2007, 2008, 2009) on isoprene emission. Thus, this thesis is filling the gap concerning the

understanding of effects of climate change on BVOC emissions other than isoprene, from boreal and subarctic ecosystems.

Table 3: *Four effects of climate change examined on the BVOC emissions from boreal and subarctic ecosystems and the hypotheses tested.*

Effect of climate change	**Hypothesis tested**
1) Warming	Warming increases the BVOC emissions (Guenther et al. 1995; Duhl et al. 2008; Tiiva et al. 2008; Hartikainen et al. 2009)
2) Water table drawdown	Water table drawdown decreases the BVOC emissions (Tiiva et al. 2009)
3) Change in the vegetation composition	Change of the vegetation composition affects the BVOC emission signature (Tiiva et al. 2009)
4) Enhanced UV-B radiation	Enhanced UV-B radiation increases BVOC emissions (Tiiva et al. 2007)

Table 4 describes briefly each of the experiments presented in this thesis. Figure 4 shows the locations of the study sites in northern Finland and Sweden and the boreal peatland from which material was collected for the experiments done in plant growth chambers. Figure 5 shows photos of each experiment.

Table 4: *Brief description of the experiments of this thesis with their chapters in which they are presented in detail.*

Experiment	**Ecosystem**	**Location**	**Treatment**	**Experiment type**	**Duration of exposure**	**Chapter**
Effect of warming on BVOC emissions	Subarctic heath	Abisko, northern Sweden	-Warming by 3-4°C -Litter addition	Field experiment	7-8 years	2
Effect on enhanced UV-B radiation on BVOC emissions	Subarctic peatland	Sodankylä, northern Finland	-Enhancement of UV-B radiation by 46%	Field experiment	3-5 years	3
Effect of vegetation removal and water table drawdown on BVOC emissions	Boreal peatland	Kuopio, Finland	-Vegetation removal -Water table drawdown of 20 cm	Microcosms in plant growth chambers	7 weeks	4
Effect of warming and water table drawdown on BVOC emissions	Boreal peatland	Kuopio, Finland	-Warming by 5°C -Water table drawdown of 20 cm	Microcosms in plant growth chambers	7 weeks	5

Figure 4. Locations of the study sites in this thesis. The experiments in chapters 2 and 3 were done in Abisko and Sodankylä, respectively. The material for the microcosms used in the studies in chapters 4 and 5 were collected on a boreal peatland in Suonenjoki and the experiments were done in the plant growth chambers at the University of Eastern Finland, Kuopio.

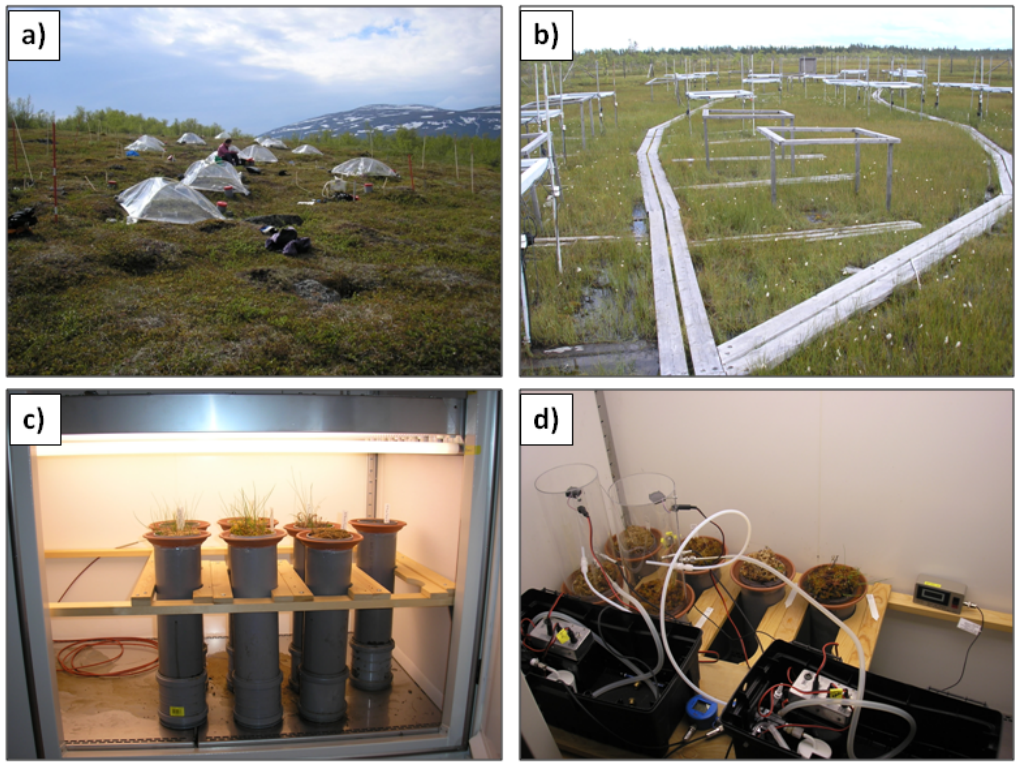

Figure 5. Photos of the experiments presented in this thesis: a) subarctic heath with the open top chambers (chapter 2), Abisko, northern Sweden, b) subarctic peatland with the UV-A and UV-B lamps (chapter 3), Sodankylä, northern Finland, c) hummock and hollow microcosms in plant growth chambers (chapter 4), University of Eastern Finland, Kuopio, d) BVOC measurements from lawn microcosms in plant growth chambers (chapter 5), University of Eastern Finland, Kuopio.

The aim of the study in chapter 2 was to assess the effects of climatic warming on the BVOC emissions (excluding isoprene, which is presented in Tiiva et al. 2008) from a wet subarctic heath in Abisko, northern Sweden (Table 4; Figures 4, 5a). The experiment simulating climatic warming was established in 1999 (that is, seven years prior to the commencement of the measurements) and has been maintained since then (Rinnan et al. 2007, 2008a). BVOC emissions were measured in the growing seasons of 2006 and 2007. The experiment included a control, warming treatment, a litter addition treatment and their combination. The warming treatment was applied using open-top chambers covered with transparent plastic layer increasing the air temperature by 3-4°C. The open-top chambers were installed for the growing season, from early June to late August. The litter addition treatment consisted of adding 90 g DW m^{-2} of air-dried mountain birch litter yearly in late August. The motive behind the litter addition treatment was to simulate the change in litter type and quality following the migration of deciduous tree species northward due to longer growing season with warming in the Subarctic (Cornelissen et al. 2007). The warming treatment was predicted to increase the monoterpene and sesquiterpene emissions (Guenther et al. 1995; Duhl et al. 2008; Hartikainen et al. 2009) as it did for isoprene (Tiiva et al. 2008). The litter addition treatment was predicted to change the BVOC emission signature either directly, with compounds released from the litter itself (Isidorov and Jdanova 2002; Leff and Fierer 2008; Ramirez et al. 2010), or indirectly, through alterations of the belowground processes (that is, microbes, mineralization, carbon turnover and nutrient pool; Rinnan et al. 2007, 2008a). The emissions of some compounds were expected to increase and those of others to decrease.

The aims of the study in chapter 3 were to report an estimate of the BVOC emissions from a subarctic peatland in Sodankylä, northern Finland (Table 4; Figures 4, 5b). Moreover, the aims

were to estimate the long-term effect of enhanced UV-B on the BVOC emissions. The measurements were done in the growing seasons of 2006 and 2008. The experiment was established in 2003 and consisted of plots exposed to ambient solar radiation and enhanced UV-B radiation targeted to a 46% increase in the UV-B flux. A UV-A control was used in order to compensate for the slight UV-A radiation increase by the UV-B lamps. BVOC emissions were predicted to increase under enhanced UV-B radiation as it was measured for isoprene emission (Tiiva et al. 2007). The net ecosystem CO_2 exchange (NEE) and CH_4 emission were also measured to determine the relationship between the carbon emitted as BVOCs and the total net carbon exchange.

The study in chapter 4 was done in plant growth chambers and it had the objective to distinguish the BVOC emissions released by vascular plants, mosses and peat in boreal peatland microcosms of hummock and hollow microtopographies (Table 4; Figures 4, 5c). The effect of water table drawdown (-20 cm) was also assessed on the BVOC emissions from hollows. The third aim was to investigate if the potential effects of vegetation and water table drawdown would also show in the BVOC emissions from the peat soil measured separately after the 7-week-long experiment. The microcosms were collected from an ombrotrophic peatland in Suonenjoki, central Finland (Figure 4). The light and temperature conditions during the experiment were the July averages in central Finland. Vascular plants, mosses and peat were predicted to release distinct BVOC emission mixtures. The water table drawdown was expected to decrease the BVOC emissions, as measured for isoprene in the same experiment (Tiiva et al. 2009), following an uptake by microbial community under increased oxic conditions (Cleveland and Yavitt 1998; Insam and Seewald 2010; Seewald et al. 2010).

The last experiment presented in chapter 5 was also done in plant growth chambers and it aimed to assess the effect of warming and water table drawdown, both alone and in concert,

on the BVOC emissions from boreal peatland microcosms of lawn microtopography (Table 4; Figures 4, 5d). The BVOC emissions from the peat soil were also measured separately at the end of the 7-week-long experiment to investigate if the warming and water table treatment could also have had an effect on the peat emissions. The microcosms were collected from the lawns of the same peatland as for the study of chapter 4 (Figure 4). The warming treatment consisted of increasing the air temperature to 5°C above the average found in central Finland in July, and the water table drawdown was done to the depth of 20 cm. Emissions of isoprene, monoterpenes and sesquiterpenes were expected to increase according to their temperature dependence (Monson et al. 1992; Guenther et al. 1995; Duhl et al. 2008). Water table drawdown was predicted to decrease all BVOC emissions as a result of degradation by the microbial activity under increased aerobicity (Cleveland and Yavitt 1998; Tiiva et al. 2009; Insam and Seewald 2010; Seewald et al. 2010). Thus, warming and water table drawdown were expected to have antagonistic effects on the BVOC emissions. The NEE and CH_4 exchange were measured in order to estimate the carbon emitted as BVOCs in relation to the net carbon exchanges.

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2. Doubled volatile organic compound emissions from subarctic tundra under simulated climate warming

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New Phytologist 187: 199-208

3. Non-methane biogenic volatile organic compound emissions from a subarctic peatland under enhanced UV-B radiation

Faubert P, Tiiva P, Rinnan Å, Räsänen J, Holopainen JK, Holopainen T, Kyrö E and Rinnan R (2010)

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4. Effect of vegetation removal and water table drawdown on the non-methane biogenic volatile organic compound emissions in boreal peatland microcosms

Faubert P, Tiiva P, Rinnan Å, Räty S, Holopainen JK, Holopainen T and Rinnan R (2010)

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5. Effect of warming and water table drawdown on the non-methane biogenic volatile organic compound emissions from boreal peatland microcosms

Faubert P, Tiiva P, Nakam TA, Holopainen JK, Holopainen T and Rinnan R

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6. General Discussion

6.1 BVOC EMISSIONS FROM BOREAL AND SUBARCTIC PEATLANDS AND A HEATH

Only few studies have reported BVOC emissions from boreal and subarctic ecosystems (see Table 2, section 1.6). The present section discusses the natural BVOC emissions (measured from the control plots) from the study sites in the field, that is, the subarctic heath in Abisko (chapter 2) and the subarctic peatland in Sodankylä (chapter 3), and the experiments in plant growth chambers (chapters 4 and 5). All those emissions are summarized in table 5 and I will compare the scales of each group of BVOC emissions with the most similar previous studies (table 2 of the section 1.6). The BVOC emissions were not standardized to the standard conditions of PPFD 1000 μmol s^{-1} m^{-2} and 30°C used in the well known algorithms built by Guenther et al. (1993, 1995). These algorithms were built with BVOC measurements taken from tree species (Guenther et al. 1993, 1995). The BVOC measurements in the studies of chapters 2 to 5 were made on plant communities consisting of different species than those used for building the algorithms and most importantly, all BVOC measurements included the soil component for which no algorithm is presently available. Moreover, no algorithm has been built for ORVOC and other VOC emissions that are presented in chapters 2 to 5. Therefore, the use of algorithms would have increased the uncertainty in the estimations of the BVOC emissions measured from the boreal and subarctic ecosystems in chapters 2 to 5.

Table 5: *Summary of the natural non-standardized BVOC emissions (mean ± SE) measured from the control plots from the boreal and subarctic ecosystems studied in chapters 2 to 5 (Faubert et al. 2010a, b, c).*

Emissions ($\mu g\ m^{-2}\ h^{-1}$)	**Subarctic heath (chapter 2)**		**Subarctic peatland (chapter 3)**		**Boreal peatland microcosms (chapters 4 and 5)**		
	2006	**2007**	**2006**	**2008**	**Hollow**	**Lawn**	**Hummock**
Isoprene	n. p.	n. p.	n. p.	7.9 (1.7)	n. p.	17.3 (1.6)	n. p.
Monoterpenes	1.5 (0.6)	9.8 (2.7)	0.31 (0.06)	0.52 (0.06)	1.3 (0.3)	4.5 (0.8)	1.1 (0.3)
Sesquiterpenes	2.7 (0.8)	3.4 (1.0)	n. d.	n. d.	1.0 (0.3)	2.0 (0.4)	0
ORVOCs	3.3 (1.6)	0.9 (0.2)	1.2 (0.3)	0.43 (0.06)	16.4 (2.0)	3.1 (0.5)	14.1 (1.5)
Other VOCs	3.4 (0.8)	0.4 (0.07)	0.24 (0.05)	0.17 (0.05)	2.9 (0.2)	4.1 (0.7)	1.1 (0.2)

n. p.: not presented in this thesis but measured in Tiiva et al. (2007a, 2008, 2009)

n. d.: not detected

The mean isoprene emission from the subarctic peatland in the growing season of 2008 (Table 5) was lower than the emission of 59.3 ± 13.0 μg m^{-2} h^{-1} measured in 2006 (Tiiva et al. 2008). The low isoprene emission in 2008 is most probably explained by the steadily high water table that decreased the emission from the submerged plants (chapter 3). In the lawn microcosms of a boreal peatland, the mean isoprene emission was slightly lower than those measured by Tiiva et al. (2009) in hummock and hollow microcosms, which were of 30 ± 6 and 45 ± 6 μg m^{-2} h^{-1}, respectively. Klinger et al. (1994) and Janson et al. (1999) measured higher isoprene emissions than those presented in this thesis from boreal peatlands using chamber methods. Klinger et al. (1994) measured isoprene emissions ranging between 0.8 and 104.2 mg C m^{-2} h^{-1} (non-standardized emissions) from a boreal fen and a bog in the Hudson Bay lowland. However, isoprene emission was only measured from 2 plots in the fen and 3 plots in the bog (Klinger et al. 1994). Janson et al. (1999) measured averaged isoprene emissions of 55 and 408 μg C m^{-2} h^{-1} (non-standardized emissions) from a *Sphagnum* fen in the southern boreal zone of Sweden for June and August, respectively. The highest isoprene emissions measured by Klinger et al. (1994) and Janson et al. (1999) were considerably higher than those in this thesis. This could be explained by differences in measurement techniques. Klinger et al. (1994) and Janson et al. (1999) used a static chamber technique. Briefly, Klinger et al. (1994) sampled the BVOCs from air samples taken with syringes from canisters and Teflon bags (volumes not reported) in which air was circulated without a fan. Janson et al. (1999) sampled BVOCs with a stainless steel chamber (volume 235 liters) with the inner wall covered with Teflon. In both studies, BVOC sampling was not done under steady state and BVOCs were analyzed with the GC-FID technique (Klinger et al. 1994; Janson et al. 1999). Other factors such as the water table level, vegetation composition, and temperature and light conditions during the measurements could also be responsible for the different isoprene emissions

measured in Klinger et al. (1994) and Janson et al. (1999) compared with those presented in this thesis.

The monoterpene emissions from the subarctic peatland in Sodankylä were one order of a magnitude lower than those from the subarctic heath in Abisko and the boreal peatland microcosms (Table 5). This could be explained by differences in vegetation composition. Klinger et al. (1994) and Janson et al. (1999) measured higher monoterpene emissions than from the experiments presented in this thesis. Klinger et al. (1994) reported non-standardized monoterpene emissions ranging between 0-146.3 mg C m^{-2} h^{-1} from a fen and a bog in the Hudson Bay lowland, whereas Janson et al. (1999) measured non-standardized emissions ranging between 19-90 μg C m^{-2} h^{-1} from a *Sphagnum* fen in the southern boreal zone of Sweden. As mentioned above for isoprene, several factors could explain the different emissions measured by Klinger et al. (1994) and Janson et al. (1999).

To the best of my knowledge, no other studies have reported emissions of sesquiterpenes, ORVOCs and other VOCs from boreal and subarctic ecosystems measured by chamber technique. The sesquiterpene emissions from the subarctic heath and the hollow and lawn microcosms were in the same range (Table 5). However, it appears that the vegetation types in the subarctic peatland in Sodankylä and hummock microcosms do not release sesquiterpenes.

The vegetation types in the hummocks and hollows of the boreal peatland released higher ORVOC emissions than the vegetation of the lawn microcosms, the subarctic heath and the subarctic peatland (Table 5). The other VOC emissions in all the experiments varied within one order of magnitude (Table 5).

There are some cautions in comparing BVOC emissions between studies. The table 2 in the introduction demonstrates well the difficulties of comparing pure BVOC emissions from ecosystems.

Different studies use different methods (e.g. chambers, eddy covariance towers) to measure BVOC emissions at variable scales or time periods. In addition, there can be a large variation in the BVOC emissions between individuals of the same species (Hakola et al. 2001; Haapanala et al. 2009), which makes generalizations and comparisons difficult if the number of measured samples is not adequate. Some of the studies use models to estimate the BVOC emissions on large scales (e.g. Tarvainen et al. 2007). Other studies use the popular algorithms developed by Guenther et al. (1993, 1995) to standardize the emissions, which makes the comparisons difficult if one is interested in the pure emissions. However, it is also difficult to compare pure emissions between experiments due to differences in the measurement conditions and vegetation composition.

There are also some weaknesses in the chamber method used in this thesis. During the measurements, there can be problems related to the increase in air humidity in the chamber, temperature control, air replacement/mixing ratio and the time needed to reach the steady state (Ortega and Helmig 2008). In all the studies of this thesis, the BVOC sampling started immediately after the chamber was put onto the sampling plot, thus the system had not reached the steady state. The waiting time needed for reaching the steady state would have been long due to the large chamber volume relative to the low air flow rate. A prolonged chamber enclosure would have altered too much the natural conditions, which would have disturbed the BVOC emissions. Thus, the lack of steady state could have been a source of uncertainty in the studies of chapters 2 to 5 and this could have resulted in an underestimation of the emission rates reported.

Davidson et al. (2002) and Loescher et al. (2006) show how to calculate uncertainties related to chamber methods for CO_2 fluxes. However, such calculations for uncertainties cannot be applied in this thesis as BVOCs are released in a totally different

manner than CO_2. For instance, BVOC emissions are released through different physiological pathways than CO_2 (see section 1.4). Moreover, BVOC emissions respond differently than CO_2 under various stresses.

Another source of uncertainty in the chamber method used was the changing temperature and CO_2 concentration inside the chamber during the sampling period. Moreover, it was not possible to estimate if some compounds may have adhered on the chamber wall and living material, thus these compounds would not have been adsorbed on the adsorbent in the ATD tube. These uncertainties are rather complex to quantify. Nevertheless, an attempt was made to calculate another uncertainty concerning the underestimation that could have resulted from the dilution by the air added during the 30-min sampling period. During all BVOC collections, 6.45 liters of clean air was added in the chamber headspace while 6 liters were taken out and passing through the ATD tube. Thus, simplifying, 0.45 liters of air was not sampled and could have resulted in an underestimation of the emission rates in this thesis by 7.5%.

Despite many potential sources of error, the used sampling technique was ideal and convenient for comparison of treatment effects of the well-replicated field experiments in remote locations or in plant growth chamber experiments. The main objective of all the studies in this thesis was to compare treatment effects and for this purpose the chamber method was adequate. For other purposes such as observational measurements and reports of pristine emissions, it is recommended to use sophisticated on-line methods, such as the proton transfer reaction mass spectrometer (PTR-MS), for more accurate quantification of the natural variability of ecosystem emissions.

6.2 BVOC EMISSIONS FROM VEGETATION, LITTER AND PEAT

6.2.1 BVOC emissions and vegetation types

The different vegetation types in the hummock and hollow microcosms from the boreal peatland had different BVOC signatures, as it was predicted (section 1.8; chapter 4; Figures 6, 7). As expected, the vegetation treatments in the hummock microcosms showed clearly that the microcosms with intact vegetation released higher BVOC emissions than those with only moss and/or peat (Figure 6). This result has also been reported for isoprene emission in the same experiment (Tiiva et al. 2009). The presence of vascular plants in the hummock microcosms with intact vegetation released significantly higher monoterpene emissions than the peat microcosms. However, vascular plants did not affect the emissions of sesquiterpenes, ORVOCs and other VOCs. The vascular species in the hummock microcosms consisted of the ericaceous shrubs *Andromeda polifolia*, *Empetrum nigrum* and *Vaccinium oxycoccos*, and the sedges *Eriophorum vaginatum* and *Carex pauciflora* (Tiiva et al. 2009). Thus, this species assemblage in the hummock microcosms with intact vegetation was responsible for the higher monoterpene emissions compared with the microcosms with the moss and peat cover. Isebrands et al. (1999) also measured high monoterpene emissions from ericaceous species. Moreover, the sister species of *E. vaginatum* in North America, *E. spissum*, releases monoterpenes such as α-pinene and limonene (Helmig et al. 1999). Low monoterpene emissions were also released from the *Sphagnum* species in the hummock microcosms but the emissions were not sufficiently high to be distinguished from the peat microcosms (chapter 4). The hollow microcosms had two types of vegetation treatments, intact vegetation and a complete removal of aboveground vegetation leaving only the bare peat surface (chapter 4; Figure 7). The species composition of the intact vegetation consisted mainly of the vascular plants *Rhynchospora alba* and *Scheuchzeria palustris*, and the moss *Sphagnum majus* (Tiiva et al. 2009). This species

assemblage appeared to be a source of sesquiterpenes as the vegetation removal decreased only the sesquiterpene emissions.

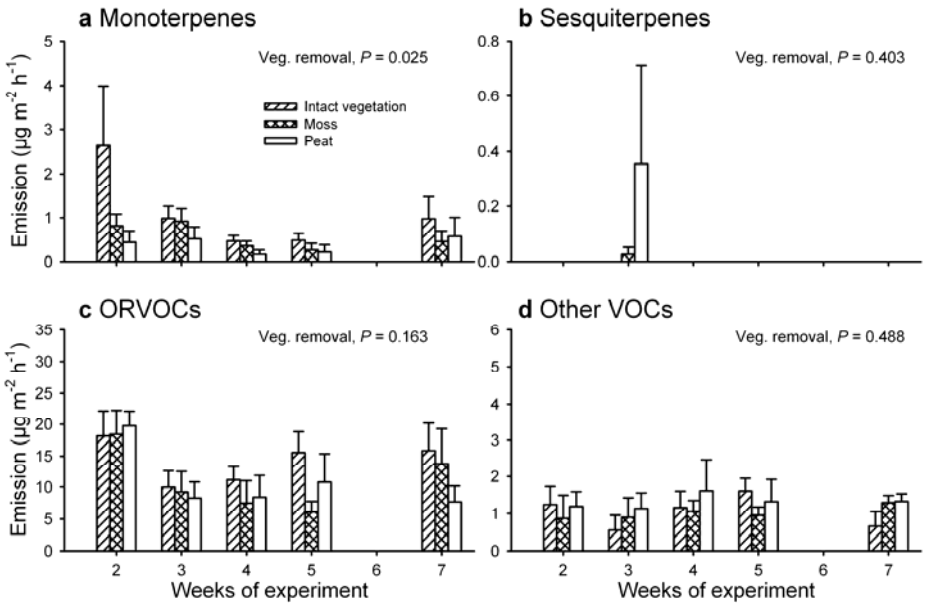

Figure 6. BVOC emissions from hummock microcosms in chapter 4 (Faubert et al. 2010c). The (a) monoterpene, (b) sesquiterpene, (c) ORVOC and (d) other VOC emissions (mean + SE, n = 4) for the intact vegetation, moss and peat surface treatments during the 7-week-long experiment. Note the different Y-axis scales. The *P*-values for vegetation treatment effect in repeated measurements are presented for each compound group.

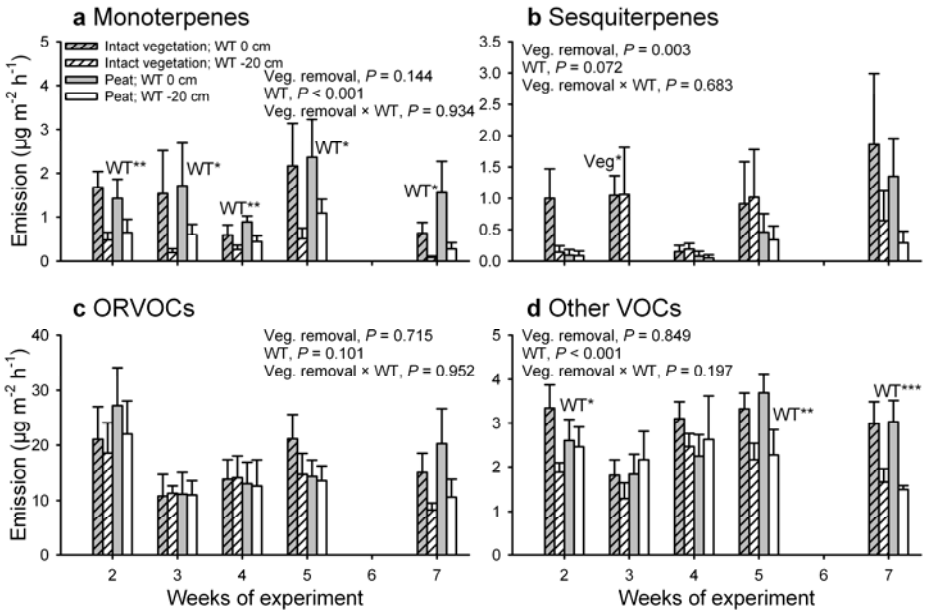

Figure 7. BVOC emissions from hollow microcosms in chapter 4 (Faubert et al. 2010c). The (a) monoterpene, (b) sesquiterpene, (c) ORVOC and (d) other VOC emissions (mean + SE, n = 6) for the intact or removed vegetation (peat surface) and natural water table (WT 0 cm) or water table drawdown (WT -20 cm) treatments during the 7-week-long experiment. Note the different Y-axis scales. The *P*-values from the linear mixed model analysis in repeated measurements are presented for each compound group. The asterisks indicate a significant difference between the treatments within a week; **P* < 0.05, ***P* < 0.01, ****P* < 0.001.

The moss *Warnstorfia exannulata* from the subarctic peatland in Sodankylä was investigated separately for its BVOC emissions in laboratory conditions (chapter 3). The major compounds released by *W. exannulata* were the other VOCs benzoic acid and toluene, and the ORVOC geranylacetone. These BVOCs are comparable to the benzoic derivatives and toluene that were released from *Sphagnum* moss tissue (Rasmussen et al. 1995). Rinnan et al. (2005) also measured similar compounds from boreal peatland microcosms dominated by a *Sphagnum* cover. The mean (± SE) emissions of monoterpenes, ORVOCs and other VOCs from *W. exannulata* were 1.1 ± 0.3, 26.7 ± 7.4 and 23.0 ± 6.1 ng g^{-1} (DW) h^{-1} (chapter 3). Tiiva et al. (2007a) measured an

isoprene emission of 22.9 ± 5.6 ng g^{-1} (DW) h^{-1} (non-standardized) from *W. exannulata*, which is in the same magnitude as the emission of the other BVOC groups.

6.2.2 Effect of the addition of mountain birch leaf litter on the BVOC emissions at the ecosystem scale

Mountain birch leaf litter was added in the warming experiment of the subarctic heath in Abisko (chapter 2) to simulate the expansion of birch species in the Subarctic (ACIA 2005) following the expected longer growing seasons under climate warming (Peñuelas and Filella 2001; Zhou et al. 2001). The litter addition was not a significant source of BVOCs relative to the ecosystem emissions. However, some tendencies of increased monoterpene and sesquiterpene emissions were measured under the combined warming plus litter addition treatment (chapter 2). More specifically, the principal component analysis (PCA) showed that the emissions of the sesquiterpenes selinene, humulene and selina-3,7(11)-diene were relatively higher under the litter addition and combined warming plus litter addition treatments than from treatments without litter (Figure 8). Litter decomposition by microbial activity (Isidorov and Jdanova 2002; Leff and Fierer 2008; Ramirez et al. 2010) as well as the fungi potentially living on the litter (Jelén et al. 1995; Jelén 2002) could have been responsible for this increasing emission tendency. In addition, (Rinnan et al. 2007, 2008a) reported that litter addition increased the phosphorus fertilization on this subarctic heath. Therefore, plant nutrient limitation may have been alleviated by the increased phosphorus fertilization in the combined warming plus litter addition treatment, which has the potential to increase the emissions of certain BVOCs.

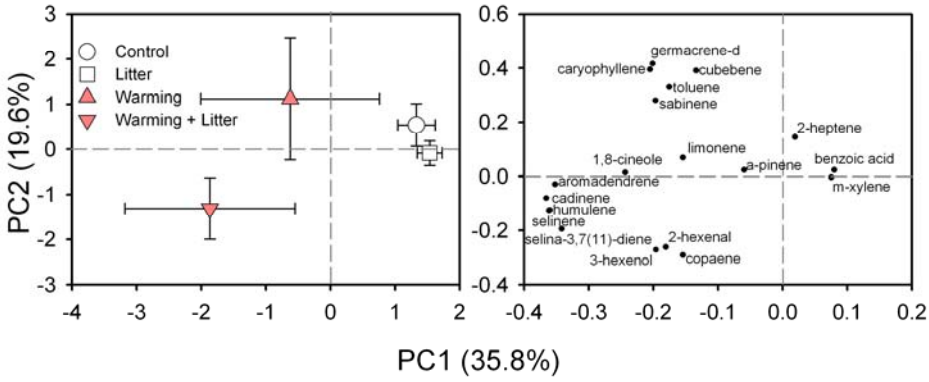

Figure 8. PCA on the BVOC emission profiles from the measurements on 25 July 2006 on the subarctic heath, Abisko, northern Sweden (chapter 2; Faubert et al. 2010a). The mean scores (± SE, n = 5-6) of PC1 and PC2 for the control, litter addition, warming and the combined treatment and the loading variables are presented. The variation explained by each PC is in parentheses.

The BVOCs emitted from the dry birch leaf litter used for the litter addition treatment were sampled in laboratory conditions. The dry litter was first moisturized to field humidity. After incubation of the moist litter in uncovered sterilized glass jars for eight days, the glass jars were sealed with Teflon covered caps and BVOCs were collected for one hour at an air temperature of 19.5°C and under a PPFD of 100 μmol m^{-2} s^{-1}. The ORVOCs were the most emitted compounds from the dry birch litter (Faubert et al. unpublished). Emissions of several ORVOCs have also been measured from leaf litter of the birch *Betula pendula* (Isebrands et al. 1999) and litter from various other ecosystems (Leff and Fierer 2008; Ramirez et al. 2010). The three most emitted compounds were linalool oxide, vitispirane and 2-pentylfuran. The sesquiterpenes selinene and selina-3,7(11)-diene were also released by the litter in laboratory conditions, which can explain why these emissions were characteristic for the plots with litter addition and combined warming plus litter addition treatments in the field experiment.

6.2.3 BVOC emissions from peat

The peat soil was sampled separately at the end of the microcosm experiments presented in chapters 4 and 5. These experiments showed that water table drawdown, change of the vegetation composition and warming applied on the microcosm surfaces affected the BVOC emissions from the peat layer. One common result regardless of the treatment applied on the microcosms was that peat did not release isoprene (Tiiva et al. 2009, chapters 4 and 5). Monoterpenes were the most emitted group from the peat in the control microcosms of hummocks with an emission rate of 76.0 ± 43.4 ng g^{-1}(peat DW) h^{-1} (chapter 4). The most emitted single compounds from the peat in the hummocks (controls) were the monoterpenes 3-carene, limonene, α-pinene, β-phellandrene and β-myrcene at rates of 30.0 ± 27.6, 12.9 ± 5.8, 8.7 ± 4.8, 7.5 ± 3.2 and 3.9 ± 2.9 ng g^{-1}(peat DW) h^{-1}, respectively. The other VOCs was the most emitted group from the peat in the controls of the hollow microcosms with an emission rate of 27.8 ± 27.5 ng g^{-1}(peat DW) h^{-1} (chapter 4). The most emitted compounds from the peat in the hollows (controls) were toluene (other VOC), 2-undecanone (ORVOC), aromadendrene (sesquiterpene), 3-octanol (ORVOC) and 2-ethyl-1-hexanol (ORVOC) with rates of 26.9 ± 26.8, 3.3 ± 0.6, 0.9 ± 0.3, 0.8 ± 0.8 and 0.8 ± 0.8 ng g^{-1}(peat DW) h^{-1}, respectively. In the controls of the lawn microcosms, the most emitted group from the peat was also the other VOCs with an emission rate of 193.3 ± 94.0 ng g^{-1}(peat DW) h^{-1}(chapter 5). The most emitted compounds from the peat in the lawns (controls) were toluene (other VOC), tert-butylbenzene (other VOC), 3-menthene (ORVOC), limonene (monoterpene) and α-pinene (monoterpene) with emission rates of 113.9 ± 75.3, 78.6 ± 73.4, 26.5 ± 23.4, 20.4 ± 8.2 and 9.6 ± 4.0 ng g^{-1}(peat DW) h^{-1}, respectively. Biogenic toluene emission has also been measured from the anoxic hypolimnion in a stratified lake (Jüttner and Henatsch 1986) and from peat cores (Beckmann and Lloyd 2001; Rinnan et al. 2005).

Water table drawdown decreased the BVOC emissions from the peat samples in both experiments presented in chapters 4 and 5. Water table controls the aerobicity of the peat soil. Therefore, the increased oxic conditions in the microcosms with water table drawdown probably favored microbial activity degrading BVOCs, thereby reducing the emissions (Cleveland and Yavitt 1998; Insam and Seewald 2010). In contrast, natural water table kept at the surface level maintained anoxic conditions in the peat soil and seemed to favor the activity of anaerobic microbes releasing BVOCs by fermentative processes (Insam and Seewald 2010; Seewald et al. 2010).

In the peat soil of the hummock microcosms, removing the aboveground part of the vascular plants decreased the sesquiterpene emissions while removing all aboveground vegetation in the hollow microcosms decreased the emissions of monoterpenes, sesquiterpenes and ORVOCs (chapter 4). Microcosms with the aboveground vegetation left intact had fresh roots during the peat BVOC sampling as the sampling was done immediately after having extracted the peat from the microcosms (see the material and methods in chapter 4). In contrast, roots in the microcosms with aboveground vascular plants removed were no longer active because the aboveground part had been removed seven weeks prior to the peat BVOC samplings (that is, in the beginning of the experiment). Thus, this suggests that the living roots of the vascular plants were responsible for the highest BVOC emissions in the peat soil of the microcosms with intact vegetation. In woody plant roots, the sesquiterpene concentration can reach up to 50% of that in leaves (Chen et al. 2009). In *Arabidopsis*, the interactions between roots and microorganisms are sources of BVOCs (Steeghs et al. 2004). In Scots pine, the pure cultures of fungi isolated from roots also release short-chain carbonyls and terpenoids (Bäck et al. 2010).

Warming did not affect the BVOC emissions from the peat samples (chapter 5). This result follows the trend observed at the

surface of the microcosms where warming affected only isoprene emission, which was not released by peat. Moreover, the actual warming treatment was not applied during the peat BVOC sampling done at the complete end of the experiment. The peat BVOC sampling was done outside the growth chamber using peat material extracted from the microcosms (see material and methods in chapter 5). However, the PCA revealed that peat emissions of several BVOCs were associated with the microcosms with natural water table and warming treatment that released specific peat BVOC emission signatures (chapter 5). This suggests that the anaerobic conditions maintained by the natural water table combined with warming could have led to an increased microbial growth and a change in the microbial community (Biasi et al. 2005; Rinnan et al. 2007). This could have increased the emissions of BVOCs associated with the control and warming treatment.

6.3 CARBON EMITTED AS BVOCS RELATED TO THE CARBON EXCHANGE

The carbon emitted as BVOCs was measured in the experiments presented in chapters 3 and 5 because it has been shown to represent a significant proportion of the total carbon balance in various ecosystems (Llusià and Peñuelas 2000; Kesselmeier et al. 2002; Kuhn et al. 2007; Tiiva et al. 2007a; Bäckstrand et al. 2008). Thus, NEE and CH_4 exchanges were measured as background variables in chapters 3 and 5. The carbon emitted as BVOCs was less than 1% of the CO_2-C uptake on the subarctic peatland and in boreal peatland microcosms with natural water table, which was a small change in terms of carbon losses from the ecosystems. This is the same proportion as estimated for carbon emitted as isoprene on the subarctic peatland in Sodankylä during the growing seasons 2005-06 (Tiiva et al. 2007a). Isoprene emission accounted for less than 1% of the carbon uptake except during a warm period where it accounted for 10% (Tiiva et al. 2007a). Tiiva et al. (2009) estimated a proportion of carbon

emitted as isoprene of 0.1% of the CO_2-C uptake in hollow microcosms with natural water table during the last two weeks of the experiment (same experiment as in chapter 4). This was similar to the proportion of all BVOC emissions from the lawn microcosms during the whole experiment presented in chapter 5. On a subarctic peatland in northern Sweden, Bäckstrand et al. (2008) estimated that carbon emitted as BVOCs was 5% of the CO_2-C uptake, which is a higher proportion than those reported in this thesis. Kuhn et al. (2007) estimated proportions of carbon emitted as BVOCs of 1 to 6% of the CO_2-C uptake in a tropical rainforest in central Amazonia. Kesselmeier et al. (2002) estimated proportions of carbon emitted as isoprenoids varying between 0.07 and 12.4% of the CO_2-C uptake in net primary production in species of Mediterranean and Amazonian ecosystems. Thus, the proportions of the emitted BVOC-C of the CO_2-C uptake are in the same range or higher in Mediterranean and Amazonian species and ecosystems than in the subarctic peatland and lawn microcosms of a boreal peatland.

In the subarctic peatland in Sodankylä and the boreal peatland microcosms with natural water table, carbon emitted as BVOCs was in the range of 0.3-1.3% and 1.5-3% of the CH_4-C emissions, respectively (chapters 3 and 5). These proportions are slightly smaller than those reported for the relationship between isoprene emission and CH_4-C emissions on the subarctic peatland in July 2005 (6%; Tiiva et al. 2007a) and the experiment on boreal peatland microcosms in chapter 4 (2% in the last two weeks of the experiment; Tiiva et al. 2009).

6.4 WATER TABLE EFFECT ON BVOC EMISSIONS

The water table level of peatlands exerted a major control on the BVOC emissions. The water table effect surpassed the effect of enhanced UV-B radiation on the subarctic peatland in Sodankylä (chapter 3), and the effect of vegetation change

(chapter 4) and warming (chapter 5) in the boreal peatland microcosms.

The water table levels differed greatly between the growing seasons of 2006 and 2008 on the subarctic peatland in Sodankylä (chapter 3). The water table in the growing season of 2006 went below the moss and soil surfaces from late June onwards whereas it was submerging most of the vegetation for the whole season of 2008. During the dry growing season of 2006, low water table level favored ORVOC and other VOC emissions that were the highest emitted BVOC groups. Some ORVOCs such as 2-methylfuran and heptanal and an "other VOC" benzoic acid were highly emitted in 2006, whereas they were not even detected in 2008. It appears that the exposed peat soil and the dominant moss *W. exannulata* were the sources for those ORVOCs and other VOCs that were emitted more in 2006 than in 2008. Furan emissions and emissions of several ORVOCs and other VOCs have been measured for peat cores and soils of various ecosystems where these compounds have been released by the activity of microorganisms (Beckmann and Lloyd 2001; Leff and Fierer 2008; Bäck et al. 2010; Ramirez et al. 2010). Moreover, the compounds 2-methylfuran and benzoic acid were also detected in the separate sampling done with the moss *W. exannulata*. In the wet season of 2008, monoterpene emissions, with α-pinene as the most emitted compound, were higher than ORVOC and other VOC emissions. In this case, it seemed that the sedges and other vascular plants protruding from the submerging water table were the sources of monoterpene emissions. Emission of α-pinene has been measured for *E. spissum* (Helmig et al. 1999) that is in the same genus as the dominant sedge on the site, *E. russeolum*.

The water table drawdown to the depth of 20 cm decreased the emissions of monoterpenes and other VOCs from the hollow microcosms of the boreal peatland (chapter 4; Figure 7). The PCA of the dataset also revealed that the effect of water table drawdown was stronger than the removal of the aboveground

part of vegetation. Specific monoterpenes (α-pinene, limonene), the ORVOC ethylbenzene and the other VOC benzene were relatively more emitted from the microcosms with the water table at the surface. On the other hand, the ORVOCs 1-pentanol and octadecane were relatively more emitted from the microcosms with water table drawdown. This confirms partly the prediction that emissions of all BVOC groups decrease with water table drawdown. For the lawn microcosms, water table drawdown had stronger effects as it decreased the emissions of all BVOC groups, which confirms the prediction (chapter 5; Figure 9). The PCA revealed that several monoterpenes (β-phellandrene, α-pinene, sabinene, β-myrcene, camphene, p-mentha-1(7),8-diene and limonene) had relatively larger emissions from the lawn microcosms with water table at the surface than from those with water table drawdown.

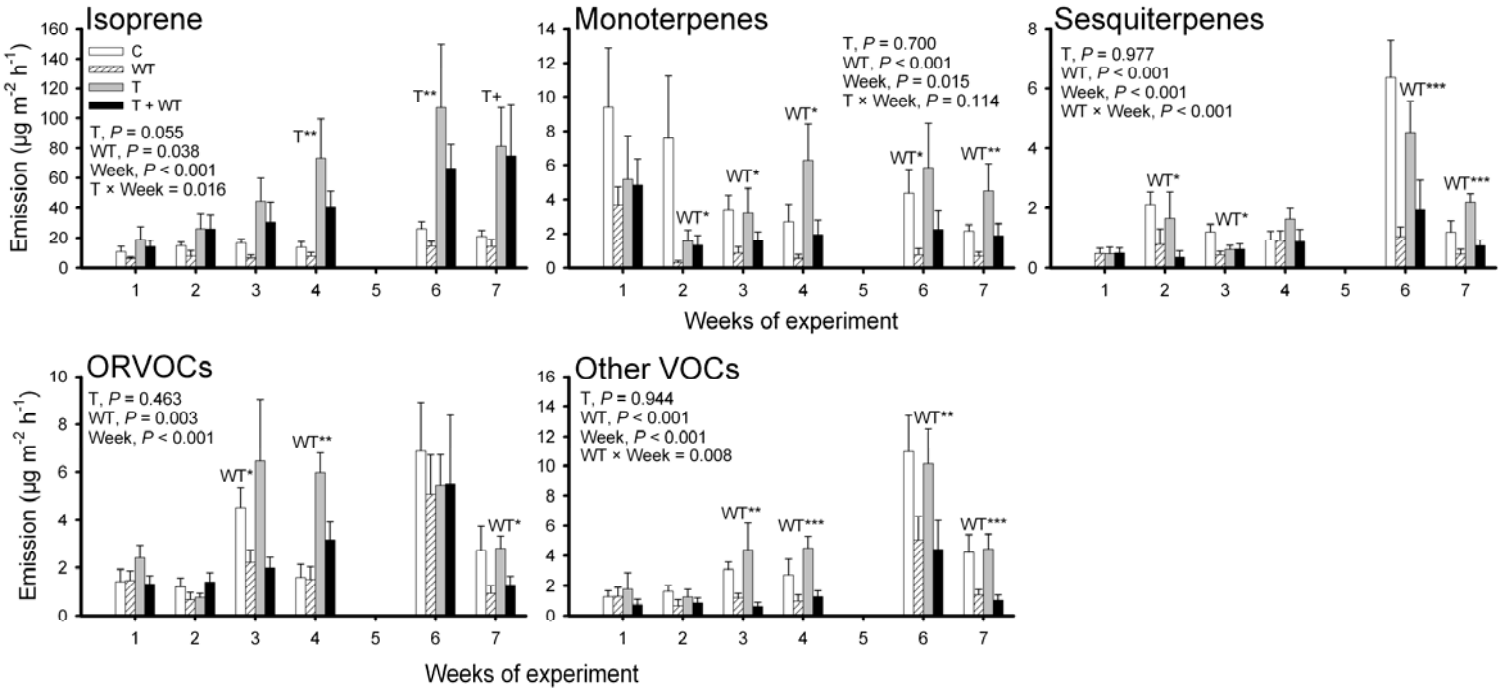

Figure 9. The mean (+ SE, n = 2-3) emissions of isoprene, monoterpenes, sesquiterpenes, ORVOCs and other VOCs from boreal peatland microcosms under control (C), water table drawdown (WT), warming (T) and combined treatments (T + WT) during the 7-week-long experiment in chapter 5. Note the different Y-axis scales. The *P*-values included in the linear mixed model analysis with warming, water table and time as fixed factors and growth chamber as a random factor are presented for each compound group. Plus sign and one, two and three asterisks signify treatment effects at $P < 0.1$, $P < 0.05$, $P < 0.01$ and $P < 0.001$ within a week, respectively.

It appears that water table drawdown decreased the BVOC emissions from the hollow and lawn microcosms by inducing a water stress on the plants. Isoprene emission was decreased by water table drawdown from the lawn microcosms as showed by Tiiva et al. (2009) for the hollow microcosms. Water stress also decreased isoprene emission from other plant species (Sharkey and Loreto 1993; Pegoraro et al. 2004). Water stress decreased monoterpene emissions from Mediterranean species under drought stress (Bertin and Staudt 1996; Llusià et al. 2006; Lavoir et al. 2009). Water table drawdown also increased the volume of the aerobic layer in the peat soil and the CO_2 emission (Tiiva et al. 2009; chapter 5). The water table drawdown increased the aerobicity, which may have favored the degradation of BVOCs by the activity of microorganisms in peat (Cleveland and Yavitt 1998; Asensio et al. 2007; Insam and Seewald 2010). In addition, the lack of carbon substrates, as more carbon was emitted as CO_2 under water table drawdown, may have affected the BVOC synthesis (Bertin and Staudt 1996; Funk et al. 2004; Brilli et al. 2007; Lavoir et al. 2009; Niinemets 2010).

The effect of water table drawdown was not the same between the hollow and lawn microcosms of the boreal peatland (chapters 4 and 5; Figures 7, 9). In hollow microcosms, only the emissions of isoprene (Tiiva et al. 2009), monoterpenes and other VOCs were decreased by water table drawdown (chapter 4) whereas emissions of all BVOC groups were decreased in the lawn microcosms (chapter 5). The different effect of the water table drawdown could be explained by the different vegetation composition. Vegetation in the hollow microcosms was mainly composed of the sedges *R. alba* and *S. palustris* (Tiiva et al. 2009), and the vegetation in lawns was dominated by the sedge *E. vaginatum* and the dwarf shrub *A. polifolia* (chapter 5). This difference in the vegetation composition could have induced different BVOC signatures on which the water table drawdown effect was different. Another experiment would be needed to test this hypothesis where only water table treatment would be applied on hollows and lawns.

6.5 WARMING EFFECT ON BVOC EMISSIONS

Warming increased the emissions of monoterpenes and sesquiterpenes (chapter 2) and isoprene (Tiiva et al. 2008) from the subarctic heath. Warming also increased isoprene emission from the lawn microcosms of the boreal peatland (chapter 5).

Warming increased the monoterpene emissions by 85% in 2006 and 120% in 2007 on the subarctic heath in Abisko (chapter 2; Figure 10). The sesquiterpene emissions increased by 250% in 2006 and 130% in 2007 under warming (chapter 2; Figure 10). In contrast, the emissions of ORVOCs and other VOCs were not significantly increased by warming. The prediction for this experiment was that warming would have increased emissions of monoterpenes and sesquiterpenes due to their temperature dependence (Guenther et al. 1995; Duhl et al. 2008; Hartikainen et al. 2009). Thus, this prediction was fulfilled although such a high increase was not expected following a moderate warming. The warming treatment increased the air temperatures in the chamber headspace by 1.9°C in 2006 and 2.5°C in 2007 (chapter 2), which is a realistic increase for the following decades (IPCC 2007).

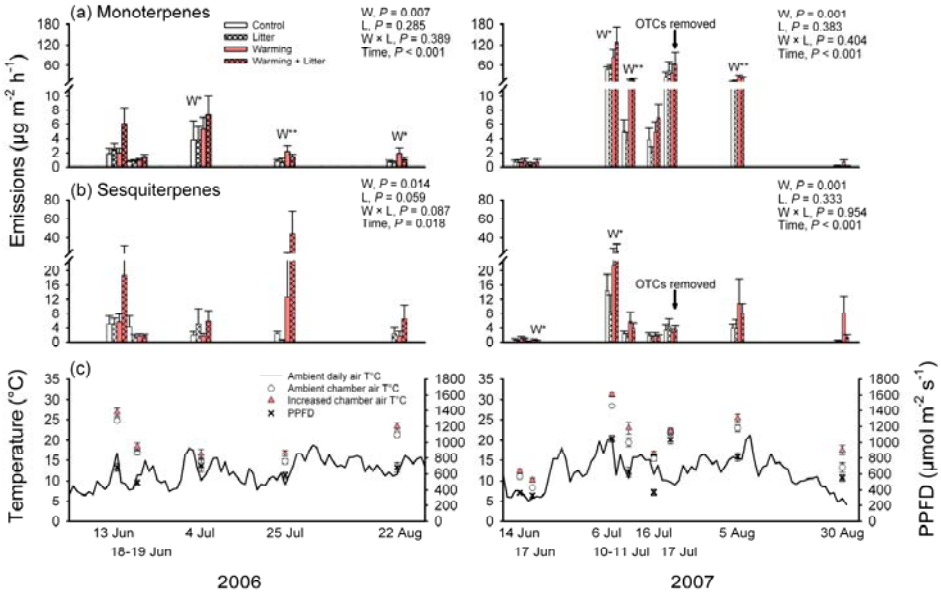

Figure 10. BVOC emissions from a subarctic tundra heath subjected to warming and litter addition in chapter 2, Abisko, northern Sweden (Faubert et al. 2010a). (a) The mean monoterpene and (b) sesquiterpene emissions of the measurements (+ SE, n = 5-6) from the control, litter addition (L), warming (W), and the combined treatment in the growing seasons of 2006 and 2007. The *P*-values from the linear mixed model analysis with W, L and Time as fixed factors and block as a random factor are shown for each compound group. One and two asterisks signify treatment effects at $P < 0.05$ and $P < 0.01$ within a date, respectively. Note the different Y-axis scales. The measurement date with OTCs removed, 17 July 2007, is indicated by an arrow, and was not included in the analysis in repeated measurements. (c) The mean daily (7:00-19:00) ambient air temperature, the mean chamber air temperature (± SE, n = 11-12) and PPFD (± SE, n = 22-24) during the measurements.

The current models on the exponential relationship between the emission rates of monoterpenes and sesquiterpenes and temperature (Guenther et al. 1993, 1995; Hakola et al. 2001; Helmig et al. 2007) do not predict such high increases. Here is the algorithm of Guenther et al. (1993) used in the current models:

$$E = E_s \times e^{(\beta(T-Ts))}$$

where E is the emission rate at temperature T (°C), E_s is the emission rate at standard temperature T_s (°C) and β (°C^{-1}) is an empirical coefficient. For a warming of 2°C, the models predict an increase of 18-25% for the monoterpene emissions, using a β coefficient of 0.09°C^{-1} (Guenther et al. 1993; chapter 2). For the sesquiterpene emissions, the models predict an increase of 37-60%, using a β coefficient of 0.17-0.19°C^{-1} (Hakola et al. 2001; Helmig et al. 2007). If new β coefficients were calculated by inferring from the averages of the measurements between the non-warmed *vs.* the warmed plots, they would be 0.33 and 0.32°C^{-1} for monoterpenes, and 0.67 and 0.34°C^{-1} for sesquiterpenes for the growing seasons of 2006 and 2007, respectively. Therefore, the current models (Guenther et al. 1993, 1995; Hakola et al. 2001; Helmig et al. 2007) appear to underestimate the effect of warming on the plant communities in the Subarctic. Holst et al. (2010) also showed that the temperature dependence of the BVOC emissions from a wetland located close to the heath in Abisko was stronger than that for the emissions from temperate or subtropical ecosystems. More field measurements in subarctic ecosystems would be needed to adjust the β coefficients of the current models for increasing the accuracy of the predictions of BVOC emissions from the Subarctic under climate warming. An increase in the mean global air temperature by 2-3°C is expected to occur in the next decades and could increase the global BVOC emissions by 30-45% (Peñuelas and Llusià 2003; Peñuelas and Staudt 2010). This increase of BVOC emissions could be much higher in the Subarctic when considering the higher temperature increase predicted for the Arctic (ACIA 2005), and the high increases measured for monoterpene and sesquiterpene emissions on the subarctic heath in response to warming (chapter 2).

Warming and litter addition treatments also increased the plant biomass on the subarctic heath as estimated by measurements of normalized differential vegetation index (NDVI; Rinnan et al. 2008a). Thus, one could hypothesize that the increase of plant biomass in the warmed plots could have caused the increases of

monoterpene and sesquiterpene emissions. This hypothesis was tested during a BVOC sampling without open-top chambers (OTC; used to apply the warming treatment, see chapter 2; Figure 10) in 2007. No significant differences were found between the monoterpene and sesquiterpene emissions of the warmed and non-warmed plots, indicating that the higher plant biomass was not responsible for the increases in the BVOC emissions. This refutes the hypothesis and does not agree with the finding that emissions in longer term increase when plants are grown under elevated temperature (Sharkey et al. 1999; Pétron et al. 2001). Thus, it appears that the warming effect was direct and acted at the physicochemical and physiological levels by increasing the synthesis, volatility and diffusion gradient of the monoterpene and sesquiterpene emissions from the plant synthesizing pathways and storage organs (reviewed by Niinemets et al. 2004).

Warming effect on the lawn microcosms of the boreal peatland was not as strong as on the subarctic heath (chapter 5; Figure 9). The warming by 5°C increased only isoprene emission. This finding confirmed the prediction that isoprene emission would increase under warming. However, it refuted the prediction for monoterpene and sesquiterpene emissions as they were also expected to increase under warming. Warming also increased the amount of *E. vaginatum* leaves in the lawn microcosms (chapter 5). This indirectly increased isoprene emission as *E. vaginatum* is an isoprene emitter (Tiiva et al. 2007b, 2009).

The absence of warming effect on monoterpene and sesquiterpene emissions in the microcosm experiment on the lawns disagrees with their well known temperature dependence (Guenther et al. 1995; Duhl et al. 2008). Moreover, the increase in the number of *E. vaginatum* leaves under warming would have been expected to increase the monoterpene emissions considering that this species is likely to be a monoterpene emitter as it is the case for the similar species *E. spissum* (Helmig et al. 1999). Monoterpene emissions were higher under warming

during the last four weeks of the experiment but this increase was not statistically significant (chapter 5; Figure 9). The low amount of replicates in the experiment (n = 2-3) would have reduced the statistical power to confirm the significance of this increase in monoterpene emissions under warming. Furthermore, the strong effect of the water table drawdown combined with the relatively short time frame of the experiment (seven weeks) could also have been responsible for the lack of significant warming responses of monoterpene and sesquiterpene emissions from the lawn microcosms.

6.6 UV-B EFFECT ON BVOC EMISSIONS

Enhanced UV-B radiation had minor effects on the BVOC emissions during the growing seasons of 2006 and 2008 in the subarctic peatland in Sodankylä (chapter 3; Table 6). This result refutes the prediction of an increase in the emissions, which occurred for isoprene emission in 2006 (Tiiva et al. 2007a).

Table 6: Mean (± SE) BVOC emissions of the measurements (n_{2006} = 70, n_{2008} = 60) from a subarctic peatland in the growing seasons of 2006 and 2008 under ambient radiation (Ambient control), UV-A control and enhanced UV-B (Faubert et al. 2010b).

Emission (µg m^{-2} h^{-1})	**2006**			**2008**		
	Ambient control	**UV-A control**	**Enhanced UV-B**	**Ambient control**	**UV-A control**	**Enhanced UV-B**
Isoprene	n. p.	n. p.	n. p.	7.88 (1.69)	9.12 (2.13)	9.66 (2.06)
Monoterpenes						
(+)-Pin-2(3)-ene	0.07 (0.03)	0.06 (0.02)	0.09 (0.03)	0.02 (0.01)	0.02 (0.01)	0.06 (0.02)
α-Pinene	0.15 (0.04)	0.20 (0.06)	0.15 (0.04)	0.36 (0.05)	0.35 (0.07)	0.23 (0.03)
Camphene	n .d.	n. d.	n. d.	< 0.01	< 0.01	< 0.01
3-Carene	0.02 (0.01)	0.03 (0.01)	0.02 (0.01)	0.04 (0.01)	0.06 (0.02)	0.05 (0.01)
Limonene	0.08 (0.01)	0.10 (0.02)	0.09 (0.01)	0.10 (0.01)	0.14 (0.04)	0.07 (0.01)
Total monoterpenes	0.31 (0.06)	0.39 (0.08)	0.35 (0.06)	0.52 (0.06)	0.58 (0.11)	0.41 (0.05)
ORVOCs						
2-Methylfuran	1.13 (0.28)	0.49 (0.12)	1.26 (0.45)	n. d.	n. d.	n. d.
2-Heptene	n. d.	n. d.	n. d.	0.28 (0.04)	0.25 (0.04)	0.27 (0.05)
1-Octene	n. d.	n. d.	n. d.	0.03 (0.01)	0.02 (0.01)*	0.06 (0.01)
Heptanal	0.07 (0.02)	0.10 (0.03)	0.10 (0.03)	n. d.	n. d.	n. d.
Octanal	n. d.	n. d.	n. d.	0.03 (0.01)	0.03 (0.01)	0.04 (0.01)
Tridecane	n. d.	n. d.	n. d.	< 0.01	0.02 (0.01)	0.01 (0.01)
Tetradecane	n. d.	n. d.	n. d.	0.01 (0.01)	0.02 (0.01)	0.02 (0.01)
Pentadecane	n. d.	n. d.	n. d.	0.08 (0.02)	0.10 (0.04)	0.11 (0.03)

Emission (µg m^{-2} h^{-1})	2006			2008		
	Ambient control	UV-A control	Enhanced UV-B	Ambient control	UV-A control	Enhanced UV-B
Total ORVOCs	1.20 (0.28)	0.59 (0.12)	1.35 (0.45)	0.43 (0.06)	0.45 (0.08)	0.51 (0.07)
Other VOCs						
Toluene	0.08 (0.02)	0.09 (0.03)	0.08 (0.02)	0.17 (0.05)*	0.17 (0.04)*	0.35 (0.06)
1-Chloro-4-methoxy-benzene	< 0.01	0.08 (0.03)	0.04 (0.02)	n. d.	n. d.	n. d.
Benzoic acid	0.15 (0.05)	0.22 (0.09)	0.14 (0.04)	n. d.	n. d.	n. d.
Total other VOCs	0.24 (0.05)	0.39 (0.10)	0.26 (0.05)	0.17 (0.05)*	0.17 (0.04)*	0.35 (0.06)
Total BVOCs	1.75 (0.30)	1.37 (0.19)	1.96 (0.44)	1.13 (0.11)	1.20 (0.19)	1.27 (0.12)

n. p.: not presented in this thesis but measured in Tiiva et al. (2007a)

n. d.: not detected

*Significant difference from the enhanced UV-B treatment within the year

The major influence of the water table level probably partly explains the lack of enhanced UV-B effect on the emissions of other BVOCs than isoprene (chapter 3; Table 6; Tiiva et al. 2007a). Moreover, the absence of effect on the other compounds could be explained by the unaffected physiology of the dominant sedge *E. russeolum* by enhanced UV-B (Scharf 2006). In another experiment done on peat monoliths from an oligotrophic fen in central Finland, the physiology of *E. vaginatum* (species of the same genus as *E. russeolum*) was also unaffected by enhanced UV-B radiation (Niemi et al. 2002). Thus, BVOC emissions were not affected by enhanced UV-B in the absence of physiological stress on the dominant species. Furthermore, it is not unusual that plants of the Subarctic have small responses to enhanced UV-B (reviewed in Callaghan et al. 2004 and Rozema et al. 2005). This is possibly due to a tolerance that several species developed during their evolution in which they were exposed to higher UV-B radiation levels than in the current time, and the physical protection against UV-B (e.g. thick epidermal layer, hair, wax) that several subarctic species have (reviewed in Callaghan et al. 2004 and Rozema et al. 2005).

The emissions of only two compounds, an ORVOC 1-octene and an "other VOC" toluene, were increased by enhanced UV-B radiation in 2008 (chapter 3; Table 6). This increase could have been induced through an indirect effect of enhanced UV-B on the peat microbial communities and the belowground parts of the plants (Rinnan et al. 2008b). The aboveground parts were not affected (Scharf 2006). Toluene emission was measured from the moss *W. exannulata* in laboratory conditions. The emissions of toluene and 1-octene were also measured from the peat in the microcosm experiments (chapters 4 and 5). On this subarctic peatland, Rinnan et al. (2008b) showed that enhanced UV-B affected the microbial community by reducing the growth rate and altering the community composition, probably through an effect on the plant photosynthate allocation and root exudation. This indirect effect on the microbial community could have been responsible for the emission of a different BVOC emission

signature in which the emissions of 1-octene and toluene were increased. Alterations of the soil microbial community caused by enhanced UV-B have also been reported for other ecosystems in the Subarctic (Callaghan et al. 2004).

Contrasting results were shown for isoprene as the emission was increased by enhanced UV-B in 2004-2006 (Tiiva et al. 2007a), especially during warm periods, whereas it was unaffected in 2008 (chapter 3; Table 6). This could be explained by the relations between isoprene emission, NEE and water table (chapter 3). In 2006, enhanced UV-B was partly responsible for an increased carbon emission as isoprene while NEE increased and ecosystem respiration decreased (Tiiva et al. 2007a; Haapala et al. 2009). Moreover, isoprene emission increased when the water table was below the surface of the dominant moss *W. exannulata*, recognized as an isoprene emitter (Tiiva et al. 2007a). In 2008, the relations between isoprene emission, NEE and water table were different. Enhanced UV-B radiation did not affect NEE, and NEE did not correlate with isoprene emission as it did in 2006. This could explain the absence of effect of UV-B on isoprene emission. Moreover, the water table submerged the vegetation and covered the isoprene emitter *W. exannulata*. Thus, the submerging water table surpassed the effect of enhanced UV-B by decreasing the isoprene emission in all treatments.

6.7 CONCLUSIONS AND IMPLICATIONS

There is a need to pursue the research on boreal and subarctic ecosystems for which little knowledge is currently available concerning their BVOC emissions. This thesis demonstrates that boreal and subarctic ecosystems emit significant quantities of BVOCs. The research presented fills a part of the gap concerning the lack of knowledge on BVOC emissions from northern ecosystems. The results also increase the knowledge on the

BVOC emissions originating from boreal peatland vegetation, peat and mountain birch leaf litter at the ecosystem scale.

Most importantly, this thesis gives some answers to the current demands for research concerning the relationships between climate change and BVOC emissions (Peñuelas and Staudt 2010), especially for the scarcely studied areas of the north. The experiments demonstrate that climate change has complex effects on the BVOC emissions from boreal and subarctic ecosystems. The BVOC emission responses were studied on four effects of climate change:

1) the direct effect of warming, and its indirect effects via
2) water table drawdown
3) change in the vegetation composition
4) enhanced UV-B radiation

Table 7 summarizes the work done by revisiting the hypotheses presented in section 1.8 (Table 3) that are either confirmed or refuted by the results obtained in the chapters. Most of the hypotheses were confirmed by the results except for the effect of warming that did not affect the BVOC emissions when it was combined with a water table drawdown in boreal peatland microcosms. Table 8 presents in detail the overall BVOC emission responses to the climate change parameters addressed in chapters 2 to 5.

Table 7: *Four effects of climate change examined on the BVOC emissions from boreal and subarctic ecosystems, the hypotheses tested and the results obtained in each study of the thesis.*

Effect of climate change	Hypothesis tested	Result
1) Warming (chapters 2 and 5; Faubert et al. 2010a)	Warming increases the BVOC emissions (Guenther et al. 1995; Duhl et al. 2008; Tiiva et al. 2008; Hartikainen et al. 2009)	- On a subarctic heath, warming doubles the monoterpene and sesquiterpene emissions - For lawn microcosms of a boreal peatland, warming has no effect on the BVOC emissions when the effect is combined with water table drawdown
2) Water table drawdown (chapters 4 and 5; Faubert et al. 2010c)	Water table drawdown decreases the BVOC emissions (Tiiva et al. 2009)	- For hollow and lawn microcosms of a boreal peatland, water table drawdown decreases the BVOC emissions
3) Change in the vegetation composition (chapter 4; Faubert et al. 2010c)	Change of the vegetation composition affects the BVOC emission signature (Tiiva et al. 2009)	- For hollow and hummock microcosms of a boreal peatland, change of the vegetation composition affects the BVOC emission signature
4) Enhanced UV-B radiation (chapter 3; Faubert et al. 2010b)	Enhanced UV-B radiation increases BVOC emissions (Tiiva et al. 2007)	- On a subarctic peatland, enhanced UV-B radiation has no effect on the monoterpene, ORVOC and other VOC emissions

Table 8: The overall responses of BVOC emissions to the climate change parameters.

Compound group	**Warming by 2°C (chapter 2)**	**Warming by 5°C[b] (chapter 5)**	**Enhanced UV-B radiation (chapter 3)**	**Water table drawdown of 20 cm (chapters 4 and 5)**		**Change of the vegetation composition (chapter 4)**	
Ecosystem	**Subarctic heath**	**Boreal peatland**	**Subarctic peatland**	**Boreal peatland**		**Boreal peatland**	
				Hollow[d]	**Lawn**	**Hollow[f]**	**Hummock**
Isoprene	Increase by 56% (2006) and 83% (2007)[a]	Increase by 280%	Increase by 101% in 2006[c] but no effect in 2008	Decrease by 25%[e]	Decrease by 50%	Decrease by 92%[e]	Decrease by 90%[e,g]
Monoterpenes	Increase by 85% (2006) and 120% (2007)	No effect	No effect	Decrease by 332%	Decrease by 160%	No effect	Decrease by 187%[h]
Sesquiterpenes	Increase by 250% (2006) and 130% (2007)	No effect	Not emitted	No effect	Decrease by 160%	Decrease by 151%	No effect
ORVOCs	No effect	No effect	No effect	No effect	Decrease by 61%	No effect	No effect
Other VOCs	No effect	No effect	No effect	Decrease by 54%	Decrease by 162%	No effect	No effect

[a]Tiiva et al. 2008; [b]Effect combined with a water table drawdown of 20 cm; [c]Tiiva et al. 2007a, calculated from non-standardized emission; [d]For the microcosms with intact vegetation; [e]Tiiva et al. 2009; [f]Removal of all the vegetation and for microcosms with natural water table, i.e. even with the vegetation surface; [g]For microcosms with moss or peat vs. intact vegetation; [h]For microcosms with peat vs. intact vegetation

By the end of this century, warming induced by climate change is projected to increase the mean annual air temperature in the area north of 60°N by 3.7°C, which is twice the average increase of temperature expected over the globe (ACIA 2005). The experiment on the subarctic heath in Abisko shows that a warming of only 2°C doubles the emissions of monoterpenes and sesquiterpenes (Table 8). This experiment also reveals that the current models underestimate the BVOC emissions under climate warming in the Subarctic, justifying the need for more studies to adjust the models (Faubert et al. 2010a).

The water table level in boreal peatlands is expected to decrease following an indirect effect of warming induced by climate change (Roulet et al. 1992). The experiments in this thesis show that water table drawdown has an opposite effect to warming because it decreases the BVOC emissions. The experiment done on the lawn microcosms from the boreal peatland showed that even monoterpene and sesquiterpene emissions, known for their temperature dependence, were mainly decreased by water table drawdown although a warming treatment was applied in concert (Table 8). In this perspective, boreal and subarctic peatland ecosystems may maintain their BVOC emission rates at the current level if they are subjected to concomitant effects of warming and water table drawdown as these could even out each other. In the experiment done on the hollow microcosms from a boreal peatland, water table drawdown also had stronger effect than a complete removal of the aboveground part of vegetation. This supports the results measured in the lawn microcosms that water table exerts a major control on peatland BVOC emissions.

Water table drawdown is also expected to induce changes in the vegetation composition of the boreal peatlands (Strack et al. 2008). Such changes are projected to be important in ombrotrophic peatlands where the patterns in the vegetation composition are driven by the microtopograhy (Strack et al. 2008). The experiment done on hummock microcosms from the

boreal peatland shows that vascular plants are responsible for the highest BVOC emissions, while vegetation dominated by *Sphagnum* appear to have BVOC emissions that are not different from bare peat surfaces (Table 8; Faubert et al. 2010c). On the subarctic heath, the simulated increased leaf litter fall also affects moderately the BVOC emission mixture at the ecosystem scale (Table 8; Faubert et al. 2010a). Thus, this thesis shows that the vegetation changes projected to occur following warming and water table drawdown in boreal and subarctic ecosystems modify the BVOC emission signature.

The BVOC emissions from the subarctic peatland, besides that of isoprene (Table 8; Tiiva et al. 2007a), are not affected by enhanced UV-B radiation (Faubert et al. 2010b). This follows the common tendency that enhanced UV-B has mild effect on plants in polar regions (reviewed in Callaghan et al. 2004 and Rozema et al. 2005). The differences between the water table levels during the growing seasons exerted a major control and surpassed the effect of enhanced UV-B. Thus, this experiment also provides evidence of the important control the water table poses on the BVOC emissions.

We still do not know how the biological interactions would be affected by modified BVOC emissions under climate change. For instance, a change in the BVOC emissions could affect the direct and indirect plant defenses against herbivores, the attraction of pollinators and plant-plant communications (Knudsen et al. 2006; Holopainen and Gershenzon 2010). Modified BVOC emissions would also have consequences on the atmospheric chemistry but the net effect is still unknown. BVOC emissions are involved in multiple oxidative reactions with OH radicals and oxides of nitrogen (Peñuelas and Staudt 2010). These oxidative reactions lead to the formation of tropospheric O_3, secondary organic aerosols and CO_2. The OH radicals are also scavenged by BVOCs, which lengthens the lifetime of CH_4. Therefore, the concrete consequences of a change in the BVOC

emission mixture under climate change still need further interdisciplinary studies.

The results of the experiments presented in this thesis are a step forward and make a significant contribution in improving the modeling of BVOC emissions for a better understanding of atmospheric chemistry and climate change effects in the boreal and subarctic regions.

6.8 REFERENCES

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Responses of Non-Methane Biogenic Volatile Organic Compound Emissions to Climate Change in Boreal and Subarctic Ecosystems

This thesis reports on the responses of non-methane biogenic volatile organic compound (BVOC) emissions to climate change on boreal and subarctic vegetation. Boreal and subarctic areas are predicted to experience warming twice as high as the warming averaged over the globe, which can considerably affect the BVOC emissions. The thesis presents results from field experiments that simulated the effect of climate change and shows that BVOC emissions will be more affected than what was previously expected. These results make a significant contribution to improving the modeling of BVOC emissions for a better understanding of atmospheric chemistry and climate change effects in the boreal and subarctic regions.

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