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Isoprene Emission from Northern Ecosystems Under Climate Change

Doctoral dissertation

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ABSTRACT

Introduction. Isoprene (C_5H_8, 2-methyl-1,3-butadiene) is a highly reactive volatile organic compound emitted to the atmosphere predominantly by vegetation. Under stressful conditions, plants can release a substantial part of their recently assimilated carbon as isoprene. However, the ultimate reason for these emissions from the plant's point of view is still under debate. In the atmosphere, isoprene is present in trace amounts (parts per billion) but it still participates in various reactions leading to secondary organic aerosol formation, ozone destruction or formation and reduction in the oxidative capacity of the atmosphere. Therefore, through its reactivity in the atmosphere, isoprene interacts with the changing climate. The current estimate of the yearly global isoprene emission is 440 - 660 $\times 10^{12}$ g carbon. Isoprene emissions from arctic and boreal ecosystems other than forests have been largely unexplored. These ecosystems are significant sinks of the greenhouse gas carbon dioxide (CO_2) and they are subjected to the most pronounced climate change. How the changing climate affects isoprene emissions from these northern ecosystems is investigated in this thesis.

Experiments. In the experiments detailed in this thesis, isoprene emissions were measured in boreal peatland and subarctic peatland and heath ecosystems with the dynamic chamber technique combined with analysis by gas-chromatography mass-spectrometry. Each of the studied ecosystems was subjected to a simulated aspect of climate change: warming, enhanced ultraviolet-B radiation (UV-B, 280-320 nm), elevated ozone concentration or water table drawdown. Isoprene emission was compared to the net CO_2 assimilation in the ecosystems. Contribution of different plant species/groups to the emissions was also estimated in each experiment.

Subarctic heath and warming. Warming clearly increased isoprene emission from a subarctic heath ecosystem with a simultaneous reduction in net carbon assimilation. Isoprene emission correlated positively with abundance of the sedge *Carex vaginata* and the herb *Tofieldia pusilla*.

Subarctic peatland and UV-B. Enhanced UV-B radiation increased isoprene emission from a subarctic minerotrophic fen. Furthermore, under unusually warm weather conditions, isoprene emissions were unexpectedly high and comprised a substantial amount of the assimilated carbon in the studied peatland. The sedge *Eriophorum russeolum* and the moss *Warnstorfia exannulata* were mainly responsible for the emission at the site.

Boreal peatland and ozone. Elevated ozone concentration did not clearly affect isoprene emissions from boreal slightly minerotrophic fen microcosms. However, warm weather periods together with elevated ozone led to high but very variable emissions. Isoprene emission was related to the density of the sedge *Eriophorum vaginatum* in the peatland microcosms.

Boreal peatland and water table drawdown. Lowering of the water table decreased isoprene emissions from boreal ombrotrophic bog microcosms. However, net carbon assimilation was more dramatically reduced which led to a substantial increase in the loss of assimilated carbon as isoprene under water table drawdown. Vascular plants were the main source of isoprene in these peatland microcosms.

Conclusions. Warming, increased levels of UV-B radiation and ozone concentration and changes in water table depth will affect isoprene emissions from northern ecosystems. The emissions are destined to increase, or the carbon loss as isoprene will increase due to reduced net carbon assimilation, if climate change proceeds as predicted for the Northern Hemisphere. This may affect the composition of the atmosphere, but it may also have implications for the carbon sequestration in these ecosystems.

ACKNOWLEDGEMENTS

ABBREVIATIONS AND TERMS

CO_2	Carbon dioxide
CH_4	Methane
VOC	Volatile organic compound
UV-B	Ultraviolet-B radiation
O_3	Ozone
NO_x	Nitrogen oxides
MVA	Mevalonic acid pathway
DMAPP	Dimethylallyl pyrophosphate
Acetyl-CoA	Acetyl coenzyme A
MEP	Methyl-erythritol pathway
DW	Dry weight
SOA	Secondary organic aerosol
OH	Hydroxyl radical
NEE	Net ecosystem CO_2 exchange
Minerotrophic peatland, fen	Peatland receiving nutrients from surface waters or groundwater
Ombrotrophic peatland, bog	Peatland receiving nutrients only from precipitation
Oligotrophic	Nutrient poor
Mesotrophic	Moderately nutrient rich
GC-MS	gas chromatography-mass spectrometry

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications referred to in the text by their chapter numbers

Chapter 2 Tiiva P, Faubert P, Michelsen A, Holopainen T, Holopainen JK, Rinnan R (2008) Climatic warming increases isoprene emission from a subarctic heath. *New Phytologist* 180: 853-863.

Chapter 3 Tiiva P, Rinnan R, Faubert P, Räsänen J, Holopainen T, Kyrö E, Holopainen JK (2007) Isoprene emission from a subarctic peatland under enhanced UV-B radiation. *New Phytologist* 176: 346-355.

Chapter 4 Tiiva P, Rinnan R, Holopainen T, Mörsky SK, Holopainen JK (2007) Isoprene emissions from boreal peatland microcosms; effects of elevated ozone concentration in an open field experiment. *Atmospheric Environment* 41: 3819-3828.

Chapter 5 Tiiva P, Faubert P, Räty S, Holopainen JK, Holopainen T, Rinnan R. Contribution of vegetation and water table on isoprene emission from boreal peatland microcosms. Submitted to *Biogeochemistry* (2008).

CONTENTS

CHAPTER 1

GENERAL INTRODUCTION

GENERAL INTRODUCTION

1.1 Changing climate in the north

1.1.1 Climatic warming

The annual mean global temperature has been constantly rising by 0.13 ºC per decade during the last 50 years (IPCC 2007). Warming has been most evident in the northern hemisphere where the last 50 years have probably been the warmest 50-year-period for 1300 years (IPCC 2007). Indeed, in the Arctic, the temperatures have increased at a rate twice the global average during the last century, and they are predicted to increase by a further 4-7 ºC over the next 100 years (ACIA 2004). There is a scientific consensus that human activities (fossil fuel combustion and land clearance), which strengthen the natural greenhouse effect, are the main contributors to these changes.

Climatic warming is most pronounced in the Arctic where the lengthening snow-free period and melting sea ice decrease albedo (reflectance) and, thus, provide positive feedback for further increase in temperature (ACIA 2004). Consequences of the warming climate have already been detected in arctic vegetation communities as a northward and upslope migrating treeline and increasing abundance of deciduous shrubs (Sturm *et al.* 2001, Tape *et al.* 2006). Increasing woody shrubs and their litter further decrease the albedo (ACIA 2004), but they also alter the quality of the soil (Rinnan *et al.* 2008) and change the ground vegetation by shading (Cornelissen *et al.* 2001).

The warming climate leads to increased evapotranspiration rates, altered distribution of rain, periods of heavy rains, but also summer droughts in northern land areas (Meehl *et al.* 2007). These changes will affect water balance in the vast boreal and arctic peatlands, which are significant sinks of carbon dioxide (CO_2) and sources of methane (CH_4), both important greenhouse gases (ACIA 2004). Water table largely determines the fluxes of these gases in northern peatlands (reviewed by Jungkunst

and Fiedler 2007). In the Arctic, thawing permafrost in peatlands can increase CO_2 and CH_4 efflux from these ecosystems and, thus, accelerate warming (ACIA 2004, Jungkunst and Fiedler 2007). This emphasises the sensitivity and importance of northern areas under a warming climate.

1.1.2 Solar ultraviolet-B radiation

Increased levels of ultraviolet-B radiation (UV-B, 280-320 nm), the most photochemically reactive portion of solar energy that reaches the Earth's surface, have been reported, especially in the Arctic. Worldwide, increases in UV-B irradiance of 6-14 % have been measured since the early 1980s (UNEP/WMO 2002). This trend has continued in the 1990s despite great variation in UV-B fluxes and the interactive effects of changing cloudiness and albedo (UNEP 2006).

Depletion of the stratospheric ozone (O_3) layer by man-made O_3-destroying chemicals (e.g. chlorofluorocarbons, CFCs) is well known to facilitate the passage of UV-B radiation to the troposphere, although many other factors (e.g. altitude, cloudiness, aerosols, albedo, atmospheric temperature) also affect UV-B fluxes (ACIA 2004, UNEP 2006). Stratospheric O_3, together with oxygen (O_2), absorbs all of the damaging UV-C (200-280 nm), most of the UV-B and only little of the UV-A (320-400 nm) radiation reaching the atmosphere. The depletion of the O_3 layer has been most severe in polar regions; the average daily reduction of stratospheric O_3 in the Arctic have occasionally reached 45 % (since 1979) in springtime when the strongest depletion occurs (ACIA 2004).

Despite ceased use and emissions of O_3 destroying substances, the stratospheric O_3 layer is not expected to totally recover in the next decades (ACIA 2004, McKenzie *et al.* 2006, Weatherhead and Andersen 2006). The long life-times of some O_3 destroying chemicals delay the recovery of the O_3 layer, but there is also evidence that the changing climate may complicate it (McKenzie *et al.*

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2006). Greenhouse gases do not only warm the troposphere but they also cool the lower stratosphere enhancing the conditions there for O_3 destructive chemistry (Shindell *et al.* 1998, ACIA 2004, Weatherhead and Andersen 2006). As O_3 losses in the stratosphere strongly depend on temperature, and due to the high natural variability in O_3 abundance, predicting the recovery of the O_3 layer is difficult especially in the Arctic where the interaction between O_3 depletion and climate change may be most pronounced (McKenzie *et al.* 2006). Recent results show no further O_3 depletion for most parts of the world (Weatherhead and Andersen 2006) but in the Arctic, springtime O_3 losses are expected to continue (McKenzie *et al.* 2006). Therefore, elevated doses of UV-B radiation are predicted to persist in the Arctic for the next decades (ACIA 2004).

1.1.3 Tropospheric ozone trends
While stratospheric O_3 protects the biosphere from deleterious UV doses, in the troposphere O_3 is an important air pollutant and a greenhouse gas. O_3 is photochemically formed in the atmosphere in reactions involving volatile organic compounds (VOCs), such as isoprene, and nitrogen oxides (NO_x) (Finlayson-Pitts and Pitts Jr. 1997, Fowler *et al.* 1998). While VOCs mainly originate from biogenic sources, NO_x are released by anthropogenic activities (e.g. combustion of fossil fuels, biomass burning). Therefore, concentrations of NO_x and, subsequently, levels of O_3 have significantly increased since the preindustrial times (IPCC 2007, Vingarzan 2004). The current annual O_3 concentrations range from 20 to 45 ppb worldwide indicating that the levels have doubled since the late 19th century (Vingarzan 2004). This trend is expected to continue in the 21st century (Vingarzan 2004, Meehl *et al.* 2007). While 60-80% increase in tropospheric O_3 concentrations are predicted for the tropics and subtropics by 2050, the global increase is estimated at 20-25% by 2050 and 40-60% by 2100 (Meehl *et al.* 2007).

High O_3 episodes are not only a problem in densely populated and industrialised areas,

although the highest levels of O_3 are often measured in such regions. Remote areas can be exposed to elevated O_3 levels due to long-distance transport and biogenic emissions of O_3 precursors (Fowler *et al.* 1998). Therefore, O_3 concentrations are highly variable in both space and time.

1.2 Characteristics and the biogenic emission of isoprene

1.2.1 Properties and the origin of isoprene
Isoprene (C_5H_8, 2-methyl-1,3-butadiene) is a highly reactive VOC commonly produced in nature by all living cells in various amounts. Isoprene is also produced anthropogenically as a by-product in the oil industry, and is used in the production of synthetic rubber. At room temperature isoprene is a colourless, flammable liquid which readily evaporates and reacts with other compounds in the air. Isoprene is easily soluble for example in methanol but not in water.

Table 1. Chemical properties of isoprene.

IUPAC name	2-Methyl-buta-1,3-diene
CAS number	78-79-5
Structure	C=C(C)C=C
Molecular formula	C_5H_8
Molar mass	68.11 g mol^{-1}
Density	0.681 g cm^{-3}
Melting point	-145.95 °C
Boiling point	34.067 °C

In unnaturally large concentrations in the air, isoprene has a typical odour and is considered reasonably carcinogenic to humans (National Toxicology Program, 2005). In addition, the photo-oxidation products of isoprene have adverse health effects when inhaled (Doyle *et al.* 2004). However, isoprene is widely produced by human cells (approximately 0.15 µmol kg^{-1} h^{-1}, National Toxicology Program 2005), and exhaled in low concentrations (40-80 ppbv) (e.g. Lechner *et al.* 2006). Yet other organisms, especially numerous plant species, are a more important source of

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isoprene (Kesselmeier and Staudt 1999). Therefore, isoprene in the atmosphere is mainly of biogenic origin. The chemical properties of isoprene are summarised in Table 1.

1.2.2 Isoprene synthesis and emission from plants

With the exception of CH_4, isoprene is the most common volatile organic compound emitted by vegetation (Kesselmeier and Staudt 1999). The emission was first detected in leaves of acacia (*Robinia pseudoacacia*), poplar (*Populus nigra*) and willow (*Salix alba*) in the mid-1950s (history reviewed by Sanadze 2004). Since then, emission screenings have shown that isoprene is emitted by several plant families, but no phylogenetic pattern for isoprene emission among plant genera or families has been found (Harley *et al*. 1999, reviewed by Sharkey *et al*. 2008). Thus, a plant genus may include both emitters and non-emitting species. The majority of strong isoprene emitters are woody species (Harley *et al*. 1999). However, significant emissions have also been detected from several mosses (Hanson *et al*. 1999) and a graminoid, common reed (*Phragmites australis*) (Loreto and Velikova 2001), which are both dominant vegetation groups in the peatland ecosystems studied in this thesis. A comprehensive list of known isoprene emitting species can be found on the internet: http://www.es.lancs. ac.uk/cnhgroup/iso-emissions.pdf.

Isoprene is produced via two distinct metabolic pathways in cells. Firstly, the mevalonic acid (MVA) pathway, which occurs in the cytosol, produces the immediate precursor of isoprene, dimethylallyl pyrophosphate (DMAPP), from acetyl-CoA. DMAPP is then converted to isoprene non-enzymatically (Deneris *et al*. 1985). This pathway runs independent of light, and it is common to cells of eukaryotes and many bacteria (Sanadze 2004). The other pathway (MEP, methyl-erythritol pyrophosphate pathway) for DMAPP production is present in some bacteria, but most importantly, in photosynthesising plastids of algae and plants. In the MEP pathway, which is light-dependent, the substrates for DMAPP are pyruvate and glyceraldehyde-3-phosphate (Lichtenthaler *et al*. 1997, Sharkey and Yeh 2001). DMAPP is ultimately converted to isoprene by the enzyme isoprene synthase (Silver and Fall 1991).

Both pathways for isoprene production are present in photosynthesising plant cells, but they have been shown to operate independent of each other in black poplar (*Populus nigra*) and common reed (Loreto *et al*. 2004). Isoprene emission is related to freshly assimilated carbon in chloroplasts (Loreto and Sharkey, 1990). However, isotopic studies with ^{13}C have revealed that stored carbon can also be used in the production, especially when photosynthesis is limited under stressful conditions (Affek and Yakir 2003, Funk *et al*. 2004, Schnitzler *et al*. 2004, Brilli *et al*. 2007).

After production in chloroplasts, isoprene diffuses through membranes into intercellular space and exits the cell through stomata. However, stomatal closure does not control the flux of isoprene. This is because isoprene production is not affected by the concentration of isoprene in the intercellular space. When the concentration of isoprene inside the leaf increases, it counteracts the diffusion resistance and, consequently, isoprene diffuses out of the leaf even when the stomata are closed (Fall and Monson 1992, see reviews by Sharkey and Yeh 2001, Lerdau and Gray 2003).

1.2.2.1 Light and temperature dependency

Isoprene emission is sensitive to many environmental parameters but most importantly to light and temperature (Kesselmeier and Staudt 1999). The response to light of isoprene emission and photosynthesis follow a similar pattern: the emission increases linearly until a certain saturating level of light intensity is reached (Rasmussen and Jones 1973, Guenther *et al*. 1993, Harley *et al*. 1996a). For example, isoprene emission and photosynthesis of sweetgum (*Liquidambar styraciflua*) saturate at 400-800 μmol m^{-2} s^{-1} (Harley *et al*. 1996a).

Isoprene emission is rapidly induced by illumination, it responds fast to changes in light intensity once induced, and finally, decreases rapidly when lights are switched off (Monson *et al.* 1991).

Isoprene emission responds almost instantly to changes in temperature. The emission increases exponentially when temperature increases and declines after reaching an optimum, usually at 40-42 °C (Harley *et al.* 1999).

The short-term light and temperature dependency of isoprene emission is described by the common algorithm established by Guenther *et al.* (1993):

$$E_s = E /(C_L \times C_T)$$

where E_s is the standardised emission in chosen light and temperature conditions (usually 30°C and 1000 µmol m^{-2} s^{-1} of photosynthetically active radiation), E is the measured emission, and C_L and C_T are factors for light and temperature dependency:

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{1 + \alpha^2 L^2}} \quad \text{and}$$

$$C_T = \frac{\exp \dfrac{C_{T1}(T - T_S)}{RT_S T}}{1 + \exp \dfrac{C_{T2}(T - T_M)}{RT_S T}}$$

where α, C_{L1}, C_{T1}, C_{T2}, and T_M are empirical coefficients, R is ideal gas constant (8.314 J K^{-1} mol^{-1}), and L and T are the measured light intensity and temperature.

Standardising emission rates with the algorithm means that emission rates reported by researchers from various environments can be made comparable. Even though the algorithm was based on measurements from a few single species, and it does not account for long-term light and temperature conditions (Harley *et al.* 1996a, Pétron *et al.* 2001) or the developmental stage of plants

(Monson *et al.* 1994), it has been widely used in emission modelling and emission rate standardisation for different species. Most of the variation in isoprene emission even at ecosystem level in peatlands has been explained by short-term changes in light and temperature described by the algorithm (Janson and De Serves 1998, Haapanala *et al.* 2006, Hellén *et al.* 2006).

1.2.2.2 Contribution of other environmental factors

In addition to light and temperature, many environmental stress factors affect isoprene emissions from plants.

O_3 is an important greenhouse gas contributing to climatic warming (IPCC 2007), but also a strong oxidant that has adverse effects on humans, animals, plants and, subsequently, on crop yields and ecosystem functioning (Ashmore 2005, Sitch *et al.* 2007). Effects of O_3 on isoprene emission have been inconsistent. High levels of O_3 have been shown to instantly increase isoprene emission in common reed (Velikova *et al.* 2005a). However, in downy oak (*Quercus pubescens*) the emission was first increased several days after the exposure (Velikova *et al.* 2005b). Different O_3 regimes during leaf development of white poplar (*Populus alba*) caused isoprene emission to either decrease or increase in mature leaves after high O_3 exposure (Fares *et al.* 2006). On the other hand, Blande *et al.* (2007) did not detect significant change in isoprene emission in hybrid poplars (*Populus tremula × tremuloides*) under chronic exposure to moderate O_3 levels. No plant community or ecosystem scale studies on isoprene emission under O_3 exposure have been conducted so far.

The effects of increasing solar UV-B radiation on plants, animals and ecosystems have been intensively studied since the discovery of depletion of the stratospheric O_3 layer. However, the effects of UV-B on isoprene emission have attracted little interest. So far, only Harley *et al.* (1996b) have shown that enhanced UV-B radiation increases the emission of isoprene from

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gambel oak (*Quercus gambelii*) as a result of increased leaf biomass.

Mild water stress is known to stimulate or to have only minor effects on isoprene emission. However, when mild water stress turns to severe drought, isoprene emission is reduced as shown at leaf level (e.g. Sharkey and Loreto 1993, Pegoraro *et al.* 2004) as well as at ecosystem scale in controlled mesocosms (Pegoraro *et al.* 2005a).

Leaf level studies have revealed that typically less than 2 % of recently assimilated carbon is re-emitted back to the atmosphere as isoprene in isoprene emitting plants at 30 ℃ (Sharkey and Loreto 1993, Harley *et al.* 1999). However, under stressful conditions a substantial amount (even up to 50 %) of the assimilated carbon can be lost as isoprene (Sharkey and Loreto 1993, Harley *et al.* 1999, Pegoraro *et al.* 2004). Even under severe drought, when reduced isoprene emission has been observed, the loss of carbon as isoprene was increased as photosynthesis decreased even more dramatically than isoprene emission (Funk *et al.* 2004, Pegoraro *et al.* 2004, 2005a). This significant loss of carbon raises the question of why plants emit isoprene.

1.2.3 Function of isoprene for plants
The isoprene molecule is a build-up component of terpenoids (also called isoprenoids) in plants. Many terpenoids, such as monoterpenes, are VOCs and have an important role in attracting pollinators and parasitoids, deterring herbivores, mediating plant-plant communication and also in defence mechanisms against abiotic stresses (reviewed by Holopainen 2004, Peñuelas and Munné-Bosch 2005). The function of isoprene in plants is a matter of debate, but isoprene emission has been postulated to help plants cope with various stress conditions harmful to photosynthesis (Peñuelas and Munné-Bosch 2005, Sharkey *et al.* 2008).

Several experiments have shown that isoprene-emitting plants are less damaged by O_3. Isoprene can act as an antioxidant by quenching O_3 and by reducing peroxidation of membrane lipids in several isoprene emitting species (Loreto and Velikova 2001, Velikova *et al.* 2005b), as well as in isoprene-fumigated non-emitting species (Loreto *et al.* 2001, 2006).

Isoprene does not only inhibit damage by exogenous oxidants such as O_3 but it can also protect the plant tissues against endogenous oxidative agents which are produced inside plants under harmful conditions such as high temperatures (Velikova *et al.* 2006). The cellular membrane properties can also be changed by isoprene under thermal stress (Sharkey and Singsaas 1995). The hypothesis that isoprene conveys increased thermotolerance has received strong support, but the mechanisms involved are still unclear (Sharkey and Singsaas 1995, Hanson *et al.* 1999, Sharkey *et al.* 2001, Behnke *et al.* 2007, review by Sharkey *et al.* 2008). So far, only Siwko *et al.* (2007) have shown that isoprene can dissolve in a phospholipid membrane and thereby enhance the membrane stability as much as a substantial decrease in temperature.

It has been hypothesised that there is no specific role for every VOC, including isoprene, and that it is rather the volatility of the compounds that determines their emission from plants (Peñuelas and Llusià 2004, Owen and Peñuelas 2005). However, for some compounds, the emission has turned into an evolutionary advantage such as the protective mechanisms (Peñuelas and Llusià 2004) described above. One basis for this opportunistic hypothesis is the suggestion that emission of isoprene is a way to dissipate excess energy in high light conditions and, thus, protect the photosynthetic apparatus (Peñuelas and Munné-Bosch 2005). The opportunistic hypothesis has been criticised on the basis of evolutionary aspects as various advantageous functions for several VOCs have been found (Pichersky *et al.* 2006) and there are also more effective ways to consume excess energy, such as photorespiration, in plants (reviewed by Sharkey *et al.* 2008). However, Niinemets *et al.* (2004) have underlined the physicochemical characteristics (e.g.

volatility and diffusivity) that determine the emissions of some VOCs, which supports the opportunistic hypothesis for VOC emissions.

1.2.4 Isoprene emission at ecosystem level

The recent estimate of global yearly biogenic isoprene emission is $440 - 660 \times 10^{12}$ g carbon (Guenther *et al*. 2006). Tropical and temperate areas strongly contribute to the global emission and have therefore gained most interest in emission inventories. Isoprene emissions from boreal forest ecosystems have been recently studied, but other ecosystems in this area and also in the Arctic region (here defined as the area north of the Arctic Circle) have received less attention.

1.2.4.1 Boreal and arctic ecosystems

In the boreal zone, Norway spruce (*Picea abies*) dominated forests have been shown to emit substantial amounts of isoprene; the emission is estimated at approximately 1000 μg m^{-2} h^{-1} (1 μg g^{-1} DW h^{-1}, needle density of 1000 g DW m^{-2}) (Janson *et al*., 1999, Lindfors and Laurila 2000, Hakola *et al*. 2003). However, isoprene emissions from the deciduous trees aspen (*Populus tremula*) and willow (*Salix* sp.) are an order of magnitude larger (Hakola *et al*. 1998). These deciduous species rarely dominate in the boreal ecosystems but their contribution to the total isoprene emission is important especially in late summer after leaf maturation (Tarvainen *et al*. 2007). However, Lindfors and Laurila (2000) and Tarvainen *et al*. (2007) have estimated that less than 10 % of the total Finnish forest VOC emissions consist of isoprene while monoterpenes are the dominant group of compounds.

Boreal peatlands are a significant source of atmospheric isoprene. In contrast to forests, isoprene dominates VOC emissions from peatlands (Janson *et al*. 1999, Haapanala *et al*. 2006, Hellén *et al*. 2006). Haapanala *et al*. (2006) and Hellén *et al*. (2006) have detected isoprene emissions of 0-400 and 50-103 μg m^{-2} h^{-1}, respectively, from a boreal oligotrophic fen (nutrient poor minerotrophic peatland) in southern Finland (Siikaneva). Janson *et al*. (1999) and Janson and De

Serves (1998) observed mean emissions of the same magnitude from oligotrophic fens in central Sweden (Stormossen) and eastern Finland (Salmisuo). However, they also noted that the emission can reach up to several mg m^{-2} h^{-1} during warm weather conditions. Dry microsites, hummocks, emitted significantly less isoprene than wet microsites, flarks (Janson and De Serves, 1998, Janson *et al*. 1999).

Peat mosses (*Sphagnum* sp.) typically dominate the ground layer in boreal bogs (ombrotrophic, extremely nutrient poor peatland) and most fens. Several *Sphagnum* species and other mosses are isoprene emitters (Hanson *et al*. 1999) and their contribution to peatland isoprene emission has been demonstrated at an oligotrophic fen (Hellén *et al*. 2006). Sedges (*Cyperaceae*) and several dwarf shrubs are also common in peatlands, but their contribution to isoprene emission has received little attention. However, in a recent study Bai *et al*. (2006) concluded that sedge species (*Carex* sp.) can be important isoprene emitters in grasslands. In a subarctic peatland, the sedges *C. rostrata* and *Eriophorum angustifolium* have also been shown to emit isoprene (A. Ekberg, Lund University, personal communication).

Very few isoprene emission measurements have been conducted in the vast arctic zone so far. Rinne *et al*. (2000) observed an emission of 14 μg m^{-2} h^{-1} from a mountain birch (*Betula pubescens* subsp. *czerepanovii*) and Siberian spruce (*Picea abies* subsp. *obovata*) dominated forest in northern Finland. Isoprene emissions from open heath (also called tundra), a common ecosystem type in the Arctic (Bliss and Matveyeva 1992), have not previously been studied.

Due to slow and incomplete degradation of organic material, boreal and arctic peatlands and other ecosystems in those regions sequester huge amounts of carbon into the soil (Turunen *et al*. 2002, Post *et al*. 1982). However, peatlands also emit substantial amounts of CH$_4$, an important greenhouse gas. Therefore, intensive research on carbon balance and its atmospheric impact has been

conducted in these areas during recent years. The investigations have focused almost exclusively on CO_2 and CH_4 fluxes in the ecosystems while emissions of isoprene and other VOCs have gained less interest. However, recently, Bäckstrand *et al.* (2008) observed a considerable (5%) loss of assimilated carbon as non-methane-VOCs during a growing season at a subarctic peatland. This suggests that VOC emissions, including isoprene, can have an effect on the carbon balance in the ecosystem.

1.2.4.2 The contribution of soil to isoprene emissions

Several soil microorganisms can produce (Schöller *et al.* 2002) and also degrade isoprene (Cleveland and Yavitt 1998, Fall and Copley 2000). Studies on temperate, mediterranean and tropical forest soils have shown that isoprene and other VOCs can be taken up by the soil in modest amounts (Cleveland and Yavitt 1998, Pegoraro *et al.* 2005b, Asensio *et al.* 2007). Small emissions of monoterpenes have been detected mainly from the litter (Hayward *et al.* 2001).

Isoprene uptake in soil is an aerobic process strongly controlled by soil water content. An optimum water content of 25-60 % for isoprene uptake in temperate soil was determined by Cleveland and Yavitt (1998). Drought has been shown to decrease isoprene uptake in tropical forest soil (Pegoraro *et al.* 2005b) whereas mediterranean forest soil has turned from a source into a slight sink of other VOCs during drought (Asensio *et al.* 2007). Contribution of soil to isoprene fluxes is probably small but it needs to be taken into account when estimating isoprene budgets at ecosystem and larger scales.

1.2.5 Isoprene in the atmosphere

Isoprene is an important contributor to the composition of the atmosphere because of its large annual emission and fast reactivity in the atmosphere. The chemistry of isoprene in the atmosphere is complex and involves several interactions with components of climate change.

Firstly, photo-oxidation of isoprene in the atmosphere leads to formation of condensable compounds, which are required for secondary organic aerosol (SOA) formation (Claeys *et al.* 2004, Kourtchev *et al.* 2005). Aerosols scatter and absorb solar radiation and act as cloud condensation nuclei (Novakov and Penner 1993, Andreae and Crutzen 1997). Thus, aerosols provide a negative radiative forcing (cooling) in the atmosphere (IPCC 2007) but the effect of SOA in particular is still under debate (Meehl *et al.* 2007).

Secondly, O_3 is formed in the atmosphere from interactions between VOCs and NO_x in sunlight (Atkinson and Arey, 2003). This results in especially high O_3 concentrations in urban areas with high NO_x pollution from combustion, large emissions of VOCs from vegetation and intensive sunlight. However, in conditions of low NO_x concentrations, the atmospheric reactions of VOCs consume O_3 (Atkinson and Arey, 2003). Despite this, increasing emissions of VOCs, especially isoprene from broadleaved trees, is predicted to increase O_3 formation in continental regions of the northern hemisphere in the next decades (Meehl *et al.* 2007).

Finally, isoprene and other VOCs contribute to the oxidative capacity of the atmosphere. Oxidative chemistry of the atmosphere is dominated by the gas-phase reactions of hydroxyl radicals (OH). Isoprene and other organic gases react rapidly with OH, the concentration of which can be subsequently reduced in the atmosphere. Several studies have revealed significant (up to 70 %) decreases in local OH concentrations due to reactions with isoprene (reviewed by Monson and Holland, 2001). On the contrary, Lelieveld *et al.* (2008) postulated a mechanism by which OH can be recycled through reactions with VOC oxidation products over tropical forest. Oxidative reactions with OH are also an important sink of CH_4 from the atmosphere. Atmospheric chemistry models suggest that the lifetime of CH_4 is significantly lengthened when emissions of isoprene and other VOCs from

ecosystems increase and consume more of atmospheric OH (Kaplan *et al.* 2006).

1.3 Research objectives and outline of experiments

The main purpose of this thesis was to assess whether various climate change factors affect isoprene emission from representative subarctic and boreal ecosystems. The specific questions of interest were if isoprene emission is affected by (1) warming, (2) increasing UV-B radiation, (3) increasing tropospheric O_3 concentration, or (4) by peatland water table drawdown. Secondly, the aim was to assess the general magnitude of isoprene emissions and its relationship to different plant species or vegetation groups in the studied ecosystems.

No isoprene emission measurements have previously been conducted in arctic tundra ecosystems. In peatlands, a few earlier studies exist, but they have concentrated on oligotrophic boreal fens dominated by *Sphagnum* mosses (reviewed by Tarvainen *et al.* 2007). Several *Sphagnum* mosses are known to emit isoprene (Hanson *et al.* 1999). There is no information of isoprene emissions from the many other peatland types or of the contributions made by other moss or vascular plant species to the emissions.

Laboratory experiments on single plant species have indicated that increasing fluxes of UV-B and concentrations of O_3 can increase isoprene emissions (e.g. Harley *et al.* 1996b, Velikova *et al.* 2005a, 2005b). Warming is likely to increase the emissions as they strongly depend on temperature in individual species (e.g. Harley *et al.* 1999). Water table drawdown can decrease isoprene emission, as recently shown at ecosystem level in a mesocosm experiment (Pegoraro *et al.* 2005a). To my knowledge, there are no reports in the literature on effects of these climate change factors on isoprene emissions from boreal or arctic ecosystems.

The experiments in this thesis were conducted either in field conditions or in growth chambers (Table 2). Figure 1 shows the locations of the field experiments and the origin of the peatland microcosms that were studied in the experimental field and in growth chambers. The experiments in the field (Figs. 2 and 3a, Chapters 2, 3 & 4) were especially designed for studies on the susceptibility and functioning of the ecosystems under realistic, long-term changes in climate. The short-term growth chamber experiment (Fig. 3b, Chapter 5) provided information on a short time scale, but in a controlled environment, which is necessary to perform the water table treatment. Isoprene emissions observed in the variable conditions in the field were standardised by the common algorithm (Guenther *et al.* 1993) to enhance the comparability of the results. By studying isoprene emission in these experiments I could begin filling the gaps in information concerning isoprene emission from boreal and arctic ecosystems and its response to the changing climate.

Figure 1. Dots indicate the locations of the experiments of this thesis. Triangles show the origin of the peatland microcosms.

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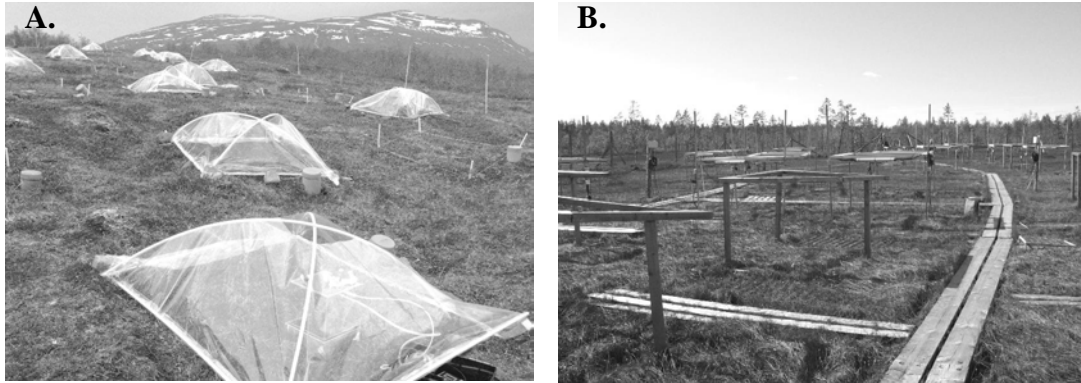
Figure 2. Field experiments used in this thesis. (A) Subarctic heath under climatic warming in Abisko, Northern Sweden. (B) Subarctic peatland under enhanced UV-B in Sodankylä, Northern Finland.
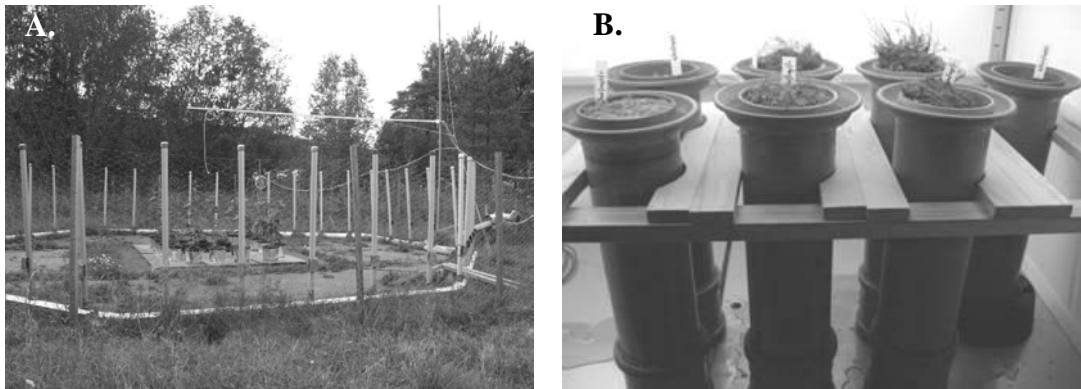
Figure 3. Facilities for the microcosm experiments in this thesis. (A) Open-field facility for ozone exposure in Kuopio, Central Finland. (B) Peatland microcosms in a growth chamber at the University of Kuopio.

Table 2. Summary of the experiments studied in the current work. Chapter numbers refer to the following publications where detailed descriptions of the experiments can be found.

Experiment	Treatments	Exposure duration	Ecosystem	Experiment type	Experiment location	Chapter
1. Effects of warming on isoprene emission	3-4°C warming, litter addition	7-8 years	Subarctic heath	*In situ* field experiment	Abisko, Sweden	2
2. Effects of increasing UV-B on isoprene emission	46 % enhanced UV-B radiation	2-4 years	Subarctic peatland	*In situ* field experiment	Sodankylä, Finland	3
3. Effects of elevated O$_3$ on isoprene emission	2 × ambient O$_3$ concentration	2-3 years	Boreal peatland	Microcosms on experimental field	Kuopio, Finland	4
4. Effects of vegetation and water table drawdown on isoprene emission	Vegetation removal, -20 cm lowered water table	9 weeks	Boreal peatland	Microcosms in growth chambers	Kuopio, Finland	5

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