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Mengistu Mengesha Maja

Volatile organic compounds emitted from silver birch and European aspen in response to environmental stresses

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ABSTRACT

Deciduous trees face increasing biotic and abiotic stresses as a result of climate warming and respond in various ways including the emission of volatile organic compounds (VOCs). There is an urgent need to quantify VOC emissions of deciduous trees in response to environmental stresses in order to understand their contribution to the atmospheric carbon and air quality in the face of climate change. The aim of this thesis was to assess VOC emission responses of silver birch (*Betula pendula* Roth) to short- and long-term herbivory and environmental changes as a result of provenance translocation along a latitudinal gradient. It also assesses the effects of single and combined warming and enhanced UV-B exposure on VOC emission from European aspen (*Populus tremula* L.).

In the first experiment, long-term (30 days) and short-term (0-48 hours) foliar herbivory experiments were carried out on potted silver birch plants by infesting them with geometrid moth species (*Agriopis aurantiaria* Clerck) and *Erannis defoliaria* Hübner). Besides foliar herbivory, there was a bark herbivory by pine weevil (*Hylobius abietis* L.) on silver birch plants for 21 days. In the second experiment, VOC emissions were measured from three provenances (Loppi (60 °N), Vehmersalmi (62 °N) and Kittilä (67 °N)) of silver birch at two common garden sites (Joensuu (62° N) and Kolari (67° N)) in Finland. The plants were growing in the field for approximately two years before the VOC sampling. In the third experiment carried out with European aspen, plants were exposed to a single and combined warming (ambient + 2°C) and enhanced UV-B radiation (30.9%) in field conditions. VOC emissions in the field were measured using dynamic head space collection method and analysed by gas chromatography-mass spectrometry (GC MS), whereas the online monitoring was performed by proton transfer time-of-flight mass spectrometry (PTR-TOF-MS).

Short-term herbivory led to a rapid induction of green leaf volatiles (GLVs) and a steady increase in terpenoid emission during the feeding period. The feeding pattern of the larvae roughly matched the VOC emission peaks. Long-term foliage herbivory in the field led to a genotype-dependent, transient increase in the emission rates of monoterpenes (MTs) but the differences in emission due to treatments and genotypic differences declined as the season progressed. There was no clear difference in VOC emission rates as a result of bark damage. VOC emissions differed between experimental sites but provenance translocation along a latitudinal gradient had no significant effect. However, VOC composition was significantly affected by translocation during the second experimental year. In the third experiment, warming increased isoprene emission from European aspen; it also modified VOC emission responses to UV-radiation. VOC emissions from the rhizospheres of both silver birch and European aspen showed no significant treatment effects.

The results suggest that VOC emission rates of silver birch to foliar herbivory are substantial immediately after herbivore damage and measurements from fresh damages are important to estimate biotic stress-induced VOC emission rates. The lack of clear provenance translocation effect on VOC emission responses of silver birch suggests that this species might be rather tolerant to environmental changes in the short-term. However, emission differences between sites indicate that abiotic condition especially cumulative temperature plays a role. Increased emission from European aspen as a result of combined warming and UV-B radiation suggests that abiotic stresses have significant interactive effects on VOC emission from deciduous trees and may further affect atmospheric chemistry.

Universal Decimal Classification: 504.3, 504.7, 57.045, 57.047, 581.135.5, 582.632.1, 582.681.81

CAB Thesaurus: volatile compounds; organic compounds; isoprenoids; terpenoids; emissions; *Betula pendula*; *Populus tremula*; environmental factors; stress; herbivory; translocation; provenance; latitude; environmental temperature; ultraviolet radiation; rhizosphere; climate change; global warming

Yleinen suomalainen asiasanasto: haihtuvat orgaaniset yhdisteet; päästöt; koivu; haapa; ympäristötekijät; ympäristökuormitus; kasvinsyöjät; siirto; leveyspiirit; lämpötila; lämpeneminen; ultraviolettisäteily; juuristo; ilmastonmuutokset

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This study was conducted in the Department of Environmental Science at the University of Eastern Finland, Kuopio campus. I wish to acknowledge the Department of Environmental Science for providing facilities and financial support to conduct the research. Science is a collaborative endeavour and I could not have completed my study without the involvement and encouragement of many people.

My deepest gratitude goes to my main supervisor, prof. Jarmo Holopainen, who gave me the opportunity to pursue my MSC and PhD studies, and introduced me to the world of plant volatiles. He has been in the heart of planning and execution of experiments, including sitting behind the wheels for hours during long trips to Kolari experimental site in Lapland.

I would like to acknowledge prof. Toini Holopainen, second supervisor, for her significant involvement in the planning of all the experiments. She was so meticulous in her constructive comments during writing and publication processes of all manuscripts, and preparation of summary of the thesis. Her support and encouragement were so valuable.

Dr. Anne Kasurinen was my third supervisor, and has been involved in most of the research planning, execution and preparation of the manuscripts. She was my immediate refuge whenever I had trouble in statistical analyses, and provided vital help on technical issues. I would like to express my special thanks to her and her large store of statistical knowledge is greatly appreciated. I have learnt a lot from her during my time as MSc and PhD student.

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Mengistu Mengesha

Kuopio, December 2015

“It is paradoxical, yet true, to say, that the more we know, the more ignorant we become in the absolute sense, for it is only through enlightenment that we become conscious of our limitations. Precisely one of the most gratifying results of intellectual evolution is the continuous opening up of new and greater prospects.”

Nicola Tesla, September 9, 1915

LIST OF ABBREVIATIONS

ATP	Adinosine triphosphate
CFC	Chlorofluorocarbon
CH_4	Methane
CO_2	Carbon dioxide
DMAPP	Dimethylallyl pyrophosphate
DMNT	(E)-4,8-Dimethyl-1,3,7-nonatriene
DNA	Deoxyribonucleic acid
FDP	Farnesyl diphosphate
GAP	Glyceraldehyde 3-phosphate
GC MS	Gas chromatography-mass spectrometry
GPP	Geranyl pyrophosphate
GLVs	Green leaf volatiles
IPCC	Intergovernmental Panel on Climate Change
IPP	Isopentenyl pyrophosphate
LOX	Lipoxygenase
MEP	Methyl-erythritol phosphate pathway
MT	Monoterpene
MVA	Mevalonic acid pathway
NADPH	Nicotinamide adenine dinucleotide phosphate
NO_x	Nitrogen oxide radicals
NO_2	Nitrogen dioxide
O_3	Ozone

PAR	Photosynthetically active radiation
PC	Principal component
PET	Polyethylene terephthalate
PPFD	Photosynthetic photon flux density
PTR-TOF-MS	Proton transfer time of flight mass spectrometry
RNA	Ribonucleic acid
SE	Standard error
SOA	Secondary organic aerosol
SQT	Sesquiterpene
Tg	Tera gram
ROS	Reactive oxygen species
UV	Ultraviolet
UV-A	Ultraviolet A radiation (320-400 nm)
UV-B	Ultraviolet B radiation (280-320 nm)
UV-C	Ultraviolet C radiation (100-280 nm)
VOC	Volatile organic compound

LIST OF ORIGINAL PUBLICATION

This thesis is based on data presented in the following three articles, referred to in the text by their chapter numbers 2-4

Chapter 2	Maja MM, Kasurinen A, Yli-Pirilä P, Joutsensaari J, Klemola T, Holopainen T, Holopainen JK. Contrasting responses of silver birch VOC emissions to short- and long-term herbivory. Tree Physiology 34: 241–252, 2014.
Chapter 3	Maja MM, Kasurinen A, Holopainen T, Kontunen-Soppela S, Oksanen E, Holopainen JK. Volatile organic compounds emitted from silver birch of different provenances across a latitudinal gradient in Finland. Tree Physiology 35: 975–986.
Chapter 4.	Maja MM, Kasurinen A, Holopainen T, Julkunen-Tiitto R, Holopainen JK (2015) The effect of warming and enhanced ultraviolet radiation on gender-specific emissions of volatile organic compounds from European aspen (*Populus tremula L.)* (Submitted manuscript)

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AUTHOR'S CONTRIBUTION

Mengistu M. Maja contributed to the field work, data analyses and was the first author in all the papers (chapters 2-4). Mengistu M. Maja also participated in planning of herbivory experiment (chapter 2) and assessments of VOC emission as a result of changes in environmental conditions following translocation of provenances of silver birch along a latitudinal gradient (chapter 3), and also warming and UV-B radiation exposure on European aspen (chapter 4). VOC sampling rounds were performed in collaboration with supervisors and with research teams led by Prof. Elina Oksanen (chapter 3) and by Prof. Riitta Julkunen-Tiitto (chapter 4). In the first paper (chapter 2) Pasi Yli-Pirilä contributed to PTR-TOF-MS VOC sampling at laboratory and performed data analysis, and Tero Klemola provided eggs of insects used to infest the plants in the first experiment.

Contents

1 General introduction

1.1 BACKGROUND

It is widely accepted that global climate change manifested primarily by changes in surface air temperature is the greatest environmental threat of all ecosystems. In the last 100 years, global surface air temperature has shown rapid increase as a result of imbalance of incoming and outgoing radiation (IPCC, 2014). According to the third assessment report of the Intergovernmental Panel on Climate Change (IPCC), the global average surface air temperature is forecasted to increase by 1.4-5.8°C over the period of 1990 to 2100 (IPCC, 2001). There is a consensus that at least part of the rise in temperature is attributable to greenhouse gas emissions from anthropogenic sources (Barnett et al., 2005; IPCC, 2014). Water vapour, carbon dioxide (CO_2), methane (CH_4), ozone (O_3), nitrogen oxides (NO_X) and chlorofluorocarbon (CFC) compounds are the main greenhouse gases that contribute to the rise in surface temperature. The emission of these gases is facilitated by human activities such as fossil fuel burning, land use change, and agricultural and industrial activities. As a result of the rapid increase in their concentration, the global average temperature is approaching a level of 2°C above pre-industrial levels, which is considered a threshold for irreversible change in the biosphere (Meinshausen et al., 2009; IPCC, 2014).

Some of the greenhouses gases associated with climate warming impact the concentration of stratospheric O_3, which filters harmful UV-B radiation. Although the role of chloro- and bromocarbons in depleting stratospheric O_3 is declining due to Montreal protocol (McKenzie et al., 2011), springtime ozone depletion will continue to increase for many decades at polar latitudes (Manney et al., 2011). Furthermore, increasing concentration of replacements of O_3 depleting substances and other trace gases such as nitrogen dioxide (NO_2) continue to degrade stratospheric O_3 (Ravishankara et al., 2009; Stolarski et al., 2015) leading to increased UV-B radiation in some areas and simultaneously changing seasonal weather pattern (Bornman et al., 2015). UV-B radiation can independently interfere with the cellular function injuring deoxyribonucleic acid (DNA), ribonucleic acid (RNA) and membranes (Jansen et al., 1998). UV-radiation and seasonal variations in other abiotic and biotic factors may have interactive effects on plant metabolism (Bornman et al., 2015).

Forest ecosystems across various latitudes have shown changes, notably the composition, structure and functional processes are affected by climatic factors (Dale et al., 2001; Kellomäki et al., 2001), but these changes are more consequential at high latitudes compared to low latitude ecosystems (Serreze et al., 2000; Parmesan and Yohe, 2003). Climate warming coupled with continuous CO_2 enrichment of the air is expected to increase carbon sequestration (Nemani et al., 2003) and thus enhance tree and forest growth in areas where soil nutrients are not a limiting factor (Oren et al., 2001). Climate warming also enhances expansion of vegetation zones and treeline further north and upslope making new habitats for other organisms (IPCC, 2014). On the other hand, treeline expansion reduces surface albedo (Beringer et al., 2005) which further enhances warming of the lower atmosphere. Warmer temperature and northward expansion of host species provide favourable conditions for herbivorous insect species that can cause extensive damage to forest trees (Jepsen et al., 2008).

Herbivorous insects are subject to both direct and indirect effects of climate warming (Bale et al., 2002; Deutsch et al., 2008). Climate warming can directly increase overwintering survival, advance generation time and enhance growth of insects (Ayres and Lombardero, 2000; Volney and Fleming, 2000). It can also have indirect effect through changes in phenological synchrony between host plant and herbivorous insects (Stange and Ayres, 2010; Pureswaran et al., 2014) and through regulation of the abundance of insect population by enhancing the performance of the natural enemies of insects (Ayres and Lombardero, 2000; Parmesan and Yohe, 2003; Delava et al., 2014). Temperature-mediated changes in community composition and species dynamics increase frequency of insect outbreaks and cause extensive defoliation in boreal forests (Jepsen et al., 2008).

Climate change factors lead to a wide range of responses in plants, including structural, physiological as well as phenological changes (Root et al., 2003). They also activate various defence strategies in plants (Atkinson and Urwin, 2012). For example, the responses of plants to climate change factors and herbivory involve production and emission of chemical compounds. Environmental stresses induce the emission of various volatile organic compounds (VOCs) (Kesselmeier and Staudt, 1999), which are organic compounds with low boiling point and high vapour pressure at normal conditions (Dudareva et al., 2006). Plant VOCs are used in defence against herbivorous insects and relieve stress caused by abiotic factors. They also play roles in multitrophic communication between plants, herbivorous insects, predators and parasitoids (Holopainen, 2004) and are involved in biosphere-atmosphere-climate feedback system (Laothawornkitkul et al., 2009; Ehn et al., 2014). At global scale, VOCs are emitted in large quantities with vegetation contributing the major share (Guenther et al., 2000). The large scale of emission, multitrophic communication in the ecosystem and their involvement in the atmospheric chemistry as a result of their reactive property makes plant VOCs important to the physical and chemical properties of the atmosphere (Fineschi et al., 2013). In order to understand the effects of environmental stresses on VOC emissions and the resultant effects on atmospheric chemistry and air quality, there is urgent need to investigate the VOC emission responses of climate change sensitive deciduous trees.

This thesis discusses the changes in VOC emission responses of deciduous trees (silver birch and European aspen), with particular emphasis on insect herbivory, warming, and enhanced UV-radiation. It also reports on how translocation of different provenances of silver birch to experimental sites located at different latitudes in Finland, that differ in both biotic and abiotic factors, affects VOC emissions from different provenances. Since most environmental stresses change simultaneously, the effects of these factors on plant metabolism may add up or neutralize each other. Therefore, this thesis also explores the effect of abiotic factors (UV-radiation and warming) singly and in combination on the quality and quantity of VOCs emitted from European aspen. Moreover, it addresses sex-specific differences in VOC emission from different genotypes of European aspen in response to warming and enhanced UV-B radiation. To my knowledge, no previous studies have investigated single or combined effects of warming and UV-B radiation on VOC emissions from European aspen.

1.2 WARMING-RELATED CHANGES IN BOREAL FORESTS

The boreal forests, being the largest terrestrial biome, account for large proportion of primary or unmanaged forests of the world and contribute to climate system by keeping significant amount of carbon in the vegetation and soil under the canopy (Bonan, 2008; Olsson, 2009). Recent climate projections indicate that warming will be greatest in the northern boreal region with an expected increase of about 4-5^{o}C at the end of this century (IPCC, 2014). As a result, boreal forest ecosystems are likely to be strongly influenced by climate change (Kellomäki et al., 2001). Some of the changes include enhanced tree growth as a result of increased CO_2 availability and longer growing season leading to gradual expansion of treeline (Kellomäki et al., 2008; Ruckstuhl et al., 2008). Climate warming also alters species composition as evergreen trees are gradually replaced by deciduous trees leading to continuous transformation of boreal ecosystems (Chen et al., 2011; Koven, 2013; Kellomäki et al., 2008). For instance, the proportion of silver birch is increasing while coniferous species are declining in the Scandinavian region (Kellomäki et al., 2001; Engelkes et al., 2008; Elmhagen et al., 2015).

There is now ample evidence that plants are showing climate warming-induced phenological shifts (Sparks and Menzel, 2002; Walther et al., 2002; Parmesan, 2007). Most spring phenological events of boreal forests (e.g., bud break, leaf maturation, and flowering) take place earlier (Visser and Both, 2005; Menzel et al., 2006). In the last few decades, the beginning of growing seasons across Europe has advanced by eight days (Chmielewski and Rötzer, 2002) leading to an expected increase of growing season by 3-4 days per decade (Peñuelas et al., 2009). Faster plant development and longer growing season coupled with increased precipitation and CO_2 enrichment enhance plant biomass (Chmielewski and Rötzer, 2001; Boisvenue and Running, 2006). Chemical composition of plants may also change due to enrichment of atmospheric CO_2, which has the potential to change carbon to nitrogen ratios in plant tissues (Kostiainen et al., 2006) and can affect the amount of foliage consumed by herbivorous insects (Hunter, 2001).

1.3 EFFECTS OF CLIMATE CHANGE ON INSECTS

Insects occupy a wide range of terrestrial and aquatic habitats and play a major role in the succession, functioning and carbon cycling in ecosystems (Ayres and Lombardero, 2000). Since insects are ectotherms, their physiology, development and biogeographical distribution are highly sensitive to climate change (Carroll et al., 2003; Stange and Ayres, 2010). In the last century alone, an average of 120 km northward displacement of climatic isotherm was reported over Europe (Beniston and Tol, 1998), which caused considerable impact on metabolic processes of insects. For example, approximately 10°C rise in temperature can roughly double metabolic rates of insects (Clarke and Fraser, 2004). Faster metabolism enhances growth and reproduction leading to shorter generation, which in turn increases density of insects (Deutsch et al., 2008). Besides creating more benign thermal environment in areas previously limited by low temperature, climate warming enhances dispersal abilities of insects (Travis et al., 2013) contributing to the range expansion of Lepidopterans in Europe (Parmesan et al., 1999; Hill et al., 2002; Saarinen et al., 2003). A survey of 35 non-migratory European butterflies with known boundaries has indicated that approximately 63% have expanded northwards (35-240 km) (Parmesan et al., 1999). Some geometrid moth species including winter (*Operophtera brumata* L*)* and autumnal (*Epirrita autumnata* Borkh*)* moths have increased their distribution range northwards in recent years in Scandinavia (Jepsen et al., 2008; Ammunét et al., 2012). Battisti et al (2006) have reported an upslope expansion of approximately 99m in altitudinal range for pine processionary moth (*Thaumetopoea pityocampa* Denis and Schiffermüller) in a 30-year period. The projections for 21st century are more alarming as a 2°C rise in temperature in the northern latitudes might move the current climate conditions by 600 km northward and 330m upslope (IPCC, 2001). This shift in bioclimatic envelopes may cause convergence of insects and increased outbreak in some parts of Scandinavian countries especially in birch forests (Tenow et al., 1999; Ruohomäki et al., 2000; Neuvonen et al., 2005).

1.4 VOLATILE ORGANIC COMPOUNDS EMITTED BY PLANTS

Plants produce over 100,000 chemical products, of which, over 1,700 are known to be volatile (Dicke and Loreto, 2010). Isoprenoids (isoprene, tepenes) are the largest group of these VOCs and their production and functions are well researched (Dudareva et al., 2006). In 1960, the global terpene emission rate from vegetation was estimated to be 175 Tg C year^{-1} (1Tg=10^{12}g) (Went 1960), but this underestimation has been rectified through advancement in measurement techniques and better map of global vegetation. Current estimation of the mean annual emission of biogenic VOCs including methane stands around 760 Tg C (Sindelarova et al., 2014). The emission rate of VOCs costs plants up to 10% of fixed carbon and accounts for 80% of reactive VOCs added to the atmosphere (Peñuelas and Llusià, 2003). Plant VOCs are emitted from almost all plant parts including branches and leaves (Loreto and Schnitzler, 2010), roots (Steeghs et al., 2004), flowers (Knudsen et al., 1993) and fruits (Dudareva and Pichersky, 2008). Physiological and physicochemical factors as well as other external constraints can alter the quality and quantity of plant VOCs (Paré and Tumlinson, 1999; Niinemets, 2010b; Schaub et al., 2010).

1.4.1. Isoprenoids (isoprene, mono- and sesquiterpenes)

Isoprenoids represented mainly by isoprene (C_5), monoterpenes (C_{10}) and sesquiterpenes (C_{15}) are the largest and most diverse class of plant volatiles (Dudareva et al., 2013) derived from five carbon precursors isopentenyl diphosphate (IPP) and its isomer dimethylalyl pyrophosphate (DMAPP) (McGarvey and Croteau, 1995). They are synthesized through the mevalonic acid (MVA) and methyl-erythritol phosphate (MEP) pathways (Rodríguez-Concepción et al., 2004). The two pathways are almost independent but recent studies have revealed that there is some interaction through metabolic cross-talk at IPP level (Laule et al., 2003). The MVA pathway takes place in cytoplasm while the MEP pathway is operational in chloroplasts (Figure 1) (Owen and Peñuelas, 2005). Isoprenoids are synthesized constitutively or induced by environmental stresses and released immediately after synthesis or stored in some special storage organs (resin ducts, glandular trichomes on the leaf surface, glands in leaf tissues) (Fineschi et al., 2013).

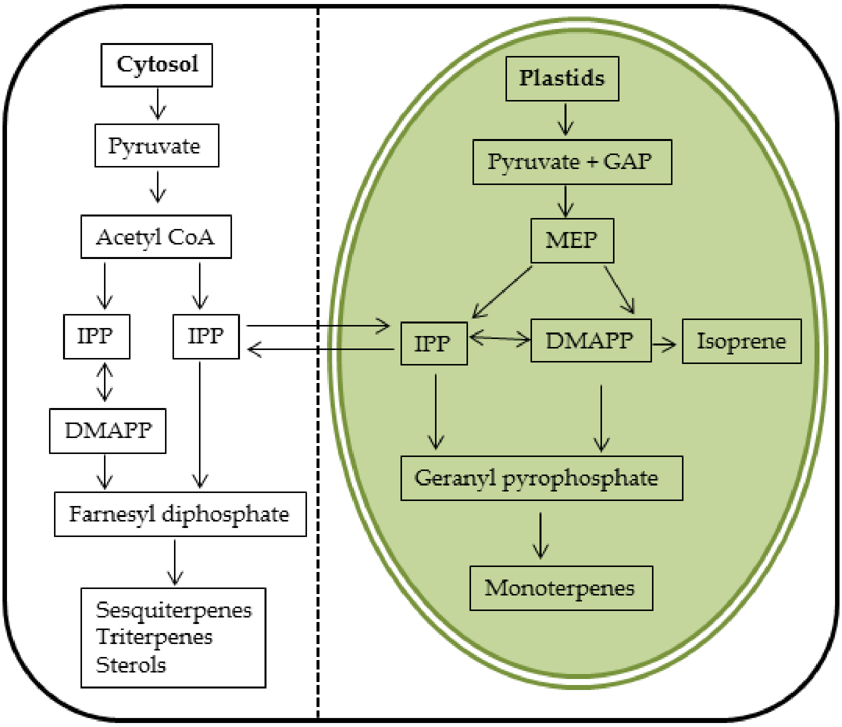

Figure 1. A simple diagram of the MVA and MEP pathways through which isoprenoids are synthesized (modified from Li and Sharkey, 2013)

Isoprene (2-methyl-1, 3-butadiene) is the most abundant hydrocarbon compound emitted mainly from perennial plant species in terrestrial ecosystems (Fineschi et al., 2013). Only 30% of extant plant species today emit isoprene, which might be due to evolution of isoprene emission capability under various environmental conditions (Harley et al., 1996). Globally, isoprene accounts for 44% of the total biogenic VOC emission with an estimated emission rate of about 500 to 700 Tg C year^{-1} (Guenther et al., 1995; Guenther et al., 2006). It is synthesized in chloroplasts via the MEP pathway and emitted immediately after synthesis in a light- and temperature-dependent manner (Guenther et al., 1993). As a result of its high reactivity and very short life time in atmosphere, isoprene influences atmospheric chemistry through the formation of secondary organic aerosols (SOA) (Atkinson and Arey, 2003).

Isoprene has multiple functions to plants, particularly in stressful conditions as it strengthens thylakoid membranes and scavenges reactive oxygen and nitrogen species (Sharkey et al., 2008). Recent studies have shown that isoprene also provides protection against insect herbivores because of its repellent nature to herbivorous insects (Laothawornkitkul et al., 2008a; Loivamäki et al., 2008). Isoprene emission rates are affected by climate warming-related environmental factors such as high temperature, increased CO_2 concentration and drought conditions (Pegoraro et al., 2004; Niinemets, 2010a; Calfapietra et al., 2013).

Monoterpenes (MTs) are an important class of plant volatiles with an estimated annual emission rate of about 85 Tg C year^{-1} (Sindelarova et al., 2014). They are synthesized through the MEP pathway in chloroplasts from head-to-head combination of geranyl pyrophosphate (GPP) and IPP (Dudareva et al., 2013). After biosynthesis, MTs are stored in specialized storage organs in terpene storing plants and are emitted later following stress or developmental changes, whereas in non-storing species they are emitted immediately after synthesis (Li and Sharkey, 2013). The biosynthesis and emission of MTs are controlled by a wide range of environmental conditions (Trowbridge et al., 2014) which is discussed in the coming sections. MTs are emitted from different parts of plants and involved in direct and indirect defence against biotic and abiotic stresses. As they represent the majority of reactive VOCs emitted into the atmosphere, they play an important role in the formation of SOA. Plant VOCs most often related to environmental stresses and their molecular structures are shown in figure 2.

Sesquiterpenes (SQTs) are structurally diverse, semi-volatiles hydrocarbons synthesized through the MVA pathway in cytosol by condensation of farnesyl diphosphate (FDP) and IPP facilitated by FDP synthase (Kesselmeier and Staudt, 1999). They account for a small portion of the volatile carbon released into the atmosphere due to their semi-volatile nature and high reactivity in the atmosphere (Li and Sharkey, 2013). However, their highly reactive nature makes them relevant in the atmosphere as their photo-oxidation leads to the formation of aerosols which in turn generate more cloud condensation nuclei (Bonn and Moortgat, 2003; Kulmala et al., 2004). SQTs are emitted constitutively mainly from flowers; but they are also emitted from foliage during and after herbivore and pathogen attack (Loreto and Schnitzler, 2010). Their emission rate shows seasonal and diurnal variability (Hakola et al., 2006), which suggests dependence on temperature, light and other abiotic factors (Duhl et al., 2008) and also on changes in physiology of plants. SQTs play an important role in multitrophic interactions involving plants, herbivorous insects and parasitoids (Holopainen, 2004).

1.4.2. Green leaf volatiles and other compounds

Green leaf volatiles are hydrocarbon compounds synthesized through the lipoxygenase (LOX) pathway, and consist of saturated and unsaturated C_6 aldehydes, alcohols, and their esters produced by oxidative breakdown of membrane lipids (Paré and Tumlinson, 1999). GLVs have distinctive "cut grass scent" (Schaub et al., 2010) and are emitted in large quantities during or immediately after herbivore damage and/or mechanical wounding to plant tissues (Brilli et al., 2012). Some GLVs just leak out from cell walls of a rapidly expanding leaves and decomposing cell walls in senescing leaves with no specific purpose (Trowbridge and Stoy, 2013). GLVs can be emitted as a result of abiotic environmental stresses such as severe drought stress that can damage the cell wall and cell membrane (Capitani et al., 2009), and anoxic conditions caused by flooding (Copolovici and Niinemets, 2010). Acute ozone exposure induces the emission of several GLVs (Heiden et al., 1999), but ozone also degrades GLVs in the atmosphere (Pinto et al., 2007). GLVs serve as important signalling molecules to the surrounding conspecifics or natural enemies of herbivorous insects. In addition to isoprenoids and GLVs, aromatic products of the shikimate pathway such as methyl salicylates and methyl chavicol are also released from plants in response to aphid infestation (Blande et al., 2010) or ozone exposure (Heiden et al., 1999). The quantity of methyl salicylate and other VOCs tends to correlate with the severity of biotic and abiotic stresses (Beauchamp et al. 2005; Karl et al., 2008; Copolovici et al., 2011). In addition to GLVs, plant tissue-damage is associated with products of octadecanoid pathway (Kessler and Baldwin 2002). This pathway produces phytohormone jasmonic acid, which is responsible for induction of defence genes.

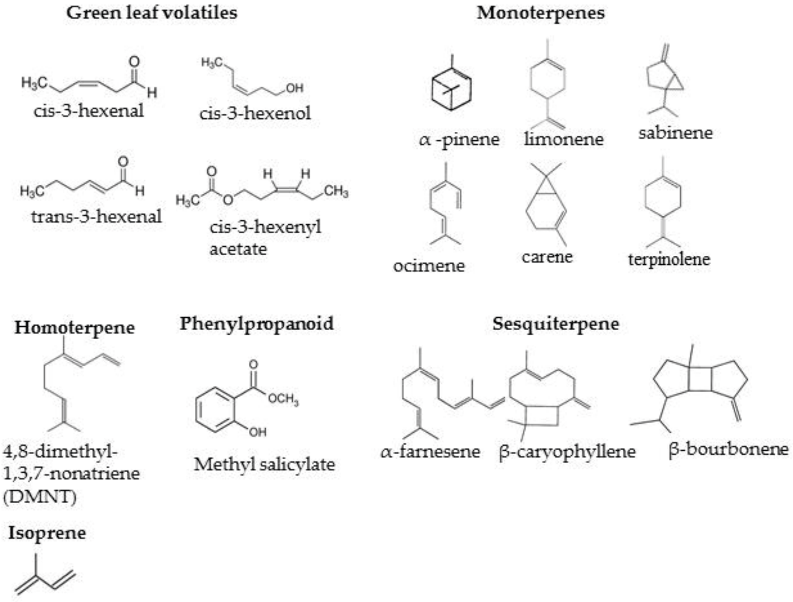

Figure 2. Molecular structures of the most common VOCs emitted from plants used in this study.

1.5 MAJOR ENVIRONMENTAL FACTORS THAT AFFECT VOC EMISSIONS

1.5.1. Abiotic factors

Abiotic stresses such as high temperature (Singsaas et al., 1997), drought (Capitani et al., 2009), air pollution (Pinto et al., 2007) and flooding (Copolovici and Niinemets, 2010) create suboptimal conditions for plants thus affecting the rate of primary metabolism which in turn influences the synthesis and emission of plant VOCs. Moreover, some of these factors have been shown to enhance the production of harmful molecules inside plant tissues that impact metabolic pathways producing VOCs (Vickers et al., 2009). Most abiotic stresses are predicted to further increase in frequency

and intensity as a result of anthropogenic contributions (IPCC, 2014), thus plants are likely to be exposed to more stressful environments in the future.
Increasing temperature can induce biosynthesis of plant VOCs through its control on plant physiology (Niinemets et al., 2004). Enzymes that regulate the rate of primary metabolism, especially respiration, which supplies intermediates for VOC biosynthesis, are affected by changes in temperature (Niinemets et al., 2004). These enzymes show temperature dependence up to 40-45°C (Sharkey, 2005). However, such high temperature can be harmful to sustain other processes necessary for the synthesis of substrates of VOCs (Singsaas and Sharkey, 2000). Increases in temperature also affect the physicochemical characteristics of individual compounds such as volatility and diffusion (Niinemets et al., 2004; Harley, 2013). Diffusion in particular leads to more partitioning of the VOCs to gaseous phase leading to higher VOC emission from plants (Possell and Loreto, 2013). Studies at controlled conditions have shown that high temperature induces the emission of isoprene, (E)-4,8-Dimethyl-1,3,7-nonatraine (DMNT), SQTs and GLVs from plants (Ibrahim et al., 2010). Some of these compounds may have protective role against reactive oxygen species (ROS) and other oxidizing agents that can cause major damage to photosynthetic apparatus (Peñuelas and Llusià, 2003). Isoprene emitted during high temperatures stabilizes thylakoid membranes from transient heat shocks (Sharkey and Singsaas, 1995) hence maintaining the dynamic properties of the membranes.

Light effects on VOCs are usually attributed to changes in metabolite pool size, and availability of ATPs and NADPH (Li and Sharkey, 2013). Increase in the atmospheric aerosols is likely to increase the fraction of diffuse light (Mercado et al., 2009) which enhances photosynthesis and supply of substrates for biosynthesis of VOCs (Kulmala et al., 2013). Thus, as incident radiation increases, the isoprenoid emission increases due to high supply of energy and substrates (Gray et al., 2005) but that trend depends on other factors such as temperature and availability of water (Fineschi et al., 2013).

UV-radiation is another important abiotic factor which changes significantly as a result of anthropogenic emissions to the atmosphere and influences both plant metabolism (Holopainen, 2011) and VOC emissions (Filella and Peñuelas, 1999). For example, UV-B radiation has the potential to decrease photosynthetic capacity of plants by down-regulating genes encoding proteins of photosynthetic apparatus (Hollosy, 2002). On the other hand, UV-B radiation can also induce VOC synthesis by encoding enzymes of the octadecanoid pathway (Izaguirre et al., 2003). Johnson et al (1999) found increased VOC emission response as a result of increased dose of UV-B radiation on sweet basil while higher concentration of some MTs and SQTs was found in peppermint (Dolzhenko et al., 2010). Similarly, Harley et al (1996) found increased emission of isoprene from *Quercus gambelii* and Gil et al (2013) reported higher MT emission from grapevine (*Vitis vinifera* L. cv. Malbeck) as a result of exposure to UV-radiation. Isoprene emission from subarctic fen was also found to increase following exposure to UV-B radiation at a dose of 20% stratospheric ozone depletion (Tiiva et al., 2007). However, some studies found reduction (Ambasht and Agrawal, 1997) or no change (Blande et al., 2009) in the emission of VOCs as a result of exposure to supplemental UV-B radiation. Nonetheless, there are not enough studies for the majority of plant species to clearly see the pattern of the responses of VOC emission to UV-B radiation. In addition, most studies on the effects of UV-radiation focus more on chemical traits other than VOCs, and those studies on VOCs have mainly focused on isoprene emission (Blande et al., 2009). Since plants are exposed to multiple environmental factors, then UV-radiation, warming and other abiotic factors may have interactive effects on VOC emissions.

1.5.2. Biotic factors

Plants face constant attack from herbivorous insects, mammalian herbivores and pathogens, which has the potential to influence primary and secondary metabolism. Herbivore damage by insects is of great interest as frequency and intensity of insect outbreaks are increasing in areas that are experiencing climate warming (Jepsen et al., 2008). Although there are temporal and spatial differences, plants lose approximately 7-11% of their tissues per year due to herbivory in various ecosystems (Coley and Barone, 1996). Some studies have suggested that herbivory is higher at low latitude ecosystems than at high latitude ecosystems (Coley and Aide, 1991; Schemske et al., 2009) although others argue against this pattern (e.g., Moles, 2013).

Herbivory profoundly affects VOC emission from a range of plant species as it has genetic and physiological control over VOC emission. Herbivore damage breaks the storage structures and diffusive barriers leading to large release of stored compounds (Monson, 2013). It also stimulates the metabolic pathways of VOCs, and thus induces de novo synthesis of some VOCs (Laothawornkitkul et al., 2008b; Fineschi et al., 2013). VOCs induced by herbivore damage are involved in bottom-up and top-down plant defence (Monson, 2013). In bottom-up defence, herbivore-induced VOCs reduce fitness of insects through direct toxicity or affect host preference through repellence (Kessler and Baldwin, 2001), whereas in top-down defence, these chemicals attract the natural enemies of insect herbivores. Some of these compounds play important roles in multitrophic communication between organisms as they serve as cues to locate host plants by specialist insects and preys by natural enemies of plant defoliating insect species (Holopainen, 2004). The induction of VOCs by herbivorous insects varies depending on plant species, age and developmental stage of plants, damage type and intensity, tissue type being attacked, insect species and feeding mode (Takabayashi et al., 1994; Cardoza and Tumlinson, 2006; Kessler and Halitschke, 2007).

In recent years, many insect species have reached outbreak threshold and caused extensive defoliation of many tree species in temperate regions. With the expected rise in temperature, herbivore damage of trees in boreal regions is expected to increase in the coming decades. This is primarily because insects are expanding their geographical range northwards due to more favourable thermal conditions in previously cold temperate regions and colonize new habitats (Jepsen et al., 2011; Ammunét et al., 2012). In addition, climate warming-induced abiotic stresses such as drought and high temperature episodes increase the susceptibility of the host plants to herbivore pressure (Adams and Zhang, 2009; Klapwijk et al., 2013). For instance, an outbreak of geometrid moth species defoliated large swath of birch forest in northern Finland (Ayres and Lombardero, 2000; Dale et al., 2001). This type of defoliation is likely to induce large emission of VOCs with potential effect on the atmospheric chemistry (Joutsensaari et al., 2015).

The independent effects of climatic factors can enhance, reduce or have no effect on plant growth, development and defence, but they can also have additive or opposing effects when they occur simultaneously. The combined effects of multiple environmental stresses on VOC emission are not adequately assessed although it has been suggested as an area of research that needs further attention (Holopainen and Gershenzon, 2010). Copolovici et al (2014) showed that the combination of herbivory and drought induces higher emission of (E)-β-ocimene and DMNT from *Alnus glutinosa* (L.) Gaertn. Similarly, spider mite infestation and acute ozone-exposure induced the emission of DMNT and cis-3-hexenyl acetate from lima bean (*Phaseolus lunatus* L.) (Vuorinen et al., 2004). In contrast, others found no significant effect of combined stress of herbivory and ozone exposure on the VOC emission from hybrid aspen (e.g. Blande et al., 2007). The likelihood of warming and UV-B radiation concurrently challenging deciduous trees at high latitudes is high, but their combined effect on VOC emission response has not yet been investigated.

In addition to aboveground effects, both biotic and abiotic factors can enhance the emission of VOCs from the rhizospheres of deciduous trees. Many studies have shown that plants release great amount of photosynthetically fixed carbon to the rhizosphere for various reasons (Wenke et al., 2010). Several compounds including MTs, GLVs and light carbon compounds are released into the soil and play defensive and communication roles in the rhizosphere (Lin et al., 2007; Wenke et al., 2010). The effects of aboveground stresses on the VOC emission responses from rhizospheres have received less attention so in this study we examined the effects of aboveground herbivory and abiotic stresses on VOC emission from the rhizospheres of silver birch and European aspen.

1.6 SILVER BIRCH AND EUROPEAN ASPEN ARE ECOLOGICALLY AND ECONOMICALLY IMPORTANT TREE SPECIES

Silver birch is an important deciduous tree species in the Northern Hemisphere with multiple ecological and economic roles. It is a pioneer species that serves as a raw material for pulp and paper industries and hosts several species to sustain biodiversity. Recent studies have revealed that both basal area and wood production of silver birch in boreal region are increasing as a result of increasing temperature and CO_2 concentration in the atmosphere (Briceño-Elizondo et al., 2006; Kellomäki et al., 2008). However, silver birch is susceptible to changes in both biotic and abiotic environmental stresses which are exacerbated by climate warming (Oksanen et al., 2007; Ibrahim et al., 2010). Herbivore pressure and warming are among the factors that are increasing in magnitude and frequency and threaten performance of silver birch and other deciduous trees in boreal regions. Furthermore, the change in the length of growing season can interfere with the function of the internal clock of this species.

Silver birch has large genotypic diversity and phenotypic plasticity which could play an important role in its resistance against biotic and abiotic stresses (Silfver et al., 2009). In the face of cyclic outbreaks of some geometrid moth species, the genetic diversity could contribute to enhance resistance or tolerance against herbivory (Neuvonen et al., 2005). The large genotypic variation means that different provenances adapted to their respective locality might vary in their VOC emission potential and thus respond differentially to environmental stresses. Silver birch emits a wide diversity of VOCs in its natural environment (Hakola et al., 1998) and in larger quantities following damage to tissues or due to abiotic stresses (Vuorinen et al., 2007; Ibrahim et al., 2010). In addition to geometrid moth species, polyphagous pine weevil (*Hylobius abietis* L.) could damage this species and may induce systemic emission of VOCs.

European aspen, which grows in mixed stands with spruce, pine and birches, is a widespread deciduous tree species in most parts of Eurasia (Worrel, 1995). Aspen is an ecologically important keystone species in boreal forests where it supports wide range of species including some critically endangered species (Kouki et al., 2004). It also plays a role in balancing the soil pH of boreal forest with its high calcium content in the foliage (Suominen et al., 2003). This species is also used for phytoremediation purpose as it can remove heavy metals such as cadmium and zinc from polluted habitats (Hassinen et al., 2009). It contributes economically mainly through its use in pulp and paper industry and making of plywood. Aspen is a prominent isoprene emitter; it also emits significant quantities of MTs such as α-pinene and carene (Hakola et al. 1998) and GLVs (Fall et al., 1999). Exposure to high temperature, herbivory and high ozone concentration showed greater emission of these compounds from aspen (*Populus* spp.) (Hartikainen et al., 2009; Blande et al., 2007).

1.7 OBJECTIVES OF THE RESEARCH

Silver birch is expected to suffer from more intense herbivory as a result of frequent insect outbreaks in the future (Ammunét et al., 2012; Kozlov et al., 2015). This tree species is known to emit wide range of terpenes in nature (Hakola et al., 1998) and also as a result of biotic (Vuorinen et al., 2007) and abiotic stresses (Ibrahim et al., 2010). However, there are only a few studies on herbivore-induced VOC emission from different provenances in field conditions. Moreover, no studies have used online monitoring to examine the timing and pattern of VOC emission from silver birch while larvae were feeding on the foliage. Climate change factors are likely to affect plant performance thus altering also VOC emissions. But it is not known how silver birch, a species with large genetic diversity, will respond to the changes in terms of VOC emission. Plants are also challenged by multiple environmental factors and their reactions are vital for their survival. How simultaneously appearing abiotic stresses, like warming and UV-radiation, impact the VOC emission from European aspen has not been investigated.

The main aim of this thesis was to assess the VOC emission responses of deciduous trees to biotic and abiotic environmental stresses. More specifically, the aim was to assess the effect of short- and long-term herbivore damage caused by larvae of two geometrid moth species on the emission rates and VOC blend from shoots and the rhizospheres of different genotypes silver birch. This will provide information about the quality and quantity of VOCs emitted from different provenances/genotypes of silver birch in the field and laboratory conditions to aforementioned stresses. The thesis also aims to assess the changes in VOC emission from shoots and rhizospheres of different provenances of silver birch in response to changes in abiotic and biotic following translocation of the provenances across a latitudinal gradient of seven degrees in Finland. Moreover, this thesis explores the VOC emission responses of European aspen to combined effects of warming and UV-radiation in the field condition. The thesis was based on three experiments summarized in Table 1. The main questions addressed in this thesis are:

1) Does insect herbivory alter VOC emission response of silver birch? (chapter 2)

2) What happens to the VOC emission responses when different provenances of silver birch are translocated across a latitudinal gradient? (chapter 3)

3) Does combined enhancement of temperature and UV-B radiation affect VOC emission of European aspen? (chapter 4)

1.8 SUMMARY OF THE EXPERIMENTS

This thesis is comprised of three experiments on VOC emission response of deciduous trees to environmental stress (Table 1). The first two were conducted on silver birch and the last one was performed on European aspen. In the first experiment (chapter 2), silver birch plants (two micropropagated clones and one seed origin) were infested with larvae of two geometrid moth species (*Agriopis aurantiaria* Clerck and *Erannis defoliaria* Hübner) at field condition in the research garden of the University of Eastern Finland, Kuopio. Side branches were enclosed in two separate mesh bags, each containing two larvae and the bags were tied to the base of the branches. Herbivory lasted for approximately 30 days during the summers of 2011 and 2012 and VOC measurements from shoot were carried out once in 2011 and three times in 2012. Besides foliage herbivory, a bark damage experiment was set up in the same field using two adult pine weevils (*H. abietis*) on plants not used for the moth herbivory experiment. The bark feeding lasted for 21 days and VOCs were sampled twice during the feeding period from the shoots. The VOC emissions from the rhizospheres were also sampled for both foliage and bark herbivory during 2011 and 2012. The VOCs from the rhizosphere were sampled by enclosing the whole root system inside the PET bags.

In addition to field measurements, VOC emission was monitored online for 48 hours while larvae were feeding on a Hausjärvi provenance trees at laboratory condition in 2012.

In the second experiment (chapter 3), six different provenances of silver birch were micropropagated and transferred to experimental sites established in Tuusula (southern site), Joensuu (central site) and Kolari (northern site) across a latitudinal gradient (north-south) of seven degrees in Finland. The VOC measurement study was part of a broader study that was designed to assess acclimation of silver birch to climate change across a latitudinal gradient in Finland (Heimonen et al., 2015). For VOC assessment, three provenances representing the southern (Loppi), central (Vehmersalmi) and northern (Kiitilä) population were selected. There were three to six genotypes for each provenance at each site but VOC assessment was limited to three genotypes from each provenance. In order to examine the effect of variation in abiotic factors and levels of herbivory on VOC emission, VOC samples were collected from shoots and rhizospheres of selected saplings at both central and northern sites in the summers of 2012 and 2013. Moreover, level of natural herbivore damage on the branches enclosed in PET bags was monitored during VOC measurements.

The last experiment (chapter 4), was carried out at an experimental site located in the Botanical Garden of Joensuu, Finland. The site was established to study the effect of multiple environmental change factors on evolution of sexually dimorphic species (Randriamanana et al., 2014, 2015) and the VOC assessment study was a part of it. Branches of aspen plants collected from different locations in southern and eastern Finland were micropropagated and the plantlets were transferred to the experimental site in 2012. The plantlets were planted in 36 plots in the field to which six treatments and treatment combinations (UV-A, UV-B, UVA+T, UVB+T, T, and control) were randomly assigned. In this experiment, the VOC emission measurements from shoot and rhizosphere were conducted twice in 2014. One male and one female sapling (total of 72 saplings) were considered from each plot for VOC sampling while clones were randomly selected in each plot.

A number of hypotheses were tested to assess the effect biotic and abiotic stresses on the VOC emission responses of silver birch and European aspen. The research topics and hypotheses tested are summarized in table 1.

Table 1. Summary of the research topics, experiments and hypotheses related to each topic

Research topic	Basic information/treatments	Hypotheses tested
Effect of insect herbivory on VOC emission (experiment 1)	Species: silver birch Treatment: foliar herbivory by geometrid moth larvae and bark herbivory by pine weevil Method: Online monitoring from shoot and headspace VOC collection from shoot and the rhizosphere Analysis: PTR-TOF-MS, GC MS	Foliage herbivory by geometrid moth species could activate systemic defence and increase VOC emission from shoots and the rhizospheres of silver birch Bark damage by pine weevil induces systemic emission of VOCs from the shoots and rhizosphere of silver birch Different genotypes have variable VOC emission responses to foliage or bark herbivory at field condition
Effect of provenance translocation across a latitudinal gradient in Finland (experiment 2)	Species: silver birch Factors: Changes in biotic and abiotic stresses across locations Method: Headspace VOC collection from shoot and the rhizosphere Analysis: GC MS	The quality and quantity of VOC emissions would differ between experimental sites and among silver birch provenances so that northward translocation of southern and central provenances reduce VOC emissions while southward translocation of northern provenances increases VOC emissions There is greater herbivore stress at lower latitudes than at higher latitudes resulting in a greater induction of VOCs at lower latitudes
Effects of Enhanced UV-radiation, elevated temperature on VOC emission from European aspen (experiment 1)	Species: European aspen Treatment: UV-B radiation (30.9%), UV-A, warming (ambient +2ºC) and their combination Method: Headspace VOC collection from shoot and the rhizosphere Analysis: GC MS	Warming and UV-B radiation influence VOC emission from shoots and rhizospheres of European aspen. The combined enhancement of UV and temperature have different effect than their separate effects on the VOC emission Female plants emit more VOCs than male plants in response to elevated temperature and UV-radiation

1.9 DESCRIPTION OF THE VOC MEASUREMENTS AND ANALYSIS

Most of the VOC measurements reported in this thesis were conducted using a dynamic head space collection method (Stewart-Jones and Poppy, 2006; Amo et al., 2013). VOC measurements in the field were performed using a portable VOC collection system designed for field sampling which consists of power batteries, air filtering system, air flow tubing, and the Tenax tubes (Figure 3). Before VOC sampling, pre-heated (120°C, 1 hr) polyethylene terephthalate (PET) bags were used to enclose branches from which VOCs were sampled. During VOC collection, air inside the bags was pulled at a rate of 200ml/min while filtered air was pushed into the bags (300 ml/min) to make sure that there was continuous replacement air inside the bag. The volume of replacement air was slightly higher compared to air pulled by the sampling line in order to prevent contamination and compensate possible leakage. The compounds that were pulled through the sampling line were adsorbed in an Automatic Thermal Desorption (ATD) steel tube filled with Tenax-TA adsorbents. Immediately after collection, the samples were kept in cool boxes for transportation and stored in a refrigerator until analysis.

During VOC collection, temperature and photosynthetically active radiation (PAR) were monitored by HOBO Micro Station (Onset Computer Corporation, Bourne, MA, USA). The emission rates of VOCs from shoots of silver birch (chapter 2 and 3) and European aspen (chapter 4) were standardized for +30°C according to temperature dependent algorithms of Guenther et al (1993) for MTs and Duhl et al (2008) for SQTs. However, the effects of light levels on the monoterpene and SQT emission rates were not considered mainly because there is no light dependent algorithm available for silver birch. In many field studies of *Betula* spp. at northern ecosystems, only temperature correction is used for monoterpene and SQT emissions (Schollert et al. 2015; Rinnan et al. 2011). This is partly based an observation that both MT and SQT emissions of mountain birch were slightly better explained by the solely temperature dependent algorithm (Guenther et al. 1993) than using the temperature and light based algorithm (Haapanala et al. 2009). In the aspen experiment (chapter 4), isoprene emission rates were standardized also for light to a photosynthetic photon flux density (PPFD) of 1000 μmol m^{-2} s^{-1} and temperature levels according to Guenther et al (1993).

VOC samples were also collected from the rhizosphere by using a plastic collar designed for this purpose. A week before VOC collection, the ground in close proximity of the plants was weeded and the soil was dug with hand forks to soften the surface before inserting the collars into the ground (about 2 cm). The VOC measurements from the rhizosphere were carried out in similar way to VOC collection from the shoot but the duration was longer (1 hr). The online VOC monitoring discussed in chapter II was performed by using high-resolution proton-transfer reaction time-of-flight mass spectrometer (PTR-TOF 8000, Ionicon Analytik, Innsbruck Austria). The online monitoring was conducted in laboratory conditions on the Hausjärvi provenance trees only.

The VOC samples were analysed by gas chromatography-mass spectrometry (GC MS) and the compounds were identified according to the mass spectra in the Wiley library, and quantified by pure standard compounds. In order to determine the accuracy of emission from plant parts, blank samples were collected from PET bags alone as well as the plastic collars and any emission found was subtracted from the total emission to determine the actual emission from the plants. In order to determine the VOC emission rates, photos of the leaves were taken by digital camera against millimetre paper as a background and leaf area of the enclosed leaves was calculated. Then the emission rates from the shoots were expressed in nanograms per square metre of leaf area per second (ng $m^{-2}s^{-1}$). The rhizosphere emission rates were expressed in nanograms per square metre of soil surface area inside the plastic collars.

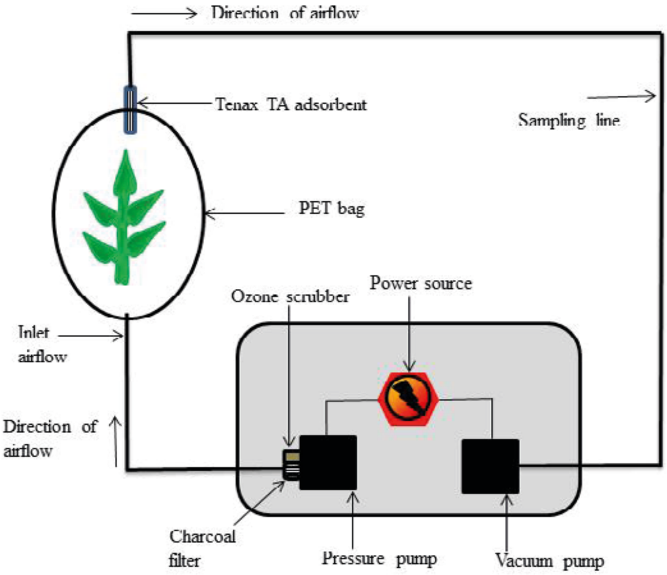

Figure 3. Schematic presentation of the collection system used to sample VOCs from headspace of living tree branch in the field

5 General Discussion

5.1 SHORT- AND LONG-TERM HERBIVORY INDUCED VOC EMISSIONS FROM SILVER BIRCH

5.1.1 Short-term foliar herbivory caused burst of green leaf volatiles (GLVs)

The online monitoring by PTR-TOF-MS showed a rapid induction of GLVs due to herbivore damage by the geometrid moth larvae. The large burst of GLVs peaked at a certain order; aldehydes were released first while alcohols and acetates were released after a delay of a few minutes. Alcohols are produced through oxidation of aldehydes whereas acetates are the result of acetyl transfer by acetyl transferase. Typical wound volatiles such as cis-3-hexenal, trans-3-hexenal and trans-2-hexenal were emitted immediately after damage and the same was reported in previous insect herbivory or mechanical damage studies on a range of plant species (Dudareva et al., 2006). There was a lag period in the emission of acetates. Fall et al (1999) reported similar delayed emission of alcohols and acetates from mechanically wounded aspen plants.

The emission of these compounds oscillated a great deal during the feeding hours and the peaks seemed to follow the feeding pattern of insects (chapter 2, Figure 1). The oscillation of the peaks suggests that each biting and tearing of the plant tissue might have caused the breakdown of the fatty acids of plant cell membranes and led to the large release while the resting phase of the larvae was shown by gaps in the peaks of the GLVs. This is in line with previous studies that observed induction of certain GLVs following insect herbivory (Paré and Tumlinson, 1997, 1999). Although methanol emissions did not show feeding-dependent response, there was a large burst especially in the morning which could be explained by tight stomatal control over its emission. Methanol usually builds up during overnight and is released in large quantities in the morning following the opening of the stomata (Niinemets and Reichstein, 2003). The emission rate of isoprenoids was not as substantial as GLVs because silver birch does not have storage structures to release terpenoids in large quantities after damage, but emission rates increased gradually throughout the monitoring period possibly due to activation of metabolic pathways. Measurements from intact shoots while larvae were feeding on side branch showed low emission rates, but there was no difference in VOC profile between intact and damaged shoot. The rapid emission immediately after the beginning of herbivory indicates that herbivore-induced GLVs are released soon after damage and rapidly disappear into atmosphere due to their volatile nature. Thus, timing of the measurements of herbivore-induced VOCs is important to get more accurate emission rates.

5.1.2 Long-term foliar herbivory induced VOC emission

There was a transient increase in the emission rates of total MTs due to long-term foliar herbivory by larvae of the geometrid moth (chapter 2, Figure 2). However, the increase in the total MTs emission was observed only in genotype 14 (gt14) while herbivore damage caused a slight reduction in the emission rates of total MTs from genotype 15 (gt15) and Hausjärvi provenance trees. The effect of herbivory and genotype differences on VOC emission was greater in 2011 but declined in 2012. The VOC emission response might be affected by differences in climatic conditions in each year, or probably the plants had acclimatized to herbivore damage in the second year. In general, VOC emissions from birch plants were higher in June than August. This is attributable to higher temperature and light condition in June which can influence the amount of inducible volatiles (Takabayashi and Dicke, 1996). Moreover, differences in developmental stages played a role as plants have more actively growing tissues in June, thus any damage to these tissues can induce more emissions compared to mature or senescing leaves. The variability in the emission rates between the genotypes suggests that VOC emission responses are genetically controlled.

Principal component analysis of field VOC data revealed that emissions of GLVs (cis-3-hexenol, cis-3-hexenyl acetate, cis-3-hexenyl butyrate and methyl salicylate) were more associated with Hausjärvi trees than with the micropropagated genotypes during the second measurement. Thus, it is logical to suggest that Hausjärvi provenance trees might be more palatable or more responsive to herbivory than micropropagated genotypes. However, the GLVs were not detected in large quantities during all measurements indicating that these compounds are usually emitted immediately after fresh damages as discussed in section 5.1.1, and the systemic emission from intact parts might also follow similar pattern. On the other hand, Hausjärvi provenance trees emitted more SQTs, especially β-caryophyllene as a result of herbivory while β-bourbonene was associated more to gt14 plants. In general, the emission of different VOCs lacked consistent pattern over the course of the two experimental years in the field condition. Although the VOC data were temperature corrected, other abiotic factors could have affected the substrate supply for the synthesis of VOCs. In addition to environmental variation, the differences in VOC blend are the result of genetic control over synthesis of VOCs particularly terpenoids (Nerg et al., 1994). Vuorinen et al (2007) and Mäntylä et al (2008) reported similar VOC emission responses of silver birch to foliage herbivory but the VOC blend was slightly different compared to the VOC blend in this study. Ocimenes, DMNT as well as linalool were emitted in higher quantities from silver birch as a result of herbivory by *E. autumnata* (Vuorinen et al., 2007) and the response to herbivory was much stronger than what has been observed in our study. That might be explained by the fact that Vuorinen et al., (2007) performed their study on younger seedlings in more actively growing stage than those used in this study.

5.1.3 No systemic effect of bark herbivory on VOC emission

Bark beetle outbreak is a concern in some areas of boreal region as bark damaging insects can also take advantage of climate warming (Williams and Liebhold, 2002), and damage to the bark is capable of inducing VOCs from surrounding tissues (Heijari et al. 2011). In the bark herbivory experiment, similar to foliar herbivory, there was a genotype x herbivory interaction effect as herbivore-infested gt14 plants had higher emission rates of total MTs and total VOCs than gt15 and Hausjärvi provenance trees. The genotype effect was clearer in 2011 as micropropagated genotypes seem to be more sensitive to bark damage as these plants emitted more inducible GLVs than Hausjärvi provenance trees due to bark herbivory (chapter 2). In the last measurement, conducted in late summer of 2012, Hausjärvi provenance trees emitted more GLVs than micropropagated saplings. GLVs were also released in large quantities from control plants indicating that other herbivores and plant pathogens might have affected emission rates from control plants. Despite variabilities in emission rates of different VOCs, this study is significant as it was able to quantify genotype-dependent effects of herbivore damage on VOC emission from silver birch in the field conditions.

5.2 VOC EMISSION RESPONSES OF SILVER BIRCH TO PROVENANCE TRANSLOCATION ACROSS A LATITUDINAL GRADIENT

Abiotic and biotic conditions determine the optimum strategy on the type and amount of resources allotted to both constitutive and inducible plant defences (Rasmann et al., 2014). As expected, the quality and quantity of VOC emission differed between the two experimental sites, Joensuu and Kolari, separated by over 500 km. All provenances emitted higher rates of different VOCs at central site in 2012 but the vice versa was true in 2013 (chapter 3, Figure 2). The higher emission of total MTs, total SQTs and total VOCs from plants at central site in 2012, and plants at northern site (which has more maritime climate than continental) in 2013 might be explained by higher cumulative temperature at the respective sites up until the VOC measurement days. The accumulated average daily temperature can affect phenology (e.g. bud burst and leaf out) and stages of VOC emission from different plant species (Hakola et al., 2001). There was a large variability in emission rates between different sampling dates; so environmental factors that are not included in the adjustment equation might have contributed to it. The variabilities also suggest that there are still uncertainties surrounding VOC collections at field condition. Therefore, interpretation of VOC data acquired from natural settings needs caution to achieve more precise flux estimation in the face of changing environmental conditions. Moreover, there is a substantial annual difference in cumulative temperature and precipitation due to the 500 km difference between sample sites, which means that longer than 2 years monitoring period is needed to reliably assess the effects of local climate.

Plant provenances are usually adapted to local conditions and thus can differ in their response to a wide range of environmental conditions. In line with the hypothesis, the results in this study showed that VOC emission rates and profile of the compounds were significantly altered according to provenance origin. Some existing literature points out that plants of southern origin are more adapted to higher herbivory than those from the north (Pennings and Silliman, 2005) and therefore develop better defence against it (Van Alstyne et al., 2001). In the present study, southern provenance (Loppi) trees had the lowest total VOC emission at both sites, which is opposite to the long held assumption that plants of lower latitude have higher defence traits than plants of higher latitudes (Coley and Aide, 1991; Van Alstyne et al., 2001). Kivimäenpää et al (2012) found variation in terpene emission from cut surfaces of Scots pine depending on provenance origin. In their study, the southernmost provenance (Tartu 58°N) emitted higher proportions of compounds such as carene, sabinene, γ-terpinene and terpinolene than Suonenjoki (62°N) and Kemijarvi (66 °N) provenances. However, Nerg et al (1994) reported that seed origin does not affect the concentration of secondary compounds in Scots pine seedlings. On the other hand, chemical defence traits, including resin concentration (Wainhouse et al. 1998) and lignin content (Wainhouse and Ashburner, 1996), have shown differences based on provenance origin. Contrary to expectations, transferring the southern and central provenances to the northern site or the northern provenance to the central site, had no effect on VOC emission. Only the VOC blend showed differences mainly because northern saplings emitted more GLVs at the central site while the southern and central provenance emitted more terpenoids at the northern site (chapter 3, Figure 4c). Although transferring plants along a latitudinal gradient may have negative effects on plant performance (Ovaska et al., 2005) the effect on secondary chemistry of silver birch was not clear.

Herbivore assessment on branches showed variation in herbivore-damage at both sites during the experimental seasons. The northern and central provenance saplings showed no difference in the level of herbivore damage at both sites with the northern having higher damage level compared to the other provenances (chapter 3, Figure 5). In 2013, all provenances had more herbivore damage at northern site during the first sampling but the trend was not the same in the second sampling as all provenances had nearly similar levels of herbivore damage with the exception of southern provenance having higher damage at central site. In general, herbivory was higher at northern site suggesting that plants are more prone or more palatable to herbivory at higher latitudes (Ho and Pennings, 2013). However, the level of herbivore damage was not necessarily reflected on the VOC emission except higher emission of herbivore-damage induced VOCs (cis-3-hexenol, cis-3-hexenyl acetate and cis-3-hexenyl butyrate) at northern site in 2013.

Herbivore damage assessment was performed only on enclosed part of the branch which might have over- or underestimated the damage intensity in trees resulting to lack of clear relationship between herbivore damage and VOC emissions. In addition, there was no knowledge when the damages first occurred and some of the damages were not fresh and thus might no longer induce VOCs. In the same experimental sites, herbivore damage assessment was carried out on actively growing part of the shoot in 2011 and 2012. There was an increase in the level of herbivore damage down the latitudinal gradient in 2011 but no clear trend was found in 2012 (Heimonen et al., 2015). Their herbivore assessment was on many actively growing shoots of the top canopy unlike our assessment which was limited to the branch used for VOC collection. This translocation experiment is relevant as it showed the variable responses of different provenances of silver birch along a latitudinal gradient. The VOC emission is one of traits that could contribute to the understanding of acclimation potentials of silver birch provenances/genotypes in the face of climate warming in boreal regions.

5.3 COMBINED ENHANCEMENT OF UV-RADIATION AND TEMPERATURE ALTERS VOC EMISSIONS FROM EUROPEAN ASPEN

As expected, warming enhanced the emission rates of isoprene and total VOCs from aspen saplings, but there was no significant effect on the emission rates of total MTs, SQTs and GLVs (chapter 4, Figure 1). This is consistent with results in various studies that have demonstrated temperature dependence of emissions of different VOCs in a range of plant species (Guenther et al., 1993; Singsaas et al., 1999; Niinemets et al., 2004). Aspens emit large quantities of isoprene (Hakola et al., 1998) and that was also seen here as isoprene accounted for approximately 90% of the total VOC emissions. Isoprene emitting species are better evolved to deal with oxidative stress and high temperature (Velikova and Loreto, 2005) through isoprene's capacity for heat removal, membrane stabilization or antioxidant functions that provide thermotolerance (Peñuelas et al., 2005). Therefore, higher levels of isoprene might enable aspens to adapt to higher temperature levels by protecting important organs through its antioxidative or membrane stabilizing role (Niinemets and Sun, 2014). High temperature affects the physico-chemical properties of isoprene and the diffusion resistance of the VOC emission channels inside leaves. Temperature can also affect VOC biosynthesis by regulating the reaction rate via its effect on enzymes that catalyse reactions for production of intermediates and substrates of isoprene (Niinemets and Sun, 2015). Hartikainen et al (2009) reported increase in MT and GLV emission but no significant enhancement in isoprene emission from genotypes of European aspen as a result of moderate air and soil warming (ambient + 0.8-1^{o}C), which they associated with the continuous nature of temperature exposure rather than repeated episode.

In addition to emission rates, VOC blends were also affected by warming as there were increased emissions of trans-β-caryophyllene and β-ocimene related to warming treatments. These compounds are often emitted as a result of environmental stress (Staudt et al., 2003; Grote et al., 2013). MTs are known to have role in protecting plants against stresses (Loreto and Schnitzler, 2010). However, in the present study warming was not reflected on the total MTs emission rates although some MTs (e.g., α-pinene, limonene and carene) were found to be more related to warming treatments.

In the present study, the combined effects of warming and UV-B radiation enhanced the emission rates of isoprene and total VOCs from European aspen. The two factors have somewhat different biochemical mechanism via which VOC emission is induced. Plants have evolved to protect themselves against reactive oxygen species production inside the tissue due to high temperature, while UV-B radiation causes injuries to proteins and membranes (Jansen et al., 1998) and thus may affect the emission of VOCs. How UV-B and warming caused additive effects on the emission of isoprene is not well understood, and thus the underlying mechanisms are open to be explored. The total MTs, total SQTs and total GLVs were similarly increased by the combined stresses, with the clearest effect found in July measurement (chapter 4, Figure 2).

European aspen is a dioecious (male and female reproductive structures on separate plants) species and its resource allocation to growth, development and defence can be gender specific. Variation in plant quality as a result of inter-sexual differences (Boecklen et al., 1990) might play role on plant defence traits including VOC emissions. In the present study, gender effects were seen in the emission rates of different compounds as females had higher emission of total MTs under UV-A and UV-B treatments with or without warming. Moreover, female saplings had more variation with regards to VOC blend composition compared to male saplings (chapter 4, Figure 3, 4). Females are slow growers and invest more resources on defensive compounds in stressful conditions (Cornelissen and Stiling, 2005). This suggests that in addition to defence against biotic stresses, sex-related differences play a role in resistance against abiotic stresses such as warming and UV-radiation. On the other hand, more resource allocation to reproductive parts in females may consume resources that might be used for synthesis of chemical compounds (Bañuelos et al., 2004) as the case reported in male Spanish plum (*Spondias purpurea* L.) plants (Maldonado-Lopez et al., 2014).

The results of this experiment are significant because they quantify for the first time the VOC emission responses of European aspen to the combined warming and UV-radiation at field condition. In light of predicted climate change factors in the coming decades, it is vital to understand how trees in boreal region, which are expected to face large effect of climate change, respond to multiple environmental factors. The results of this study indicate that emission rates and composition of VOCs are subject to change in the future as a result of expected changes in climate with a potential effect on air quality and atmospheric chemistry.

5.4 RHIZOSPHERE EMISSIONS

Only MTs were detected in the rhizosphere samples of both foliar and bark herbivory experiments on silver birch. Contrary to the expectation, the emission rates were unaffected by genotype, herbivory or interaction of these factors. Similar results were reported in a previous study performed in cotton as herbivore damage on above-ground parts did not cause significant effect on VOC emission the rhizosphere (Bezemer et al., 2004). The VOC emission from roots in forested sites accounts for about half of the carbon emission from soil (Gray et al., 2014), but in this study the quantities of VOCs are not in the same order of magnitude as the compounds were detected only in small quantities. In provenance translocation experiment, VOC emissions from the rhizospheres of silver birch were not affected by provenance effect, and in general only few VOCs were detected from samples. In addition to terpenoids, GLVs found in the rhizosphere emissions may be attributable to mechanical damage sustained by birch roots during weeding. The result indicates that non-terpene storing roots of deciduous trees are not so responsive to above-ground stress as terpene-storing conifer roots (Ghimire et al., 2013). Similarly, emissions from the rhizospheres of European aspen were not affected by above ground warming and UV-B radiation treatments. Only low-molecular-weight compounds such as toluene, which is associated to stressful conditions such as ozone level (Heiden et al., 1999), were detected but there was no clear difference in emission rates between control and treated plants.

5.5 LIMITATIONS OF THE STUDY

As most of the VOC measurements (except online monitoring) were carried out in the field conditions where many external factors such as wind and relative humidity that could not be controlled during VOC measurements, these factors might have affected plants and the sampling procedure. Therefore, it is likely that some of these factors have caused physical injury and influenced tree physiology contributing to the large variability of VOC emissions. In the field conditions, the surrounding plants are also probably affecting the VOC responses and natural background herbivory is difficult to fully exclude.

In provenance translocation study, the southern site (Tuusula) had to be excluded due to high mortality of the saplings as a result of fungal diseases. This means that VOC measurements were carried out from the central (Joensuu) and northern (Kolari) sites only, and this limited the possibility of making the planned comparison of larger latitudinal gradient measurements and full understanding of its effect on VOC emissions. This study also indicated that not only latitudinal gradient (i.e. temperature change and herbivore pressure along the latitude) affected the VOCs but there were probably also some masking factors like photoperiod and edaphic factors which affected responses.

Several previous studies have used similar VOC collection method, i.e., dynamic headspace VOC collection technique (Stewart-Jones and Poppy, 2006; Blande et al., 2007; Ibrahim et al., 2010). Some of the constraints in this method include the mechanical induction of VOCs while fixing the lines and changes in air flow rates after flushing the empty PET bags. The changing flow rates of incoming air can affect photosynthesis of experimental plants, which may in turn influence VOC synthesis and emission. However, this measurement procedure was the same for all the plants from which VOCs were sampled, thus it may not be considered as a serious flaw. This method is the best method thus far to conduct VOC measurements in remote sites and enable to collect several simultaneous samples by saving time between measurements. The VOC measurement from rhizosphere has its own limitations as the collection system or the sampling times used might not be sensitive enough to detect the VOC flux from the roots and rhizosphere system, so future methodological considerations are necessary to acquire more accurate VOC emission rates.

5.6 CONCLUSIONS AND IMPLICATIONS

This study revealed contrasting pattern in VOC emission to short- and long-term herbivore damage to silver birch by geometrid moth species (*A. aurantiaria* and *E. defoliaria*). Herbivory showed strong influence on VOC emission on short-term whereas a long-term response was transient and variable throughout the measurement period. VOC emissions to both foliar and bark herbivory were altered based on genotype differences, but aboveground herbivory had no significant influence on VOC emission from rhizosphere.

The VOC emission response of silver birch at common garden experimental sites varied based on provenance origin and the responses of VOC blends was genotype-specific which suggests that there was genetic control over VOC biosynthesis. However, provenance translocation across latitudinal gradient had no effect on VOC emissions or herbivore damage intensity. This indicates that provenances of silver birch may not be very sensitive to changes in environmental conditions at least in short-term. Moreover, the study does not support the classical theory that plants have higher defence at lower latitudes than at higher latitudes.

The study also showed that combined environmental factors (warming and UV-radiation) had additive effects on the emission rates of VOCs from European aspen. As the impacts of these factors increase as a result of climate change, it is likely that they might alter VOC emission rates from different plant species, especially for those in boreal regions.

In conclusion, the VOC emission response of deciduous trees is dependent on biotic and abiotic factors at laboratory and field conditions. Herbivory effect on VOC emission seemed to be greater immediately after damage and declines gradually. In order to get accurate VOC emission rates to insect herbivory, measurements need to be carried out immediately after herbivore attack. Performing emission rates right away after herbivory from individual plant species will enable to scale up estimation of annual stress-induced VOC emission at regional and global scale. As a model plant species, the response of aspen to warming and enhanced UV-B radiation is an important step in understanding how future changes in the environment might affect defence traits. Higher isoprene emission in response to combined climatic factors might be a resistance trait that provides protection against these stresses, but the mechanisms underlying the additive effect need further investigation. High emission of isoprene in response to these stresses from deciduous trees should not be overlooked in the face of predicted changes in temperature and other abiotic stresses.

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MENGISTU MENGESHA MAJA

Volatile organic compounds emitted from silver birch and European aspen in response to environmental stresses

Climate change-related stresses are increasing in extent and frequency especially in boreal region, which leads to a wide range of plant responses including the emission of volatile organic compounds (VOC). This thesis discusses the effects of biotic (insect herbivory) and abiotic (warming and UV-radiation) stresses on VOC emissions from deciduous tree species. This information contributes to the understanding of stress-induced VOC emissions from deciduous trees in the face of global change.

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