FINNISH METEOROLOGICAL INSTITUTE

CONTRIBUTIONS

NO. 72

DEVELOPMENT OF BIOGENIC VOC EMISSION INVENTORIES FOR THE BOREAL FOREST

Virpi Tarvainen

ACADEMIC DISSERTATION in physics

To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public criticism in Auditorium E204, Physicum (Gustaf Hällströmin katu 2a) on May 14, 2008, at 12 o'clock noon.

Finnish Meteorological Institute

Helsinki 2008

Author(s)
Virpi Tarvainen

Title
Development of biogenic VOC emission inventories for the boreal forest

Abstract

The volatile organic compounds (VOCs) emitted by vegetation, especially forests, can affect local and regional atmospheric photochemistry through their reactions with atmospheric oxidants. Their reaction products may also participate in the formation and growth of new particles which affect the radiation balance of the atmosphere, and thus climate, by scattering and absorbing shortwave and longwave radiation and by modifying the radiative properties, amount and lifetime of clouds.

Globally, anthropogenic VOC emissions are far surpassed by the biogenic ones, making biogenic emission inventories an integral element in the development of efficient air quality and climate strategies. The inventories are typically constructed based on landcover information, measured emissions of different plants or vegetation types, and empirical dependencies of the emissions on environmental variables such as temperature and light.

This thesis is focused on the VOC emissions from the boreal forest, the largest terrestrial biome with characteristic vegetation patterns and strong seasonality. The isoprene, monoterpene and sesquiterpene emissions of the most prevalent boreal tree species in Finland, Scots pine, have been measured and their seasonal variation and dependence on temperature and light have been studied. The measured emission data and other available observations of the emissions of the principal boreal trees have been used in a biogenic emission model developed for the boreal forests in Finland. The model utilizes satellite landcover information, Finnish forest classification and hourly meteorological data to calculate isoprene, monoterpene, sesquiterpene and other VOC emissions over the growing season.

The principal compounds emitted by Scots pine are Δ^3-carene and α-pinene in the south boreal zone and α- and β-pinene in the north boreal zone. The monoterpene emissions are dependent on temperature and have a clear seasonal cycle with high emissions in spring. For the first time, Scots pine was found to emit also sesquiterpenes and 2-methyl-3-buten-2-ol (MBO), with maximum emissions in the summer months.

According to the model calculations the main compounds emitted by the boreal forest throughout the growing season in Finland are α- and β-pinene and Δ^3-carene, with a strong contribution of sabinene by the deciduous trees in summer and autumn. The emissions follow the course of the temperature and are highest in the south boreal zone with a steady decline towards the north. The isoprene emissions from the boreal forest are fairly low - the main isoprene emitters are the low emitting Norway spruce and the high emitting willow and aspen, whose foliage, however, only represents a very small percentage of the boreal leaf biomass. This work also includes the first estimate of sesquiterpene emissions from the boreal forest. The sesquiterpene emissions initiate after midsummer and are of the same order of magnitude as the isoprene emissions. At the annual level, the total biogenic emissions from the forests in Finland are approximately twice the anthropogenic VOC emissions.

ILMATIETEEN LAITOS

Tekijä(t)
Virpi Tarvainen

Nimeke
Boreaalisen metsän hiilivetypäästöjen arviointimenetelmän kehittäminen

Tiivistelmä

Luonnosta haihtuvat orgaaniset yhdisteet (VOC-yhdisteet), joita pääsee ilmaan etenkin metsistä, voivat vaikuttaa paikalliseen ja alueelliseen ilmanlaatuun, koska ne reagoivat ilmakehän hapettavien yhdisteiden kanssa. Niiden reaktiotuotteet voivat myös osallistua uusien hiukkasten muodostumiseen ja kasvuun, millä voi olla vaikutusta ilmakehän säteilytaseeseen ja tätä kautta myös ilmastoon. Hiukkaset absorboivat ja sirottavat auringon säteilyä ja maapallon lämpösäteilyä minkä lisäksi ne vaikuttavat pilvien säteilyominaisuuksiin, määrään ja elinikään.

Koko maapallon mittakaavassa luonnosta tulevat VOC-päästöt ylittävät ihmistoiminnan aiheuttamat päästöt moninkertaisesti. Tämän vuoksi luonnon päästöjen arviointi on tärkeää kun halutaan kehittää tehokkaita ilmanlaatu- ja ilmastostrategioita. Päästöarviot perustuvat yleensä maankäyttötietoihin ja eri kasveilla tai kasvillisuustyypeillä tehtyihin päästömittauksiin. Lisäksi sovelletaan kokemusperäistä tietoa siitä miten päästöt muuttuvat esimerkiksi lämpötilan ja valoisuuden muuttuessa.

Tämä tutkimus käsittelee boreaalisen metsän hiilivetypäästöjä. Boreaalinen metsä eli pohjoinen havumetsä on suurin maanpäällinen ekosysteemi, ja se ulottuu lähes yhtenäisenä nauhana koko pohjoisen pallonpuoliskon ympäri. Boreaaliselle metsälle on tyypillistä puulajien suhteellisen pieni kirjo sekä olosuhteiden ja kasvun voimakkaat vuodenaikaisvaihtelut. Työssä on tutkittu Suomen yleisimmän boreaalisen puun eli männyn isopreeni-, monoterpeeni- ja seskviterpeenipäästöjen vuodenaikaisvaihtelua sekä päästöjen riippuvuutta lämpötilasta ja valosta. Saatuja tuloksia on käytetty yhdessä muiden boreaalisilla puilla tehtyjen päästömittaustulosten kanssa Suomen metsiä varten kehitetyssä päästömallissa. Malli perustuu lisäksi maankäyttötietoihin, Suomen metsille kehitettyyn luokitukseen ja meteorologisiin tietoihin, joiden avulla se laskee metsien hiilivetypäästöt kasvukauden aikana.

Eteläboreaalisella vyöhykkeellä männyn päästöjä hallitsevat Δ^3-kareeni ja α-pineeni kun taas pohjoisessa tärkeimmät päästöissä olevat yhdisteet ovat α- ja β-pineeni. Monoterpeenipäästöt ovat riippuvaisia lämpötilasta ja niillä on selvä vuodenaikainen sykli, jossa suurimmat päästöt tapahtuvat keväällä. Tässä esitetyissä mittauksissa havaittiin ensimmäisen kerran, että männyn päästöissä on myös seskviterpeenejä ja 2-metyyli-3-buten-2-olia (MBO), joiden runsaimmat päästöt ajoittuvat kesäkuukausiin.

Mallilaskelmien perusteella Suomen boreaalisen metsän päästöt koostuvat koko kasvukauden ajan suurelta osin α- ja β-pineenistä sekä Δ^3-kareenista. Kesällä ja syksyllä päästöissä on myös paljon sabineenia, jota tulee etenkin lehtipuista. Päästöt seuraavat lämpötilan keskimääräistä vaihtelua, ovat suurimmillaan maan eteläosissa ja laskevat tasaisesti pohjoiseen siirryttäessä. Metsän isopreenipäästö on suhteellisen pieni – Suomessa tärkein isopreeniä päästävä puu on vähäpäästöinen kuusi, koska runsaspäästöisten pajun ja haavan osuus metsän lehtimassasta on hyvin pieni. Tässä työssä on myös laskettu ensimmäinen arvio boreaalisen metsän seskviterpeenipäästöistä. Seskviterpeenipäästöt alkavat Juhannuksen jälkeen ja ovat kasvukauden aikana samaa suuruusluokkaa kuin isopreenipäästöt. Vuositasolla Suomen metsien VOC-päästöt ovat noin kaksinkertaiset ihmistoiminnasta aiheutuviin päästöihin verrattuna.

CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This thesis consists of an introductory review, followed by five research articles, hereafter referred to by their Roman numerals (I-V). The papers are reproduced with the kind permission of the journals concerned.

I. Tarvainen V., Hakola H., Hellén H., Bäck J., Hari P., and Kulmala M., 2005. Temperature and light dependence of the VOC emissions of Scots pine. Atmospheric Chemistry and Physics 5, 989-998.

II. Hakola H., Tarvainen V., Bäck J., Ranta H., Bonn B., Rinne J., and Kulmala M., 2006. Seasonal variation of mono- and sesquiterpene emission rates of Scots pine. Biogeosciences 3, 93-101.

III. Lindfors V. and Laurila T., 2000. Biogenic volatile organic compound (VOC) emissions from forests in Finland. Boreal Environment Research 5, 95-113.

IV. Lindfors V., Laurila T., Hakola H., Steinbrecher R., and Rinne J., 2000. Modeling speciated terpenoid emissions from the European boreal forest. Atmospheric Environment 34, 4983-4996.

V. Tarvainen, V., Hakola, H., Rinne, J., Hellén, H., and Haapanala, S., 2007. Towards a comprehensive emission inventory of terpenoids from boreal ecosystems. Tellus 59B, 526-534.

AUTHOR'S CONTRIBUTIONS

Papers I and II: The author was responsible for the data analyses and model calculations and bore the main (Paper I) and joint (Paper II) responsibility for writing the papers, while H. Hakola was responsible for the experimental setup at the sampling sites and the laboratory analyses.

Papers III-V: The author developed the methodology for the construction of biogenic emission inventories for boreal ecosystems, carried out the model calculations, and bore the main responsibility for writing the papers.

REVIEW OF THE PAPERS

Paper I reports volatile organic compound (VOC) emission measurements of Scots pine carried out during the growing season in 2003 in southern Finland and in spring and early summer in 2002 in northern Finland. A clear seasonal cycle was observed with high emission rates in early spring, and the emissions were found to be temperature dependent and well described by a simple exponential emission algorithm. For the first time the boreal Scots pine was identified as both sesquiterpene and 2-methyl-3-buten-2-ol (MBO) emitter.

Paper II reports the VOC emission measurements of Scots pine in southern Finland for a second growing season (2004) with a higher temporal resolution to cover the gaps in the previous data set. The effect of new needle growth on the emissions was studied by sampling two identical branches, one of which was debudded while the other was allowed to grow new needles. The role of Scots pine as a copious sesquiterpene emitter in the summer months was confirmed as well as the stronger temperature dependence of the sesquiterpene emissions when compared to the monoterpene emissions.

Paper III presents the first inventory of the biogenic VOC emissions from the North European boreal forest in Finland. A forest classification was developed based on LANDSAT land use data and Finnish forest inventory data. The Biogenic Emission Inventory System of the Finnish Meteorological Institute (FMI-BEIS emission model) was built based of the Biogenic Emission Inventory System of the U.S. Environmental Protection Agency (EPA). The model was adapted to the North European conditions and complemented with emission potentials measured in actual boreal forests. Isoprene, monoterpene and other VOC (OVOC) emission estimates were calculated for the growing seasons of the years 1995-1997 for the different boreal regions in Finland. Norway spruce was found to be the main isoprene emitter in the North European boreal forest due to its high biomass.

Paper IV presents a seasonal species speciated terpenoid emission inventory for the North European boreal forest for the year 1997. The FMI-BEIS model was upgraded by assigning early and late summer emission potentials and terpenoid emission spectra for the boreal trees. The seasonal development of the deciduous leaf biomass was included through a simple temperature sum parameterization, and the calculation period was extended to cover also the month of October. The main emitted compounds in the North European boreal forest were found to be α- and β-pinene, carene and linalool.

Paper V presents the first estimate of sesquiterpene emissions from the North European boreal forest, together with improved isoprene and monoterpene estimates. The seasonal emission potentials in FMI-BEIS were revised to reflect the latest experimental data and the parameterization of the sesquiterpene emissions was built in the model. The VOC emission inventory was further complemented by the inclusion of wetland isoprene emissions. The emissions were calculated for the different boreal zones in Finland for the years 1997, 1999, 2000, and 2003. The main emitted compounds throughout the country were α-pinene and Δ^3-carene. Due to the revised emission potentials the role of Norway spruce as the main isoprene and monoterpene emitter in the North European boreal forest was subdued. The sesquiterpene emissions were of the same order of magnitude as the isoprene emissions, with maximum emission rates in the summer months.

1. INTRODUCTION

The exchange of gases between the biosphere and atmosphere is a fundamental element of the Earth System, and to a great extent responsible for the present composition and chemical properties of the atmosphere (e.g. *Warneck*, 2000). Plant life is an integral contribution to this exchange as plants are involved in photosynthesis, i.e. the uptake and processing of carbon dioxide and emission of water vapor and oxygen by living organisms, which also makes our planet fit for animal life. During the last decades, it has become evident that plants are also capable of emitting trace amounts of numerous other gases with important atmospheric effects – their role accentuated now that the human imprint is starting to show in the Earth System as altered atmospheric chemical composition and climate forcing (*IPCC*, 2007).

A good understanding of both anthropogenic and biogenic emission sources is essential for the development of efficient emission control policies and climate strategies. A central instrument in their formulation are emission inventories, constructed based on information about anthropogenic and biogenic activities and emission source strengths, combined with mathematical modeling (e.g. *Brasseur et al.*, 2004). The emission inventories are then used as input to regional or global models describing the atmospheric transport and chemical transformation of the emitted trace gases (e.g. *Williams and Koppmann*, 2007). The inclusion of the biogenic sectors in the emission inventories is especially important for gases such as the nonmethane volatile organic compounds (VOCs) which react readily with atmospheric oxidants and whose anthropogenic emissions are clearly surpassed by the natural ones (e.g. *Atkinson and Arey*, 2003; *Guenther et al.*, 1995; *Kanakidou et al.*, 2005).

This thesis is focused on the volatile organic compound emissions from the boreal forest, especially those of terpenoids, i.e. isoprene and mono- and sesquiterpenes. These compounds have been identified as participants in tropospheric ozone chemistry and secondary organic aerosol (SOA) formation, both of which are major issues in the abatement of local and regional air pollution and the considerations of air quality and

climate change interactions (e.g. *Chameides et al.*, 1992; *Tunved et al.*, 2006). The boreal forest represents the largest terrestrial biome, forming an almost continuous belt across the Northern Hemisphere. It has characteristic vegetation patterns and strong seasonality, and it is one of the major sources of biogenic VOCs to the atmosphere at the global scale.

The key questions which this thesis seeks to answer are:

- What are the principal compounds emitted by the Scots pine, the most prevalent boreal tree species in Finland, and how do the emissions vary seasonally and spatially?
- How well can the emissions of Scots pine be described using emission algorithms based on observed emissions of more southern plant species growing in warmer climates?
- What are the emissions of the North European boreal forest in different parts of the boreal zone in Finland and are the strong seasonal features of boreal climatology reflected in the emissions?
- What are the sesquiterpene emissions of the boreal forest in Finland?
- What are the specific features in the emissions from the boreal forest in Finland when compared with emissions from other ecosystems?

2. BIOGENIC VOC EMISSIONS

In 1960 Went proposed that significant amounts of organic compounds are released to the atmosphere by plants, and that these compounds then oxidize in the air leading to the formation of the blue hazes commonly observed in summer over vegetated land masses and mountain areas (*Went*, 1960b). The first estimate of this emission source at the global level was 175 Tg a^{-1} - almost and order of magnitude higher than the contemporary anthropogenic emissions of 20 Tg a^{-1} (*Went*, 1960a). However, the global biogenic emission estimate was soon revised to be 438 Tg a^{-1} (*Rasmussen and Went*, 1965), surpassing the anthropogenic emissions even more clearly.

Table 1. Estimated annual global VOC and methane emissions from different sources according to Guenther (1999).

Source	Annual emission (TgC a^{-1})			
	Isoprene	Monoterpenes	Other VOCs	Methane
Canopy foliage	460	115	500	<1
Terrestrial ground cover and soils	40	13	50	175
Flowers	0	2	2	0
Ocean and freshwater	1	<0.001	10	15
Animals, humans and insects	0.003	<0.001	0.003	100
Anthropogenic (incl. biomass burning)	0.01	1	93	220
Total	**~500**	**~130**	**~650**	**~510**

After almost half a century of research, the global biogenic VOC emissions are now estimated to be 1150-1180 Tg a^{-1} (*Guenther et al.*, 1995; *Guenther*, 1999) or, more recently, within the range of 312-1062 Tg a^{-1} (*Wiedinmyer et al*, 2004). Again, this is severalfold the estimated global anthropogenic VOC emissions of 110-149 Tg a^{-1} (*Müller et al.*, 1992; *Picott et al.*, 1992). Most of the biogenic emissions originate from canopy foliage, with lesser contributions by other terrestrial vegetation, water bodies and soils, as summarized in Table 1 (*Guenther*, 1999).

The predominant VOCs emitted by vegetation belong to terpenoids, a family of over 22 000 identified compounds. Terpenoids play diverse physiological, metabolic and structural roles in plants, and are also used for communication and defense (e.g. *McGarvey and Croteau*, 1995). The basic building unit of terpenoids is isoprene (2-methyl-1,3-butadiene) which has the chemical formula C_5H_8. Isoprene is presently considered the single most important biogenic hydrocarbon because of its copious emissions and high chemical reactivity. Other important terpenoid classes are the monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$). The structures of some typical terpenoids emitted by vegetation are shown in Figure 1.
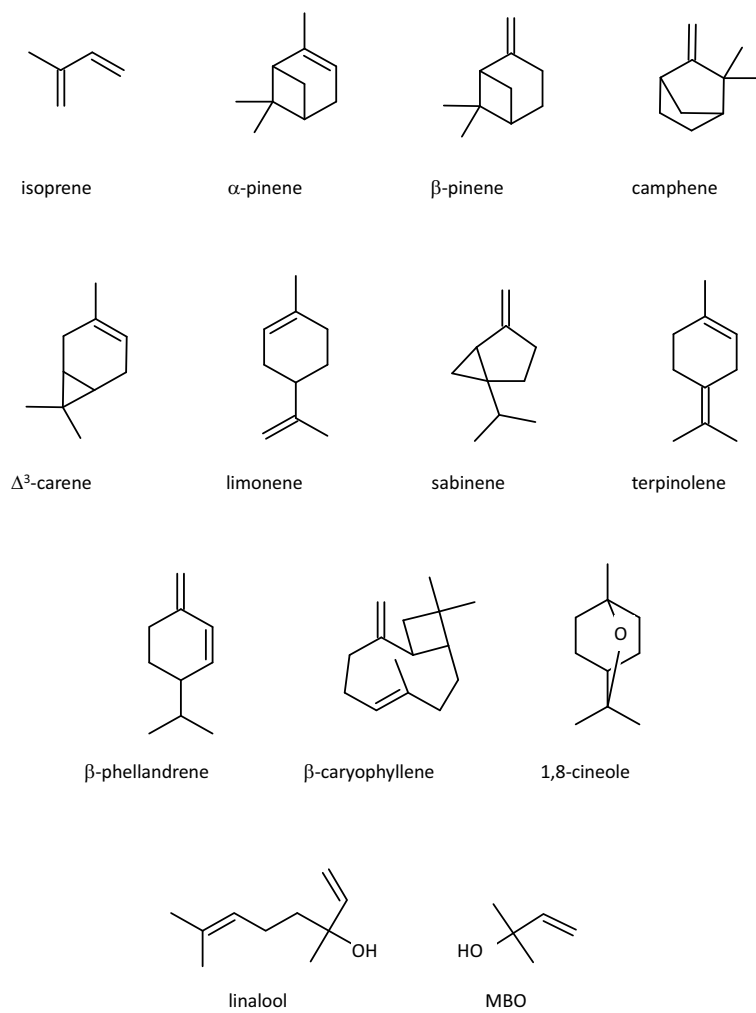
Figure 1. The structures of terpenoid compounds commonly emitted by vegetation.

Table 2. Chemical species that dominate the annual global VOC emission from vegetation according to Wiedinmyer et al. (2004).

Annual emission (TgC a^{-1})	Compound
250-750	Isoprene
50-250	Methanol, α-pinene
10-50	Acetaldehyde, acetone, β-pinene, Δ-carene, ethanol, ethene, hexenal, hexenol, hexenyl-acetate
2-10	Propene, formaldehyde, hexanal, butanone, sabinene, limonene, methyl-butenol, butene, β-phellandrene, p-cymene, myrcene
0.4-2.0	Formic acid, acetic acid, ethane, toluene, camphene, terpinolene, a-terpinolene, α-thujene, cineole, ocimene, γ-terpinene, bornyl acetate, β-caryophyllene, camphor, piperitone, linalool, tricyclene

In addition to terpenoids, plant emissions also comprise alkanes, other alkenes, carbonyls, alcohols, esters, ethers, and acids. Despite the overwhelming multitude of individual organic compounds found in plants only a relatively small number are considered relevant to atmospheric chemistry, either due to their large emissions or/and high reactivity. These compounds are listed in Table 2 ranked according to their average annual emission (*Wiedinmyer et al.*, 2004). The processes leading to the synthesis and subsequent emission of biogenic VOCs in the various living organisms are complex - and quite beyond the scope of this thesis - with even the purpose of the emissions often widely under debate (e.g. *Steiner and Goldstein,* 2007).

Once emitted, the biogenic VOCs enter intricate atmospheric reaction chains whose details, likewise, remain outside of the scope of this work. The reactions involve the principal atmospheric oxidants, the hydroxyl and nitrate radicals (OH, NO$_3$) and ozone (O$_3$), and occur in scales ranging from minutes to several days (*Atkinson and Arey*, 2003). It is now firmly established that the reactions of biogenic VOCs may significantly contribute to local and regional photochemistry and secondary organic aerosol (SOA) formation (e.g. *Chameides et al.*, 1992; *Carter*, 1996; *Hoffmann et al.*, 1997; *Calogirou et al.*, 1999; *Griffin et al.*, 1999a,b; *Bonn and Moortgat*, 2003; *Jaoui et al.*, 2003; *Claeys et al.*, 2004; *Chung and Seinfeld*, 2002; *Kanakidou et al.*, 2005). The climatic impact of biogenic VOCs comes through the effect of SOA on the radiation balance of the

atmosphere and the consumption of the atmospheric oxidants in the reactions of the VOCs which may have implications on the lifetime of atmospheric methane (e.g. *Tunved et al.*, 2006; *Kaplan et al.*, 2006). The radiation balance is influenced by SOA both directly and indirectly. The direct effect is caused by the scattering and absorption of shortwave and longwave radiation by the aerosol particles, while the indirect effect is caused by the modification of the radiative properties, amount and lifetime of clouds (e.g. *Kanakidou et al.*, 2005; *IPCC*, 2007).

2.1. Isoprene

According to a central biogenic volatile organic compound emission database maintained by the Biosphere-Atmosphere Interactions Research Group in the National Center for Atmospheric Research in Boulder, Colorado (http://bai.acd.ucar.edu/Data/BVOC/ (accessed March 27, 2008), hereafter referred to as the BAI database), cited and widely discussed by *Wiedinmyer et al.* (2004), close to a thousand plant species are presently classified as isoprene emitters. However, measured data is only available for about 20 % of the listed emitters and the classification is done under the broad assumption that species within the same genus exhibit similar isoprene emission characteristics (*Wiedinmyer et al.*, 2004). The most notable isoprene emitters with measured data in the BAI database are woody species, especially deciduous trees such as oak, eucalyptus, poplar, aspen and willow. The observed isoprene emissions from conifers appear to be restricted to various spruce species. Besides trees, isoprene is also emitted by mosses and ferns.

The reported normalized isoprene emission rates i.e. emission potentials in standard conditions of temperature (30 ºC) and light (photosynthetically active photon flux density, PPFD, 1000 μmol m^{-2} s^{-1}) are usually expressed as the mass of emissions per mass of leaf biomass (dry weight) per time. Depending on the plant species and their growing environment the emission potentials can vary from not detectable to a few hundred μg g^{-1} h^{-1} (*Kesselmeier and Staudt*, 1999). *Geron et al.* (2001) have estimated the emission potential of isoprene emitting broadleaved trees in the U.S. to vary between 0.1-

100 μg g^{-1} h^{-1}. North American spruces (genus *Picea*) have emission potentials of about 20 μg g^{-1} h^{-1} (*Wiedinmyer et al.*, 2004) while *Hakola et al.* (2003) have reported the maximum isoprene emission potential of the Norway spruce (*Picea abies*) in the North European boreal forest to be 1.3 μg g^{-1} h^{-1}.

The prerequisite of isoprene synthesis and emission from plants is light, and the emission is also dependent on temperature (e.g. *Sharkey and Yeh*, 2001; *Sanadze*, 2004). Isoprene is not stored in the plant, and while the emission occurs through the stomatal pores it is not controlled by their aperture (*Fall and Monson*, 1992). In the atmosphere isoprene is oxidized via complex pathways, producing formaldehyde, methylvinylketone (MVK), methacrolein (MACR), organic nitrates and various other compounds which then react further (*Atkinson and Arey*, 2003). In the presence of nitrogen oxides, isoprene can be an important contribution to ozone and photochemical smog formation (*Chameides et al.*, 1992; *Pierce et al.*, 1998).

Why plants emit isoprene has been - and still is - under wide speculation. *Steiner and Goldstein* (2007) have summarized the suggested roles which include providing thermotolerance for the plant, acting as an antioxidant, and facilitating the release of excess energy and/or carbon. However, not all plants emit isoprene, and the reason for this, likewise, remains a mystery. Recently, *Loreto and Fares* (2007) have shown that isoprene helps protect the plant against damage caused by ozone. The role of isoprene as an ozone forming compound has then led *Lerdau* (2007) to speculate with a feedback loop in which isoprene released by plants as a response to elevated ozone concentration is consumed in reactions producing even more ozone. For plants without the capability of synthesizing isoprene and thus protecting themselves against ozone damage, the outcome of such a feedback loop could be devastating and result in the alteration of regional species diversity and also the atmosphere (*Lerdau*, 2007).

2.2. Monoterpenes

The BAI database currently lists some 300-400 plant species which emit monoterpenes – of these measured data is presented for approximately 80 %. Prominent among the emitters are all coniferous species, but significant emissions have also been reported from several broadleaved trees, such as eucalyptus, oak, birch, aspen, and willow (*Hakola et al.*, 1998; *Kesselmeier and Staudt*, 1999).

All monoterpene-producing plants synthesize an array of monoterpenes instead of just one compound (*Fall*, 1999). Unlike isoprene, the monoterpenes are generally stored in specialized structures in the plants, such as resin ducts (pines) or resin blisters (firs), and catabolized along specific pathways, their emission dependent on the prevailing temperature and the volatility of the individual compounds (*Lerdau*, 1991; *Tingey et al.*, 1991; *Fall*, 1999). Recently, however, it has been found that monoterpene emission can also occur directly after synthesis without storage, in a similar light and temperature dependent manner as isoprene emission, and that in some plant species the monoterpene emission is a result of both of these pathways (e.g. *Staudt and Seufert*, 1995; *Kuhn et al.*, 2002; *Rinne et al.*, 2002; see also summary by *Wiedinmyer et al.*, 2004).

The maximum normalized monoterpene emission rates (emission potentials) from plants are generally lower than the reported isoprene emission potentials, varying from not detectable to 50 or 60 μg g^{-1} h^{-1} (*Kesselmeier and Staudt*, 1999). Among the tree species, emissions of stored monoterpenes are thought to be highest in conifers (*Pinus* and *Abies*), which have emission potentials of 1-5 μg g^{-1} h^{-1} (at standard temperature 30 ºC) (*Wiedinmyer et al.*, 2004).

In the atmosphere, monoterpenes undergo oxidation, yielding various volatile or semivolatile reactive intermediates, as well as formaldehyde, acetone, formic acid, and organic nitrates (*Atkinson and Arey*, 2003). Ever since the insightful paper by *Went* (1960b) plant emissions have received attention as a possible source of secondary organic

particulate matter (SOA), and monoterpenes are now considered to be the major precursor for SOA from biogenic VOCs (*Kanakidou et al.*, 2005).

Monoterpenes are toxic to insects and fungal pathogens, which suggests a defensive role for their emission (*Tingey et al.*, 1991). In his review, *Fall* (1999) lists the ecological roles for monoterpene emission as direct defense against herbivores and pathogens, attraction of pollinators or enemies of herbivores, and allelopathic (plant harming another plant with specific biomolecules) effects on competing plants. The light and temperature dependent (non-stored) monoterpene emissions are thought to perform a similar biological function as isoprene (e.g. *Steiner and Goldstein*, 2007).

2.3. Sesquiterpenes

Sesquiterpenes have long been known to be both contained in plants and emitted by them (*Tingey et al.*, 1991 and references therein). However, as recently as 1999, a leading review of biogenic VOC emissions considered sesquiterpenes to be only of minor importance to atmospheric chemistry (*Kesselmeier and Staudt*, 1999). This early misconception was partly due to the fact that these compounds are highly reactive in the atmosphere, with lifetimes generally of the order of minutes (*Atkinson and Arey*, 2003), rendering them not detectable in ambient air samples (e.g. *Hakola et al*. 2000, 2003). The quantification of sesquiterpenes in plant emissions also presents several analytical challenges due to their low volatility and high reactivity (*Ciccioli et al.*, 1999; *Helmig et al.*, 2004), and it is only recently that more information about their emission characteristics is becoming available (e.g. *Hansen and Seufert*, 2003; **Papers I** and **II**; *Helmig et al.*, 2006; *Holzke et al.*, 2006).

Like monoterpenes, sesquiterpenes are also emitted from storage pools (e.g. *Wiedinmyer at al.*, 2004). However, the details of their synthesis or the factors controlling their emissions are not explicitly known at present (*Wiedinmyer at al.*, 2004; *Kanakidou et al.*, 2005; *Steiner and Goldstein*, 2007). In plant emissions sesquiterpenes perform similar functions to monoterpenes (e.g. *McGarvey and Croteau*, 1995).

Despite the unpretentious outset, sesquiterpenes emitted by plants quickly gained momentum as participants in the atmospheric chemistry in forest environments and are now considered important sinks for oxidants and precursors to aerosols in rural regions (*Wiedinmyer et al.*, 2004, *Steiner and Goldstein*, 2007). Especially the potential for SOA formation from sesquiterpenes is high (*Hoffman* et al., 1997; *Griffin et al.*, 1999a; *Jaoui et al.*, 2003) which implicates them as a potentially important contributor also to climate change (e.g. *Kanakidou et al.*, 2005).

2.4. Other compounds

Besides terpenoids, plants also emit a variety of other reactive VOCs (Table 2). They are often referred to by the term other VOCs, or OVOCs. Among the most important OVOC compound groups are carbonyls, such as acetaldehyde, acetone and formaldehyde. The contribution of carbonyls to the total VOCs emitted by forest ecosystems has been estimated as 24% (*Wiedinmyer et al.*, 2004). *Janson et al.* (1999) and *Janson and De Serves* (2001) have reported significant carbonyl emissions from two boreal tree species, Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*), and *Rinne et al.* (2007) have observed high methanol, acetaldehyde and acetone fluxes above a Scots pine stand in Central Finland.

According to *Steiner and Goldstein* (2007), methanol is the OVOC with the highest concentration in rural areas. Apparently all plants emit methanol, especially when their leaves are expanding (e.g. *MacDonald and Fall*, 1993; *Fuentes et al.*, 2000; *Fall*, 2003). Another important alcohol emitted by plants is 2-methyl-3-buten-2-ol (MBO), whose emissions have been estimated to be a an important contribution to the reactive carbon in the atmosphere (*Harley et al.*, 1998) and e.g. the main source of atmospheric acetone in a pine forest region in the USA (*Goldstein and Schade*, 2000). MBO emissions have also been reported from Scots pine in the boreal zone (**Paper I**).

Compared to terpenoids, carbonyls and methanol are less reactive towards the principal atmospheric oxidants (*Atkinson and Arey*, 2003) and thus they may exit the boundary layer and be transported over large distances before entering the atmospheric chemical cycles. In addition, *Nozière and Esteve* (2005) have shown that the reactions of some biogenic carbonyls may affect the optical properties of atmospheric aerosol particles.

2.5. Biogenic emission measurements

Biogenic emissions have traditionally been measured using enclosure or micro-meteorological methods with air sampling and subsequent off-line analysis of the VOC concentrations. Recently, however, new analytical techniques have been developed which allow also on-line measurement of the biogenic fluxes. The details of the measurement and analysis techniques are outside the scope of this thesis, and they are only briefly discussed here, based on the reviews of *Cao and Hewitt* (1999), *Wiedinmyer et al.* (2004) and *Steiner and Goldstein* (2007).

The micrometeorological techniques used in biogenic emission measurements include the gradient profile, relaxed eddy accumulation and eddy covariance methods. All methods provide emission fluxes representative of canopy or larger areal scales and involve the measurement of meteorological parameters in addition to chemical concentrations. They often require fast response sensors and may set strict constraints to the measurement site or environmental conditions. Their primary use has been the evaluation and validation of emission modeling procedures, but after recent technological improvements they are now also used to establish average areal emission factors in regions with high species diversity where the characterization of individual plant emissions is not practicable (*Wiedinmyer et al.*, 2004).

Leaf, branch or even larger enclosures have been used to characterize the emissions from individual plant species ever since the early days of biogenic VOC emission studies (e.g. *Rasmussen and Went*, 1965). In a dynamic flow-through enclosure system a bag or container made of inert material, typically glass (in laboratory conditions) or Teflon (in

field conditions), is placed around the plant or plant part to be studied. Ambient air is then pumped into the enclosure or pulled through it and sampled at both inlet and outlet. The emission rate E (mass of emissions per mass of leaf biomass per time) is determined according to

$$E = \frac{F}{m}(C_{out} - C_{in}),$$
(1)

where F is the flow rate of air through the enclosure, m is the biomass in the enclosure (dry weight) and C_{in} and C_{out} are the VOC concentrations in the air sampled at the inlet and outlet of the enclosure, respectively. The dynamic enclosure technique has been used in the emission rate measurements of Scots pine presented in **Papers I** and **II**.

The sampling methods of biogenic VOCs include whole air sampling and adsorbent sampling, with the samples taken to a laboratory and stored until analysis by gas chromatography. Whole air samples are drawn or pumped into evacuated containers made of inert material, such as Teflon bags or passivated stainless steel canisters. Ozone must be removed from the air to prevent sampling losses of the more reactive compounds. Sample stability during storage has to be ensured, and the samples must be concentrated prior to being analyzed, especially if the concentrations of the studied compounds are low. Due to losses of the heavier molecules to the container walls, canister sampling is only suitable for truly gas-phase VOCs, which limits its use to compounds lighter than C_{10} (*Cao and Hewitt*, 1999).

The most commonly used sampling methodology for atmospheric VOCs is adsorbent sampling, i.e. collection of the compounds onto solid adsorbents either by pumping or by diffusion (*Cao and Hewitt*, 1999). The adsorbents have different collection efficiencies for different compounds and often a combination of them is used to cover a wide range of VOCs. In the emission measurements presented in **Papers I** and **II**, the adsorbent cartridges were filled with Tenax-TA and Carbopack-B, which together cover the range

C_4-C_{26} (*EPA*, 1999a). Prior to the analysis, the volatiles must be extracted from the adsorbent by thermal desorption.

The most widely used and recommended method for the separation, identification and quantification of the VOCs from air samples has been gas chromatography (GC) followed by mass spectrometry (MS) (*Cao and Hewitt*, 1999; *EPA*, 1999b). The GC/MS technique has also been used in the analysis of the VOC samples collected during the emission measurements described in **Papers I** and **II**.

Currently, the newly developed proton-transfer-reaction mass-spectrometry (PTR-MS) on-line measurement technique (*Lindinger et al.*, 1998) is becoming increasingly popular in biogenic VOC measurements. In the North European boreal forest it has already been applied e.g. in studies of atmospheric VOC concentrations (*Rinne et al.*, 2005), emissions of Scots pine (*Ruuskanen et al.*, 2005), and the hydrocarbon fluxes above a Scots pine forest canopy (*Rinne et al.*, 2007).

3. BIOGENIC EMISSION MODELING AND EMISSION INVENTORIES

In order to estimate the importance of biogenic emissions to the atmosphere their composition and magnitude must be assessed in representative temporal and spatial scales. This requires the parameterization of the emission fluxes as a function of the driving environmental variables, i.e. the development of emission algorithms for different compounds and plant species. To be viable when constructing regional or global emission inventories the emission algorithms should be robust, universally applicable, and computationally efficient. If the inventories are used as input to atmospheric chemistry models, the algorithms must be able to capture the short term variations of the emissions. In addition, the amount and distribution of the emitting biomass needs to be gleaned from various land use and vegetation surveys. Both the emission fluxes and the emitting biomass may exhibit seasonal behavior which should be included in the inventory calculations.

3.1. Emission algorithms

The dependence of both isoprene and monoterpene emissions on temperature has been seen in all emission studies (e.g. *Kesselmeier and Staudt*, 1999), and also sesquiterpene emissions have been found to be temperature dependent (e.g. *Ciccioli et al.*, 1999; *Hansen and Seufert*, 1999; **Papers I** and **II**). *Tingey et al.* (1980) found that while monoterpene emissions were not affected by light they increased exponentially with temperature, and presented a log-linear formulation of the temperature dependence. This formulation was also adopted by *Guenther et al.* (1993) as

$$E(T) = E_S e^{\beta(T-T_S)} \tag{2}$$

where $E(T)$ is the emission rate (µg g^{-1} h^{-1}) at leaf temperature T, β is the slope $\dfrac{d \ln E}{dT}$, and E_S is the emission rate at standard temperature T_S (usually set at 30 °C) (*Tingey et al.*, 1980; *Kesselmeier and Staudt*, 1999). The emission rate at standard temperature is also called the emission potential of the plant species and while it is sometimes held to be a constant it may show variability related to e.g. season or the plant developmental stage (e.g. *Hakola et al.*, 1998, 2001, 2003; **Papers I** and **II**). The value of the β coefficient is obtained from experimental data, and based on literature reviews the slope 0.09 is generally recommended to be used in monoterpene emission calculations (*Fehsenfeld et al.*, 1992; *Guenther et al.*, 1993). In the following, equation (2) is referred to as the TEMP algorithm.

As discussed e.g. in the review of *Sanadze* (2004), the light dependent nature of isoprene synthesis and emission was discovered already in early studies of plant emissions. In 1993 Guenther and coworkers proposed a parameterization for isoprene emissions which took into account both the temperature and light dependence and which still is a staple of the profession
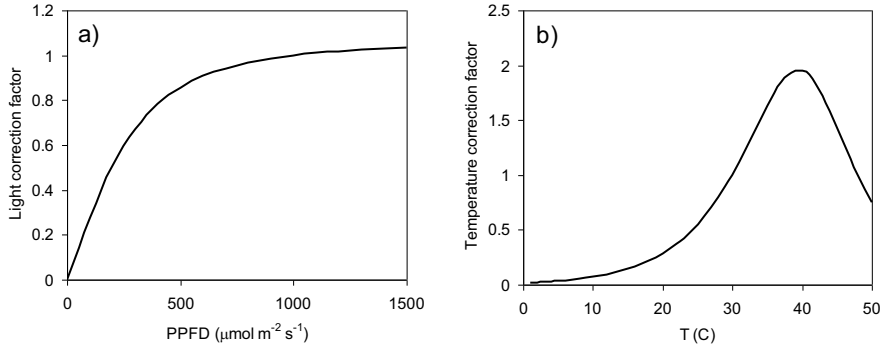
Figure 2. The variation of the light correction (a) and temperature correction (b) factors of the G93 algorithm over typical PPFD and temperature ranges.

$$E(L,T) = E_S C_L C_T . \tag{3}$$

Here $E(L,T)$ is the emission rate at photosynthetically active photon flux density L (µmol m^{-2} s^{-1}) and leaf temperature T (K), E_S is the emission rate at standard conditions of radiation and temperature (usually set at 30 °C and 1000 µmol photons m^{-2} s^{-1}) (*Guenther et al.*, 1993; *Kesselmeier and Staudt*, 1999; *Wiedinmyer et al.*, 2004). C_L and C_T are dimensionless environmental correction factors, accounting for the light and temperature effects on the emissions, with the formulations

$$C_L = \frac{\alpha c_{L1} L}{\sqrt{1 + \alpha^2 L^2}} \tag{4}$$

and

$$C_T = \frac{\exp\dfrac{c_{T1}(T - T_S)}{RT_S T}}{c_{T3} + \exp\dfrac{c_{T2}(T - T_M)}{RT_S T}} , \tag{5}$$

respectively. Here R is the universal gas constant (8.314 J K^{-1} mol^{-1}), and α (0.0027), c_{L1} (1.066), c_{T1} (95 000 J mol^{-1}), c_{T2} (230 000 J mol^{-1}), c_{T3} (0.961), and T_M (314 K) are empirical constants obtained from experimental data (*Guenther et al.*, 1993; *Guenther*, 1997). In the following, equation (3) is referred to as the G93 algorithm.

The light and temperature correction factors in equation (3) are shown in Figure 2 over typical ranges of photosynthetically active radiation and temperature encountered in plant emission measurements. The light correction is formulated as a rectangular hyperbola, based on the assumption that the light response of isoprene emission is similar to that of photosynthesis (*Guenther et al.*, 1993). Thus, the light correction is nearly linear at low light levels and approaches saturation above 500 μmol photons m^{-2} s^{-1}. The formulation of the temperature correction factor is adopted from simulations of the temperature response of enzymatic activity (*Guenther et al.*, 1993), as isoprene emission is driven by the activity of the isoprene synthase enzyme, with increasing emissions at increasing temperatures. At high enough temperatures, however, the enzyme denatures and thus the temperature correction also exhibits a temperature optimum and high-temperature falloff (*Guenther et al.*, 1993).

The TEMP and G93 algorithms have been widely applied in simulating the short term variability of the emissions of stored (temperature control) and newly synthesized (light and temperature control) VOCs from plant foliage. They are still the generally accepted approach to biogenic emission modeling, although there are many regions of the Earth where they have not yet been validated against observations (e.g. *Wiedinmyer et al.*, 2004; *Steiner and Goldstein*, 2007). The applicability of the TEMP and G93 algorithms to the emissions of boreal tree species in boreal environmental conditions is studied in **Papers I** and **II**.

3.2. Emission inventories

Following the methodology developed by *Guenther et al.* (1993, 1995) for inventorying foliar emissions, the VOC flux F (in μg m(ground area)$^{-2}$ h^{-1}) can be described as

$$F = D\varepsilon\gamma \tag{6}$$

where D is the foliar biomass density (g(dry weight) m(ground area)$^{-2}$), ε is the emission potential (μg g^{-1} h^{-1}) i.e. the emission rate for a particular plant species at standard conditions (30 °C and 1000 μmol photons m^{-2} s^{-1}), and γ is a nondimensional environmental correction factor. The correction factor accounts for the temperature and light effects on the emissions but it can also incorporate other aspects such as seasonality or plant phenology. Thus a general form of the correction factor is

$$\gamma = \gamma_T \gamma_L \gamma_{other}. \tag{7}$$

For pool emissions $\gamma_T\gamma_L = e^{\beta(T-T_S)}$, and for emissions occurring after *de novo* synthesis $\gamma_T\gamma_L = C_T C_L$, as described above.

As discussed above, some plants may emit terpenoids via a combination of temperature controlled and light dependent pathways. In this case the total emission flux is obtained from a combination of the pool and synthesis emissions (e.g. *Schuh et al.*, 1997)

$$F_{total} = F_{pool}(T) + F_{synthesis}(L,T) \tag{8}$$

This methodology has been employed when constructing global (e.g. *Guenther et al.*, 1995), continental scale (e.g. *Simpson et al.*, 1999) and regional biogenic emission inventories (e.g. *Guenther et al.*, 2000). In **Papers III-V** the methodology is applied in the calculation of the biogenic VOC emissions from boreal forests in Finland.

Recently, the methodology of *Guenther et al.* (1993, 1995) has been further developed to include other processes such as the chemical reactions and deposition within the forest canopy, and to take into account past temperature and PPFD conditions when calculating the isoprene emissions (*Guenther et al.*, 2006). In the future, when this new approach

called MEGAN (Model of Emissions of Gases and Aerosols from Nature) is extended to cover other compounds besides isoprene, it is likely to become the recommended method of constructing biogenic emission inventories.

3.2.1. Land cover and foliar biomass

The density of the emitting foliar biomass can be obtained in various ways utilizing e.g. local or regional vegetation inventories, general land use data, mathematical models of primary productivity or leaf area index measured from satellites (e.g. *Steiner and Goldstein*, 2007). In **Paper III** a methodology is developed for calculating boreal forest biomass densities from a detailed analysis of satellite land cover information and existing estimates of the relation of growing stock to leaf biomass in Finland.

3.2.2. Seasonality

In addition to the short term variability of temperature and light, biogenic emissions are profoundly affected by the seasonal cycles and developmental stages of the emitting plants. An obvious example is the emergence, maturing, senescence and falling of the leaves of deciduous trees which results in a constant change of the emitting biomass during the growing season. In the boreal region, the severe environmental conditions in winter keep the deciduous trees bare for a large part of the year and the evergreens dormant, resulting in very small or nonexistent emissions (e.g. *Hakola et al.*, 2003). In addition to the seasonal variation of the biomass, the emission potentials and the spectra of emitted compounds also change during the growing season (e.g. *Staudt et al.*, 1997, 2000; *Hakola et al.*, 1998, 2001, 2003; *Llusià and Peñuelas*, 2000; **Papers I** and **II**).

In the boreal region, *Hakola et al.* (1998) observed high monoterpene emission rates from newly developing leaves of boreal deciduous trees in spring as well as the onset of isoprene emission from willow and aspen only after the early growth period was over. The main boreal deciduous trees, silver birch and downy birch were found to emit different monoterpenes at different stages of the growing season (*Hakola et al.*, 2001). A

clear seasonality was also observed in both the emission potential and the spectrum of monoterpenes emitted by Norway spruce (*Hakola et al.*, 2003), which is one of the main boreal conifers in Europe. The seasonal variation of the emissions of the other main European boreal conifer, Scots pine, is studied in **Papers I** and **II**. In **Paper IV** a simple parameterization is developed for the variation of the boreal deciduous biomass during the growing season.

3.3. The BEIS approach

The Biogenic Emissions Inventory System (BEIS) was developed at the U.S. Environmental Protection Agency (EPA) in order to obtain an estimate of biogenic VOC emissions required by the 1990 Clean Air Act Amendments and to provide hourly emissions of isoprene, α-pinene, other monoterpenes, and OVOCs for regional model calculations of tropospheric ozone concentrations (*Pierce and Baugues*, 1991). In 1995 the model was updated to version 2 which also included soil nitrogen oxide emissions (*Birth and Geron*, 1995; *Pierce*, 1996; *Pierce et al.*, 1998), and later to BEIS3 with state of the art emission algorithms and improved treatment of landcover data (http://www.epa.gov/AMD/biogen.html (accessed March 27, 2008)).

In the BEIS approach a regional emission rate (ER_i, μg h^{-1}) of a chemical species (i) is calculated as a sum over all the vegetation types (j):

$$ER_i = \sum_{j=1}^{n}[A_j FD_j EP_{ij} F_{ij}(L,T)]. \tag{9}$$

Here A_j is the land area (m^2) of vegetation type j, FD_j (g(leaf biomass) m(land area)$^{-2}$) is the foliar density of vegetation type j, EP_{ij} (μg g(leaf biomass)$^{-1}$ h^{-1}) is the emission potential of chemical species i from vegetation type j, and $F_{ij}(L,T)$ is the dimensionless environmental correction factor accounting for the light and temperature control of the emission of chemical species i from vegetation type j.

The input data to BEIS consists of land use and emission factor data bases and the hourly time series of temperature and solar radiation. Alternatively, cloud cover data can be supplied, from which the visible solar radiation is then calculated in BEIS. A canopy parameterization is included in the model which adjusts the above canopy solar radiation to photosynthetically active radiation intercepted at 5 vertical levels within different types of forest canopies (*Geron et al.*, 1994). The temperature is not adjusted, however, thus the model assumes that the above canopy ambient temperature applies throughout the canopy (*Lamb et al.*, 1996).

In **Paper III**, the methodology used in BEIS version 2.2 has been adapted for the calculation of isoprene, monoterpene and OVOC emissions from boreal forest canopies. The adapted modeling system is henceforth called FMI-BEIS. In **Paper IV** the parameterization in FMI-BEIS is further developed to account for the variation of both the emission potentials and emission spectra of boreal trees as well as the changes in the deciduous foliage along the course of the growing season. In **Paper V** FMI-BEIS is updated according to new experimental data on the emissions of boreal trees, and the compound selection of the model is expanded to cover also the calculation of sesquiterpene emissions from boreal forests. As a further improvement, **Paper V** also includes the first estimate of the isoprene emissions from wetland ecosystems.

4. RESULTS

4.1. Emissions of Scots pine

The VOC emission rate measurements of Scots pine (*Pinus sylvestris*) described in **Papers I** and **II** cover two growing seasons at the site of Hyytiälä in the south boreal zone (61º51'N, 24º17'E). In 2003 the measurements were carried out from March to October and in 2004 from April to October. The 2003 measurements included an intensive three-week campaign period (24 March to 14 April) during which several samples were taken daily, while the rest of the data consisted of samples on one or two

Figure 3. Map of Finland with black dots denoting the locations where the emissions from boreal tree species referred to in this work have been measured. The division of Finland to the south boreal (dark grey), middle boreal (medium gray) and north boreal (light gray) forest zones is also indicated.

days each month. For the measurements in 2004, samples were taken daily except on weekends. In addition, the emissions of Scots pine were also measured in Sodankylä in the north boreal zone (67º22'N, 26º39'E) on five selected days in spring and early summer 2002. The measurement sites, together with other locations where the emissions of the Finnish boreal tree species have been measured are presented in Figure 3.

4.1.1. Emission spectra and seasonality

The dominant monoterpenes emitted by Scots pine in the south boreal zone were Δ^3-carene and α-pinene. Other observed monoterpenes were β-pinene, camphene, sabinene, terpinolene, limonene, 1,8-cineol, and β-phellandrene. In addition, sesquiterpene and

MBO emissions were detected, especially during the summer months. The main emitted sesquiterpene was β-caryophyllene and two other compounds were tentatively identified as α-farnesene and α-caryophyllene. A small isoprene emission was also found, but as it occurred simultaneously with MBO emission and was well correlated with it, it was considered to be an artifact rather than a real finding (**Papers I** and **II**). The compounds emitted by the Scots pine measured in the north boreal zone were mostly the same, except that no carene emissions were detected and instead the emissions were dominated by α- and β-pinene (**Paper I**).

The observed monthly average noontime emission rates (as nanograms per gram of leaf biomass (dry weight) per hour) during the two growing seasons in the south boreal zone are presented in Figure 4 together with the average noontime temperatures. The emission rates follow the course of the average temperature during spring and summer, but the emissions start to fall off already in August when the temperature is still high. In September and October the emission rates decline further. It is notable that the average emission rates in April are lower than in March. In the 2003 data this was at least partly explained by a severe cold spell which occurred during the April measurements (**Paper I**). However, the same type of behavior with high emission rates in early spring when the plants first start to emit and a decline towards late spring and early summer was also observed in the measurements carried out in the north boreal zone in 2002 (**Paper I**) and to a lesser extent also in the measurements in the south boreal zone in 2004, where the total monoterpene emission rate in April was 25% lower than in March even though the temperatures showed no anomaly.

Sesquiterpene and MBO emissions initiated in early summer and their emission rates increased after midsummer. The emissions continued, although declining, all the way to September. Throughout the growing season the other monoterpenes consisted mostly of camphene, sabinene, and β-pinene, each with an average contribution of 20%. In addition, limonene and β-phellandrene were emitted in the early growing season, as well as terpinolene whose emissions then increased as the summer progressed, reaching 30%
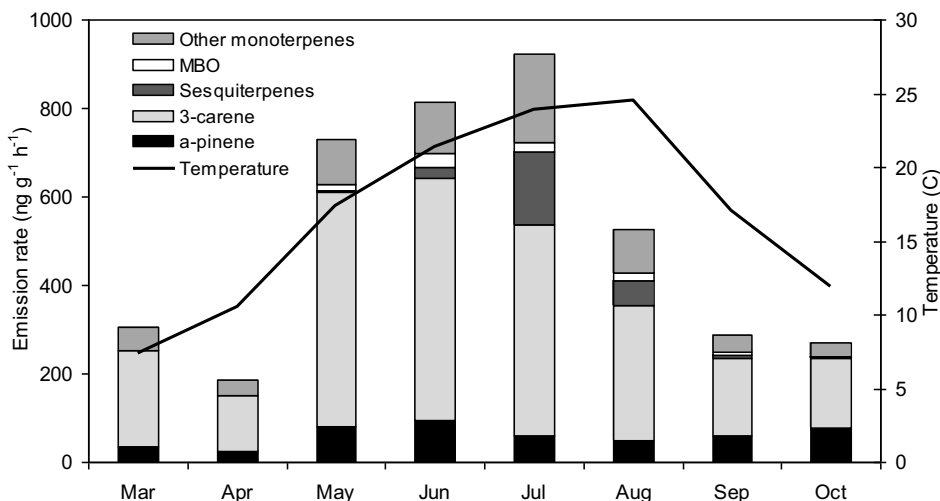
Figure 4. Observed monthly average noontime emission rates of Scots pine during the course of the growing seasons in 2003 and 2004 in Hyytiälä in the south boreal zone. Other monoterpenes include β-pinene, camphene, sabinene, limonene, 1,8-cineol, terpinolene, and β-phellandrene. Sesquiterpenes are mainly β-caryophyllene, with lesser contributions of two tentatively identified compounds (α-farnesene and α-caryophyllene). The monthly average noontime temperature during the measurements is also shown on right axis.

in October. 1,8-cineol emissions initiated in April, increased to a maximum of 20% of other monoterpenes in July-August and then dropped close to zero.

The percentage contribution of the different compounds to the VOC emissions of Scots pine in the south boreal and north boreal zones are shown in Table 3. The difference in the dominant emission in different parts of the boreal zone is most probably explained by the fact that there are two genotypes of Scots pine of Finland, one of which emits Δ^3-carene while the other does not (**Paper I**). Similar differences in the main emitted compounds have been found in the emissions of individual Scots pines growing in southern Germany (*Komenda and Koppmann*, 2002; *Holzke et al.*, 2006). Unfortunately no other trees at these boreal locations were measured at the time, so it can not be

Table 3. The percentage contribution of different compounds to the VOC emissions of Scots pine in the south boreal zone during the growing seasons in 2003 and 2004. The corresponding values from the measurements carried out in the north boreal zone in spring and early summer 2002 are given in parenthesis.

	α-pinene	Δ^3-carene	Other monoterpenes	Sesquiterpenes	MBO
March	11%	71%	17%	0%	0%
April	13% (36%)	67% (0%)	19% (64%)	0% (0%)	1% (0%)
May	11% (70%)	73% (0%)	14% (28%)	0% (0.1%)	2% (0.3%)
June	12% (41%)	67% (0%)	14% (32%)	3% (24%)	4% (1%)
July	7%	53%	22%	16%	3%
August	9%	58%	18%	12%	2%
September	20%	61%	14%	3%	2%
October	28%	59%	11%	0%	1%

deduced from this data whether this finding can be generalized to represent the emission spectra of pine trees in the respective parts of the boreal zone. However, such a generalization might be warranted according to the results of *Nerg et al.* (1994) who studied the proportional amounts of Δ^3-carene and α-pinene in Scots pine seedlings as a function of the latitude of seed origin in the boreal zone. The highest proportional quantities of Δ^3-carene were found in seedlings originating in the south boreal zone and the lowest in seedlings originating in the north boreal zone, while the opposite was true for α-pinene (*Nerg et al.*, 1994).

A notable feature of the seasonal emission spectrum is the large contribution of sesquiterpenes to the total emission in the north boreal zone in June. The only sesquiterpene included in this analysis of the north boreal data is β-caryophyllene, although some other sesquiterpenes were also tentatively identified (longifolene and elemene) but not quantified (**Paper I**). The high contribution of other monoterpenes to the emission in the north boreal zone in early spring consisted mainly of β-pinene which equaled the α-pinene emission in April.

4.1.2. Emission potentials

In order to be comparable with other work, the VOC emission rates measured in field conditions must be standardized to remove the effects of the varying environmental parameters. This is achieved by utilizing the known dependencies of the emission rates on light and temperature. The generally accepted method is to use equations (2) and (3) for standardizing the temperature and temperature and light dependent emissions, respectively, to 30 ºC and 1000 µmol photons m^{-2} s^{-1}.

The standardized emission rates, hereafter referred to as emission potentials, of Scots pine during the growing season in the south boreal zone are presented in Figure 5. The emission potentials were calculated using equation (2) for monoterpenes and sesquiterpenes and equation (3) for MBO. The β coefficients in equation (2) were taken as 0.10 and 0.19 for monoterpenes and sesquiterpenes, respectively (**Papers I** and **II**).

The monoterpene emission potentials exhibit a maximum in early spring when the emissions start, after which they settle to a lower level which stays remarkably even for the rest of the growing season, except for an apparently temporary drop in August. The emission potentials of sesquiterpenes and MBO show a more sinusoidal distribution, with maxima in June (MBO) and July (sesquiterpenes). In July the sesquiterpene emission potential of Scots pine is about 260 ng g^{-1} h^{-1}. This surpasses the concomitant α-pinene emission potential, is of the same order of magnitude than that of other monoterpenes and is approximately 30% of the emission potential of Δ^3-carene which remains the main emitted compound throughout the growing season.

When compared with the other main European boreal conifer, Norway spruce, the emission potentials of Scots pine show some noteworthy differences. *Hakola et al.* (2003) found that the main monoterpenes emitted by Norway spruce during the growing season were α- and β-pinene, and only very small Δ^3-carene emissions were detected in the summer months. A small sesquiterpene emission was detected from spruce in June and October – however, in July, sesquiterpenes were the main emitted compounds with an
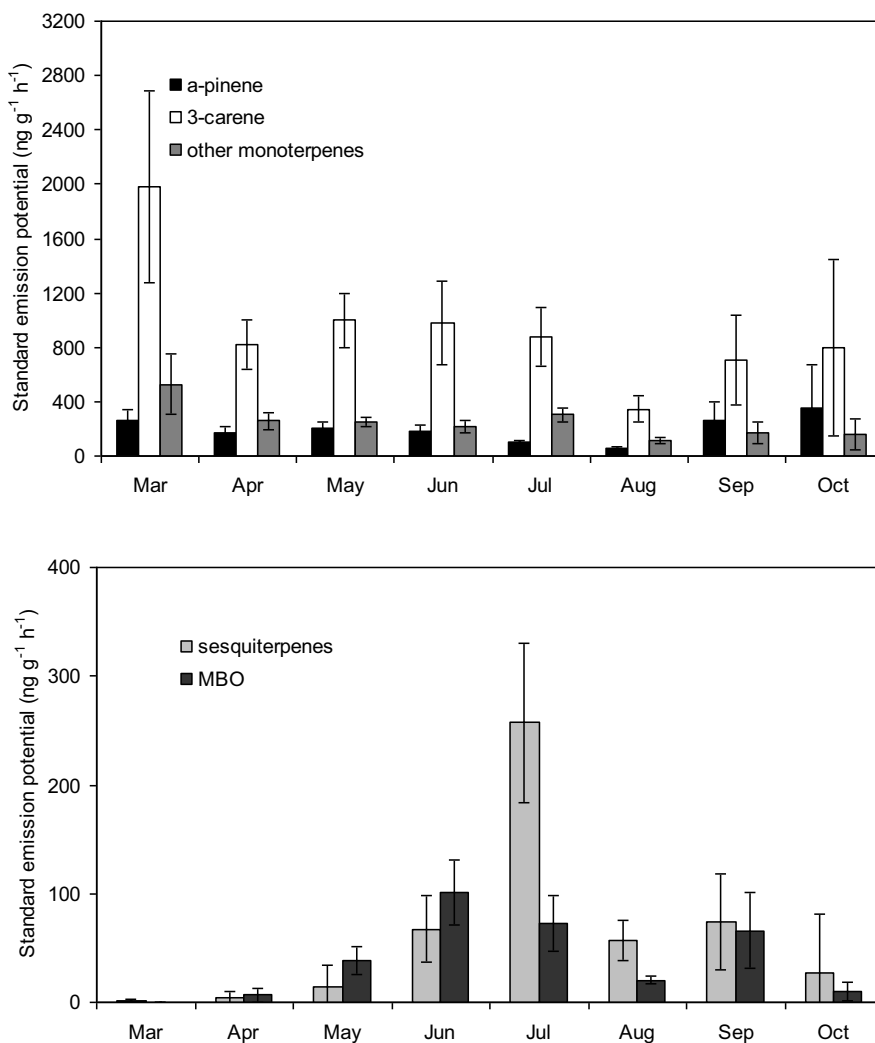
Figure 5. Monthly averages of the monoterpene (upper panel), sesquiterpene and MBO (lower panel) emission potentials of Scots pine based on the measurements carried out in the south boreal zone in 2003 and 2004. The error bars represent the 95% confidence limits calculated as $2 \cdot STD / \sqrt{N}$ where STD is the standard deviation of the emission potential and N the number of observations.

emission potential close to 600 ng g^{-1} h^{-1}, i.e. more than twice as high as the maximum sesquiterpene emission potential of Scots pine. In addition to mono- and sesquiterpenes,

spruce also emitted isoprene with fair emission potentials especially in early summer while no isoprene was found to be emitted by Scots pine. The seasonal pattern of the total emission potential of Norway spruce during the growing season showed no sudden emission burst in spring but was sinusoidal with maximum in May-June and a smooth decrease towards autumn (*Hakola et al.*, 2003).

4.1.3. Temperature and light dependence - applicability of emission algorithms

The 2003 Scots pine data set included experiments where samples were taken from an artificially darkened enclosure (**Paper I**). The results from these experiments suggested a possible light dependence of the MBO and 1,8-cineol emissions while all other measured compounds appeared to be unaffected by the darkening. Light dependent behavior of MBO emissions from North American pine species has been reported by e.g. *Goldan et al.* (1993), *Harley et al.* (1998), and *Schade et al.* (2000) and *Kesselmeier et al.* (1997) and *Staudt et al.* (1997; 2000) have observed that the 1,8-cineol emissions from Mediterranean pine trees are influenced by light. *Shao et al.* (2001), on the other hand found light dependence in some monoterpene emissions of Scots pine seedlings measured in laboratory conditions but this finding was not supported by our results.

The dependence of the emissions of Scots pine on temperature and light was further studied by applying the TEMP and G93 emission algorithms to the observed data (**Papers I** and **II**). Nonlinear regression was used to fit the β and E_S in equation (2) and E_S in equation (3). It was found that, with the exception of the spring period, the emission rate variability of most of the compounds measured in 2002 and 2003 could be simulated using the TEMP algorithm whereas the G93 algorithm performed poorly (**Paper I**). The only exception was 1,8-cineol, which was well simulated also with the G93 algorithm. This was taken as a tentative confirmation of the light dependent nature of the cineol emission of Scots pine indicated by the darkening experiments. However, no similar conclusion could be made for the MBO emissions as their variability was much better simulated by the TEMP algorithm.

In addition to the TEMP and G93 algorithms the temperature and light dependence of sesquiterpenes and 1,8-cineol during their intense emission period in July (2004 data set) was investigated also using a modification of the G93 algorithm where the light dependence was more moderate (**Paper II**). It turned out that all three algorithms performed almost equally well in simulating variability of the sesquiterpene and 1,8-cineol emissions – this illustrates the difficulty of discerning the effect of individual environmental parameters on the emissions in measurements carried out in field conditions, where the solar radiation and temperature are strongly correlated (**Paper II**). For instance the measurements carried out in the south boreal zone in 2004 were always conducted under high light conditions. This leads to the saturation of the light algorithm in most cases so that the only driver of any observed short term variability of the emission rates appears to be the temperature. Thus, even though these results can be used to show that the "universal" emission algorithms developed for more southern biomes are, with some exceptions, applicable also in the boreal regions, they can not be used for a proper validation or further development of the algorithms.

An important result already discussed above and confirmed by the emission algorithm studies is the variability of the standard emission potentials of both the total terpenoids and individual compounds from Scots pine during the course of the growing season. This implies that e.g. annual boreal emission inventories should not be constructed using just one emission potential or emission spectrum per tree species for the whole year. An equally important finding is the variability of the strength of the temperature dependence – in the results presented in **Paper I** the β coefficient values obtained for different monoterpenes ranged from 0.025 to 0.19, with an average of 0.10. This is close to the generic value of 0.09 which is recommended to be used in the TEMP algorithm (*Guenther et al.*, 1993). However, the nonlinear regression analysis of the observed sesquiterpene emission rates against temperature consistently produced higher values for β, indicating a much stronger temperature dependence for the sesquiterpene emissions than for monoterpenes (**Papers I** and **II**). Earlier *Hakola et al.* (2001) found similar strong temperature dependence of the sesquiterpene emissions from downy birch, with the beta coefficients ranging from 0.14 to 0.22. Thus, based on this and the previous work

we now recommend that the β coefficient 0.19 should be used when standardizing the sesquiterpene emissions of boreal trees.

4.2. Emissions from the boreal forest

During the last 15 years, the emission characteristics of the European boreal ecosystems have been intensively studied (e.g. *Janson*, 1993; *Schürmann*, 1993; *Hakola et al.*, 1998, 2001, 2003; *Rinne et al.*, 1999, 2000a,b, 2005, 2007; Janson et al., 1999, 2001; Janson and De Serves, 2001; **Papers I** and **II**; *Ruuskanen et al.*, 2005, 2007; *Hellén et al.*, 2006; *Haapanala et al.*, 2007). Especially the emissions of the main boreal tree species, Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies*), and the deciduous Downy birch (*Betula pubescens*) and Silver birch (*Betula pendula*) have been measured over extended periods in different parts of the European boreal zone. This now allows the compilation of a truly boreal VOC emission data base as a subset of the existing global data bases, with the immediate benefit that it represents the emission characteristics of the European boreal tree species in their natural environment, enabling the construction of more accurate boreal biogenic emission inventories.

4.2.1. Development of the FMI-BEIS emission model

The classification of the forests in Finland to south boreal, middle boreal and north boreal zones applied in this thesis is presented in Figure 3 (page 30). The development of the methodology of inventorying the biogenic emissions from the boreal forest has been a continuous process ever since the first inventory (**Paper III**) was published in 2000 as an outcome of the first large scale boreal VOC emission measurement project (*Laurila and Lindfors*, 1999). In this early inventory much attention was given to the manipulation of the 10x10 km grid analysis of LANDSAT satellite data in order to obtain the forest and species coverage and foliar biomass information in different parts of the boreal zone in Finland.

*Table 4. The species profiles of the three boreal forest types used in the emission inventory calculations in **Papers III-V**. The deciduous species are classified as high-isoprene, low-isoprene and non-isoprene emitters as explained in the text.*

Forest type	Deciduous species			Coniferous species	
	high-iso	low-iso	non-iso	pine	spruce
Pine	1%	16%	1%	82%	0%
Spruce	0.5%	10%	0.5%	0%	89%
Deciduous	3.5%	64%	3.5%	16%	13%

For this, all forests in Finland were reallocated to two coniferous and one deciduous forest categories, each with a different species profile to account for the blend of the main tree species. The deciduous trees were further categorized in three classes based on their isoprene emission potential: high isoprene emitters (e.g. *Populus* and *Salix* sp.), low isoprene emitters (e.g. *Betula* sp.), and non-isoprene emitters (e.g. *Alnus* sp.). The profiles of the three forest types are presented in Table 4.

In the first boreal emission inventory only three kinds of emissions were distinguished: isoprene, monoterpenes and other VOCs. One emission potential per tree species was used for each compound group in the calculations throughout the six-month modeling period (April to September). Moreover, some of the emission potentials were generic or based on literature rather than actual measured data, and the emitting foliar biomass, whether coniferous or deciduous, was assumed constant during the modeling period. For all tree species, the isoprene emission was parameterized using the G93 algorithm and the monoterpene and OVOC emissions were parameterized using the TEMP algorithm.

In the second inventory (**Paper IV**) speciated monoterpene emission profiles were introduced for each of the main boreal tree species. Based on existing experimental data, the emission potentials were revised and separate emission potentials and monoterpene emission profiles were assigned for the deciduous trees for early and late summer. The additional temperature and light dependent monoterpene emission pathway suggested for Norway spruce and Scots pine (*Steinbrecher et al.*, 1999) was incorporated in the FMI-

BEIS parameterization according to equation (8). The second inventory was also temporally extended to cover the month of October.

A simple temperature based parameterization for the seasonal variation of the boreal deciduous foliage was also incorporated in FMI-BEIS for the second emission inventory (**Paper IV**). The leaf development was assumed to initiate when the effective temperature sum (cumulative sum of daily average temperatures > +5ºC) reach a threshold value of 49 degree days (*Lappalainen*, 1993) and complete by July 31. During this period the percentage *P(i)* of full foliage on each day (*i*) is calculated from

$$P(i) = \sum_i Sc \log \left[\frac{ETS(\text{July31}) - 49}{ETS(i) - 49} \right]. \tag{10}$$

Here *ETS(i)* is the effective temperature sum on day *i*, and *Sc* is a scaling factor fitted individually for each study location so that *P(July31)* = 100%. After maturity, maximum foliage is maintained until senescence which is assumed to start two weeks before complete leaf shedding - this generally occurs between September 20 in the North and October 10 along the South-West coast (*Havas and Sulkava*, 1987). During the senescence *P(i)* is assumed to decrease linearly until the tree is bare (*P(i)* = 0%). Average *P(i)* in different parts of the boreal zone in Finland according to this parameterization, calculated at the meteorological stations used in the inventory for the years 1997, 1999, 2000, and 2003, is presented in Figure 6.

For the third emission inventory (**Paper V**) the biogenic emission data base in FMI-BEIS was completely revised to reflect the accumulated new experimental data on the seasonal variation of the emission potentials and emission spectra of the boreal tree species. In addition to the deciduous trees, early (April-June) and late (July-October) growing season emission potentials were assigned also for the conifers. The assumption of dual emission pathways (pool and synthesis) for Scots pine was relinquished as it was not supported by the findings in **Papers I** and **II**. While sesquiterpenes were included already in the second
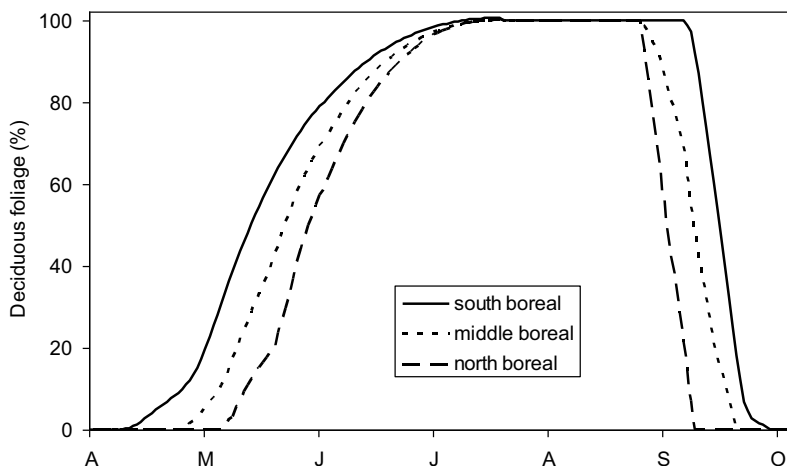
Figure 6. The development of deciduous foliage in the south boreal, middle boreal and north boreal zones in FMI-BEIS. The lines represent the averages of the years 1997, 1999, 2000, and 2003.

inventory through their contribution to the total monoterpene emission spectra of the deciduous (*Betula*) species (despite the fact that they are not monoterpenes) the new findings (*Hakola et al.*, 2003, **Papers I** and **II**) had revealed substantial sesquiterpene emissions also from Norway spruce and Scots pine. This warranted complementing FMI-BEIS with a separate parameterization for sesquiterpene emissions using the TEMP algorithm with seasonal sesquiterpene emission potentials and the recommended new β coefficient value of 0.19 based on this work (**Papers IV** and **V**) and the work of *Hakola et al.* (2001). The new early and late growing season emission potentials of boreal trees, recommended to be used in future emission inventories in the European boreal zone, are presented in Table 5.

4.2.2. Emission spectra

The main compounds emitted by the European boreal forests are α- and β-pinene and Δ^3-carene, which dominate the emissions almost through the whole growing season. The

Table 5. The emission potentials (in $\mu g\ g^{-1}\ h^{-1}$) of boreal tree species at standard conditions (30 °C and 1000 μmol photons $m^{-2}\ s^{-1}$) in early (April-June) and late (July-October) growing season. The values recommended for the north boreal zone are given in parenthesis, and the emission potentials assigned separately for pool (pool) and synthesis (synth) emissions are indicated.

	Isoprene		Monoterpenes		Sesquiterpenes	
	Early	Late	Early	Late	Early	Late
Deciduous trees						
Betula pendula and *Betula pubescens*	0.1	0.1	0.84	3.35	0	2.69
Populus, *Salix* sp.	34	34	3	0.3	0	0
Alnus sp.	0	0	0.72	0.72	0	0
Coniferous trees						
Pinus sylvestris	0.1	0.1	2.39	1.46	0.05	0.13
Picea abies	0.90 (0.6)	0.22 (0.6)	0.81 pool 0.45 synth	0.81 pool 0.45 synth	0	0.16

average monthly emission spectra from forests in the middle boreal zone are shown in Figure 7 (upper panel). The emissions of the forests in the south and north boreal zones are quite similar, although somewhat higher in magnitude in the south and somewhat lower in the north. Isoprene is emitted mainly in the summer months and a prominent sesquiterpene emission starts after midsummer and then decreases towards autumn. From the end of June to September there is a large sabinene emission, contributed mainly by the birch species. Limonene and linalool are also emitted in summer and cineol in late spring and summer.

Figure 7 (lower panel) also shows the monthly average atmospheric concentrations of terpenoids at a middle boreal forest research site, measured around midday during 1997 and 1998 (*Hakola et al.*, 2000). Compared to the emissions, the more reactive emitted terpenoids (such as sesquiterpenes, limonene and linalool) are depleted in the ambient air while the relative abundance of e.g. isoprene and α-pinene which have longer atmospheric lifetimes against oxidation (*Atkinson and Arey*, 2003) is amplified. Besides emissions from the trees, the atmospheric concentrations are affected by emissions from

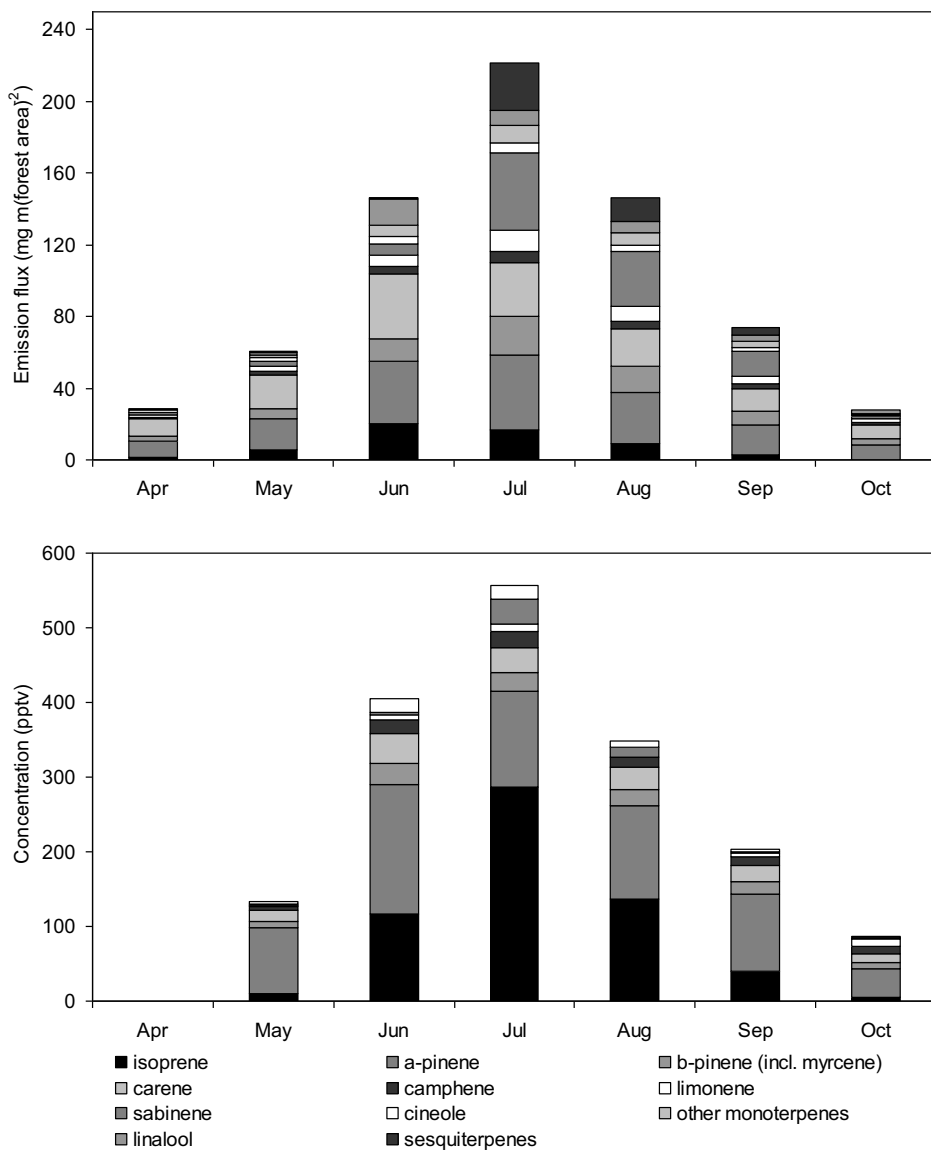*Figure 7. Average terpenoid emission fluxes (mg m(forest area)$^{-2}$ per month) from forests in the middle boreal zone (upper panel) and the monthly average midday concentrations (lower panel) measured at a forest measurement site in Pötsönvaara in eastern Finland in 1997 and 1998 (Hakola et al., 2000).*

other vegetation and the forest floor, which are not parameterized in FMI-BEIS. A large amount of isoprene is also emitted by wetlands. In the middle boreal zone this contribution is close to 20% (**Paper V**). This may also explain why the enhancement of the atmospheric isoprene concentration in Figure 7 appears somewhat disproportionate when compared to α-pinene as there were large wetland areas in the vicinity of the measurement site.

4.2.3. Seasonal and spatial variation of emissions

The monthly average emission fluxes of isoprene, monoterpenes, and sesquiterpenes from forests in different parts of the boreal zone in Finland are presented in Figure 8. The values are calculated as the averages of the years 1997, 1999, 2000, and 2003, and the interannual variation of the emissions is indicated by the error bars which show the maximum and minimum fluxes.

The isoprene emissions exhibit a maximum in June in the south boreal and middle boreal zones, whereas in the north the maximum emission occurs in July. In the southern parts of Finland the isoprene emissions are dominated by spruce which contributes 53% and 49% of the forest isoprene emission in the south and middle boreal zones, respectively. In the north boreal zone, where the spruce biomass is assumed to be divided between the higher emitting Norway spruce (*Picea abies*) and its lower emitting subspecies Siberian spruce (*Picea abies* ssp. *obovata*), the contribution of spruce is 46%. On the other hand, the deciduous trees contribute 42%, 46%, and 50% in the south boreal, middle boreal and north boreal zones, respectively. Thus, in the north the seasonality of the deciduous biomass has a more profound effect on the seasonal pattern of isoprene emissions than in the southern parts of the country.

The differences in the isoprene emissions in different parts of the boreal zone are most prominent in spring, when the forest emission fluxes in the middle and north boreal zones are approximately 65% and 30% of those in the south boreal zone, respectively. In July, however, the emission fluxes in the north boreal zone are almost equal to the emissions in
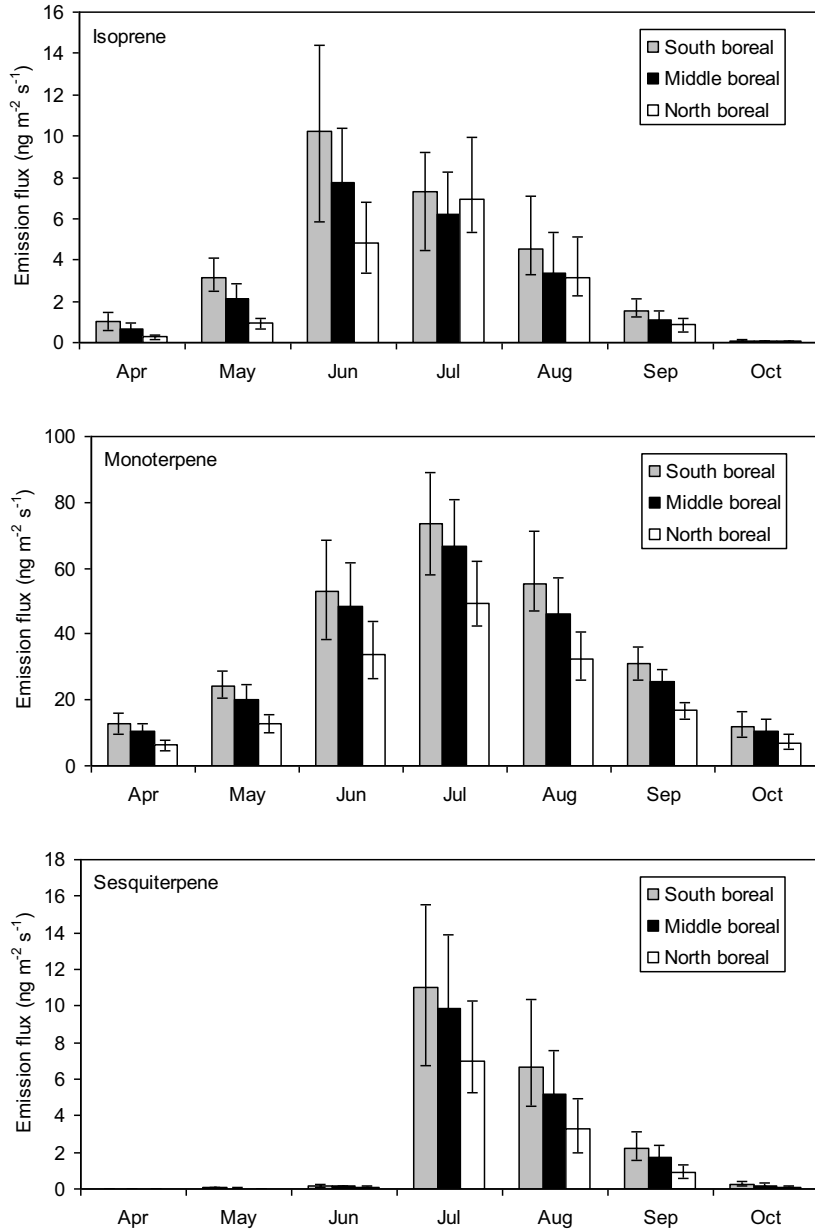
Figure 8. Monthly average terpenoid emission fluxes (ng m(forest area)$^{-2}$ s^{-1}) from forests in the south, middle and north boreal zones. The values are averages for the years 1997, 1999, 2000, and 2003. The error bars give the range of the monthly averages in the individual years.

the south boreal zone, surpassing the emissions in the middle boreal zone. After this, the emissions in the middle and north boreal zones decline but remain of almost equal magnitude all the way until the end of the growing season. Thus, the relative shortness of the growing period in the north appears to be compensated by a more intense isoprene emission during the summer months.

Paper V also includes an estimate of the wetland isoprene emissions in different parts of the boreal zone in Finland based on new experimental data (*Haapanala et al.*, 2006). In the south boreal zone the total wetland isoprene emissions were 3% of the forest isoprene emissions, while in the middle and north boreal zones the corresponding percentages were 23% and 45%, respectively, indicating the increasing importance of the wetland ecosystems in the total isoprene budget in the northern parts of the European boreal zone.

The monoterpene emissions are dependent on the temperature and this is also evident in their seasonal cycle which closely follows that of the temperature, with maximum emissions in July in all parts of the country. Spruce contributes about half of the monoterpene emissions in all parts of the boreal zone, with the contributions of pine and deciduous trees approximately 30% and 20%, respectively. A clear decreasing trend is seen in the monoterpene emission fluxes when moving from the south boreal zone towards north, with the emission fluxes between 80-90% and 50-70% of those in the south in the middle boreal zone and in the north boreal zone, respectively.

The sesquiterpene emissions also depend on the temperature and thus their seasonal behavior in different parts of the boreal zone is similar to that of monoterpenes. Similarly to monoterpenes, the impact of different forest types to the sesquiterpene emissions is quite similar in all parts of the boreal zone in Finland, with the pine, spruce and deciduous contributions 7%, 23%, and 70%, respectively. During their main emission period, the sesquiterpene emission fluxes in the middle boreal zone are between 70-90% and those in the north between 40-60% of the fluxes in the south. The extremely low sesquiterpene emissions in early summer and the abrupt onset of high emissions in the beginning of July, however, are obvious artifacts produced by the choice of the

parameterization of the emission potentials in FMI-BEIS using only the early and late growing season categories. It would probably be beneficial, and not only for this compound group, to use monthly emission potentials in future emission inventory calculations. At present, however, Scots pine is the only boreal tree for which it would be feasible to develop monthly emission potentials – the emissions of Norway spruce and the deciduous trees still need to be investigated in closer detail to facilitate this.

4.2.4. Comparison with other inventories – boreal characteristics

The average forest emission fluxes in July obtained in the boreal emission inventory (**Paper V**) were 25 and 210 $\mu g\ m^{-2}\ h^{-1}$ for isoprene and monoterpenes, respectively. In global model calculations by *Guenther et al.* (1995) the July isoprene emission fluxes in Finland were estimated to be approximately 340 $\mu g\ m^{-2}\ h^{-1}$ and monoterpene fluxes between 70 and 540 $\mu g\ m^{-2}\ h^{-1}$ (rough estimates from color plates in the reference). The isoprene emission estimated by the global model is more than an order of magnitude higher that the results obtained in the boreal emission inventory, while the monoterpene emissions are of the same order of magnitude. Similar differences have been pointed out by the authors themselves between the global inventory and several regional inventories and attributed mostly to the use of different base emission factors or differences in land cover estimates in the respective models (*Guenther et al., 1995*).

According to the boreal emission inventory the total annual biogenic isoprene and monoterpene emissions in Finland are 15 ± 5 and 114 ± 2 kilotonnes. This also includes the 2.4 kilotonnes of isoprene emitted by wetlands. In the detailed European biogenic emission inventory of *Simpson et al.* (1999), the annual isoprene and monoterpene emissions from the forests in Finland were estimated to be 39 and 168 kilotonnes, respectively, and the wetland isoprene emissions 1-5 kilotonnes. Thus, the boreal isoprene emissions are overestimated also in the European inventory – although not so grossly as the July emissions in the global model. The monoterpene emissions are also overestimated, but of the same order of magnitude with the boreal estimate.

In a biogenic hydrocarbon emission inventory for the U.S.A., *Lamb et al.* (1993) calculated maximum isoprene and terpene emission fluxes in the different EPA regions of the country. In EPA region 10, which includes the states of Alaska, Idaho, Oregon, and Washington, the maximum forest emission fluxes in July were 964 and 754 μg m^{-2} h^{-1} for isoprene and terpenes, respectively. In July the maximum isoprene emission flux from the boreal forests in Finland was 33 μg m^{-2} h^{-1} and the maximum monoterpene flux 260 μg m^{-2} h^{-1}, i.e. the isoprene flux only 3% and the monoterpene flux 34% of the corresponding U.S. values. However, of the states in the EPA region 10, only Alaska lies at the same northern latitudes with Finland while the other states are between 40 and 50 ºN; in addition, the vegetation in the U.S. forests is quite different from that in Finland, with a number of high isoprene emitters such as oak, poplar, cottonwood and aspen (e.g. *Geron et al.*, 2001).

In a Swiss emission inventory, the annual isoprene and monoterpene emissions from the forests in the country were estimated to be 87 kilotonnes (*Andreani-Aksoyoglu and Keller*, 1995). The forests in Switzerland are predominantly coniferous and dominated by Norway spruce which together with Scots pine represents over half of the total forest area (*Andreani-Aksoyoglu and Keller*, 1995). Taking the forest area of Switzerland to be 10845 km^2 as given by *Simpson et al.* (1999) this yields an annual average terpenoid emission flux of 900 μg m^{-2} h^{-1} for the Swiss forests. *Komenda and Koppmann* (2002), on the other hand, measured the emissions of Scots pine in a forest in southern Germany and calculated monthly monoterpene emissions. According to their results the emission fluxes in July varied between 58 and 936 μg m^{-2} h^{-1}. The Central European emissions thus appear to be up to three times the emissions obtained in the boreal emission inventory, even though the same tree species are present in the forests.

The above examples show that the characteristics of the European boreal forests, such as the small selection of tree species and the seasonally changing emission potentials which also appear to be dependent on the growth environment of the trees, are not necessarily adequately represented in large scale emission models. This can result in the overestimation of the boreal emissions, especially with regard to isoprene. Furthermore,

*Table 6. Global and regional estimates of the mass percentage of some monoterpene and other reactive VOC emissions adopted from the review by Kanakidou et al. (2005) and the results of the present study (**Paper V**; growing season average over all boreal zones).*

Compound	Mass % contribution			
	Global	Southern Europe and Mediterranean	North America	North European boreal forest
α-pinene	24.8	30 - 58	12 - 53	27.1
β-pinene	16.4	8 - 33	10 - 31	10.8
Sabinene*	10.0	2.5 - 14	2 - 5	11.9
Δ^3-carene	3.0	0	4 - 9	23.9
Limonene	16.4	0 - 5	6 - 10	6.0
Terpinolene	1.4	n.d.	0 - 2	1.2
Myrcene	3.5	0 - 4	2 - 7	0.2
Terpenoid alcohols (Linalool**)	14.9	0 - 20	n.d.	4.3
Ocimene	1.5	0 - 1	0 - 1	1.5
Sesquiterpenes	7.4	n.d.	n.d.	4.6
Other	0.6	2 - 5	0 - 6	1.5

* Kanakidou et al. (2005) also include terpenoid ketones with sabinene.
** Linalool is the only terpenoid alcohol considered in the present study.

emission estimates carried out in other parts of the world appear not to be applicable as such to the North European boreal forest, even though the same tree species may grow in both environments.

The emission spectrum of the boreal forest is also somewhat different than those in other parts of the world. *Kanakidou et al.* (2005) have summarized the relative contributions of SOA forming terpenoids from some recent studies representing North American, South European/Mediterranean and global emission estimates. This summary is presented in Table 6, complemented with the corresponding results of the present work. The conspicuous feature of the North European boreal emission spectrum when compared to the other regions is the high relative amount of Δ^3-carene in the emissions. The boreal α-pinene and sesquiterpene emissions are close to the global averages, while e.g. the

contributions of β-pinene, limonene and linalool are lower than the global values. When compared to the emissions in southern Europe and the Mediterranean region, the boreal emission spectrum is enriched with respect to carene and sesquiterpenes, while the other emissions mostly fit within the boundaries of the more southern estimates. Compared to North America, the notable differences in the emissions from the North European boreal forest are the high proportions of sabinene, Δ^3-carene, linalool, and sesquiterpenes. However, regarding the missing sesquiterpenes in the Mediterranean and North American inventories, one should keep in mind that – partly due to their high reactivity and analytical difficulties – these compounds have only recently became the focus of attention in emission estimates. Thus, it must be only a question of time before they can be accounted for also in the other emission inventories.

The anthropogenic VOC emissions in Finland in 2006 were 132.6 kilotonnes (Statistics of the Ministry of the Environment in Finland). This is slightly less than the annual total of 138.1 kilotonnes obtained as a sum of the terpenoid emissions in the boreal emission inventory (**Paper V**). In addition to terpenoids, however, the biogenic emissions also comprise a number of other VOC compounds, which probably contribute an amount of the same magnitude to the grand total (e.g. *Simpson et al.*, 1999; **Paper III**). Thus, it can be estimated that the biogenic emissions from the boreal forest and wetland ecosystems in Finland are approximately twice the anthropogenic emissions. This is typical of remote sparsely populated areas in Europe, such as the boreal regions, while for instance at the European continental level, the biogenic emissions are not significant when compared to the anthropogenic ones (*Simpson et al.*, 1999).

4.3. Uncertainties

Due to the many different aspects involved in generating biogenic emission inventories, they are prone to several kinds of uncertainties. One obvious source of error is the lack of sufficiently detailed information about the emission potentials and their temporal, spatial, genetic or phenological variability. Even though this work is based on the best available information on the emissions of the main boreal tree species, there are still gaps and open

questions regarding for instance the seasonal patterns of sesquiterpene emissions from deciduous trees or the extrapolation of the few measured tree specimen to represent the whole species in different parts of the boreal forest. A second important factor in emission inventory calculations is the level of accuracy of the land use and emitting biomass information, and the final aspect is the capability of the chosen emission parameterizations to depict the dependence of the emissions on the environmental conditions.

When developing the U.S. national biogenic VOC emission inventory *Lamb et al.* (1987) estimated that the uncertainties involved with emission rate measurements range between ±30 to ±55% depending on the measurement method, while the uncertainties involved with land use distributions and biomass densities were ±15% and ±25%, respectively. The overall uncertainty of the inventory was estimated to be a factor of three (*Lamb et al.*, 1987).

In their global model of natural VOC emissions *Guenther et al.* (1995) estimated that the uncertainties associated with isoprene and monoterpene emissions in some temperate regions are at least a factor of 3 and even higher in tropical regions. In the European emission inventory of *Simpson et al.* (1995), an uncertainty of a factor of 5 was associated with the model calculations of biogenic isoprene emissions to cover episodic situations when the emission data was used in tropospheric ozone simulations. Based on the review of *Wiedinmyer et al.* (2004) *Kanakidou et al.* (2005), however, conclude that the overall uncertainty of global isoprene emission estimates is a factor of 3 and that of the monoterpene and sesquiterpene emissions a factor of 5.

In **Paper IV**, the overall uncertainty of the boreal emission inventory was estimated to be ±70%, due to the fact that the emission potentials used in the model calculations were based on measurements carried out on plants growing in actual boreal conditions in Finland. In **Paper V** the emission potentials were further revised to reflect the latest experimental data and the variation of the monthly average emission fluxes (presented in Fig. 8) was within ±85%, ±43%, and ±107% for isoprene, monoterpenes, and

sesquiterpenes, respectively, which are of the same order of magnitude with the previous overall error estimate. Thus the uncertainty of the present emission inventory is a factor of 2-3 for monoterpenes, several times that for isoprene and even higher for sesquiterpenes, reflecting the strong interannual variability of the meteorological conditions in the boreal region.

5. CONCLUSIONS

According to the results obtained in this work the principal compounds emitted by Scots pine are Δ^3-carene and α-pinene in the south boreal zone and α- and β-pinene in the north boreal zone. For the first time, Scots pine has also been found to be a copious sesquiterpene emitter, and emit MBO especially in the summer months. The emissions of Scots pine show a strong seasonality; the monoterpene emissions are very high in spring, then decline and closely follow the course of the temperature for the rest of the growing season. The sesquiterpene and MBO emissions, however, have a sinusoidal seasonal distribution, with maximum emissions in July.

The variability of the observed monoterpene emissions of Scots pine is generally well described by the simple temperature dependent emission algorithm with the strength of the temperature dependence ($\beta = 0.10$) very close to the universally recommended parameter value ($\beta = 0.09$). The only exception is the extremely high emissions in early spring, which are probably related to the plant developmental stages and thus not included in the simple emission parameterization. The observed variability of the sesquiterpene emissions can also be described using the simple temperature algorithm, although the dependence of the emissions on temperature is much stronger ($\beta = 0.19$) than that of monoterpenes. The only compound emitted by Scots pine whose emissions appear to be controlled both by light and temperature is 1,8-cineol – however, this allocation is only tentative.

The main compounds emitted by the boreal forest throughout the growing season in Finland are α- and β-pinene and Δ^3-carene, with a strong contribution from sabinene in summer and autumn. The emission fluxes are highest in the south boreal zone, and decline steadily towards north. The terpenoid emissions generally follow the average course of the temperature during the growing season, with maximum emissions in July. The only exception is isoprene, whose emissions show a maximum already in June in the south boreal and middle boreal zones due to the strong dominance of spruce with its high early summer emission potential in these parts of the country.

A first estimate of sesquiterpene emissions from the boreal forest is presented in this work. The highly reactive sesquiterpenes have now been shown to be emitted in copious amounts by all main boreal tree species in Finland, and an assessment of their emission is acutely needed. The sesquiterpene emissions from the boreal forests in Finland initiate after midsummer and are of the same order of magnitude as the isoprene emissions. Experimental data on sesquiterpene emissions from Norway spruce and the deciduous trees during the early growing season, however, is still sparse, and additional measurements of these species in spring and early summer would considerably improve the sesquiterpene emission inventory.

The boreal forests in Finland are characterized by a relatively sparse selection of tree species, with the emitting foliage almost totally represented by Norway spruce, Scots pine, and the deciduous Downy birch and Silver birch. The main isoprene emitters in Finland are the low emitting Norway spruce and the high emitting willow and aspen species – the latter, however, only occupy less than one per cent of the total forest land area of the country. In addition to the low isoprene emissions, the second outstanding feature of the emissions from the Finnish forests is the strong dominance of Δ^3-carene in the terpenoid spectrum. One must, however, be careful when interpreting this as a typical characteristic of the European boreal forests, as the emission spectra of the main monoterpene emitters, Norway spruce and Scots pine are still based on only a few measured trees. In particular, it would be important to study the relative distribution of

the two emitting genotypes of the Scots pine in different parts of the European boreal zone in order to obtain representative Δ^3-carene and a-pinene emission potentials.

The results presented in this thesis show that it is well warranted to develop biogenic emission inventories for specific ecosystems as they can account for the emission characteristics of the plants and the local environmental conditions in much closer detail than is currently possible when using global or continental scale emission models. The terpenoid emission fluxes obtained in the emission model calculations can be used as input to atmospheric chemistry and transport models for e.g. regional air quality forecasts or simulations of aerosol formation. The methodology developed in this work for the European boreal forests can also be adapted to cover the forested regions in e.g. western Russia and beyond when data on the emissions of the prevalent tree species become available.

REFERENCES

Andreani-Aksoyoglu, S. and Keller, J., 1995. Estimates of monoterpene and isoprene emissions from the forests in Switzerland, *Journal of Atmospheric Chemistry* 20, 71-87.

Atkinson, R. and Arey, J., 2003. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, *Atmospheric Environment* 37 Supplement No. 2, S197-S219.

Birth, T. L. and Geron, C. D., 1995. User's guide to the personal computer version of the biogenic emissions inventory system (PC-BEIS), Version 2.0, U.S. Environmental Protection Agency, Research Triangle Park, N.C.

Bonn, B. and Moortgat, G. K., 2003. Sesquiterpene ozonolysis: origin of atmospheric new particle formation from biogenic hydrocarbons, *Geophysical Research Letters* 30, 1585, doi:10.1029/2003GL017000.

Brasseur, G. P., Steffen, W., and Granier, C., 2004. Atmospheric composition and surface exchanges. In: Emissions of atmospheric trace compounds, Granier, C. et al. (eds), Kluwer Academic Publishers, Dordrecht, The Netherlands, 115-170.

Calogirou, A., Larsen, B. R. and Kotzias, D., 1999. Gas-phase terpene oxidation products: a review, *Atmospheric Environment 33*, 1423-1439.

Cao, X.-L. and Hewitt, C. N., 1999. The sampling and analysis of volatile organic compounds in the atmosphere. In: Reactive hydrocarbons in the atmosphere, Hewitt, C. N. (Ed.), Academic Press, San Diego, California, 119-157.

Carter, W. P. L., 1996. Condensed atmospheric photooxidation mechanisms for isoprene, *Atmospheric Environment* 30, 4275-4290.

Chameides, W. L., Fehsenfeld, F., Rodgers, M. O., Cardelino, C., Martinez, J., Parrish, D., Lonneman, W., Lawson, D. R., Rasmussen, R. A., Zimmerman, P., Greenberg, J., Middleton, P., and Wang, T., 1992. Ozone precursor relationships in the ambient atmosphere, *Journal of Geophysical Research* 97(D5), 6037-6055.

Chung, S. H. and Seinfeld, J. H., 2002. Global distribution and climate forcing of carbonaceous aerosols, *Journal of Geophysical Research* 107(D19), 4407, doi:10.1029/2001JD001397.

Ciccioli, P., Brancaleoni, E., Frattoni, M., Di Palo, V., Valentini, R., Tirone, G., Seufert, G., Bertin, N., Hansen, U., Csiky, O., Lenz, R., and Sharma, M., 1999. Emissions of reactive terpene compounds from orange orchards and their removal by within-canopy processes, *Journal of Geophysical Research* 104(D7), 8077-8094.

Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pahynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P. and Maenhaut, W., 2004. Formation of secondary organic aerosols through photooxidation of isoprene, *Science* 303, 1173-1176.

EPA, 1999a. Compendium method TO-17: Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes. In: Compendium of methods for the determination of toxic organic compounds in ambient air, 2nd edn. US Environmental Protection Agency, 53 pp.

EPA, 1999b. Compendium method TO-15: Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS). In: Compendium of methods for the determination of toxic organic compounds in ambient air, 2nd edn. US Environmental Protection Agency, 67 pp.

Fall, R., 1999. Biogenic emissions of volatile organic compounds from higher plants. In: Reactive hydrocarbons in the atmosphere, Hewitt, C. N. (Ed.), Academic Press, San Diego, California, 41-96.

Fall, R., 2003. Abundant oxygenates in the atmosphere: A biochemical perspective, *Chemical Reviews* 103, 4941-4951.

Fall, R. and Monson, R. K., 1992. Isoprene emission rate and intercellular isoprene concentration as influenced by stomatal distribution and conductance, *Plant Physiology* 100, 987-992.

Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A. B., Hewitt, C. N., Lamb, B., Liu, S., Trainer, M., Westberg, H., and Zimmerman, P., 1992. Emissions of volatile organic compounds from vegetation and their implications for atmospheric chemistry, *Global Biogeochemical Cycles* 6(4), 389-430.

Fuentes., J. D., Lerdau, M., Atkinson, R., Baldocchi, D., Bottenheim, J. W., Ciccioli, P., Lamb., B., Geron, C., Gu, L., Guenther, A., Sharkey, T. D., and Stockwell, W., 2000. Biogenic hydrocarbons in the atmospheric boundary layer: A review, *Bulletin of the American Meteorological Society* 81(7), 1537-1575.

Geron, C. D., Guenther, A. B., and Pierce, T. E., 1994. An improved model for estimating emissions of volatile organic compounds from forests in eastern United States, *Journal of Geophysical Research* 99(D6), 12,773-12,791.

Geron, C. D., Harley, P., and Guenther, A., 2001. Isoprene emission capacity of US tree species, *Atmospheric Environment* 35(19), 3341-3352.

Goldan, P. D., Kuster, W. C., and Fehsenfeld, F. C., 1993. The observation of a C5 alcohol amission in a North American pine forest, *Geophysical Research Letters* 20, 1039-1042.

Goldstein, A. H and Schade, G. W., 2000. Quantifying biogenic and anthropogenic contributions to acetone mixing ratios in a rural environment, *Atmospheric Environment* 34, 4997-5006.

Griffin, R. J., Cocker III, D. R., Flagan, R. C., and Seinfeld, J. H., 1999a. Organic aerosol formation from the oxidation of biogenic hydrocarbons, *Journal of Geophysical Research* 104(D3), 3555-3567.

Griffin, R. J., Cocker III, D. R., Seinfeld, J. H., and Dabdub, D., 1999b. Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons, *Geophysical Research Letters* 26(17), 2721-2724.

Guenther, A., 1997. Seasonal and spatial variations in natural volatile organic compound emissions, *Ecological applications* 7(1), 34-45.

Guenther, A., 1999. Modeling biogenic volatile organic compound emissions to the atmosphere. In: Reactive hydrocarbons in the atmosphere, Hewitt, C. N. (Ed.), Academic Press, San Diego, California, 97-118.

Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R., 1993. Isoprene and monoterpene emission rate variability: Model evaluation and sensitivity analyses, *Journal of Geophysical Research* 98(D7), 12,609-12,627.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M, McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P., 1995. A global model of natural volatile organic compound emissions, *Journal of Geophysical Research* 100, 8873-8892.

Guenther, A., Geron, C., Pierce, T., Lamb, B., Harley, P., and Fall, R., 2000. Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America, *Atmospheric Environment* 34, 2205-2230.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C., 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmospheric Chemistry and Physics* 6, 3181-3210.

Haapanala, S., Rinne, J., Pystynen, K.-H., Hellén, H., Hakola, H., and Riutta, T., 2006. Measurements of hydrocarbon emissions from a boreal fen using the REA technique. *Biogeosciences* 3, 103-112.

Haapanala, S., Rinne, J., Hakola, H., Hellén, H., Laakso, L., Lihavainen, H., Janson, R., O'Dowd, C., and Kulmala, M., 2007. Boundary layer concentrationa and landscape scale emissions of volatile organic compounds in early spring, *Atmospheric Chemistry and Physics* 7, 1869-1878.

Hakola, H., Rinne, J., and Laurila, T., 1998. The hydrocarbon emission rates of Tea-Leaved Willow (Salix phylicifolia), Silver Birch (Betula pendula) and European Aspen (Populus tremula), *Atmospheric Environment* 32(10), 1825-1833.

Hakola, H., Laurila, T., Rinne, J., and Puhto, K., 2000. The ambient concentrations of biogenic hydrocarbons at a Northern European, boreal site, *Atmospheric Environment* 34, 4971–4982, 2000.

Hakola, H., Laurila, T., Lindfors, V., Hellén, H., Gaman, A., and Rinne, J., 2001. Variation of the VOC emission rates of birch species during the growing season. *Boreal Environment Research* 6, 237-249.

Hakola, H., Tarvainen, V., Laurila, T., Hiltunen, V., Hellén, H., and Keronen, P., 2003. Seasonal variation of VOC concentrations above a boreal coniferous forest, *Atmospheric Environment* 37, 1623–1634, 2003.

Hansen, U. and Seufert, G., 1999. Terpenoid emission from *Citrus sinensis* (L.) OSBECK under droughts stress, *Physics and Chemistry of the Earth B* 42, 681-687.

Hansen, U. and Seufert, G., 2003. Temperature and light dependence of β-caryophyllene emission rates, *Journal of Geophysical Research* 108(D249, 4801, doi:10.1029/2003JD003853.

Harley, R., Fridd-Stroud, V., Greenberg, J., Guenther, A., and Vasconcellos, P., 1998. Emission of 2-methyl-3-buten-2-ol by pines: A potentially large natural source of reactive carbon to the atmosphere, *Journal of Geophysical Research* 103(D19), 25,479-25,486.

Havas, P. and Sulkava, S., 1987. Suomen luonnon talvi, Kirjayhtymä, Helsinki, 222 pp (in Finnish).

Hellén, H., Hakola, H., Pystynen, K.-H., Rinne J., and Haapanala, S., 2006. C2-C10 hydrocarbon emissions from a boreal wetland and forest floor. *Biogeosciences.* 3, 167-174.

Helmig, D., Bocquet, F., Pollmann, J., and Revermann, T., 2004. Analytical techniques for sesquiterpene emission rate studies in vegetation enclosure experiments, *Atmospheric Environment* 38, 557-572.

Helmig, D., Ortega, J., Guenther, A., Herrick, J. D., and Geron, C., 2006. Sesquiterpene emissions from loblolly pine and their potential contribution to biogenic aerosol formation in the Southeastern US, *Atmospheric Environment* 40, 4150-4157.

Hoffmann, T., Odum, J. R., Bowman, F., Collins, D., Klockow, D., Flagan, R. C. and Seinfeld, J. H., 1997. Formation of organic aerosols from the oxidation of biogenic hydrocarbons, *Journal of Atmospheric Chemistry* 26, 189-222.

Holzke, C., Hoffmann, T., Jaeger, L., Koppmann, R., and Zimmer, W., 2006. Diurnal and seasonal variation of monoterpene and sesquiterpene emissions from Scots pine (*Pinus sylvestris* L.), *Atmospheric Environment* 40, 3174-3185.

IPCC, 2007. Climate Change 2007. The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 996 pp.

Janson, R., 1993. Monoterpene emissions from Scots pine and Norwegian spruce, *Journal of Geophysical Research* 98, 2839-2850.

Janson, R. and De Serves, C., 2001. Acetone and monoterpene emissions from the boreal forest in northern Europe, *Atmospheric Environment* 35, 4629-4637.

Janson, R., De Serves, C., and Romero, R., 1999. Emission of isoprene and carbonyl compounds from a boreal forest and wetland in Sweden, *Agricultural and Forest Meteorology* 98-99, 671-681.

Janson, R., Rosman, K., Karlsson, A., and Hansson, H.-C., 2001. Biogenic emissions and gaseous precursors to forest aerosols, *Tellus* 53B, 423-440.

Jaoui, M., Leungsakul, S. and Kamens R.M., 2003. Gas and particle products distribution from the reaction of β-caryophyllene with ozone, *Journal of Atmospheric Chemistry* 45, 261-287.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J., 2005. Organic aerosol and global climate modelling: a review, *Atmospheric Chemistry and Physics* 5, 1053-1123.

Kaplan, J. O., Folberth, G., and Hauglustaine, D. A., 2006. Role of methane and biogenic volatile organic compound sources in late glacial and Holocene fluctuations of atmospheric methane concentrations, *Global Biogeochem. Cycles* 20(2), GB2016, 10.1029/2005GB002590 ???

Kesselmeier, J., Bode, K., Hofmann, U., Müller, H., Schäfer, L., Wolf, A., Ciccioli, P., Brancaleoni, E., Cecinato, A., Frattoni, M., Foster, P., Ferrari, C., Jacob, V., Fugit, J. L., Dutaur, L., Simon, V., and Torres, L., 1997. Emission of short chained organic acids, aldehydes and monoterpenes from *Quercus ilex* L. and *Pinus pinea* L. in relation to physiological activities, carbon budget and emission algorithms. *Atmospheric Environment* 31(SI), 119-133.

Kesselmeier, J. and Staudt, M., 1999. Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology. *Journal of Atmospheric Chemistry* 33, 23-88.

Komenda, M. and Koppmann, R., 2002. Monoterpene emissions from Scots pine (*Pinus sylvestris*): Field studies of emission rate variabilities. *Journal of Geophysical Research* 107(D13), 10.1029/2001JD000691.

Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Ciccioli, P., Brancaleoni, E., Frattoni, M., Tavares, T. M., and Kesselmeier, J., 2002. Isoprene and monoterpene emissions of Amazonian tree species during the wet season: Direct and indirect investigations on controlling environmental functions. *Journal of Geophysical Research* 107(D20), 10.1029/2001JD000978.

Lamb, B., Guenther, A., Gay, D., and Westberg, H., 1987. A national inventory of biogenic hydrocarbon emissions. *Atmospheric Environment* 21(8), 1695-1705.

Lamb, B., Gay, D., and Westberg, H., 1993. A biogenic hydrocarbon emission inventory for the U.S.A. using a simple forest canopy model. *Atmospheric Environment* 27A(11), 1673-1690.

Lamb, B., Pierce, T., Baldocci, D., Allwine, E., Dilts, S., Westberg, H., Geron, C., Guenther, A., Klinger, L., Harley, P., and Zimmerman, P., 1996. Evaluation of forest caopy models for estimating isoprene emissions. *Journal of Geophysical Research* 101(D17), 22,787-22,797.

Lappalainen, H., 1993. Relations between climate and plant phenology; examples of plant phenological events in Finland and their relation to effective temperature sum. Licentiate Thesis, University of Helsinki, Department of Botany, 115 pp.

Laurila, T. and Lindfors, V. (Eds), 1999. Biogenic VOC emissions and photochemistry in the boreal regions of Europe. Air Pollution Research Report No 70, Commission of the European Communities, Luxembourg, ISBN 92-828-6990-3, 158 pp.

Lerdau, M. T., 1991. Plant function and biogenic terpene emission. In: Trace Gas Emissions by Plants, Sharkey, T. D. et al., (eds), Academic Press, Inc. San Diego, California*,* 121-134.

Lerdau, M., 2007. A positive feedback with negative consequences, *Science* 316, 212-213.

Lindinger, W., Hansel, A., and Jordan, A., 1998. Proton-transfer-reaction mass spectrometry (PTR–MS): on-line monitoring of volatile organic compounds at pptv levels, *Chemical Society Reviews* 27, 347-354.

Llusià, J. and Peñuelas, J., 2000. Seasonal patterns of terpene content and emission from seven Mediterranean woody species in field conditions. *Botany* 87(1), 133–140.

Loreto, F. and Fares, S., 2007. Is ozone flux inside leaves only a damage indicator? Clues from volatile isoprenoid studies, *Plant Physiology* 143, 1096-1100.

MacDonald, R. and Fall, R., 1993. Detection of substantial emissions of methanol from plants to the atmosphere. *Atmospheric Environment* 27, 1709–1713.

McGarvey, D. J. and Croteau, R., 1995. Terpenoid metabolism, *The Plant Cell* 7, 1015-1026.

Müller, J.-F., 1992. Geographical distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gases, *Journal of Geophysical Research* 97(D4), 3787-3804.

Nerg, A., Kainulainen, P., Vuorinen, M., Hanso, M., Holopainen, J. K., and Kurkela, T., 1994. Seasonal and geographical variation of terpenes, resin acids and total phenolics in nursery grown seedlings of Scots pine (*Pinus sylvestris* L.), *New Phytologist* 128, 703-713.

Nozière, B. and Esteve, W., 2005. Organic reactions increasing the absorption index of atmospheric sulfuric acid aerosols, *Geophysical Research Letters* 32, L03812, doi:10.1029/2004GL021942.

Picott, S. D., Watson, J. J., and Jones, J. W., 1992. A Global inventory of volatile organic compound emissions from anthropogenic sources, *Journal of Geophysical Research* 97(D9), 9897-9912.

Pierce, T. E., 1996. Update to PC-BEIS: Release of Version 2.2. U.S. Environmental Protection Agency, Research Triangle Park, N.C.

Pierce, T. E. and Baugues, K. A., 1991. User's guide to the personal computer version of the biogenic emissions inventory system (PC-BEIS). Office of Air Quality Planning and Standards, EPA-450/4-91-017, U.S. Environmental Protection Agency, Research Triangle Park, N.C.

Pierce, T., Geron, C., Bender, L., Dennis, R., Tonnesen, G., and Guenther, A., 1998. Influence of increased isoprene emissions on regional ozone modeling. *Journal of Geophysical Research* 103(D19), 25,611-25,629.

Rasmussen, R. A. and Went, F. W., 1965. Volatile organic material of plant origin in the atmosphere, *Proceedings of the National Academy of Sciences of the United States of America* 46, 215-220.

Rinne, J., Hakola, H., and Laurila, T., 1999. Vertical fluxes of monoterpenes above a Scots pine stand in the boreal vegetation zone, *Physics and Chemistry of Earth (B)* 24, 215-220.

Rinne, J., Hakola, H., Laurila, T., and Rannik, Ü., 2000a. Canopy scale monoterpene emissions of *Pinus Sylvestris* dominated forests, *Atmospheric Environment* 34, 1099-1107.

Rinne, J., Tuovinen, J.-P., Laurila, T., Hakola, H., Aurela, M., and Hypén, H., 2000b. Measurements of hydrocarbon fluxes by a gradient method above a northern boreal forest, *Agricultural and Forest Meterology* 102, 25-37.

Rinne, H. J. I., Guenther, A. B. 1, Greenberg, J. P., and Harley, P. C., 2002. Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature, *Atmospheric Environment* 36(14), 2421-2426.

Rinne, J., Ruuskanen, T. M., Reissell, A., Taipale, R., Hakola, H., and Kulmala, M., 2005. On-line PTR-MS measurements of atmospheric concentrations of volatile organic compounds in a european boreal forest ecosystem, *Boreal Environment Research* 10, 425-436.

Rinne, J., Taipale, R., Markkanen, T., Ruuskanen, T. M., Hellén, H., Kajos, M. K., Vesala, T., and Kulmala, M., 2007. Hydrocarbon fluxes above a Scots pine forest canopy: measurements and modeling, *Atmospheric Chemistry and Physics* 7, 3361-3372.

Ruuskanen, T. M., Kolari, P., Bäck, J., Kulmala, M., Rinne, J., Hakola, H., Taipale, R., Raivonen, M., Altimir, N., and Hari, P., 2005. On-line field measurements on monoterpene emissions from Scots pine by proton-transfer-reaction mass spectrometry, *Boreal Environment Research* 10, 553-567.

Ruuskanen, T. M., Hakola, H., Kajos, M. K., Hellén, H., Tarvainen, V., and Rinne, J., 2007. Volatile organic compound emissions from Siberian larch, *Atmospheric Environment* 41, 5807-5812.

Sanadze, G. A., 2004. Biogenic isoprene (a review), *Russian Journal of Plant Physiology* 51(6), 729-741.

Schade, G. W., Goldstein, A. H., Gray, D. W., and Lerdau, M. T., 2000. Canopy and leaf level 2-methyl-3-buten-2-ol fluxes from a ponderosa pine plantation, *Atmospheric Environment* 34, 3535-3544.

Schuh, G., Heiden, A. C., Hoffmann, T., Kahl, J., Rockel, P., Rudolph, J., and Wildt, J., 1997. Emissions of volatile organic compounds from sunflower and beech: Dependence on temperature and light intensity, *Journal of Atmospheric Chemistry* 27, 291-318.

Shao, M., Czapiewski, K. V, Heiden, A. C., Kobel, K., Komenda, M., Koppmann, R., and Wildt, J., 2001. Volatiel organic compound emissions from Scots pine: Mechanisms and description by algorithms, *Journal of Geophysical Research* 106(D17), 20483-20491.

Sharkey, T. D. and Yeh, S., 2001. Isoprene emission from plants, *Annual Review of Plant Physiology and Plant Molecular Biology* 52, 407-436.

Schürmann, W., Ziegler, H., Kotzias, D., Schönwitz, R., and Steinbrecher, R., 1993. Emission of biosynthesized monoterpenes from needles of Norway spruce. *Naturwissenchaften*, 80, 276-278.

Simpson, D., Guenther, A., Hewitt, and Steinbrecher, R., 1995. Biogenic emissions in Europe 1. Estimates and uncertainties. *Journal of Geophysical Research* 100(D11), 22,875-22,890.

Simpson, D., Winiwarter, W., Börjesson, G., Cinderby, S., Ferreiro, A., Guenther, A., Hewitt, C. N., Janson, R., Khalil, M. A. K., Owen, S., Pierce, T. E., Puxbaum, H., Shearer, M., Steinbrecher, R., Tarrasón, L., and Öquist, M. G., 1999. Inventorying emissions from nature in Europe. *Journal of Geophysical Research* 104(D7), 8113-8152.

Staudt, M. and Seufert, G., 1995. Light-dependent emission of monoterpenes by Holm Oak (Quercus ilex L.). *Naturwissenschaften* 82, 89-92.

Staudt, M., Bertin, N., Hansen, U., Seufert, G., Ciccioli, P., Foster, P., Frenzel, B., and Fugit, J.-L., 1997. Seasonal and diurnal patterns of monoterpene emissions from *Pinus pinea* (L.) under field conditions. *Journal of Atmospheric Chemistry* 35, 77-99.

Staudt, M., Bertin, N., Frenzel, B., and Seufert, G., 2000. Seasonal variation in amount and composition of monoterpenes emitted by young *Pinus pinea* trees – Implications for emission modeling. *Atmospheric Environment* 31(SI), 145-156.

Steinbrecher, R., Hauff, K., Hakola, H., and Rössler, J., 1999. A revised parameterisation for emission modelling of isoprenoids for boreal plants. In: Biogenic VOC emissions and photochemistry in the boreal regions of Europe, Laurila, T., Lindfors, V. (eds), Air Pollution Research Report No 70, Commission of the European Communities, Luxembourg, ISBN 92-828-6990-3, 29-43.

Steiner, A. H. and Goldstein, A. L., 2007. Biogenic VOCs. In: Volatile organic compounds in the atmosphere, Koppmann, R. (Ed.), Blackwell Publishing Ltd, Oxford, 82-128.

Tingey, D. T., Manning, M., Grothaus, L. C., and Burns, W. F., 1980. Influence of light and temperature on monoterpene emission rates from slash pine, *Plant Physiology* 65, 797-801.

Tingey, D. T., Turner, D. P., and Weber, J. A., 1991. Factors controlling the emissions of monoterpenes and other volatile organic compounds. In: Trace Gas Emissions by Plants, Sharkey, T. D. et al., (eds), Academic Press, Inc. San Diego, California, 93-119.

Tunved, P., Hansson, H.-C., Kerminen, V.-M., Ström, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P. P., Komppula, M. and Kulmala, M., 2006. High natural aerosol loading over boreal forests, *Science* 312, 261-263.

Warneck, P., 2000. Chemistry of the natural atmosphere, second edition, Academic Press, Inc. San Diego, CA, U.S.A. and London, United Kingdom, 927 pp.

Went, F. W., 1960a. Organic matter in the atmosphere, and its possible relation to petroleum formation, *Proceedings of the National Academy of Sciences of the United States of America* 46, 212-221.

Went, F. W., 1960b. Blue hazes in the atmosphere, *Nature* 187, 641-643.

Wiedinmyer, C., Guenther, A., Harley, P., Hewitt, N., Geron, C., Artaxo, P., Steinbrecher, R., and Rasmussen, R., 2004. Global organic emissions from vegetation. In: Emissions of atmospheric trace compounds, Granier, C. et al. (eds), Kluwer Academic Publishers, Dordrecht, 115-170.

Williams, J. and Koppmann, R., 2007. Volatile organic compounds in the atmosphere: An overview. In: Volatile organic compounds in the atmosphere, Koppmann, R. (Ed.), Blackwell Publishing Ltd, Oxford, United Kingdom, 82-128.