REPORT SERIES IN AEROSOL SCIENCE
N:o 101 (2009)

MEASUREMENTS OF VOLATILE ORGANIC COMPOUNDS – FROM BIOGENIC EMISSIONS TO AMBIENT CONCENTRATIONS

TAINA MARIA RUUSKANEN

Division of Atmospheric Sciences and Geophysics
Department of Physics
Faculty of Science
University of Helsinki
Helsinki, Finland

Academic dissertation

To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public criticism in auditorium E204, Gustaf Hällströmin katu 2, on February, Friday 13th, 2009, at 12 o'clock.

Helsinki 2009

ISBN 978-952-5822-00-7
ISSN 0784-3496
Helsinki 2009
Yliopistopaino

ISBN 978-952-5822-01-4 (E-thesis version)
http://ethesis.helsinki.fi/
Helsinki 2009
Helsingin yliopiston verkkojulkaisut

Acknowledgements

The research for this thesis as well as much other scientific work has been an unlimited source of joy and challenges to me. Firstly, I wish to thank the head of the Department of Physics, Professor Juhani Keinonen, for providing work facilities at Physicum and Exactum. I also owe my thanks to Professor Markku Kulmala for giving me the opportunity for this long and fascinating journey with experts from all fields, for the instruments and equipment (including limitless amounts of Teflon tube), and especially for the excellent cross-disciplinary facilities of SMEAR II. I am also grateful to the Nordic Centre of Excellence, BACCI, for the important contacts with colleagues in Nordic atmospheric research, as well as for the opportunities to have travel discussions, that enabled research supervision, with Markku. I am indebted to my supervisor Docent Janne Rinne for his guidance and active support.

I also wish to thank Docent Hannele Hakola for her always enjoyable and effective steering, and helpful comments that were followed with an “and..”, not a “but..”. I thank Dr. Heidi Hellén, too, for her reliable and invariably high quality sample analyses, Dr. Anni Reissell for guidance at the beginning of my Ph.D. and for sharing her knowledge on volatile organic compounds in the atmosphere, Toivo Pohja for long and valuable talks on the properties of hardware in its true meaning that were started with a story on something completely different, Erkki Siivola for opening my eyes to the opportunities for fun in research, such as skiing during maintenance trips to SMEAR I at Värriö. I thank Docent Hanna Vehkamäki for sharing views on research and life, and for selling her old car that enabled the transport of light (less than 100 kg) equipment to the measurement site. I also want to thank my fellow VOC researchers: Heidi, Risto, Maija, Johanna and Sami, as well as all my co-authors and colleagues for their support and the fun we have had together in everyday science.

I acknowledge the Finnish Academy, the Finnish Centre of Excellence research unit in Physics, Chemistry and Biology of Atmospheric Composition and Climate Change, the Nordic Centre of Excellence research unit in Biosphere-Atmosphere-Cloud-Climate Interactions (BACCI), the University of Helsinki Rectors fund and the Nessling foundation for the funding they have provided.

I want to express my gratitude for the love and support of my parents Vesa and Aune, to my extended family, especially Matti for Olli’s daycare in the winter of 07-08. I value my friends, also those that I’m at home with, even when the previous time we met was two years ago. I hope our paths keep crossing despite the long distances and my poor letter writing and phone-calling skills. I thank Tytöt for sharing honest views as well as numerous bottles of red wine.

Finally I wish to thank my husband Janne Metsomäki: you make my life good. I hope our son Olli will find his own path in life and live it without fear.

Measurements of Volatile Organic Compounds - from Biogenic Emissions to Concentrations in Ambient Air

Taina Maria Ruuskanen
University of Helsinki, 2009

Volatile organic compounds (VOCs) affect atmospheric chemistry and thereafter also participate in the climate change in many ways. The long-lived greenhouse gases and tropospheric ozone are the most important radiative forcing components warming the climate, while aerosols are the most important cooling component. VOCs can have warming effects on the climate: they participate in tropospheric ozone formation and compete for oxidants with the greenhouse gases thus, for example, lengthening the atmospheric lifetime of methane. Some VOCs, on the other hand, cool the atmosphere by taking part in the formation of aerosol particles. Some VOCs, in addition, have direct health effects, such as carcinogenic benzene. VOCs are emitted into the atmosphere in various processes. Primary emissions of VOC include biogenic emissions from vegetation, biomass burning and human activities. VOCs are also produced in secondary emissions from the reactions of other organic compounds. Globally, forests are the largest source of VOC entering the atmosphere. This thesis focuses on the measurement results of emissions and concentrations of VOCs in one of the largest vegetation zones in the world, the boreal zone.

An automated sampling system was designed and built for continuous VOC concentration and emission measurements with a proton transfer reaction - mass spectrometer (PTR-MS). The system measured one hour at a time in three-hourly cycles: 1) ambient volume mixing-ratios of VOCs in the Scots-pine-dominated boreal forest, 2) VOC fluxes above the canopy, and 3) VOC emissions from Scots pine shoots. In addition to the online PTR-MS measurements, we determined the composition and seasonality of the VOC emissions from a Siberian larch with adsorbent samples and GC-MS analysis.

The VOC emissions from Siberian larch were reported for the fist time in the literature. The VOC emissions were 90% monoterpenes (mainly sabinene) and the rest sesquiterpenes (mainly α-farnesene). The normalized monoterpene emission potentials were highest in late summer, rising again in late autumn. The normalized sesquiterpene emission potentials were also highest in late summer, but decreased towards the autumn. The emissions of mono- and sesquiterpenes from the deciduous Siberian larch, as well as the emissions of monoterpenes measured from the evergreen Scots pine, were well described by the temperature-dependent algorithm. In the Scots-pine-dominated forest, canopy-scale emissions of monoterpenes and oxygenated VOCs (OVOCs) were of the same magnitude. Methanol and acetone were the most abundant OVOCs emitted from the forest and also in the ambient air. Annually, methanol and mixing ratios were of the order of 1 ppbv. The monoterpene and sum of isoprene – 2-methyl-3-buten-2-ol (MBO) volume mixing-ratios were an order of magnitude lower. The majority of the monoterpene and methanol emissions from the Scots-pine-dominated forest were explained by emissions from Scots pine shoots. The VOCs were divided into three classes based on the dynamics of the summer-time concentrations: 1) reactive compounds with local biological, anthropogenic or chemical sources (methanol, acetone, butanol and hexanal), 2) compounds whose emissions are only temperature-dependent (monoterpenes), 3) long-lived compounds (benzene, acetaldehyde). Biogenic VOC (methanol, acetone, isoprene–MBO and monoterpene) volume mixing-ratios had clear diurnal patterns during summer. The ambient mixing ratios of other VOCs did not show this behaviour. During winter we did not observe systematical diurnal cycles for any of the VOCs. Different sources, removal processes and turbulent mixing explained the dynamics of the measured mixing-ratios qualitatively. However, quantitative understanding will require long-term emission measurements of the OVOCs and the use of comprehensive chemistry models.

Keywords: Hydrocarbons, VOC, fluxes, volume mixing-ratio, boreal forest

Nomenclature:

α	ratio of transmission coefficient for water cluster to that for primary ion
A	all-sided shoot needle area
β	temperature-dependent emission factor
c	concentration of a VOC
C_a	concentration of a VOC in ingoing air to a manual chamber or initial concentration of a VOC in an automated online chambers
C_f	concentration of a VOC in outgoing air from a manual chamber or final concentration of a VOC in an automated online chambers
C_{L1}, C_{T1}, C_{T2}, C_{T3}	empirical constants given for *E(T,PPFD)* by Guenther (1997)
E	applied electric field in drift tube (reaction chamber),
E_{VOC}	emission of a VOC
E(T)	temperature-dependent emission
E(T,PPFD)	temperature and light-dependent emission
E_0	emission potential, traditionally normalized to emission at 30°C
F	flow rate
F	flux
F_{VOC}	fragmentation fraction of a VOC
φ	empirical constant for given by Guenther (1997)
γ	activity factor depending on environmental conditions
$\gamma(T,PPFD)$	activity factor depending on temperature and light
σ_{voc}	calibration coefficient of a VOC (from direct standard gas calibration)
$[H_3O^+]$	concentration of hydronium ion
I_{norm}	primary ion signal used for normalization (10^6 cps)
$I(VOCH^+)_{norm}$	VOC signal normalized with I_{norm} in cps and p_{norm}
$I(VOCH^+)$	ion signal of a protonated VOC (hydrocarbon) in cps
$I(VOCH^+)_{zero}$	ion signal during zero (signal background) measurement of a VOC in cps
$I(H_3O^+)$	primary ion signal in cps
$I(H_2O\ H_3O^+)$	water cluster signal in cps
k_{VOC}	reaction rate constant of a VOC
L	length of drift tube (reaction chamber)
λ	photosynthetic photon flux density for *E(T,PPFD)*

m	dry weight of needle biomass
N	number density of gas molecules in air
N_0	number density of air at standard temperature and pressure (273.15 K and 1013.25 hPa)
N_A	Avogadro's constant
p_{amb}, p_r, p_{norm}	ambient pressure, pressure of reaction chamber, pressure used for normalization (2 hPa)
n	number of measurements
R	universal gas constant
S_{norm}	normalized sensitivity of a VOC from a direct gas calibration
t_r	reaction time in reaction chamber
T, T_r, T_{amb}	temperature, temperature in reaction chamber, ambient temperature
T_M	empirical temperature constant given by Guenther (1997)
$trans_{voc}$, $trans_{voc,rel}$	transmission factor of a VOC, relative to primary ion H_3O^+
$trans_{H_3O^+}$, $trans_{H_2OH_3O^+}$	transmission factor of primary ion (at M21 or more exactly 21 amu mass-to-charge ratio), water cluster (at M39)
V_m	molar volume of ideal gas
$VOCH^+$	protonated volatile organic compound
$[VOCH^+]$	concentration of a protonated volatile organic compound
VMR_{ppb}	volume mixing-ratio in parts per billion
μ_o	normalized ion mobility of primary ions

Abbreviations:

amu	atomic mass unit
asl	above sea level
BVOC	biogenic volatile organic compound
cps	counts per second
DEC	disjunct eddy covariance
GC	gas chromatograph
M21	21 amu mass-to-charge ratio, notation for PTR-MS measurements
OVOC	oxidized volatile organic compound
PTR-MS	proton transfer reaction - mass spectrometer
PPFD	photosynthetic photon flux density
ppbv	parts per billion by volume
ppmv	parts per million by volume
pptv	parts per trillion by volume
QMS	quadrupole mass spectrometer
SEM	secondary electron multiplier
SMEAR	station for measuring forest ecosystem - atmosphere relations
VOC	volatile organic compound
VMR	volume mixing-ratio

Key compounds

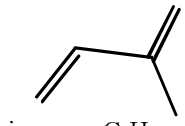
water	H_2O
hydronium, primary ion	H_3O^+
water clusters	$(H_2O)_nH_2O$, n = 1,2,3...
protonated water clusters	$(H_2O)_nH_3O^+$, n = 1,2,3...
manganese oxide	MnO

Volatile organic compounds (VOCs):

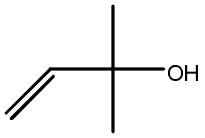
acetonitrile	C_2H_3N
acetaldehyde	C_2H_4O
acetone	C_3H_6O
benzene	C_6H_6
isoprene	C_5H_8
methanol	CH_4O
monoterpenes: α-pinene β-pinene camphene Δ^3-carene limonene	$C_{10}H_{16}$
methacrolein (MACR)	C_4H_6O
2-methyl-3-buten-2-ol (MBO)	$C_5H_{10}O$
methyl-ethyl-ketone (MEK)	C_4H_8O
methyl-vinyl-ketone (MVK)	C_4H_6O
sesquiterpenes: α-farnesene α-caryophyllene β-caryophyllene β-bourbonene β-cubinene longifolene isolongifolenene s-cadinene	$C_{15}H_{24}$
toluene	C_7H_8

Chemical structures of key terpenoids

Hemiterpenoids

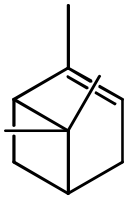


isoprene, C_5H_8

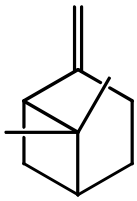


2-methyl-3-buten-2-ol, $C_5H_{10}O$ (MBO)

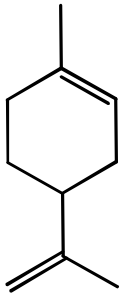
Monoterpenes, $C_{10}H_{16}$



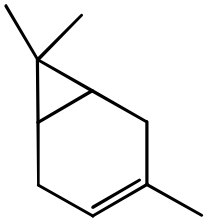
α-pinene



β-pinene

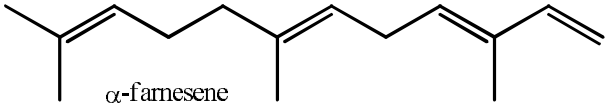


limonene

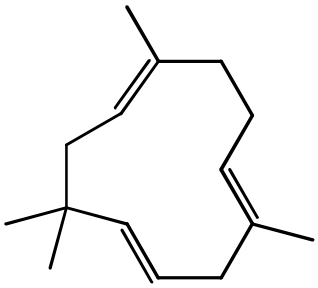


Δ^3-carene

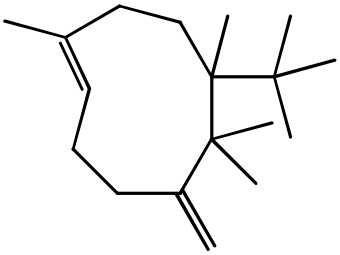
Sesquiterpenes, $C_{15}H_{24}$



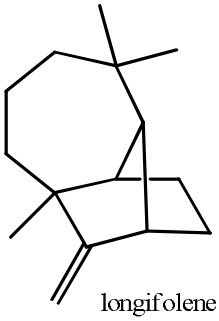
α-farnesene



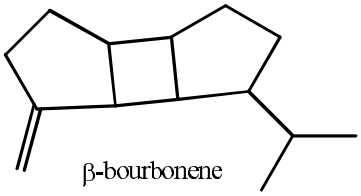
α-caryophyllene



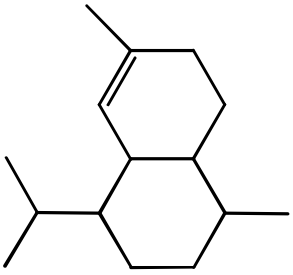
β-caryophyllene



longifolene



β-bourbonene



cubinene

Contents

List of publications

This thesis consists of an introductory review and six peer-reviewed research articles. Papers I, II and IV are reproduced with the kind permission of the journals concerned and papers III, V and VI under Creative Commons Attribution Licence. In the Introduction, the papers are cited according to their Roman numerals.

I 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 of monoterpene emissions from Scots pine by proton-transfer-reaction mass spectrometry. *Boreal Env. Res.* 10, 553–567.

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

III 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. *Atmos. Chem. Phys.* 7, 3361-3372.

IV 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 Env. Res.* 10, 425-436.

V Taipale R., Ruuskanen T.M., Rinne J., Kajos M.K., Hakola H., Pohja T. and Kulmala M. 2008. Technical note: Quantitative long-term measurements of VOC concentrations by PTR-MS – measurement, calibration, and volume mixing ratio calculation methods. *Atmos. Chem. Phys.* 8, 6681-6698.

VI Ruuskanen T.M., Taipale R., Rinne J., Kajos M.K., Hakola H. and Kulmala M. 2009. Quantitative long-term measurements of VOC concentrations by PTR-MS: Annual cycle of ambient concentrations at a boreal forest site. *Atmos. Chem. Phys. Disc.* 9, 81-134.

1 Introduction

Volatile organic compounds (VOCs) are emitted from biogenic and anthropogenic sources. Primary emissions of VOCs include biogenic emissions from vegetation, biomass burning and human activities. In addition, VOCs are produced in secondary emissions from the reactions of other organic compounds. Globally, biogenic emissions are estimated to be ten times higher than anthropogenic emissions, with only densely-populated and urban areas being dominated by anthropogenic emissions (e.g. Müller, 1992; Müller et al., 2008; Piccot et al., 1992; Guenther et al., 1995; Simpson et al., 1995; 1999; Lindfors et al., 2000, Hellén et al., 2006a).

Biogenic VOC (BVOC) emissions are usually of the order of 0.2-10% of the carbon assimilated by a plant, depending on the vegetation, time of the year, temperature or water availability (e.g. Sharkey et al., 1996; Guenther, 2002; Kesselmeier et al., 2002). However, for a few days the emissions can amount up to 20-70% of the assimilated carbon e.g. when the plants are under water or heat stress (Kesselmeier et al., 2002). The estimated VOC fluxes are small in relation to net and gross primary productivity, however, the VOC emissions can be of the same order of magnitude as net carbon uptake in tropical (Guenther, 2002) and Mediterranean vegetation zones (Kesselmeier et al., 2002). The estimates of the VOC emissions vary largely and are problematic due to the variation, within- and between-species, of the amount and composition of the emitted VOCs from the plant, the strong seasonality of the emissions, and the large number of emitted compounds. Compounds emitted by the vegetation include isoprenoids or terpenoids including: isoprene (C_5H_8), 2-methyl-3-buten-2-ol (MBO, formally formed from one isoprene unit and OH-group aka $C_5H_{10}O$) monoterpenes (two isoprene units aka $C_{10}H_{16}$) and sesquiterpenes (three isoprene units aka $C_{15}H_{24}$). Another important group of emitted compounds comprise of oxygenated VOCs (OVOCs), mainly of methanol (CH_4O), acetone (C_3H_6O) and acetaldehyde (C_2H_4O), and also minor contribution of methyl-ethyl-ketone (MEK, C_4H_8O) and methyl-vinyl-ketone (MVK, C_4H_6O). The BVOCs are emitted by all vegetation: including trees, shrubs, crops, grass. On the global scale, the largest BVOC sources are the tropical and other forests, with their large isoprene, monoterpene and methanol emissions (Guenther et al., 1995; 2006). The tropical, temperate and boreal forests cover areas of the same order of magnitude 17.6, 10.4 and 13.7 million km^2, respectively (IPCC 2000). However, the total carbon stock, including all vegetation but not carbon stored in soil, of the tropical forests is 212 gigatons of carbon (GtC), while the boreal forest store 88 GtC and temperate forests only 59 GtC (IPCC 2000). Global VOC emission estimates are, so far, most reliable for isoprene. Guenther et al. (2006) estimated that of the global isoprene emissions 75% is from the tropical vegetation zone from which 45% is from forests and 28% is from shrubs. The rest are from arid shrubs (11%), and only few percents of the global isoprene emissions are from Mediterranean and boreal zones. However, unlike the isoprene emitting tropical forest, the boreal forest tree species are mostly monoterpene emitters. Tarvainen et al. (2007) calculated that of the terpene emissions from boreal forests in Finland over 80% are monoterpenes, and less than 10% isoprene and sesquiterpenes, respectively. Using the annual estimate of VOC emissions (Tarvainen et al., 2007) and the annual carbon uptake, measured at SMEAR II (Suni et al., 2003), the VOC emissions are between 0.3 and 0.7 % of the assimilated carbon in the boreal forest in Finland. A similar value was estimated for a boreal fen: the proportion of assimilated carbon emitted as VOC is of the order of 0.5% (Aurela et al., 2007).

Biomass burning is an important source of VOCs into the atmosphere. Globally biomass burning is a large source of aromatic hydrocarbons (including benzene, C_6H_6, and toluene, C_7H_8), nitriles (including acetonitrile, C_2H_3N), and OVOCs (Crutzen & Andreae, 1990; Andreae & Merlet, 2001; Karl et al., 2007; Yokelson et al., 2007). In urban and residential areas in Finland for the winter concentrations of VOC the wood combustion can be distinguished from other VOC sources in the ambient air (Hellén et al. 2006a). However, since the emitted VOCs are the same from all types of biomass burning, it is impossible to distinguishing between controlled biomass burning, such as wood combustion in fireplaces, from anthropogenic or natural fires.

Boreal forest BVOC emissions have been widely studied (e.g. Isidorov et al., 1985; Rinne at al., 1999; 2000a; 2000b; Janson, 1993; Hakola et al., 2000; 2003; Lindfors & Laurila, 2000; Lindfors et al., 2000; Janson & de Serves, 2001; Spanke et al., 2001; Karl et al., 2003; Hellén et al., 2004; 2006a; Hayward et al., 2004; Spirig et al., 2005; Haapanala et al., 2007; Tarvainen et al., 2005; 2007). Traditionally the focus has been on isoprene and monoterpene emissions. Direct emissions after synthesis depend on enzyme kinetics and thus are light and temperature driven whereas the emissions from storage pools depend on diffusion and thus are driven by temperature only (Grote & Niinemets, 2008). Emitted terpenoids depend on the plant: an aspen (*Populus tremula*) emits isoprene but not monoterpenes; while Scots pine (*Pinus sylvestris*) does not emit isoprene and emits monoterpenes. Isoprene storage pools are small and the synthesis and emission rates are practically equal, whereas mono- and sesquiterpene of conifers are stored in large resin ducts and synthesis and emission rates can be effectively decoupled (Grote & Niinemets, 2008). These have been modelled with a) leaf temperature and b) photosynthetic photon flux density (PPFD) and leaf temperature that have both been normalized with a species-specific basal emission rate (Tingey et al., 1980; Guenther et al., 1993; Guenther, 1997; Schuh et al., 1997, Grote & Niinemets, 2008). Often, air temperature is used for the leaf temperature and visible light is used for the PPFD, which is the intensity of solar irradiation of wavelengths used in photosynthesis. The emission response to environmental conditions depends on the physiological state of the plant, the development stage and the age of leafs or needles as well as on acclimation to the environment during previous hours or days (Grote & Niinemets, 2008). Annually and inter-annually, changes in BVOC emissions can be parameterized by leaf maturity, past weather conditions, growth environment, as well as nutrient and water availability (Guenther et al., 2006). The emissions of monoterpene from Scots pine are dominated by emissions from storage pools, and thus they are well described by the temperature algorithm (Shao et al., 2001). However, emissions of some monoterpenes have been observed to also depend on irradiation (Shao et al., 2001). In addition, the monoterpene emissions of Scots pine are very sensitive to mechanical stress: rough handling can increase them by 50-fold (Juuti et al., 1990). The mono- and sesquiterpenes are even emitted from conifer needle litter (Isidorov et al., 2003) and tree stumps (Hakola et al., 2008). Monoterpene emissions from Scots pine and other boreal evergreens have a clear seasonality. Their basal emission rates change during the growing season (e.g. Shao et al., 2001; Komenda & Koppmann, 2002; Staudt et al., 2000; Hakola et al., 2003; 2006; Bäck et al., 2005; Tarvainen et al., 2005). The understanding of BVOC emissions has advanced tremendously in the past decades. However, some old questions remain unanswered and new ones have emerged. At the moment, the key gaps in the knowledge of emissions of BVOC from

the Eurasian boreal forests are the lack of mechanistic models with both direct emissions from synthesis and those from storage pools, as well as, understanding emission mechanisms of OVOCs (Rinne et al., 2008).

The ambient concentrations of monoterpenes in a boreal forest are dominated by local and regional emissions, since their lifetimes are generally of the order of hours or less (Spanke et al., 2001; Karl & Guenther, 2004). Sesquiterpenes are even more reactive and can be effectively removed from the ambient air even during short range transport. For example, β-caryophyllene, the major sesquiterpene emitted from Scots pine is (e.g. Hakola et al., 2003; 2006), has an atmospheric lifetime of the order of minutes (Shu and Atkinson, 1995). Methanol, however, has an atmospheric lifetime of the order of days or weeks (Atkinson, 1994) and thus can be transported over long distances. Biogenic emissions are clearly the dominant source of methanol into the atmosphere, as reviewed by Heikes et al. (2002). They estimated that secondary formation from methane oxidation is the second-most-important source, contributing about 10% of the global budget. In addition a few percents of methanol come from primary anthropogenic emissions and biomass burning. Once emitted, the fate of a VOC depends on numerous processes that are sketched out in Figure 1.

Organic compounds take part in ozone formation in the troposphere, and react with OH, ozone and NO_3, thus affecting the oxidative capacity of the atmosphere and air quality (e.g. Chameides et al., 1992; Fehsenfeld et al., 1992; Simpson, 1995; Atkinson & Arey, 2003). Some VOCs also have direct health effects, such as carcinogenic benzene. The oxidation products of VOCs may remain volatile and undergo further oxidation until they eventually form CO_2 and H_2O. Oxidation also forms less volatile organic compounds that can deposit on surfaces or take part in secondary aerosol formation by condensing on pre-existing particles (review by Kroll & Seinfeld, 2008). The organic compounds may also take part in aerosol particle nucleation, e.g. Zhang et al. (2004) suggest that organic acids enhance new particle formation of sulphuric acid in the atmosphere. Atmospheric particles are formed practically everywhere in the world in various different environments (review by Kulmala et al., 2004b), and it has been estimated that 20-90% of the particulate mass in troposphere is organic (review by Kanakidou et al., 2005). Globally, the majority of the organic particulate matter is from secondary organic aerosol (SOA) formation and the minority from different primary emissions (Kanakidou et al., 2005). Even in aging urban pollution plumes the majority of the organic particulate matter is from secondary organic aerosol formation of anthropogenic VOCs and minority from primary emissions e.g. from fossil fuel burning (de Gouw et al., 2008). The SOA-formation includes both growth of pre-existing aerosol particles and formation of new particles. On global scale majority of the SOA precursors are biogenic VOCs (Kanakidou et al., 2005). However, determining the key compounds is very difficult and only few of the compounds have been identified. Isoprene, as an example, was thought not to take part in SOA formation before Claeys et al. (2004) determined its oxidation products in aerosol particles over tropical forests. Later studies have suggested that isoprene related SOA formation is common and that even marine aerosols grow from the isoprene produced by phytoplankton (Meskhidze & Nenes, 2006). Secondary organic aerosol formation has been observed over boreal forests (e.g. Kulmala, 2003; Kulmala et al., 2004a; Tunved et al., 2006; Bonn et al., 2008). Organic compounds that have been identified in the aerosols include oxidation products of monoterpenes (e.g. Kavouras et al., 1999; Yu et al., 1999; Kourtchev et

al., 2008) and isoprene (Claeys et al., 2004a; 2004b; Kourtchev et al., 2005). Even new particle formation or nucleation from natural BVOC emissions from boreal forest has been suggested (Bonn et al., 2008; Boy et al., 2008), but so far this has only been directly measured in laboratory conditions (VanReken et al., 2006).

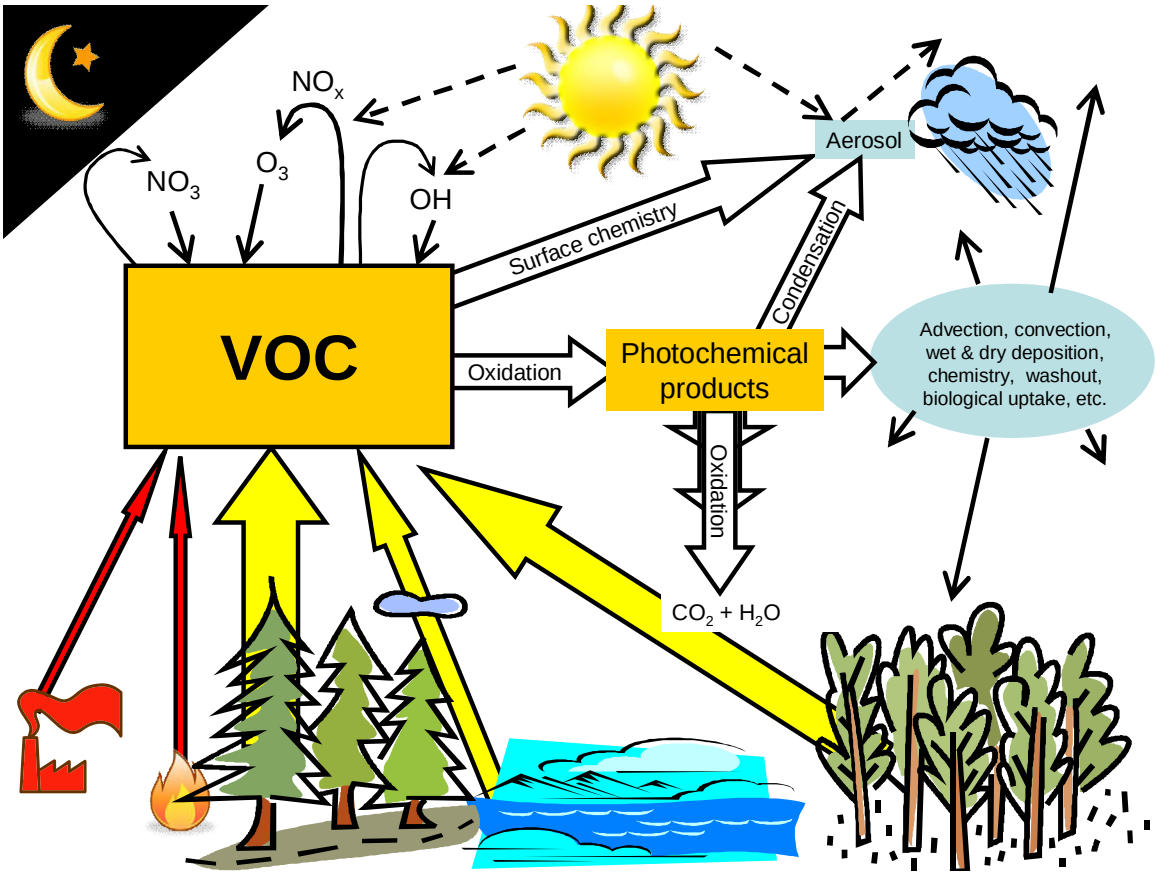


Figure 1. Schematic figure of the various processes which determine the fate of VOCs in the atmosphere, revised from Williams & Koppmann (2007).

In order to understand the various ways in which VOCs participate in atmospheric processes, reliable measurements of VOC composition and how it varies on different spatial and temporal scales are required. The traditional analytical methods for VOC measurements have been chromatographic analysis of VOCs trapped in different adsorbents such as Tenax-TA and Carbopack-B - suitable for hydrocarbons, or derivative adsorbent DNPH-coated C_{18}-cartrages - suitable for carbonyls. In recent decades the detection levels of analytical methods have come down to the ambient level. This has enabled the use of such instruments online, without sampling and pre-treatment to concentrate the measured compounds. These online measurement methods enable long-term datasets with high time resolution. One of the new instruments is proton transfer reaction - mass spectrometry (PTR-MS), and it has been widely applied in atmospheric online concentration measurements (for a review see de Gouw & Warneke, 2007). The PTR-MS is able to detect ambient concentration of a wide range of compounds including monoterpenes, aromatic hydrocarbons and OVOCs (methanol, acetone etc). The PTR-MS is a fast online method that has also enabled direct micrometeorological flux measurements of VOCs. Its use was introduced with the eddy covariance method by Karl et al. (2001) and with the disjunct eddy covariance method using grab samples by Rinne et al. (2001) or consecutively-detected masses by Karl et al. (2002). The results presented

in this thesis are based on PTR-MS measurements that have been complemented with traditional adsorbent samples.

This thesis focuses on the measurements of emissions and concentrations of VOCs in one of the largest vegetation zones in the world, the boreal zone. We measured 1) emissions from Siberian larch (mono- and sesquiterpenes) and Scots pine (monoterpenes), 2) monoterpene and oxygenated VOC (OVOC) above-canopy fluxes, and 3) VOC volume mixing-ratios in the air of a Scots-pine-dominated forest. The measurements were conducted at the SMEAR II station and the Hyytiälä Forestry field station. The main aim was to understand the factors influencing the seasonal and diurnal variation of the volume mixing-ratios of the major VOCs in the ambient air; with the following sub aims (Figure 2):

- To develop and present a method for continuous, long-term stand-alone VOC measurements, with quantitative calibration and volume mixing-ratio calculations.
- To quantify major VOCs (including several oxygenated VOCs) in boreal forest air and their changes on different temporal scales, their diurnal patterns and their seasonality.
- To measure canopy-level emissions of monoterpenes, methanol, acetone and acetaldehyde and compare them with up-scaled emissions from the shoot-level.
- To determine, for the first time, the VOC emission composition of the Siberian larch (*Larix sibirica*) and how it changes during the growing season. Siberian larch is a dominant, natively grown, tree species in the boreal vegetation zone area from western Russia to central Siberia.
- To determine the emission potentials and driving environmental variables of the terpenoid emissions of two different kinds of conifer: monoterpenes from the evergreen Scots pine (*Pinus sylvestris*) and mono- and sesquiterpenes from the deciduous Siberian larch.

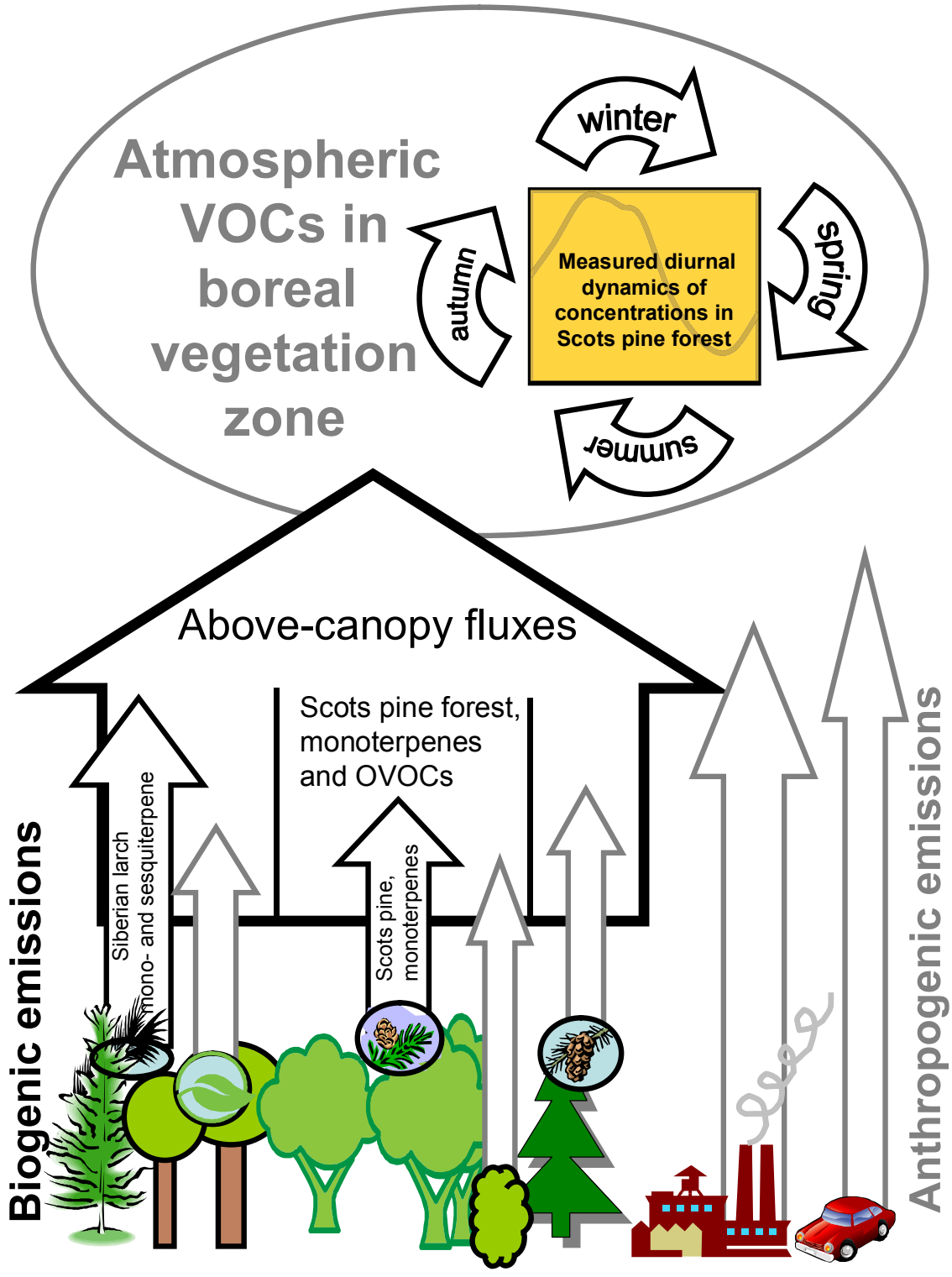


Figure 2. Schematic figure of the main aims of the measurements of VOCs from emission to ambient concentrations.

2 Experimental methods

The measurements were carried out at the SMEAR II measurement station (Station for Measuring Forest Ecosystem-Atmosphere Relations (Hari & Kulmala, 2005) at Hyytiälä in southern Finland (61°51´N, 24°17´E, 180 m above sea level). The measurements were done during the years 2004-2007 (Figure 3). The area is part of the southern boreal zone and mostly covered by forest (70%) dominated by Scots pine (*Pinus sylvestris*) with some Norway spruce (*Picea abies*), aspen (*Populus tremula*) and birch (*Betula*). A detailed description of the surroundings is given in **Paper VI**. The Scots pine forest at the SMEAR II site was sown in 1962 after a controlled burning and during these studies the height of the trees was about 16 m. Chamber measurements (methods in more detail in sections 2.1 and 2.3.1) of VOC emissions were conducted at the top of the crown of the trees to minimize shading effects. A scaffolding tower was used to access the Scots pine crowns for the VOC emissions measurements from the 40-year-old trees at SMEAR II (**Paper I**). The VOC emissions from Siberian larch (*Larix sibirica*) (**Paper II**) were measured from 5-year-old trees that had been planted at the Forestry Field station three years before the study. Ambient volume mixing-ratios inside and above the canopy (methods in more detail in sections 2.2 and 2.5) and above-canopy fluxes (methods in more detail in sections 2.2 and 2.4.) were measured from another scaffolding tower about 30 metres from the chamber measurements (Picture 1).

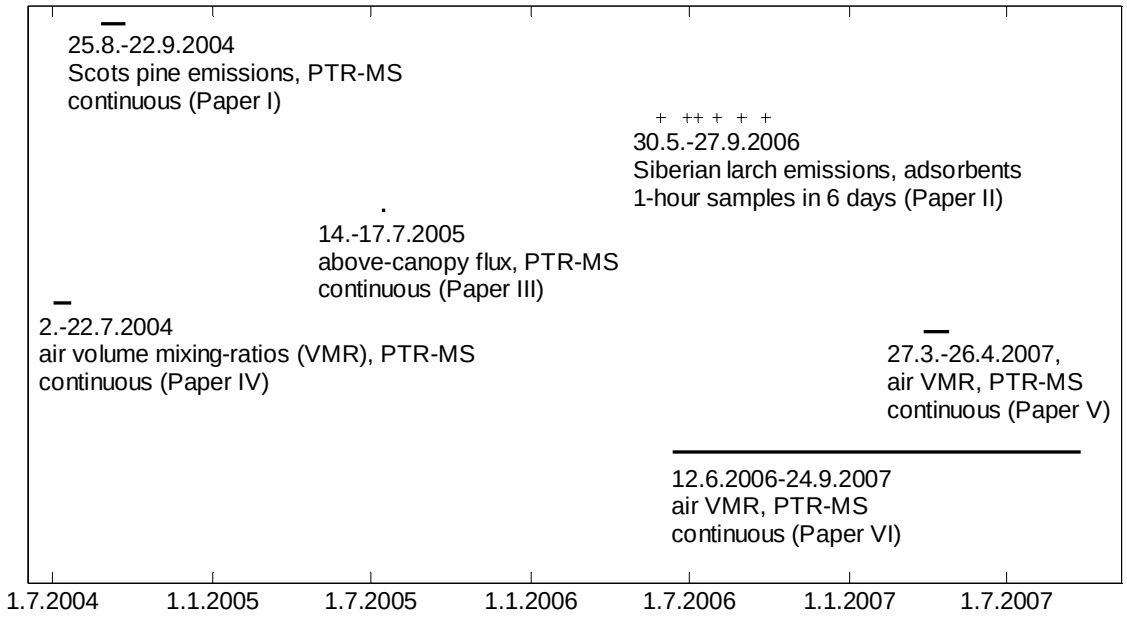


Figure 3. The timeline of the VOC measurements and the main measurement method used in Papers I-VI.

Picture 1. The measurement tower used for the VOC volume mixing-ratio and above-canopy flux measurements at SMEAR II.

2.1 Adsorbent samples of VOCs

Adsorbent samples were used to determine VOC concentrations in the ambient air (**Papers I** and **IV**), as well as to determine shoot-scale emissions from concentrations in the ingoing and outgoing air of the chambers (**Papers I** and **II**, see section 2.3.1). The samples were taken each for one-hour at a time and during a period from few hours to few days at a time. The adsorbents were packed in stainless steel tubes filled with Tenax-TA and Carbopack-B. The sampling and analysis procedures are well documented (Hakola et al., 2003; Hakola et al., 2006).

2.1.1 VOC sampling

The sampling time was about one hour and sampling flow rate about 100 ml min^{-1}. The sample flow was measured before sampling. In the chamber studies, ozone was removed from the air to prevent oxidation of the adsorbed molecules during the sampling. This was done with MnO_2-coated copper nets (Pollmann et al., 2005) prior to the chamber. This procedure did not produce measurement artefacts in the emission measurements. However, in ambient measurements, the MnO_2-coated copper nets removed some compounds including 10% of the camphene and all of the linalool, but not α- and β-pinene, limonene or Δ^3-carene (Hakola et al., 2003). After sampling the adsorbents were stored in a refrigerator.

2.1.2 Analysis

The adsorbent tubes were analyzed using a thermodesorption instrument (Perkin-Elmer ATD-400), connected to a gas chromatograph (GC) (HP 5890) with a HP-1 column (60 m, i.d. 0.25mm) and a mass-selective detector (HP 5972). The samples were analyzed for a number of compounds, depending on the study. Oxygenated VOCs, such as methanol and acetone, cannot be measured using these techniques. However, the analysis always contained the most abundant monoterpenes in the boreal forest, α- and β-pinene, Δ^3-carene and camphene. The monoterpene detection limits were of the order of 1-6 pptv, depending on the compound in question.

2.2 Online VOC measurements

Online measurements of VOCs (**Papers I, III-VI**) were conducted with a proton transfer reaction - mass spectrometer (PTR-MS, Ionicon GmbH, Innsbruck, Austria). This is a fast-response analyzer suited for the measurement of VOCs with a higher proton affinity than water. Compounds that can be measured with the instrument include methanol, acetone, benzene and monoterpenes. The method does not separate compounds with the same molecular mass, and thus, as in the case of monoterpenes, we measured their sum. The measurement set-up, summarized in Figure 4, included online measurements of ambient volume mixing-ratios (section 2.5), shoot-scale emissions (section 2.3.2) and ecosystem scale fluxes (section 2.4).

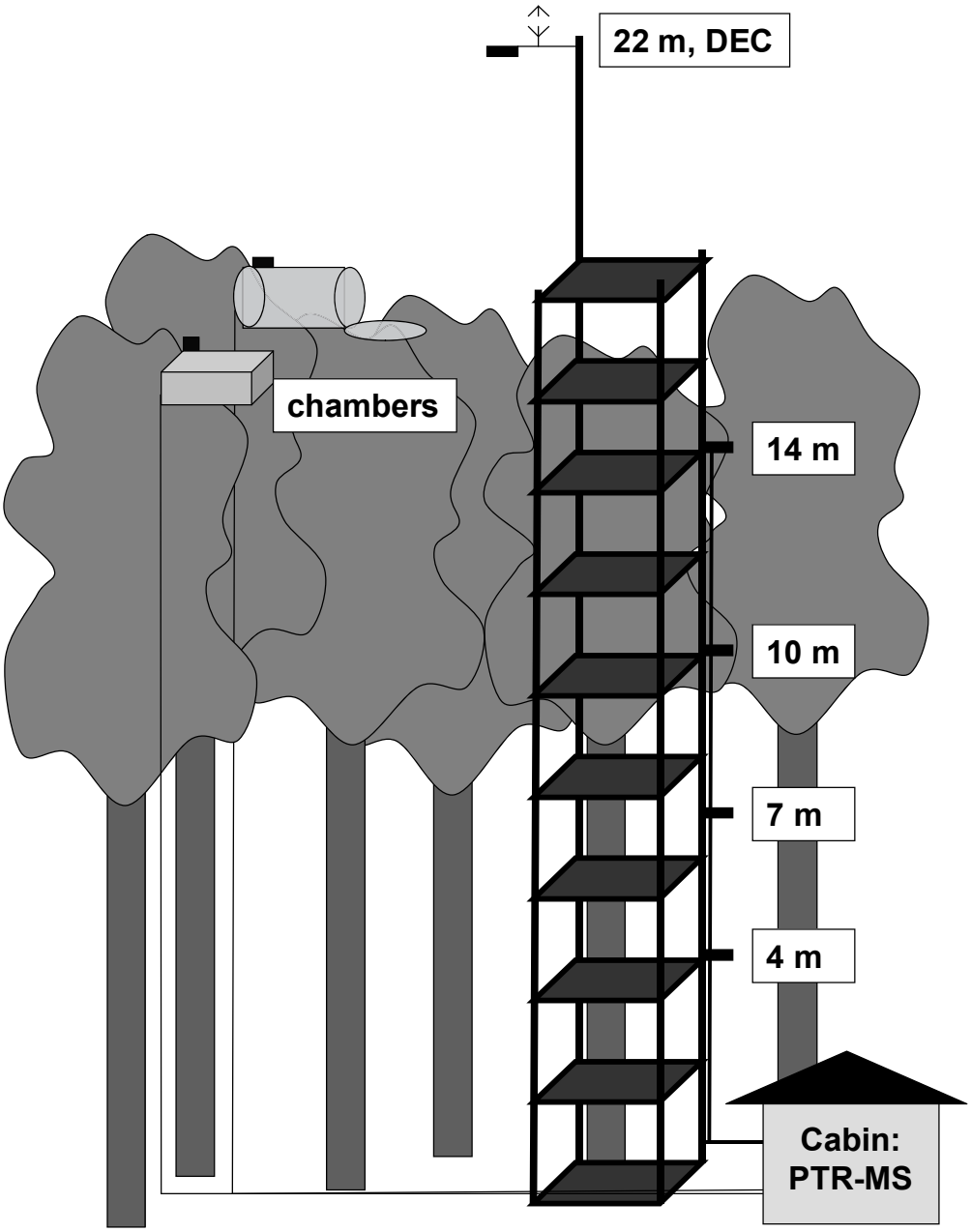


Figure 4. Schematic presentation of the measurement set-up that was used in the ambient volume mixing-ratio, the above-canopy flux, and the online shoot emission measurements. The automated chambers were sampled with 64-m-long heated and covered Teflon (FEP) tubes in autumn 2004 and again after March 2007. In October 2006, ambient measurements were reduced to three heights below, in and above-the canopy at 4, 14 and 22 m heights. Each height was sampled with 30-m-long Teflon (PTFE) tubes, 8 mm id, each with a flow of 15 l min^{-1} before October 2006 and 17.5 l min^{-1} after. The tubes were heated after November 2006. A zero air generator with a 1 l min^{-1} flow was used until November 2006, when it was changed to another one with a 3.5 l min^{-1} flow. In June 2006 - March 2007 ambient volume mixing-ratios at each height and a mass scan at a height of 14 m were measured every second hour; during the following hour zero air and above-canopy fluxes were measured. Measurements of shoot fluxes were included in the measurement cycle March 2007 - September 2007, when the timing changed and everything was measured every third hour.

2.2.1 PTR-MS

The use of PTR-MS in atmospheric measurements of VOCs is summarized by de Gouw and Warneke (2007). The PTR-MS analyzer is described in detail by Lindinger et al. (1998) and Hansel et al. (1998). The measurement time of the PTR-MS was allocated between ambient volume mixing-ratio (**Papers IV-VI**, section 2.5) and mass scan measurements (not presented here), and at times to shoot-scale emission measurements (**Paper I**, section 2.3.2) and ecosystem scale flux measurements with the micrometeorological disjunct eddy covariance method (**Paper III**, section 2.4).

The instrument is comprised of four main components: an ion source, a drift tube, a quadrupole mass filter and an ion detector/amplifier. The pressure inside the instrument is lowered with a membrane pump and three turbo molecular pumps from an initial pressure close to ambient down to about 10^{-5} mbar in the detection chamber.

A constant flow of pure water vapour into the hollow cathode ion source produces primary ions H_3O^+ and protonated water clusters $(H_2O)_nH_3O^+$ (n = 1, 2, 3..). In the drift tube VOCs, denoted as *R*, with a higher proton affinity than water (700 kJ mol^{-1}) undergo proton transfer reaction with primary ions:

$$H_3O^+ + R \rightarrow RH^+ + H_2O. \qquad \text{(R1)}$$

Most VOCs that are detected with the PTR-MS method are also protonated in the proton transfer reaction with water clusters or in ligand switching reactions and a rearrangement of products that result in:

$$(H_2O)_nH_3O^+ + R \rightarrow RH^+ + (H_2O)_{n+1}, \quad \text{where n = 1, 2...} \qquad \text{(R2)}$$

Also, depending on the organic compound in question, reverse reactions and complex ion chemistry can occur, but for simplicity we will not consider these here. Since the proton transfer from a protonated water cluster (R2) requires more energy than for proton transfer from protonated water (R1), compounds with a proton affinity close to that of water are only protonated by the primary ion. However, all of the compounds we reported (**Papers I, III-VI**) have proton affinities that are clearly higher than that of water. The distribution of protons to primary ions and protonated water clusters depends on 1) the water vapour flow into the ion source, 2) the pressure in the reaction chamber, 3) the applied electric field in the reaction chamber, and 4) the humidity of the sample air.

The initial inlet flow into the instrument is 10 ml min^{-1}; a small fraction of this is led into the reaction chamber. Only a fraction of the protonated molecules is directed into the quadrupole mass spectrometer (QMS) that selects one mass (more accurately mass-to-charge ratio) to pass into the secondary electron multiplier (SEM) -detector. All of these steps and the detection of molecules are more or less compound or mass dependent, resulting in a discrimination of the transmission of compounds through the PTR-MS. The differences between the transmissions of different compounds depend on the instrument set-up and operation parameters. Often the transport and detection is most effective for compounds that weigh about 80-100 amu and less effective for lighter and heavier compounds. Correspondingly, also the detection limits depends on the measured mass.

The detection limit of a compound can be lowered by extending the duration of the detection of the mass in question. In general, integration, or dwell, times of the order of 1-10 seconds are sufficient for measurements of VOCs volume mixing ratios of the order of 10-100 pptv (de Gouw & Warneke, 2007). However, the detection limits of different compounds vary substantially and depend also on the background signal and fragmentation. We estimated detection limits for the individual measurements of VOCs with integration time of 2 seconds (**Paper VI**). For example, the detection limit was 18 pptv for benzene and 300 pptv for methanol, which has a high background signal. Neither of the example compounds is considered to fragment. Altogether, integration time between 0.2 and 10 second were used for the VOC measurements (**Papers I, III-VI**). However, detection of atmospheric volume mixing ratios of heavy and fragmenting compounds can require much longer detection time. As an example the sesquiterpenes are a group of compounds known to fragment in the PTR-MS. Kim et al. (2008) suggest that the observation of about 20 pptv of sesquiterpenes (measured from a major ion at the unfragmented mass 205 amu) can be achieved with a dwell time of 10 minute or more.

2.2.2 Calibration procedure

Two types of calibration procedures were used. Initially, only the relative transmission of compounds with various molecular masses was determined (**Papers I** and **IV**). In spring 2005 a gas calibration set-up was built, and this enabled regular calibration of the PTR-MS instrument (**Papers III, V** and **VI**); this will be presented here in chronological order.

The transmission measurements (used in **Papers I** and **IV**) resulted in relative transmission factors that were used for calculating concentrations, or more accurately volume mixing-ratios, from the measurement signal. The transmission of each compound was measured by inserting an unknown amount of the compound into a plastic bag to obtain a relatively stable concentration that was high enough to cause a drop of the order of 10% in the primary ion signal. It was assumed that the flow of the primary ion into the reaction chamber remained effectively constant, and that the only change was due to the proton transfer reaction R1. It was also assumed the concentration of the primary ion was much larger than the concentration of the protonated VOC ($[H_3O^+]>>[VOCH^+]$). The transmission of the compound was calculated:

$$trans(VOCH^+) = \frac{\Delta I(H_3O^+)}{\Delta I(VOCH^+)}, \qquad \text{(Eq. 1)}$$

from the ratio of the change in the primary ion signal $I(H_3O^+)$ and the protonated VOC signal $I(VOCH^+)$, both signals being measured in as counts per second (cps). The transmissions were normalized so that the highest transmission was 1, and extrapolated for lighter and heavier masses.

The measured transmissions give information on the mass discrimination of the instrument and, by comparing successive transmission curves, of the changes in the instrument operation over time. The measured relative transmissions of the compounds mentioned in Table 1 were used to determine a transmission curve for the range of measured masses.

Table 1. Compounds used in calibrations of the PTR-MS. In transmission an unknown amount of the VOC was added to ambient air. The standard A was used in the calibrations conducted in March and April 2007 and the standard B was used in July and August 2007. The manufacturer (Apel-Riemer Environmental, Inc.) estimated that the uncertainty of the volume mixing-ratio (VMR) was not more than 6% for cis-3-hexenol and methyl-vinyl-ketone (in A) and not more than 5% for the other compounds. In the last column are given the proton transfer reaction rate coefficients (k) reported by Zhao & Zhang (2004).

protonated mass [amu]	VOC	formula	not fragmenting	transmission calibration	VMR in gas A [ppmv]	VMR in gas B [ppmv]	k [10^{-9} cm^3s^{-1}]
33	methanol	CH_4O	•	#	1.03	1.05	2.33
42	acetonitrile	C_2H_3N	•		1.08	1.01	4.47
45	acetaldehyde	C_2H_4O	•		1.06	0.99	3.36
47	ethanol	C_2H_6O			1.06	-	
59	acetone	C_3H_6O		#	1.09	1.05	
69	isoprene	C_5H_8			1.09	1.02	
71	methacrolein	C_4H_6O	•		1.08	-	3.55
71	methyl vinyl ketone	C_4H_6O	•		0.92	0.92	3.83
73	methyl ethyl ketone	C_4H_8O	•	#	1.08	1.06	3.48
79	benzene	C_6H_6	•		1.07	1.03	1.97
93	toluene	C_7H_8	•	#	1.07	1.04	2.12
101	cis-3-hexenol	C_6H_{12}			0.96	-	
101	hexanal	C_6H_{12}			0.97	0.90	
107	m-xylene	C_8H_{10}	•	#	1.07	1.03	2.26
107	o-xylene	C_8H_{10}	•	#	1.07	1.05	2.32
121	1,2,3-trimethyl benzene	C_9H_{12}	•		-	0.98	2.40
129	naphthalene	$C_{10}H_8$	•		-	1.00	2.59
137	α-pinene	$C_{10}H_{16}$		#	1.05	0.93	
182	1,2,4-tricloro benzene	$C_6H_3Cl_3$	•		-	1.01	

• These compounds do not fragment significantly in the drift tube of the PTR-MS.

From spring 2005 onwards the PTR-MS was calibrated (**Papers III, V** and **VI**) for the online VOC measurements weekly or every second week as presented in **Paper V**. Prior to the calibration, the SEM voltage was checked and adjusted if raising the detector voltage by 100 V resulted in more than a 20% change in the primary ion signal. The calibration started with the determination of the background signal by half-an-hour of measurements of VOC-free air that was obtained from the ambient air with a zero air generator. Model 1001 zero air generator (Parker ChromGas), with a flow of 1 l min^{-1}, was used until November 2006 and model 3501, with 3.5 l min^{-1} flow or less thereafter.

The efficiencies of the zero air generators used were determined in laboratory measurements. The zero air generators effectively removed the compounds used in the calibrations, except for the model 1001 generator which was unable to remove all of the toluene. After the zero air measurement, a VOC calibration gas standard (Apel-Riemer Environmental Inc.) was added to the system for one and a half hours. The standard gas contained compounds associated with most measured masses (Table 1). The standard gas flows resulted in volume mixing-ratios of the order of 50 ppbv with the smaller and 15-20 ppbv with the larger zero air generator. After this, the standard and zero air flows were measured, and finally zero air was measured for another half-an-hour. The flows were measured with a primary flow meter (Bios International Corp., DryCal DC-2M) that was connected into the system only during the flow measurements. In addition to the weekly calibrations, the zero air generators were used to measure the background signals of VOCs every second or third hour during the online measurements.

2.2.3 Calculation of volume mixing-ratios

The volume mixing-ratio calculations were initially based on relative transmissions and reactions with the primary ion signal (**Papers I** and **IV**). The calculation was then improved with the use of coefficients from direct gas calibration, with the subtraction of the frequently-measured background signal, and with the use of water cluster abundance in addition to the primary ion (**Paper III**). Eventially, in the final papers (**Papers V** and **VI**), we also included normalization of the measurement signals, more accurate isotope ratios and different transmissions for primary ions and water clusters. The calculation methods are presented here in the order in which the accuracy of the volume mixing calculations was enhanced.

For **Papers I** and **IV**, the volume mixing-ratios of compounds that contributed to the measured masses were calculated based on reaction R1 and equation Eq. 1, as suggested by the manufacturer (Ionicon GmbH, 2004), by:

$$VMR_{ppb} = \frac{I(VOCH^+)10^9 V_m T_{amb} p_{amb}}{\left[\frac{k_{VOC} t_r I(H_3{}^{18}O^+)\cdot 500}{trans_{H_3O^+}}\right] N_A T_r p_r trans_{VOCH^+} F_{VOC}}, \qquad \text{(Eq. 2)}$$

where $I(H_3{}^{18}O^+)$ is the signal of the ^{18}O isotope of the primary ion in counts per second (cps) multiplied by the isotope ^{16}O: ^{18}O ratio (500:1), $I(VOCH^+)$ is the signal of the protonated compound in cps. T is temperature in Kelvin, p is pressure in Pa, k_{voc} is the reaction rate constant, t_r is reaction time in seconds, *trans* is the unitless transmission factor and F_{VOC} the unitless fragmentation fraction. V_m is the molar volume in moles per litre of the ideal gas at 273.15 K and 1013.25 hPa, N_A is

Avogadro's constant of molecules in a mole. Subscript *r* refers to the reaction chamber and *amb* to the ambient conditions, where constant temperature and pressure were used. For the monoterpene emission study in **Paper I** we used a k_{voc} of 2.44 10^{-9} cm^3 s^{-1} (specific for each compound in question, e.g., Tani et al. 2003), an F_{voc} of 0.65 and a $trans_{voc}$ of 0.36. During all of the measurements the PTR-MS was operated at a reaction chamber pressure of about 2.0 hPa, and a temperature of 50 °C; the parameter E/N, affecting fragmentation pattern, was about 106 Td and the reaction time about 120 µs.

Eq. 2 was also used for the ambient volume mixing-ratios during July 2004 (**Paper IV**). The k_{voc} time constant value of $2 \cdot 10^{-9}$ cm^3 s^{-1} was used for all compounds. The only compounds that were considered to fragment were the monoterpenes. The monoterpenes were measured as the sum of the unfragmented protonated mass M137 and the main protonated fragment M81. The background signal was measured from VOC-free air after the campaign, and the signal was subtracted from the measured volume mixing-ratio.

For the volume mixing-ratio calculation for the above-canopy fluxes in July 2005 (**Paper III**) water clusters and calibration coefficients were also included. Taking into account reactions R1 and R2, and assuming linear response to change in mixing-ratio we derived that:

$$VMR_{ppb} = \sigma_{voc}\left[\frac{I(VOCH^+)}{500I(H_3{}^{18}O^+)+I(H_2{}^{16}OH_3{}^{16}O^+)}-\frac{I(VOCH^+)_{zero}}{500I(H_3{}^{18}O^+)+I(H_2{}^{16}OH_3{}^{16}O^+)}\right] \quad \text{(Eq. 4)}$$

The calibration coefficient σ_{voc} (in ppb) was determined for each VOC from direct standard gas calibration and calculated by solving Eq. 4 with respect to σ_{voc}. The measurement signals (in cps) of each VOC, $I(VOCH^+)$, primary ion $I(H_3{}^{18}O^+)$ containing ^{18}O isotope multiplied by isotope ^{16}O: ^{18}O ratio (500:1) and water cluster $I(H_2{}^{16}OH_3{}^{16}O^+)$ were measured during each measurement cycle. The VOC background signals $I(VOCH^+)_{zero}$ in cps were obtained from VOC-free air measurements every second hour.

For the quantitative long-term measurements (**Papers V** and **VI**) the accuracy of the online VOC measurements was enhanced from the initial procedure by 1) using coefficients from direct and regular gas standard calibrations of the measured compounds when possible, 2) normalizing all calculations to a set primary ion and water cluster count rates and reaction chamber pressure 3) including protonated water clusters in all calculations 4) introducing the factor α, the ratio of the transmission coefficient for a water cluster to that of the primary ion, 5) taking hydrogen and oxygen isotopes into account when calculating primary ion and water cluster signals, and 6) subtracting the background signal that was measured between VOC measurements. Taking the above and Eq. 4 into account and reformulating (presented in more detail in **Paper V**) the VOC volume mixing-ratios were calculated using:

$$VMR_{ppb} = 10^9 \frac{p_r}{I_{norm} p_{norm}} \frac{\mu_0 N_0}{k_{VOC} L} \frac{E}{N^2} \frac{trans_{H_3O^+}}{F_{VOC} trans_{VOC}} I(VOCH^+)_{norm}, \quad \text{(Eq. 5)}$$

where 10^9 converts the fraction to parts per billion (ppb), subscript *r* denotes reaction chamber (drift tube) and *norm* denotes normalization (I_{norm} is 10^6 cps and p_{norm} is 2 hPa). *trans* is the unitless transmission coefficient, *p* is pressure in Pa, μ_o is the normalized ion mobility of the primary ions cm s^{-1}. *N* is the number density of the air in the drift tube and N_0 is the number density of air at standard pressure and temperature (1013.25 hPa and 273.15 K). k_{voc} is the reaction rate constant in cm^3 s^{-1} of the proton transfer reaction from the primary ion to the VOC in question. *L* is the length of the drift tube in cm (reaction chamber), *E* is the applied electric field (in V cm^{-1}) in the drift tube (reaction chamber), F_{voc} is the unitless fragmentation factor. $I(VOCH^+)_{norm}$ is the normalized ion count rate in cps of the measured compound and thus can be written as:

$$I(VOCH^+)_{norm} = I(VOCH^+)\left(\frac{I(H_3O^+)+\alpha^{-1}I(H_2OH_3O^+)}{I_{norm}}\right)^{-1}\left(\frac{p_r}{p_{norm}}\right)^{-1} - \frac{1}{n}\sum_{i=1}^{n} I(VOCH^+)_{zero,i}\left(\frac{I(H_3O^+)_{zero,i}+\alpha^{-1}I(H_2OH_3O^+)_{zero,i}}{I_{norm}}\right)^{-1}\left(\frac{p_{r,zero,i}}{p_{norm}}\right)^{-1} \quad \text{(Eq. 6)}$$

where $I(H_3O^+)$ is in cps 487·I(M21), M21 stands for mass 21, equal to the measured primary ion isotope $H_3{}^{18}O^+$. $I(H_2O\ H_3O^+)$ is in cps 243·I(M39), and M39 stands for mass 39, equal to the measured water cluster isotope with one ^{18}O isotope. In the primary ion and water cluster coefficients, the abundances of the oxygen and hydrogen isotopes are taken into account. *n* is the number of zero air measurements, zero denotes the measured background signal, and factor α is the unitless ratio of the transmission coefficient of a water cluster to that of the primary ion:

$$\alpha = \frac{\text{trans}_{H_2OH_3O^+}}{\text{trans}_{H_3O^+}} \quad \text{(Eq. 7)}$$

For the compounds that existed in the gas standard, the normalized sensitivities in cps ppb^{-1} were determined, assuming linear response to change in volume mixing-ratio, from direct calibrations:

$$S_{norm} = \frac{I(VOCH^+)_{norm}}{VMR_{ppb}} \quad \text{(Eq. 8)}$$

The atmosphere contains a wide range of VOCs, and in addition the VOC composition can change, for example seasonally, at a given place. Thus all the relevant compounds were not included in the calibration gas standard. The transmissions of VOCs relative to the transmission of the primary ion were determined, according to Eqs 5 and 8, as:

$$trans_{voc,rel} = \frac{trans_{VOC}}{trans_{H_3O^+}} = 10^9 \frac{p_r}{I_{norm}p_{norm}} \frac{\mu_0 N_0}{k_{VOC}L} \frac{E}{N^2} S_{norm}, \quad \text{(Eq. 9)}$$

and a transmission curve was fitted to these measured values. Thus relative unitless transmission factors were determined from 20 to 170 amu, i.e., for all masses in the measurement range.

One major problem that remains is that reaction coefficients are not available for all compounds, and especially measurements of VOC water cluster proton transfer rates are lacking. Also a marginal error comes from different reaction times, as the water clusters are heavier and spend more time in the reaction chamber than do the primary ions (Dotan et al., 1976). These problems can be bypassed by direct calibrations with measured compounds. In practice this would require a calibration system that would enable the use of liquid standards and the adjustment of compounds used in the direct calibration to fit the composition of the VOC in the measurements. However, at the present, flexible calibration systems that could be used for the calibration of VOCs in ambient concentrations are not available.

2.3 Shoot emissions

Manual dynamic flow-through chambers (section 2.3.1), with one-hour adsorbent samples, were used to determine 1) the VOC emissions and their seasonal changes from a Siberian larch (**Paper II**) and 2) the monoterpene emission spectra from a 40-year-old Scots pine (**Paper I**). Automated chambers were used for online monoterpene emission measurements from a Scots pine (**Paper I,** section 2.3.2). A temporal resolution of a few minutes was achieved with the automated chamber system that was originally built for CO_2 measurements. All chambers were open in between the measurements. Branches were selected so that shading was minimized and the measured shoots were fully sunlit.

2.3.1 Manual flow-through chambers

The volume of the cylinder-shaped Teflon enclosure (Picture 2), with a transparent Teflon film cover, was approximately 20 litres (Hakola et al., 2006). We assumed that equilibrium between the gas and the Teflon was reached during the one-hour sampling time. Possible memory effects caused by the Teflon, that Helmig et al. (2003) observed, were not estimated. The enclosure had inlet and outlet ports, where the air samples were collected onto adsorbent tubes simultaneously. The flow-through the enclosure was about 5 l min^{-1} and a small fraction of it was taken for the VOC sample.

The Siberian larch had been planted in the field three years earlier (**Paper II**). The VOC emission measurements were started when the Siberian larch needles appeared fully grown and ended when they started to shed. The emission rates were measured during a few days every month from June to September in 2006. During each period, samples were taken in varying conditions of light (from dark to fully sunlight) and temperature (between 5 and 40°C). A new fully lit shoot, at various heights, was inserted at least four hours before each measurement period and a purge flow was maintained in the chamber at all times. The Siberian larch shoots were cut directly after each measurement. Dry needle weight was determined by drying the needles at 75°C until a consistent weight was achieved. Temperature was measured inside the enclosure and photosynthetic photon flux density (PPFD) at the SMEAR II station located 650 m away. The photosynthetic activity and respiration of the Siberian larch was monitored with an infrared gas analyzer (EGM-4, PP-systems, Hitchin, UK) from the sample ports every time the VOC sample cartridges were changed.

Picture 2. The VOC emission measurements from a Siberian larch with manual flow-through chamber (Paper II).

The Scots pine measurements with the manual chamber were conducted at the tree crown from a branch of the same tree as was used for the online measurements (**Paper I**). The shoot was inserted well before the two-week campaign, and remained inside the chamber for the whole period. The transparent Teflon film cover also remained over the shoot the whole time. However, the lid of the chamber was removed in between sampling. One-hour samples were taken daily at midday from the Scots pine according to the procedures used by Hakola et al. (2003). The needle area and weight of the Scots pine shoot was estimated based on measurements of similar branches.

The VOC emission rate and carbon dioxide exchange rate was determined according to:

$$E_{VOC} = \frac{(C_f - C_a)F}{m}, \qquad \text{(Eq. 10)}$$

where C_f is the concentration in µg per cm^{-3} in the outgoing air, C_a is the concentration in µg per cm^{-3} in the ingoing air, F is the flow rate in litres per second into the enclosure, and m is the biomass inside the enclosure in grams of dry needle weight (g_{dw}).

2.3.2 Automated online chambers and PTR-MS set-up

Online measurements were applied to measure monoterpene emissions from a 40-year-old Scots pine (**Paper I**). The shoots were inserted several months before, and remained inside the chamber for the two week campaign. The needles were gently bent into the horizontal plane and debudded of new shoot growth. The needle area and weight of the Scots pine shoot was based on previous measurements of similar shoots. In addition, the gas exchange from an empty chamber was measured to determine measurement artifacts. The effect of surface contamination was demonstrated by inserting a cut branch inside the empty chamber for four days, after which emissions from the contaminated surfaces were measured for the following days up to the end of the campaign.

The automated chambers were 1-litre rectangular boxes built from metacrylat, except for a quartz glass cover wall (Picture 3). However, in 2007 VOC emissions were measured using a 3.5-litre cylinder-shaped acrylic plastic chamber (Picture 4). The acrylic plastic parts were coated in spring with a fresh Teflon (Fluoro Ethylene Propylene (FEP)) film. For a detailed description on the automated chamber see Raivonen et al. (2003) and for the sampling set-up Altimir et al. (2002). The chambers were closed intermittently three times an hour for less than two minutes at a time, resulting in 70 measurements per day. During closure, air was drawn from the chambers into the gas analyzers along heated and covered 64 m long Teflon (FEP) sampling lines and replaced by ambient air at an equal flow rate. The tube flow was lower in between sampling. The measurement started when the chamber was open and ambient atmospheric concentrations were measured.

Picture 3. The monoterpene emission measurements from a Scots pine with an automated online chamber August-September 2004 (Paper I).

Picture 4. The monoterpene emission measurements from a Scots pine with an automated online chamber, March-September 2007 (unpublished data).

The changes in concentration during the chamber closure were used to determine the gas fluxes. We estimated that during a closure the monoterpene concentration reached a steady state in the chamber. The emission of monoterpene was determined in ng m^{-2} s^{-1}, using initial and final concentrations, by the mass balance equation, rather than mass as in Eq. 10, with area:

$$E_{VOC} = \frac{(C_f - C_a) \cdot F}{A}, \qquad \text{(Eq. 11)}$$

where C_a is ambient (initial) concentration, and C_f is final concentration, determined at the end of the measurement period and considered constant, the concentrations were converted from ppbv to units of ng cm^{-3}. F is the flow rate in litres per second and A is the all-sided shoot needle area in cm^{-2}.

2.3.3 Determination of emission potentials

The observed emission rate of VOCs is parameterized as:

$$E_{VOC} = E_0 \gamma \,, \qquad \text{(Eq. 12)}$$

where γ is a unitless activity factor depending on the environmental conditions. E_0 is the basal emission rate or emission potential (typically expressed per dry needle weight in ng g_{dw}^{-1} h^{-1}) in standard conditions (traditionally at 30°C and 1000 µmol photons m^{-2} s^{-1}) and specific to a given vegetation type. The emission potential has been observed to change seasonally, and was determined separately for each measurement period, as described by Tarvainen et al. (2005).

The temperature dependence of VOC emissions (*E(T)*) from the Siberian larch (**Paper II**) and of monoterpenes from the Scots pine (**Paper I**), was investigated using a temperature-dependent emission algorithm (e.g. Tingey et al., 1980, Guenther et al., 1993):

$$E(T) = E_0 \exp\left[\beta\left(T - 30^\circ C\right)\right], \qquad \text{(Eq. 13)}$$

where E_0 is the fitted emission potential, and β is the emission factor (expressed in $^oC^{-1}$). We tested how well this algorithm described the measured emissions. Emission inventory models typically use a constant β value (0.09 $^oC^{-1}$) and emission potentials were also calculated with this value. We also tested how well the VOC emissions of the Siberian larch (**Paper II**) were described by the temperature and light-dependent isoprene algorithm (Guenther, 1997):

$$E(T, PPFD) = E_0 \gamma(T, PPFD), \qquad \text{(Eq. 14)}$$

with one fitted parameter (E_0) and

$$\gamma(T, PPFD) = \left[\frac{\varphi\, C_{L1} \lambda}{\sqrt{1+\varphi^2\lambda^2}}\right]\left[\frac{e^{\left(\frac{C_{T1}/(T-T_S)}{RT_sT}\right)}}{C_{T3} + e^{\left(\frac{C_{T2}(T-T_M)}{RT_sT}\right)}}\right] \qquad \text{(Eq. 15)}$$

where λ is photosynthetic photon flux density (PPFD) in µmol$m^{-2}s^{-1}$, here T is temperature in Kelvin, T_S is the standard temperature (303.15 K), R is the universal gas constant (J mol^{-1} K^{-1}), and φ (=0.0027), C_{L1} (=1.066), C_{T1} (=95 000 J/mol), C_{T2} (=230 000 J/mol), C_{T3} (=0.961) and T_M (=314 K) are empirical constants given by Guenther (1997).

2.4 Above-canopy fluxes

The disjunct eddy covariance (DEC) method was used to determine the fluxes of methanol (M33), acetaldehyde (M45), acetone (M59) and monoterpenes (M137 and a fragment at M81) above the Scots pine canopy (**Paper III**). Each VOC signal was measured for 0.5 seconds at a time and the primary ion isotope (M21) and water clusters (at several masses) for 0.2 seconds at a time. The measurement cycle lasted about 6 seconds, resulting in a dataset for each compound with a 0.5 second measurement every 6 seconds. Air was drawn from a VOC sampling point at a height of 22 metre through a 8 mm inner diameter (id) Teflon (PTFE) tube at a flow rate of 15 l min^{-1}. Next to the sampling point the three-dimensional wind speed was

measured at a rate of 10 Hz with a sonic anemometer (Gill Instruments Ltd., Solent HS1199).

2.4.1 Calculation of flux using the Disjunct Eddy Covariance

The above-canopy flux was calculated using the disjunct eddy covariance (DEC) method developed by Rinne et al. (2001) as the covariance of the vertical wind speed and the VOC volume mixing-ratio:

$$f = \langle w' c' \rangle = \frac{1}{n} \sum_{i=1}^{n} w_i' c_i', \qquad \text{(Eq. 16)}$$

where *w'* is the momentary variation of vertical wind speed (m s^{-1}) from the 45-minute average value and *c'* (ng cm^{-3}) is the corresponding momentary variation of the VOC volume mixing-ratio.

The momentary values must be measured with a fast-response instrument, within one second, to take into account the rapid fluctuations in the flux. In traditional eddy covariance (EC) the values are measured continuously. Using a disjunct time series does not lead to systematic errors. However, the disjunct sampling does increase the random uncertainty of the measured flux value. In field comparisons of the EC and DEC methods, Ammann et al. (2006) and Rinne et al. (2008) observed that the sampling lines and instrumentation caused larger discrepancies to the measured flux than the actual disjunct measurements. The major systematic errors came from the sampling, from the residence time inside the tube and interactions between the measured species and the tube walls. The time lag due to the transfer time in the tubing was determined by finding the maximum covariance, which is a standard method used in CO_2 flux measurement networks (Aubinet et al., 2000).

2.5 Ambient volume mixing-ratios

Concentrations of VOCs vary diurnally and seasonally. For calculation of the volume mixing-ratios see section 2.3.3 (for **Papers I, III-VI**) and for operation parameters see section 2.3.1. The VOC composition changes over time at any given location. We must take into account the fact that, using the PTR-MS, we might not observe this change for compounds with the same molecular mass. As an example, during the summers M69 is likely to be dominated by isoprene and 2-methyl-3-buten-2-ol (MBO) emitted from regional vegetation; during winter, on the other hand, M69 is dominated by compounds from anthropogenic sources. In addition, compounds can have several sources and processes contributing to the ambient volume mixing-ratio.

The integration, or dwell time, used depended on the abundance of the measured mass. The integration time of the primary ion isotope at M21 was only 0.2 s, monoterpenes were observed at M137 for 2-10 s, while even 20 seconds was too short to observe a significant signal of sesquiterpenes at mass M205. For comparison of the online measurements, adsorbent samples (see 2.1) were taken from a corresponding height inside the canopy (**Paper IV**).

Sampling artifacts are minimized by the use of open path sensors and by minimizing the residence time in the sampling line. However, many methods, such as the PTR-MS, require air flow into the instrument and sampling is inevitable. This is also the case when the same instrument is used for measurements from different locations, e.g., from several heights. In the quantitative long-term ambient

measurement described in **Papers V** and **VI** we estimated that the average sample residence time was 6 seconds or less, since we used a flow rate of 15-17.5 l min^{-1}. The sample flow is limited by a reasonable tube diameter and the pump capacity. It is often desirable to keep the pressure drop in the tube reasonable. For example the PTR-MS operational pressure must be above 0.6 bar, and this was achieved with the use of 8 mm id tubes.

The sampling line material is also a trade-off of properties. Glass is an inert, smooth material: however, installing and fastening a 30-metre-long rigid and easily-broken glass tube to a measurement tower is not realistic. For the sample lines, Teflon (PTFE) tube was chosen since it is flexible and chemically inert. However, Teflon is porous, and some compounds may linger on the surface, as Helmig et al. (2003) observed. Initially, the sampling system was a few metres long 1/8 inch Teflon tube that sampled air from two metres height (**Paper IV**). For the quantitative long-term measurements (**Papers V** and **VI**), the set-up consisted of sampling from several heights below, in and above the canopy, as well as background signal and calibration measurement systems (details of the set-up are shown in Figure 4).

3 Review of the papers

The papers in this thesis are based on studies of VOCs measurements conducted at the SMEAR II station and the Hyytiälä Forestry field station. We have measured 1) terpenoid emissions from Siberian larch (mono- and sesquiterpenes) and Scots pine (monoterpenes) shoots using manual and automated chambers, and 2) monoterpene and oxygenated VOC (OVOC) emissions above as well as 3) VOC volume mixing-ratios below, inside and above the canopy of a Scots-pine-dominated forest. The focus of this thesis is on the VOCs of biogenic origin.

Paper I describes an automated online chamber system for fast-response measurements of Scots pine shoot monoterpene emission rates on a time-scale of minutes. The system was combined with continuous measurements of plant physiological phenomena (CO_2 exchange and transpiration), exchange of other trace gases (NO_x, O_3), and environmental variables (PPFD, temperature and RH) at the SMEAR II station. The system was operated for a month and the monoterpene emission rates determined were compared with hourly samples from well-established manual chamber method measurements from an adjacent shoot.

Paper II presents seasonal isoprene, mono- and sesquiterpene emissions from a Siberian larch (*Larix sibirica*) measured throughout the growing season from fully-grown needles to the start of shedding of the needles. Each month, VOCs were collected as one-hour adsorbent samples over at least a 24-hour period from the in- and outgoing air of the manual dynamic flow-through chamber, with simultaneous temperature and solar radiation measurements. The tree's CO_2 exchange was measured adjacent to the VOC samples to confirm that the tree was photosynthesizing during daylight hours and respiring in the dark. Each month the emissions were determined during both daylight and night hours to obtain results in varying light and temperature conditions. Different algorithms were tested to determine factors controlling emission rates, emission factors and emission potentials.

Paper III presents measurements of VOC fluxes above a Scots pine (*Pinus sylvestris*) stand during four summer days and the application of a stochastic Lagrangian transport model. In the model a simple chemical degradation scheme was used to evaluate how compounds of different reactivity are chemically removed during their transport to the measurement point. The sensitivity of the above-canopy fluxes and their vertical profiles to the oxidation and photolysis were assessed for the compounds that were observed in the flux measurements, as well as for a more reactive compound. Measured monoterpene fluxes were fitted with a traditional emission algorithm and the monoterpene and non terpenoid VOC fluxes were compared with previous studies of Scots pine emissions.

Paper IV presents the diurnal variation and vertical profiles of atmospheric VOC volume mixing-ratios, and introduces continuous on-line volume mixing-ratio measurements of VOCs in and above a Scots pine stand. Factor analysis was used to classify the measured VOCs, based on the correlation of local meteorology with ambient summertime volume mixing-ratios, into different groups, and to estimate factors driving the behaviour of their atmospheric volume mixing-ratios.

Paper V presents a method for quantitative volume mixing-ratio calculations, including the calibration procedure and a measurement set-up, for long-term, stand-alone field measurements of VOCs with an online PTR-MS. The performance of the measurement, calibration, and calculation methods were investigated in measurements of VOC volume mixing-ratios in a boreal forest.

Paper VI presents quantitative long-term online measurements of atmospheric volume mixing-ratios of methanol, acetaldehyde, acetone, isoprene - 2-methylbuten-2-ol, benzene, monoterpenes and other VOCs. Seasonal and diurnal variations of the VOC mixing-ratios, meteorology and inorganic trace gas volume mixing-ratios were observed at the boreal forest site.

4 Author's contributions

I alone am responsible for the summary of this thesis. In **Paper I,** I was responsible for the measurements, contributed to the data interpretation and the figures and wrote the main bulk of the article. In **Paper II**, I was responsible for the on-line measurements of monoterpenes, contributed to the data interpretation and to the figures and wrote the main bulk of the article. In **Paper III**, I participated in the VOC measurements, and wrote part of the VOC volume mixing-ratio measurements methods. In **Paper IV**, I was responsible for the on-line VOC measurements, participated in the interpretation of the results and wrote the main bulk of the description of the measurements. In **Paper V**, I was responsible for the design and building of the calibration set-up and participated in the development of the volume mixing-ratio calculation method. In **Paper VI**, I was responsible for the mixing-ratio data processing, figures, interpretation of the results and writing the main bulk of the article.

5 Results and discussion

In this thesis the development of methods for VOC measurements were central. We introduced the use of an automated online chamber system for continuous VOC emission measurements in **Paper I**. An automated sampling system (partly presented in **Paper V** and summarized in Figure 4) was build for long-term VOC measurements with a PTR-MS. The PTR-MS measured in three-hour cycles for one hour at a time: 1) the volume mixing-ratio of VOCs in forest air, 2) above-canopy emissions with the DEC method, and 3) Scots pine shoot emissions with the automated chamber method. The emission, photosynthetic process and environmental variable measurements allow development of mechanistic emission models of terpenoid and OVOC emissions with both plant physiological and physicochemical parameters. The novel approach was to determine emission dynamics in field conditions together with atmospheric changes. In addition to the short measurement period presented here (section 4.1.) the long-term stand alone method enables observation of seasonal changes. The developed automated sampling system enables systematic and reliable long-term field measurement system that captures diurnal and seasonal behaviour of biogenic terpenoid and OVOC emissions and the simultaneous changes in the VOC concentrations in the atmosphere. Results of simultaneous emission and ambient volume mixing-ratio measurements are presented for a four day period for monoterpenes and methanol in chapter 4.1.

The development of systematic maintenance and calibration protocols, presented in **Paper V**, were the backbone for the reliable long-term measurements of ambient VOC volume mixing-ratios presented in **Paper VI**. Another technical essentiality for reliable PTR-MS measurements, the volume mixing-ratio calculation procedure, was developed. The final calculation method (presented in **Paper V)** includes 1) coefficients from direct and regular gas standard calibrations of the measured compounds when possible, 2) normalizing all of the measured VOC signals to a given primary ion and water cluster count rates and reaction chamber pressure 3) reactions with protonated water clusters 4) different transmission coefficients of water cluster and primary ion, 5) accounting for hydrogen and oxygen isotopes in the primary ion and water cluster signals, and 6) subtracting the background signal measured at regular intervals between VOC measurements.

5.1 Summertime emissions and volume mixing-ratios of monoterpenes and methanol

A four-day period of unpublished results of measurements made in SMEAR II is presented in this chapter. I will introduce and compare simultaneously-measured 1) emissions from a Scots pine shoot, 2) above-canopy fluxes and 3) ambient volume mixing-ratios below, within and above the canopy in the Scots-pine-dominated forest for two VOCs, monoterpenes and methanol. These until now unpublished results will also be compared with the results obtained during different years between 2004 and 2007 that have already been presented in **Papers I** and **III-VI**.

The monoterpene emissions from the shoot exhibited a clear diurnal pattern with daily maximum in the afternoon (Figure 5). The DEC method is based on turbulent transport of the emissions, and measurement become unreliable at night when mixing is suppressed; the typical diurnal emission pattern is thus less distinct for

the above-canopy fluxes than for the branch scale measurements. Similar diurnal pattern was observed in the measurements from shoots in autumn in **Paper I** and from canopy-level measurements in summer in **Paper III**. The diurnal afternoon emission maximum is typical for Scots pine, and is related to the variation of temperature (e.g. Janson, 1993; Tarvainen et al., 2005; Hakola et al., 2006). The majority of the Scots pine monoterpene emissions originate from evaporating storage pools in mature needles, although a part of the monoterpene emissions have been observed to depend on irradiation (Shao et al., 2001). However, separating the influences of irradiation and temperature on emissions is problematic in field measurements. That was also the case, during the four-day period when the air temperature clearly followed the solar radiation measured as the photosynthetic photon flux density (Figure 5).

The monoterpene emission rates measured with the DEC method above the canopy and by the automated online chamber method were between 10 and 270 $\mu g m^{-2} h^{-1}$ and between -30 and 360 $\mu g m^{-2} h^{-1}$, respectively (Figure 5). The chamber measurements of a Scots pine shoot were up-scaled to canopy-scale by assuming that all emissions originated from the needles and that the needle mass per ground area ratio was 540 $g_{dw}\ m^{-2}$ (for more details see **Paper III**). Chemical degradation during the transport was studied in **Paper III**. We estimated that it could result in a 10% loss of the emitted monoterpenes before flux measurement. The loss would result in a lower emission measured with DEC than expected from the shoot measurements. However, we observed the opposite. In addition to the shoots, minor monoterpene emissions from the forest floor have been observed in summer at Hyytiälä (Hellén et al., 2006b) and from a mixed Scots pine – Norway spruce forest floor (Janson et al., 1999). The midday monoterpene emissions (Figure 5) measured with the automated online chamber method were lower and with the DEC method higher than the midday emissions measured previously from the same site. However, the obtained flux values vary even when determined with the same method. Rinne et al. (2000b) and Spanke et al. (2001) determined independently monoterpene emissions with the gradient method during a two-day period in August and obtained midday emission values of 300 $\mu g m^{-2}\ h^{-1}$ and 200 $\mu g m^{-2}\ h^{-1}$, respectively. The automated online chamber measurements resulted in negative values at night, probably due to measurement artefacts such as deposition to the chamber walls.

Monoterpene emissions from boreal conifer trees are traditionally modelled as a function of temperature (Tingey et al., 1980; Guenther et al., 1993). The determined temperature dependency of monoterpene emission, expressed as β-coefficient in Eq. 13, was $0.17 ºC^{-1}$ when measured from a Scots pine shoot in **Paper I**, $0.11 ºC^{-1}$ when measured at the canopy-scale in **Paper III** and varies generally between $0.05 ºC^{-1}$ and $0.2 ºC^{-1}$ (e.g. Juuti et al., 1990; Hakola et al., 2006; Janson & de Serves, 2001; Komenda & Koppmann, 2002; Tarvainen et al., 2005). The standardized emission potential was initially 7.2 $\mu g\ g_{dw}^{-1}\ h^{-1}$, increasing after a frost night to 19.7 $\mu g\ g_{dw}^{-1}\ h^{-1}$ in **Paper I.** A value of 2.5 $\mu g\ g_{dw}^{-1}\ h^{-1}$ was determined in **Paper III**. Both methods, automated online chambers in **Paper I** and DEC in **Paper III,** resulted in higher

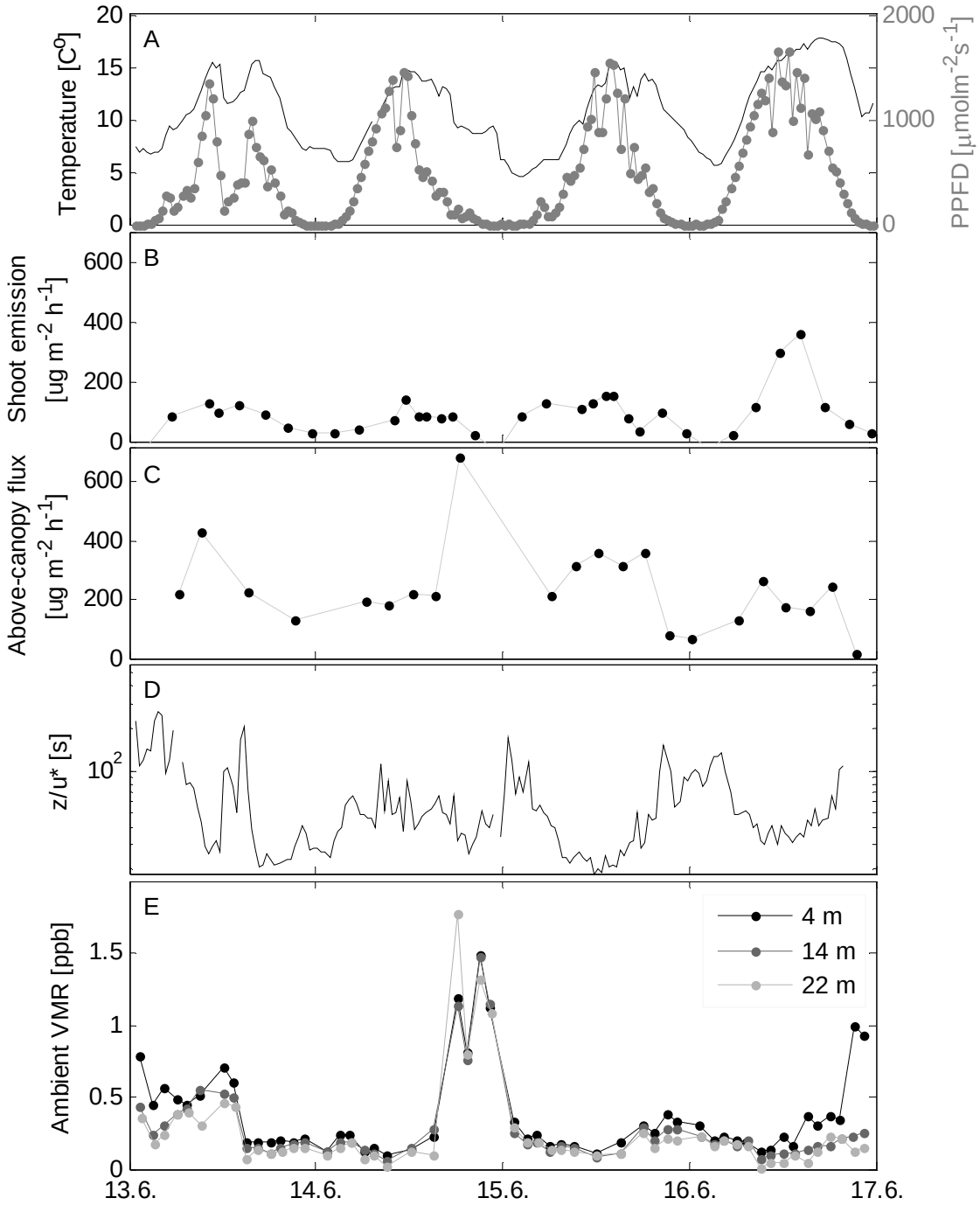


Figure 5. Results of online monoterpene measurements at SMEAR II from summer 2007 (all calculated from M137). A) air temperature and photosynthetic photon flux density (PPFD), B), monoterpene emission measured from a shoot in an automated online chamber and up-scaled to canopy level using a biomass of 540 $g_{dw}m^{-2}$, C) monoterpene flux above the canopy determined with the DEC method, D) turbulent mixing time-scale at above-canopy height z=22 m (t = z/u*), and E) monoterpene volume mixing-ration in ambient air at three heights.

emission potentials than previously determined at the same site using the gradient method (Rinne et al., 2000a) and manual chambers with adsorbent sampling and CG analysis (Hakola et al., 2006). However, there is a large variation between branches of different ages on the same tree (Komenda & Koppmann, 2002), as well as between different seasons (Janson & de Serves, 2001; Komenda & Koppmann, 2002; Tarvainen et al., 2005; Hakola et al., 2006). Tarvainen et al. (2005) also observed a large seasonal variation in the standardized monoterpene emission potential of Scots pine, being highest, 4.9 μg g_{dw}^{-1} h^{-1}, during early summer, 0.9 μg g_{dw}^{-1} h^{-1} in late summer and increasing again to 4.8 μg g_{dw}^{-1} h^{-1} in the autumn. The seasonal behaviour of the monoterpene emission is affected by complex physicochemical controls of VOC synthesis and emissions related to the biological processes within needles (e.g. Niinemets et al., 2004; Bäck et al., 2005; Grote & Niinemets, 2008). For the deciduous trees the effect of phenology is very clear, as in the case of isoprene from aspen (*Populus tremula*), and the emissions begin 2-3 weeks after leafing and cease before the leaves are shed (Hakola et al., 1998). However, also evergreen trees may have seasonal controls in the activation of monoterpene synthesis, as well as the following emissions, as suggested by Grote & Niinemets (2008). In addition to the acclimation to the growth climate and nutrient availability, the needle age may affect the monoterpene emissions and the synthesis capacity appears to be largest during the first year when the needles are grown (Grote & Niinemets, 2008). However, majority of the emission measurements are done in controlled conditions, due to limited resources often only from one-year old shoots or during a short period ranging from few days to few weeks and thus the seasonal and inter-annual changes in synthesis and emission capacity are not captured.

The ambient air volume mixing-ratios are affected by the emission rate, loss due to photochemistry and dilution by turbulent mixing (Figure 6). The ambient monoterpene volume mixing-ratio median was 0.2 ppbv during these four days, slightly lower than the summer medians reported in **Paper VI.** High momentary peaks in the monoterpene mixing-ratio are seen in Figure 5 and were observed also in **Papers IV-VI**. The monoterpene volume mixing-ratio in rural and remote locations is low in winter and high in summer (Hakola et al., 2003; **Paper VI**). Night-time maximum is typical for the diurnal pattern of the summer-time monoterpene volume mixing-ratio in a conifer boreal forest, as observed in **Papers IV** and **VI,** due to the temperature-dependent emissions and the daily cycle in turbulent mixing.

Methanol emissions between 10 and 200 μgm^{-2} h^{-1} were determined from canopy-scale measurements with the DEC and automated online chamber method (Figure 7 and 8). The Scots pine shoot emissions were up-scaled with a needle mass per ground area ratio of 540 g_{dw} m^{-2}. The methanol emissions from shoot-level and above-canopy measurements showed a clear diurnal pattern following that of solar radiation and evapo-transpiration (Figure 7). The lowest emissions were measured by night and the highest before noon. Unlike monoterpenes, methanol is water-soluble, and emissions from Scots pine are affected by the opening of the stoma (Nemecek-Marshall et al., 1995; Niinemets & Reichstein, 2003). Harley et al. (2007) observed stomatal and temperature-controlled methanol emission as well as an emission burst after dark periods as predicted by Niinemets & Reichstein (2003). Niinemets & Reichstein (2003) link methanol emissions to the opening of stomata and partitioning between the water and gas phases. Due to the water solubility of methanol, measurement artifacts are susceptible to formation of water films in the sampling

system. Kolari et al. (2004) observed that water vapour is adsorbed onto the surface of the heated sampling tubes when the relative humidity is higher than 75%. The observed water fluxes, measured with the automated online chamber set-up, are about 60% of the actual flux (Kolari et al., 2004) and it is likely that the effect is in the same range for methanol fluxes. However, deposition of methanol on wet surfaces, such as dew formed during night-time, may even affect the ambient volume mixing-ratios. Emissions determined with the DEC and automated online chamber methods followed well the ambient temperature (Figure 8). However, since during the four-day period methanol emissions, temperature, the opening of stoma and evapo-transpiration all followed solar radiation, we could not distinguish between the effects of the different processes.

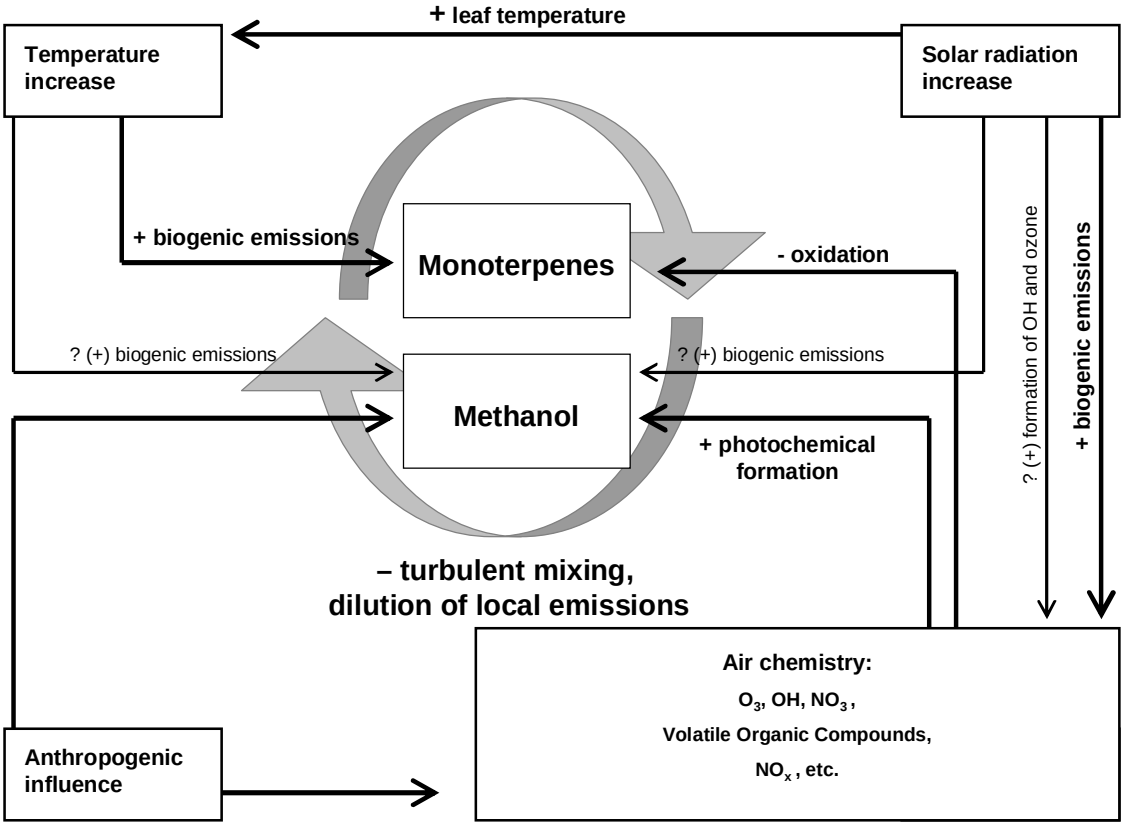


Figure 6. Possible effects of changes in environmental variables on volume mixing-ratios based on the annual variation of summer measurements of monoterpenes and methanol. Signs + and – indicate positive and negative response and (?) that the influence is uncertain. The arrows in the centre portray turbulent eddies that transport compounds and dilute local emission. Adapted from Figure 13 in Paper VI, published under Creative Commons Attribution Licence.

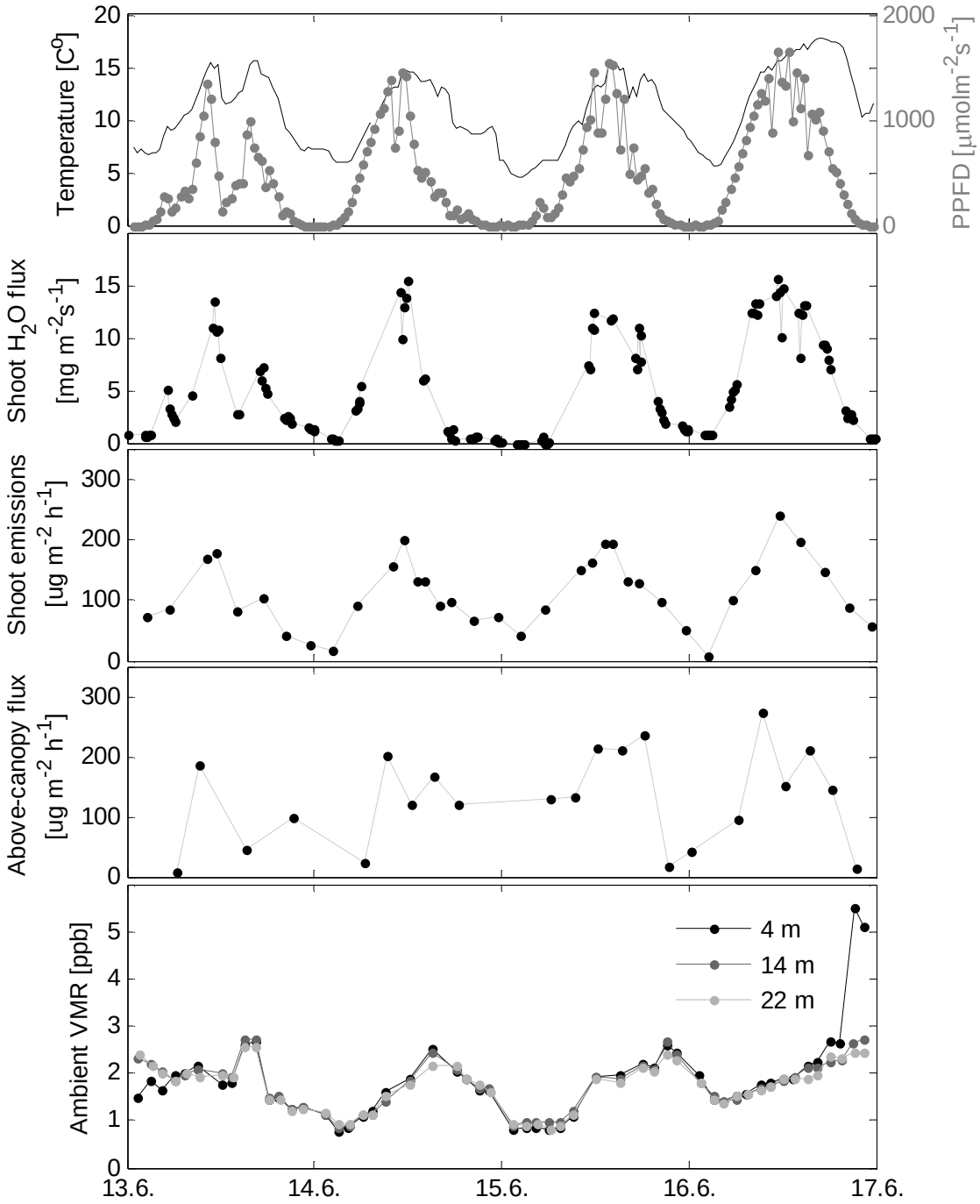


Figure 7. Results of online methanol (M33) measurements at SMEAR II from summer 2007. A) air temperature and photosynthetic photon flux density (PPFD), B), shoot water flux, from evaporation and transpiration in the automated online chamber C) methanol emission measured from a shoot in the automated online chamber and up-scaled to canopy level using a biomass of 540 $g_{dw}m^{-2}$, D) methanol flux above the canopy determined with the DEC method, and E) methanol volume mixing-ratio in ambient air at three heights.

The methanol volume mixing-ratio was between 0.4 and 5 ppbv during the four-day measurement period (Figure 7), and similar values were measured during three summers in **Papers IV** and **VI**. The diurnal cycle of the methanol volume mixing-ratio, with afternoon maximum observed here and also in **Paper III**, can be explained by the emission pattern of methanol. Although the monoterpene emissions peak only a few hours later, their mixing-ratio is highest at night-time. The differences are mainly due to the different emission processes leading to different diurnal patterns: methanol emissions are both light and temperature-controlled, and emissions diminish at sunset, while monoterpene emissions are governed by temperature, and continue through the night. The methanol and monoterpene emissions were of the same order of magnitude. However, the ambient volume mixing-ratios of methanol (Figure 7) were almost an order of magnitude larger than those of the monoterpenes (Figure 5). This is due to their different lifetimes; these were investigated in **Paper III**. Many monoterpenes are oxidized in less than an hour; the lifetime of methanol, however, is several days. Due to its long lifetime and wide-ranging emissions, methanol is often the dominant oxygenated hydrocarbon in the rural atmosphere (e.g. Fehnsenfeld et al., 1992). About 90% of the methanol emissions on the global scale come from biogenic sources (Heikes et al., 2002). At the SMEAR II site the majority of the ambient methanol and monoterpenes probably come from the trees of the surrounding forests during the summer (Figures 5 and 7). The differences between the sources and processes affecting methanol and monoterpene emissions and their ambient volume mixing-ratios are summarized in Figure 6.

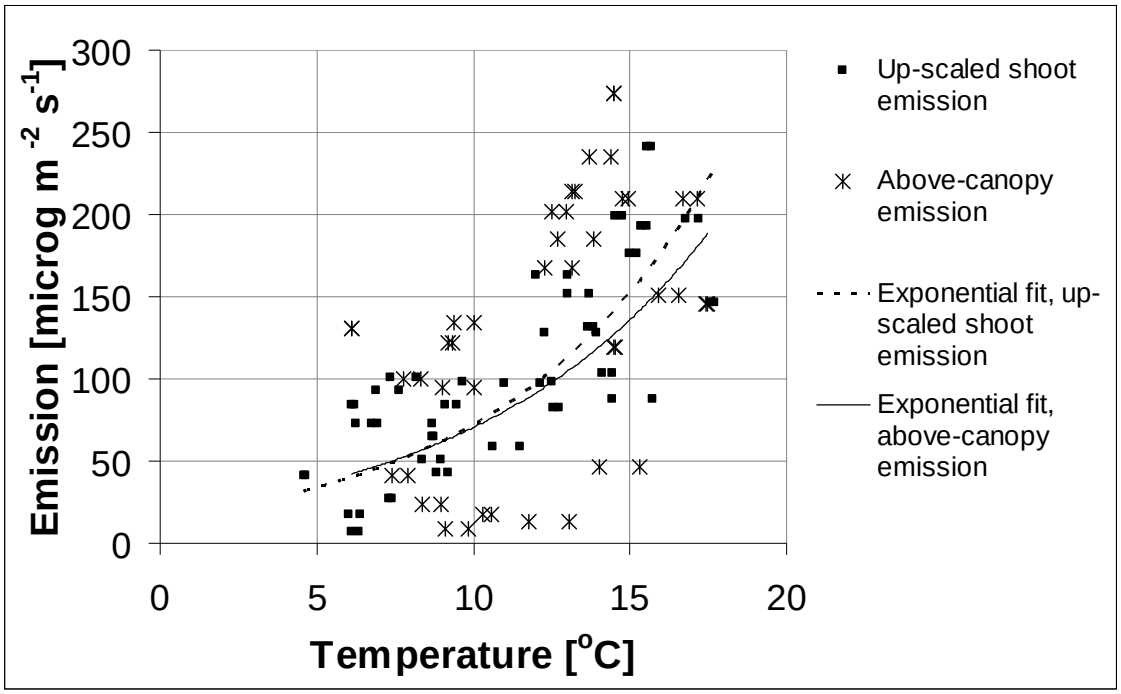


Figure 8. Methanol (M33) emissions measured at SMEAR II 13.-17.6.2007 as a function of air temperature. The methanol emission measured from a shoot in an automated online chamber is up-scaled to canopy level using a biomass density of 540 $g_{dw}m^{-2}$; methanol flux above the canopy was measured using the DEC method. The lines indicate an exponential fitting to temperature: up-scaled shoot $E_s = 16.1\ e^{0.15x}$ and above-canopy $E_c = 18.8\ e^{0.13x}$.

5.2 Biogenic VOC emissions

In addition to the monoterpene and methanol emissions from Scots pine, presented in the previous chapter, we measured the seasonal VOC emission spectra and determined emission potential of Siberian larch (**Paper II**) and determined monoterpene emission potentials of Scots pine in autumn (**Paper I**). In addition, we compared the canopy-scale emissions of monoterpenes and methanol, acetone and acetaldehyde (**Paper III**).

Monoterpene and sesquiterpene emissions from Siberian larch were reported in **Paper II** for the first time in literature. About half of the monoterpene emission was sabinene and the rest was mostly Δ^3-carene, β- and α-pinene. The major sesquiterpene emitted was α-farnesene; during spring and summer it contributed to about 10% of the terpenoid emissions. Before the Siberian larch shed its needles the sesquiterpene emissions declined to a third. The mono- and sesquiterpene emissions, measured from mature needles until the end of growing season, were well described by a temperature-dependent algorithm. The monoterpene emission potentials (according to Eq. 13) were between 0.056 and 21 μg $g_{dw}^{-1}h^{-1}$ using a β value of $0.09°C^{-1}$. The sesquiterpene emission potentials (according to Eq. 13) were between 0.4 and 1.8 μg $g_{dw}^{-1}h^{-1}$ using a β value of 0.143 $°C^{-1}$. In a review of sesquiterpene emissions from vegetation, Duhl et al. (2008) summarized that the emissions typically increase with temperature. Comparing sesquiterpene emissions is problematic, since practices in reporting them are not standardized. The temperature dependency we determined was of the same magnitude as the values determined in other studies as synthesised by Duhl et al. (2008).

Monoterpene emissions from a Scots pine shoot during autumn (**Paper I**), a time when Scots pine is hardening for the winter, were well described by temperature-dependent algorithm. The emissions had clear diurnal patterns, with maxima in the afternoons and minima during the night-time. The normalized monoterpene emission rates were increased three-fold after a cold night from 2.1 to 4.4 μg $g_{dw}^{-1}h^{-1}$. We observed also that mechanical stress and re-emissions from chamber walls can cause notable measurement artefacts.

Oxygenated VOC (OVOC) and monoterpene fluxes were measured in June 2005 above a Scots pine canopy (**Paper III**). The combined flux of oxygenated VOCs (methanol, acetone and acetaldehyde) was of the same order of magnitude as the monoterpene emissions. The average monoterpene emission rate was 460 $\mu g m^{-2}h^{-1}$, while methanol, acetone and acetaldehyde emission rates were 160, 120 and 45 $\mu g m^{-2}h^{-1}$, respectively. Compared to earlier chamber measurements of Scots pine shoots the acetone emissions were of the same order of magnitude (Janson et al., 1999; Janson & de Serves, 2001) and had a similar diurnal pattern (Janson et al., 1999). The chemical degradation of the monoterpenes was estimated to be about 10% during the transport from the emission to the measurement point, and less for the OVOCs.

5.3 Dynamics of ambient VOC concentrations

We measured the diurnal (**Papers IV-VI**) and seasonal (**Paper VI**) patterns of VOC volume mixing-ratios. The summertime diurnal patterns of monoterpenes differed from those of the other VOCs that were emitted from local sources (**Papers IV** and **VI**). The methanol, acetone and isoprene-MBO volume mixing-ratio diurnal maxima were before midnight a few hours earlier than the typical diurnal monoterpene maximum at midnight.

In **Paper VI** the diurnal patterns and seasonality of the VOC volume mixing-ratios in boreal forest air were measured from June 2006 to September 2007. The volume mixing-ratios of methanol, acetone, isoprene–MBO and monoterpene, compounds mainly deriving from biogenic emissions and gas-phase chemistry, were highest during summer and lowest in winter. Benzene, dominated by anthropogenic emissions and photochemical removal, behaved in the opposite way with winter maximum. The seasonality of acetaldehyde and methacrolein - methyl-vinyl-ketone (MACR–MVK) volume mixing-ratios were less distinct. Biogenic VOCs, methanol, acetone, isoprene–MBO and monoterpene volume mixing-ratios had clear diurnal patterns during the summers, while other VOCs did not show this behaviour (**Papers IV** and **VI**). The high summer volume mixing-ratios indicate that also the summer time emissions are higher than in spring and autumn. However, also removal processes might have the opposite effect on seasonal patterns since OH chemistry is assumed to slow down in autumn and reach a maximum during midsummer. This complicates the data interpretation. The ambient concentrations can be used as information on emissions when used with a model that describes the emission, transport and chemical processes. During winter we did not observe a systematical diurnal cycle in the VOCs volume mixing-ratios (**Paper VI**).

The measured volume mixing-ratios and their diurnal and seasonal changes were qualitatively explained by considering the sources, removal processes and turbulent mixing (**Paper VI**). A quantitative description, however, would require the use of a comprehensive chemistry model with the appropriate emissions, chemistry, deposition, mixing and transport for each compound in question. Over the whole year, methanol and acetone were the most abundant VOCs, the annual averages of their volume mixing-ratios being of the order of 1 ppbv (**Paper VI**). The methanol volume mixing-ratio was highest in June (**Paper VI**) after the time of the fastest growth rate of new shoots as well as wood in the stem that was observed from the growth of the new needles and shoots (Lappalainen et al., 2008); MacDonald & Fall (1993) linked methanol emissions to cell wall growth as they observed that twofold methanol emissions are observed from young as compared to mature leaves. Both methanol and acetone volume mixing-ratios were highest in June between 7 and 4 ppb, and lowest in January between 0.1 and 0.2 ppbv (**Paper VI**). The seasonality of the sum of C_6-compounds, including hexanal and hexenol, was less significant. On an annual level, however, the volume mixing-ratio of the sum of the C_6-compounds was also of the order of 1 ppb. The monoterpene and isoprene–MBO volume mixing-ratios were an order of magnitude lower, between summer values of 1 and 0.4 ppbv and winter values of 0.06 and 0.03 ppb, respectively. The annual median volume mixing-ratios of other VOCs were: acetaldehyde 0.2 ppb, MACR-MVK 0.1 ppb, benzene 0.1 ppb. The volume mixing-ratios of acetaldehyde and benzene ranged from undetectable to 1 ppb. The isoprene, MBO and monoterpenes have shorter lifetimes than most

OVOCs and their concentrations were dominated by local emissions. Methanol and acetone have relatively long lifetimes, and in addition to local sources receive contributions from the long range transport of anthropogenic emissions, as well as from secondary production from the oxidation of other VOCs.

In **Paper IV,** the measured compounds were divided into three classes based on the correlation of local meteorology with ambient summertime volume mixing-ratios: 1) The compound class which was correlated with the ambient air temperature and light included reactive compounds with local biological, anthropogenic or chemical sources (e.g. methanol, acetone, MVK + MACR, butanol and hexanal). 2) The compound class which was correlated with the mixing time-scale included compounds whose emissions are dependent only on temperature (monoterpenes). 3) The compound class which was not correlated with local meteorology included rather long-lived compounds (benzene, acetaldehyde).

6 Conclusions

VOCs affect atmospheric chemistry and thereafter also on the climate change in many ways. IPCC (2007) listed the long lived greenhouse gases (carbon dioxide, methane, nitrous oxide and halocarbons) and tropospheric ozone as the most important warming radiative forcing components, and aerosols as the most important cooling component, in the industrial era (1750-2005). VOCs can have warming effects on the climate: they participate in tropospheric ozone formation and compete on oxidants with the greenhouse gases thus, for example, lengthening the atmospheric lifetime of methane. Some VOCs, on the other hand, may have a cooling effect on the atmosphere by taking part in the formation of aerosol particles. In this thesis I added to knowledge about BVOC emissions and the atmospheric VOC composition: we described, for the first time in the literature, the composition and seasonality of mono- and sesquiterpene emissions from Siberian larch (*Larix sibirica*), an important tree species in the boreal vegetation zone. We contributed to the knowledge on monoterpene and oxygenated compound emissions by comparing these from a single Scots pine (*Pinus sylvestris*) shoot and from a Scots-pine-dominated forest. We also reported the ambient volume mixing-ratio composition and seasonality of VOCs measured in a Scots-pine-dominated forest.

The main conclusions of this thesis are based on the online measurements with a proton transfer reaction - mass spectrometer, with the exception of the Siberian larch emission measurements, for which adsorbent samples were analysed with thermodesorption-GC-MS analysis. The PTR-MS was used in long-term stand-alone measurements and frequent background signal measurements and systematic calibrations as well as maintenance, all essential for reliable VOC measurements, were developed. In the continuous measurements we observed that the PTR-MS has to be calibrated and the detector, secondary electron multiplier (SEM), operation voltage checked regularly, at least twice a month. In addition, a volume mixing-ratio calculation procedure relying on these measurements was developed. An automated sampling system was built for continuous measurements of emissions and ambient VOC concentrations with the PTR-MS. The system measures one hour at a time in three-hour cycles 1) ambient atmospheric volume mixing-ratios of VOCs in the boreal forest, 2) VOC fluxes above the canopy, and 3) VOC emissions from Scots pine shoots. The results obtained with the developed measurement system were systematical and in good agreement with results of previous studies suggesting that it provided reliable data. However, rigorous validation is still needed.

Siberian larch, a deciduous conifer that accounts for nearly half of the forest in Siberia (Shepashenko et al., 1998), emitted mono- and sesquiterpenes. The monoterpenes, mainly sabinene, accounted for 90% of the terpenoid emissions during summer. The rest of the emissions were sesquiterpenes, mainly α-farnesene. The normalized monoterpene emission potentials were highest in late summer, rising again in late autumn. The sesquiterpene emission potentials were also highest in late summer, but decreased towards the autumn. The emission spectrum was clearly different from those observed from the native Finnish conifers. However, more measurements are needed from fully grown mature trees and also from several individuals since there are clear genetical differences in the emission spectrum even within species (e.g. in Scots pine).

The monoterpene emissions from Siberian larch and Scots pine were well described by the temperature-dependent algorithm (Eq. 13), as were also the sesquiterpene emissions from Siberian larch. The normalized emission potentials, according to the temperature-dependent algorithm were: 1) between 0.056 and 21 µg $g_{dw}^{-1}h^{-1}$ for monoterpene emissions from Siberian larch during May-August, 2) between 2.1 and 4.4 µg $g_{dw}^{-1}h^{-1}$ for monoterpene emissions from Scots pine during August-September, and 3) between 0.4 and 1.8 µg $g_{dw}^{-1}h^{-1}$ for sesquiterpene emissions from Siberian larch. The emission potentials were calculated using a β value of 0.09 $°C^{-1}$ for monoterpenes and 0.143 $°C^{-1}$ for sesquiterpenes.

In the Scots-pine-dominate forest, canopy-scale emissions of monoterpenes and OVOCs (methanol, acetone and acetonitrile) were of the same order of magnitude. Methanol and acetone were the most abundant OVOCs emitted by the forest and in the ambient air. The majority of the monoterpene and methanol emissions from the Scots-pine-dominated forest were qualitatively explained by emissions from Scots pine shoots. Different sources, removal processes and turbulent mixing explained the measured volume mixing-ratios. The VOCs were divided into three classes based on the correlation of local meteorology with ambient summertime volume mixing-ratios: 1) Correlation with air temperature and light, reactive compounds with local biological, anthropogenic or chemical sources (methanol, acetone, MVK-MACR, butanol and hexanal). 2) Correlation with mixing time-scale, compounds whose emissions are only temperature-dependent (monoterpenes). 3) Not correlated with local meteorology (benzene, acetaldehyde).

Methanol and acetone were the most abundant VOCs at the boreal forest site; the volume mixing-ratios of both compounds were between 4 ppbv and 7 ppbv in June, and 0.1 ppbv and 0.2 ppbv in January. The annual medians of methanol, acetone and sum of C_6-compounds were of the order of 1 ppbv. Monoterpene and isoprene–MBO volume mixing-ratios were an order of magnitude lower. The mixing-ratios of monoterpenes were between summer 1 ppbv and winter 0.06 ppbv and of isoprene–MBO were between summer 0.4 ppbv and winter 0.03 ppb. Other typical annual volume mixing-ratio values included: 0.2 ppbv of acetaldehyde, 0.1 ppbv of MACR-MVK, 0.1 ppbv of benzene, with their mixing-ratios ranging from undetectable to 1 ppb. Biogenic VOC (methanol, acetone, isoprene–MBO and monoterpene) volume mixing-ratios had clear diurnal patterns during both summers. Other VOCs did not show this behaviour. During winter we did not observe a systematical diurnal cycle for any of the VOCs.

Future work includes:

- Continuous emission measurements of monoterpenes, methanol and other VOCs together with environmental variables and photosynthesis, aimed at the development of mechanistic models describing the diurnal, seasonal and annual dynamics of BVOC emissions.
- Direct calibration of the PTR-MS with a wider range of measured compounds. At the moment, only a fraction of the measured compounds are included in the calibration gas standard. Volume mixing-ratios of other compounds are calculated using a less reliable method, utilizing a relative transmission curve. In practice this improvement could be achieved with a combination of: 1) a calibration gas standard with more compounds, and 2) a calibration system that could use liquid standards. However, at the moment calibration systems

using liquid standards for the calibration of VOCs in ambient concentrations are not commercially available, and thus method development is required.

- Continuous measurements of emissions and ambient volume mixing-ratios of heavier VOCs, such as sesquiterpenes. Separation of VOCs containing oxygen or nitrogen from hydrocarbons with similar mass. These are feasible with 1) an online gas chromatographic separation prior a mass spectrometer or 2) a time of flight (TOF) PTR-MS (PTR-TOF-MS). In contrast to the quadrupole MS, that is used in the current PTR-MS, the sensitivity increases with the compounds mass and the instrument can achieve more than a hundred times better mass resolution.
- A comprehensive study of the atmospheric chemistry of the VOCs using models that describe emission, transport and chemical processes.
- Development of the automated online chambers to better suit VOC measurements. Reducing surface effects is essential, especially for measurements of water-soluble VOCs, such as methanol, and heavy compounds that are more susceptible to condensing, such as sesquiterpenes. Possible steps are: 1) minimizing the surface area in the chamber, 2) minimizing surface per volume in the sampling lines, and 3) constructing chambers from physically and chemically inert materials.

References

Altimir N., Vesala T., Keronen P., Kulmala M. and Hari P. 2002. Methodology for direct field measurements of ozone flux to foliage with shoot chambers. *Atmos. Environ.* 36, 19-29.

Ammann C., Brunner A., Spirig C. and Neftel A. 2006. Technical note: Water vapour concentration and flux measurements with PTR-MS. *Atmos. Chem. Phys.* 6, 4643–4651.

Andreae M.O. and Merlet P. 2001. Emission of trace gases and aerosols from biomass burning. *Global Biogeochemical Cycles* 15, 955–966.

Atkinson R. 1994. Gas-phase tropospheric chemistry of organic compounds. *J. Phys. Chem. Ref. Data.* Monograph No. 2, 1-216.

Atkinson R., and Arey J. 2003. Atmospheric degradation of volatile organic compounds. *Chem. Rev.* 103, 4605–4638.

Aubinet M., Grelle A., Ibrom A., Rannik Ü., Moncrieff J., Foken T., Kowalski A.S., Martin P.H., Berbigier P., Bernhofer C., Clement R., Elbers J., Granier A., Grunwald T., Morgenstern K., Pilegaard K., Rebmann C., Snijders W., Valentini R. and Vesala T. 2000. Estimates of the annual net carbon and water exchange of forests: The EUROFLUX methodology. *Adv. Ecol. Res.* 30, 113–175.

Aurela M., Riutta T., Laurila T., Tuovinen J.-P., Vesala T., Tuittila E.-S., Rinne J., Haapanala S. and Laine J. 2007. CO2 exchange of a sedge fen in southern Finland - the impact of a drought period. Tellus B 59, 826-837.

Bonn B., Kulmala M., Riipinen I., Sihto S.-L. and Ruuskanen T.M. 2008. How biogenic terpenes govern the correlation between sulfuric acid concentrations and new particle formation, *J. Geophys. Res.* 113, D11209, doi:10.1029/2007JD009327.

Boy M., Karl T., Turnipseed A., Mauldin R.L., Kosciuch E., Greenberg J., Rathbone J., Smith J., Held A., Barsanti K., Wehner B., Bauer S., Wiedensohler A., Bonn B., Kulmala M. and Guenther A.. 2008. New particle formation in the Front Range of the Colorado Rocky Mountains. *Atmos. Chem. Phys.* 8, 1577–1590.

Bäck J., Hari P., Hakola H., Juurola E. and Kulmala M. 2005. Dynamics of monoterpene emissions in Pinus sylvestris during early spring. *Boreal Env. Res.* 10, 409–424.

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

Claeys M., Wang W., Ion A.C., Kourtchev I., Gelencsér A. and Maenhaut W. 2004b.Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide. *Atmos. Environ.* 38, 4093–4098.

Chameides W. L., Fehsenfeld F., Rogers M., 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. *J. Geophys. Res.* 97, 6037-6055.

Crutzen P.J. and Andreae M.O. 1990. Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles. *Science* 250, 1669-78.

Dotan I. and Lindinger W. 1976. Mobilities of CO_2^+, N_2H^+, H_3O^+, $H_3O^+ \cdot H_2O$, and $H_3O^+ \cdot (H_2O)_2$ in N_2. *J. Chem. Phys.* 65, 5028-5030.

Duhl T.R., Helmig D. and Guenther A. 2008. Sesquiterpene emissions from vegetation: a review. *Biogeosciences* 5, 761–777.

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

de Gouw J. and Warneke C. 2007. Measurements of volatile organic compounds in the Earth's atmosphere using proton-transfer-reaction mass spectrometry. *Mass Spectrom. Rev.* 26, 223–2577.

de Gouw J.A., Brock C. A., Atlas E.L., Bates T.S., Fehsenfeld F.C., Goldan P.D., Holloway J.S., W.C. Kuster, Lerner B.M., Matthew B.M., Middlebrook A.M., Onasch T.B., Peltier R.E., Quinn P.K., Senff C.J., Stohl A., Sullivan A.P., Trainer M., Warneke C., Weber R.J. and Williams E.J. 2008. Sources of particulate matter in the northeastern United States in summer: 1. Direct emissions and secondary formation of organic matter in urban plumes. *J. Geophys. Res.* 113, D08301, doi:10.1029/2007JD009243.

Grote R. and Niinemets Ü. 2008. Modeling volatile isoprenoid emissions - A story with split ends. *Plant Biology* 10, 8-28.

Guenther A. 1997. Seasonal and spatial variations in natural volatile organic compound emissions. *Ecological Applications* 7, 34–45.

Guenther A. 2002. The contribution of reactive carbon emissions from vegetation to the carbon balance of terrestrial ecosystems. *Chemosphere* 49, 837-844.

Guenther A., Zimmerman P.R., Harley P.C., Monson R.K. and Fall R. 1993. Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses. *J. Geophys. Res.* 98, 12609-12617.

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. *J. Geophys. Res.* 100, 8873–8892.

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). *Atmos. Chem. Phys.* 6, 3181–3210.

Haapanala S., Rinne J., Hakola H., Hellén H., Laakso L., Lihavainen H., Janson R., O'Dowd C. and Kulmala M. 2007. Boundary layer concentrations and landscape scale emissions of volatile organic compounds in early spring. *Atmos. Chem. Phys.*, 7, 1869–1878.

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

Hakola H., Tarvainen V., Laurila L., Hiltunen V., Hellén H. and Keronen P. 2003. Seasonal variation of VOC concentrations above a boreal coniferous forest. *Atmos. Environ.* 37, 1623-1634.

Hakola H., Tarvainen V., Bäck J., Rinne J., Ranta H., Bonn B. and Kulmala M. 2006. Seasonal variation of mono- and sesquiterpene emission rates of Scots pine. *Biogeosciences* SRef-ID: 1726-4189/bg/2006-3-93, 93–101.

Hakola H., Haapanala S., Rinne J., Vestenius M. and Tarvainen V. 2008. VOC Emissions from Tree Stumps. *Report Series in Aerosol Science* 93, 33–36.

Hansel A., Jordan A., Warnike C., Holzinger R. and Lindinger W. 1998. Improved detection limit of the Proton-transfer Reaction Mass Spectrometer: On-line monitoring of volatile organic compounds at mixing ratios of few pptv. *Rapid Commun. Mass Spectrom.* 173, 191-241.

Hari P. and Kulmala M. 2005. Station for Measuring Ecosystem–Atmosphere Relations (SMEAR II). *Boreal Env. Res.* 10, 315–322.

Harley P., Greenberg J., Niinemets U. and Guenther A. 2007. Environmental controls over methanol emission from leaves. *Biogeosciences* 4, 1083–1099.

Hayward S., Tani A., Owen S. and Hewitt N. 2004. Online analysis of volatile organic compound emissions from Sitka spruce (*Picea sitchensis*). *Tree Physiol.* 24, 721-728.

Heikes B.G., Chang W., Pilson M.E.Q., Swift E., Singh H.B., Guenther A., Jacob D.J., Field B.D., Fall R., Riemer D. and Brand L. 2002. Atmospheric methanol budget and ocean implication. *Global Biogeochemical Cycles* 16, doi:10.1029/2002GB001895.

Hellén H., Hakola H., Reissell A. and Ruuskanen T.M. 2004. Carbonyl compounds in coniferous forest air in Hyytiälä, Southern Finland. *Atmos. Chem. Phys.* 4, 1771–1780.

Hellén H., Hakola H., Pirjola L., Laurila T. and Pystynen K.-H. 2006a. Ambient air concentrations, source profiles, and source apportionment of 71 different C2-C10 volatile organic compounds in urban and residential areas of Finland. *Environmental Science & Technology* 40, 103–108.

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

Helmig D., Revermann T., Pollmann J., Kaltschmidt O., Hernandez A.J., Bocquet F. and David D. 2003. Calibration system and analytical considerations for quantitative sesquiterpene measurements in air. *J. Chromatogr. A.* 1002 (1-2), 193-211.

IPCC 2000. Land use, land use change and forestry. A special report. Cambridge, UK, Cambridge University Press. ISBN 978 0521 804950.

IPCC 2007. Climate Change 2007 - The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the IPCC. Cambridge University Press, ISBN 978 0521 88009-1.

Ionicon GmBH. 2004. Manual for operating the PTR-MS.

Isidorov V. A., Zenkevich I.G. and Ioffe B. V. 1985**.** Volatile organic compounds in the atmosphere of forests. *Atmos. Environ.* 19, 1-8.

Isidorov V.A., Vinogorova V.T. and Rafalowski K. 2003. HS-SPME analysis of volatile organic compounds of coniferous needle litter. *Atmos. Environ.* 37, 4645–4650.

Janson R. W. 1993. Monoterpene emissions from Scots pine and Norwegian spruce. *J. Geophys. Res.* 98, 2839-2850.

Janson R. and de Serves C. 2001. Acetone and monoterpene emissions from the boreal forest in northern Europe. *Atmos. Environ.* 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. *Agric. For. Meteorol.* 98, 671–681.

Juuti S., Arey J. and Atkinson R. 1990. Monoterpene emission rate measurements from a Monterey pine. *J. Geophys.* Res. 95, 7515-7519.

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. *Atmos. Chem. Phys.* 5, 1053–1123.

Karl T. and Guenther A. 2004. Atmospheric Variability of Biogenic VOCs in the Surface Layer Measured by Proton-Transfer-Reaction mass spectrometry. *Int. J. Mass Spectr.* 239, 77-86.

Karl T., Guenther A., Jordan A., Fall R. and Lindinger W. 2001. Eddy covariance measurements of biogenic oxygenated VOC emissions from hay harvesting. *Atmos. Environ.* 35, 491-495.

Karl T.G., Spirig C., Rinne J., Stroud C., Prevost P., Greenberg J., Fall R. and Guenther A. 2002. Virtual disjunct eddy covariance measurements of organic trace compound fluxes from a subalpine forest using proton transfer reaction mass spectrometry. *Atmos. Chem. Phys.* 2, 279–291.

Karl T., Guenther A., Spirig C., Hansel A. and Fall R. 2003. Seasonal variation of biogenic VOC emissions above a mixed hardwood forest in northern Michigan. *Geophys. Res. Lett.* 30, 2186, doi:10.1029/2003GL018432.

Karl T.G., Christian T. J., Yokelson R. J., Artaxo P., Hao W. M. and Guenther A. 2007. The Tropical forest and fire emissions experiment: method evaluation of volatile organic compound emissions measured by PTR-MS, FTIR, and GC from tropical biomass burning. *Atmos. Chem. Phys.* 7, 5883-5897.

Kavouras I., Mihalopoulos N. and Stephanou E. G. 1999. Formation and gas/particle partitioning of monoterpenes photo-oxidation products over forests. *Geophys. Res. Lett.* 26, 55–59.

Kesselmeier J., Ciccioli P., Kuhn U., Stefani P., Biesenthal T., Rottenberger S., Wolf A., Vitullo M., Valentini R., Nobre A., Kabat P. and Andreae M.O. 2002. Volatile organic compound emissions in relation to plant carbon fixation and the terrestrial carbon budget. *Global Biogeochemical Cycles,* 16, 1126, doi:10.1029/2001GB001813.

Kim S., Karl T., Helmig D., Daly R., Rasmussen R. and Guenther A. 2008. Measurement of atmospheric sesquiterpenes by proton transfer reaction-mass spectrometry (PTR-MS). *Atmos. Meas. Tech. Discuss.*, 1, 401–433.

Kolari P., Keronen P. and Hari P. 2004. The accuracy of transpiration measurements with a dynamic cuvette system. *Report Series in Aerosol Science*, 68, 112–114.

Komenda M. and Koppmann R. 2002. Monoterpene emissions from Scots pine (Pinus sylvestris): field studies of emission rate variabilities. *J. Geophys. Res.* 107(D13) 4161, doi:10.1029/2001JD000691.

Kourtchev I., Ruuskanen T., Maenhaut W., Kulmala M. and Claeys M. 2005. Observation of 2-methyltetrols and related photo-oxidation products of isoprene in boreal forest aerosols from Hyytiala, Finland. *Atmos. Chem. Phys.* 5, 2761-2770.

Kourtchev I., Ruuskanen T.M., Keronen P., Sogacheva L., Dal Maso M., Reissell A., Chi X., Vermeylen R., Kulmala M., Maenhaut W. and Claeys M. 2008. Determination of isoprene and alpha-/beta-pinene oxidation products in boreal forest aerosols from Hyytiala, Finland: diel variations and possible link with particle formation events. *Plant biology* 10, 138-49.

Kroll J.H. and Seinfeld J.H. 2008. Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmos. Environ.* 42, 16, 3593–3624.

Kulmala M. 2003. How Particles Nucleate and Grow. *Science* 302, 1000-1001 doi:10.1126/science.1090848.

Kulmala M., Suni T., Lehtinen K.E.J., Dal Maso M., Boy M., Reissell A., Rannik Ü, Aalto P., Keronen P., Hakola H., Bäck J., Hoffmann T., Vesala T. and Hari H. 2004a. A new feedback mechanism linking forests, aerosols, and climate. *Atmos. Chem. Phys.* 4, 557-562.

Kulmala M., Vehkamäki H., Petäjä T., Dal Maso M., Lauri A., Kerminen V.-M., Birmili W. and McMurry P.H. 2004b. Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J. Aerosol Science* 35, 2, 143-176.

Lappalainen H.K. Sevanto S., Bäck J., Ruuskanen T.M., Rinne J., Taipale R., Kolari P., Kulmala M. and Hari P. 2008. Day-time concentrations of biogenic volatile organic compounds in a boreal forest canopy and their relation to environmental and biological factors, in preparation.

Lindfors V. and Laurila T. 2000. Biogenic volatile organic compound (VOC) emissions from forests in Finland. *Boreal Env. Res.* 5, 95–113.

Lindfors V., Laurila T., Hakola H., Steinbrecher R. and Rinne J. 2000. Modeling speciated terpenoid emissions from the European boreal forest. *Atmos. Environ.* 34, 4983–4996.

Lindinger W., Hansel A. and Jordan A. 1998. On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) - Medical applications, food control and environmental research. *Int. J. Mass Spectrom.* 173,191-241.

MacDonald R.C. and Fall R. 1993. Detection of substantial emissions of methanol from plants to the atmosphere. *Atmos. Environ.* 27A, 1709–1713.

Meskhidze N. and Nenes A. 2004. Phytoplankton and cloudiness in the southern ocean. *Science* 314, 1419-1423, DOI: 10.1126/science.1131779.

Müller J.-F. 1992. Geographical distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gases. *J. Geophys. Res.* 97, 3787–3804.

Müller J.-F., Stavrakou T., Wallens S. De Smedt I., Van Roozendael M., Potosnak M. J., Rinne J., Munger B., Goldstein A. and Guenther A.B. 2008. Global isoprene emissions estimated using MEGAN, ECMWF analyses and a detailed canopy environment model. *Atmos. Chem. Phys.* 8, 1329-1341.

Nemecek-Marshall M., MacDonald R.C., Franzen J.J., Wojciechowski C.L. and Fall R. 1995. Methanol emission from leaves: Enzymic detection of gas-phase methanol and relation of methanol fluxes to stomatal conductance and leaf development. *Plant Physiol.* 108, 1359–1368.

Niinemets Ü. and Reichstein M. 2003. Controls on the emission of plant volatiles through stomata: Differential sensitivity of emission rates to stomatal closure explained. *J. Geophys. Res.* 108, 4208, doi:10.1029/2002JD002620.

Niinemets Ü., Loreto F. and Reichstein M. 2004. Physiological and physicochemical controls on foliar volatile organic compound emissions. *Trends in Plant Science* 9, 180-186, doi:10.1016/j.tplants.2004.02.006.

Piccot S. D., Watson J. J. and Jones J. W. 1992. A global inventory of volatile organic compound emissions from anthropogenic sources. *J. Geophys. Res.* 97, 9897–9912.

Pollmann J., Ortega J. and Helmig D. 2005. Analysis of atmospheric sesquiterpenes: sampling losses and mitigation of ozone interferences. *Environ. Sci. Technol.* 39, 9620–9629.

Raivonen M., Keronen P., Vesala T., Kulmala M. and Hari P. 2003. Measuring shoot-level NO_x flux in field conditions: the role of blank chambers. *Boreal. Env. Res.* 8, 445-455.

Rinne J., Hakola H. and Laurila T. 1999. Vertical fluxes of monoterpenes above a Scots pine stand in the boreal vegetation zone. *Phys. Chem. Earth (B)* 24, 711-715.

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

Rinne J., Tuovinen J.-P., Laurila T., Hakola H., Aurela M. and Hypén H. 2000b. Measurements of isoprene and monoterpene fluxes by a gradient method above a northern boreal forest. *Agric. For. Meteorol.* 102, 25–37.

Rinne H.J.I., Guenther A.B., Warneke C., de Gouw J.A. and Luxembourg S.L. 2001. Disjunct eddy covariance technique for trace gas flux measurements. *Geophys. Res. Lett.* 28, 3139-3142.

Rinne J., Douffet T., Prigent Y. and Durand P. 2008. Field comparison of disjunct and conventional eddy covariance techniques for trace gas flux measurements. *Environmental Pollution* 152, 630-635.

Rinne J., Bäck J. and Hakola H. 2008. Biogenic volatile organic compound emissions from Eurasian Taiga: Current knowledge and future directions. *Boreal. Env. Res*. submitted

Schuh G., Heiden A.C., Hoffmann T.H., 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. *J. Atmos. Chem.* 27, 291-318.

Shao M., Czapiewski K.V., Heiden A.C., Kobel K., Komenda M., Koppman R. and Wilt J. 2001. Volatile organic compound emissions from Scots pine: mechanism and description by algorithms. *J. Geophys Res.* 106, 20,483-20491.

Sharkey T.D., Singsaas E.L., Vanderveer P.J. and Geron C.D. 1996. Field measurements of isoprene emission from trees in response to temperature and light. *Tree Physiology* 16, 649-54.

Shepashenko, D., Shvidenko, A., Nilsson, S., 1998. Phytomass (live biomass) and carbon of Siberian forests. *Biomass and Bioenergy* 14 (1), 21–31.

Shu Y. and Atkinson R. 1995. Atmospheric lifetimes and fates of a series of sesquiterpenes. *J. Geophys. Res.* 100, 7275–7281.

Simpson D. 1995. Biogenic emissions in Europe, 2, Implications for ozone control strategies. *J. Geophys. Res.* 100, 22,891–22,906.

Simpson D., Guenther A., Hewitt C.N. and Steinbrecher R. 1995. Biogenic emissions in Europe, 1, Estimates and uncertainties. *J. Geophys. Res.* 100, 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., Skiba U., Steinbrecher R., Tarrasón L. and Öquist M.G. 1999. Inventorying Emissions from Nature in Europe. *J. Geophys. Res.* 104, 8113–8152.

Spanke J., Rannik Ü., Forkel R., Nigge W. and Hoffman T. 2001. Emission fluxes and atmospheric degradation of monoterpenes above a boreal forest: field measurements and modeling. *Tellus* 53B, 406–422.

Spirig C., Neftel A., Ammann C., Dommen J., Grabmer W., Thielmann A., Schaub A., Beauchamp J., Whisthaler A. and Hansel A. 2005. Eddy covariance flux measurements of biogenic VOCs during ECHO 2003 using proton transfer reaction mass spectrometry. *Atmos. Chem. Phys.* 5, 465-481.

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. *J. Atmos. Chem.* 35, 77-99.

Suni T., Rinne J., Reissell A., Altimir N., Keronen P., Rannik Ü., Dal Maso M., Kulmala M. and Vesala T. 2003.Long-term measurements of surface fluxes above a Scots pine forest in Hyytiälä, southern Finland, 1996-2001. Bor. Env. Res. 8, 287-301.

Tani A., Hayward S. and Hewitt CN. 2003. Measurement of monoterpenes and related compounds by proton transfer reaction-mass spectrometry (PTR-MS). *Int. J. Mass Spectrom.* 223 (1-3), 561-578.

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. *Atmos. Chem. Phys.* 5, 989-998.

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, doi:10.1111/j.1600-0889.2007.00263.x.

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.

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.

VanReken, T.M., Greenberg, J.P., Harley, P.C., Guenther, A.B. and Smith, J. N. 2006. Direct Measurement of Particle Formation and Growth from the Oxidation of Biogenic Emissions. *Atmos. Chem. Phys.* 6, 4403-4413.

Williams J. and Koppmann R. Volatile Organic Compounds in the Atmosphere: An Overview. In: Koppmann R., (ed.) Volatile Organic Compounds in the Atmosphere. Blackwell Publishing, ISBN: 978-1-4051-3115-5, 2007.

Yokelson R. J., Karl T., Artaxo P., Blake D.R., Christian T.J., Griffith D.W.T., Guenther A. and Hao W.M. 2007. The tropical forest and fire emissions experiment: Overview and airborne fire emission factor measurements. *Atmos. Chem. Phys.* 7, 5175–5196.

Yu J., Griffin R.J., Cocker D.R. III, Flagan R.C., Seinfeld J.H. and Blanchard P. 1999. Observation of gaseous and particulate products of monoterpene oxidation in forest atmospheres. *Geophys. Res. Lett.* 26, 1145-1148.

Zhang R., Suh I., Zhao J., Zhang D., Fortner E.C., Tie X., Molina L.T. and Molina M.J. 2004. Atmospheric new particle formation enhanced by organic acids. *Science* 304, 1487-1490.