

REPORT SERIES IN AEROSOL SCIENCE
N:o 133 (2012)

**EMISSION MEASUREMENTS OF BIOGENIC
VOLATILE ORGANIC COMPOUNDS IN
MULTIPLE SCALES**

SAMI HAAPANALA

Division of Atmospheric Sciences
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 2a, on 29 September 2012, at 12 p.m.*

Helsinki 2012

Author's address: Department of Physics
P.O. Box 64
FI-00014 University of Helsinki
sami.haapanala@helsinki.fi

Supervisor: Docent Janne Rinne, Ph.D.
Department of Physics
University of Helsinki
Finland

Reviewers: Professor Jaakko Kukkonen, Ph.D.
Air Quality Research
Finnish Meteorological Institute
Finland

Associate professor Riikka Rinnan, Ph.D.
Department of Biology
University of Copenhagen
Denmark

Opponent: Professor Gabriel Katul, Ph.D.
Nicholas School of the Environment
Duke University
United States

ISBN 978-952-5822-59-5 (printed version)

ISSN 0784-3496

Helsinki 2012

Unigrafia Oy

ISBN 978-952-5822-60-1 (PDF version)

<http://ethesis.helsinki.fi/>

Helsinki 2012

Helsingin yliopiston verkkojulkaisut

Acknowledgements

The work presented in this thesis was carried out at the Department of Physics of the University of Helsinki. I thank Professor Juhani Keinonen, head of the Department, for providing me the working facilities at the department. I wish to thank Professor Markku Kulmala, head of the Division of Atmospheric Sciences, for the opportunity to work at this truly multidisciplinary and inspiring community. I thank Professor Timo Vesala, leader of the micrometeorology group, for introducing me to micrometeorology.

I am grateful to my supervisor Docent Janne Rinne for all guidance and support I have received, and for sharing his endless pool of good research ideas. I thank Professor Hannele Hakola and Doctor Heidi Hellén from the Finnish Meteorological Institute for sharing their invaluable expertise in VOC science, and for patiently analyzing a vast number of my samples. Competent technical support from Eki Siivola, Petri Keronen, Pasi Aalto, Heikki Laakso, Janne Levula and Topi Pohja has been essential for conducting successful measurements. I'm grateful to my closest VOC scientist colleagues Taina Ruuskanen, Risto Taipale, Johanna Patokoski, Maija Kajos and Pekka Rantala as well as to all my other workmates for good company during the years.

I thank Professor Jaakko Kukkonen and Associate professor Riikka Rinnan for reviewing this thesis and for their valuable comments to improve it.

The Academy of Finland as well as Maj and Tor Nessling foundation are gratefully acknowledged for the financial support to my research. Magnus Ehrnrooth foundation, Vilho, Yrjö and Kalle Väisälä fund, and ACCENT-BIAFLUX are acknowledged for financial support to travels.

Finally, I would like to express my gratitude to my family for their endless support and interest towards my work, and to Päivi for love and care.

Emission Measurements of Biogenic Volatile Organic Compounds in Multiple Scales

Sami Antero Haapanala
University of Helsinki, 2012

Abstract

Volatile organic compounds (VOCs) are reactive trace gases abundant in the atmosphere. As strongly reactive constituents they have many impacts on the atmospheric chemistry. To properly understand the processes involved in VOC cycles within the biosphere and atmosphere, we must have comprehensive knowledge on the biogenic and anthropogenic emissions and atmospheric concentrations. In this thesis, the emissions of VOCs were measured in many scales from various Fennoscandian ecosystems, utilizing several methods.

First, enclosure method was applied to study the branch scale VOC emission from mountain birch. The measurements were conducted during two successive growing seasons. Significant emissions of sesquiterpenes were observed in the first year but not in the second one. Second, relaxed eddy accumulation (REA) method was used to study the ecosystem scale emissions of light hydrocarbons from a wetland. In addition to methane, the only significant emission was that of isoprene. Isoprene emission potential was found to be about $680 \mu\text{g m}^{-2} \text{h}^{-1}$. The REA method was further developed by studying the possible stability dependency of the method. Another ecosystem scale flux measurement method, disjunct eddy accumulation (DEA), was applied to study monoterpene emissions from a timber felling area. The emissions of monoterpenes were very high for a few months after felling, peaking at $5200 \mu\text{g m}^{-2} \text{h}^{-1}$. Despite of the short period those emissions seem to be of great importance for the atmospheric VOC burden. Third, profiles of boundary layer concentrations of some biogenic and anthropogenic VOCs were measured using a hot air balloon as a platform. Landscape scale emissions were inferred using the concentration data.

Overall, our understanding of the previously poorly known VOC emissions from some Fennoscandian ecosystems was increased. This study highlights the importance to quantify emission hotspots of even marginal ecosystems to get comprehensive understanding for emission inventories and future predictions. The correct choice of measuring methods and experiment setup is essential for reliable field data.

Keywords: VOC, isoprene, monoterpenes, sesquiterpenes, emission, turbulent fluxes, ecosystem

Nomenclature

ABL	Atmospheric Boundary Layer
ASL	Atmospheric Surface Layer
BVOC	Biogenic Volatile Organic Compound
DEA	Disjunct Eddy Accumulation
EA	Eddy Accumulation
EC	Eddy Covariance
ECD	Electron Capture Detector
EZ	Entrainment Zone
FID	Flame Ionization Detector
ISR	Intermediate Storage Reservoir
PTFE	Polytetrafluoroethylene
PTR-MS	Proton Transfer Reaction - Mass Spectrometer
REA	Relaxed Eddy Accumulation
SNR	Signal-to-Noise Ratio
VOC	Volatile Organic Compound

Contents

List of publications	7
1 Introduction	8
2 Background	11
2.1 Atmospheric boundary layer	11
2.2 Surface flux measurement methods	12
2.3 Flux estimates inferred from the mixed layer concentrations	15
2.4 Dependence of BVOC emissions on temperature and light.....	16
3 Experimental methods and the measurements	18
3.1 Study sites	18
3.2 Field measurement methods.....	19
3.2.1 REA method.....	19
3.2.2 DEA method	20
3.2.3 Mixed box budget method	21
3.2.4 Enclosure method.....	22
3.3 Sampling and chemical analyses.....	23
3.3.1 Light VOC analysis.....	23
3.3.2 Analysis of terpenes and aromatic hydrocarbons.....	24
3.3.3 Methane analysis.....	24
4 Results and discussion	25
4.1 Emissions of VOCs from selected ecosystems	25
4.1.1 Emissions of hydrocarbons from a boreal fen.....	25
4.1.2 Emissions of VOCs from mountain birches.....	26
4.1.3 VOCs emitted from forest felling areas	27
4.2 Landscape scale emissions of VOCs from boreal forest zone	28
5 Review of the papers and author's contribution	30
6 Conclusions	32
References.....	34

List of publications

This thesis consists of an introductory review followed by five original research articles. **Papers I, III, IV** and **V** are reprinted under the Creative Commons Attribution License. **Paper II** is reproduced with the kind permission of the journal. In the review, the papers are cited according to their Roman numerals.

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

II Grönholm T., Haapanala S., Launiainen S., Rinne J., Vesala T. and Rannik Ü. The dependence of the β coefficient of REA system with dynamic deadband on atmospheric conditions. *Environmental Pollution*, **152**, 597-603, 2007.

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

IV Haapanala S., Ekberg A., Hakola H., Tarvainen V., Rinne J., Hellén H. and Arneth A. Mountain birch – potentially large source of sesquiterpenes into high latitude atmosphere. *Biogeosciences*, **6**, 2709-2718, 2009.

V Haapanala S., Hakola H., Hellén H., Vestenius M., Levula J. and Rinne J. Is forest management a significant source of monoterpenes into the boreal atmosphere? *Biogeosciences*, **9**, 1291-1300, 2012.

1 Introduction

Volatile organic compounds (VOCs) are a diverse group of gaseous, reactive, carbon containing compounds. Since the pioneering days of Went (1960), the importance of VOCs in the atmospheric chemistry and physics has been gradually understood. Emerging concern about the climate change has increased our interest towards the complex processes within biosphere-atmosphere continuum. As a consequence, the multiple roles of VOCs have become under intensive research.

VOCs are released into the atmosphere by various biogenic (of natural origin) and anthropogenic (of human origin) sources. Globally, the biogenic sources are estimated to dominate the VOC emissions by a factor of about ten (Piccot et al., 1992; Guenther et al., 1995). Anthropogenic sources include fuel production, distribution and consumption, solvent use, chemical industry and biomass burning. Biogenic sources mean plants, soils and oceans. Plants emit a large number of different VOCs. The known emitted compounds include isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$), MBO (2-methyl-3-buten-2-ol; $C_5H_{10}O$), alcohols, carbonyls, and many others (e.g. Koppmann, 2007).

A small portion of the carbon assimilated by plants ends up as VOCs in the complex processes inside plant tissues. Some portion of the VOCs produced by plants is released directly whereas some VOCs are stored within the plants (e.g. Grote & Niinemets, 2008; Ghirardo et al., 2010). For example coniferous trees store a large amount of monoterpenes in their resin ducts and part of the emission is passive evaporation of stored VOCs from those in-plant reservoirs. In addition, plants actively produce and release VOCs for many, partly unknown, purposes. These include plant-to-plant signaling, plants defending themselves against herbivory or extreme environmental conditions, etc. (see e.g. Yuan et al., 2009 and Loreto & Schnitzler, 2010 for overview).

VOCs are important for the atmosphere in many ways. Once emitted to the atmosphere, VOCs take part in many reactions and undergo chemical transformations. These reactions are initiated mainly by atmospheric oxidants: ozone (O_3), hydroxyl radical ($OH\cdot$) and nitrate radical ($NO_3\cdot$). Nitrate radical is abundant in the troposphere only in the nighttime due to fast photolysis in the presence of sunlight. The compounds resulting from the oxidation processes of higher molecular weight VOCs are often less volatile and capable of condensing into liquid or solid phase (see Calogirou et al., 1999 for review). Therefore, the VOCs or their oxidation products can act as a precursor for aerosol particle growth (e.g. Kavouras et al., 1998; Kulmala, 2003). By affecting the number, size and composition of aerosol particles, the VOCs have indirect effect on the radiation balance of the atmosphere (IPCC, 2007). Depending on the specific

composition of the VOC mixture present in the atmosphere, the resulting particle population may have different properties and thus different radiative forcing.

Within the lower troposphere, the presence of VOCs affects ozone concentration. In clean air, where NO_x concentration is low, the oxidative reactions between VOCs and ozone consume both thus decreasing the ozone concentration. However, large concentration of VOCs together with NO_x present in polluted air may also lead to ozone formation (Seinfeld & Pandis, 1998; Atkinson, 2000). Ozone concentration in the lower troposphere is of great importance since in too high concentrations it is toxic to plants and animals (e.g. Iriti & Faoro, 2008 and the references therein). Moreover, ozone is also a significant greenhouse gas. Increasing ozone concentration in the troposphere leads to positive radiative forcing which is, however, partly counterbalanced by negative forcing due to stratospheric ozone depletion.

By consuming atmospheric oxidants and thus affecting the oxidative capacity of the atmosphere, the VOCs alter the lifetimes of atmospheric reactive constituents. For example, the main sink of atmospheric methane is oxidation by tropospheric $\text{OH}\cdot$. By consuming the $\text{OH}\cdot$, the presence of VOCs will slow down the oxidation of methane thus making its lifetime longer and atmospheric concentration higher (Kaplan et al., 2006). That will have small positive effect on radiative forcing (IPCC, 2007). Similarly to methane, reduced oxidative capacity of atmosphere will increase the CO concentration in the atmosphere. Furthermore, CO is produced from oxidation of VOCs.

As the VOCs are obviously important for understanding the chemistry and physics of the atmosphere, much effort has been made to measure them. Traditionally, the VOC concentrations have been analyzed using various gas chromatographic methods. These methods are well established and accurate but labor-intensive. Lately, proton transfer reaction mass spectrometry (PTR-MS; Hansel et al., 1995; Lindinger et al., 1998) has become a key instrument in VOC science, mostly as a result of its relatively high time resolution. The major disadvantage of the PTR-MS is the limited capability of separating compounds with the same mass.

To get a comprehensive understanding of VOCs in the atmosphere and biosphere, both atmospheric concentrations and source/sink strengths of different VOCs must be measured. Emission or deposition rates in a small scale (leaf, branch, surface community) are measured using enclosures. In the ecosystem scale, emission or deposition fluxes are measured using a repertoire of micrometeorological methods. The mean surface emission in the landscape scale can be estimated using boundary layer budget or mixed layer gradient methods. Even larger scale regional fluxes can be inferred from the boundary layer

concentration measurements using atmospheric transport modeling. However, in the case of reactive VOCs this requires very sophisticated air chemistry modeling simultaneously.

The objectives of this work were to evaluate different methods to measure VOC emissions from natural sources in different scales, to evaluate existing measurement systems and further develop them, and to characterize the previously poorly known VOC emissions from some ecosystems in Fennoscandia. The specific aims were:

- to determine the branch scale emissions of mono- and sesquiterpenes from mountain birches (*Betula pubescens* ssp. *czerepanovii* (Orlova) Hämet-Ahti) and to evaluate their possible importance to the atmospheric VOC burden in high latitudes;
- to determine the ecosystem scale emissions of light hydrocarbons, halogenated hydrocarbons and methane from a boreal fen, and to construct a field deployable REA (Relaxed Eddy Accumulation) measurement system for this purpose;
- to determine whether forest felling causes significant emissions of terpenoids, and to construct a field deployable DEA (Disjunct Eddy Accumulation) system for this purpose, and
- to compare landscape scale emissions, obtained from boundary layer concentration data, to previously measured ecosystem scale fluxes over boreal forest zone.

2 Background

2.1 Atmospheric boundary layer

Atmospheric boundary layer (ABL) is the lowest part of the troposphere. Properties of this layer are influenced by the Earth's surface in the time scale of an hour or less. The flow within the ABL is characterized by turbulence, i.e. chaotic changes in the velocity field. Similar fluctuations occur in other properties of the air, namely scalar concentrations, density and temperature. Wind shear, typical for the air flow above a surface, produces turbulent kinetic energy. During the daytime, convection triggered by the solar heating at the surface is another important source of turbulent kinetic energy into the ABL. In the nighttime the turbulence is suppressed by the thermal stability (Stull, 1988).

Turbulent eddies cover a large size range from sub-millimeter up to the length scale limited by the ABL height (usually between 100 m and 2 km). Turbulent energy formation occurs in the largest length scales. Turbulent energy is then being transported into smaller and smaller eddies. In this inertial sub-range turbulent energy is not produced nor dissipated. Finally, the turbulent energy is transported into smallest eddies and dissipated into heat by molecular viscosity.

Atmospheric boundary layer can be separated into several sections (see Fig. 1). At the bottom of the ABL there is a sub-layer called atmospheric surface layer (ASL). Within the ASL, but well above the roughness elements of the surface (i.e. trees, buildings etc.), the surface fluxes of energy and matter are considered to be independent of height. This is an important layer for surface flux measurements to be discussed below in the Section 2.2. Closer to the roughness elements, up to about their height plus inter-element spacing, the assumption of constant flux is not valid. Moreover, the statistical properties of turbulence are dependent also on the distance from the roughness elements, i.e. horizontal location (Arya, 2001). The upmost zone of the ABL is defined as entrainment zone (EZ) where the interactions between the ABL and free troposphere take place. During the daytime, between the surface layer and the entrainment zone there is a mixed layer as a result of strong convective mixing. In the mixed layer the properties of air (e.g. trace gas concentrations, potential temperature) are almost constant in height and they are not directly affected by the surface below but rather by the average conditions within a scale of hundreds of kilometers (Gloor et al., 2001). In the nighttime, as the convective mixing ceases, the mixed layer gradually becomes residual layer and a stable nocturnal boundary layer evolves from bottom as a result of surface cooling (Stull, 1988). During the high latitude winter the daily pattern of the ABL structure disappears due to absence of solar radiation, and the boundary layer may remain stable throughout the day.

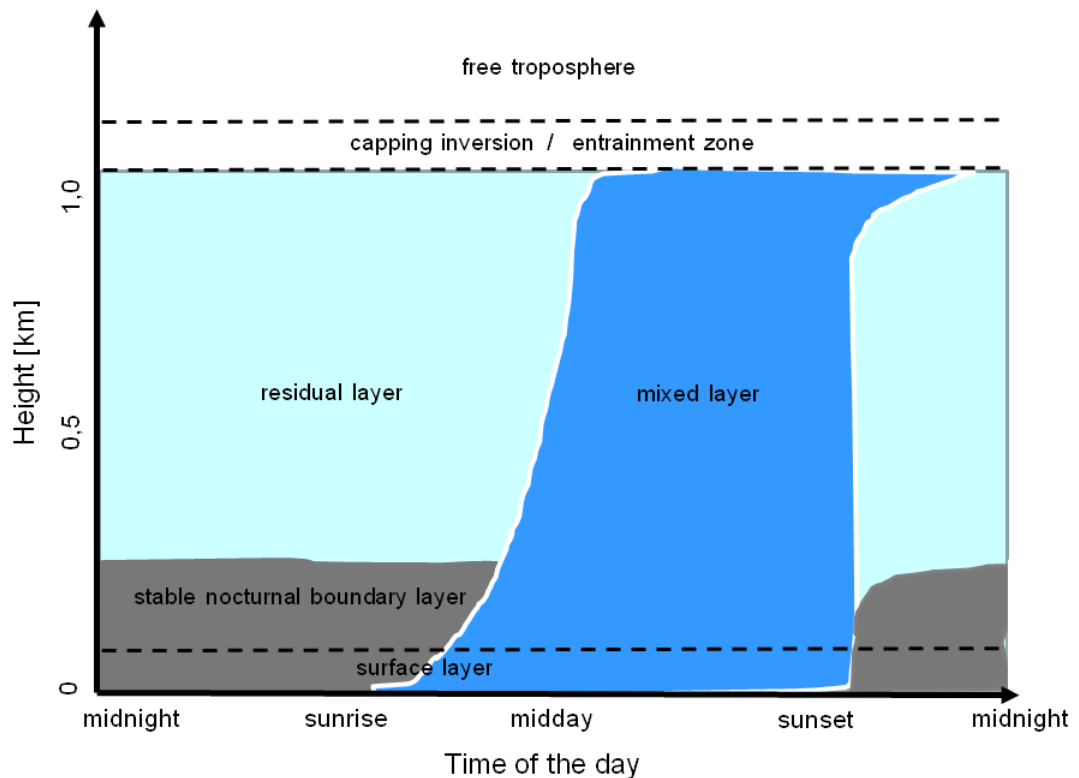


Figure 1. Schematic illustration of typical boundary layer structure and daily development during summer season. Modified based on Stull (1988).

2.2 Surface flux measurement methods

Interaction between the atmosphere and the biosphere is determined by the energy and matter fluxes between the two. Considering ecosystem scale fluxes, energy and matter transport by turbulent eddies is orders of magnitudes more efficient than molecular diffusion. Therefore, measuring just the vertical turbulent transport above an ecosystem determines the energy and matter transport between the ecosystem and the atmosphere.

Eddy covariance (EC) is a direct method to measure turbulent fluxes (e.g. Kaimal & Finnigan, 1994; Aubinet et al., 2000). For the flux calculation, high-frequency time series of wind components and mixing ratio of the compound of interest are measured near the same point. Afterwards, the average values \bar{x} are removed from the time series to yield the fluctuations $x' = x - \bar{x}$ and subsequently the covariance between the time series of vertical wind speed fluctuations w' and mixing ratio fluctuations c' is calculated to yield the flux density F ,

$$F = \bar{\rho} \overline{w'c'}, \quad (1)$$

where $\bar{\rho}$ is the average density of air during the measurement period.

The theory behind the EC method makes several assumptions of the conditions and environment where the EC measurements are conducted. First of all, the conditions must be stationary, so that the statistical properties of turbulence do not change in time. Second, the terrain must be horizontal and uniform so that the average vertical wind and horizontal net flux become negligible. In addition, the turbulence must be intense enough so that the turbulent transport dominates over other transport mechanisms. To properly interpret the results, the flux source area (footprint) must be uniform within a certain range. Eq. (1) is an idealized form of the flux calculation. In reality, the flux needs to be corrected for finite frequency response of the analyzers, displacement of the sensors and density fluctuations caused by humidity and temperature variations.

Established practice is to calculate EC fluxes over a time span of 30 minutes, however a range of about 15 minutes to several hours have been used. It is important to select long enough averaging period so that all relevant turbulent time scales are represented. On the other hand, the period should be short enough to keep the conditions stationary.

For several compounds, such as carbon dioxide, water vapor, ozone and methane, the eddy covariance measurements are easy to carry out due to existence of fast response analyzers. For many other compounds, such as VOCs, availability of fast response analyzers is limited. To overcome such practical problems, some variants of the EC method have been developed.

Desjardins (1977) proposed an eddy accumulation (EA) method which is, similarly to EC, a direct technique to measure turbulent fluxes. In EA the properties of air (e.g. temperature), or the air itself to be analyzed afterwards, is sampled into two separate reservoirs depending on the sign of the vertical wind velocity. The sampling must be done at an amount proportional to the vertical wind velocity which in the case of trace gas flux measurement requires the sampling flow to be adjusted according to the instantaneous vertical wind velocity. The vertical flux density F is calculated from the averaged measurands

$$F = \overline{w_{UP}} c_{UP} + \overline{w_{DOWN}} c_{DOWN}, \quad (2)$$

where $\overline{w_{UP}}$ and $\overline{w_{DOWN}}$ are the mean vertical velocities during updrafts ($w > 0$) and downdrafts ($w < 0$), respectively. c_{UP} and c_{DOWN} are the mean concentrations of the

updraft and downdraft samples, respectively. In practice, EA system is extremely difficult to implement for trace gases which should then be accumulated using flow proportional to the instantaneous vertical wind velocity.

Businger and Oncley (1990) proposed a method where the requirement of the sampling flow to change along with vertical wind velocity can be avoided. In this method, relaxed eddy accumulation (REA), sample collection is conducted based on the direction of the vertical wind velocity only, independent of its magnitude. The vertical flux density F becomes

$$F = \beta \sigma_w (c_{UP} - c_{DOWN}), \quad (3)$$

where β is a theoretically or empirically determined dimensionless coefficient of proportionality, σ_w is the standard deviation of vertical wind velocity and c_{UP} and c_{DOWN} are the mean concentrations of the updrafts and downdrafts, respectively. Eq. 3 can be theoretically derived using joint probability distribution of w and c .

In order to increase the concentration difference between the reservoirs, a sampling threshold (dead band) is often used around $w=0$. Between the threshold values the air samples are not collected at all. Increased concentration difference is often a great advantage since the accuracy of chemical analysis of trace species is limited. If the dead band is dynamic, i.e. proportional to the running mean of the standard deviation of the vertical wind speed, it will keep the coefficient β constant and independent of atmospheric conditions such as stability and turbulence intensity (e.g. **Paper II** and the references therein). The optimal dead band width to maximize the signal-to-noise ratio (SNR) is discussed by e.g. Oncley et al. (1993). They conclude that the dead band of about $w > \pm 0.6\sigma_w$ gives the best signal-to-noise ratio, however the maximum of SNR is broad.

In addition to the continuous measurements, turbulent fluxes can be determined from a discontinuous time series. Disjunct eddy covariance (DEC) is a method where the flux is calculated in a similar manner than in the EC method, but using a subset of the continuous time series (see Rinne and Ammann, 2012). In the disjunct eddy accumulation (DEA), fast grab samples are taken at regular intervals (e.g. every 30 s). Each sample is stored in the updraft or downdraft reservoirs according to the direction of the vertical wind at the time of the sample grabbing and the amount of the sample is determined by the magnitude of the vertical wind (Rinne et al., 2000). The resulting concentrations can be analyzed using slow methods, e.g. gas chromatography. Disjunct methods will give unbiased estimates of turbulent fluxes. However, the random error is significantly increased as a result of small number of samples (Rinne et al., 2008; Turnipseed et al., 2009).

2.3 Flux estimates inferred from the mixed layer concentrations

Landscape scale surface fluxes can be inferred using concentration measurements within the mixed layer. In the mixed box approach, the mixed layer is considered to be a well mixed box where the sources (surface flux) and sinks (chemical degradation and entrainment) together with horizontal advection define change of the concentration of a compound. A complete mass conservation equation can be written in the form

$$\frac{\partial c}{\partial t} + U \frac{\partial c}{\partial x} + \frac{\overline{w'_{z_i} c'_{z_i}} - \overline{w'_0 c'_0}}{z_i} = S, \quad (4)$$

where c is the mean concentration within the mixed layer, U is wind speed along the mean wind direction, $\frac{\partial c}{\partial x}$ is horizontal concentration gradient along the direction of U , $\overline{w'_{z_i} c'_{z_i}}$ and $\overline{w'_0 c'_0}$ are the turbulent fluxes at the top and bottom of the mixed layer, respectively, z_i is the height of the mixed layer, and S represents the chemical sources and sinks within the mixed layer. This representation assumes the vertical flux profile to be linear within the mixed layer, and that the horizontal turbulent flux and the mean vertical advection are negligible (Guenther et al., 1996).

To calculate the surface flux using practically feasible measurements, we need to further simplify the expression. Assuming that the concentration has reached a steady state and is homogenous in space we can neglect the two leftmost terms of Eq. (4). If we further assume entrainment flux at the top of the boundary layer to be negligible, the surface flux can be written as

$$\overline{w'_0 c'_0} = z_i S, \quad (5)$$

Entrainment flux can be assumed negligible in case of rapidly reacting compounds, such as VOCs, since the chemical sink dominates strongly. For VOCs without significant sources above the surface, the chemical sink term S can be written as

$$S = \sum_j c_{VOC} c_{oxidant,j} k_{oxidant,j}, \quad (6)$$

where c_{VOC} is the mean concentration of the VOC along the vertical column, $c_{oxidant,j}$ are the concentrations of relevant oxidants and $k_{oxidant,j}$ are the second order reaction rate constants between the VOC and oxidant in question. Finally, the surface flux density can be calculated from

$$\overline{w_0 c_0} = z_i \sum_j c_{VOC} c_{oxidant,j} k_{oxidant,j}. \quad (7)$$

2.4 Dependence of BVOC emissions on temperature and light

The emission rates of biogenic VOCs are generally dependent on temperature. The emissions originating purely from existing storage pools within plant tissues, such as resin ducts in coniferous trees, are often explained by

$$I = I_S \exp(\gamma(T - T_S)), \quad (8)$$

where I is the observed emission, I_S is the standard emission potential in temperature T_S , γ is the temperature sensitivity factor (β in **Papers III, IV and V**) and T is the actual temperature (Guenther et al., 1993). This formulation is based on empirical observations on monoterpene emission from plants, and it resembles the temperature dependence of vapor pressure of those compounds. Despite of its simplicity, this relationship is found to be very useful to predict e.g. monoterpene emissions from variety of plants.

Some compounds are not stored within the plants but are emitted almost directly after biosynthesis. In addition to temperature, synthesis rate of VOCs follow photosynthesis and thus available light. Commonly applied, semiempirical description for such emission is

$$I = I_S C_L C_T, \quad (9)$$

where I is the observed emission and I_S is the standard emission potential at photosynthetic photon flux density of $L_0=1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ and leaf temperature of $T_0=30^\circ\text{C}$. C_L is a light dependency factor predicting rate of electron transport, saturating at L_0 and it is defined as

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{1 + \alpha^2 L^2}}, \quad (10)$$

where α and C_{L1} are empirically determined coefficients and L is the photosynthetic photon flux density. C_T is a temperature dependency factor explaining the enzymatic activity within chloroplast, having its maximum below 40°C . C_T is defined as

$$C_T = \frac{\exp\left(\frac{C_{T1}(T-T_S)}{RT_S T}\right)}{C_{T3} + \exp\left(\frac{C_{T2}(T-T_M)}{RT_S T}\right)}, \quad (11)$$

where C_{T1} , C_{T2} , C_{T3} and T_M are empirically determined coefficients, T_S is the standard temperature (303 K), R is the universal gas constant and T is the measured temperature (Guenther et al., 1993; Guenther, 1997). This type of algorithm is found to explain well e.g. isoprene emission (e.g. Rinne et al., 2002; Kuhn et al., 2004).

In practice, the emissions from many plants are a combination originating from storage pools and directly from de novo biosynthesis. This can be modeled using hybrid algorithms that are rarely applied to flux measurement data (Steinbrecher et al., 1999; Spanke et al., 2001; Holzke et al., 2006; Taipale et al., 2011; **Paper IV**) and have recently been shown to be justified by well controlled laboratory experiments (Ghirardo et al., 2010). The approach used in **Paper IV** is a linear combination of the Eqs. (8) and (9). The weight coefficients are determined to maximize the level of explanation of the measured flux.

3 Experimental methods and the measurements

3.1 Study sites

The measurements presented in this thesis were conducted in two areas in Fennoscandia (see Fig. 2). The studies of **Papers I, II, III** and **V** were carried out in southern Finland, near the SMEAR II –measurement station in Hyytiälä (61°51'N, 24°17'E, 181 m above sea level). The station is further described by Hari & Kulmala (2005). The Hyytiälä area belongs to the south boreal vegetation zone. Coniferous forests, dominated by Norway spruce (*Picea abies* L.) and Scots pine (*Pinus sylvestris* L.), account for about 70% of the area. The long-term mean annual temperature of the area is about 3°C and the mean precipitation about 700 mm (Drebs et al., 2002).

The study presented in **Paper IV** was carried out in northern Sweden, in the Stordalen Nature Reserve (68°20'N, 18°49'E, 388 m above sea level), near Abisko village. The area is located in the northern border of north boreal vegetation zone. The long-term mean annual temperature of the area is about -1°C and the mean precipitation 300 mm (Alexandersson et al., 1991).



Figure 2. A map of Fennoscandia indicating the locations of the measurement sites Hyytiälä and Abisko.

3.2 Field measurement methods

Several methods for measuring the fluxes of VOCs were used in this study. The methods cover a large range of size scales, from branch scale up to landscape scale. Each method has pros and cons and consequently the selection of method depends on the specific needs.

3.2.1 REA method

As discussed in Section 2.2, relaxed eddy accumulation (REA) is a micrometeorological method to measure ecosystem scale net flux. In **Paper I** it was used to measure the flux of isoprene and some other light hydrocarbons over a wetland. As opposite to the direct flux measurement method, eddy covariance, the REA method does not need fast chemical analysis of the compounds. This is important for VOCs as there are only a few compounds that can be analyzed in real time at a rate adequate to eddy covariance method.

In the REA method, samples of updraft and downdraft air are accumulated into two reservoirs. Sorting the updraft and downdraft air parcels is based on the instantaneous vertical wind speed measured by a 3-D sonic anemometer. Because the sorting of samples is conducted online, no coordinate rotations or other post processing corrections are possible. Therefore, it is essential to ensure that the sonic is orientated correctly or avoid vertical wind measurement to be contaminated from horizontal wind components. The flux density is directly proportional to the concentration difference between the reservoirs, and to the standard deviation of the vertical wind velocity (see Eq. 3).

In our implementation (see Fig. 3), the REA valves allowing updraft and downdraft samples to be collected were located on the mast, just below the sonic anemometer. Upstream of the valves there were ozone scrubbers to remove ozone from the air samples. This is important since otherwise the O_3 would destroy VOCs from the samples before analysis (e.g. Helmig et al., 2004 and the references therein). A dead-band valve was used in order to maintain a constant flow and pressure downstream of the reservoirs, when both sampling valves are closed. The samples were accumulated into bags made of Tedlar. The bags were located inside airtight containers that were slightly under pressurized by a constant drain flow of about 1 l min^{-1} . The valves and tubes that were in touch with the sample air were made of PTFE (polytetrafluoroethylene) to prevent VOCs from sticking into the surfaces and thus causing memory effect in the measurements. The REA system employed a dynamic dead-band with sampling threshold of $-0.5\sigma_w > w > 0.5\sigma_w$, where σ_w is a running mean of the standard deviation of the vertical wind velocity. Dynamic dead-band was considered to maintain β constant and no tracer measurements were used to define β separately for each period (**Paper II**).

After a 30 minutes sampling period, the sample air from the bags were pumped into electro polished stainless steel canisters to be analyzed in the laboratory. Also the pump had Teflon membranes in order to minimize contamination of the samples.

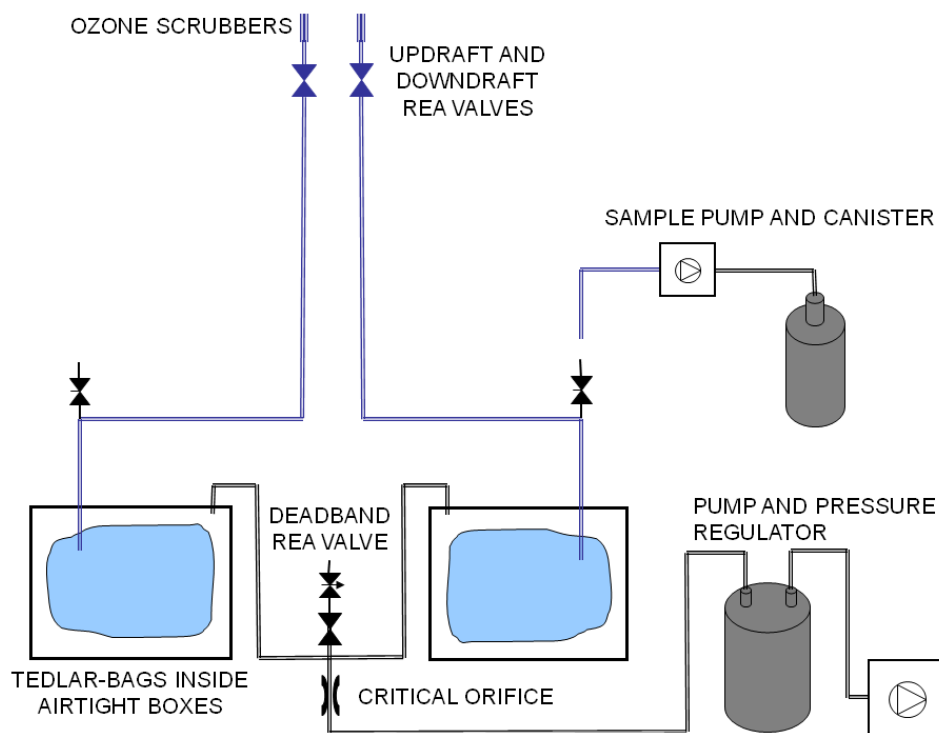


Figure 3. Schematic illustration of the structure of the REA flow system used in **Paper I**. Blue color indicates parts made of PTFE.

3.2.2 DEA method

Besides REA, another micrometeorological method, disjunct eddy accumulation (DEA), was used (**Paper V**). The aim in the present study was to measure monoterpene flux from a forest cut area. In the DEA system (see Fig. 4), a sample of air was grabbed very quickly (in about 0.1 s) into an intermediate storage reservoir (ISR). As the ISR an electro polished stainless steel bottle was used. The bottle was evacuated to below 10 hPa (about 1% of the atmospheric pressure) before each sampling cycle. The under pressure inside the ISR allowed it to fill with the sample air during the short valve opening without a pump in the sampling line. At the same time with the sample grabbing, the vertical wind speed measured by a 3-D sonic anemometer was recorded. As in the case of REA, no post processing including coordinate rotation is possible when using DEA.

After each sampling, a portion of the sampled air was passed into the updraft or downdraft reservoir based on the direction of the vertical wind at the time of the sampling. The amount of sample passed into the reservoir was directly

proportional to the vertical wind velocity at the time of the sample grabbing. As a result, a direct flux measurement was achieved. Cartridges filled with Tenax TA and Carbopack II adsorbents were used as the final reservoirs. To collect enough samples we operated the DEA for 55 minutes. A disadvantage of the DEA method is the small amount of samples per flux reading which causes large random error in the measurement (e.g. Rinne et al., 2008; Turnipseed et al., 2009).

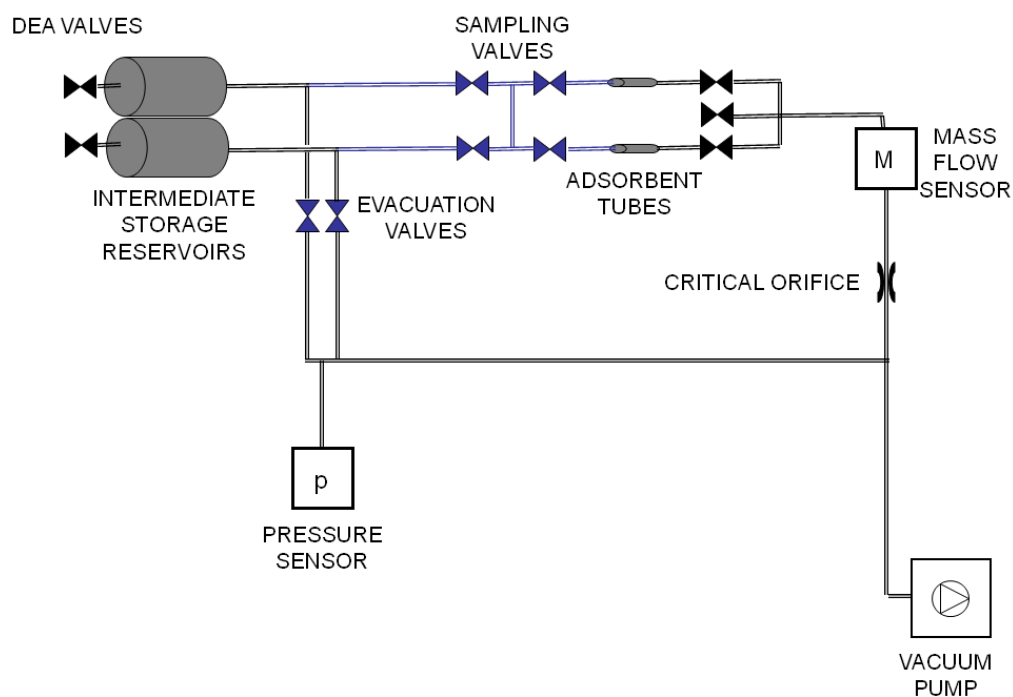


Figure 4. Schematic illustration of the structure of the DEA flow system used in **Paper V**. Blue color indicates parts made of PTFE.

3.2.3 Mixed box budget method

In **Paper III**, the landscape scale emissions of VOCs were estimated using mixed box budget method (e.g. Guenther et al., 1996). In this method, we assume a closed and well mixed box within the atmospheric boundary layer, where the sources (surface flux) and sinks (chemical degradation and entrainment) of a compound are in balance. For compounds with relatively short atmospheric lifetime, as many VOCs are, we can neglect the entrainment at the top of the boundary layer as the chemical degradation is much faster. For monoterpenes, the entrainment flux is shown to be less than 20% of the chemical degradation (Guenther et al., 1996; Spirig et al., 2004; **Paper III**). To calculate the chemical degradation rate within the boundary layer, we need to know the average concentration of the compound of interest, the concentrations of relevant oxidizers as well as the corresponding reaction rate constants. In the study presented in

Paper III the concentrations of VOCs were measured throughout the boundary layer using a light aircraft and a hot air balloon as the platform.

3.2.4 Enclosure method

In addition to meteorological flux measurement methods, enclosure method was used. Enclosures are an established method to study the gas exchange in the small scale (e.g. Livingston & Hutchinson, 1995). In this method, the object of interest (e.g. plant leaf or branch, soil surface etc) is closed in an enclosure where the gas exchange can be studied. Assuming negligible chemistry inside the enclosure, a complete mass balance of the enclosure can be written as

$$V \frac{dc_C}{dt} = F + q_{IN}c_{IN} - q_{OUT}c_C, \quad (12)$$

where V is the volume of the enclosure, c_C is the concentration inside the chamber, F is the efflux from the enclosed object, c_{IN} and c_{OUT} are the concentrations in the inlet and outlet air, respectively, and q_{IN} and q_{OUT} are the flow rates of the inlet and outlet air, respectively. In the case of steady-state through-flow chamber the time derivative of the concentration can be neglected and the efflux is calculated from

$$F = q(c_{OUT} - c_{IN}), \quad (13)$$

where q is the net flow through the chamber.

Generally enclosure measurement disturbs the object to be studied. First, the environmental condition (temperature, humidity, radiation) of the plant are altered just by placing the plant into the enclosure. In addition, the concentrations of trace gases in the enclosure can change significantly thus modifying the production rates and diffusion gradients within the tissues. Particularly in the case of VOC emission measurements, the enclosure may disturb or even damage the plant tissues mechanically causing generally the emission to increase. This can be avoided by careful installation of the chamber, and by letting the plant to recover from installation before starting the measurements (for a review of good practices in VOC enclosure measurements, see Niinemets et al., 2011).

Enclosure method was used in **Papers IV** and **V** to study the VOC emissions from specific sources. In **Paper IV** the emission source was a single branch of mountain birch and in the **Paper V** it was a tree stump. The enclosures used in these studies were made of transparent Teflon film. In **Paper IV** the enclosure was constructed over a frame covered by Teflon, and had an internal volume of about 20 l. In **Paper V** a Teflon bag with inlet- and outlet ports attached at the top was used as the enclosure.

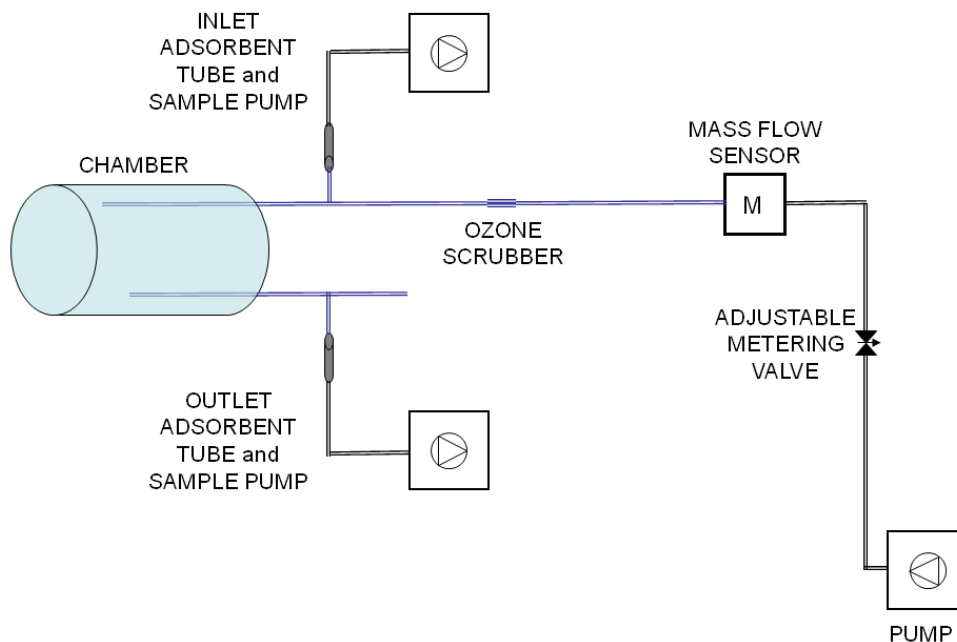


Figure 5. Schematic illustration of the enclosure measurement systems used in *Papers IV and V*.

In this open dynamic enclosure method (see Fig. 5), a known airflow is pumped into a chamber through an inlet port. Inlet air is purged from ozone to avoid VOC losses inside the chamber and adsorbent tubes. The outlet port allows excess air to exit from the enclosure thus maintaining a constant pressure inside. As the chamber is not completely airtight, some part of the airflow exits other routes. For the chemical analysis, small amounts of the inlet and outlet air are collected as described below in Section 3.2.2. Finally, the emission rates of the compounds of interest are calculated using Eq. 13 and normalized to the dry leaf biomass (**Paper IV**) or to the enclosed stump area (**Paper V**).

3.3 Sampling and chemical analyses

3.3.1 Light VOC analysis

Light C₂-C₆ hydrocarbons were analyzed from air samples. The samples were collected in previously evacuated electro polished stainless steel canisters with internal volume of 0.85 l. The samples were always passed through ozone trap (MnO₂ coated copper nets) to avoid ozone to enter the canister and destroy the

VOCs before the analysis. When analyzed, the samples were first pre-concentrated in two cold traps and subsequently passed into a HP-6890 gas chromatograph with flame ionization detector (FID) and electron capture detector (ECD). A calibration was conducted using a gaseous standard mixture of 27 different hydrocarbons. For further information, see Hakola et al. (2000) and Hellén et al. (2006).

3.3.2 Analysis of terpenes and aromatic hydrocarbons

Concentrations of terpenes and aromatic hydrocarbons were analyzed from adsorbent samples collected into a cartridge filled with Tenax TA and Carbopack II adsorbents. Similarly to the light hydrocarbon sampling, ozone was scrubbed from the air sampled, or from the enclosure inlet air. The adsorbent samples were analyzed using a thermodesorption unit (Perkin Elmer ATD-400) connected to a HP-5890 gas chromatograph with a mass-selective detector (HP-5972). A five-point calibration was conducted using liquid standards in a methanol solution. For further information, see Hakola et al. (2000) and Hellén et al. (2006).

3.3.3 Methane analysis

Methane concentrations were analyzed from 40 ml air samples taken into polypropylene syringes. The samples were analyzed within 24 h of sampling using an HP-5890A gas chromatograph equipped with 6 ft×1/8” analytical column and a FID.

4 Results and discussion

4.1 Emissions of VOCs from selected ecosystems

4.1.1 Emissions of hydrocarbons from a boreal fen

The REA measurement technique was successfully applied to measure the fluxes of methane, C₂-C₆ hydrocarbons and some halogenated hydrocarbons from a boreal fen, Siikaneva (**Paper I**). The measurements were conducted during two successive summers, 8 Jul - 6 Oct 2004 and 14 Apr - 1 Jul 2005. Methane fluxes varied between 0 and 10 mg m⁻² h⁻¹, the average value being 4.3 mg m⁻² h⁻¹. This is in the same range as the average methane fluxes of 7.9 mg m⁻² h⁻¹ and 3.5 mg m⁻² h⁻¹, measured at the same site using enclosures (Riutta et al., 2007) and eddy covariance (Rinne et al., 2007), respectively.

Isoprene was the only detected non-methane hydrocarbon emitted by the fen. The emission typically varied between 0 and 500 µg m⁻² h⁻¹. Isoprene emission from plants follows leaf temperature and available light (e.g. Guenther, 1997; Fall & Wildermuth, 1998). The measurement data was fitted to Eq. 10 (see Figure 6). The resulting isoprene emission potential was 680 µg m⁻² h⁻¹. This agrees well with the previous results by Janson and DeServes (1998) who reported isoprene emission potential of about 700 µg m⁻² h⁻¹ from flarks of boreal fens. Hellén et al. (2006) found considerably lower isoprene emission potential of about 220 µg m⁻² h⁻¹ at the same wetland using enclosure measurement data. However, their measurements were conducted in lower temperature and illumination levels (i.e. lower C_T and C_L) which raises a question whether the emission is not well explained by Eq. 10. This conclusion was also supported by our dataset. If we take into account only the data C_TC_L<0.2 the resulting emission potential becomes as low as 330 µg m⁻² h⁻¹.

At the fen, chambers suffered from severe condensation on the inner surface. This effect was pronounced during high radiation and temperature conditions. This effect may at least partly explain the observed discrepancy between the REA and chamber results. In these conditions REA method would be preferred to get reliable results.

Despite of the special emphasis, no fluxes of halogenated hydrocarbons were detected. Varner et al. (1999) and Dimmer et al. (2001) have reported significant emissions of halogenated hydrocarbons from wetlands. Those wetlands, however, are close to oceans and thus sea spray may be the source of chlorine in the wetland, needed to form large amounts of the observed halogenated compounds (Hellén et al., 2006; Blei & Heal, 2011).

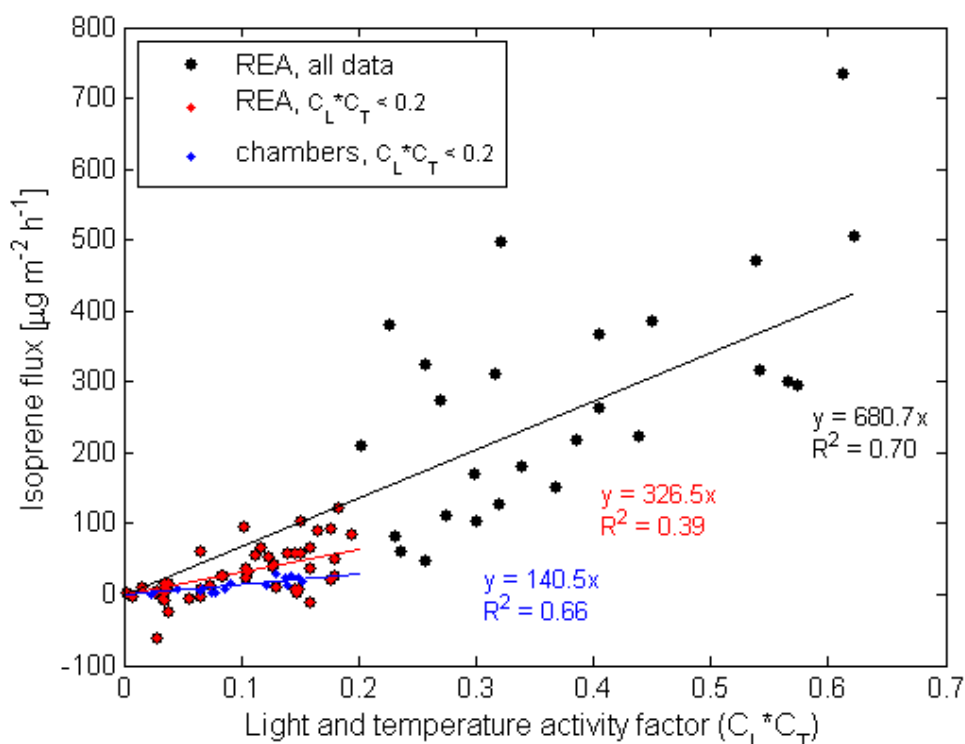


Figure 6. Isoprene flux from a boreal fen as a function of light and temperature activity factor $C_L C_T$ of the isoprene emission algorithm described by Guenther (1997). Data adapted from **Paper I** and from Hellén et al., (2006).

The experimental isoprene emission factor obtained in **Paper I** was later utilized in an emission inventory for boreal area (Tarvainen et al., 2007). According to the inventory, about 16% of the isoprene emission of the Finnish boreal area originates from wetlands. As wetlands nowadays cover significant area only in the Northern Finland, the local differences might be significant and in the north boreal area up to 31% of the isoprene emission originates from wetlands.

4.1.2 Emissions of VOCs from mountain birches

Branch scale emissions of linalool, monoterpenes and sesquiterpenes from mountain birches were measured in Abisko, northern Sweden during two growing seasons (**Paper IV**). These measurements show large emissions of monoterpenes and sesquiterpenes from the leaves. A very special feature in the sesquiterpene emission was the dramatic change of the emission rate and composition between the two successive years. During the first year, sesquiterpene α -farnesene was emitted at the average rate of about $2300 \text{ ng g}_{\text{dw}}^{-1} \text{ h}^{-1}$ and β -caryophyllene at the average rate of about $300 \text{ ng g}_{\text{dw}}^{-1} \text{ h}^{-1}$. One year later, α -farnesene emission was not detected at all and the emission of β -caryophyllene had dropped to less than $20 \text{ ng g}_{\text{dw}}^{-1} \text{ h}^{-1}$. The emissions of monoterpenes were almost equal during these

years, the average emission rates being $1100 \text{ ng g}_{\text{dw}}^{-1} \text{ h}^{-1}$ and $1200 \text{ ng g}_{\text{dw}}^{-1} \text{ h}^{-1}$ in the first and second year, respectively.

We speculated that the high sesquiterpene emission may be caused by the herbivory outbreak that occurred in the area a couple of years before. There is a strong evidence that herbivory damage causes increased terpenoid emissions from plants (Paré & Tumlinson, 1999; Holopainen, 2004; Duhl et al., 2008), also from mountain birch and they may last several years (Ruuhola et al., 2007; Mäntylä et al., 2008). However, there are also other factors that may affect the observed change in the emissions. From that dataset it was also obvious that both mono- and sesquiterpene emission approaches zero in low illumination. This suggests the emissions to originate directly from biosynthesis, and not from storage pools, which was later confirmed for Silver birch (*Betula pendula* L.) by Ghirardo et al. (2010) employing $^{13}\text{CO}_2$ labelling experiments.

4.1.3 VOCs emitted from forest felling areas

Increased VOC emissions due to forestry operations were studied in **Paper V**. Coniferous trees store large amount of monoterpenes within resin ducts, and they become easily available when wood tissue is damaged (Juuti et al., 1990). The sparse literature on the issue have demonstrated increased emissions of monoterpenes from logging areas (Schade et al., 2003) and increased air concentrations close to forestry work (Strömvall & Petersson, 1991; Räisänen et al., 2008a). We measured the specific emissions from tree stumps using enclosures as well as the ecosystem scale flux, including emissions from stumps and logging residue, using disjunct eddy accumulation. The results show large emissions of monoterpenes from fresh stumps and logging residue. The highest landscape scale emissions were $5200 \mu\text{g m}^{-2} \text{ h}^{-1}$. The emissions decay rapidly in time and after about six months from the logging, the emissions become negligible. We upscaled the results to represent annual forestry operations in Finnish Scots pine forests. The resulting annual monoterpene release is about 15 kilotonnes per year. For comparison, Tarvainen et al., (2007) estimated the annual monoterpenes release from Finnish forests to be about 114 kilotonnes. Despite of the short emission period, the amount of monoterpenes released into the atmosphere seems to be significant at least in the local scale.

Our results suggest the total release of monoterpenes to exceed the initial monoterpene content of the logging debris left on the site. Table 1 show the estimated amount of each debris fraction left on the site, the average monoterpene content of the fraction based on literature (Manninen et al., 2002; Lin et al., 2007; Räisänen et al., 2008b; Isidorov et al., 2010), and the resulting total monoterpene mass of the fraction. The total monoterpene content of the debris fall in the range of $2.4 - 6.7 \text{ g m}^{-2}$ which is somewhat lower than the monoterpene release of 8.5 g

m^{-2} obtained in the study of **Paper V**. This discrepancy may be explainable by the microbial production of monoterpenes from the debris biomass as discussed e.g. by Isidorov & Jdanova, 2002 and Isidorov et al., 2010. This interesting observation needs further studies to verify our result and to quantify the different sources within the felling area.

Table 1. The amount, estimated monoterpene content and the resulting monoterpene mass per land area of each of the debris fraction found in the seed tree felling area.

Fraction of the debris	Amount of the fraction in the area	Estimated monoterpene content in the fraction	Mass of monoterpenes in the fraction
needles	$280 \text{ g}_{\text{dw}} \text{ m}^{-2}$	$2.5 - 8.0 \text{ mg g}_{\text{dw}}^{-1}$	$0.7 - 2.2 \text{ g m}^{-2}$
brushwood	$1000 \text{ g}_{\text{dw}} \text{ m}^{-2}$	$1.0 - 1.6 \text{ mg g}_{\text{dw}}^{-1}$	$1.0 - 1.6 \text{ g m}^{-2}$
roots	$1800 \text{ g}_{\text{dw}} \text{ m}^{-2}$	$0.4 - 1.6 \text{ mg g}_{\text{dw}}^{-1}$	$0.7 - 2.9 \text{ g m}^{-2}$

4.2 Landscape scale emissions of VOCs from boreal forest zone

In order to take into account emissions from all different ecosystems within the region, landscape scale flux measurements were applied. In **Paper III** mixed box budget method was used to study the emissions of some biogenic and anthropogenic VOCs. The measurements were conducted early in the spring when biogenic emissions are still expected to be small due to low temperatures. However, this period is interesting because the maximum of new aerosol particle formation events in the boreal zone occurs in the spring (Dal Maso et al., 2005) and condensable vapors from oxidation of VOCs is assumed to contribute significantly to the growth of fresh aerosol particles.

Monoterpenes and aromatic hydrocarbons were abundant throughout the mixed boundary layer. Relatively high concentrations can be explained by low oxidant concentrations due to early spring. The VOC concentrations showed decreasing trends upwards. However, the gradients were seldom monotonous. Surface fluxes, estimated from the average boundary layer concentrations, are shown in Table 2.

Boundary layer concentration data of VOCs was further used to estimate the production rate of condensable vapors from VOC oxidation. The estimated formation rate of condensable vapors was in the range of $10^4 \text{ cm}^{-3} \text{ s}^{-1}$. This rate is about an order of magnitude too small to alone explain the observed aerosol particle growth rates during nucleation events in Hyytiälä. Similar results were obtained in previous studies (Kulmala et al., 2000; Spirig et al., 2004; Boy et al., 2004).

Table 2. The average landscape scale emission rates of VOCs measured during the two campaigns near Hyttiälä. Adapted from Paper III.

Compound	QUEST II	LABACET
	21 Mar - 2 Apr 2003	10 - 17 Mar 2006
	Emission [$\mu\text{g m}^{-2} \text{h}^{-1}$]	Emission [$\mu\text{g m}^{-2} \text{h}^{-1}$]
isoprene	B.D.L.	1.7±0.6
α -pinene	13±8.2	27±16
β -pinene	1.7±1.4	0.4±1.0
Δ^3 -carene	3.9±3.2	8.6±8.0
camphene	1.5±1.7	0.3±0.5
Σ MONOTERPENES	20±9	38±18
benzene	1.1±0.6	0.4±0.2
toluene	1.0±0.4	0.9±0.5
p/m xylene	3.3±2.4	4.6±1.7
o xylene	0.9±0.6	4.2±1.6

B.D.L. = Below the detection limit.

5 Review of the papers and author's contribution

This thesis consists of five research articles examining the emissions of volatile organic compounds from natural sources and measurement methodologies of these emissions.

Paper I studies the ecosystem scale emissions of hydrocarbons from a natural wetland area. For the measurements, a relaxed eddy accumulation (REA) system was constructed and used during two successive growing seasons. The compounds analyzed included methane, C₂-C₆ substances and halogenated hydrocarbons. The main findings were large emission of isoprene and lack of emissions of halogenated hydrocarbons. The observed methane release (on average 4.3 mg m⁻² h⁻¹) was in line with the other measurements at the same site.

Paper II includes simulations of one of the main issues in the REA methodology, namely the value of proportionality parameter β and its dependence on atmospheric conditions. The analysis is based on six month dataset of the measurement data from SMEAR II station in Hyytiälä. The results confirm the previous findings about the independence of β from the atmospheric stability and friction velocity.

Paper III describes the measurements of VOC concentrations from atmospheric boundary layer. These measurements were carried out using a light aircraft and hot air balloon. From the measured boundary layer mean concentration, the landscape scale emissions of VOCs were calculated using mixed box budget method. The results show negligible emissions of isoprene and some emissions of monoterpenes. Anthropogenic VOCs were abundant throughout the boundary layer.

Paper IV reports enclosure measurements of VOC emissions from mountain birches. Special attention was paid to the controls of terpenoid emissions, including environmental parameters and stress factors of the trees. The results suggest that mountain birches may occasionally act as very strong sesquiterpene emitters. Due to their high reactivity, this may have consequences to the local air chemistry.

Paper V reports measurements of VOCs emitted into the atmosphere due to forestry operations. The emission rates and composition from tree stumps were studied using enclosures, and the ecosystem scale emissions from a felling area using disjunct eddy accumulation (DEA) method. The monoterpene emissions were remarkably high for a few months after forest felling. The results were upscaled to represent whole Finland and compared to the results from previous emission inventory. Despite of the short emission period and relatively low

coverage of felling areas, timber felling may contribute significantly to the national monoterpene inventory.

I am alone responsible for writing the summary of this thesis. In **Paper I**, I was responsible for constructing the measurement setup (except the REA software), conducting the field measurements and methane concentration analyses. I performed the data analysis and wrote most of the paper. In **Paper II**, I contributed to the data interpretation and writing the paper. In **Paper III**, I participated in the hot air balloon flights by operating the instruments and samplers, where part of the field data was collected. I was responsible for the major part of the data analysis and writing the paper. In **Paper IV**, I conducted part of the field measurements. I performed the data analysis and wrote major part of the paper. In **Paper V**, I was responsible for constructing the DEA measurement setup and conducting most of the field measurements. I did major part of the data analysis and writing the paper. **Paper II** will be included also in the doctoral thesis of Tiia Grönholm.

6 Conclusions

We applied several micrometeorological methods and an enclosure method to study the emissions of VOCs from various natural sources.

We constructed measurement devices for REA and DEA methods, and applied them successfully for measuring ecosystem scale VOC fluxes from a boreal fen and from forest felling area. The REA method was further developed by studying the variability of the β coefficient due to atmospheric conditions. In that study, it was concluded that β varies randomly around the mean value. The mean value is only very weakly dependent on the atmospheric conditions such as friction velocity and stability. This result justifies the usage of a constant β in the flux measurements using a REA system with a dynamic dead-band. The emissions of non-methane hydrocarbons from a boreal fen were clearly dominated by isoprene. Despite of small green biomass on fen, the total terpenoid release was about one third of the release from local forest. Probably the most important finding of this work was the large monoterpene emission from felling residue left behind after forest management. This finding highlights the need to quantify the release of biogenic VOCs not only from living plants but also from storage reservoirs. High emissions from storage reservoirs are likely to take place during timber felling and sawmill or pulp processing. From the atmosphere point of view these emissions may be as important as undisturbed biogenic emissions, at least in the local scale.

Concentrations of some biogenic and anthropogenic VOCs were measured throughout the atmospheric boundary layer and used to estimate the landscape scale fluxes of those compounds. In addition, the production rate of condensable vapors from oxidation of VOCs was estimated. Supporting the previous literature, it was concluded that the terpenoid oxidation alone cannot explain the observed growth rates of aerosol particles.

Branch scale terpenoid emissions of mountain birches were found to be highly variable between successive years. The reason remains unclear; however there is evidence that herbivory might have affected the emissions. During the peak emission years, increased sesquiterpene emissions may affect the local air chemistry and even favor the growth of aerosol particles.

This work underlines the importance of proper experiment design and selection of measurement method. To properly understand the mechanisms behind VOC synthesis and emissions of VOCs from plants, well controlled chamber studies are essential.

To evaluate the contribution of biogenic VOCs to atmospheric chemistry, larger scale measurements are valuable since upscaling problems hinder the value of

chamber works. The chemical analysis of adsorbent or whole air samples by gas chromatography is laborious and time consuming task. In practice, use of these methods leads to limited dataset sizes and lengths. On the other hand, it gives detailed information on the chemical composition of the emissions which in turn is valuable to understand the details of atmospheric chemistry. This work encourages well designed and long-term terpenoid emission measurements from mountain birches and forest felling areas to properly quantify their impact on atmospheric VOC burden.

References

- Alexandersson H., Karlström C., and Larsson-McCann S. Temperature and precipitation in Sweden 1961-1990, reference normals. SMHI, Norrköping, 88 pp., ISSN 0283-7730, 1991.
- Atkinson R. Gas-phase tropospheric chemistry of organic compounds. *J. Phys. Chem. Ref. Data Monog.* **2**, 1994.
- Atkinson R. Atmospheric chemistry of VOCs and NOx. *Atmos. Environ.*, **34**, 2063-2101, 2000.
- Aubinet M., Grelle A., Ibrom A., Rannik Ü., Moncrieff J., Foken T., Kowalski A., Martin P., Berbigier P., Bernhofer Ch. Clement R., Elbers J., Granier A., Grünwald T., Morgenstern K., Pilegaard K., Rebmann C., Snijders W., Valentini R., and Vesala T. Estimates of the annual net carbon and water exchange of forests: the EUROFLUX methodology. *Adv. Ecol. Res.*, **30**, 113-175, 2000.
- Arya S.P. Introduction to micrometeorology. Academic press, ISBN 0-12-059354-8, 2001.
- Blei E., and Heal M. Methyl bromide and methyl chloride fluxes from temperate forest litter. *Atmos. Environ.*, **45**, 1543-1547, 2011.
- Boy M., Petäjä T., Dal Maso M., Rannik Ü., Rinne J., Aalto P., Laaksonen A., Vaattovaara P., Joutsensaari J., Hoffmann T., Warnke J., Apostolaki M., Stephanou E.G., Tsapakis M., Kouvarakis A., Pio C., Carvalho A., Römpf A., Moortgat G., Spirig C., Guenther A., Greenberg J., Ciccioli P., and Kulmala M. Overview of the field measurement campaign in Hyytiälä, August 2001 in the framework of the EU project OSOA. *Atmos. Chem. Phys.*, **4**, 657-678, 2004.
- Businger J. A. and Oncley S. P. Flux Measurement with Conditional Sampling. *J. Atmos. Ocean. Technol.*, **7**, 349-352, 1990.
- Calogirou A., Larsen B. R., and Kotzias D. Gas-phase terpene oxidation products: a review. *Atmos. Environ.*, **33**, 1423-1439, 1999.
- Dal Maso M., Kulmala M., Riipinen I., Wagner R., Hussein T., Aalto P. P., and Lehtinen K. E. J. Formation and growth of fresh atmospheric aerosols: eight years of aerosol size distribution data from SMEAR II, Hyytiälä, Finland. *Boreal Environ. Res.*, **5**, 323-336, 2005.

Desjardins R. L. Description and evaluation of a sensible heat flux detector. *Bound-lay. Meteorol.*, **11**, 147-154, 1977.

Dimmer C. H., Simmonds P. G., Nickless G., and Bassford M. R. Biogenic fluxes of halomethanes from Irish peatland ecosystems. *Atmos. Environ.*, **35**, 321–330, 2001.

Drebs A., Nordlund A., Karlsson P., Helminen J., and Rissanen P. Climatological statistics of Finland 1971-2000. Finnish Meteorological Institute, Helsinki, 99 pp, ISBN 951-697-568-2, 2002.

Duhl T., Helmig D., and Guenther A. Sesquiterpene emission from vegetation: a review. *Biogeos.*, **5**, 761-777, 2008.

Fall R., and Wildermuth M.C. Isoprene synthase: from biochemical mechanism to emission algorithm. *J. Geophys. Res.*, **103**, 25599-25609, 1998.

Ghirardo A., Koch K., Taipale R., Zimmer I., Schnitzler J.-P., and Rinne J. Determination of *de novo* and pool emissions of terpenes from four common boreal/alpine trees by ¹³CO₂ labelling and PTR-MS analysis. *Plant Cell Environ.*, **33**, 781–792, 2010.

Gloor M., Bakwin P., Hurst D., Lock L., Draxler R., and Tans P. What is the concentration footprint of a tall tower? *J. Geophys. Res.*, **106**, 17831-17840, 2001.

Guenther A. B., Zimmerman P. R., Harley P. C., Monson R. K., and Fall R. Isoprene and Monoterpene Emission Rate Variability: Model Evaluations and Sensitivity Analyses. *J. Geophys. Res.*, **98**, 12609-12617, 1993.

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

Guenther A., Zimmerman P., Klinger L., Greenberg J., Ennis C., Davis K., Pollock W., Westberg H., Allwine G., and Geron C. Estimates of regional natural volatile organic compound fluxes from enclosure and ambient measurements, *J. Geophys. Res.*, **101**, 1345–1359, 1996.

Guenther A. Seasonal and spatial variations in natural volatile organic compound emissions. *Ecol. Appl.*, **7**, 34-45, 1997.

Grote R., and Niinemets Ü. Modeling volatile isoprenoids – a story with split ends. *Plant Biology*, **10**, 8-28, 2008.

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

Hansel A., Jordan A., Holzinger R., Prazeller P., Vogel W., and Lindinger W. Proton transfer reaction mass spectrometry: on-line trace gas analysis at the ppb level. *Int. J. Mass Spectrom.*, **149/150**, 609-619, 1995.

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

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

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

Holopainen J. K. Multiple functions of inducible plant volatiles. *Trends Plant Sci.*, **9**, 529–533, 2004.

Holzke C., Hoffmann T., Jaeger L., Koppmann R., and Zimmer W. Diurnal and seasonal variation of monoterpene and sesquiterpene emission from Scots pine (*Pinus sylvestris* L.), *Atmos. Environ.*, **40**, 3174–3185, 2006.

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

Iriti M., and Faoro F. Oxidative stress, the paradigm of ozone toxicity in plants and animals. *Water Air Soil Pollut.*, **187**, 285-301, 2008.

Isidorov V., and Jdanova, M. Volatile organic compounds from leaves litter. *Chemosphere*, **48**, 975–979, 2002.

Isidorov V. A., Smolewska M., Purzyńska-Pugacewicz A., and Tyszkiewicz Z. Chemical composition of volatile and extractive compounds of pine and spruce leaf litter in the initial stages of decomposition, *Biogeos.*, **7**, 2785–2794, doi:10.5194/bg-7-2785-2010, 2010.

Janson R. W. and De Serves C. Isoprene emissions from boreal wetlands in Scandinavia. *J. Geophys. Res.*, **103**, 25 513–25 517, 1998.

Juuti S., Arey J., and Atkinson, R. Monoterpene Emission Rate Measurements From a Monterey Pine. *J. Geophys. Res.*, **95**, 7515-7519, 1990.

Kaimal J.C., and Finnigan J.J. Atmospheric Boundary Layer Flows – Their Structure and Measurements. Oxford University Press. ISBN 0-19-506239-6, 1994.

Kaplan J. O., Folberth G., and Hauglustaine D. A. Role of methane and biogenic volatile organic compound sources in late glacial and Holocene fluctuations of atmospheric methane concentrations. *Global Biogeochem. Cy.*, **20**, GB2016, 2006.

Kavouras I. G., Mihalopoulos N., and Stephanou E.G. Formation of atmospheric particles from organic acids produced by forests. *Nature*, **395**, 683-686, 1998.

Koppmann R. (ed.). Volatile Organic Compounds in the Atmosphere. Blackwell Publishing Ltd. ISBN 978-1-4051-3115-5, 2007.

Kuhn U., Rottenberger S., Biesenthal T., Wolf A., Schebeske G., Ciccioli P., Brancaleoni E., Frattoni M., Tavares T. M., and Kesselmeier, J. Seasonal differences in isoprene and light-dependent monoterpene emission by Amazonian tree species. *Glob. Change Biol.*, **10**, 663–682, 2004.

Kulmala M., Hämeri K., Mäkelä J.M., Aalto P.P., Pirjola L., Väkevä M., Nilsson E.D., Koponen I.K., Buzorius G., Keronen P., Rannik Ü., Laakso L., Vesala T., Bigg K., Seidl W., Forkel R., Hoffmann T., Spanke J., Janson R., Shimmo M., Hansson H.-C., O’Dowd C., Becker E., Paatero J., Teinilä K., Hillamo R., Viisanen Y., Laaksonen A., Swietlicki E., Salm J., Hari P., Altimir N., and Weber R.: Biogenic aerosol formation in the boreal forest. *Boreal Env. Res.*, **5**, 281-297, 2000.

Kulmala, M. How particles nucleate and grow. *Science*, **302**, 1000-1001, 2003.

Lin C., Owen S. M., and Peñuelas J. Volatile organic compounds in the roots and rhizosphere of *Pinus* spp. *Soil Biol. Biochem.*, **39**, 951–960, 2007.

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

Livingston G.P., and Hutchinson G.L. Enclosure-based measurement of trace gas exchange: applications and sources of error. In: Matson P.A., and Harriss R.C. (eds.): *Biogenic Trace Gases: Measuring Emissions from Soil and Water*. Blackwell Science, ISBN 0-632-03641-9, 1995.

Loreto F., and Schnitzler J.-P. Abiotic stresses and induced BVOCs. *Trends Plant Sci.*, **15**, 154-166, 2010.

Manninen A.-M., Tarhanen S., Vuorinen M., and Kainulainen, P. Comparing the variation of needle and wood terpenoids in Scots pine provenances, *J. Chem. Ecol.*, **28**, 211–228, 2002.

Mäntylä E., Alessio G.A., Blade J. D., Heijari J., Holopainen J. K., Laaksonen T., Piirtola P., and Klemola T. From plants to birds: Higher avian predation rates in trees responding to insect herbivory. *PLoS ONE*, **3**, e2832, 2008.

Niinemets Ü., Kuhn U., Harley P.C., Staudt M., Arneth A., Cescatti A., Ciccioli P., Copolovici L., Geron C., Guenther A., Kesselmeier J., Lerdau M.T., Monson R.K., and Peñuelas J. Estimations of isoprenoid emission capacity from enclosure studies: measurements, data processing, quality and standardized measurement protocols. *Biogeos.*, **8**, 2209-2246, 2011.

Oncley S.P., Delany A.C., and Horst T.W. Verification of flux measurement using relaxed eddy accumulation. *Atmos. Environ.*, **27**, 2417-2426, 1993.

Paré P. and Tumlinson J. Plant volatiles as a defence against insect herbivores. *Plant Physiol.*, **121**, 325–331, 1999.

Piccot S. D., Watson, J. J., and Jones J. W. A global inventory of Volatile Organic Compound Emissions From Anthropogenic Sources. *J. Geophys. Res.*, **97**, 9897-9912, 1992.

Rinne J, and Ammann C. Disjunct Eddy Covariance Method. In: Aubinet M., Vesala T., and Papale D. (eds.): *Eddy Covariance - A Practical Guide to Measurement and Data Analysis*. Springer, ISBN 978-94-007-2350-4, 2012.

Rinne J., Delany A., Greenberg J., and Guenther, A. A true eddy accumulation system for trace gas fluxes using disjunct eddy sampling method. *J. Geophys. Res.*, **105**, 24791-24798, 2000.

Rinne J., Guenther A., Greenberg J., and Harley P. Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature. *Atmos. Environ.*, **36**, 2421–2426, 2002.

Rinne J., Riutta T., Pihlatie M., Aurela M., Haapanala S., Tuovinen J.-P., Tuittila E.-S., and Vesala T. Annual cycle of methane emission from a boreal fen measured by the eddy covariance technique. *Tellus*, **59B**, 449-457, 2007.

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

Riutta T., Laine J., Aurela M., Rinne J., Vesala T., Laurila T., Haapanala S., Pihlatie M. and Tuittila E.-S. Spatial variation in plant community functions regulates carbon gas dynamics in a boreal fen ecosystem. *Tellus*, **59B**, 838–852, 2007.

Ruuhola T., Salminen J.-P., Haviola S., Yang S., and Rantala M. J. Immunological memory of mountain birches: Effects of Phenolics on performance of the autumnal moth depend on herbivory history of trees, *J. Chem. Ecol.*, **33**, 1160–1176, 2007.

Räisänen T., Ryyppö A., and Kellomäki S. Impact of timber felling on the ambient monoterpene concentration of a Scots pine (*Pinus sylvestris* L.) forest. *Atmos. Environ.*, **42**, 6759-6766, 2008a.

Räisänen T., Ryyppö A., Julkunen-Tiitto R., and Kellomäki S. Effects of elevated CO₂ and temperature on secondary compounds in the needles of Scots pine (*Pinus sylvestris* L.), *Trees*, **22**, 121–135, 2008b.

Schade G. W., and Goldstein A.H. Increase of monoterpene emissions from a pine plantation as a result of mechanical disturbances. *Geophys. Res. Lett.*, **30**, 1380, 2003.

Seinfeld J.H., and Pandis S. N. Atmospheric Chemistry and Physics, From Air Pollution to Climate Change. John Wiley & Sons, Inc., New York, ISBN 0-471-17815-2, 1998.

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

Spirig C., Guenther A., Greenberg J. P., Calanca P., and Tarvainen V. Tethered balloon measurements of biogenic volatile organic compounds at a Boreal forest site, *Atmos. Chem. Phys.*, **4**, 215–229, 2004.

Steinbrecher R., Hauff K., Hakola H., and Rössler J. A Revised Parametrisation for Emission Modelling of Isoprenoids for Boreal Plants, in: Biogenic VOC emissions and photochemistry in the boreal regions of Europe, edited by: Laurila T. and Lindfors V., Air pollution research report No 70, Commission of the European Communities, Luxembourg, 158 pp., ISBN 92-828-6990-3. 29-43, 1999.

Strömvall A.-M., and Petersson G. Conifer monoterpenes emitted to air by logging operations. *Scand. J. Forest Res.*, **6**, 253-258, 1991.

Stull R. B. An introduction to boundary layer meteorology, Kluwer Academic Publishers, Dordrecht, ISBN 90-277-2768-6, 1988.

Taipale R., Kajos M. K., Patokoski J., Rantala P., Ruuskanen T. M., and Rinne J. Role of the novo biosynthesis in ecosystem scale monoterpene emissions from a boreal Scots pine forest. *Biogeos.*, **8**, 2247-2255, 2011.

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

Turnipseed A., Pressley S., Karl T., Lamb B., Nemitz E., Allwine E., Cooper W., Shertz S., and Guenther, A. The use of disjunct eddy sampling methods for the determination of ecosystem level fluxes of trace gases. *Atmos. Chem. Phys.*, **9**, 981-994, 2009.

Varner R. K., Crill P. M., and Talbot R. W. Wetlands, a potentially significant source of atmospheric methyl bromide and methyl chloride. *Geophys. Res. Lett.*, **26**, 2433–2436, 1999.

Went F. W. Organic matter in the atmosphere, and its possible relation to petroleum formation. *P. Natl. Acad. Sci. USA.*, **46**, 212-221, 1960.

Yuan J. S., Himanen S. J., Holopainen J. K., Chen F., and Stewart C. N. Jr. Smelling global climate change: mitigation of function for plant volatile organic compounds. *Trends Ecol. Evol.*, **24**, 323–331, 2009.