LUND UNIVERSITY

Emission of biogenic volatile organic compounds from intact & clearcut boreal forest

Multi-year observations of BVOC fluxes at a Swedish boreal forest and the ecosystem-scale BVOC impacts of clearcut forestry

Petersen, Ross

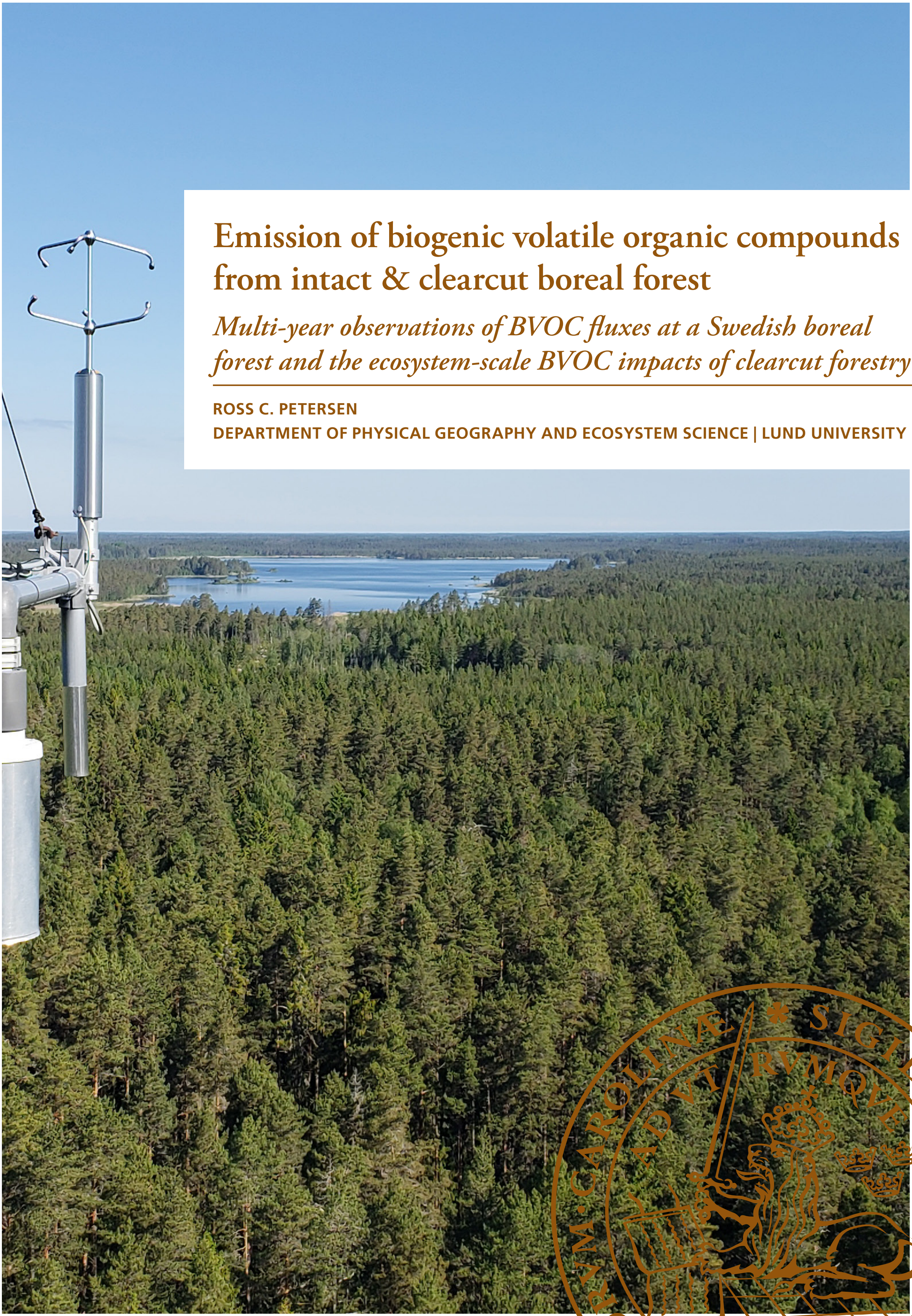
2025

Citation for published version (APA):
Petersen, R. (2025). *Emission of biogenic volatile organic compounds from intact & clearcut boreal forest: Multi-year observations of BVOC fluxes at a Swedish boreal forest and the ecosystem-scale BVOC impacts of clearcut forestry*. Lund University, Faculty of Science.

Total number of authors:
1

LUND UNIVERSITY

PO Box 117
221 00 Lund
+46 46-222 00 00



Emission of biogenic volatile organic compounds from intact & clearcut boreal forest

Multi-year observations of BVOC fluxes at a Swedish boreal forest and the ecosystem-scale BVOC impacts of clearcut forestry

ROSS C. PETERSEN
DEPARTMENT OF PHYSICAL GEOGRAPHY AND ECOSYSTEM SCIENCE | LUND UNIVERSITY

Emission of biogenic volatile organic compounds from intact & clearcut boreal forest

Multi-year observations of BVOC fluxes at a Swedish boreal forest and the ecosystem-scale BVOC impacts of clearcut forestry

Emission of biogenic volatile organic compounds from intact and clearcut boreal forest

Multi-year observations of BVOC fluxes at a Swedish boreal forest and the ecosystem-scale BVOC impacts of clearcut forestry

Ross C. Petersen

LUND
UNIVERSITY

DOCTORAL DISSERTATION

Doctoral dissertation for the degree of Doctor of Philosophy (PhD) at the Faculty of Science at Lund University to be publicly defended on Tuesday, the 20th of May 2025 at 10:00 am in Pangea auditorium, Geocentrum II, Sölvegatan 12, Lund

Faculty opponent
Dr. Delphine Farmer, Colorado State University, Colorado, USA

Organization: LUND UNIVERSITY Faculty of Science Department of Physical Geography & Ecosystem Science

Document name: DOCTORAL DISSERTATION **Date of issue:** 2025-03-08

Author(s): Ross C. Petersen **Sponsoring organization:**

Title and subtitle: Emission of biogenic volatile organic compounds from intact and clearcut boreal forest - Multi-year observations of BVOC fluxes at a Swedish boreal forest and the ecosystem-scale BVOC impacts of clearcut forestry

Abstract: Vegetation is the major source of volatile organic compounds (VOCs) in the atmosphere, which affect both air quality and climate. Long-term ecosystem-level data on biogenic VOC (BVOC) emissions, however, are limited. This is especially true regarding the impacts of landscape-scale disturbances like clear-cutting on the short-term and longer seasonal-scale emissions of boreal forests, particularly with respect to emissions in prior years.

Presented in this PhD thesis document is an overview of BVOC concentration and flux measurements and results spanning several years, leading up to the summer 2022 clear-cutting of a boreal forest located at the ICOS (Integrated Carbon Observation System) and ACTRIS (Aerosol, Clouds, and Traces Gases Research Infrastructure) station Norunda (located at 60°05′N, 17°29′E, ca. 30 km north of Uppsala) in Sweden. This managed boreal forest, between 80 and 120 years old, primarily consisted of a mix of Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*). Beginning in summer 2020, BVOC mixing ratios were measured using a Vocus proton-transfer-reaction time-of-flight mass spectrometer (Vocus PTR-ToF-MS). These Vocus measurements (at 10 Hz) were collected at 35 m on the station flux tower to determine BVOC fluxes using the eddy-covariance method. During several intensive BVOC sampling periods in 2020 and 2022, hourly adsorbent samples were also collected, at 37 and 60 m, for subsequent automated-thermal-desorption gas-chromatography mass-spectrometry (ATD-GC-MS) analysis to determine compound-speciated BVOC concentrations. These samples were additionally used to estimate the changes in the fluxes of speciated monoterpene (MT) compounds using the surface-layer-gradient (SLG) and modified Bowen-ratio (MBR) methods. As part of the research to investigate boreal BVOC emissions, new software tools were also developed for processing high-frequency Vocus PTR-ToF-MS campaign datasets for the eddy-covariance analysis of long-term BVOC fluxes above the Norunda forest canopy.

The results of this thesis indicate a large variety of VOC compounds being emitted by the forest system, including among terpenoids - e.g., isoprene, monoterpenes (MTs) and sesquiterpenes (SQTs). The most common MT compounds emitted were α-pinene and Δ^3-carene. A seasonal investigation of the vertical distribution of BVOC sources and sinks within and below the intact Norunda forest canopy also found a significant proportion of the forest's MT emission in autumn originating from the forest floor. During the 2022 clearcut, MT emissions increased by 1-2 orders of magnitude during active-cutting, with persisting MT emission increases from clearcut residue which continued for several months. In comparison, many BVOCs lacking storage reservoirs in plant tissues (e.g., isoprene) were relatively unaffected by active-cutting. Fluxes and the mixture of speciated MT compounds observed before, during, and post-cut are compared, and the additional total and speciated MT emissions due to clear-cutting are estimated. For context, in Sweden 69% of total land cover is forest, of which 84% is productive forest for clear-cut forestry (~58% of total land cover). From Swedish forestry information of yearly absolute timber removal and on-site residue volumes following typical clearcuts, these results show that current Swedish boreal forest MT emission inventory estimates may be significantly underestimated.

Key words:

Classification system and/or index terms (if any) Supplementary bibliographical information

Language **ISSN and key title**:

ISBN: (print): 978-91-89187-57-3 (e) : 978-91-89187-58-0

Recipient's notes **Number of pages**: 173

Price Security classification

I, the undersigned, being the copyright owner of the abstract of the above-mentioned dissertation, hereby grant to all reference sources permission to publish and disseminate the abstract of the above-mentioned dissertation.

Signature Date 2025-05-20

Emission of biogenic volatile organic compounds from intact and clearcut boreal forest

Multi-year observations of BVOC fluxes at a Swedish boreal forest and the ecosystem-scale BVOC impacts of clearcut forestry

Ross C. Petersen

LUND
UNIVERSITY

Coverphotos by Ross C. Petersen

Faculty of Science
Department of Physical Geography and Ecosystem Science

ISBN (print): 978-91-89187-57-3
ISBN (e): 978-91-89187-58-0

Printed in Sweden by Media-Tryck, Lund University
Lund 2025

NORDIC SWAN ECOLABEL
Printed matter
3041 0903

Media-Tryck is a Nordic Swan Ecolabel
certified provider of printed material.
Read more about our environmental
work at www.mediatryck.lu.se
MADE IN SWEDEN

For my parents, wife, family, and mentors along the way

Table of Contents

Abstract

Vegetation is the major source of volatile organic compounds (VOCs) in the atmosphere, which affect both air quality and climate. Long-term ecosystem-level data on biogenic VOC (BVOC) emissions, however, are limited. This is especially true regarding the impacts of landscape-scale disturbances like clear-cutting on the short-term and longer seasonal-scale emissions of boreal forests, particularly with respect to emissions in prior years.

Presented in this PhD thesis document is an overview of BVOC concentration and flux measurements and results spanning several years, leading up to the summer 2022 clear-cutting of a boreal forest located at the ICOS (Integrated Carbon Observation System) and ACTRIS (Aerosol, Clouds, and Traces Gases Research Infrastructure) station Norunda (located at 60°05′N, 17°29′E, ca. 30 km north of Uppsala) in Sweden. This managed boreal forest, between 80 and 120 years old, primarily consisted of a mix of Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*). Beginning in summer 2020, BVOC mixing ratios were measured using a Vocus proton-transfer-reaction time-of-flight mass spectrometer (Vocus PTR-ToF-MS). These Vocus measurements (at 10 Hz) were collected at 35 m on the station flux tower to determine BVOC fluxes using the eddy-covariance method. During several intensive BVOC sampling periods in 2020 and 2022, hourly adsorbent samples were also collected, at 37 and 60 m, for subsequent automated-thermal-desorption gas-chromatography mass-spectrometry (ATD-GC-MS) analysis to determine compound-speciated BVOC concentrations. These samples were additionally used to estimate the changes in the fluxes of speciated monoterpene (MT) compounds using the surface-layer-gradient (SLG) and modified Bowen-ratio (MBR) methods. As part of the research to investigate boreal BVOC emissions, new software tools were also developed for processing high-frequency Vocus PTR-ToF-MS campaign datasets for the eddy-covariance analysis of long-term BVOC fluxes above the Norunda forest canopy.

The results of this thesis indicate a large variety of VOC compounds being emitted by the forest system, including among terpenoids - e.g., isoprene, monoterpenes (MTs) and sesquiterpenes (SQTs). The most common MT compounds emitted were α-pinene and Δ^3-carene. A seasonal investigation of the vertical distribution of BVOC sources and sinks within and below the intact Norunda forest canopy also found a significant proportion of the forest's MT emission in autumn originating from the forest floor. During the 2022 clearcut, MT emissions increased by 1-2 orders of magnitude during active-cutting, with persisting MT emission increases from clearcut residue which continued for several months. In comparison, many BVOCs lacking storage reservoirs in plant tissues (e.g., isoprene) were relatively unaffected by active-cutting. Fluxes and the mixture of speciated MT compounds observed before, during, and post-cut are compared, and the additional total and speciated MT emissions due to clear-cutting are estimated. For context, in Sweden 69% of total land cover is forest, of which 84% is productive forest for clear-cut forestry (~58% of total land cover). From Swedish forestry information of yearly absolute timber removal and on-site residue volumes following typical clearcuts, these results show that current Swedish boreal forest MT emission inventory estimates may be significantly underestimated.

List of Papers

Paper I

Petersen, R. C., T. Holst, M. Mölder, N. Kljun, and J. Rinne (2023). Vertical distribution of sources and sinks of VOCs within a boreal forest canopy, *Atmospheric Chemistry and Physics*, 23, 7839-7858.

Paper II

Petersen, R. C., T. Holst, C. Wu, R. Krejci, J. Chan, C. Mohr, and J. Rinne (2024). BVOC and speciated monoterpene concentrations and fluxes at a Scandinavian boreal forest, *EGUsphere 2024*, 1-45. Submitted to *Atmospheric Chemistry and Physics*

Paper III

Petersen, R. C., C. Wu, C. Mohr, R. Rinnan, T. Holst, E. Jaakkola, N. Kljun, R. Krejci, and J. Rinne (2025). Speciated BVOC fluxes from a boreal forest clearcut, short-term and persistent long-term impact on emissions. *Prepared manuscript for submission.*

Paper IV

Petersen, R. C., L. Fischer, T. Holst, C. Wu, and J. Rinne (2025). An efficient Julia-language tool package (TT3) for processing long-term high-frequency Vocus PTR-ToF-MS data. *Prepared manuscript for submission.*

Contributions

Paper I: **RCP**, JR, and TH initiated the study. JR and TH supervised the study and acquired the primary funding to support this research. **RCP** conducted the main study analysis and prepared the manuscript and figures, with contributions from JR, TH, MM, and NK. TH provided the PTR-MS and ozone data from the 2014–2016 campaign at ICOS Norunda. NK provided airborne lidar mapping data of tree height and assistance in estimating the flux footprint climatology for the campaign period using the FFP footprint model (Kljun et al., 2015). MM provided the sonic anemometer data from the collection on the Norunda flux tower and technical feedback on the Lagrangian inversion analysis. All the authors contributed to scientific discussion and revision of the manuscript.

Paper II: **RCP**, JR, and TH initiated the study. JR and TH supervised the study and acquired the primary funding to support this research. **RCP**, CW, and CM conducted the Vocus PTR-ToF-MS campaign measurements, and TH assisted with Vocus field calibration preparation and measurements. **RCP** performed the TD gradient sampling and laboratory analysis at Lund University. JC assisted with post-processing of GC-MS laboratory files following TD sample analysis. **RCP** conducted the main study analysis and prepared the manuscript and figures, with contributions from all co-authors.

Paper III: **RCP**, JR, and TH initiated the study. **RCP** designed the study. **RCP**, CW and CM performed the Vocus PTR-ToF-MS site and instrumentation preparation and Vocus-oriented fieldwork. **RCP** performed the adsorption tube gradient sampling preparation and fieldwork. RR and their group performed the GC-MS laboratory analysis of adsorbent tube samples at Copenhagen University. EJ performed GC-MS data post-processing. **RCP** conducted the main study analysis and prepared the manuscript and figures, with contributions from all co-authors.

Paper IV: **RCP** initiated and designed the study. **RCP**, JR, TH, CW, and CM contributed to the collection of Vocus PTR-ToF-MS field data that was used for the software analysis undertaken by this study. **RCP** conducted the main study analysis and prepared the manuscript and figures, with contributions from all co-authors.

Abbreviations

ABL	Atmospheric Boundary Layer
ACTRIS	Aerosols, Clouds and Trace Gases Research Infrastructure
ATD-GC-MS	Automated-Thermal-Desorption GC-MS
BVOC	Biogenic Volatile Organic Compound
GC-MS	Gas-Chromatography Mass-Spectrometry
ICOS	Integrated Carbon Observation System
MT	Monoterpene
PAR	Photosynthetically Active Radiation
PPFD	Photosynthetic Photon Flux Density
PTR-ToF	Proton Transfer Reaction – Time of Flight
SOA	Secondary Organic Aerosol
SQT	Sesquiterpene
TD	Thermal Desorption
VOC	Volatile Organic Compound

Introduction

In the early second-half of the 20th century, Dr. F W. Went (Went, 1960) first published his hypothesis regarding the link between vegetation and the source of blue haze that often covers remote vegetated areas. Since then, significant advances has been made in the understanding of the role of Biogenic Volatile Organic Compounds (BVOCs) in atmospheric chemistry as well as within ecosystems as a whole. The ecosystem-atmosphere BVOC flux has important impacts on tropospheric oxidative capacity and the formation of secondary organic aerosol (SOA), influencing air quality and climate (e.g., Kulmala et al., 2013). In the Northern hemisphere, this is particularly true in boreal forests, where BVOC emissions often dominate over anthropogenic sources of VOC.

Volatile organic compounds (VOCs) in the atmosphere are all gas-phase organic compounds (i.e., a compound containing one or more covalently linked carbon atoms) excluding carbon monoxide (CO) and carbon dioxide (CO_2) that have a high vapor-pressure at room temperatures (Seinfeld and Pandis, 2016). Biogenic VOCs – BVOCs - are those VOC compounds which are derived from a biological source (Niinemets and Monson, 2013). The types of BVOC compounds are diverse, and in addition to the terpenoids (isoprene, monoterpenes, sesquiterpenes, etc.), include alcohols, alkanes, alkenes, aldehydes, ethers, esters and carboxylic acids. While it is an organic, typically methane (CH_4) is considered separately from other VOCs.

According to chemical structure, BVOCs can be classified into many groups, with examples including terpenoids, alkanes, alkenes alcohols, aldehydes, esters, ethers, and carboxylic acids (Maffei, 2010). Among the most abundant BVOCs in terrestrial forest ecosystems are the terpenoids, such as isoprene, the monoterpenes (MTs), and the sesquiterpenes (SQTs). The terpenes share many structural similarities, built around blocks of two or more isoprene (C_5H_8) units. For example, the MT group typically consists of two units ($C_{10}H_{16}$) while the SQT group consists of three ($C_{15}H_{24}$).

1.1 Role and plant synthesis of BVOCs

BVOCs are emitted from plant tissues (leaves, bark, flowers, fruits, roots), and from microbial activity in the soil as well. Thousands of BVOC compounds have been identified from a variety of ecosystem sources (e.g., Dudareva et al., 2013; Knudsen et al., 2006). BVOCs perform many important physiological and ecological functions (Schuman et al., 2016). BVOCs frequently act as protective or signal-mediating compounds within plants, between plants in a population, and perform ecological functions among other organisms within an ecosystem (e.g., Heil and Silva Bueno, 2007; Holopainen, 2011). Many plant-synthesized BVOCs directly deter herbivores from feeding on them, or indirectly by attracting the predators or parasitoids of herbivore species - direct and indirect defense (Fineschi and Loreto, 2012). BVOCs are also important attractors of plant-pollenating species (Kessler et al., 2008). A notable feature, herbivory-induced and stress-induced BVOCs can also induce preemptive defensive responses in nearby undamaged plants (Heil and Silva Bueno, 2007). BVOCs can also act as enhancing plant tolerance towards environmental stresses (Loreto and Schnitzler, 2010). It has been found that isoprene can act to protect plants from heat-shock stress in leaves (Sharkey et al., 2007) as well as stomatal ozone exposure, and that terpene compounds can relieve plants of internal oxidative stresses by scavenging excess reactive oxygen species within plant tissues (Loreto and Schnitzler, 2010).

The synthesis of BVOCs in plants begins with photosynthesis. Plants produce primary metabolites via photosynthesis which are used for growth and development. Some of these are then utilized through secondary metabolic steps, in which BVOCs are produced through various synthesis pathways. Depending on whether the plant is exposed to stress or other factors, different pathways may be promoted or suppressed (Li et al., 2017; Loreto and Schnitzler, 2010). Isoprene and the primary monoterpenes are produced from the same pathway - the methylerythriol phosphate (MEP) pathway (Li and Sharkey, 2013). While the MEP pathway can also produce some SQTs, the majority of SQT compounds are produced through the mevalonate (MVA) pathway (Loreto and Schnitzler, 2010). Other BVOCs are created within plants from other synthesis pathways. For example, green leaf volatiles (GLVs; C_6) are synthesized through the lipoxygenase (LOX) pathway (Loreto and Schnitzler, 2010). The LOX-pathway is activated upon plant damage (Matsui and Engelberth, 2022).

Subsequent emission of BVOCs then depends on the chemical characteristics of the volatile, the internal structure of the plant tissues, and physiological state (stressed or unstressed) of the plant. Isoprene, due to its relatively high Henry’s law constant (i.e., high vapor pressure at equilibrium partitioning between water and air), is emitted directly following photosynthesis. This isoprene-emission is light- and temperature-dependent, and is independent from the stomatal opening or closing

(Fall and Monson, 1992; Sharkey, 1991). In many boreal species, such as conifers like Norway spruce and Scots pine, terpenes like MTs and SQTs are produced throughout the plant and subsequently stored either in specialized tissue storage structures, such as resin ducts, trichomes, or glands (Loreto and Schnitzler, 2010), or in non-specific pools such as between cell membranes. The emission of these storage-pool terpenes under constitutive conditions is primarily temperature-dependent. Terpene emission rates can also be significantly impacted by stress-related processes, such as herbivory-induced plant defense-responses and mechanical damage to plant tissues. When under significant stresses such as insect herbivory or drought, boreal forests are also known to be significant sesquiterpene emitters (Niinemets, 2010; Rinne et al., 2009).

In the earliest modeling of boreal MT emissions, it was modeled as purely temperature-dependent emission (i.e, storage-pool emission) (Guenther et al., 1993). Depending on the individual plant and species, however, some of the synthesized terpenes can be (partially) emitted directly to the atmosphere after *de novo* synthesis rather than being stored internally. For example, using isotopic labeling to track recently fixed carbon, Ghirardo et al. (2010) found that for the boreal conifers Scots pine and Norway spruce, roughly 30 – 60 % of emitted MT in their study originated from *de novo* emission rather that from storage-pool emission. Distinguishing between these two types of emission behavior types is a key component of future measurement and BVOC emission modeling work.

1.2 Biotic and abiotic BVOC emission responses

BVOC emissions can generally be considered in two distinct categories: *constitutive* emissions and *induced* emissions. Emissions of BVOCs under typical, unstressed conditions generally occur continuously and follow primarily light and/or temperature-dependent behavior (e.g., Guenther et al., 2012), are referred to as constitutive emissions (Holopainen, 2011). When plants are exposed to biotic or abiotic stress, significant changes in the magnitude and composition of BVOC emissions can be induced (Laothawornkitkul et al., 2009).

For example, plant exposure to transiently high-temperature and light levels has been shown to be capable of inducing large BVOC emissions, particularly for C_6-compounds and acetaldehyde (Loreto et al., 2006). While heat stress can initially increase of isoprene and MT emissions, such emissions decline below typical levels under persisting vegetation heat stress (Possell and Loreto, 2013). While the effects on isoprene and MT by moderate drought can be mixed, depending on plant species, long-term water stress from severe drought ultimately will significantly reduce BVOC emissions (Laothawornkitkul et al., 2009). Mechanical wounding or herbivory can induce significant increases of MT and SQT emissions from conifer tree species (Litvak and Monson, 1998) a stable of boreal forest regions. Plant wounding can also induce strong, rapid emissions of green leaf volatiles (GLVs). In the case of boreal forest clearcutting, a common forestry practice in Sweden and Finland, the clearcut damage and mechanical disturbance from tree harvesting also ruptures storage structures within plants, facilitating higher emission rates from the terpene storage-pool of residue biomass that is left behind in the forest following clearcutting (Figure 1).

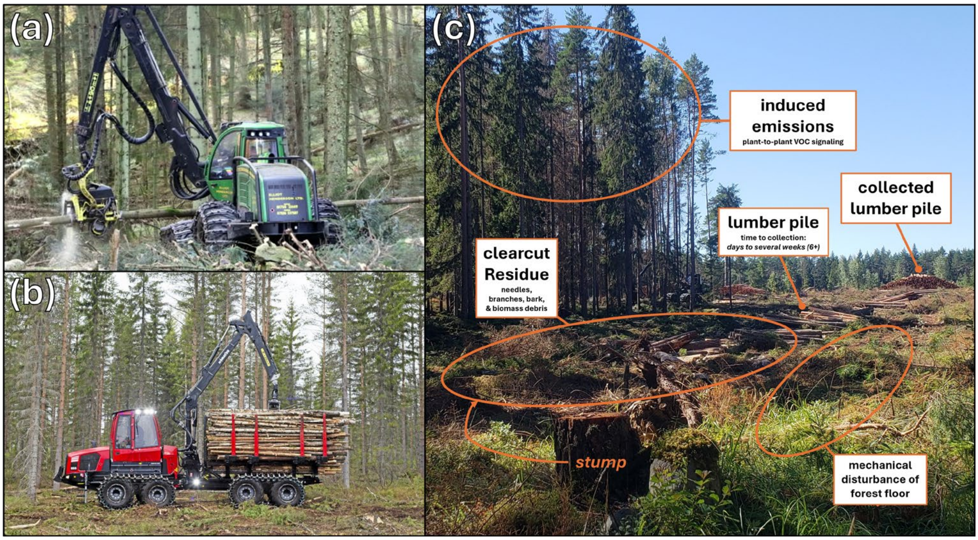


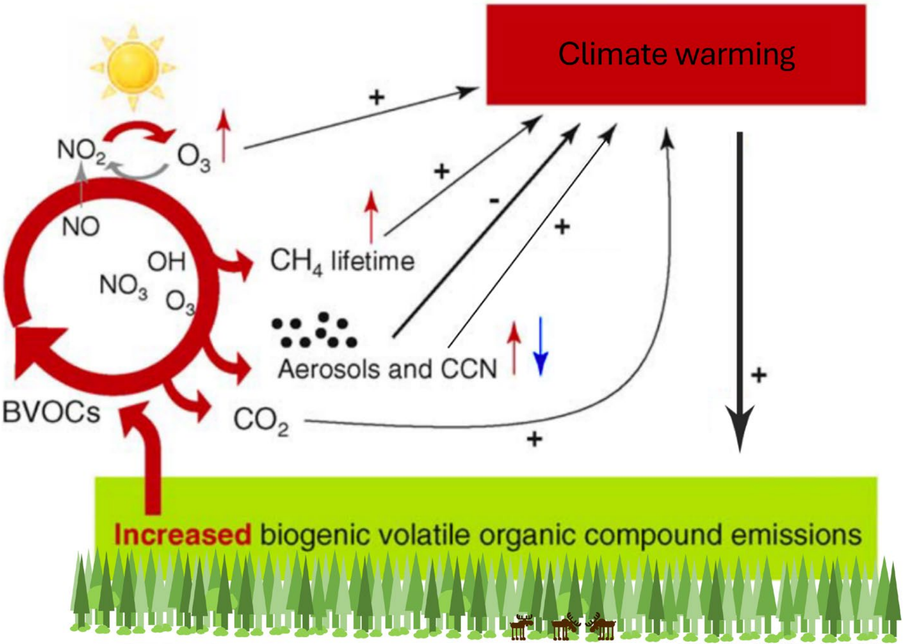
Figure 1. Example of clearcut equipment contributing to mechanical disturbance within forest area. (a) Lumber harvester with cutting implement on a crane arm (measures & cuts lumber to selected length. Discards branches, bark, and other residue on forest floor). (b) Collecting tractor (*Skotare*), a forestry vehicle which sorts fresh lumber into piles on the forest floor and subsequently removes the forest lumber piles (weeks to months) from the area to roadside for transport. (c) Sources of enhanced VOC emission (particularly MTs and SQTs) during and after a boreal forest clearcut. Images taken during the 2022 clearcut of the ICOS Norunda boreal forst research station near Uppsala, Sweden.

Typically, BVOC emissions are modeled as constitutive emissions, following either light- and temperature-dependent (*de novo* emission), exclusively temperature-dependent (storage pool emission) behavior, or a combination of *de novo* and storage pool emission, depending on specified plant functional types assigned for a particular biome region (Guenther et al., 1995; Guenther et al., 2012; Guenther et al., 1993). Improving the characterization of biotic and abiotic induced emissions is another important and developing task for BVOC emission and modeling research.

1.3 BVOCs and the atmosphere

BVOCs have important impacts on climate and atmospheric chemistry (Figure 2). BVOC emissions from plants are estimated to contribute approximately 400-800 Tg of carbon to the atmosphere per year globally (Guenther et al., 1995; Sindelarova et al., 2014). Individually, a plant can re-emit up to 10% of its fixed carbon by producing and emitting BVOCs (Fineschi et al., 2013).

BVOCs have a significant role in the production of tropospheric ozone (Chameides et al., 1992) and impact on the lifetimes of methane (Collins et al., 2002). In addition, BVOCs serve as a major precursor source for the formation and growth of organic aerosols (e.g., Andreae and Crutzen, 1997). Oxygenated VOC compounds, such as acetone, can also modifiy hydroxyl radical concentrations in the upper troposphere (Fehsenfeld et al., 1992; Mckeen et al., 1997), and/or contribute to the formation of peroxyacetic nitric anhydride (PAN) compounds that can act as a reservoir for nitrogen oxides (NO_x) (Roberts et al., 2002).



Adapted from Peñuelas & Staudt (2010)

Figure 2. Atmospheric chemistry and climate effects of BVOC emissions. Adapted figure broadly illustrates the coupling and feedback of BVOC emissions and atmospheric changes in a warming global climate scenario: Increased temperature increases BVOC emission rates (+). Increased BVOC emissions increases aerosol formation and growth rates, subsequently increasing aerosol and cloud condensation nuclei (CCN) concentrations. Increased aerosol and CCN concentrations decreases temperature (–) due to increased reflection of sunlight from low clouds to space. + and - symbols indicate positive and negative feedbacks, respectively. As Peñuelas & Staudt (2010) note, however, other climate feedbacks of BVOC/climate interactions are also present and require further research.

1.4 Boreal forest BVOCs and the influence of forestry

Boreal forests are a major source of BVOCs in the atmosphere (Guenther et al., 1995). While boreal zone vegetation on average tend to have lower emission rates than forests in warmer biomes, due to the cooler boreal climate and lower biomass density, the large areal coverage of ca. 15.8×10^6 km^2 (Archibold, 1995) of boreal forest, representing about 30 % of the world's total forest area (Gauthier et al., 2015), makes it an important VOC source. For comparison, tropical rainforest extent in the Amazon basin covers 6.3×10^6 km^2. Furthermore, as large areas covered by boreal forests are sparsely populated, the biogenic emissions tend to dominate over anthropogenic ones in these areas. Across all plant functional types (e.g., Guenther et al., 2012), boreal MT emissions make up as much as ca. 26.3 % of the global summertime MT emission inventory (June: 28.3 %, July: 29.7 %, and August: 20.7 %), and up to ca. 37.1 % of it (June: 39.2 %, July: 41 %, and August: 30.5 %) for the Northern Hemisphere (Sindelarova et al., 2022).

Boreal forest regions typically include a mix of tree types, including evergreen conifer species (e.g., pine, spruce), deciduous species (e.g., larch, birch, willow, alder, aspen), as well as various kinds of understory vegetation (e.g., Rinne et al., 2009). The two dominant tree species at ICOS Norunda, Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) are widespread evergreen tree species in the boreal zone, comprising about 83% of the forests in Sweden (Alin and Sundberg, 2003; Pettersson, 2007). Both species are significant emitters of MT and SQT (Rinne et al., 2009). Below the canopy, the understory vegetation, subsurface roots, and microbiological activities all contribute to forest floor BVOC emissions (Hayward et al., 2001; Lin et al., 2007). Needle litter has also been recognized as a significant source of forest floor BVOC emissions in coniferous boreal forest (e.g., Hayward et al., 2001; Hellén et al., 2006).

Long-term observations of BVOC concentrations and fluxes from boreal forests are, unfortunately, represented by relatively few datasets. There are also relatively few examples demonstrating the ecosystem-scale changes in BVOC emission due to stresses, such as drought or (in particular) commercial forest logging (Schade and Goldstein, 2003; Seco et al., 2015). Such information is important to improve understanding of biosphere-atmosphere feedbacks and to refine future climate models. A further compounding factor is the lack of information regarding the quantitative impact of human disturbance on boreal BVOC emissions.

To the knowledge of the author, there are only three BVOC flux studies (Haapanala et al., 2012; Petersen et al., 2024; Schade and Goldstein, 2003) and two ambient BVOC concentration studies (Räisänen et al., 2008; Strömvall and Petersson, 1991) regarding the impact of forest thinning (the forest-management practice of clearing younger trees so that more mature trees can develop better for eventual harvesting) or clear-cutting on boreal forest BVOC emissions. Of the two emission studies not presented as part of this PhD thesis, Haapanala et al. (2012) studied felling residue emissions using chamber measurements and the disjunct eddy-accumulation flux method for several-day periods in 2017 and 2018, while Schade and Goldstein (2003) investigated the effects of thinning on a ponderosa pine forest in the continental United States. In their general estimates regarding the VOC emission impacts of US forestry, Schade and Goldstein (2003) found that the total MT emissions annually in the US may be underestimated by between 0.5 and 5.5%.

Worldwide, about two-thirds of boreal forests are managed, mainly for timber production (Gauthier et al., 2015). In the different areas of the boreal zone, the percentage of managed forests is about 35 to 40 % in Canada (Burton et al., 2010; Venier et al., 2014), about 58% in Russia (Gauthier et al., 2015), and 90% in Fennoscandian region (Burton et al., 2010). In light of this discrepancy between the significant extent of boreal forest management and the relative lack of studies investigating the influence of forestry on BVOC emissions, improving our knowledge regarding the impacts of forestry on boreal BVOC emissions is an important next step in boreal BVOC research.

Aims & objectives

VOC emissions of biogenic origin are the major driver of atmospheric chemistry in the troposphere. In Northern hemisphere regions, at such as Sweden, boreal forests are the major contributor to these BVOC emissions – particularly of reactive terpenes such as monoterpenes and sesquiterpenes. While long-term information regarding these emission rates is already limited, even less is known about the seasonal-scale impacts of landscape disturbances such as boreal forest clearcutting (a common forestry practice in Northern Europe and worldwide). This thesis aims to investigate the seasonal and long-term dynamics of BVOC emissions in boreal forests, with a particular focus on the multi-year trends in BVOC emission behaviors and their chemical speciation at landscape-scale throughout the years. It also examines the impact of forest management practices, such as clearcutting, on BVOC emissions and their potential consequences for atmospheric chemistry and climate, carried out through unique and detailed BVOC measurements in the years before, during, and after the clear-cutting of a more than 100-year-old boreal forest. Additionally, this thesis involves the development of timely and powerful analytical tools for processing high-frequency BVOC flux measurements - contributing to both a more comprehensive understanding of BVOC emissions from boreal forests for interpreting, and accessibility for researchers to study, ecosystem-scale BVOC emissions and their role in biosphere-atmosphere interactions.

The main objectives of this PhD thesis were the following:

1. Investigate the seasonal BVOC emission and vertical source distribution in boreal forests (**Paper I**).

2. Quantify the seasonal speciation of BVOC fluxes from a boreal forest (**Paper II**).

3. Investigate and quantify the long-term (i.e, 2-3 years) BVOC emissions from a boreal forest on an ecosystem-scale (**Paper II & III**).

4. Investigate the BVOC emissions from a managed boreal forest vs. BVOC emissions during/after boreal forest clear-cutting (**Paper II & III**).

5. Develop the required analytical tools to evaluate and process the BVOC flux-related measurements (i.e., raw 10-Hz Vocus PTR-ToF-MS data) collected at Norunda over the course of the PhD studies (**Paper IV**).

Material and Methods

3.1 Research site (ICOS Norunda)

The study site, ICOS research station Norunda (SE-Nor), is located at 60°05′N, 17°29′E, near Uppsala, Sweden. The station is surrounded by mixed-conifer forest areas of Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*). At the time of the forest clearcut in summer 2022, the Norunda forest was between 80 and 120 years old (Lagergren et al., 2005) and had a canopy height of about 28 m (Petersen et al., 2023; Petersen et al., 2024). The forest has been managed forest for approximately the last 200 years. The flux measurement station at Norunda has operated since 1994, measuring forest-atmosphere CO_2 exchange, and is currently a labeled ICOS ecosystem and atmosphere station. The station is equipped with a 102 m tower for flux and atmospheric measurements (Lindroth et al., 1998; Lundin et al., 1999).

Soils around the Norunda station area are predominantly sandy-loamy till with a high stone content of all sizes (typically up to ~1 m diameter). These soils are podzolized and classified as dystric regosols (e.g., Lundin et al. 1999). Prior to the 2022 clear-cutting of the forest, Norway spruce (53.4 %) and Scots pine (39.8 %) constituted about 93 % of all trees (number per hectare) found in the forest. The forest's leaf area index (LAI) typically ranged from 3 to 6 m^2/m^2. There was also a small number of deciduous trees, consisting primarily of Black Alder (*Alnus glutinosa (L.) Gaertn*; 2.5 %) and Downy Birch (*Betula pubescens Ehrh.*; 3.9 %). Below the canopy, the dominant understory vegetation was bilberry (*Vaccinium myrtillus*) followed by lingonberry (*Vaccinium vitis-idaea*). Also present were several species of dwarf shrubs, ferns, and grasses. The bottom-layer vegetation consisted predominantly of a thick layer of boreal feather mosses (*Pleurozium schreberi* and *Hylocomium splendens*). The location of ICOS Norunda in Sweden and a map of forest tree heights surrounding the station prior to the 2022 clearcut is displayed in Figure 3.

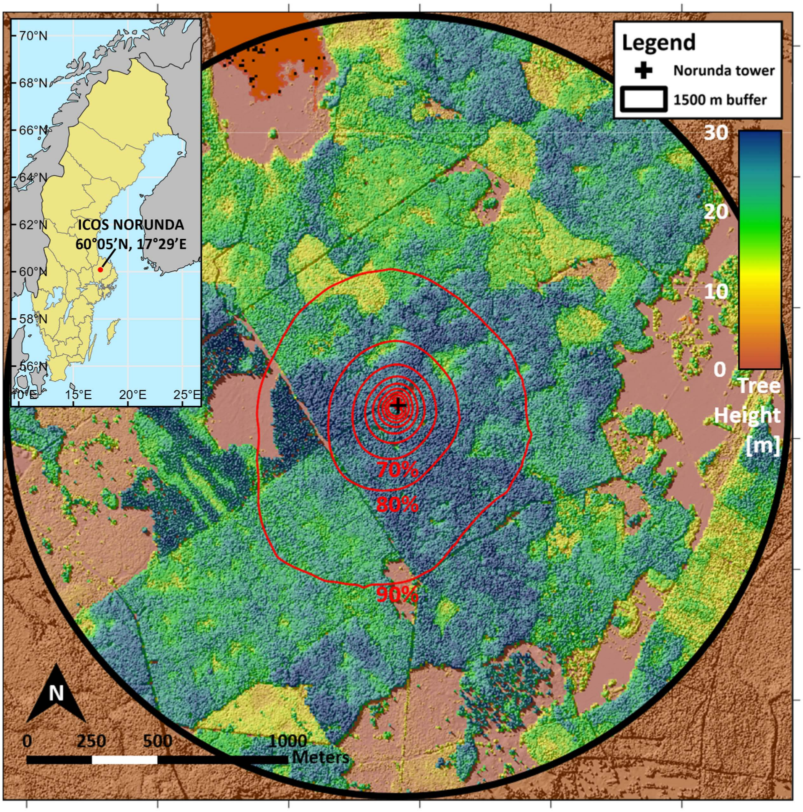


Figure 3. *Adapted from paper I*. Location of ICOS station Norunda (a) relative to Sweden as a whole. (b) A map of tree heights surrounding the station as seen from above (airborne LiDAR; 2011), prior to the 2022 forest clearcut. Included is an example of a typical flux footprint (red contours) at 36 m on the Norunda tower. Contours calculated using the Flux Footprint Prediction (FFP) model (Kljun et al., 2015).

Tower BVOC infrastructure

As part of the ICOS network, the Norunda station had an extensive set of monitoring instrumentation on the Norunda station flux tower, which provided supplemental data to the main BVOC campaign measurements.

Instrumentation for PTR measurements at Norunda and related equipment was housed in an instrument shed ca. 10 m from the flux tower base. Previous studies have investigated BVOC emissions from the mixed pine/spruce forest as well, providing useful information through chamber emission measurements (Van Meeningen et al., 2017; Wang et al., 2017). In 2014 to 2016, as part of a campaign conducted by Dr. Thomas Holst, the station flux tower was equipped with ⅜"-outer-diameter PTFE-Teflon tubing for BVOC sampling at six inlet heights (4, 8.5, 13.5, 19, 24.5, and 32 m) using a PTR-quadrupole MS (Ionicon). These raw measurements were later processed and analyzed to investigate the vertical-profile behavior of VOC concentrations within the Norunda canopy (**Paper I**).

In 2019, for this PhD thesis research, new Teflon tubing infrastructure was installed on the Norunda tower to carry out BVOC eddy-covariance (EC) flux measurements **(papers II & III**) above the forest canopy. In 2020 and throughout the forest clearcut in 2022, BVOCs were sampled at 35 m using a Vocus PTR-ToF-MS. The different inlet setups for BVOC sampling on the Norunda flux tower are shown in Figure 4. Regular daytime sampling at 37 and 60 m was conducted in 2020 and 2022. In 2022, a STS-25 sequential tube sampler was also installed on the tower at 35 m to enable nighttime adsorbent sampling during the 2022 campaign.

Due to a separate long-term project run by station staff member Dr. Meelis Molder, extensive sonic-profile measurements were also available throughout the 2014-2016 and 2020-2022 periods at Norunda from a collection of 3d-sonic anemometers installed at 14 heights on the Norunda station flux tower (located at 1.8, 4.4, 14.8, 20.8, 26.6, 29.6 32.8, 35, 37.9, 44.8, 59.5, 74,88.5, and 101.8 m). This long-term profile information was applied to the inverse Lagrangian dispersion analysis featured in **paper I** and was helpful with the analyses for **papers II** and **III**.

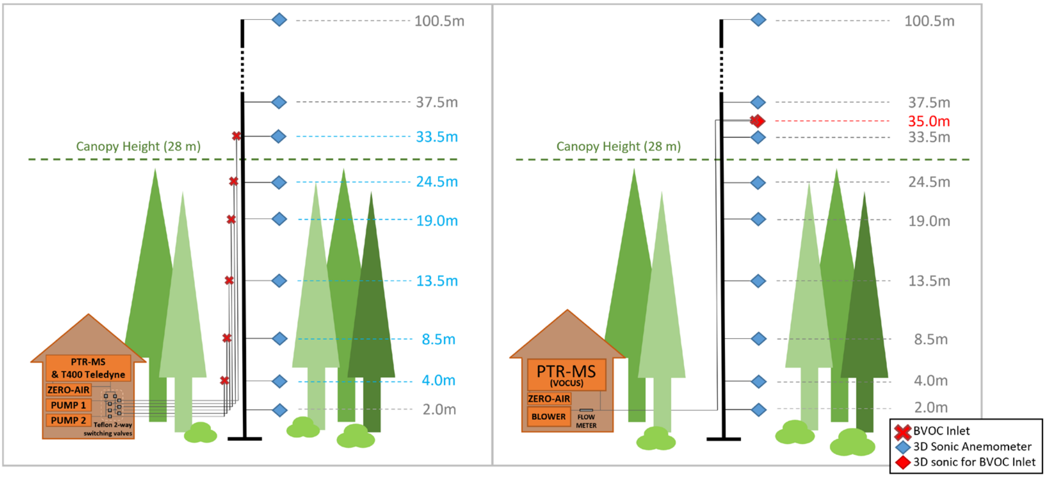


Figure 4. BVOC Inlet setup at ICOS station Norunda. (a) The inlet setup for the 2014-2016 BVOC concentration profile measurements (Paper I). (b) The inlet setup for the 2020, 2021, and 2022 BVOC eddy-covariance flux measurements (Papers II & III). Shown are the heights of the 3D sonic anemometers (diamond) and BVOC inlets (cross) on the station flux tower. To the left is shown a diagram of the BVOC instrumentation building. The forest canopy height (dashed green line) is shown at 25m.

Norunda forest clearcut

The typical growth and cutting cycle timing for managed boreal forests in Sweden like Norunda is well established. At the start of this PhD research, it was known that

Norunda forest would likely be clearcut within 2-4 years. Figure 5 shows a map of the cutting schedule for the forested areas surrounding the ICOS Norunda Station. This allowed long-term BVOC campaigns to be planned and performed in anticipation of a forest clearcutting event.

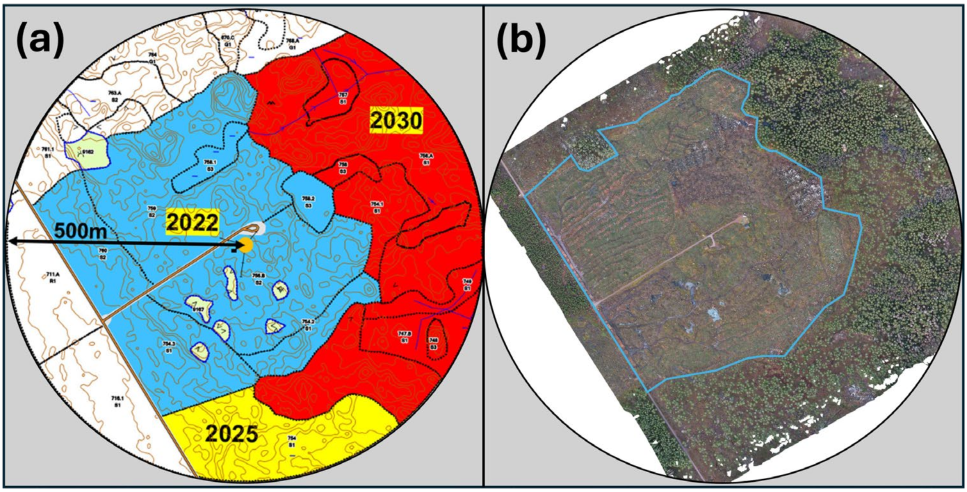


Figure 5. Maps of planned and final Norunda forest clearcutting. (a) map of station showing planned clearcutting areas. (b) Aireal drone map showing the final area cleared by the end of the 2022 clearcutting period.

Beginning in July 2022 and concluding in the autumn, the forest area within approximately 300 m of the station tower base (an area of ca. 30.5 hectares in total) was harvested by clearcut-forestry equipment, with all trees (>14000 individuals) cut down and the clearing of the vegetation understory. During clearcutting, following typical harvesting practice, only the stems (i.e., logs) were removed. This logging amounted to a total of about 11000 m^3fpb (where *m^3fpb* indicates volume (m^3) of logs including bark - ca. 320 m^3fpb per hectare). Tree bark alone, which is removed and left on-site during harvesting, amounts to about 1500 m^3 in biomass volume. Branches, tree-tops, and smaller trees were also left on-site. Based on allometric equations for Norway spruce and Scots pine relating the relative proportion of tree biomass among needles, twigs, branches, bark and stem wood, biomass left on-site following the clearcut was then roughly 90 m^3 per hectare. The vegetation understory layer previously present was destroyed during this clearcutting process.

A year following the clearcut (autumn 2023), soil scarification was performed to prepare the ground for replanting the forest. In spring 2024, the forest area was replanted with mainly pine (~90%) and spruce (~10%).

3.2 BVOC measurement and flux techniques

There are several ways to measure BVOCs, from the landscape-scale to leaf-level emissions as well as differing temporal scales. The two instrumental approaches (1&2) for measuring BVOCs that were used in this thesis research:

1a) Proton-transfer-reaction mass-spectrometry (PTR-MS)

2a) Adsorption sampling for subsequent off-line laboratory analysis by gas-chromatography mass-spectrometry (GC-MS).

Meanwhile, the two main approaches were utilized for evaluating BVOC fluxes in this PhD research:

1b) eddy-covariance flux method for PTR-based measurements

2b) gradient-flux methods for adsorbent-based sampling measurements

Each measurement and flux approach has advantages and disadvantages. For example, BVOC air sampling for GC-MS analysis can be conducted off-line or on-line (i.e., *in-situ* sampling and analysis with GC-MS instrumentation housed in the field or portable adsorbent sampling of ambient air for later laboratory analysis). The later makes it possible to bring portable sampling equipment into a field-setting with relative ease and analyze samples later in the laboratory. Additionally, GC-MS analysis of BVOC samples can identify and quantify specific VOC compounds. However, the time required to sufficiently separate VOC compounds within the GC column for MS peak-identification is relatively slow (typically >20 min and up to 1 hr, depending on instrumentation and settings). Even specialized GC implementations such as fastGC (e.g., Materić et al., 2015), designed specifically to reduce this time delay, require more than 1 min. While not necessarily an issue for chamber-based emission studies, this is a significant obstacle for ecosystem and landscape-scale BVOC flux research, since it is too slow to subsequently implement EC or even disjunct EC flux analysis. Various methods, such as relaxed eddy-accumulation and gradient-flux applications, have been developed in an attempt to address this drawback.

Meanwhile, PTR-ToF-MS instrumentation brings excellent sensitivity and is well-suited to measuring EC fluxes. However, it can only directly quantify BVOC compounds according to the mass-to-charge ratio of their positively-charged ion. For example, it cannot differentiate between a-pinene and Δ^3-carene (both monoterpenes: $m/z^+ = 137$). Fragmentation of ions within the PTR instrument must also be accounted and corrected for during calibration and analysis. In **papers II** and **III**, the best of both these options were combined to provide EC total BVOC-group fluxes (such as total MT and total observed SQT flux) and speciated BVOC flux measurement capability to the Norunda field campaigns.

In addition to above-canopy flux methods, the seasonality of VOC exchange within and below the Norunda canopy was also explored. During 2018 to spring-2020, while ICOS Norunda was being prepared with the equipment and flux tower infrastructure for PTR-ToF-MS flux measurements, an investigation was performed to evaluate the vertical distribution of BVOC sources and sinks, and the seasonal behavior of this distribution, within and below the forest canopy. **Paper I** is an example of a combined evaluation of vertical exchange within the forest canopy. This investigation of vertically-resolved BVOC sources and sinks was performed using concentration profile measurements of BVOC concentration within the canopy (2014-2016 field campaigns via PTR-quadrupole-MS) and by applying an analysis utilizing an inverse Lagrangian transport theory method (see section 3.2).

Paper II and **paper III** demonstrate two flux measurement approaches: eddy-covariance flux using Vocus PTR-ToF-MS and the surface layer gradient (SLG) approach utilizing manual adsorbent tube sampling of BVOCs on the Norunda flux tower. After sampling these tubes were analyzed using ATD-GC-MS. In **Paper II**, the impact of chemical degradation on observed isoprene, MT, and SQT fluxes was also investigated using an analysis from stochastic Lagrangian transport modeling, presented in Rinne et al. (2012), for boreal forest canopies.

All such methods rely on the ability to accurately measure BVOC trace gas concentrations. In the case of eddy-covariance flux measurements, it also requires high-frequency (10-20 Hz) measurements as well. **Paper IV** presents the software tools (*TT3*) that were developed and implemented to process the high-frequency (10 Hz) Vocus PTR-ToF-MS data from eddy-covariance analysis of the BVOC flux above the Norunda forest canopy.

3.2.1 Vocus PTR-ToF-MS

Proton-transfer-reaction mass-spectrometry (PTR-MS) has been widely used to study BVOCs in the atmosphere (e.g., Lindinger et al., 1998; Yuan et al., 2017). A PTR-MS instrument uses an ion source to produce H_3O^+ ions from water vapor (H_2O) via cathode discharge. The H_3O^+ ions are directed through a drift-tube containing BVOC sample gas from the instrument's inlet system, where these VOCs undergo the following chemical reaction with the H_3O^+ ions.

$$H_3O^+ + R \rightarrow RH^+ + H_2O,$$

where R and RH^+ are the reactant gas molecule (i.e., VOC) and its ion, respectively. The VOC ions are then directed towards a mass spectrometer, where ions are separated, and subsequently detected, according to their mass-to-charge (m/z) ratio (e.g., Lindinger et al., 1998). The VOC signal intensity can then be converted to VOC concentration (ppbv) using calibration measurements of VOC gas standards at known concentrations. In recent years, it has become possible to perform quick (10 Hz) BVOC sampling over a wide range of BVOC molar masses simultaneously using fast-response ($\tau \lesssim 1$ s) PTR *Time-of-Flight* MS (PTR-ToF-MS) (Müller et al., 2010). This quick response time and the high sampling rate that a PTR-ToF-MS can provide is necessary to perform eddy-covariance flux analysis.

For the summer 2020, 2021, and 2022 (clearcut) Norunda campaign measurements, a Vocus PTR-ToF-MS instrument (Vocus-2R, TOFWERK, Thun, Switzerland) was installed at the ICOS Norunda flux tower. Featuring a Focusing Ion-Molecule Reactor (FIMR) among other design improvements, the Vocus PTR-ToF-MS is able to measure VOC compounds with a wide range of volatilities with high instrument sensitivity (Krechmer et al., 2018).

Vocus data processing

The analysis of the raw VOCUS data was performed using Julia-based analysis scripts from the software package (*TT3*), developed during this PhD research for use with the VOCUS PTR-ToF-MS dataset. To prepare the Vocus measurements for EC flux processing, these Julia-based tools were used to execute the required series of dedicated workflow procedures, including mass scale recalibration, stick-peak integration of the 10 Hz-sampled spectrum data, baseline signal subtraction, peak shape fitting, signal deconvolution, and cps-to-ppbv concentration calibration. Performing these steps, especially for high-frequency campaign datasets, is a computationally- and time-intensive task. The TT3 tools have been optimized to perform these steps efficiently, aided further by leveraging parallel-processing, and is described in detail in **paper IV**.

The daily Vocus spectra were mass-scale calibrated every 5 minutes and averaged for peak shape analysis. The program *PeakFit* (e.g., Fischer et al., 2021) was used for peak fitting and identification. *PeakFit* was used to create a mass peak list of more than 2000 identified compounds for the Vocus. Based on this mass peak list and using the *TT3* script tools, the 10 Hz time traces were obtained by integrating the spectra for non-overlapping intervals around each mass, then applying deconvolution to reduce cross-talk caused by signal contributions from neighboring masses and isotopes in each spectrum (Müller et al., 2010). The script runtime on a 10 core processor system with a 1 Tb harddrive and 96 Gb of RAM is about 2.5 hours for 24 hours of 10 Hz data. The recorded amount of raw Vocus data collected each day in the native HDF5-file format was about 20 GB.

Finally, after the 10 Hz cps-traces were extracted from the Vocus dataset, a cps-to-ppbv calibration workflow was implemented to convert the Vocus trace signals from counts-per-second (cps) to BVOC concentration (ppbv). Step-wise Vocus calibration measurements were collected during each Norunda BVOC campaign. These Vocus calibration measurements were performed using a gravimetrically prepared calibration bottle of VOC standards at known concentration (Ionimed Analytik). The calibration standard gas was diluted before sampling by the Vocus using a Gas Calibration Unit (GCU-b, Ionicon). An example of the calibration routine for 2020, implementing S_{exp}-fitting, the transmission fitting, fragmentation rate determination for available calibration standard compounds, is included in Figure 6 below.

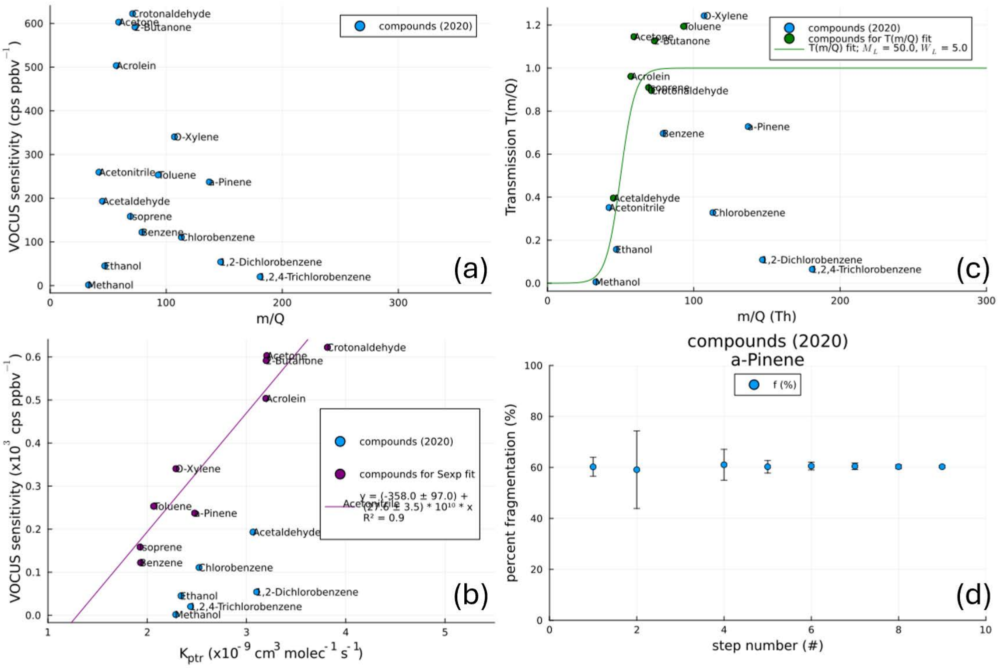


Figure 6. Examples from the 2020 Norunda campaign calibration using the calibration procedure outlined in Jensen et al. 2023. (a) The regression best-fit line for the measured calibration bottle compound sensitivities (those with low fragmentation, attenuation or other factors impacting sensitivity) and their respective proton-transfer-reaction rate constants. (b) The fitted mass-to-charge (m/Q) transmission curve. (c) The calibration-measured sensitivities (cps ppbv^{-1}) of the compounds in the standard VOC calibration bottle. (d) The measured monoterpene fragmentation rate at each calibration step-level during the 2020 calibration procedure

3.2.2 Eddy-covariance BVOC fluxes

The most direct method for measuring a chemical flux above a forest canopy is the EC flux method. It requires simultaneous high-frequency measurements of the compound concentration (c) and vertical wind velocity (w). The covariance between the time-dependent fluctuations of these variables gives the flux (F_c), with

$$F_c = \overline{w'c'} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} w'(t)c'(t)\, dt \qquad (1)$$

where the overbar denotes time-averaging from time t_1 to time t_2, $c' = c - \bar{c}$, and $w' = w - \bar{w}$. Further information regarding the EC approach can be found in the literature (e.g., Aubinet et al., 2012), and in **papers II** and **III**.

As a significant proportion of a turbulent flux in the atmospheric surface layer is carried by relatively small eddies, for the EC-flux method to accurately quantify the vertical exchange, the BVOC concentration and vertical wind speed must be measured by fast-response instrumentation. Typically, many analyzers for greenhouse gas fluxes have response times of around 0.1 s. While the Vocus PTR-ToF-MS's characteristic response time τ (i.e., time for 100 × 1/e % ≈ 63.2 % of instrument signal to fully transition between two levels of concentration) is around 1 s, due to transit time of the BVOC product ions in the Vocus drift tube reaction chamber (Krechmer et al., 2018), the effect of this is relatively minimal for evaluating BVOC EC-flux (high-frequency attenuation of total flux signal is about 1 %), and can be accounted for by a transfer function correction factor (Striednig et al., 2020). This is sufficient for fluxes measured above tall vegetation, such as forest canopies (Rantala et al., 2014).

Tower measurements

To conduct BVOC flux measurements using the EC method, a 3d-sonic anemometer (USA-1, Metek GmbH, Germany) was deployed alongside the BVOC inlet at 35 m on the Norunda flux tower to collect the required directional wind speed measurements (10 Hz sampling rate). The flow rate through the BVOC inlet tubing to the Vocus was 20 L/min. Inside the instrumentation shed, 6 L/min of the flow coming from the tower was directed through the Vocus-inlet, to minimize BVOC losses from prolonged residence time within sample tubing. A portion of this 6 L/min flow was sampled inside the Vocus-inlet into the Vocus, and the remainder was directed to the inlet exhaust. The mass flow controller for the Vocus zero-air was set to 500 mL/min. The pressure control valve for the Vocus was set to 220 mL/min. The Vocus ion source was routinely set at 2 mbar.

Fluxes from the processed high-frequency Vocus traces were calculated using InnFLUX, an open-source MatLab code for EC analysis of trace gas measurements (Striednig et al., 2020). A tilt-correction is performed on the Metek sonic data to align the instrument's coordinate system with the mean wind streamlines (e.g., Wilczak et al., 2001). Timing is important in EC analysis, and the time required for sample air to flow down the flux tower's Teflon tubing and reach the Vocus introduced a time delay. After the raw Vocus concentration data is processed to usable timeseries data and is being run through the initial analysis steps of InnFLUX, the time delay between the timeseries data for the Metek sonic's vertical wind speed and Vocus's BVOC concentrations is determined. This is done by optimizing the correlation coefficient of the Vocus concentration timeseries data with the vertical wind speed component from the sonic anemometer collocated with the VOC-inlet (e.g., Mcmillen, 1988) within a ± 1 min time window.

3.2.3 Adsorbent BVOC sampling

While a powerful tool for BVOC research, a limitation of PTR instrumentation is the inability to distinguish between VOC compounds with the same molar mass. As a result, PTR-derived measurements of concentration and flux are only possible for *total* monoterpenes (m/z+ = 137), *total* sesquiterpenes (m/z+ = 205), etc., rather than specific MT and SQT compounds. Additionally, ion fragmentation within the PTR instrument (e.g., Yuan et al., 2017) can produce interferences in the mass-signal, with MS signal from the mass-fragments of larger parent VOC ions potentially adding onto the signal detected for smaller VOC ions. This fragmentation effect in the PTR instrument must be considered to properly determine the sampled VOC concentrations. The mass-specific nature of the PTR-measurements also means that EC-fluxes derived from PTR data are also limited in the same way. To determine compound-specific MT and SQT fluxes, we must also modify our approach to measuring BVOCs.

To determine speciated BVOC concentrations, manual BVOC air sampling with adsorbent tubes was employed on the flux tower at Norunda during the 2020 and 2022 clearcut campaigns. These samples were collected using stainless-steel thermal desorption (TD) tubes (10 cm in length and 1/4 inch in diameter) that were filled with a 50/50 mix of Tenax GR and Carbograph 5TD (Markes International Inc., USA), chemically adsorbent materials designed for thermal absorption-desorption sampling of gas volatiles. Ambient air was pumped (typically 6 L total) through these adsorbent TD tubes using flow-controlled sampling pumps (Pocket Pump Pro, SKC Ltd., Dorset UK). After sampling, TD samples were then kept refrigerated and analyzed within 30 days of collection.

Two-height BVOC TD sampling on the Norunda tower

To later estimate compound-specific BVOC fluxes (see section 3.2.4), daytime sampling was conducted simultaneously at 37 and 60 m to evaluate the BVOC concentration gradient between these heights following off-line analysis (Figure 7).

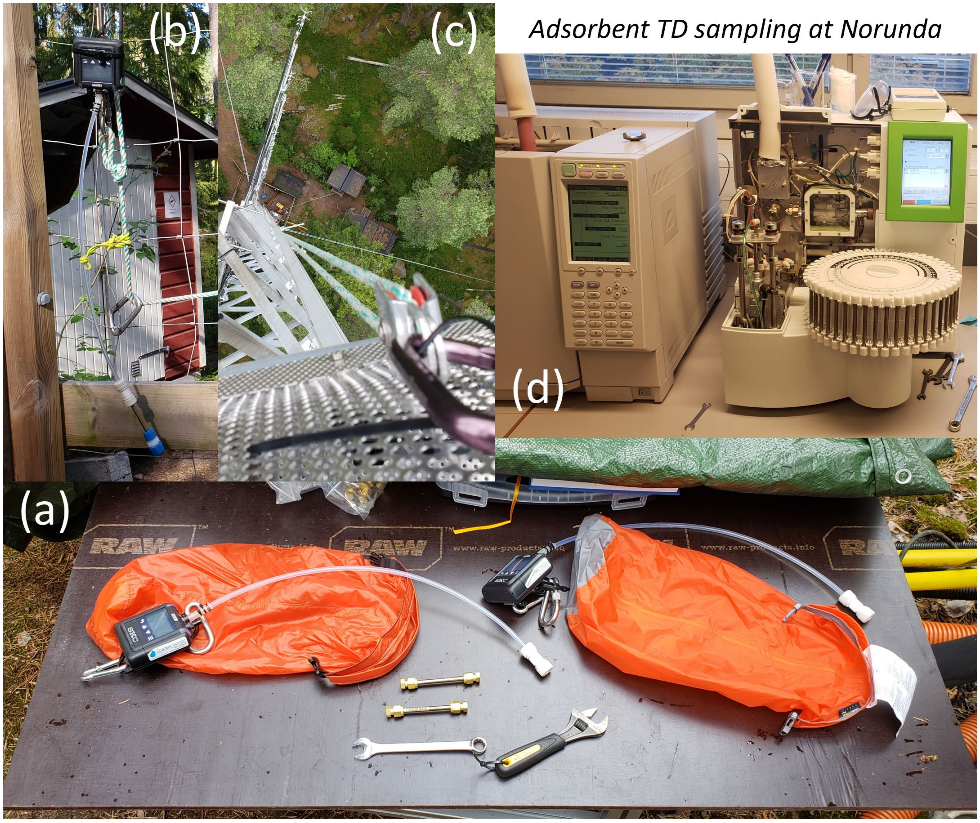


Figure 7. TD tube sampling of BVOC concentration & gradient. (a) Sampling pumps, TD tubes, and equipment for sampling of the BVOC concentration on the Norunda flux tower at 37 and 60 meters. (b) Prepared TD tubes and sampling pump. (c) TD sampling setup on the flux tower for moving the pumps and their tubes to 37 and 60 m for each 30 min sampling period. (d) The ATD-GC-MS in the laboratory used for analyzing the 2020 TD BVOC samples.

ATD-GC-MS and laboratory analysis

The BVOC sample tubes collected in 2020 and 2022 at Norunda were analyzed at two laboratories (at Lund University and Copenhagen University, respectively). Details of the laboratory procedures, analysis settings, and instrumentation model can be found in **papers II** and **III**. In both cases, the sample tubes were analyzed using automated-thermal-desorption (ATD) coupled to a gas-chromatography mass-spectrometer (GC-MS) (e.g., Noe et al., 2012).

In ATD-GC-MS analysis, the desorption of BVOCs from the adsorbent tube and into the GC-MS instrument is carried out in two steps. First, an initial thermal desorption is carried out in which the sample tube is heated (typically >300 °C) and flushed with flow gas (H_2 for these samples) to release the BVOCs onto a adsorbent cold trap inside the ATD unit. During this phase, the *cold* trap is kept at -40 °C. Next, a second thermal desorption is performed by quickly heating the cold trap (>300 °C). This second desorption is much faster, re-releasing the BVOCs at higher concentration into the flow stream for introduction to the GC-column than the initial desorption from the TD sample tube (hence improving GC-MS performance). As BVOC-ladden flow gas passes through the heated GC-column, the column separates the volatiles compounds as they pass through depending on their retention time (i.e., the time required for the compound concentration peak to pass through the GC-column to the MS). Thus isolated, VOC compounds are then identified by the MS according to their mass-spectra using a NIST spectra library. Use of an ATD-GC-MS system provided off-line identification and quantification of sampled BVOCs. Importantly, unlike PTR-MS, this measurement technique can also distinguish between different compounds with identical molar mass.

3.2.4 Gradient-flux methods

Surface layer methods for quantifying turbulent fluxes include the Surface-Layer Gradient (SLG), and Surface-Layer Profile (SLP) methods (e.g., Rantala et al., 2014). The SLG method obtains the turbulent flux by using the vertical gradient of the measured volume mixing ratios (i.e., concentrations $\bar{c}$) and a turbulent exchange coefficient K in the manner of molecular diffusion, with $F_C = -K\frac{\delta \bar{c}}{\delta z}$.

The turbulent exchange coefficient K can be obtained in several approaches, such as using results from another scalar quantity or by application of Monin-Obukhov similarity theory (Foken, 2006).

Surface Layer Gradient (SLG) method

In the case of BVOC gradient sampling using TD tubes at two heights during the Norunda BVOC field campaigns, we use (e.g., Fuentes et al., 1996; Rinne et al., 2000):

$$F_C = \frac{-ku_*[\bar{c}(z_1)-\bar{c}(z_2)]}{ln\left(\frac{z_2-d}{z_1-d}\right)+\psi_h\left(\frac{z_1-d}{L}\right)-\psi_h\left(\frac{z_2-d}{L}\right)} \qquad (2)$$

Where u_* is the friction velocity, d is the displacement height, L is the Obukhov length, ψ_h is the Monin-Obukhov stability function for heat, k is the von Kármán constant, and $\bar{c}(z_1)$ and $\bar{c}(z_2)$ are the BVOC concentrations at heights z_1 and z_2, respectively.

Modified Bowen-Ratio method

Incidentally, another approach that was available for estimating compound-specific monoterpene fluxes was the modified Bowen-ratio method (e.g., Misztal, 2016). From Modified Bowen ratio theory,

$$F_{c_2} = F_{c_1}\frac{\Delta c_2}{\Delta c_1} = k_{c_1}\Delta c_2 \tag{3}$$

Due to the Vocus, total MT flux measurements were available. Making use of these total MT fluxes, speciated MT concentration gradients from TD sampling, and total MT concentration gradient, as estimated by summing all MT compounds identified by upper and lower TD sampling heights, we have

$$F_{MT_i} = F_{MT_{tot}}\frac{\Delta MT_i}{\Delta MT_{tot}} \tag{4}$$

as an additional means of estimating the speciated MT flux. While this approach was sensitive to sampling uncertainty during conditions when MT gradients were relatively weak, it worked particularly well during the 2022 clearcut, when often there were strong concentration gradients that were well resolved.

3.2.5 Other techniques to investigate BVOC emissions

Inverse Lagrangian dispersion analysis of BVOC sources & sinks

To quantify the strength of various compound sources and sinks within the Norunda forest canopy, Lagrangian dispersion theory was applied to interpret vertical profiles of BVOC concentration that were measured during several campaigns in 2014-2016. Unlike previous investigations, which relied on empirical (Raupach et al., 1986) or fitted turbulence profiles (Karl et al., 2004) for estimating parameters such as the standard deviation of the vertical wind speed (σ_w), friction velocity (u^*), and Lagrangian time-scale (T_L), in this analysis we used sonic anemometer measurements from twelve heights on the station flux tower during this time period (see Figure 2), a fairly rare dataset to have available, to directly quantify the profiles of σ_w, u^*, and T_L. Sonic anemometer data from these heights was processed according to the methodology presented by Mölder et al. (2004). An example of what these profiles looked like is provided in Figure 8 below.

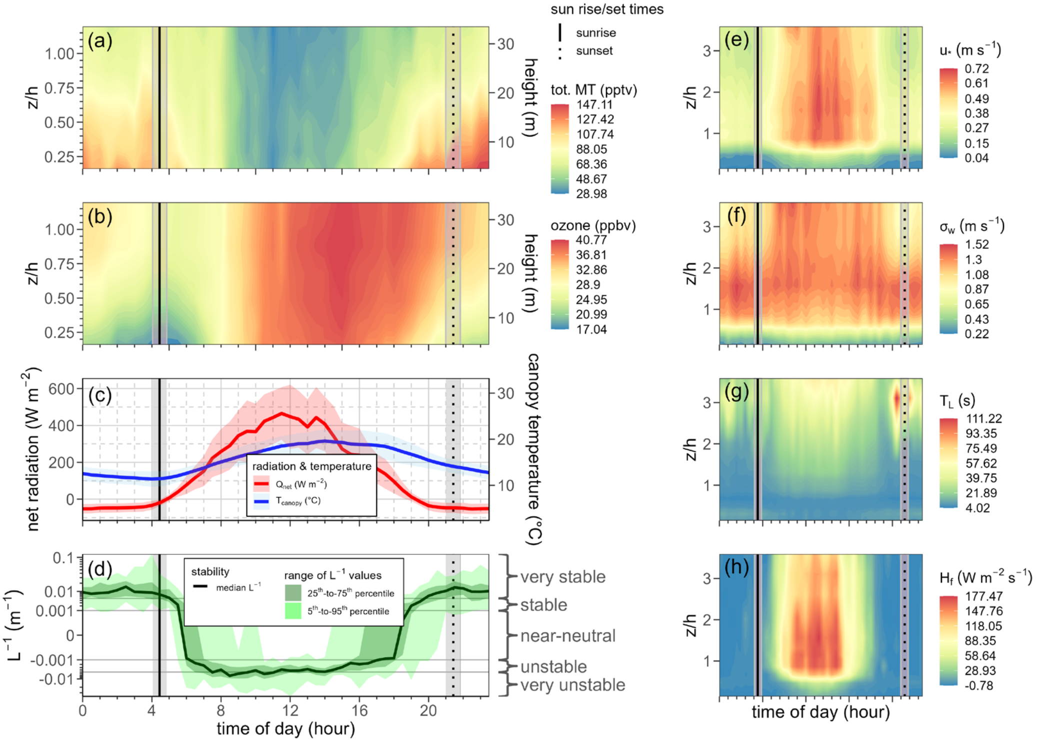


Figure 8. Average diurnal cycle of (a) total monoterpene and (b) ozone profile concentrations for a clear-weather period of summer 2015 (July 20th to August 10th). (c) Net radiation (red) and canopy temperature (blue). Net radiation and canopy temperature are measured at 55 m. Shaded regions of net radiation and canopy temperature indicate one standard deviation. (d) Plot of the inverse of the Obukhov length (L^{-1}), indicating the atmospheric stability above the canopy (measured at 36 m). Classification of stability from Obukhov-length (L) values (very stable: $0 \leq L < 200$, stable: $200 \leq L < 1000$, near-neutral: $1000 \leq |L|$, unstable: $-1000 < L \leq -200$, very unstable: $-200 < L \leq 0$). (e-h) Diurnal mean contour profiles of (e) friction velocity u_* (m s^{-1}), (g) standard deviation in vertical wind velocity σ_w (m s^{-1}), (h) Lagrangian timescale T_L (s), and (i) sensible heat flux H_f (W m^{-2} s^{-1}) with respect to the normalized height z/h in the forest. In all panels, sunrise (solid vertical line) and sunset (dotted vertical line) are indicated. Shaded region indicates the range of sunrise and sunset times during the July 20th to August 10th period.

As Lagrangian timescales T_L cannot be directly measured from one-point measurements (i.e., a sonic anemometer affixed to a stationary tower), T_L values were calculated from measured Eulerian timescale values T_E based on the approach of Raupach (1989), using the relationship

$$T_L = \beta \frac{\bar{u}}{\sigma_w} T_E \tag{5}$$

Where $\bar{u}$ is the wind velocity and β, a scaling constant, was chosen to be equal to one (Raupach et al., 1986). The timescales T_E were defined as the time delay for the autocorrelation function of vertical velocity w to decay to 36.8 % (1/e) of the maximum value (Mölder et al., 2004; Raupach, 1989). The choice of β equal to one at and below canopy height has previously been shown to be a reasonable approximation (Mölder et al., 2004; Raupach, 1989). Twelve source layers were used (from 2 m to 100.5 m) for the calculation of the source distribution. The six measurement heights for BVOC and ozone were used to calculate the concentration gradients at 6.25, 11.0, 16.25, 21.75, and 29.0 m. The values of σ_w and T_L at 2 m were described using the parameterization given by Nemitz et al. (2000). Ground-level BVOC emissions are not separated from emissions in this lowest source layer (thickness 2 m) due to the limitations of parameterizing σ_w/u* near the surface.

The ozone and BVOC source/sink distribution in and below the canopy was investigated using a Lagrangian dispersion theory approach (Karl et al., 2004; Warland and Thurtell, 2000) to quantify the source and sink layers in the forest canopy using dispersion matrix inversion. Inversion results using the CO_2 concentration profile were also analyzed for comparison to EC measurements of the CO_2 flux (see figure 2), in order to check inversion method performance. Previously, the application of Lagrangian inversion methods for studying CO_2 source and sink behavior in forest canopies, evaluating method performance as well as comparing the inversion results with CO_2 eddy-covariance fluxes, has been robustly studied (e.g., Siqueira et al., 2002; Siqueira et al., 2000). The dispersion matrix that was used for analyzing this data utilized the gradient approach formulated by Warland and Thurtell (2000). The dispersion relation is of the form given by:

$$\frac{dc}{dz}\Big|_i = \sum_{j=1}^{m} D_{ij} S_j \qquad (6)$$

where the concentration gradient at height z_i is the sum of all contributions from source/sink layers S_j at heights z_i. The elements of dispersion matrix D_{ij} are calculated as the sum of near-field and far-field dispersion terms and are given in an attached appendix of **paper I**. A damped least squares approach, weighted by solution smoothness (Siqueira et al., 2000), of the form

$$S^{est} = \left[D^T D + \epsilon^2 W_m\right]^{-1} D^T \left(\frac{dc}{dz}\right) \qquad (7)$$

was applied when performing this inversion. The use of the weighting matrix W_m (Menke, 2018) comes from the approach suggested by Siqueira et al. (2000), in that the sensitivity of the inversion to errors in the concentration (gradient) measurements is addressed by smoothness, imposed by a weighting matrix W_m (i.e, the 1st and 2nd derivative of the canopy concentration profile should be smooth). The weighting matrix W_m is given by Eq. 4 in **paper I**. For Eq. 3 above, the choice of weighting parameter ϵ for the BVOC and ozone inversion was informed by performing the same inversion calculations to quantifying the CO_2 source/sink layer strengths in the Norunda canopy, and then comparing the estimated flux (i.e. the sum the source/sink layer strengths in the canopy) to ICOS Norunda's station CO_2 flux measured by eddy-covariance above the canopy. The CO_2 mixing ratio observations used with Eqs. 1 & 2 were made at heights from 0.8 m to 100.85 m a.g.l. on the Norunda flux tower. Since BVOC measurements were only collected in the forest canopy (up to 33.5 m), only CO_2 measurements from 0.8 m up to 33 m on the tower were used for the inversion calculations.

Quantifying the effects of chemical degradation on observed MT and SQT fluxes

Chemical degradation plays a crucial role in accurately interpreting surface exchange rates for reactive trace gases such as VOCs. A common assumption in surface layer flux measurements is that the vertical flux between the surface and measurement level remains constant. However, for reactive gases, this assumption can lead to systematic errors when fluxes are interpreted as surface exchange rates. The error is particularly significant for compounds with a high Damköhler number ($Da = \tau_t/\tau_c$), which represents the ratio of turbulent mixing time-scale to chemical reaction time-scale. This is the case for certain sesquiterpenes (Rinne et al., 2012), where the chemical degradation can substantially alter surface exchange estimations.

The ratio of flux to surface exchange (R = F/E) is influenced by both the compound's chemical lifetime (τ_c), which depends on the mixing ratios and reactivities of atmospheric species like ozone (O_3), hydroxyl radicals (OH), and nitrate radicals (NO_3), and the turbulent mixing time-scale (τ_t), which is controlled by friction velocity (u_*), measurement height (z), and canopy height (h). The surface exchange rate (E) of a compound can be estimated by considering these factors:

$$E = \frac{F}{R(Da(\tau_t/\tau_c), z/h)} \tag{8}$$

Moreover, the value of R varies with emission height, such as between canopy and soil surface emissions, affecting surface exchange rates for different VOCs. For example, the Da number for isoprene ranges from 0.0003 to 0.014, for MT (based on α-pinene reactivity), Da ranges from 0.005 to 0.037, and for SQT (based on β-caryophyllene reactivity), Da ranges from 0.3 to 0.9.

In **paper II**, chemical degradation's impact on observed fluxes of isoprene, MT, and SQT was investigated through modeled estimates for the ratio F/E (Figure 9). Stochastic Lagrangian transport modeling in forest canopy by Rinne et al. (2012) had explored the effect of chemical degradation on the F/E ratio as a function of Da and height z. This study implemented those findings to estimate the surface exchange rates of isoprene, MT, and SQT, parameterizing the diurnal variation in reaction rates for OH and NO_3 as well as using locally measured ozone concentrations. A significant impact was found for SQT as well as nighttime MT exchange. Further details can be found in **paper II** and its appendix.

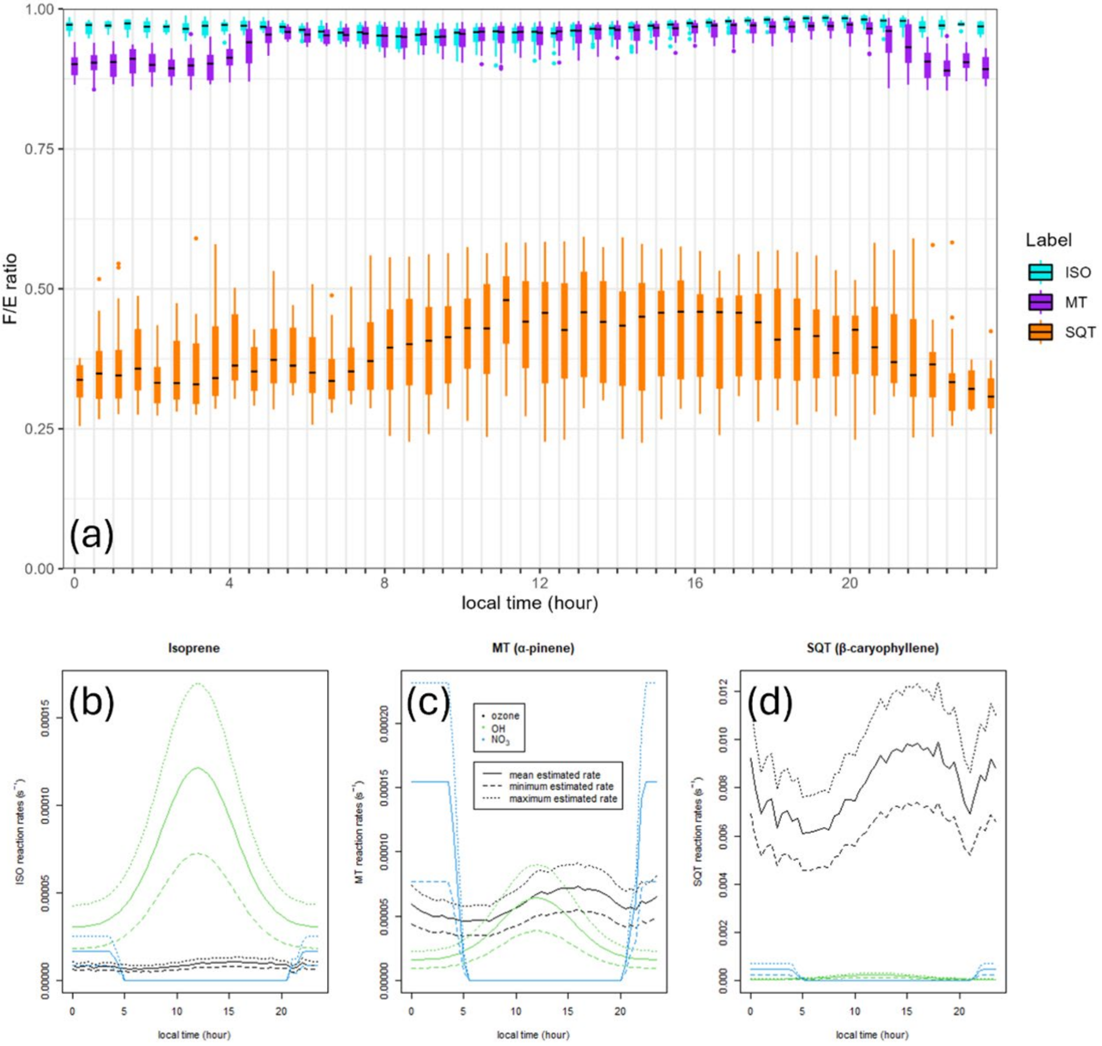


Figure 9. (modified from *Petersen et al. 2024, in disc.)* (a) Ratios for chemical degradation estimates of isoprene (cyan), MT (purple), and SQT (orange) for the 2020 Norunda BVOC campaign. Black dash of whisker plot indicates the median value. (b-d) Diurnal mean reaction rates of ozone (black), OH (green), and NO_3 (blue) for isoprene, MT (α-pinene) and SQT (β-caryophyllene). Lines indicate the mean (solid) reaction rates, as well as the minimum (dashed) and maximum (dotted) -estimated values of the reaction rates based on the concentrations of OH, O_3, and NO_3 as well as the uncertainties ΔOH, ΔO_3, and ΔNO_3.

3.3 Field campaigns before, during, and after 2022 Norunda clearcut

Vocus measurements were conducted during all Norunda PhD campaigns (2020, 2021, and clearcut 2022). In 2020, the Vocus operated from July 26 to August 28, in 2021 from June 1 to September 18, and during the main clearcut campaign study, in 2022 from July 14 (with a brief delay in measurements of a few days due to Vocus-component replacement) until October 5. In all campaigns, Vocus were sampled at 35m using a Vocus PTR-ToF-MS.

Regular daytime adsorption sampling at 37 and 60 m was conducted during the 2020 and 2022 campaigns. During the 2020 measurements, daytime adsorbent TD samples were collected over three-day periods, approximately once a month, from June to August. During the 2022 clearcut, sampling was conducted continuously for two-day periods, typically once a week, during the initial cut. Late in the clearcut campaign, this sampling schedule was extended to about once every two to three weeks. In addition to the two-height daytime sampling, during the 2022 clearcut, continuous sampling at 37 m was maintained at night during these two-day periods using sequential tube sampler (STS-25, PerkinElmer) mounted at 37 m on the station flux tower. The setup of BVOC instrumentation on and around the Norunda station tower during all campaign years is illustrated in Figure 10 below.

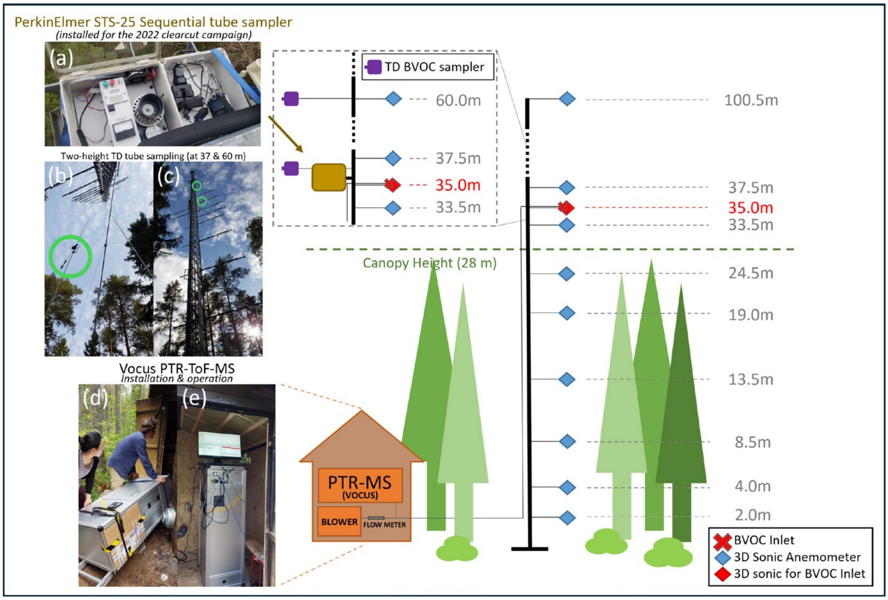


Figure 10. BVOC Inlet setup and infrastructure at ICOS station Norunda for the 2022 forest clearcut. In addition to the equipment and infrastructure already present in 2020 and 2021, a PerkinElmer STS-25 sequential tube sampler (a) was installed on the station tower at 37 for nighttime adsorption tube BVOC sampling. (b-c) Lifting and final heights of TD equipment for gradient sampling (at 37 and 60 m) on the Norunda tower. (d-e) Example showing installation and position of Vocus inside the instrument shed.

Results and Discussion

4.1 Technical advances in BVOC flux measurement

This PhD thesis has combined the best of EC-flux and gradient-flux instrumentation and flux methods for BVOC research to investigate the long-term emission of BVOCs (particularly that of terpenes) from the ICOS station Norunda (**paper II**). It has also applied the same combined BVOC-method approach to investigating the short-term and persisting impacts of boreal forest clearcutting (**paper III**) through an intensive and thorough clearcut field campaign – a notably unique study in the current annals of boreal BVOC research.

In addition to the combined EC and gradient methods, this PhD also implemented other technically-challenging approaches to studying BVOC emissions from and within boreal forests. Applying Lagrangrian dispersion analysis and inverse theory (**paper I**) this thesis research also found seasonality in the vertical distribution of sources within and below the Norunda boreal forest canopy, notably characterizing the autumnal role of forest floor MT sources in total ecosystem emissions. Another novel development was the analysis of chemical degradation (described in detail in the following subsection) and its impact on MT and (significantly impacted) SQT flux observations to estimate the original surface exchange rate of the volatiles.

Finally, during the process of this PhD research, several new and innovative advancements in computational tools for BVOC research have been developed. Described in section 3.2.1 and **paper IV** is the Julia programming-language tool package TT3, a first-of-its-kind software tool developed specifically for working with high sampling-rate (>10 Hz) Vocus PTR-ToF-MS measurements for field campaign and extended study (days to months) EC BVOC flux applications. One of the core objectives of **paper IV** is to provide a much-needed tool to the BVOC research community studying emerging EC BVOC topics.

4.1.1 The impact of chemical degradation by OH, ozone, and NO_3 on observed SQT and nighttime MT fluxes

The effect of chemical degradation on isoprene, MT, and SQT surface exchange rates (Figure 11) was explored using the modeling work of Rinne et al. (2012), which made use of a stochastic Lagrangian transport chemistry model, and by parameterizing the diurnal cycle of the reaction rates for ozone, OH and NO_3, to estimate the surface exchange rates for the 2020 Norunda campaign's terpenoid EC flux dataset. The ozone, OH, and NO_3 reaction rate constants of isoprene, MT, and SQT for the surface exchange rate (SER) analysis are from those reported by Atkinson (1997) and Shu and Atkinson (1995). A full description of the surface exchange rate calculations can be found in the appendix of **paper II**.

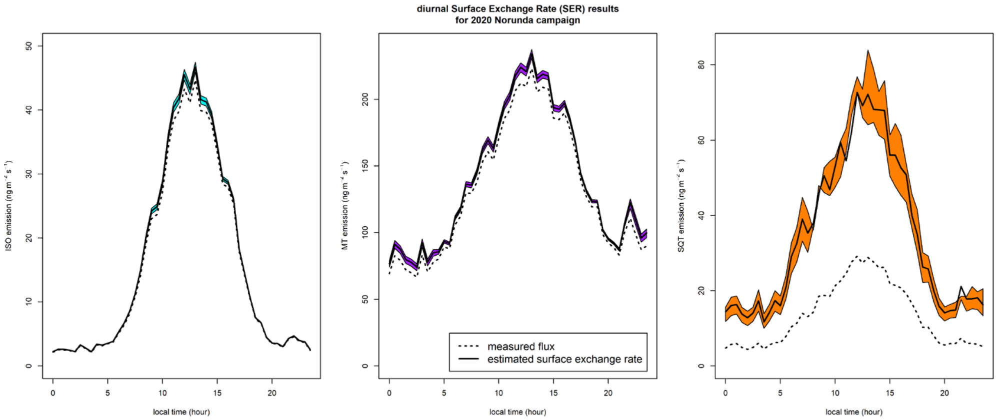


Figure 11. Mean diurnal surface exchange rates for isoprene, MT, and SQT during the 2020 Norunda campaign. Shaded region indicates the range of uncertainty for the modeled ozone, OH, and NO_3 reaction rate coefficients. Dashed black line indicates the corresponding measured flux.

The most significant impact of chemical degradation for observed flux is for SQT. For the diurnal average over the 2020 campaign, peak SQT nighttime emission rates are typically ca. 240 % to 310 % (mean ca. 290 %) greater, and SQT daytime emissions ca. 240 % to 290 % (mean ca. 260 %) greater than would otherwise be inferred solely from EC flux measurements if the impact of chemical degradation on SQT exchange and subsequent SQT flux observations were neglected.

It was noted that, while evaluating the impact of chemical degradation on MT when using the average of the reaction rate coefficients for OH, ozone, and NO_3 for the typical MT concentration mixture observed during the 2020 campaign only differed from the results for α-pinene by ~Δ1%, the varying reaction rates of different MT compounds can have a meaningful impact on their individual nighttime observed flux. For example, while the reaction rate coefficients of α-pinene yields nighttime exchange rates that are ca. 12.6 % greater (varying 7.7 to 16.9 %) than observed flux, the rates for b-myrcene during nighttime yields exchange rates that are ca. 24.6 % greater (varying from 16.7 to 33.3 %). Figure 12 provides a diurnal example of this difference with respect to the estimated emission vs. observed flux for specific MT compounds. It is therefore important to consider the varying impacts of chemical degradation on different MT species when evaluating ecosystem-atmosphere exchanges of these volatile terpene compounds.

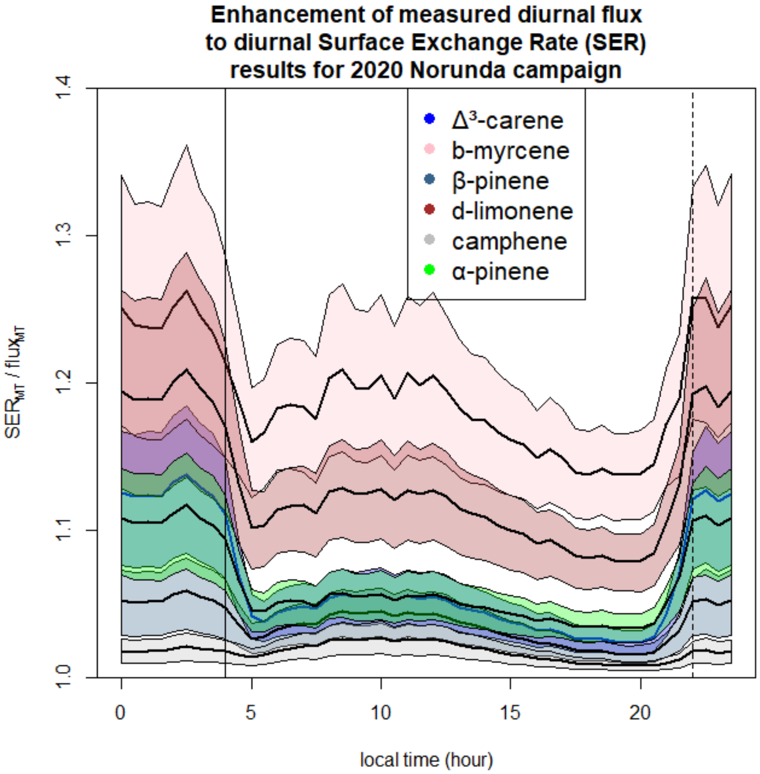


Figure 12. Ratios of estimated surface exchange rate to flux (SER/F) for the chemical degradation estimates of individual MT compounds quantified during the 2020 Norunda campaign.

4.2 BVOC emissions from intact boreal forest

Long-term observations are important for understanding the ecosystem-scale emissions of volatile organics, as these emissions, following from BVOC synthesis from secondary metabolic processes in plants, are influenced by several environmental factors. Even constitutive (i.e., unstressed) emissions respond to environmental factors such as photosynthic light availability, temperature, and CO_2 concentration (e.g., Grote et al., 2013; Li and Sharkey, 2013; Monson, 2013). The emission capacity of a plant or plant population additionally varies depending on past developmental history, the availability of nutrients and ambient CO_2 availability during plant growth (e.g., Monson, 2013; Niinemets, 2010). Hence BVOC emission rates from a forest vary on a daily, seasonal, yearly, and even longer basis. To capture the variability of BVOC emissions over a long period of time, the fieldwork sub-projects of the PhD were organized to take place over multiple consecutive years. Given the detailed nature of Vocus-based EC flux measurements and adsorbent sampling that was conducted, this added further to the knowledge of the seasonal behavior and long-term characteristics of constitutive BVOC emissions from boreal forest ecosystems.

4.2.1 Evaluating the undisturbed emission of terpenoids

BVOC emissions from the intact Norunda forest were measured using Vocus PTR-ToF-MS EC-flux measurements at Norunda in 2020, 2021, and just prior to the forest clearcut in summer 2022. Following the procedures laid down in **paper II**, the terpene fluxes (MT and SQT) we can analyze terpene emissions during the two years (2020 & 2021) of PhD field measurements at ICOS Norunda.

For example, for the month of July, the terpene emission regression results for the emission potential Eo and temperature-factor β for the first week (July 22 - 28) of the 2020 campaign and the last week (July 17 – 22) of EC fluxes analyzed during the PhD thesis for the 2021 campaign are presented in the figure below. For the isoprene flux, we used the fixed $\beta = 0.09\ ^{\circ}C{-1}$ and standard isoprene emission algorithm of Guenther et al. (1995). The fitted isoprene Eo was found to be 76.6 (± 1.2) ng $m^{-2}\ s^{-1}$. Since SQT fluxes at the Vocus inlet height can be expected to be significantly impacted by chemical degradation (chemical lifetime $\tau_c \sim$ seconds to minutes), the chemical degradation analysis presented in **paper II** for estimating the surface exchange rates of reactive VOC gases has been applied to the observed 2020 SQT fluxes at the Vocus EC-inlet height at ICOS station Norunda.

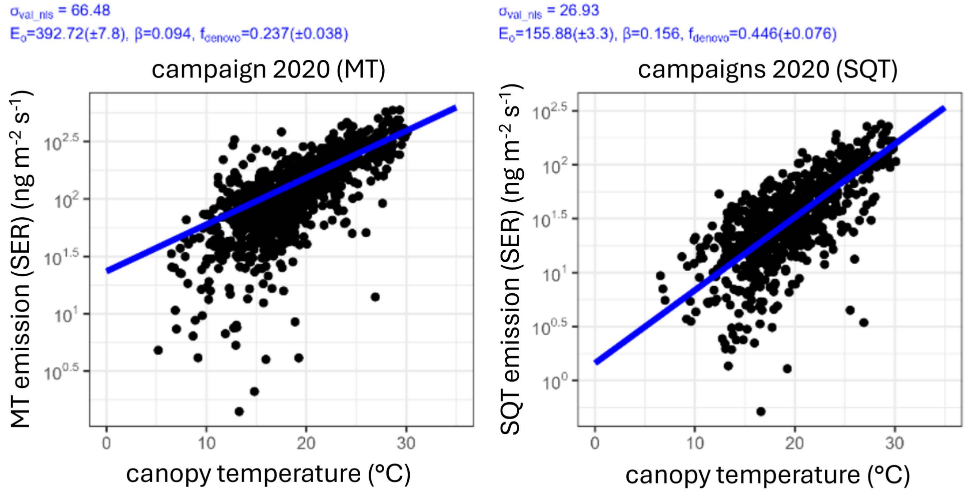


Figure 13. Hybrid emission algorithm fitting of MT and SQT emissions at pre-cut Norunda (2020 campaign). Shown are the model fitting results for MT (EC-flux) and SQT (SER-analysis) (a,b respectively) emissions. SQT emission rates shown follow application of the chemical degradation anaylsis described in paper II to the observed SQT fluxes at Norunda in 2020. Blue line shows the best-fit regression line.

For MT emissions, based on the temperature-dependent pool emission algorithm (Guenther et al., 2012; Guenther et al., 1993), E_o = 381.7 (± 4.5) ng m^{-2} s^{-1} for β fixed at 0.1 (i.e., Guenther et al., 2012). Allowing β to also vary as a regression coefficient yields 368.2 (± 8.8) ng m^{-2} s^{-1} and β = 0.09 (± 0.002). Applying the full hybrid MT emission algorithm (i.e., combined *de novo* synthesis and pool-storage emission, with relative contribution of each based on the fitting-parameter f_{denovo}) (e.g., Taipale et al., 2011) yields E_o = 381.3 (± 6.9) ng m^{-2} s^{-1}, with fitted fraction of MT emissions originating from *de novo* synthesis f_{denovo} = 19 (± 3) %. For the SQT emission estimates produced by the chemical degradation analysis, we find E_o = 184.7 (± 4) ng m^{-2} s^{-1} for β fixed at 0.17 (i.e., Guenther et al., 2012). Allowing SQT's β to also vary yields E_o = 158 (± 5.4) ng m^{-2} s^{-1} and β = 0.14 (± 0.01). Fitting SQT to the hybrid emission algorithm using this β gives E_o = 164 (± 3) ng m^{-2} s^{-1}, with the fraction of SQT emissions originating from *de novo* synthesis as f_{denovo} = 52 (± 6) %.

Based on this combined evaluation for July and the results from the 2020 Norunda campaign (Figure 13), it appears that the total SQT emission potential is likely about 1/3rd of that of the total MT emission potential found at Norunda. In general, this proportion compares well to the model parameter estimates for MT and SQT emission potentials within the plant functional type represented by the Norunda boreal forest (e.g., Guenther et al., 2012).

The total SQT emission fitting also yielded a greater fraction f_{denovo} than total MT. This difference implies that more total SQT is emitted directly following synthesis than from storage pool compared to the relative fraction for total MT. As Δ^3-carene makes up a significant portion of the overall MT emissions (from gradient-flux estimates, typically ca. 25 to 35 %), and predominantly comes from pool-storage rather than *de novo* synthesis for this general composition of spruce and pine species (Guenther et al., 2012; Vanhatalo et al., 2018), this may contribute to differences in fraction f_{denovo} observed. An overview of the isoprene, MT (including the speciation for individual MT compounds), and SQT concentration and fluxes from the Norunda 2020 campaign is presented in Figures 14 & 15.

4.2.2 Speciated & seasonal MT fluxes

Seasonality in the total MT emission potential at Norunda during 2020 and 2021 EC-flux measurements was difficult to distinguish. One reason for this is likely that the seasonality of MT emissions is very species-dependent – as has been observed for many species (e.g., Helmig et al., 2013). Helmig et al. (2013) note that it is typically not feasible to apply a universal seasonal correction factor across different vegetation species. In general, the standard emission rates at Norunda for weekly and monthly total MT emissions were highest in spring and early summer and decreased in August and September.

A weak decline in the relative Eo-fraction of Δ^3-carene was, however, observed in the speciated-MT emission measurements during the Norunda 2020 campaign. In past studies, reduced emissions in summer and autumn have been correlated with activity of some terpene synthases (e.g., Lehning et al., 1999). In their study comparing Scots pine needles collected in early spring and late summer, Vanhatalo et al. (2018) found the proportion of Δ^3-carene synthesis activity to monoterpene storage within them to be exceptionally small (by far the smallest among all MT compounds they studied and also those observed at Norunda).

In the past, the possibility of a seasonal decrease in emission potential among MT compound species due to storage pool depletion has previously been proposed (e.g., Holzke et al., 2006). The inability of new synthesis to adequately replenish storage reservoirs of a MT compound (in this case, Δ^3-carene) sufficiently to mask this effect in emission observations as time progresses, from the peak of the growing season to late summer (June-to-August in Norunda 2020 TD sampling), seems to be a possible mechanism. It has also previously been argued that Δ^3-carene may act as a protective agent against herbivory, being observed to be mainly produced in young needles (Larsson and Tenow, 1980).

Given the current knowledge for Scots pine and Norway spruce regarding the relative synthase activity vs. pool storage, as well as typical *de novo* emission fractions and MT speciation for these boreal tree species (e.g., Ghirardo et al., 2010; Vanhatalo et al., 2018), plus these current findings from 2020 Norunda BVOC investigation, this seems a reasonable proposal for future research and discussion.

The speciation of BVOCs, particularly the speciation of MT compounds, was explored in **papers II** and **III**. The flux of MT compounds at the Norunda boreal forest was observed to primarily consist of α -pinene, followed by Δ^3-carene at ca. 2/3rds of α-pinene. Limonene concentrations contributed about 5 - 10 % of total monoterpene concentrations. During the July measurements for 2020 and 2021 (and precut July 2022), alpha-pinene was the main monoterpene emitted, accounting for ca. 45 % of the total MT concentration. The typical abundance of the other MT species observed was 25 % Δ^3-carene, 11 % myrcene, 9 % limonene, and 8 % β-pinene. During the August measurements for 2020 and 2021, α-pinene was again the main monoterpene emitted, though relative amount to other MT compounds was slightly reduced, accounting for ca. 40 % of the total MT concentration. Meanwhile, the relative abundance of myrcene (18 %) and limonene (13 %) was increased. The typical abundance of Δ^3-carene was 21 %.

It has been observed that, despite the large uncertainty involved with the gradient-method speciated MT fluxes, the fraction of α-pinene flux to the other MT compound fluxes is appreciably higher than the fraction of α -pinene concentration relative to the other MT compounds. This condition is also found in other studies (e.g., Rinne et al. 2000). A potential explanation of this observation is the differing level of impact of chemical degradation on the concentrations observed at the upper and lower adsorbent sampling levels on the Norunda tower (as well as EC point-measurements of flux above the canopy in general). **Paper II**, in a short aside at the end Results section 3.3.1, briefly investigates the impact of chemical degradation on two-height concentration gradient estimation for gradient-flux measurements and finds that the impact on estimated flux is likely negligible relative to the impact on fluxes in general (<1 %). An important takeaway observation is that the relative mixture of MT species concentrations observed does not necessarily reflect the relative mixture of speciated MT fluxes observed above the forest canopy, particularly for the abundantly emitted compounds.

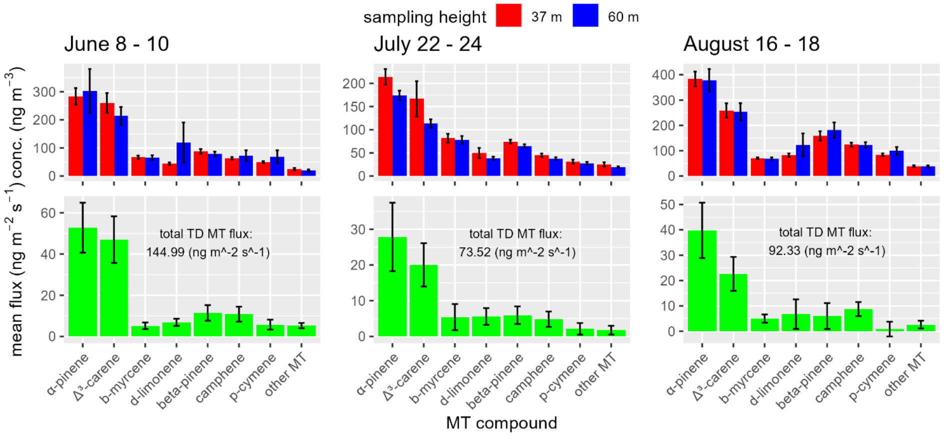


Figure 14. Monthly sampling-period average concentrations (at 37 and 60 m) and fluxes of MT compound species on the Norunda flux tower during the 2020 BVOC gradient sampling campaign. Speciated MT concentrations at 37 and 60 m are shown in red and blue, respectively. Speciated MT fluxes from gradient-method flux estimates are shown in green. From left to right, the columns show the sampling-period averages for June 8 – 10, July 22 - 24, and August 16 - 18. Vertical error bars indicate the standard mean error.

Speciated discussion

A key advantage of these speciated MT flux measurements, via the SLG gradient-flux method, allows the flux to be evaluated at an ecosystem-scale, which avoids the issue of the large variability in MT speciated emissions that can occur even among the pine and spruce members of the same population. It is entirely likely that the observed start-to-end campaign trend from June to August in Δ^3-carene would not have been observed due to tree-to-tree variation among pine and spruce individuals chosen for the limited number of chamber MT emission measurements. An important takeaway from this is that these speciated MT concentration and gradient-method fluxes are useful tools at the ecosystem-scale.

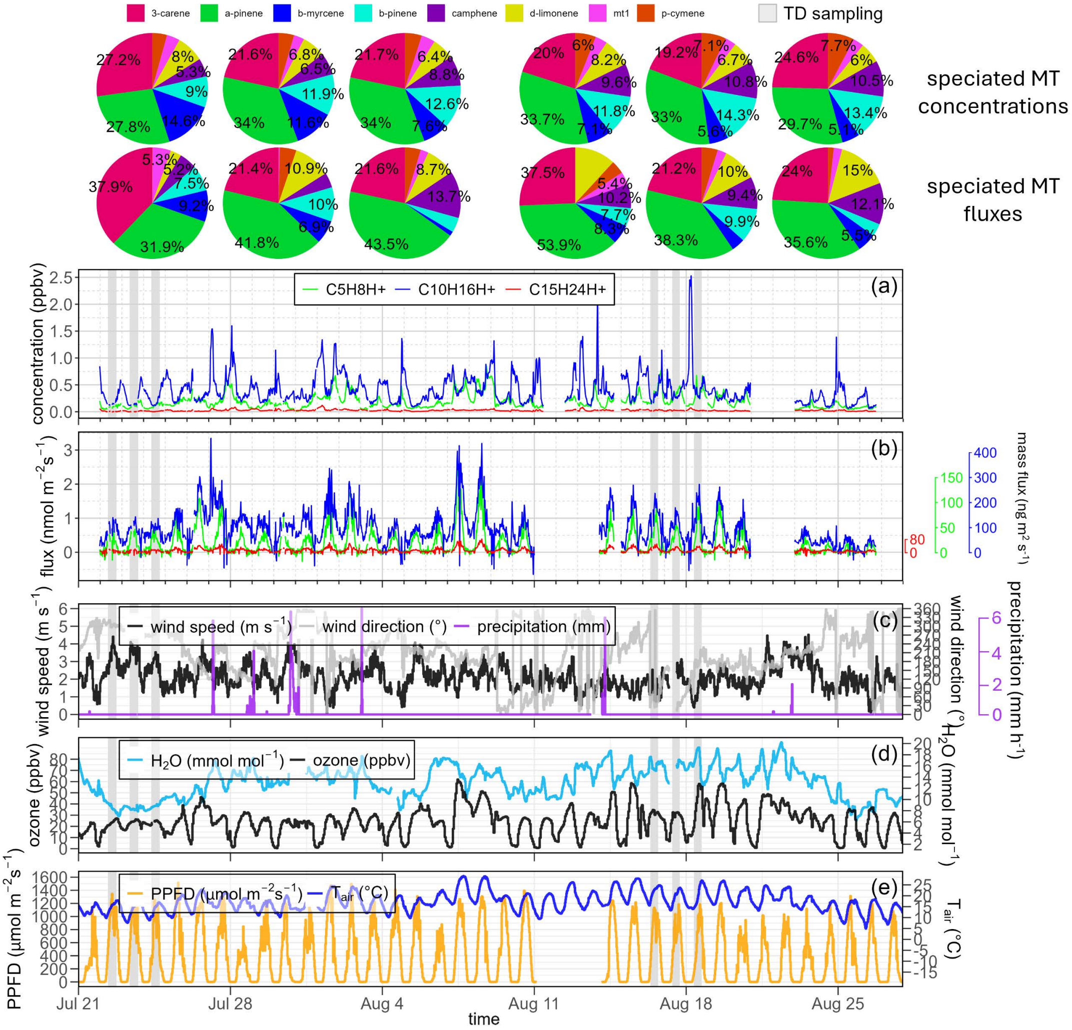


Figure 15. Overview of Vocus PTR-MS and TD sampling during the 2020 Norunda campaign. Time periods during which TD concentration and concentration gradient BVOC sampling took place are indicated in grey. Pie charts show the chemical speciation of MT concentration and flux (top and bottom rows, repectively) during each day of manual TD BVOC sampling. (a) VOCUS measurement timeseries of total MT concentration. (b) VOCUS measurement timeseries of total MT flux. (c-e) timeseries of wind speed, wind direction, precipitation, water vapor, ozone, photosynthetic photon flux density (PPFD), and temperature, respectively.

4.2.3 BVOC sources and sinks within the canopy

Vertical profiles of BVOC, ozone, and turbulence parameters were measured in a boreal forest canopy during several seasonal periods from 2014 to 2016, providing new insight into BVOC exchange processes in boreal forest (**paper I**). A Lagrangian dispersion methodology was subsequently developed to investigate the distribution of BVOC and ozone sources and sinks within and below in the Norunda forest canopy (Figure 16). The results show seasonal behavior in source and sink characteristics for BVOCs within this forest canopy, indicating that further investigations seeking additional insight of BVOC emission and deposition properties within boreal forest ecosystems are warranted.

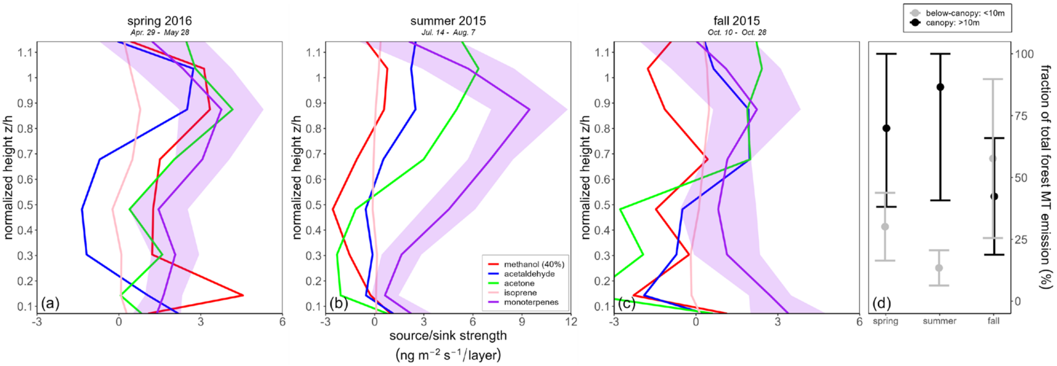


Figure 16. MT seasonal sources. Seasonal BVOC inversion results for the canopy source and sink profile distribution. (a-c) Data shown represent the average of daytime concentrations (from 1.5 h after sunrise to 1.5 h before sunset) for (a) summer 2015, July 14th to August 7th, (b) fall 2015, October 1st to October 28th, and (c) spring 2016, April 29th to May 28th. Shaded region for monoterpenes indicates ± standard error. (d) Relative contribution to total monoterpene emission from the canopy (black) and from below-canopy (gray), and (e) total inferred monoterpene flux (purple), for spring 2016, summer 2015, and fall 2015 periods shown in (a-c).

From the Lagrangian dispersion analysis, the MT source strength was found to typically peak mid-canopy (approximately 25 m), while we observed a strong source near the surface (4 m layer) during the fall. The monoterpene emission from the canopy relative to below the canopy increased (by ca. 70 % to 86 % from the canopy) from spring to summer, while in fall, emissions from the canopy and below the canopy were found to be similar in magnitude. The increased relative emissions from below the canopy are attributed to increased understory litter and soil emissions during the fall (Wang et al., 2018).

Lower levels of isoprene relative to MT were observed in the canopy. As the Norunda boreal forest is predominantly composed of Norway spruce and Scots pine, known to be low/no emitters of isoprene, this was consistent with the composition of the forest and previous isoprenoid measurements at Norunda (Wang et al., 2017). An enhancement in canopy and understory methanol sources was observed in the

Lagrangian inversion results during the spring growing season and attributed to increased methanol production and emission by new growth.

In contrast to the sources of MTs, strong episodic nighttime enhancement of nighttime sinks of methanol and other water-soluble BVOCs (acetone; acetaldehyde) was noted in the summer and fall periods (see Figure 17). This sink behavior was associated with deposition to wet surfaces due to the formation of nighttime dew in the canopy and understory vegetation. Both concentration profile and the inversion results for ozone indicate that the canopy is a significant daytime ozone sink. This likely produces a vertical canopy gradient for the photochemical lifetimes of short lived (1– 20 s) BVOC compounds, such as SQTs.

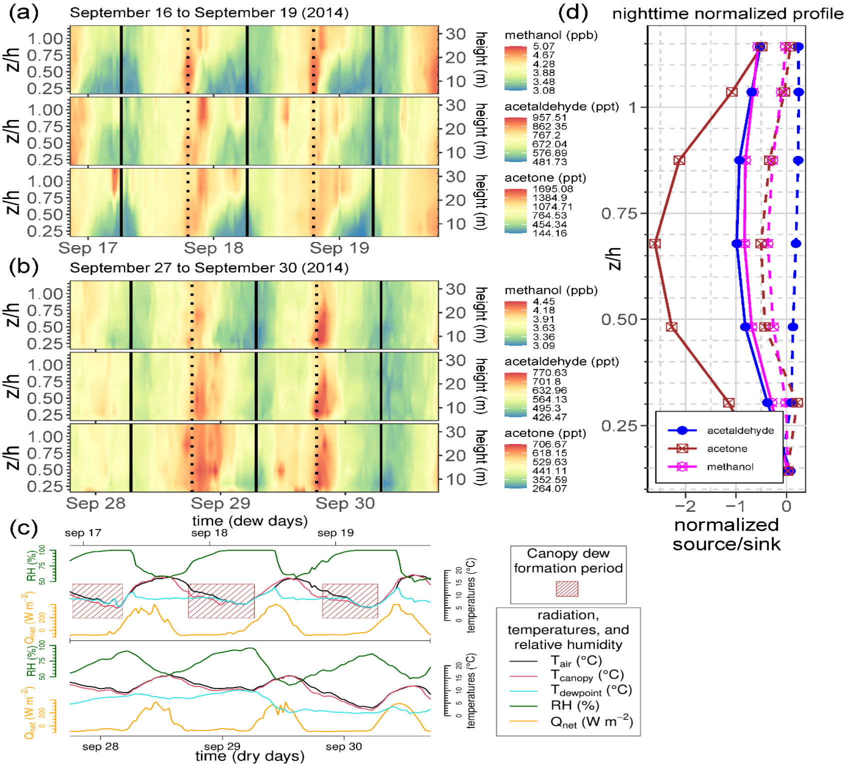


Figure 17. Methanol, acetone, & acetaldehyde sinks. Nighttime dew effects on water-soluble BVOCs in forest canopy. (a) Methanol concentration profile from Sept. 16th to 19th, during conditions where nighttime dew is assumed to have formed in the forest canopy. (b) Methanol concentration profile two weeks later, from Sept. 27th to 30th, during dry conditions. In a) and b), sunrise (solid vertical line) and sunset (dotted vertical line) are indicated. (c) 3-day time-series for meteorological conditions during the "dry" period from Sept. 27th to 30th (bottom-of-panel) and during the "dew" periods from Sept. 16th to 19th (top-of-panel). The meteorological values shown are air temperature (black) in the canopy (at 28 m), IR-measured canopy surface temperature (red), dewpoint temperature (cyan) in the canopy (at 28 m), relative humidity (green), and net radiation (orange). Relative humidity is measured at 28 m. Time periods when dew is expected to have formed in the forest canopy during the "dew" periods are indicated in panel (c) with brown boxes. (d) Normalized source and sink profiles, for methanol, acetaldehyde, and acetone, during the dew and dry periods. Both left- and right-panel profiles are normalized by the sum of the dry period profile level strengths.

4.3 Effect of disturbances on forest BVOC emissions

While large scale disturbances such as forest clearcutting has an influence on a variety of BVOCs, the main focus of the Norunda 2022 campaign (**paper III**) was on MT emission, including the speciation of MT compound concentrations and fluxes that may be observed before, during, and after a boreal forest clearcut.

Two key sources of enhanced MT emissions were evaluated from the Norunda 2022 clearcut campaign's EC Vocus flux measurements. These were (1) the active felling of forest trees (i.e., Scots pine and Norway spruce) and (2) the biomass residue left behind by the clearcut harvesting, as well as other disturbances related to clearcut forestry activity.

4.3.1 Managed vs clearcut forest fluxes

In **paper III**, measurements of BVOC concentrations and fluxes were conducted shortly before (early July), during, and after the clear-cutting in summer 2022 of the Norunda boreal forest. Hourly adsorbent samples were also collected during several intensive BVOC sampling periods for subsequent ATD-GC-MS analysis. The MT flux and concentration timeseries for the clearcut campaign, as well as the time periods when TD concentration and gradient sampling were conducted, are illustrated on the following page in Figure 18.

The largest observed MT flux during the campaign was ca. 250 nmol m^{-2} s^{-1}, more than 100 times greater than the largest flux measured in previous years. Daytime MT emissions during active-cutting periods were frequently above 55 ng m^{-2} s^{-1}. Notably, isoprene emission was comparatively unaffected by the clear-cutting activities during the 2022 campaign. This observation was previously hypothesized and anticipated before the campaign began, as emission of isoprene by plants is entirely *de novo*, lacking (as is well documented in the isoprene research literature) the physical capability for storing it.

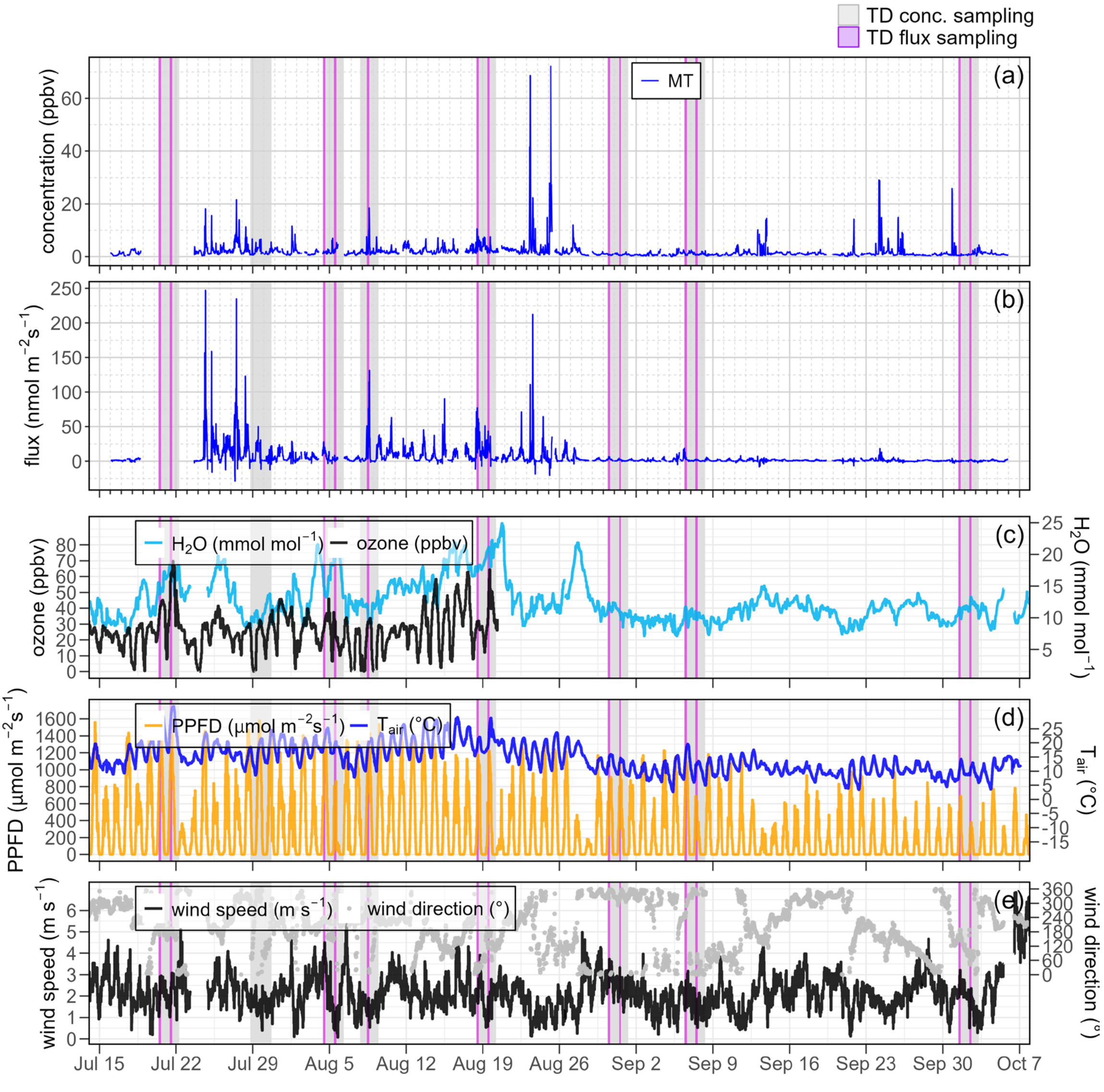


Figure 18. Campaign overview of Vocus PTR-MS and TD sampling during the 2022 Norunda clearcut. Time periods during which TD concentration sampling took place are indicated in grey and when TD concentration gradient sampling took place in purple. (a) VOCUS measurements of MT concentration. (b) VOCUS measurments of MT flux. (c-e) timeseries of water vapor, ozone, PPFD, temperature, wind speed, and wind direction, respectively.

To distinguish between days when active cutting took place, and the rest of the campaign when significant emission is expected from residue and other disturbance (such as tractors driving over the cleared forest terrain, etc.), following the precut, the MT flux dataset was separated into active days and passive days according to its daily-fitted E_o standardized emission rate. For this analysis, a day was considered to be active if its daily E_o exceeded a threshold value (set at 10x precut E_o) and an examination using daily drone maps to confirm the direction of active cutting in the forest footprint relative to the station flux tower (see Figures 19 & 20).

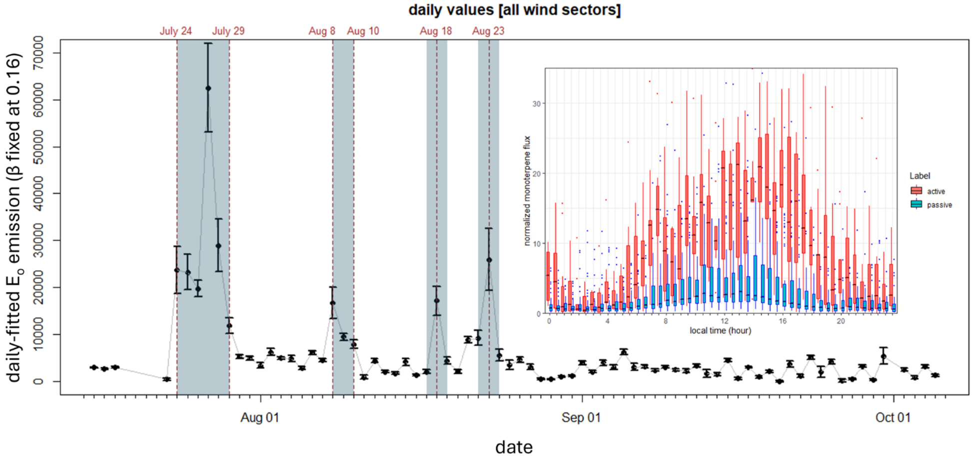


Figure 19. (main) Daily Eo fittings throughout the campaign to distinguish active-cutting vs passive days for subsequent analysis and comparison. (inset) Diurnal comparison of active-cutting vs passive Eo standardized emission rates (normalized to precut Eo).

If β is held as a fixed parameter (0.09), then the ratio of the standard emission during active cutting days to precut $E_{o,active}/E_{o,active} = 21.3 \pm 0.57$, and for passive days we find $E_{o,passive}/E_{o,precut} = 5.9 \pm 0.06$. Naturally, however, the temperature-sensitivity of emissions can be expected to be influenced as well. If we allow β to vary as a fitting parameter for the Pool emission algorithm as well, we find $E_{o,active}/E_{o,precut} = 33.8 \pm 3.65$ and $E_{o,passive}/E_{o,precut} = 8.7 \pm 0.17$ (with $\beta_{active} = 0.162 \pm 0.025$, $\beta_{passive} = 0.158 \pm 0.004$, and $\beta_{precut} = 0.134 \pm 0.003$). If β is kept fixed for the precut measurements, however, which is reasonable, as 0.09 is a consistent value for Norunda stemming from the 2020 and 2021 Vocus campaigns, then the greatest ratios for the active and passive emission are found to be $E_{o,active}/E_{o,precut} = 50.7 \pm 2.9$ and $E_{o,passive}/E_{o,precut} = 13.1 \pm 0.1$.

MT fluxes increased by more than an 1 - 2 orders of magnitude during the clearcut and continued to be significantly above the average for summer and autumn found during observations from previous years. An example of this is shown in Figure 21. Using an emission-model based on these results, the additional MT emissions due to active clear-cutting were estimated to increase emissions by a factor of greater than 50x and persisting passive emission increases from residue and related disturbance by a factor greater than of 13x. Using Sweden forestry information of absolute timber removal and on-site residue volumes from logging activities, we estimate that current Swedish boreal MT emission inventory estimates that rely on modeling approaches that neglect the impact of logging activity may be significantly underestimated.

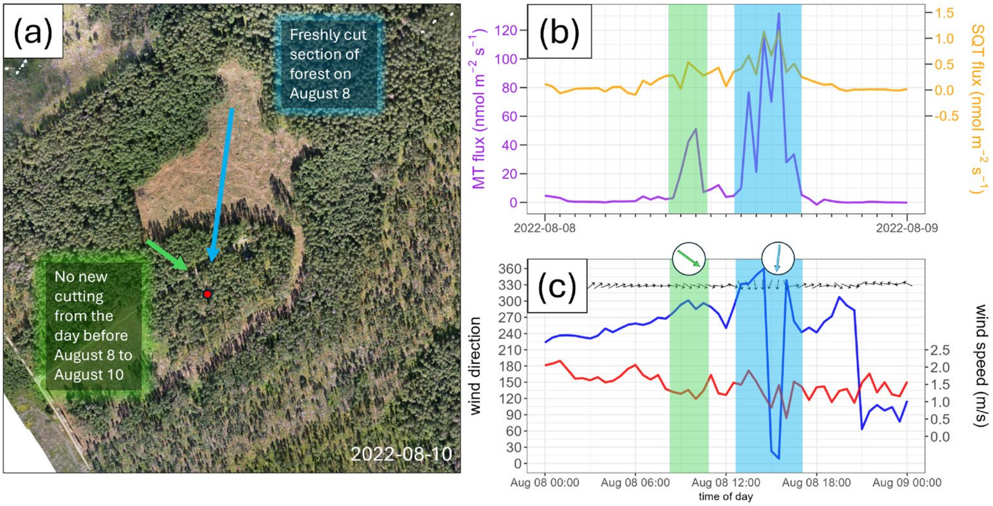


Figure 20. Example of passive disturbance (logging tractor, moving lumber, ect) and active cutting MT emission. (a) Drone map of Norunda forest following cutting activity on August 8, 2022. (b) Observed MT (purple) and SQT (orange) fluxes. (c) wind direction (arrows; blue line) and wind speed (red line). In panels b & c, time-periods illustrating passive activity (green) and active cutting (cyan) are indicated.

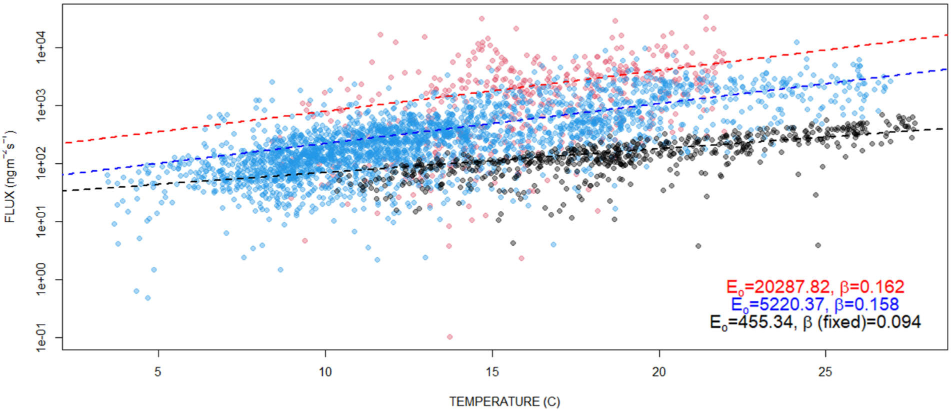


Figure 21. MT emissions before & during boreal forest clearcut. Semi-log scatterplot of fluxes (nmol m^{-2} s^{-1}) and the corresponding observations of ambient temperature during the 2022 Norunda Clearcut campaign. Shown are measurements collected during (red) active-cutting, (blue) passive emissions derived from biomass residue and other disturbances during the clearcut, and (black) pre-cut measurements from the 2021 campaign (July 12 – 22).

4.3.2 Changes in MT speciation during the Norunda 2022 clearcut and its implications

The 2022 campaign TD sampling for ATD-GC-MS analysis indicated clear changes in the relative mixture of MT compounds (Figure 22) before, during and after the forest clearcut.

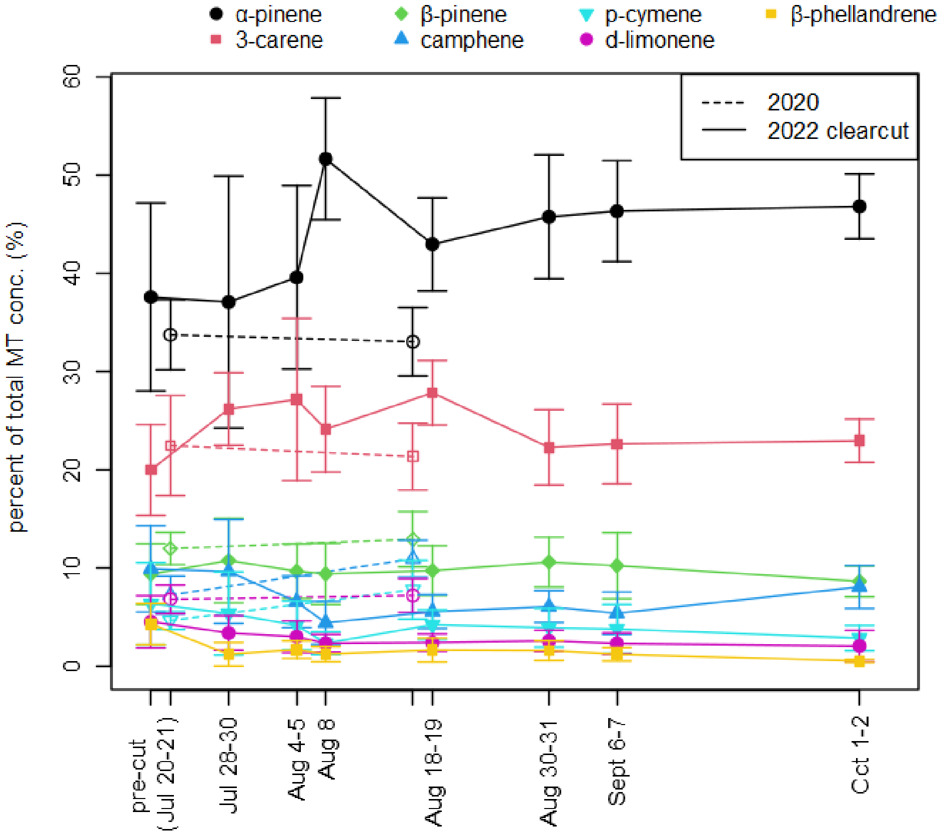


Figure 22. fraction of MT compound relative to total MT concentration at 37 m. The clearcut 2022 measurements are indictated by solid lines & dots, and 2020 campaign values (i.e., precut year fractions) by dashed lines & circles. The y-axis indicates the percent a given MT compound contributes to the total MT concentration (ng m^{-3})

In late stage of campaign (September and October), ɑ-pinene dominates the total MT mixture and is at its highest fraction (45-50 %), while Δ^3-carene returns to slightly above (~24 %) its precut level. Camphene also rebounds towards its precut level in October, while β-pinene is relatively unchanged. The percentages of the other MTs remain depressed following the precut. Interestingly, while overall emission rate decreases towards the end of the campaign (due to lower temperatures and reduced frequency of active cutting), the fraction of α-pinene consistently grows from August to October. During active cutting directly upwind of the tower on August 8, α-pinene was the only MT compound whose fraction increased relative to the overall MT compound population.

The behavior of different MT species before, during, and after the clearcut of the Norunda forest can be examined in the context of *de novo* versus storage pool emission. As observed by Vanhatalo et al. (2018), among α-pinene, β-pinene, Δ^3-carene, and camphene, there are notable differences in MT synthesis activity and fraction of total MT storage pool in needles. An example of the speciation of MT synthesis activity and pool storage (as examined via summer and autumn needle samples) is provided in the right panel of Figure 23 (credit: *Vanhatalo et al. (2018)*).

This examination comes from the SMEAR II measurement station in Finland, a similar mixed pine/spruce forest to Norunda. Both MT synthase activity and storage pool fraction is typically largest for α-pinene. Meanwhile, the storage pool of Δ^3-carene was second largest among the four compounds (about 1/3rd of total MT pool), but Δ^3-carene synthesis activity was by far the smallest. In contrast, the storage capacity of camphene relative to its synthase activity in SMEAR II forest needles, like its fraction at Norunda following the clearcut, is significantly reduced.

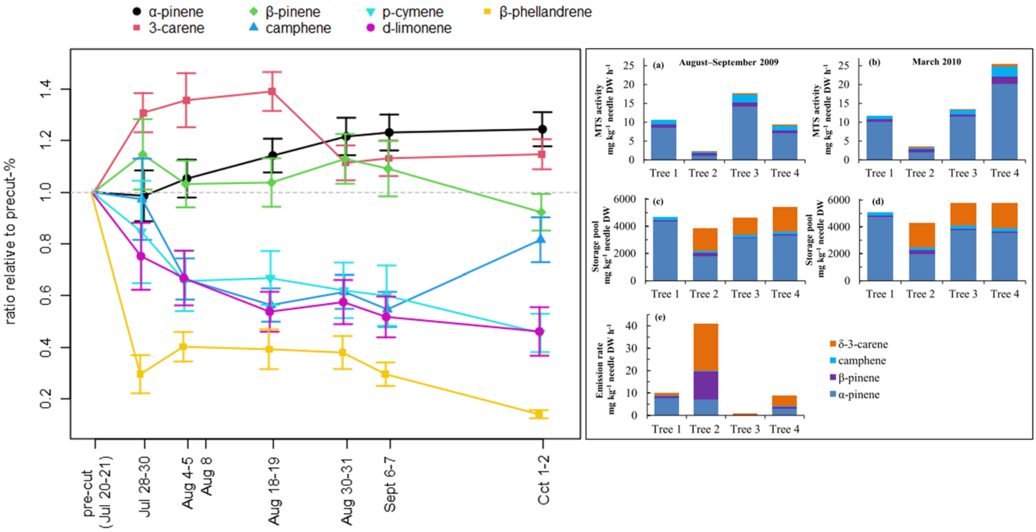


Figure 23. (left) Relative ratio of fraction of total MT concentration vs. precut fraction for the primary MT compounds observed during the Norunda 2022 clearcut. (right) MT synthase activity vs storage pool (credit: *Vanhatalo et al 2018*): (a,e; b,d) Tree-to-tree variation for 2009 needles in monoterpene synthase activity and (c) and (d) monoterpene storage in late summer/autumn (Aug.–Sept. 2009: a, c, e approx. two-month-old needles) and in early spring (March 2010: b, d approx. nine-month-old needles).

Changes in the speciated MT fraction are further illustrated in the left panel of Figure 23. During the main period of cutting in the Norunda forest, the fraction of Δ^3-carene among all MTs relative to its precut fraction ($Q_{\Delta^3\text{-carene}}$) increased, peaking in August by 30 to 40 %, and subsequently declining to 10 to 20 % by the end of the campaign in October. In comparison, the ratio $Q_{\alpha\text{-pinene}}$ for α-pinene gradually increased throughout the campaign until reaching a 15 to 25 % increase in October relative to its precut fraction. The relative ratios for d-limonene and camphene fell for the entire campaign.

As discussed in section 4.2.2, the depletion of Δ^3-carene from boreal forest storage pools has been posited previously as a potential cause for seasonal decreases in the ecosystem-scale Δ^3-carene emission potential following the peak of the growing season. Boreal forest clearcuts significantly increase storage pool MT emission by breaking open the storage structures within plant tissues. As storage likely plays an outsized role for Δ^3-carene emission relative to new synthesis in comparison to other observed MT compounds, this may play a role in the unique behavior of its relative fraction of MT compounds observed during the 2022 Norunda clearcut.

4.3.3 Discussion on boreal forest management and implications for future boreal VOC emissions

In their general estimates regarding the VOC emission impacts of US forestry, Schade and Goldstein (2003) found that the total MT emissions annually in the US may be underestimated by between 0.5 and 5.5%. Following **paper III**, a similar or larger magnitude can be anticipated for Sweden and similarly managed-forest areas of Scandinavia. In Sweden alone, forests cover ca. 70% of the country's area, with around 87 billion trees. In recent years, approximately twice as much lumber is now harvested compared to 90 years ago (Kumar et al., 2021). Forestry has a long history as an important resource for the Swedish economy (Poudel et al., 2012), leading to regular updates of national forest inventories at the regional- and county-level for over a century (Swedish National Forest Inventory). Similar to the ~1 % found by Schade and Goldstein (2003), Swedish national inventory data indicates that 1.03 % of Sweden's forests is felled for logging each year, with 1.23 % subjected to forest-thinning (SNFI). In the Svealand region, where ICOS Norunda is located, approximately 1.4 % of productive forest land was felled in 2020 (Skogsstyrelsen) with an additional 1.43 % thinned (3.8 % in total either felled, thinned, or cleaned – i.e., dead or deseased trees removed). By species, of all trees felled in Svealand in 2020, approximately 91% were either Scots or Norway spruce. The makeup of managed forests in Sweden overall is likewise dominated by a mix of these two species.

The flux measurements conducted in this PhD thesis during the 2022 clearcut of a boreal pine/spruce forest in Svealand, Sweden, indicates a range of about *30-50x* increase in base MT emission rates during active-cutting and a *8-13x* increase in persisting MT emissions from clearcut residue and other disturbances in the felled area. In particular, these persisting emissions continued for the duration of 2022 clearcut observations. Through the course of this PhD thesis, in addition to investigating the ecosystem-scale emissions during and after (2022-2023) the 2022 summer clearcut, the intensive BVOC measurements at ICOS Norunda has provided perhaps the greatest known coverage of BVOC emissions leading up to a boreal clearcut as well (cumulatively ca. 10 months from July 2020 to July 2022). When compared to the same analysis arguments as Schade and Goldstein (2003), we find annual MT emission estimates for Sweden, and for the Svealand region of Sweden where the ICOS Norunda station is located, to be underestimated to an even greater degree when neglecting the abiotic influence of forestry (> 5% yearly). This gap highlights the needs for future BVOC modeling advancements and indicates that the impact of clearcut forestry should be considered when evaluating Sweden's national BVOC emission inventory.

Impact of forestry on MT speciation

A significant implication of this work has been the role that seasonal changes can have on the speciation of MT compounds and subsequently their impact on air chemistry. From **paper III**, it appears clearcutting and similarly disruptive forest management may influence the region speciation of MT and other terpenes as well. This has significant consequences. BVOCs like MT influence the tropospheric ozone budget (Archibald et al., 2020). MTs also contribute to the formation and/or growth of atmospheric SOA due to the gas/particle partitioning of their reaction products in the troposphere. The structure of MTs has a significant role in their reactivity. For example, endocyclic MTs (e.g., limonene, α-pinene, and Δ^3-carene) have a greater aerosol formation potential and tend to react faster than compounds with exocyclic double bonds (e.g.,β-pinene and camphene). Fast-reacting MTs can also represent a significant fraction of total reactivity even at low concentrations (e.g., Yee et al., 2018). Subsequently, even small seasonal changes in their concentration can represent large changes in the reactivity of the overall MT population emitted. It therefore appears to emerge clearly from this PhD field campaign research into clearcuts that differentiating between *de novo* synthesis emission and storage pool emission, and the mechanistic effects controlling them, is key for understanding the effects of anthropogenic disturbances on landscape-scale BVOC emissions in the future.

Other influences

Outside abiotic disturbances evaluated in **paper III**, another consideration for managed boreal forest BVOC emission rates is how they may also be influenced by the age-constraints placed by forest management on the forest tree population. The impact of a plant's age on its BVOC emission potential is species-specific and can depend on environmental and biotic conditions. For example, Kim et al. (2005) found that total emission rates and the speciation of emitted MT compounds varied significantly with tree species, age, and season. In particular, in their study they found total emissions from *Pinus koraiensis* increased with tree age (yet the converse for *Chamaecyparis obtusa*). Street et al. (1997) found that emission potentials of *Pinus pinea* among mature forest trees were twice those young plantation trees growing nearby under similar environmental conditions. The common practice in boreal forest management is to periodically conduct a forest-thinning, in which younger, smaller trees are removed so that the most mature trees have greater access to nutrients and ability to grow. Hence trees in such managed forests tend to be of similar age. Aside from clearcutting and other disturbance, this skewing of age likely impacts managed forest emission potentials as well.

Future impacts

The global demand for wood (~$1.5\text{x}10^9$ m^3) is expected to increase to 2.3 - $3.5\text{x}10^9$ m^3 by 2050 (Smeets and Faaij, 2007), representing a ca. 50 – 130 % increase. Logging and forestry-related activities will likely have an increasingly large impact on boreal forests in the future. In the managed boreal forests of Finland and Sweden, annual forest growth rates and harvesting volumes have been increasing over the past 100 years, with about twice as much timber in Sweden than 90 years ago (Kumar et al., 2021). If we consider that about 1% of these managed forests are harvested each year, and conservatively estimate that the typical emission potential for MT when averaged over the year of a forest's harvest is 5x normal, then the increase in boreal MT emission potential annually is >3% greater just from boreal forest harvesting alone. This appraisal also does not account for the emission impact of other management practices, such as forest thinning and cleaning. If boreal forestry and biomass harvesting continue to increase further in the future, as expected, then this impact on boreal emissions is likely to grow.

Conclusion

This research significantly advances our understanding of Biogenic Volatile Organic Compound (BVOC) emissions in boreal forest ecosystems and their response to both seasonal ecosystem dynamics and anthropogenic disturbances. The findings presented highlight the important role that boreal forests play in the global BVOC (particularly MT) budget, with these emissions influencing atmospheric chemistry, air quality, and climate processes.

Through a series of systematic observations, from seasonal BVOC fluxes over several years to the impacts of boreal forest clearcutting, this study underscores the complexity of BVOC exchange processes and the sensitivity of these emissions to forest management practices. Specifically, the drastic increases in monoterpene (MT) emissions during and after clearcutting events suggest that current BVOC emission models may underestimate emissions in managed forest landscapes. These insights have significant implications for refining national and global BVOC emission inventories, particularly in regions like Sweden where clearcut forestry practices are prevalent.

Furthermore, the showcased development of advanced data analysis tools for high-frequency PTR-ToF-MS measurements contributes to the broader research community's ability to process and interpret complex BVOC datasets efficiently. This technical progress ensures more accurate (and manageable, in the case of large campaign datasets) assessments of BVOC fluxes and their interactions with atmospheric processes.

Looking ahead, the results emphasize the need for continued long-term BVOC measurements and support the inclusion of forest management impacts in emission models. Future research should aim to explore the mechanistic differences between *de novo* synthesis and storage pool emissions in their response to abiotic disturbance to further elucidate the effects of human-induced disturbances. Such efforts will be essential for improving biosphere-atmosphere feedback models and informing sustainable forest management policies in a changing climate.

In conclusion, the work of this PhD not only helps to fill key gaps in the current understanding of boreal BVOC emissions but also sets the stage for more comprehensive and accurate assessments of forest-atmosphere interactions in boreal regions worldwide.

Acknowledgements

This PhD work was supported by the Swedish Research Councils VR (2011-3190) and Formas (2017-01474).

The Norunda research station – at which this PhD took place - received funding from the Swedish Research Council VR, Grant 2019-00205.

All things progress - *little by little, poc a poc*. My PhD studies at Lund University was a rocket ship of new experiences, triumph, disaster – fire included, triumph again, and ultimately meeting the love of my life, Lara, and recently welcoming our son into the world. Wow. I could not have succeeded without the support and friendship of the people around me.

First, I would like to thank my main supervisor, Janne Rinne, for your guidance and encouragement through these PhD years. You gave me independence to pursue my projects and the support to do so. If you had not encouraged me to turn my PhD notes for the Vocus into my fourth thesis paper, it likely would have remained a bundle of notes and code in an office drawer. It's still there - but now other people can read it too, which seems to be a big (and rewarding) part of what being a scientist is all about. You also introduced me to the *nyckelharpa* – which I now will have time to play! Thanks goes out also to my other supervisor, Thomas Holst, for being there through thick and thin, fire and – well, it's hard to beat fire. Thank you for your help and guidance over the last few years. Easter weekend 2020 set the gold-standard in my mind for how to behave when under… well you get the idea. Really, thank you for being such a rock-solid adviser over the years. Special thanks to you both as well for the weekly PhD thesis meetings in the final stage(s) of the PhD. During my studies, I also had the chance to explore and improve my skills at teaching in a classroom, which was very fulfilling to do while also pursing my PhD studies in Lund. A special thank you to Maj-Lena for being an excellent mentor in teaching! - wishing you a wonderful retirement.

Projects like climbing on towers to measure fluxes cannot be possible without a host of other people, even if that tower is out in the middle of the woods. I am very grateful to Irene Lehner and Anders Båth for your endless help at Norunda over the years. Thanks also to Meelis Mölder for his wonderful company and discussion at lunch and on road trips. For my studies, I am also particularly grateful for his assistance with station data as well as from his tower sonic anemometers. I would like to also thank Natascha Kljun for all her assistance with flux footprints and project work at Norunda. Speaking of project work in the field, a thank you to Tobias Biermann for his help at the start of my PhD with getting the Teflon tubing for BVOC flux research up the station tower! I also appreciate all the help and advice for getting certified for mast-climbing work over the years. I would also like to thank Claudia Mohr and Cheng Wu from (at the time) Stockholm University for sharing their Vocus instrument with our Lund BVOC group at ICOS Norunda during the span of years covering my PhD studies at the station.

Thank you to all my colleagues at INES department and elsewhere. *It takes a village*. Thanks to my office partners for being there to chat. I would like to thank office partners Klas Lucander (at the start) and Renkui Guo (at the end) for a wonderful day-to-day office experience during the PhD. Special thanks to Renkui for turning my office computer back on whenever the power went out - a big help for PhD studies when you're often working remotely from several countries away. On that note, thank you to Rafael Przybyszewski and Rebecca Anderberg in INES IT. I'm also glad that there was also another PhD student studying BVOCs during my time in Lund. Thank you to Erica Jaakkola for being a great fellow BVOC researcher during our PhDs! I'm happy that we got to experience its joys and pitfalls together. I would also like to thank Jutta Holst for her assitance in the printing of this thesis book. Thanks to Katerina Sindelarova for her assistance in quantifying boreal contributions to the global and northern hemispheric MT emission inventories. Thank you to Lukas Fischer for his advice and giving the world his TOF-Tracer2 Julia scripts on GitHub – they were a workhorse that made building a Vocus workflow toolkit for powering through my PhD's Vocus PTR-ToF-MS campaign data of BVOCs at Norunda possible. Thank you to Jeremy Chan at the University of Naples. Thanks also Jing Tang, Riikka Rinnan, and everyone at the University of Copenhagen! You made a big difference in making the most of my PhD fieldwork.

Speaking of being out in the field (again), thank you to Per-Ola Olsson for the early-Lund experiences with orienteering at the start of my PhD! I really appreciated it. Additional thanks for compositing the Norunda 2022 drone photos into maps of the clearcut. A big thanks to Joel White, for great times and great flyfishing! You made my time in Lund a wonderful place to go down memory lane. I always appreciated those trips out to the Swedish coast and kanelbulle that followed. *Let me know if you ever want to go fishing in Spain.* Finally, thank you to Jaleh Taheri and Lars Olofsson, Rowan & Rainier – *you made living in Lund a home.*

Words cannot encompass how much my family and their support meant to me throughout the years I've been across the Atlantic from Colorado. From late-night calls to long-distance visits, it has meant the world to me. To my mom, dad, aunt, uncles, both brothers, cousins and relatives – thank you.

And then there is one of the two most important people in my life – my wife (*guapísima!*). Lara, I am so happy that we met and are now sharing a life together. I did not expect when moving to Sweden that I would end up living in Valencia, Spain. We have the absolute best little boy I could have ever imagined. We have a wonderful family, I'm excited to watch our son grow up and see our future together. Soon he will be riding a bike – *but not too soon*.

Poc a poc,

Ross Petersen

References

Alin, L. and Sundberg, U.: Statistical Yearbook of Sweden 2003, Statistics Sweden, Örebro, Sweden, 2003.

Andreae, M. O. and Crutzen, P. J.: Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, Science, 276, 1052-1058, 1997.

Archibald, A., Neu, J., Elshorbany, Y., Cooper, O., Young, P., Akiyoshi, H., Cox, R., Coyle, M., Derwent, R., and Deushi, M.: Tropospheric Ozone Assessment ReportA critical review of changes in the tropospheric ozone burden and budget from 1850 to 2100, Elementa: Science of the Anthropocene, 8, 2020.

Archibold, O. W.: Ecology of world vegetation, in, Springer Science & Business Media, Dordrecht, 510, 1995.

Atkinson, R.: Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes, Journal of Physical and Chemical Reference Data, 26, 215-290, 1997.

Aubinet, M., Vesala, T., and Papale, D.: Eddy covariance: a practical guide to measurement and data analysis, Springer Science & Business Media, 2012.

Burton, P., Bergeron, Y., Bogdanski, B., Juday, G., Kuuluvainen, T., McAfee, B., Ogden, A., Teplyakov, V., Alfaro, R., and Gauthier, S.: Sustainability of boreal forests and forestry in a changing environment, in: Forests and Society-Responding to Global Drivers of Change, International union of forest research organizations, 231-255, 2010.

Chameides, W., Fehsenfeld, F., Rodgers, M., Cardelino, C., Martinez, J., Parrish, D., Lonneman, W., Lawson, D., Rasmussen, R., and Zimmerman, P.: Ozone precursor relationships in the ambient atmosphere, J. Geophys. Res. Atmos., 97, 6037-6055, 1992.

Collins, W., Derwent, R., Johnson, C., and Stevenson, D.: The oxidation of organic compounds in the troposphere and their global warming potentials, Climatic Change, 52, 453-479, 2002.

Dudareva, N., Klempien, A., Muhlemann, J. K., and Kaplan, I.: Biosynthesis, function and metabolic engineering of plant volatile organic compounds, New Phytol., 198, 16-32, 2013.

Fall, R. and Monson, R. K.: Isoprene Emission Rate and Intercellular Isoprene Concentration as Influenced by Stomatal Distribution and Conductance 1, Plant Physiol., 100, 987-992, 1992.

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

Fineschi, S. and Loreto, F.: Leaf volatile isoprenoids: an important defensive armament in forest tree species, iForest - Biogeosciences and Forestry, 5, 13-17, 2012.

Fineschi, S., Loreto, F., Staudt, M., and Peñuelas, J.: Diversification of volatile isoprenoid emissions from trees: evolutionary and ecological perspectives, Biology, controls and models of tree volatile organic compound emissions, 1-20, 2013.

Fischer, L., Breitenlechner, M., Canaval, E., Scholz, W., Striednig, M., Graus, M., Karl, T. G., Petäjä, T., Kulmala, M., and Hansel, A.: First eddy covariance flux measurements of semi-volatile organic compounds with the PTR3-TOF-MS, Atmospheric Measurement Techniques, 14, 8019-8039, 2021.

Foken, T.: 50 years of the Monin–Obukhov similarity theory, Boundary Layer Meteorol., 119, 431-447, 2006.

Fuentes, J., Wang, D., Neumann, H., Gillespie, T., Den Hartog, G., and Dann, T.: Ambient biogenic hydrocarbons and isoprene emissions from a mixed deciduous forest, J. Atmos. Chem., 25, 67-95, 1996.

Gauthier, S., Bernier, P., Kuuluvainen, T., Shvidenko, A. Z., and Schepaschenko, D. G.: Boreal forest health and global change, Science, 349, 819-822, 2015.

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 $^{13}CO_2$ labelling and PTR-MS analysis, Plant Cell Environ., 33, 781-792, 2010.

Grote, R., Monson, R. K., and Niinemets, Ü.: Leaf-level models of constitutive and stress-driven volatile organic compound emissions, in: Biology, controls and models of tree volatile organic compound emissions, Springer, 315-355, 2013.

Guenther, A., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T. a., Emmons, L., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2. 1): an extended and updated framework for modeling biogenic emissions, Geosci. Instrum. Dev., 5, 1471-1492, 2012.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., and McKay, W.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100, 8873-8892, 1995.

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. Atmos., 98, 12609-12617, 1993.

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.

Hayward, S., Muncey, R., James, A., Halsall, C. J., and Hewitt, C. N.: Monoterpene emissions from soil in a Sitka spruce forest, Atmos. Environ., 35, 4081-4087, 2001.

Heil, M. and Silva Bueno, J. C.: Within-plant signaling by volatiles leads to induction and priming of an indirect plant defense in nature, Proceedings of the National Academy of Sciences, 104, 5467-5472, 2007.

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

Helmig, D., Daly, R. W., Milford, J., and Guenther, A.: Seasonal trends of biogenic terpene emissions, Chemosphere, 93, 35-46, 2013.

Holopainen, J. K.: Can forest trees compensate for stress-generated growth losses by induced production of volatile compounds?, Tree physiology, 31, 1356-1377, 2011.

Holzke, C., Dindorf, T., Kesselmeier, J., Kuhn, U., and Koppmann, R.: Terpene emissions from European beech (*Fagus sylvatica L.*): pattern and Emission Behaviour Over two Vegetation Periods, J. Atmos. Chem., 55, 81-102, 2006.

Karl, T., Potosnak, M., Guenther, A., Clark, D., Walker, J., Herrick, J. D., and Geron, C.: Exchange processes of volatile organic compounds above a tropical rain forest: Implications for modeling tropospheric chemistry above dense vegetation, J. Geophys. Res. Atmos., 109, 2004.

Kessler, D., Gase, K., and Baldwin, I. T.: Field Experiments with Transformed Plants Reveal the Sense of Floral Scents, Science, 321, 1200-1202, 2008.

Kim, J.-C., Kim, K.-J., Kim, D.-S., and Han, J.-S.: Seasonal variations of monoterpene emissions from coniferous trees of different ages in Korea, Chemosphere, 59, 1685-1696, 2005.

Knudsen, J. T., Eriksson, R., Gershenzon, J., and Ståhl, B.: Diversity and distribution of floral scent, The botanical review, 72, 1-120, 2006.

Krechmer, J., Lopez-Hilfiker, F., Koss, A., Hutterli, M., Stoermer, C., Deming, B., Kimmel, J., Warneke, C., Holzinger, R., and Jayne, J.: Evaluation of a new reagent-ion source and focusing ion–molecule reactor for use in proton-transfer-reaction mass spectrometry, Analytical chemistry, 90, 12011-12018, 2018.

Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petäjä, T., Sipilä, M., Schobesberger, S., and Rantala, P.: Direct observations of atmospheric aerosol nucleation, Science, 339, 943-946, 2013.

Kumar, A., Adamopoulos, S., Jones, D., and Amiandamhen, S. O.: Forest biomass availability and utilization potential in Sweden: A review, Waste and Biomass Valorization, 12, 65-80, 2021.

Lagergren, F., Eklundh, L., Grelle, A., Lundblad, M., Mölder, M., Lankreijer, H., and Lindroth, A.: Net primary production and light use efficiency in a mixed coniferous forest in Sweden, Plant Cell Environ., 28, 412-423, 2005.

Laothawornkitkul, J., Taylor, J. E., Paul, N. D., and Hewitt, C. N.: Biogenic volatile organic compounds in the Earth system, New Phytol., 183, 27-51, 2009.

Lehning, A., Zimmer, I., Steinbrecher, R., Brüggemann, N., and Schnitzler, J. P.: Isoprene synthase activity and its relation to isoprene emission in Quercus robur L. leaves, Plant Cell Environ., 22, 495-504, 1999.

Li, S., Harley, P. C., and Niinemets, Ü.: Ozone-induced foliar damage and release of stress volatiles is highly dependent on stomatal openness and priming by low-level ozone exposure in, Plant Cell Environ., 40, 1984-2003, 2017.

Li, Z. and Sharkey, T. D.: Molecular and pathway controls on biogenic volatile organic compound emissions, in: Biology, controls and models of tree volatile organic compound emissions, Springer, 119-151, 2013.

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.: 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. Ion Proc., 173, 191-241, 1998.

Lindroth, A., Grelle, A., and Morén, A. S.: Long-term measurements of boreal forest carbon balance reveal large temperature sensitivity, Global Change Biol., 4, 443-450, 1998.

Litvak, M. E. and Monson, R. K.: Patterns of induced and constitutive monoterpene production in conifer needles in relation to insect herbivory, Oecologia, 114, 531-540, 1998.

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

Loreto, F., Barata, C., Brilli, F., and Nogues, I.: On the induction of volatile organic compound emissions by plants as consequence of wounding or fluctuations of light and temperature, Plant Cell Environ., 29, 1820-1828, 2006.

Lundin, L.-C., Halldin, S., Lindroth, A., Cienciala, E., Grelle, A., Hjelm, P., Kellner, E., Lundberg, A., Mölder, M., and Morén, A.-S.: Continuous long-term measurements of soil-plant-atmosphere variables at a forest site, Agr. Forest Met., 98, 53-73, 1999.

Maffei, M. E.: Sites of synthesis, biochemistry and functional role of plant volatiles, S. Afr. J. Bot., 76, 612-631, 2010.

Materić, D., Lanza, M., Sulzer, P., Herbig, J., Bruhn, D., Turner, C., Mason, N., and Gauci, V.: Monoterpene separation by coupling proton transfer reaction time-of-flight mass spectrometry with fastGC, Analytical and bioanalytical chemistry, 407, 7757-7763, 2015.

Matsui, K. and Engelberth, J.: Green Leaf Volatiles—The Forefront of Plant Responses Against Biotic Attack, Plant and Cell Physiology, 63, 1378-1390, 2022.

McKeen, S., Gierczak, T., Burkholder, J., Wennberg, P., Hanisco, T., Keim, E., Gao, R. S., Liu, S., Ravishankara, A., and Fahey, D.: The photochemistry of acetone in the upper troposphere: A source of odd-hydrogen radicals, Geophys. Res. Lett., 24, 3177-3180, 1997.

McMillen, R. T.: An eddy correlation technique with extended applicability to non-simple terrain, Boundary Layer Meteorol., 43, 231-245, 1988.

Menke, W.: Geophysical data analysis: Discrete inverse theory, Elsevier, Amsterdam2018.

Misztal, P. K.: Measuring rapid changes in plant volatiles at different spatial levels, Deciphering chemical language of plant communication, 95-114, 2016.

Mölder, M., Klemedtsson, L., and Lindroth, A.: Turbulence characteristics and dispersion in a forest—tests of Thomson's random-flight model, Agr. Forest Met., 127, 203-222, 2004.

Monson, R. K.: Metabolic and gene expression controls on the production of biogenic volatile organic compounds, Biology, controls and models of tree volatile organic compound emissions, 153-179, 2013.

Müller, M., Graus, M., Ruuskanen, T. M., Schnitzhofer, R., Bamberger, I., Kaser, L., Titzmann, T., Hörtnagl, L., Wohlfahrt, G., and Karl, T.: First eddy covariance flux measurements by PTR-TOF, Atmospheric Measurement Techniques, 3, 387, 2010.

Nemitz, E., Sutton, M. A., Gut, A., San José, R., Husted, S., and Schjoerring, J. K.: Sources and sinks of ammonia within an oilseed rape canopy, Agr. Forest Met., 105, 385-404, 2000.

Niinemets, Ü.: Mild versus severe stress and BVOCs: thresholds, priming and consequences, Trends Plant Sci., 15, 145-153, 2010.

Niinemets, Ü. and Monson, R. K.: Biology, controls and models of tree volatile organic compound emissions, Springer2013.

Noe, S., Hüve, K., Niinemets, Ü., and Copolovici, L.: Seasonal variation in vertical volatile compounds air concentrations within a remote hemiboreal mixed forest, Atmos. Chem. Phys., 12, 3909-3926, 2012.

Petersen, R. C., Holst, T., Mölder, M., Kljun, N., and Rinne, J.: Vertical distribution of sources and sinks of volatile organic compounds within a boreal forest canopy, Atmos. Chem. Phys., 23, 7839-7858, 2023.

Petersen, R. C., Holst, T., Wu, C., Krejci, R., Chan, J., Mohr, C., and Rinne, J.: BVOC and speciated monoterpene concentrations and fluxes at a Scandinavian boreal forest, EGUsphere, 2024, 1-45, 2024.

Pettersson, M.: Stress related emissions of Norway spruce plants, Kemi, 2007.

Possell, M. and Loreto, F.: The Role of Volatile Organic Compounds in Plant Resistance to Abiotic Stresses: Responses and Mechanisms, in: Biology, Controls and Models of Tree Volatile Organic Compound Emissions, edited by: Niinemets, Ü., and Monson, R. K., Springer Netherlands, Dordrecht, 209-235, 2013.

Poudel, B. C., Sathre, R., Bergh, J., Gustavsson, L., Lundström, A., and Hyvönen, R.: Potential effects of intensive forestry on biomass production and total carbon balance in north-central Sweden, Environ. Sci. Policy, 15, 106-124, 2012.

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, 2008.

Rantala, P., Taipale, R., Aalto, J., Kajos, M. K., Patokoski, J., Ruuskanen, T. M., and Rinne, J.: Continuous flux measurements of VOCs using PTR-MS—reliability and feasibility of disjunct-eddy-covariance, surface-layer-gradient, and surface-layer-profile methods, Boreal Environ. Res., 19, 87-107, 2014.

Raupach, M.: Applying Lagrangian fluid mechanics to infer scalar source distributions from concentration profiles in plant canopies, Agr. Forest Met., 47, 85-108, 1989.

Raupach, M., Coppin, P., and Legg, B.: Experiments on scalar dispersion within a model plant canopy part I: The turbulence structure, Boundary Layer Meteorol., 35, 21-52, 1986.

Rinne, J., Bäck, J., and Hakola, H.: Biogenic volatile organic compound emissions from the Eurasian taiga: current knowledge and future directions, Boreal Environ. Res., 14, 2009.

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

Rinne, J., Markkanen, T., Ruuskanen, T., Petäjä, T., Keronen, P., Tang, M., Crowley, J., Rannik, Ü., and Vesala, T.: Effect of chemical degradation on fluxes of reactive compounds–a study with a stochastic Lagrangian transport model, Atmos. Chem. Phys., 12, 4843-4854, 2012.

Roberts, J. M., Flocke, F., Stroud, C. A., Hereid, D., Williams, E., Fehsenfeld, F., Brune, W., Martinez, M., and Harder, H.: Ground-based measurements of peroxycarboxylic nitric anhydrides (PANs) during the 1999 Southern Oxidants Study Nashville Intensive, J. Geophys. Res. Atmos., 107, ACH 1-1 – ACH 1-10, 2002.

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, 2003.

Schuman, M. C., Valim, H. A., and Joo, Y.: Temporal dynamics of plant volatiles: Mechanistic bases and functional consequences, Deciphering chemical language of plant communication, 3-34, 2016.

Seco, R., Karl, T., Guenther, A., Hosman, K. P., Pallardy, S. G., Gu, L., Geron, C., Harley, P., and Kim, S.: Ecosystem-scale volatile organic compound fluxes during an extreme drought in a broadleaf temperate forest of the Missouri Ozarks (central USA), Global Change Biol., 21, 3657-3674, 2015.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate change, John Wiley & Sons 2016.

Sharkey, T. D.: Stomatal control of trace gas emissions, Trace gas emissions by plants, 335-339, 1991.

Sharkey, T. D., Wiberley, A. E., and Donohue, A. R.: Isoprene Emission from Plants: Why and How, Ann. Bot., 101, 5-18, 2007.

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

Sindelarova, K., Markova, J., Simpson, D., Huszar, P., Karlicky, J., Darras, S., and Granier, C.: High-resolution biogenic global emission inventory for the time period 2000–2019 for air quality modelling, Earth Syst. Sci. Data, 14, 251-270, 2022.

Sindelarova, K., Granier, C., Bouarar, I., Guenther, A., Tilmes, S., Stavrakou, T., Müller, J. F., Kuhn, U., Stefani, P., and Knorr, W.: Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years, Atmos. Chem. Phys., 14, 9317-9341, 2014.

Siqueira, M., Katul, G., and Lai, C.-T.: Quantifying net ecosystem exchange by multilevel ecophysiological and turbulent transport models, AdWR, 25, 1357-1366, 2002.

Siqueira, M., Lai, C. T., and Katul, G.: Estimating scalar sources, sinks, and fluxes in a forest canopy using Lagrangian, Eulerian, and hybrid inverse models, J. Geophys. Res. Atmos., 105, 29475-29488, 2000.

Smeets, E. M. and Faaij, A. P.: Bioenergy potentials from forestry in 2050: an assessment of the drivers that determine the potentials, Climatic Change, 81, 353-390, 2007.

Street, R., Owen, S., Duckham, S., Boissard, C., and Hewitt, C.: Effect of habitat and age on variations in volatile organic compound (VOC) emissions from Quercus ilex and Pinus pinea, Atmos. Environ., 31, 89-100, 1997.

Striednig, M., Graus, M., Märk, T. D., and Karl, T. G.: InnFLUX–an open-source code for conventional and disjunct eddy covariance analysis of trace gas measurements: an urban test case, Atmospheric Measurement Techniques, 13, 1447-1465, 2020.

Strömvall, A. M. and Petersson, G.: Conifer monoterpenes emitted to air by logging operations, Scandinavian Journal of Forest Research, 6, 253-258, 1991.

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

van Meeningen, Y., Wang, M., Karlsson, T., Seifert, A., Schurgers, G., Rinnan, R., and Holst, T.: Isoprenoid emission variation of Norway spruce across a European latitudinal transect, Atmos. Environ., 170, 45-57, 2017.

Vanhatalo, A., Ghirardo, A., Juurola, E., Schnitzler, J.-P., Zimmer, I., Hellén, H., Hakola, H., and Bäck, J.: Long-term dynamics of monoterpene synthase activities, monoterpene storage pools and emissions in boreal Scots pine, Biogeosciences, 15, 5047-5060, 2018.

Venier, L. A., Thompson, I. D., Fleming, R., Malcolm, J., Aubin, I., Trofymow, J. A., Langor, D., Sturrock, R., Patry, C., and Outerbridge, R.: Effects of natural resource development on the terrestrial biodiversity of Canadian boreal forests, Environmental reviews, 22, 457-490, 2014.

Wang, M., Schurgers, G., Arneth, A., Ekberg, A., and Holst, T.: Seasonal variation in biogenic volatile organic compound (BVOC) emissions from Norway spruce in a Swedish boreal forest, Boreal Environ. Res., 22, 353-367, 2017.

Warland, J. S. and Thurtell, G. W.: A Lagrangian solution to the relationship between a distributed source and concentration profile, Boundary Layer Meteorol., 96, 453-471, 2000.

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

Wilczak, J. M., Oncley, S. P., and Stage, S. A.: Sonic anemometer tilt correction algorithms, Boundary Layer Meteorol., 99, 127-150, 2001.

Yee, L. D., Isaacman-VanWertz, G., Wernis, R. A., Meng, M., Rivera, V., Kreisberg, N. M., Hering, S. V., Bering, M. S., Glasius, M., Upshur, M. A., Gray Bé, A., Thomson, R. J., Geiger, F. M., Offenberg, J. H., Lewandowski, M., Kourtchev, I., Kalberer, M., de Sá, S., Martin, S. T., Alexander, M. L., Palm, B. B., Hu, W., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Liu, Y., McKinney, K. A., Artaxo, P., Viegas, J., Manzi, A., Oliveira, M. B., de Souza, R., Machado, L. A. T., Longo, K., and Goldstein, A. H.: Observations of sesquiterpenes and their oxidation products in central Amazonia during the wet and dry seasons, Atmos. Chem. Phys., 18, 10433-10457, 2018.

Yuan, B., Koss, A. R., Warneke, C., Coggon, M., Sekimoto, K., and de Gouw, J. A.: Proton-transfer-reaction mass spectrometry: applications in atmospheric sciences, Chem. Rev., 117, 13187-13229, 2017.

Printed by Media-Tryck, Lund 2025 NORDIC SWAN ECOLABEL 3041 0903

LUND
UNIVERSITY

Department of Physical Geography
and Ecosystem Science
Faculty of Science

ISBN 978-91-89187-57-3