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BVOC emission variability for Norway spruce (*Picea abies*) in Hyltemossa, Sweden

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Bachelor thesis, 15 credits, in Physical Geography and Ecosystem Science

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Abstract

Biogenic volatile organic compounds (BVOC) are known as hydrocarbons emitted into the atmosphere from the biosphere. They have physiological and ecological functions such as communication within the plant and plant – plant, protection against environmental stress factors and defense against herbivores attack. Coniferous forests are known to produce larger quantities of BVOCs, especially terpenes, where isoprene and the group of monoterpenes are the main compounds. Emitted BVOCs are highly reactive and have an impact on the atmospheric chemistry where it contributes to particle formation and growth. Hence, BVOCs mediate the relationship between the biosphere and atmosphere. Produced BVOCs are affected by environmental factors, among these factors are temperature, stress and light. Emissions may be induced in response to biotic and abiotic factors such as increased temperature, damage done by other organisms or air pollutants.

The analysis of this thesis presents the relationship between BVOC emissions and the photosynthetic rate, and how the different compounds are affected by different environmental factors such as light. This was achieved by using a flow-through conifer chamber technique combined with a portable photosynthesis system combined with adsorbent tubes to trap the BVOC emissions. Where the result revealed the differences in compounds, emission rate and photosynthetic activity. Isoprene and the group of monoterpenes, including nine different compounds were then chosen BVOCs for this study. The results from this thesis were then compared to other published literature focusing on Norway spruce (*Picea abies*) stands during the growing season. This study based on measurements in 2019 showed increased emission rates compared to another study from the same stand four years prior to this, indicating induced emission from stress. The emission rates for the seasonal average were 2.35 (± 3.83 std) for isoprene and 3.59 (± 3.24 std) for monoterpenes, these results were in line with other published research for Norway spruce.

Key words

BVOC, isoprene, monoterpenes, induced emission, light dependency, temperature, Norway spruce.

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List of abbreviations

BVOC: Biogenic volatile organic compound

VOC: Volatile organic compound

MT: Monoterpenes

SQT: Sesquiterpenes

ISO: Isoprene

PAR: Photosynthetically active radiation

CO_2: Carbon dioxide

IRGA: Infrared gas analyzer

Std: Standard deviation

1 Introduction

It is known that biological processes in terrestrial ecosystems affect the atmosphere and climate systems on Earth. A few of these emitted compounds are known to have a significant impact on the atmospheric composition (Guenther et al., 2012).

The study of BVOCs was first dated in 1960, where the first observations were hypothesized to cause the development of blue haze (Went, 1960). There have been several studies since, one conducted on Norway spruce by Janson (1993), and another on boreal coniferous forest by Hakola et al., (2003) focusing on identifying and quantifying the BVOC emissions from the biosphere, their physiological processes and effects on the environment (Sindelarova et al., 2014). BVOC compounds are known to contribute to the largest global carbon flux besides CO_2 (Holopainen et al., 2017; Niinemets et al., 2014).

BVOC consists of several different classes of compounds, such as isoprenoids, alkanes, alcohols and acids (Kesselmeier & Staudt, 1999). The three most contributing compounds are isoprene (ISO), the group of monoterpenes (MT) and sesquiterpenes (SQT) acting as e.g., defensive compounds. The two most significant of these compounds being emitted from coniferous trees are monoterpenes and isoprene (Bäck et al., 2012; Fäldt, 2000; J. Hick et al., 1999; Kesselmeier & Staudt, 1999). Sesquiterpenes are however debated to be of minor importance, as they appear in small amounts (König et al., 1995; Schuh et al., 1997). BVOCs can be emitted from all organs of the plant, flowers to roots (Laothawornkitkul et al., 2009).

High metabolic costs are raised by a release of the plant's fixed carbon when emitting BVOCs. The advantages could be considered to compensate for the loss of carbon for the trees (Dudareva et al., 2006; Niinemets, 2013), as several of the emitted compounds are assumed to protect the trees from abiotic and biotic stresses. They can also function as communication within plants and plant to plant (Dudareva et al., 2006). The cause of destructed vegetation can be due to high levels of lowered atmospheric ozone as well as other pollutants, this can cause an increase of the plants BVOC emissions that lead to lowered rates of photosynthesis, causing damage to the photosynthesis apparatus of the leaf which might lead to a reduction of photosynthetic activity (Bolsoni et al., 2018; Seyyedneja et al., 2011).

Biotic and abiotic stresses such as increased temperature, increased levels of ozone, other air pollutants or damages by other organisms are factors controlling BVOC emissions from Norway spruce. These factors tend to change with environmental changes. There is a strong temperature dependence of BVOC emissions where the emissions in all cases increase along with temperature up to a certain maximum. Beyond this maximum, both enzyme degradation and physiological responses to heat stress affect the emission pattern for BVOCs (Peñuelas & Llusià, 2003). BVOC emissions also have a strong correlation with enzyme activities during optimal and stressful conditions (Fischbach et al., 2002; Kuzma & Fall, 1993; Loreto et al., 2001). This means that BVOCs are emitted during relatively unstressed conditions and increase during stressed conditions. Total BVOC emission and its chemical composition can vary between plants (Guenther, 2013).

Van Meeningen et al., (2017) conducted a study in July 2015 in Hyltemossa, Sweden with the aim to investigate the light response and variability of terpenoids on Norway spruce. Results revealed that emission rates for especially isoprene and some monoterpenes are strongly linked with available light.

1.1 Study aim

Emission rates of BVOCs from trees vary with time of year, light and temperature conditions, and are therefore expected to differ in their magnitude and chemical compounds. Existing literature on BVOCs is primarily focusing on the growing season as well as seasonality, where boreal forests are thought to emit less BVOCs on a global scale compared to tropical regions (Guenther et al., 1995; Sindelarova et al., 2014). Local acclimation and adaptation may occur and cause different emission patterns that vary between stand locations and time of year.

Needles in the tree canopy are exposed to changing light and temperature conditions and the emission rates are most likely to differ between branches. Measuring and monitoring BVOC emissions is therefore a good contribution to science for future studies and improvement of climate models of the same species and forest stand. The result from this study is thought to enable a better understanding of how the species are affected by seasonal variety through measurements of the seasonal emission pattern between different campaign years.

The aim of this study is therefore to quantify and analyze BVOC emissions for Norway spruce during the growing season in Hyltemossa, Sweden together with photosynthetic activity. Comparing these results with previous research over a seasonal pattern for the same area using climate data derived from ICOS for 2019 and 2015, including PAR, canopy temperature, GPP and soil water content.

Following research questions are in focus:

- How might the emissions differ between branches of the same spruce compared to other spruces?
- How might the calculated seasonal pattern for this season differ compared to the calculated seasonal pattern with derived results from van Meeningen et al. (2017)?

2 Background

2.1 Definition and occurrence of BVOCs

BVOCs are compounds of biogenic descent, formed in plants as by-products of photosynthesis and different synthesis pathways (Guenther, 1997; Niinemets, 2013). These compounds are not required for the growth of plants and are referred to as secondary metabolites which are important for protection, reproduction and competition between and within plants (Dudareva et al., 2006). Isoprene, monoterpenes and sesquiterpenes are chemical compounds functioning in interactions with animals, other plants and microbes as well as protection against ultraviolet radiation and oxidants, where they directly can deter herbivores from feeding or reduce their appeal making them suitable for herbivore attack (Guenther, 2013; Heil & Bueno, 2007).

The group of the most abundant BVOC compounds is terpenoids, consisting of isoprene, monoterpenes and sesquiterpenes (Kesselmeier & Staudt, 1999). BVOCs are also reactive trace gasses that influence atmospheric chemistry. Where the majority of especially isoprene and monoterpenes are emitted by trees in forest ecosystems and contribute to air composition and the formation of ozone and secondary organic aerosols (SOAs) (Guenther et al., 1995; Kesselmeier & Staudt, 1999; Zemankova & Brechler, 2010). SOAs affect the climate by reflection or absorption of solar radiation and acting as cloud condensation nuclei (CCN) that in turn have an effect on incoming and outgoing radiation and can therefore influence environmental conditions (Kulmala et al., 2004; Laothawornkitkul et al., 2009). The boreal

zone is the largest vegetated zone in the world and emits mainly monoterpenes, it does however emit less isoprene compared to tropical regions on a global scale (Guenther et al., 1995; Šimpraga et al., 2019).

A study has also shown that the blend and intensity of different BVOC compounds being emitted from plants can change throughout the plants development stages (Loreto & Schnitzler, 2010). The emissions can be divided into two groups, constitutive and induced emissions, where the former mostly occur continuously with diurnal and seasonal patterns and are generally volatiles stored in specific compartments of the tree. These emissions could also be influenced by factors caused by stress (Holopainen, 2011; Joo et al., 2011; Loreto et al., 2006; Loreto & Schnitzler, 2010; Niinemets et al., 2004). Induced emissions are stressed-induced BVOC emissions and are typically a response to direct impacts caused by external stress factors, e.g., herbivores causing damage to the leaves or bark. Induced emissions can change the type of emitted compounds as well as the amount (Grote et al., 2019). Several plants have the ability to store BVOC, which include monoterpenes and sesquiterpenes, these could later be emitted from its storage depending on the temperature. Stress exposure can however increase the emission rate factors (Brilli et al., 2007; Christiansen et al., 1999; Martin et al., 2002).

Norway spruce is said to emit a low amount of isoprene and a moderate amount of monoterpene, where the species has the capacity to emit BVOCs from its storage through both needles and the bark. These compounds are however efficient precursors for both particle formation and growth and boreal forests are important for the atmospheric chemistry and SOA (Ghirardo et al., 2010; Paasonen et al., 2013).

2.2 Description of light and temperature dependency

BVOC emissions are affected by environmental conditions related to photosynthesis, such as light availability, temperature, nutrient and water as BVOC are synthesized from photosynthetic products (Laothawornkitkul et al., 2009; Niinemets et al., 2010; Sharkey et al., 1996). Even though photosynthesis is highly temperature-dependent, it is debated that photosynthesis rates decrease at higher temperatures. Earlier studies show that higher temperatures are correlated with higher induced volatility rates (J Berry & Bjorkman, 1980; Monson et al., 1992; Paré, 1999).

The availability of photosynthetically active radiation (PAR) influences the ability to photosynthesize, making plants light-dependent unless they are light saturated. The light dependency can be described by a light response curve that reveals how much of the carbon assimilation in plants relates to the amount of irradiance (Monson et al., 1992; Paré, 1999). Increased temperature has also shown a typical increase in carbon assimilation, this is however only accurate until a certain temperature threshold given for each species. After which potential effects and damages caused by high temperatures are irreversible and can cause injuries to the plants. This relationship can be explained by adaptation and the surrounding environment, where plants might have adapted their photosynthetic system to be optimal in regard to cooler or warmer climate (J Berry & Bjorkman, 1980). A temperature of 25°C is observed to be optimal for the process of photosynthesis for Norway spruce (Šigut et al., 2015). The relationship could as well limit the evaporation of BVOCs as the precursors for BVOC production are limited. There could however still be emissions if they were emitted from a storage (Kesselmeier & Staudt, 1999).

BVOC emission rates are regulated by both internal factors (biochemical and genetic) and external factors (light, water availability and temperature) (Kesselmeier & Staudt, 1999; Niinemets et al., 2004; Peñuelas & Llusià, 2001, 2003). The reason why the plants invest a high metabolic cost is most likely to protect themselves from biotic and abiotic stresses (Possell & Loreto, 2013). Studies have shown that isoprenoids are the most abundant BVOC and are argued to be the most advantageous protection against abiotic stresses, especially high temperatures, ozone tolerance and prevent loss of photosynthetic capacity (Behnke et al., 2012; Peñuelas et al., 2005; Sharkey & Singsaas, 1995; Sharkey et al., 2008; Velikova et al., 2011).

Research shows seasonal trends of BVOC emissions for different compounds, these seasonal trends depend on temperature and light. Where higher emissions normally occur during the growing season and lower emissions during winter (Hakola et al., 2003). Research has also shown that emission patterns of BVOCs are increasing during the morning to peak midday and decrease during the evening and night (Grabmer et al., 2004; Pio et al., 2005). Emissions produced within leaves and needles enter the atmosphere by passing either the stomata or hydrophobic cuticle, where isoprene is highly volatile and shows no significant influence of the stomatal on its emission rate. There are however some monoterpenes that are highly influenced by the stomata which are not emitted once the stomata is closed (Kesselmeier & Staudt, 1999).

Some plants can store compounds for hours or days while some compounds are emitted immediately upon formation. The compounds that are immediately emitted can be considered to be light-dependent while the stored compounds can be emitted without light and are therefore considered to be light-independent and are instead temperature-dependent (Kesselmeier & Staudt, 1999; Laothawornkitkul et al., 2009).

2.3 Monoterpenes, isoprene and sesquiterpenes

Isoprene and monoterpenes belong to the biochemical class of terpenoids which are composed of C_5 units (McGarvey & Croteau, 1995). The compounds are then subdivided where monoterpenes have a C_{10} skeleton. Plants exposed to water stress occurring in periods of increased temperatures and drought are protected from damage by isoprene and monoterpene (Laothawornkitkul et al., 2009).

Isoprene is the BVOC compound that accounts for more than 50 % of the terpenoid emissions from plants (Guenther et al., 1995). It is a highly volatile compound that is emitted immediately upon formation since no storage pool exists, it is therefore referred to as being emitted *de novo* and closely related to light intensity (Kesselmeier & Staudt, 1999; Laothawornkitkul et al., 2009). The main function of isoprene is thought to function as protection against mainly oxidative- and thermal stress (Laothawornkitkul et al., 2009). It is however debated why some plants emit isoprene while others don't since there is a significantly high metabolic cost of emitting BVOCs for plants (Possell & Loreto, 2013).

Monoterpenes with a C_{10} skeleton are produced in almost all conifer trees (Koppmann, 2007). The compounds have the characteristics of a strong scent and are hardly water soluble and may also exist as hydrocarbons with or without the presence of oxygen. Linalool is an example of such compound (Kesselmeier & Staudt, 1999), 3-carene is another compound known to act as a defensive compound known to be emitted during stress (Fäldt et al., 2003). Although, monoterpenes are temperature dependent, the dependence does however vary among the different monoterpenes. Other studies have shown that some monoterpenes are more reactive than isoprene where the lifetime can range from minutes to two days (Koppmann, 2007).

Sesquiterpenes are the third group of compounds in the group of terpenoids. They consist of C_{15} skeleton with a more complex structure than monoterpenes. Emitted sesquiterpenes are the group of terpenoids that emits at a lower rate than isoprene and monoterpene which can be explained by their high reactivity, where their lifetime in the atmosphere only is a few minutes. This group of compounds also has the same ability as monoterpenes to be stored in plant compartments (Koppmann, 2007; Peñuelas & Staudt, 2010).

2.4 Induced BVOC emissions

The magnitude of induced BVOC climate impacts is rather uncertain because of their high reactivity and rapid chemical transformations. BVOC emissions can be involved in chemical transformations that may or may not be involved in atmospheric chemical reactions. While in the atmosphere can BVOC emissions influence the atmospheric chemistry and therefore the climate (Kulmala et al., 2004; Pacifico et al., 2009).

Abiotic stress affects the secondary metabolism in different ways, stress factors commonly inhibit photosynthetic activity by reducing the uptake of CO_2. While the impact of stress on BVOC emission is more controversial as some pathways might be drawn out by stress factors (Flexas et al., 2004), it may also induce damage to the plant that can cause or induce the synthesis of other compounds with important consequences for plant protection (Vickers et al., 2009). It is however expected that plants during their lifetime will experience stress which will affect the BVOC emissions as well as their photosynthetic activity. Induced emissions caused by stress can differ depending on the stress factors. Mechanical-stress-induced BVOCs are different from other induced emissions caused by other stress factors (Paré, 1999)

Undamaged plants maintain a certain level of volatile metabolites released from its storage that often include monoterpenes and sesquiterpenes (Pare & Tumlinson, 1997). Several factors can cause stress, abiotic stress is caused by temperature, drought, irradiation and ozone exposure while biotic stress is caused by herbivory. The named factors can single-handed or in combination cause induced BVOC emissions (Vickers et al., 2009).

There are two classes of induced BVOCs, the first class includes BVOCs that is emitted immediately after the plants had been wounded (Hatanaka, 1993). This class of C6 is referred to as green leaf volatiles (GLV), which could be induced by both mechanical wounding and herbivore wounding (Rose et al., 1996). The second class is emitted hours to days after the plant has been exposed to stress (Mumm & Hilker, 2006). The main constituents of induced BVOC emissions are the monoterpenes and sesquiterpenes (Kessler & Baldwin, 2001) and acyclic isoprenoids (De Moraes et al., 1998; Heil & Silva Bueno, 2007; Rose et al., 1996). Emissions can act as a key role in the activation of defensive pathways in the plants where 3-carene α-pinene are two examples of emissions that functions as a defense (Faldt et al., 2003; Kessler & Baldwin, 2001).

Several studies have aimed for broader knowledge about BVOC emissions and their relation to stress factors, it is hypothesized that isoprene is the main group of compounds helping the photosynthetic activity to cope with high temperatures (Sharkey & Singsaas, 1995; Singsaas et al., 1997). Water availability is also a factor that affects BVOC emissions directly and indirectly depending on the stress severity (Grote et al., 2014). Changes that affect the soil water conditions and the resulting changes in BVOC exchange fluxes are also expected to influence

plant responses and their capacity to protect themselves (Peñuelas & Staudt, 2010; Rennenberg et al., 2006).

3 Method

The research questions were addressed by investigating the BVOC emissions from Norway spruce from a field study done from May to August 2019 by a Ph.D. student from the department of physical geography and ecosystem science at Lund University. The ICOS research station in Hyltemossa (HTM, 56°06´N, 13°25´E) was used for these measurements. Where two different plots were chosen with different environmental conditions. Plot one was located on a small hill where it was considered to be drier, while plot two was located at the lowest area by the station and considered to be a wetter area. Three individual Norway spruces were selected for measurements throughout the growing season, the selection was based on availability, health, where no visible signs of herbivore attacks could be seen, and distance to each other. Any trees with visible damaged or infestation were ruled out.

The seasonal pattern for 2015 and 2019 was calculated to observe the BVOC emission pattern in relation to photosynthetic activity, temperature, and soil moisture content, to then analyze the results of the two measurement years. Of either higher or lower emission patterns caused by stress in 2019 compared to 2015.

3.1 Site description and climate

This study was conducted in Hyltemossa, located a few kilometers south of Perstorp, north-western Scania, seen in Figure. 1. The area is a managed spruce forest with the ICOS research station that was established in 2014. The dominating tree species is Norway spruce covering 97.7 % of the forest stand with 597 trees /ha. The average tree height is 14.56 (± 3.96) meters. The second species within the area is a few birch trees (*Betula pendula*) covering 1.7 % of the forest stand along with sparse understory vegetation, where the forest floor is mainly covered by a thick moss layer.

Measurements taken between 1961-1990 show humid temperatures with mild summers and winters with a mean annual air temperature of 7°C and mean annual precipitation up to 830 mm (ICOS, n.d), while measurements between 1991-2020 show a mean annual air temperature of 8.2°C (SMHI, 2009). The weather conditions during the campaigns involved lower temperatures and precipitation between and during some of the measurements.

Figure 1. Study area, Hyltemossa located in north-western Scania, Sweden.

3.2 Material and data sampling

Measurements were performed on Norway spruce for two different plots (P) and three different spruces (S) in Hyltemossa, Sweden between 6th of May and 31st of July 2019.

3.2.1 Setup of needle chamber

Measurements were performed using a flow-through chamber technique (Figure 2). The tree samples were collected using a portable photosynthesis system (LI-6400 XT, LICOR, NE, USA) together with a dual infrared gas analyzer (IRGA) that was positioned in the sensor head, which analyses CO_2 and H_2O. All measurements were collected during fixed environmental conditions from the chamber. The constant reference of the CO_2 for the incoming air was set to 400 ppm, light to 1000 µmol m^{-2} s^{-1} and the temperature within the chamber was set to 20°C or 30 °C. The IRGA gas analyzer measures the differences in gas concentrations upstream and downstream the leaf chamber. The ingoing airstream was set to either 200, 300 or 500 µmol/s depending on the relative humidity within the chamber, into the chamber for the different campaigns. Each sampling was set to run for 30 min and the logger on the LI-6400 XT was set to log values of CO_2, H_2O and temperature of air and leaf for ingoing and outgoing airstream every 10 seconds.

The ingoing air to the chamber passed through a hydrocarbon trap to remove all VOCs from the incoming air stream, this was done to avoid any BVOCs in the chamber from the outside air before sampling. Measurements on BVOC emissions were conducted from the air sampled from the LI-6400 chamber through a pocket pump, where the air passed through a Tenax Carbograph adsorbent tube for 30 min to trap any BVOC emissions. The material of the

adsorbent tube is stainless steel filled with adsorbents of porous polymers and graphitized carbon blacks to capture isoprene, monoterpenes and sesquiterpenes. The flowrate from the pocket pump was set to a rate of 200 ml/min. Blank measurements were taken prior to the first measurements each day and once after the sampling was done to distinguish any emissions that might entered the system from the hydrocarbon trap. To avoid mechanically induced BVOC emissions, the chamber head was clamped on the needle shoots 1 hour prior to the sampling. For each branch measurement, two to three continuous samples were taken before repeating the method on a new branch.

These adsorbent tubes were then covered with long-term storage caps and kept cool in a refrigerator for later analysis in the lab where gas chromatography-mass spectrometry (ATD-GC-MS) was used. This method enables the compounds in the sample to be identified with high sensitivity and specificity. The samples were stored in a refrigerator at ~3°C for about 6-11 months before they were analyzed.

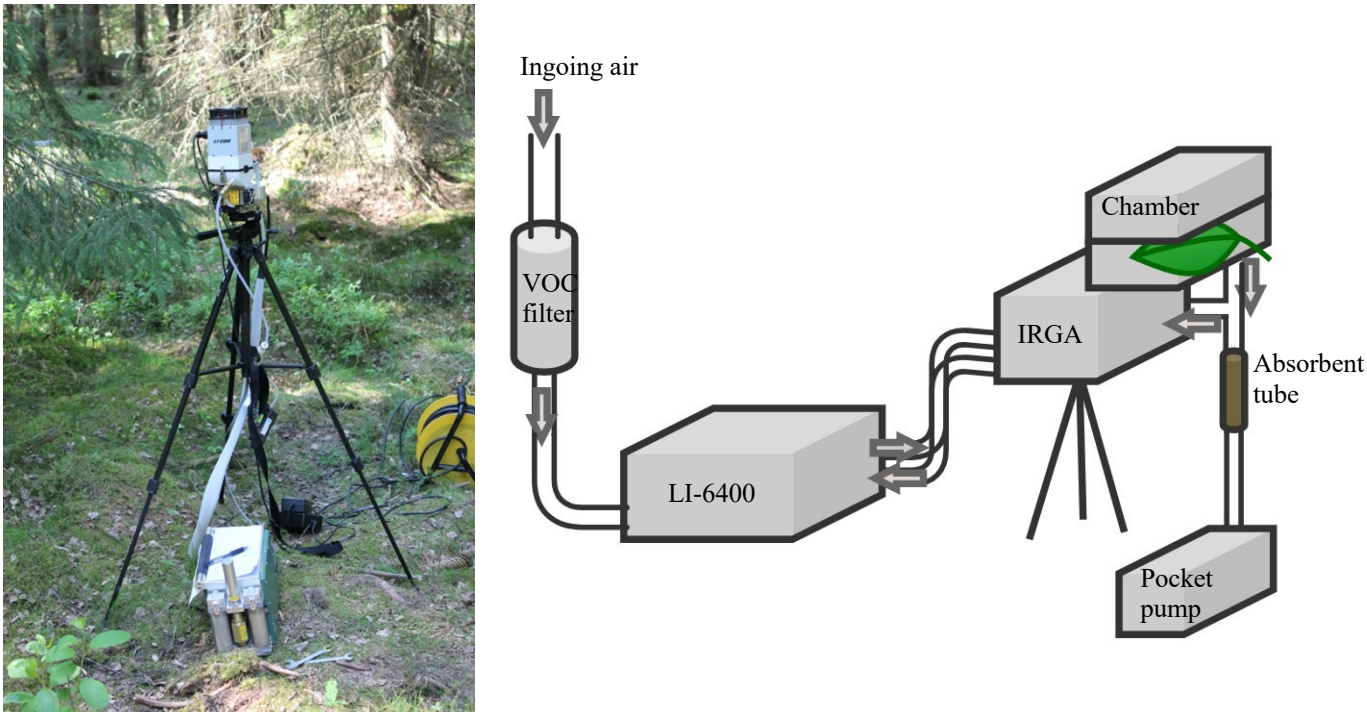

Figure 2. Instrumental setup for measuring BVOC emission and photosynthetic activity and photo taken by Jaakola (2022).

3.2.2 Analyzing BVOC emissions

Analyzing the sampled adsorbent tubes is often done by thermal desorption (TD) which is linked to the ATD-GC-MS system. The BVOC samples were analyzed by the same PhD student who conducted the field study by using a two-stage automated thermal desorption (Turbomatrix ATD 650, PerkinElmer, Waltham, MA, USA). The cartridges were heated up to 280°C in a flow of purified helium for 10 minutes to release the trapped VOCs. The compounds were then cryo-focused downstream on a Tenax TA coldtrap (Turbomatrix 650 ATD,PerkinElmer, Waltham, MA, USA) that were held at -30°C. The cold trap was then flash heated (40°C sec^{-1}) to 300°C that was maintained for 6 minutes. The volatilized VOCs were then passed through a heat transfer line to a gas chromatograph-mass spectrometry system (ATD-GC-MS, Shimadzu QP2010 Plus, Shimadzu Corporation, Japan). The oven temperature was held at 40°C for 1 minute and then raised to 210°C at the rate of 5°C min^{-1} and then further increased to 250°C at

the rate of 20°C min^{-1} and held for 2 minutes. The different BVOCs were separated using a BPX5 capillary column (50m, I.D. 0.32mm, film thickness 1.0 µm, Trajan Scientific, Australia). The chromatogram displayed peaks of the sampled compounds that were identified with the mass spectra in the library (NIST08) and analyzed with the LabSolutions ADT-GC-MS post-run analysis program (Version 4.30, Shimadzu Corporation) (Jaakola, 2022).

To establish an estimation of the biomass from the needles where they harvested and collected in containers. The average weight of the containers was found by weighing them without the needles three times before the needles were added and weighed three times again to determine the average weight of the needles. The needles were then dried in an oven at 70 °C for 24h until the weight was stable and the weight was taken three times again.

3.3 Data analysis

The derived data from the field study was then calculated and analyzed in this study. The photosynthesis data were extracted from the photosynthesis system LI-6400 XT, and the BVOC data were analyzed from the sampled adsorbent tubes using the ADT-GC-MS system to detect any peaks of the emitted compounds from the needles. The output from the ADT-GC-MS was analyzed using PARADISe version 6 (Johnsen, 2017). To then be used together with the photosynthetic data in Microsoft (Microsoft Corp., Redmond, Washington, USA) Excel 2022 version 16.6.

3.3.1 Photosynthesis

The photosynthesis measured by the LI-6400 XT is calculated directly, these measurements are however based on a cuvette that held several needles and not a single leaf covering the whole area of the cuvette which the calculations of the system are referring to. Other measurements are better considered for this study on needles to measure a more accurate estimation of the photosynthesis, where the dry biomass, CO_2 and water vapor are derived. The correct biomass was accounted for after the measurements by harvesting the needles and drying them.

The equation used (Eq. 1) for calculating the net carbon assimilation, A_n (µmol CO2 m^{-2} s^{-1}) is derived by von Caemmerer and Farquhar (1981).

$$An = \frac{F\left(Cr - Cs\left(\frac{1000 - Wr}{1000 - Ws}\right)\right)}{100S} \quad \text{(Eq. 1)}$$

Where F is the flow rate (µmol s^{-1}) and S is the leaf area present in the chamber (cm^2), C_r and C_s equals the IRGA mole fraction of CO_2 (µmol CO2 mol^{-1} air) and W_r and W_s equals the mole fraction of water vapor (mmol H2O mol air^{-1}). The leaf area, S (m^2) is derived by scaling dry needle biomass (g) to a leaf area, S (cm^2). Another study based on Norway spruce at Norunda research station by Wang et al. (2017) derived a specific leaf area (SLA) of 38.4 cm^2/g at a canopy height of 20 m. With the assumption to apply the same SLA on Norway spruce in Hyltemossa can S be derived when multiplying SLA with the dry needle biomass and then applying it to Eq. 1.

3.3.2 BVOC emissions

The needle measurements were quantitatively analyzed to compare the different types of compounds being emitted during the campaign in 2019. Calculations of the BVOC fluxes were carried out for all compounds within each sample. For the results to be comparable to other studies was the emission rate *ER* (µg C g_{dw}^{-1} h^{-1}) scaled by the weight of dry biomass. The equation used for this study is presented in Eq. 2 according to (Ortega & Helmig, 2008).

$$ER = \frac{[C_{out} - C_{in}]F}{m_{dry}} \quad \text{(Eq. 2)}$$

Where C_{out} (µg C l^{-1}) is the concentration of the compounds in the chamber, C_{in} (µg C l^{-1}) is the concentration of the compounds entering the chamber. F is the flow rate of the purge air through the chamber (1 h^{-1}) and m_{dry} is the dried mass (g) of the needles. C_{in} is the background value and is often assumed to be zero if the filters have scrubbed out all the VOC of the inlet air, the blank values were here averaged to use in Eq. 2.

3.3.3 Standardization of BVOC emissions

The measurements were conducted during several days over the season, the environmental conditions were slightly different regarding the temperature in the chamber that was set to either 20°C or 30°C. The difference in temperature was changed in field from either 20°C to 30°C to keep the branch in a natural and stable level, for some of the measurements were the temperature set to 30°C from the beginning but then changed to 20°C to be more representative for the branches. The emission rates ER at 20° C were then standardized ER_s to standard light and temperature conditions of 1000 µmol m^{-2} s^{-1} (PAR) and a temperature of 30 °C (303 K). There are different algorithms for light dependent compounds and compounds stored within the plants used for this, Eq. 3 and Eq. 6.

Eq. 3 is used for the standardization of compounds that were developed by Guenther et al., (1993) and used for light and temperature dependent compounds which include isoprene.

$$I_S = \frac{I}{(C_L \cdot C_T)} \quad \text{(Eq. 3)}$$

Where *I* is the emission rate at a given temperature T (K) and PAR flux (µmol m^{-2} s^{-1}), I_s is the isoprene emission rate at standard temperature T_s (K) and standard PAR flux (1000 µmol m^{-2} s^{-1}), the correction factors for temperature and light, C_L and C_T are defined by the following equations:

$$C_L = \frac{aC_{L_1}L}{\sqrt{1+a^2L^2}} \quad \text{(Eq. 4)}$$

$$C_T = \frac{e\left(\frac{C_{T_1}(T-T_S)}{RT_ST}\right)}{1+e\left(\frac{C_{T_2}(T-T_M)}{RT_ST}\right)} \quad \text{(Eq. 5)}$$

R is the ideal gas constant (8.314 J K^{-1} mol^{-1}), α (0.0027), C_{L1} (1.066) are empirical coefficients, C_{T1} (95 000 J mol^{-1}), C_{T2} (230 000 J mol^{-1}) and T_M (314 K), T_s (303,15 K), T is the actual temperature within the chamber (Guenther et al., 1993).

Monoterpenes and sesquiterpenes are BVOC compounds that are considered to be only temperature dependent and the following equation (Eq. 6) from Guenther et al., (1993) was used to determine the emission capacities.

$$M_S = \frac{M}{e^{\left(\beta(T-T_S)\right)}} \quad \text{(Eq. 6)}$$

M_s is the standardized emission rate (µg C g_{dw}^{-1} h^{-1}), M is the emission rate of the stored compound (µg C g_{dw}^{-1} h^{-1}) at given leaf temperature, derived from Eq. 2, and (0.09 K^{-1}) is the empirical coefficient that establishes the temperature dependency by Guenther et al. (1993).

The emission rate was plotted in a scatterplot against the photosynthetic rate, a linear trendline was applied together with the equation and R^2 value to interpret the variance between the dependent variable set as the photosynthetic rate and the independent variable set as the emission rate. Furthermore, Pearson's correlation test was used to calculate the P-value between isoprene and photosynthetic rate as well as monoterpene and photosynthetic rate to measure the statistical significance between the two factors.

3.3.4 Calculation of seasonal BVOC fluxes

Climate data for 2015 and 2019 from ICOS database (Heliasz, 2020) was derived for comparative reasons. The climate data was logged with values every 30 minutes for the whole two years. All days except May–August was deleted, and an average for all parameters was then taken between 10.00-16.00 every day where the daily patterns of PAR and temperature reached its peaks from June to August. Parameters used for the seasonal pattern were temperature (T°C from canopy) in kelvin, soil water content (SWC), GPP and PAR. The seasonal soil water content is thought to give an indication of how the two years differed in amount compared to the amount of emitted BVOCs.

Eq. 3 and 6 were then rearranged to find I and M in order to derive the actual emission rate for both years. This was done to determine the seasonal average of BVOCs based on the average standardized emission rate and standard deviation for the whole season for both monoterpenes and isoprene. I_s and M_s were derived from the total standardized average in the 2019 field study and the results conducted in July 2015. Almost all trees measured during the campaign in 2019 involved the same trees used in the campaign in 2015. Daily emission rates from May-August could then be plotted in a graph along with the standard deviation, soil moisture content and canopy temperature to see seasonal modeled emission rate patterns for the two years.

4 Results

The BVOC emissions from different plots and spruces of a Norway spruce stand were measured during a field study in 2019 to get a seasonal emission pattern. The different patterns of BVOC emissions and photosynthetic rate for each adsorbent tube, plot and spruce are seen in Figure 3,4 and 5. These figures illustrate the difference in emission rate and the relation to the

photosynthetic activity of the same spruce for each of the three plots and adsorbent tubes for the different campaigns.

Table 1 gives an overview of the standardized total emission rates for isoprene and monoterpenes (μg gdw^{-1} h^{-1}) of each spruce and photosynthetic rate (μmol CO_2 m^{-2} s^{-1}). Several of the compounds in the adsorbent tubes gave negative values from the emission rate calculations which indicates that these needles did not emit any of the specific compounds for the given tree during that campaign. The average blank measurements were higher than the emitted BVOC for some of the measurements, the concentration in the adsorbent tube ranged between 0.4 and 10.1 (n=13) (ng/tube) and the average BVOC concentration were ranging between 0.5 and 28.8 (n=31) (ng/tube). These were therefore excluded from further calculations. Several of the measurements only displayed emitted compounds once out of two to three continuous samples taken for each branch, for these measurements could no standard deviation be applied.

The emission rates of the different compounds differed, the average standardized BVOC emissions rate from the campaign in 2019 was 5.94 (±7.07 std) μg gdw^{-1} h^{-1}. Where isoprene had the average emission rate of 2.35 (±3.83) μg gdw^{-1} h^{-1} and monoterpene 3.59 (±3.24) μg gdw^{-1} h^{-1}. The composition of the detected terpenes between the campaigns varied where isoprene was the compound detected in almost all samples for the whole growing season whilst the components of monoterpenes differed between samples. The photosynthetic rate was stable throughout the measurement during May and the beginning of July for P2S1 where it then dropped to increase again in July to reach the highest photosynthetic rate for all plots that growing season, reaching 12.7 μmol CO_2 m^{-2} s^{-1} to then drop again in August. The emission rate for this plot is higher than for any of the other plots in this study. P2S2 revealed a similar irregular pattern for the photosynthetic rate (Figure 4) along with the BVOC emission rate that reached its peak during May to then decrease. The last spruce, P1S4 showed increased photosynthetic rate through the four measurements that were done for this plot, the emission rate was much higher for the measurements in July than in June.

The average air temperature from 1st of May to 30th of August in 2019 at Hyltemossa was 15°C, field notes explained colder days with precipitation and even hail prior to and during the measurements. There were a few campaigns where the temperature was held at around 20°C inside the chamber and 1000 μmol m^{-2} s^{-1} while others were held at a temperature of 30°C and 1000 μmol m^{-2} s^{-1}. The temperature inside the chamber ranged from 18.1°C - 29.9°C throughout the campaigns depending on the decided temperature from the setup.

Table 1. The total isoprene and monoterpene emission rate for all champaigns stated from dates to plots and spruces at standard light and temperature conditions (PAR 1000 μmol m^{-2} s^{-1} and T_s 303 K). No data (n.d.) indicates that no compound was detected in the sample for that branch. Given is also the average photosynthesis for each campaign (μmol CO_2 m^{-2} s^{-1}). All individual compounds within the group of monoterpenes are shown in Appendix A.

Date	Plot /spruce	Isoprene (μg gdw^{-1} h^{-1})	MT (μg gdw^{-1} h^{-1})	Photosynthesis (μmol CO_2 m^{-2} s^{-1})
190506	**P2S1**	0.64	0.21	9.60
	P2S2	0.11	6.41	11.15
190606	**P2S1**	10.26	6.26	9.35
	P2S2	0.08	2.00	6.31
190613	**P2S1**	3.36	3.59	6.44
	P2S2	0.07	0.09	9.62
	P1S4	0.02	0.47	7.65
190702	**P1S4**	n.d	n.d	9.18
190704	**P1S1**	0.77	6.64	11.21
	P2S2	n.d	0.001	11.43
190730	**P1S4**	0.61	1.88	13.51
190731	**P2S1**	10.38	9.32	12.48
	P2S2	0.46	n.d	10.55
190828	**P2S1**	1.44	6.27	8.18

4.1 Isoprene

The total emission rate for isoprene showed the highest relation to the photosynthetic activity when comparing the compounds, it did however only show a strong correlation through the R^2 value in the scatterplot (Figure 7) for P1S4. Figure 3 shows the highest isoprene emission rate for the season measured with 10.38 μg gdw^{-1} h^{-1} during the 31st of July for P2S1. Lower emission rates were also observed during the season, unsteady weather conditions with clouds and rain could be the reason why lower emission rates were observed for P2S1 (0.77 μg gdw^{-1} h^{-1}) and no emission rates for P2S2 4th of July, the rain continued to fall during the campaign according to the field notes on the 30th of July with emission rates of 0.61 μg gdw^{-1} h^{-1}.

The relationship between isoprene and the photosynthetic rate is clearly shown through the pattern in Figure 3, 4 and 5, where a higher photosynthetic rate in some measurements results in higher isoprene emissions, which could explain the emissions light response. The emission rates for P2S2 (Figure 4) were very low in relation to the photosynthetic rate in the latter part of the season compared to the rest of the study. P1S4 (Figure 5) also showed inconsistent emission rates compared to the photosynthetic activity, especially for the second adsorbent tube in June and the first adsorbent tube in July.

4.2 Monoterpene

The emission rates for each compound within the group of monoterpenes differed throughout the season and tree. α -pinene was the dominant monoterpene with an average of 7.27 (± 5.45)

µg gdw^{-1} h^{-1}, this is almost two times higher than β-pinene (3.86 ±1.44) µg gdw^{-1} h^{-1} which were the second most emitted monoterpene. The entire emission rate throughout the season is shown in Figure 6, where July and August were the months with the highest emission rates. The different compounds show a high variation throughout the different adsorbent tubes, where some measurements lacked emission data and others showed low emission rates. P2S2 (Figure 4) did however show a peak of 3-carene for the campaign done in May, this compound is known to act as a defense and therefore an indicator of stress (Fäldt et al., 2003). Another peak that stands out is α -pinene for P2S1 on the 4th of July.

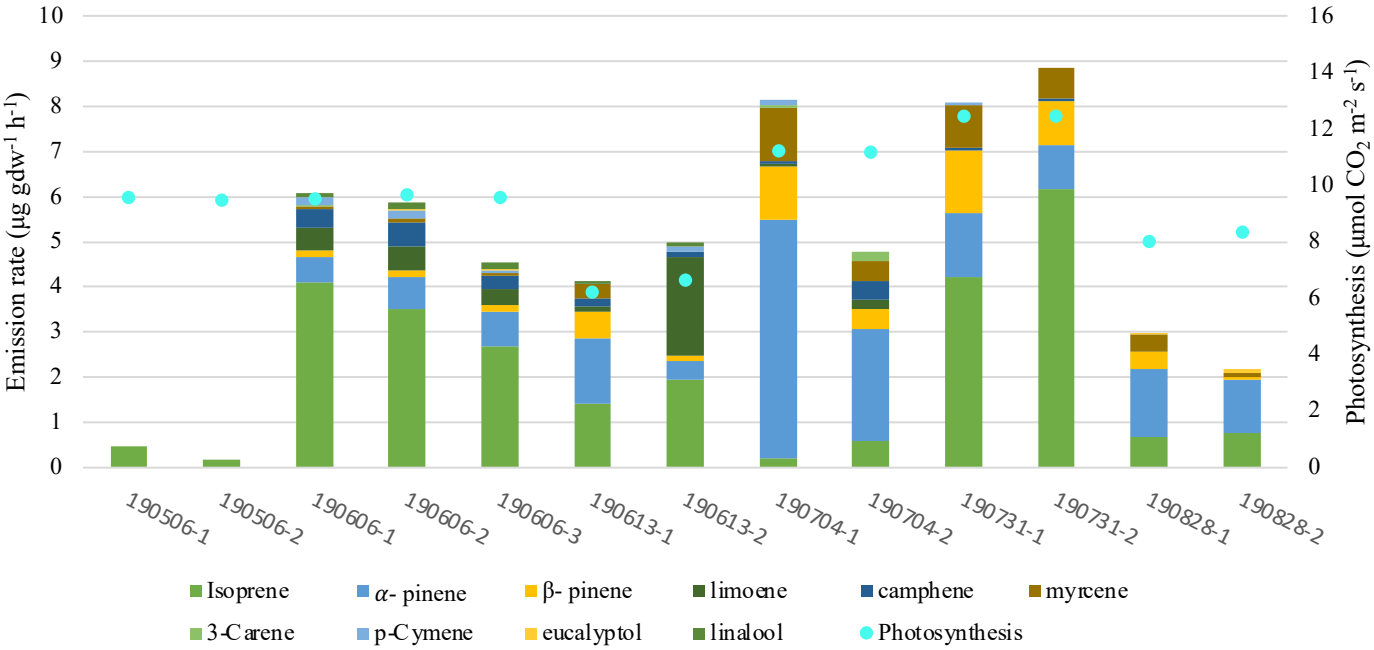

Figure 3. Total standardized MT and ISO emission rate (µg gdw^{-1} h^{-1}) and average photosynthetic rate (µmol CO2 m^{-2} s^{-1}) for each adsorbent tube for each campaign at P2S1. Each measurement is explained by the year-month-date and which tube.

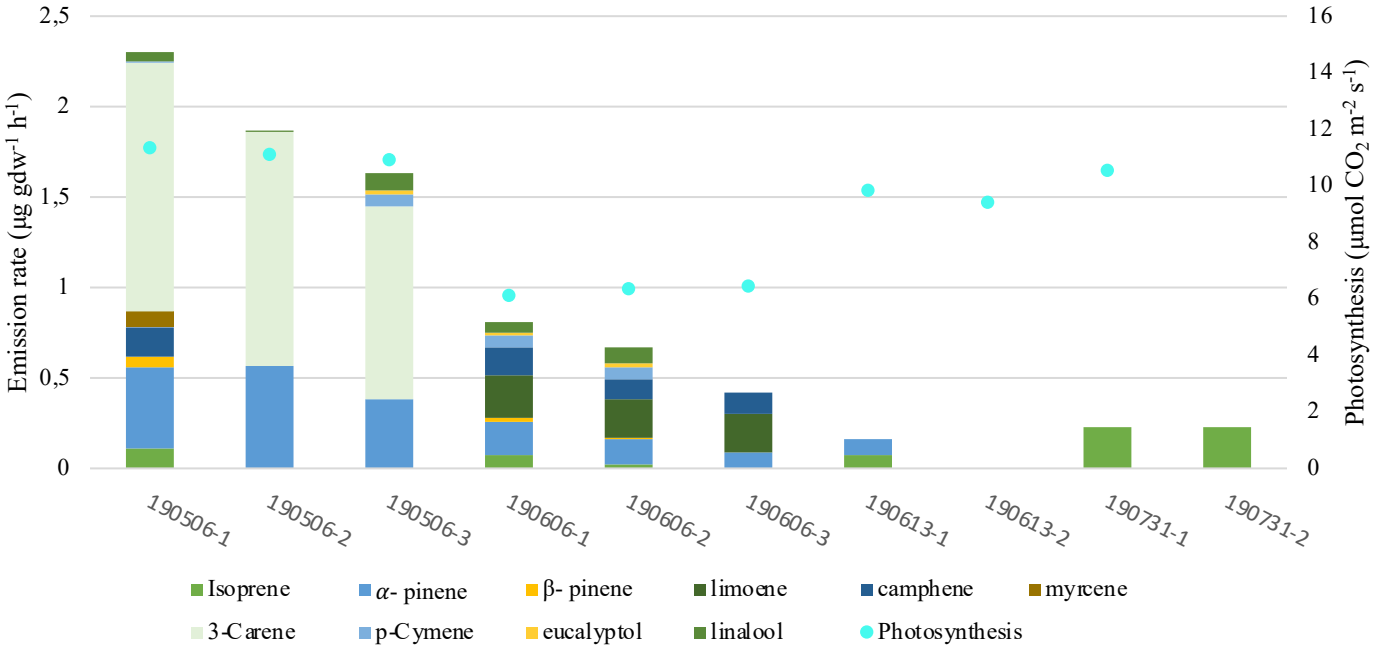

Figure 4. Total standardized MTs and ISO emission rate (µg gdw^{-1} h^{-1}) and average photosynthetic rate (µmol CO2 m^{-2} s^{-1}) for each adsorbent tube for each campaign at P2S2. Each measurement is explained by the year-month-date and which tube.

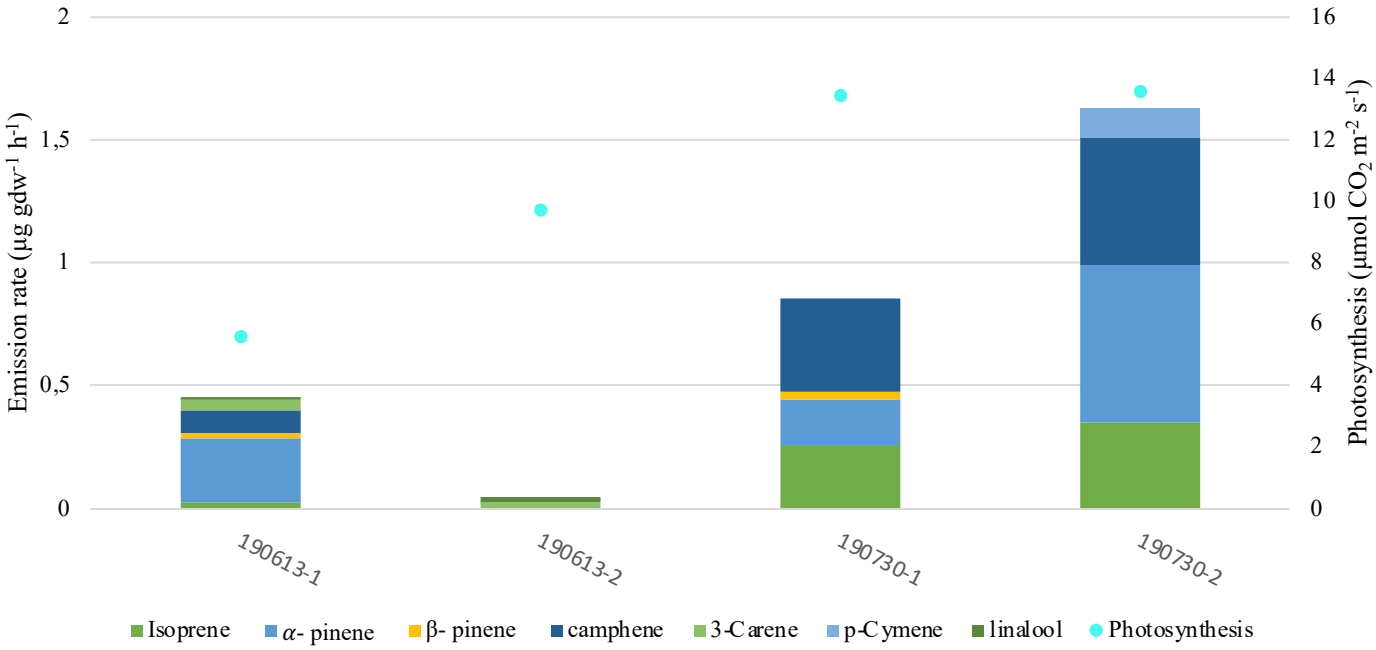

Figure 5. Total standardized MTs and ISO emission rate (µg gdw^{-1} h^{-1}) and average photosynthetic rate (µmol CO2 m^{-2} s-^{1}) for each adsorbent tube for each campaign at P1S4. Each measurement is explained by the year-month-date and which tube.

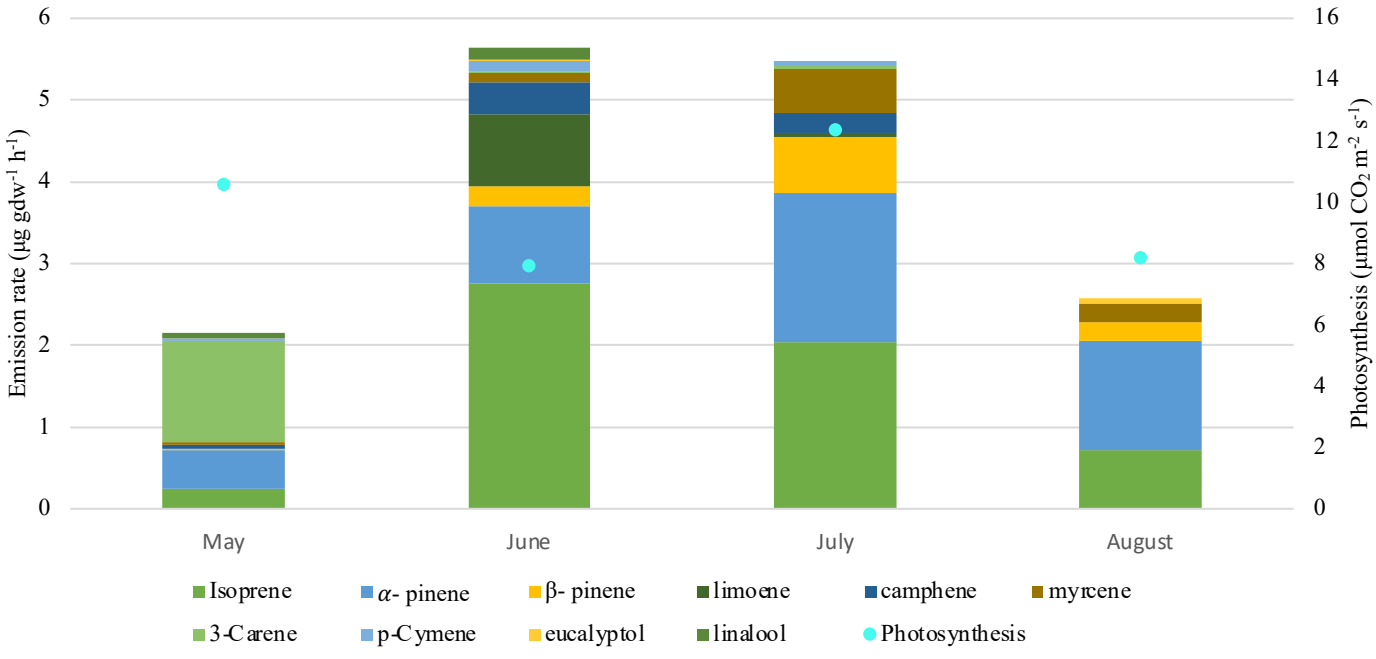

Figure 6. Total standardized BVOC emission rate (µg gdw^{-1} h^{-1}) and average photosynthetic rate for all plots and spruces (µmol CO2 m^{-2} s^{-1}) for each month of the growing season.

4.3 Difference in monoterpenes and isoprene emissions

The highest average standardized terpenoid emission rate in this study was from P2S1 (9.89 ± 2.44 µg gdw^{-1} h^{-1}) during the campaign on the 31st of July. Followed by the same tree 6th of June (5.51 ± 1.15 µg gdw^{-1} h^{-1}). Whilst P2S1 also was the tree that emitted the highest average standardized amount of both monoterpene emissions and isoprene emissions (27.07 ± 13.79 µg gdw^{-1} h^{-1}) during the whole season, followed by P2S2 (3.78 ± 1.42 µg gdw^{-1} h^{-1}) and P1S4 (1.77 ± 0.5 µg gdw^{-1} h^{-1}).

All trees had however a high variance between the different compounds and measurements. The significant difference between these emissions was that the average standardized isoprene emissions were higher for the measurements taken on the 31st of July for P2S1 (5.18 ± 1.36 µg gdw^{-1} h^{-1}). Following the trend of the increased average photosynthetic rate where it increased (12.47 µmol CO_2 m^{-2} s^{-1}) compared to the other measurements. The monthly pattern of standardized emission rates for the terpenoids was not consistent with the photosynthetic rate seen in Figure 6.

Figure 7 shows the total standardized emission rate for both monoterpenes and isoprene for all plots and spruces plotted against the photosynthetic rate for each adsorbent tube and day of measurement. Where the trendlines for all spruces and compounds show a positive correlation, P1S4 is shown to have the strongest correlation with a value of $R^2 = 0.92$. This is however the spruce with the least amount of measurements where emission rates could be derived compared to the other two trees. Isoprene shows higher correlation R^2 values from the linear trendlines compared to the monoterpenes which were expected since isoprene is a light-dependent compound. However, the significance between the photosynthetic rate and the compounds through a regression test seen in Table 2, indicating that there is no significant correlation between the compounds and the photosynthetic rate for P2S2, P2S1 and P1S4. There are nevertheless lower p-values for both P2S1 and P1S4, implying that these trees are closer to a significant correlation, although they are not significant.

Table 2. P-values of the relation between the total standardized emitted isoprene and monoterpenes and the average photosynthetic rate for each plot and spruce.

	Isoprene	**Monoterpenes**
P2S1	P=.15	P=.17
P2S2	P=.98	P=.95
P1S4	P=.14	P=.35

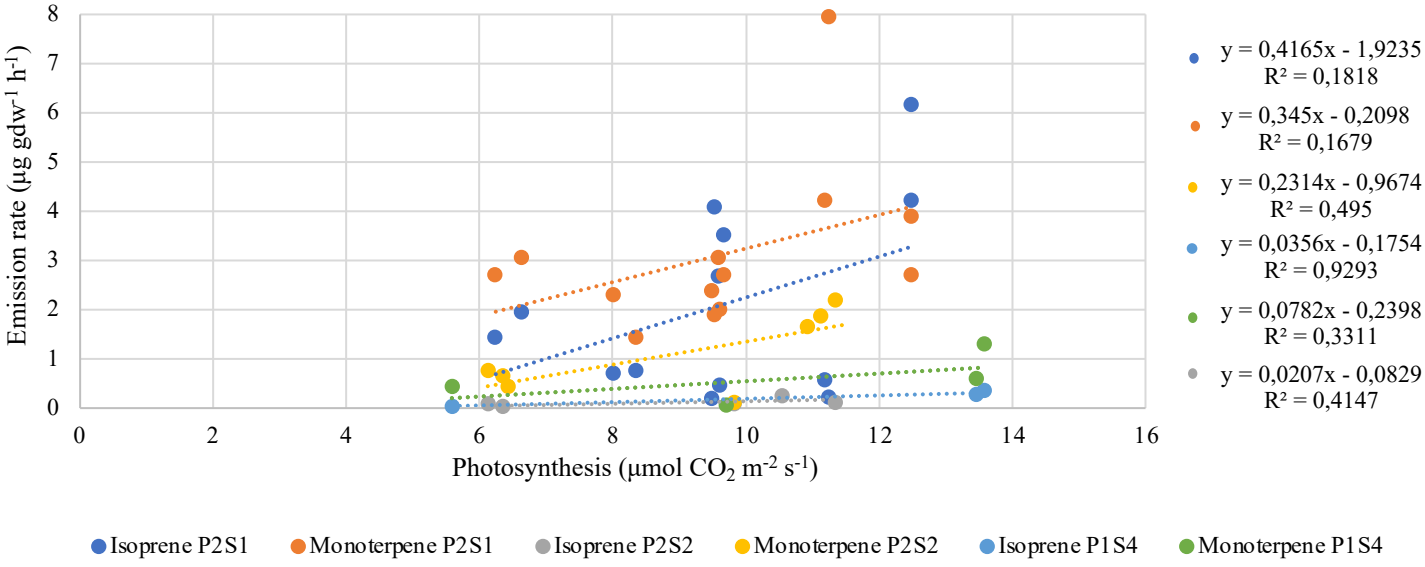

Figure 7. Total standardized BVOC emission rate (µg gdw^{-1} h^{-1}) for monoterpenes and isoprene each measurement day plotted against the photosynthetic rate µmol CO_2 m^{-2} s^{-1} from the field study in 2019 along with the R^2 value.

4.4 Calculated seasonal emission rate for 2015 and 2019

The average standardized emission rates for isoprene and monoterpenes from 2015 and 2019 were calculated by Guenther's algorithm (Eq. 3 and Eq.6) together with climate data (PAR and canopy temperature) from ICOS for respective years for comparative reasons. van Meeningen et al. (2017) had results from July 2015 while the results from this study were based on the entire season (May-August) of 2019.

Figure 11 displays the actual average monoterpene emission rate (±std) for 2015 based on the results from van Meeningen et al. (2017) see Table 3. Where the most frequent peaks occur in mid-July throughout August, whilst the highest emission rate peaks at the beginning of each month except for May 2019 (Figure 11). The BVOCs for the calculated seasonal emission rates, including both monoterpenes and isoprene follow a similar pattern as the average temperature for both years. The exception would be for isoprene in May 2019 (Figure 10) where there is a clear fluctuation in temperature but not for the emission rate. The temperature difference between the two years of measurements shows a difference of 1.9 °C from the average temperature measured in 2015 which was 16.3 °C as the lowest and 18.1 °C as the highest in 2019.

There was a clear difference in monoterpene emission rates comparing the two campaign years, 2019 showed emission rates up to 2.9 µg gdw^{-1} h^{-1} while it was 1.2 µg gdw^{-1} h^{-1} for 2015. The average emission rate for isoprene was on the other hand much lower than for monoterpene, the difference between them is however clearly visible in Figures 10 and 11. The highest average emission rate for 2015 was 0.37 µg gdw^{-1} h^{-1} and 0.07 µg gdw^{-1} h^{-1} for 2019.

The soil water content from the topsoil was derived throughout the season for both measurement years, in Figures 10-11 is the average soil water content shown for the two seasons, where the

lowest average for 2015 was 45.5 %, whilst 18.6 % for 2019. Other variables influencing the soil moisture content were however not taken into consideration.

The plant gross primary production (GPP) is a direct indicator of the biogenic activity since it describes the carbon uptake by the photosynthetic activity, GPP and temperature (T) are hypothesized to cause higher emissions of BVOC (Niinemets 2013). The relationship between the photosynthetic rate/GPP derived from ICOS and the standardized emission rate for the calculated years is shown in Figure 8 for 2015 and Figure 9 for 2019, where the relationship of an increased GPP also results in an increased emission rate of BVOC. The result for 2019 shows a more scattered pattern than for 2015.

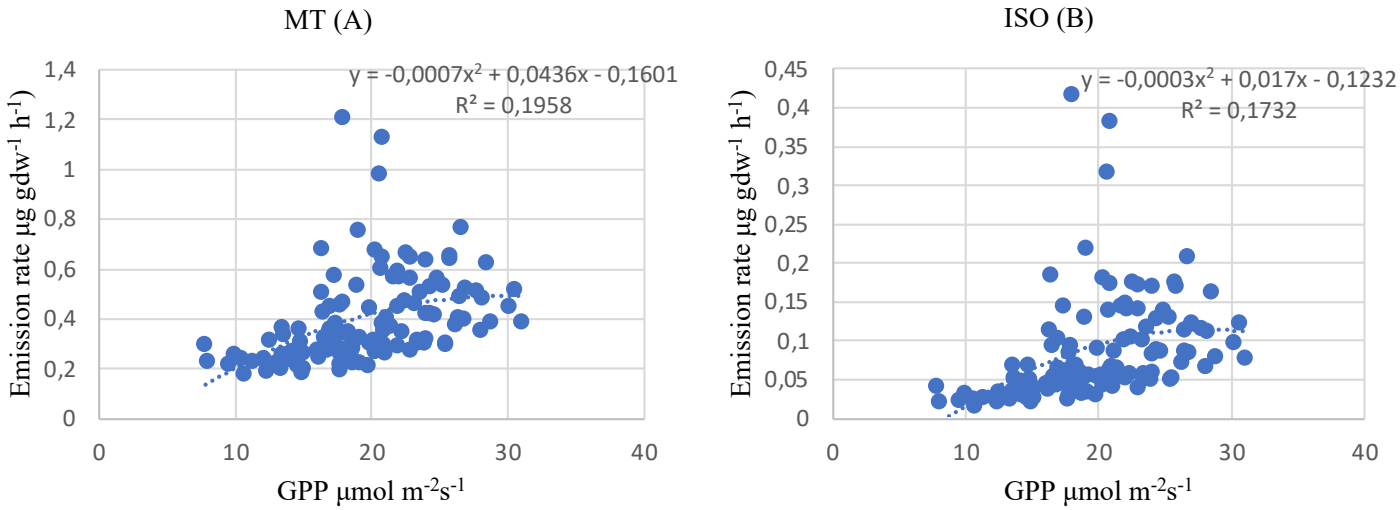

Figure 8. Monotrepene and isoprene emission rate as a function of GPP for 2015.

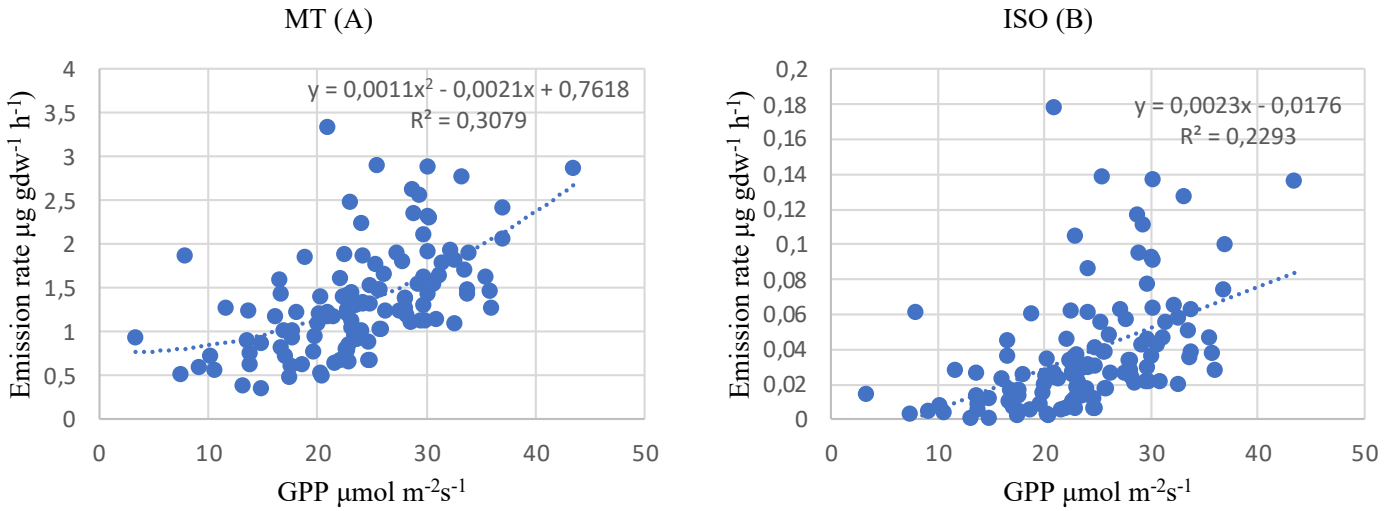

Figure 9. Monoterpene and isoprene emission rate as a function of GPP for 2019.

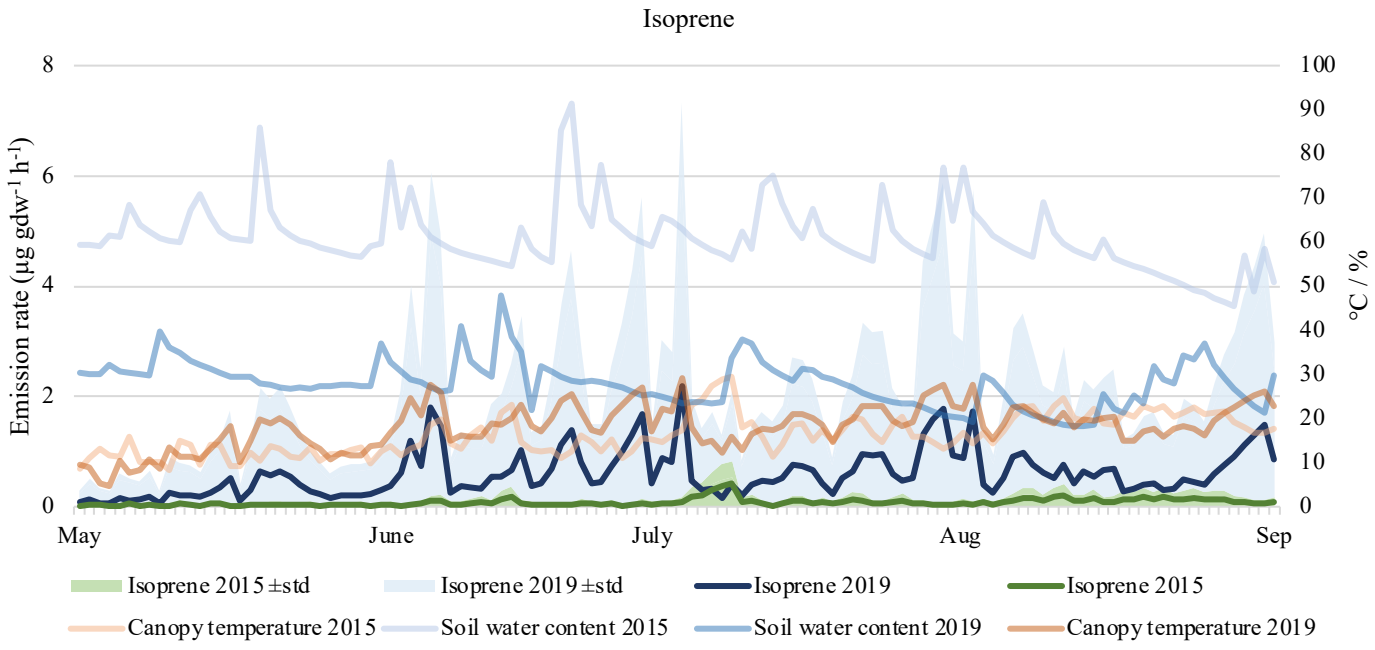

Figure 10. Calculated emission rate (±standard deviation) for isoprene based on the standardized average emission rate derived from the campaigns in 2015 from Meeningen et al., (2017) and 2019 with ICOS data (air temperature and PAR) from the same time period and the average soil water content from the topsoil

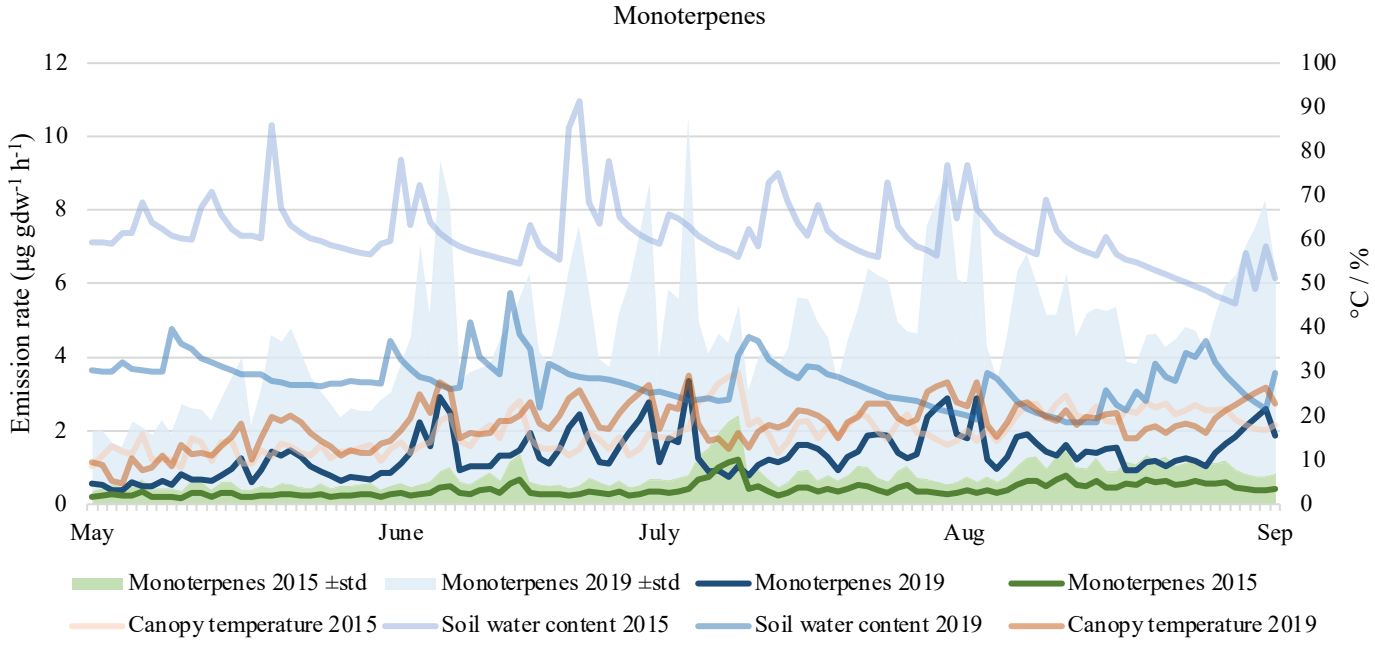

Figure 11. Calculated emission rate (±standard deviation) for monoterpenes based on the standardized average emission rate derived from the campaigns in 2015 from Meeningen et al., (2017) and 2019 with ICOS data (air temperature and PAR) from the same time period and the average soil water content from the topsoil

Table 3. Average emission rates ± standard deviation for monoterpenes and isoprene from 2015 and 2019 used to model the full seasons.

	Isoprene ($\mu g\ gdw^{-1}\ h^{-1}$)	**Isoprene ±std** ($\mu g\ gdw^{-1}\ h^{-1}$)	**Monoterpenes** ($\mu g\ gdw^{-1}\ h^{-1}$)	**Monoterpenes ±std** ($\mu g\ gdw^{-1}\ h^{-1}$)
2015	0.43	0.12	1.25	1.14
2019	2.35	3.83	3.59	3.24

5 Discussion

BVOC emissions were measured during the growing season (May-August) in 2019 from needle branches of Norway spruce to determine a short-term measurement of the seasonal behaviors. Norway spruce is an important contributor of BVOC emissions, and it has also been studied to be a common specie among coniferous trees in Europe (Rinne et al., 2009).

The results of emission rates in this study were in range of earlier studies for Norway spruce and other measurements done for some of the same trees in 2015 (van Meeningen et al., 2017). Out of the 14 measurements in 2019 were isoprene and monoterpenes found in 12 of them. Sesquiterpenes are the compounds debated to appear of minor importance (König et al., 1995; Schuh et al., 1997). And sesquiterpenes were therefore not included in here since the measurements showed no apparent signs of emissions for several of the campaigns. There were only three compounds detected from the ATD-GC-MS analysis with very low emission rates. van Meeningen et al. (2017) did however investigate four different Norway spruces in July, where SQT emissions were only found in one of the spruces. Research done in 2006 showed that Norway spruce starts to emit sesquiterpenes during late summer (Hakola et al., 2006). While another study by Bourtsoukidis et al. (2014) found low sesquiterpene emissions during spring, where the lowest emission rate was 0.0016 $\mu g\ gdw^{-1}\ h^{-1}$. An explanation for the few and low emission rates for this study could therefore be that empty storage pools were filled up instead of being emitted directly.

The difference in emission rates for the three different spruces could be a result of which time during the day the measurements were conducted. Some measurements were conducted in the morning which has been shown through research to be a time of increasing emission rates (Niinemets, 2013), while some measurements were conducted midday when the emission rates reach the peak, and other measurements were conducted during the late afternoon towards the evening when the rate is said to be low. The difference in total emission rate during the growing season in 2019 showed the highest emission rates in June while the photosynthetic activity was the lowest. July was the month with the second highest emittance and with the highest average photosynthetic rate (Figure 6). This could be an indication of why the emission rates do not show a significant correlation to photosynthetic activity.

5.1 BVOC emissions

The needles of a Norway spruce are exposed to a variety of light and temperature conditions in such a dense forest from where this study was conducted, which can result in fluctuations depending on the seasons. The temperature difference between the measurements in 2015 and 2019 shows an increase in the seasonal average by 1.9°C. Figure 10 shows the seasonal temperature for 2019, where the temperature can fluctuate from 12°C one day to 29°C the other. This could affect the emission rate of especially monoterpenes to be induced since those compounds are temperature dependent. The microclimate within the tree canopy can also influence the BVOC emission rate for all compounds, isoprene in particular since it is a light-dependent compound (Guenther, 2013). However, the seasonal change in 2019 is more pronounced since all measurements were derived from the same height for all branches, where the total average emission rate of both isoprene and monoterpenes was found in July. The seasonality of BVOC emissions of a boreal forest in southern Finland was analyzed by Hakola et al. (2003), where the emission rate for isoprene and monoterpenes were recorded to be the highest during the growing season. While the emission rate was significantly lower during the winter.

Monoterpenes were the highest emitted BVOCs in 2019 which was expected since the dominant emissions from Norway spruce usually are monoterpenes. The study by van Meeningen et al. (2017) showed results presented in Table 3 where the emission rate for monoterpene is almost three times as high as isoprene for July. The study also includes results from another site in Sweden (Norunda) in June-July where the emission rates were 0.98 (±1.25) μg gdw^{-1} h^{-1} for isoprene and 0.59 (±0.36) μg gdw^{-1} h^{-1} for monoterpenes. Results presented by Wang (2018) for the same site in 2013 showed that monoterpenes accounted for 65 % of the total terpene emissions. It did however show an increase in isoprene emissions from the same study but in 2014 where isoprene was the dominant compound emitted from July to September.

Hakola et al. (2003) studied the seasonal pattern of BVOCs, where the emissions rates peaked during the growing season, the highest emission rate for MT was found in May with 1.4 μg gdw^{-1} h^{-1} which is lower than the results found in this study for the same month. Bourtsoukidis et al. (2014) did however find monoterpene emission rates in April at 0.2031 μg gdw^{-1} h^{-1} in a forest in Germany dominated by Norway spruce, which is comparable to the results found in May for P2S1 in this study. The seasonal change of emission pattern in this study has shown to also follow the same pattern as another study conducted on Norway spruce in 1993 (Janson, 1993). Where it is clear that the amount of emission and their profile is influenced by seasonality (Hakola et al., 2003; Janson, 1993).

The average emission rate in the study from van Meeningen et al. (2017) for isoprene was 0.43 (±0.12) μg gdw^{-1} h^{-1}, and 1.25 (±1.14) μg gdw^{-1} h^{-1} for monoterpenes. This result was lower compared to the isoprene emission in 2019 which was 2.35 (± 3.83) μg gdw^{-1} h^{-1} and 3.59 (± 3.24) μg gdw^{-1} h^{-1} for monoterpenes. The difference between the two years could be an indication of induced emissions caused by stress. The result from 2019 is however based on the whole season and not just July as in the study by van Meeningen et al. (2017). This is of importance since the average of the whole growing season can change significantly over a whole season compared to a few measurements for one month. This comparison is just an overview of how one could interpret the emissions during 2015 and does not give the actual individual emission patterns of each measurement conducted in the field but an estimation.

The soil water content revealed a change of 26.9 % between the four years of measurements, whereas the water content in the topsoil in 2019 was relatively low. This could be an indication

of a year with less precipitation, or the result of climate change with higher temperatures and less precipitation that could be the cause of drier soil.

5.1.1 Seasonal emission rates

The chosen technique that was used to measure the emissions (needle-scale) can be related to the variability of the standardized emission rates. The physiological changes in plants related to different development stages are also a factor influencing the emission rates. Isoprene is suggested to vary in the development of emissions, where at least four stages are involved (Guenther, 1997; Monson et al., 1994). This could be an explanation for why the emissions varied during the measurements in 2019, especially for P2S1 (Figure 3) where the isoprene emission increased in July. The isoprene synthase activity changes through season and the physiological processes are thought to be dependent on this activity (Kuzma & Fall, 1993; Monson et al., 1992; Schnitzler et al., 2004). Though, temperature and PAR are the main factors influencing the isoprene emissions and the main reason why Eq. 3 has been commonly used to describe the emissions. However, this equation cannot explain why the standardized average emissions were higher in May for P2S2 than in July, even though the PAR and temperature were higher in July. The lack of sesquiterpenes gives an indication of a shorter emittance season or low amounts compared to the isoprene and monoterpenes, this indicates a need for additional parameters, taking seasonality into account.

The results from this study where no correlation could be found between the emission rate and photosynthetic activity for the measurements in 2019 point out the importance of how genetical influence can change the emission pattern of BVOCs, even within the same species which has been studied by Staudt et al. (2004). Plants do not necessarily respond the same to climate factors, whereas a study by Evans et al. (1985) found that the photosynthetic activity showed little influence on monoterpene emissions from spruce, another study by Steinbrecher et al. (1993) did however report a significant dependence. Another contributing factor to increased emission rates could be the age of the tree or branch. Depending on the species, where mature trees may not be as affected by damage as younger ones and could therefore be more capable to stand against any kind of damage (Palo, 1984).

5.2 Light and temperature dependence

The light response in this study can be used as a measurement of the activity. The results showed positive net assimilation with values ranging between 6.31-13.51 μmol CO_2 m^{-2} s^{-1} at a light level of 1000 μmol m^{-2} s^{-1}. Results that can be compared to the study by van Meeningen et al. (2017), where the net assimilation rates were found to range between 3.6 and 12.1 μmol CO_2 m^{-2} s^{-1} for light levels from 500 to 1000 μmol m^{-2} s^{-1}. There were however needles for the measurements in 2019 that were photosynthetically active without releasing any BVOCs given as n.d in Table 1. Isoprene was shown to vary between the measurements, higher photosynthetic rate did not in all cases in this study involve high emission rates of isoprene.

5.3 Induced BVOC emissions

Stress-induced BVOC emissions from controlling short-term climate variations are harder to include in the existing algorithms, it would however be required to better estimate the relationship between emission rates and the controlling environmental variables (Guenther, 2013). The effect temperature has on the release of BVOC from plants ranges from direct to indirect effects, biochemical reactions, and the length of the growing season. Forests in Europe are suffering from stresses of different kinds, and most of these are expected to increase with

climate change (IPCC, 2014). It is however noted that the difference in average standardized emission rate for both isoprene and monoterpene is higher in 2019 than in 2015 which could be an indication of the ongoing climate change. The calculated emission rates for 2015 were based on the average emission rate for July only, while the average emission rate for this study was based on the entire season of 2019 (May-August). This difference is an important factor taken into consideration when comparing the two seasonal patterns.

Field notes revealed hail and lower temperatures days prior to the measurement from where the high 3-carene had its peak for P2S2 (Figure 4). The high emission rate could be a result from the position of the needles on the tree, as it might be a difference in the amount of emitted compounds. Or it could also be an indication of stress from being in a cold environment to then be shocked with warmer temperatures within the chamber.

The chamber that was assembled 1 hour prior to the measurement might not have been enough for this branch to acclimatize to the temperature difference and the high emission rate could be a result of this. Another factor to this could be that the needles have been chocked from the cold weather while entering the chamber, where they might have started to photosynthesize again to simply focus on the growth and not the other factors BVOC emissions provide. Research shows that in some cases where the plant is under stress conditions is the isoprene no longer closely related to the photosynthesis, 'old' carbon does instead maintain the isoprene biosynthesis (Brilli et al., 2007).

5.4 Limitations

This chamber technique requires background reading before and after each sampling period. In cases where the concentration of BVOCs from the background reading is discovered to be higher or near the concentration that was measured is there an indication that the VOC filter has let some emissions from the outside air into the chamber. Better detection of the different BVOC emissions would therefore be to have cleaner background values, preferably 0 by using brand new clean filters for each measurement, which also might be a difficulty during an in-situ measurement station.

Another disadvantage with the needle chamber approach together with the LI-6400 XT is that the first measurement taken out of the 2-3 back-to-back measurements in the field study from 2019 might increase the risk of induced emissions from mechanical stress since the branch is handled. The results calculated for the seasonal emission patterns for the two years were based on the average emission rates of each campaign year. The results show an estimation of how the emission rate could be interpreted on a bigger scale.

The off-line sampling method conducted in this study using adsorbent tubes for later analysis has the disadvantage of having the total concentration of BVOC emissions over time which makes it hard to capture the short-term fluctuations which could have been done with on-line measurements that gives the BVOC concentration in real-time. The on-line sampling method does however not detect the specific compounds, instead only the groups of BVOC emissions. A combination of the two might be of advantage. Measurements of this kind, with an enclosed chamber require more time and most often only represent one part of the tree where the branch is measured.

5.5 Future studies

This study could be repeated several times for future studies over several different climate periods, it is essential to understand how the trees are affected by the environment and different environmental factors and how they can enhance by climate change. This study could also be conducted on other species within the same forest to study how the species react differently to climate factors or damage of some kind. A few factors are excluded here: mechanical damage, biotic herbivore or insect attack. Mechanical damage involves unpredicted weather events such as ice or hail and damage caused by humans from e.g. cutting the needles. A study to measure the emission rates caused by mechanical stress is done by measuring the emission rate before and after cutting the needles. Herbivore attacks also cause damage to the needles or tree trunk which involves other kinds of chamber techniques to measure the emission rate, and then compare these measurements with healthy trees in the area. Future studies are thus needed to investigate if emission patterns are influenced by short-term environmental effects or not. Another aspect of measuring the BVOC emission is to have several chambers throughout the canopy for each tree since the microclimate influences the emission rate.

6 Conclusion

The main objective of this study was to characterize the different BVOC emissions during the growing season of 2019 from Norway spruce in Hyltemossa, using a dynamic needle chamber along with cartridge sampling. The focus was on terpenoid emissions, specifically, monoterpenes and isoprene. To then compare this result to measurements conducted four years earlier by van Meeningen et al. (2017), to see if there were any differences in emission rate and which possible stress factors might have induced the emissions.

The measurements of Norway spruce in 2019 presented in this study confirmed a seasonal variation of emission rate as well as the fraction of each compound emitted for all branches of the same spruce as well as the other spruces. This leads to an indication of uncertainty when predicting emission patterns from only one branch on one spruce. Monoterpenes were shown to be the dominating compounds emitted during the growing season. This study shows a pattern of BVOC emissions to be in line with other published results which indicates a somewhat normal activity for the spruces, they were however elevated from previous measurements conducted four years earlier in 2015 which might be an indication of induced emission caused by stress. This could also be interpreted through the specific compounds being emitted from the spruces, where 3-carene known to be an indication of stress were found in large amounts for P2S2 (Figure 4).

The modeled results of Norway spruce presented in this study imply an increase in BVOC emissions in 2019 compared to 2015, where the average standardized monoterpene emission rate resulted in more than three times higher than four years earlier. However, the results were based on July for 2015 and the whole season for 2019. This only gives an estimation of how the pattern looked during that growing season in 2015, compared to how the emission rates in 2019 looked. There is nevertheless an indication of induced emission rates from the high difference between the two years for this study area, which may be caused by stress, most likely drought as there were no visible signs of herbivore attack. Induced emissions can greatly impact particle formation and growth as well as the regional climate. And since the observed emissions varied with sites, seasons and different branches of the same canopy height, more replications of this study would be needed to get conclusive results on the distribution of BVOC emissions.

7 References

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8 Appendix A

The total isoprene and individual monoterpene emission rate for all champaigns stated from dates to plots and spruces at standard light and temperature conditions (PAR 1000 µmol m^{-2} s^{-1} and T_s 303 K). No data (n.d.) indicates that no compound was detected in the sample for that particular tree

Date	Site	Isoprene	MT	α- pinene	β- pinene	Camphene	Myrcene	3-Carene	p-Cymene	Limonene	Eucalyptol	Linalool
	/spruce	(µg gdw-1 h-1)	(µg gdw-1 h-1)	(µg gdw-1 h-1)	(µg gdw-1 h-1)	(µg gdw-1 h-1)	(µg gdw-1 h-1)	(µg gdw-1 h-1)	(µg gdw-1 h-1)	(µg gdw-1 h-1)	(µg gdw-1 h-1)	(µg gdw-1 h-1)
190506	**S2S1**	0.64	0,21	n.d	n.d	n.d	n.d	n.d	n.d	0,21	n.d	n.d
	S2S2	0.11	6,41	1,40	0,07	0,16	0,08	3,73	0,01	0,89	n.d	0,07
190606	**S2S1**	10.26	6,26	2,08	0,42	1,22	0,22	0,05	0,41	1,42	0,03	0,41
	S2S2	0.08	2,00	0,42	0,02	0,39	n.d	n.d	0,20	0,66	0,05	0,26
190613	**S2S1**	3.36	3,58	1,85	0,73	0,30	0,31	n.d	0,11	0,14	n.d	0,15
	S2S2	0.07	0,09	0,09	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
	S1S4	0.02	0,48	0,26	0,02	0,09	n.d	0,07	n.d	n.d	n.d	0,03
190702	**S1S4**	n.d		n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	
190704	**S1S1**	0.77	6,64	0,77	2,82	0,47	1,64	0,27	0,12	0,55	n.d	n.d
	S2S2	n.d	0,00	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	0,00
190730	**S1S4**	0.61	1,87	0,82	0,04	0,90	n.d	n.d	0,12	n.d	n.d	n.d
190731	**S2S1**	10.38	9,31	5,13	2,40	0,10	1,61	n.d	0,08	n.d	n.d	n.d
	S2S2	0.46		n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
190828	**S2S1**	1.44	6,27	2,68	1,23	n.d	0,45	n.d	n.d	1,76	0,15	n.d