

BVOC emissions from a subarctic Mountain birch: *Analysis of short-term chamber measurements*



Erik Ahlberg

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Department of Earth and Ecosystem Sciences
Physical Geography and Ecosystems Analysis
Lund University
Sölvegatan 12
SE-223 62 Lund
Sweden



**BVOC EMISSIONS FROM A SUBARCTIC
MOUNTAIN BIRCH: ANALYSIS OF SHORT TERM
CHAMBER MEASUREMENTS**

ERIK AHLBERG

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Supervisor: **Thomas Holst**

Department of Earth and Ecosystem Sciences
Physical Geography and Ecosystems Analysis
Lund University

ABSTRACT

Biogenic volatile organic compounds (BVOCs) can have a large affect on atmospheric chemistry by the production or degradation of ozone and by acting as precursors to secondary organic aerosols (SOA). The most common BVOCs are isoprene and its derivatives, terpenes and terpenoids (isoprenoids). These are used by the plant in cell membranes and as steroids, but are also a means of communication and defence. Emissions of BVOCs have proved advantageous in stressful situations such as elevated temperatures and radiation, herbivore attacks and physical damage. Many of the volatile isoprenoids are the main compound in plant scents that are used to communicate and attract pollinators.

The volatilization of compounds is correlated to temperature, but production of BVOCs is dependent on photosynthetic products, and hence light. How plants regulate the production of specific compounds is largely unknown.

Emissions of BVOCs are not large in subarctic ecosystems, but are likely to change in the course of a climate warming that will affect high latitude ecosystems significantly. Research on BVOCs, that involves both carbon and radiation budgets, at northern sites, is therefore of high importance.

This study is an analysis of raw data obtained in a three day monitoring of BVOC emissions from a Mountain birch (*Betula pubescens ssp. czerepanovii*) during July, 2008. The raw data was converted into fluxes and analyzed with regards to correlation to temperature, light and photosynthesis. Emission potentials were calculated using the common algorithms developed by Alex Guenther.

Emissions were significantly lower than found in a previous study on the Mountain birches in the same area (maximum total emission rate at $300 \text{ ng g}_{\text{dw}}^{-1} \text{ h}^{-1}$), although some compounds that were emitted might not have been identified due to lack of references in the GC-MS analysis. Linalool was the main compound emitted with an emission potential of $28,5 \text{ ng g}_{\text{dw}}^{-1} \text{ h}^{-1}$ (standard temperature 20°C). A severe herbivore attack in 2004 is thought to have increased emissions during consecutive years. Earlier measurements showed a decrease in emissions from 2006 to 2007. The low values found in this study of emissions during 2008, might imply that the emission rates are returning to normal values.

Keywords: Geography, Physical geography, Volatile organic compounds, BVOC, Mountain birch.

SAMMANFATTNING

Flyktiga organiska föreningar som släpps ut från växter (BVOC- Biogenic volatile organic compounds) kan ha en stor påverkan på atmosfärisk kemi genom reaktioner som leder till ökad eller minskad ozonproduktion, och genom att de kan vara ett förstadium till aerosoler. De vanligaste flyktiga organiska föreningarna är isopren (2-metyl, 1,3-butadien) och dess derivat, terpenier och terpenoider (isoprenoider). Dessa används av växter som t.ex. uppbyggnad av cellmembran, steroider m.m., men är också ett sätt för växten att kommunicera och försvara sig mot yttre påverkan. Utsläpp av flyktiga föreningar har visat sig gynnsamt under vissa situationer, såsom förhöjd temperatur och solinstrålning, insektsangrepp och fysiska skador. Doften från många växter och blommor består i hög grad av isoprenoider, och används för att kommunicera och locka pollinatorer.

Förångning av kemiska föreningar står i korrelation till temperaturen, men växters produktion är beroende av produkter från fotosyntesen, vilket gör att utsläppen även är beroende av solljus. Hur växter reglerar produktionen av specifika kemiska föreningar är dock i hög grad okänt.

Utsläppen av flyktiga föreningar från växter är inte stora i subarktiska ekosystem, men kommer troligen förändras under en klimatuppvärmning som kommer att påverka nordliga latituders ekosystem betydligt. Därför är forskning på BVOC-området, som involverar kol- och strålningsbudgetar, av stor betydelse.

Den här studien är en analys av rådata från en tredagars mätning av BVOC-utsläpp från en Fjällbjörk (*Betula pubescens ssp. czerepanovii*) i juli 2008. Rådatan omvandlades till flöden, och analyserades med avseende på korrelationen mot temperatur, ljus och fotosyntes.

Utsläppen var betydligt lägre än i en tidigare studie på Fjällbjörkar i samma område, men det är möjligt att vissa kemiska föreningar som släpptes ut inte identifierades. Ett stort utbrott av en växtätare år 2004, tros ha triggat en ökning av utsläppen under efterföljande år. Tidigare studier har visat en nedgång i utsläpp även mellan 2006 och 2007. De uppmätta utsläppsnivåerna i denna studie kan därför vara närmare normala värden.

Nyckelord: Geografi, Naturgeografi, Flyktiga kolföreningar, BVOC, Fjällbjörk.

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1. Introduction

1.1 TERMINOLOGY AND INTRODUCTION TO BVOCs

Volatile Organic Compound (VOC) is a common name used for all organic trace gases, excluding carbon dioxide and carbon monoxide. BVOC refers to compounds of biogenic descent, which is believed to be as much as two thirds of global VOC emissions (Guenther, 1997). Other abbreviations are used to further narrow the variety of gases. BVOC is used in this thesis, including compounds emitted from terrestrial plants, excluding methane that is considered a research field on its own.

Biogenic volatile organic compounds connect the biosphere and the atmosphere, and are therefore of interest to a wide range of scientific communities. They are often highly reactive, with corresponding short life-times (Table 1), spanning from minutes to a few hours (Kesselmeier and Staudt, 1999), and influence atmospheric chemistry by the production or degradation of ozone (depending on the presence of reagents and sunlight) and by acting as precursors to aerosols (Atkinson, 2000; Matsunaga *et al.*, 2003; Sharkey *et al.*, 2008). These properties influence climate, which in turn is the major reason for an increased interest and research in the BVOC field during the last 15 years or so, assisted by improved analysis methods.

Current changes in climate and land use are predicted to alter BVOC emissions (Lathière *et al.*, 2006; Pacifico *et al.*, 2009), though the processes behind the feedbacks are uncertain (IPCC, 2007).

1.2 OBJECTIVES AND HYPOTHESIS

Most biogenic volatiles are emitted by tropical woodlands (Guenther *et al.*, 1995), but high latitude ecosystems, such as the subarctic Mountain birch forests in northern scandinavia, are thought to be more severely altered by climate warming (Sjögersten and Wookey, 2009), a fact that gives high importance to research at northern sites.

Measuring and monitoring BVOC emissions is basic research, but will also aid in the construction of better climate models. Birches, and especially the Mountain birch, show a large variation in emission patterns (Hakola *et al.*, 1998; Hakola *et al.*, 2001; Haapanala *et al.*, 2009). Adding to the scarce data available on Mountain birches is the main objective of this research.

This study, with emission data from three consecutive days of July 2008, is expected to fall into the patterns of contemporary knowledge that exists on BVOC emissions in general and Mountain birches in particular. Emission rates should show a clear dependence on light and temperature.

2. Background

2.1 ISOPRENE AND ISOPRENOIDS

Emissions of BVOCs are dominated by the alkenes isoprene (C₅) and monoterpenes (MT) (C₁₀) (Kesselmeier and Staudt, 1999; Guenther *et al.* 1995), which are also the compounds that have been studied the most (Seco *et al.*, 2007). Other BVOCs include sesquiterpenes (SQT) (C₁₅), alcohols, carbonyls, esters and acids.

Isoprene is a relatively simple hydrocarbon (Figure 1) that can be combined to form structures that are of many uses to plants. Isoprene is synthesized by plants, bacteria and animals, in two different metabolic pathways (Lombard and Moreira, 2011). The precursor to isoprene, a five-carbon unit called active isoprene, is one of nature's most versatile building units. It can be combined and modified in several thousands of ways to create terpenes and terpenoids (isoprenoids) (Lombard and Moreira, 2011) which are among the most abundant BVOCs (Kesselmeier and Staudt, 1999). Isoprenoids are one of the largest and oldest families of biological compounds and are used by plants in a wide range of areas, e.g. as parts of cell membranes, photosynthetic pigments, hormones and, for the volatile compounds, plant defence mechanisms and scents that aid in plant reproduction (Laothawornkitkul *et al.*, 2009; Lombard and Moreira, 2011; Owen and Peñuelas, 2005).

The most volatile isoprenoids other than isoprene are monoterpenes and sesquiterpenes, which are synthesized by the combination of two and three active isoprene units respectively. Adding more isoprene units gives diterpenes (C_{20}), triterpenes (C_{30}) and tetraterpens (C_{40}) (Kesselmeier and Staudt, 1999). Very long carbon chains of isoprene units (polyterpenes, $>C_{45}$) can form materials such as rubber. Only chains containing up to 15 carbon atoms (sesquiterpenes) are volatile (Owen and Peñuelas, 2005).

Monoterpenes and monoterpenoids are often strong smelling compounds, some of which gives well-known plants their distinctive smells, such as limonene, menthol, pinene and camphene (Kesselmeier and Staudt, 1999). Monoterpenes are also a common additive in food, beverages, ointments, perfumes and cleaning agents, thanks to their often pleasant smell (Mühlbauer *et al.*, 2003).

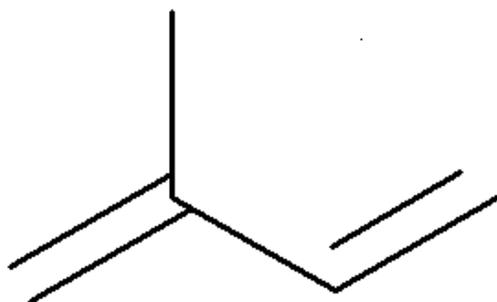


Figure 1. The molecular structure of the most abundant BVOC, isoprene, C_5H_8 , with five carbon atoms and two carbon-carbon double bonds. Combinations of this molecule create isoprenoids (terpenoids), that are one of nature's most common building blocks (Lombard and Moreira, 2011). Short chained isoprenoids are also volatile. Figure created using PLT (© Hans J. Reich, 1997-2007).

Linalool, which is a monoterpene alcohol, occurs naturally in many flower scents and is a very common additive in deodorants (Sköld *et al.*, 2004). It is used by a wide range of plants to attract pollinators, and is one of the components in bergamot and lavender oils (Raguso and Pichersky, 1999), but is also emitted from trees such as birches (Haapanala *et al.*, 2009; Hakola *et al.*, 2001) and Scots pine (Hakola *et al.*, 2006). Other uses of linalool include industrial production of vitamins and insecticides. In contact with air, the unsaturated molecule can oxidize and form organic hydroperoxides (Sköld *et al.* 2004). These contribute to secondary organic aerosol formation (Hua *et al.*, 2008). Linalool is sometimes grouped according to its derivation, and is hence considered a monoterpene (e.g. Arneth and Niinemets, 2010). In this study the grouping was chosen by molecular formula.

2.2 EMISSION CONTROLS

2.2.1 Stomatal conductance

The compounds produced in the plant enter the atmosphere via the stomata or by diffusion (Kesselmeier and Staudt, 1999). Isoprene emissions seem not to be influenced significantly by stomatal conductance. This does not mean that the gas diffuses through the leaf, since emissions have been shown to originate only from leaf sides containing stomatal pores. A decreased stomatal conductance is thought to be compensated by an increased pressure gradient for VOCs which results in emission rates not changing drastically. Compounds with a high water solubility (often caused by oxidation) are affected more by stomatal conductance (Seco *et al.*, 2007).

2.2.2 Plant benefits of VOC emission

BVOCs are essentially emitted because they are volatile, but the emission can also be advantageous for the plant, despite the high energy cost. Releasing specific compounds could be favourable under certain environmental conditions such as temperature stress (Sharkey *et al.*, 2008; Karl *et al.*, 2008), excess irradiation (Peñuelas and Munné-Bosch, 2005), presence of ozone (Vickers *et al.*, 2009) and reactive oxygen species (Sharkey *et al.*, 2008) and herbivore attacks (Arneeth and Niinemets, 2010; Dudareva *et al.*, 2004) but also act as a means of communication within the plant as well as between plants and to attract pollinators (Peñuelas *et al.*, 1995). It is also well known that mechanical stress (e.g. breaking of twigs) changes the composition and magnitudes of BVOC emissions (Laothawornkitkul *et al.*, 2009; Kesselmeier and Staudt, 1999; Vuorinen *et al.*, 2005). How the plant regulates synthesis of specific compounds is not well known (Laothawornkitkul *et al.*, 2009).

2.2.3 Temperature and light dependence

BVOC emissions are dependent on temperature and photosynthetic active radiation (PAR). All BVOC emissions show clear temperature dependence since they are volatilized by the higher energy. Isoprene emission is also known to be light dependent, due to its synthesis being dependent on photosynthetic products. This is not true for all other BVOCs that are often stored inside the plant and emitted even if dark, given high enough temperatures to volatilize the compounds (Kesselmeier, 1999). This theory has worked well on a small scale but may need revision when modelling long term and large scale emissions since temperature alone cannot explain emission variations, as shown for monoterpenes by Schurgers *et al.* 2009.

When modelling emissions, a light and temperature dependent algorithm for isoprene (called G_{TL} in this thesis), and a temperature only dependent algorithm (called G_{TEMP}) for all other BVOCs have been empirically established by Guenther *et al.* (1993) (see section 3.3). These have been rather successful in describing emission variations due to mentioned variables (Guenther *et al.*, 1995). The algorithms describing the emission's light and temperature dependence show similarities to models describing CO_2 fixing (Chopin *et al.*, 2002), with a saturation level for high PAR and an increase with temperature up to a certain level where production, and hence emission, decreases, except for stored compounds (Figure 2). The global geographic distribution of emission capacities for isoprene emitting plants is correlated to temperature and irradiation, but also at a smaller scale, such as leaves within a tree canopy, variations in emissions that are consistent with the hypothesis of thermal stress can be seen (Sharkey *et al.*, 2008; Harley *et al.*, 1996).

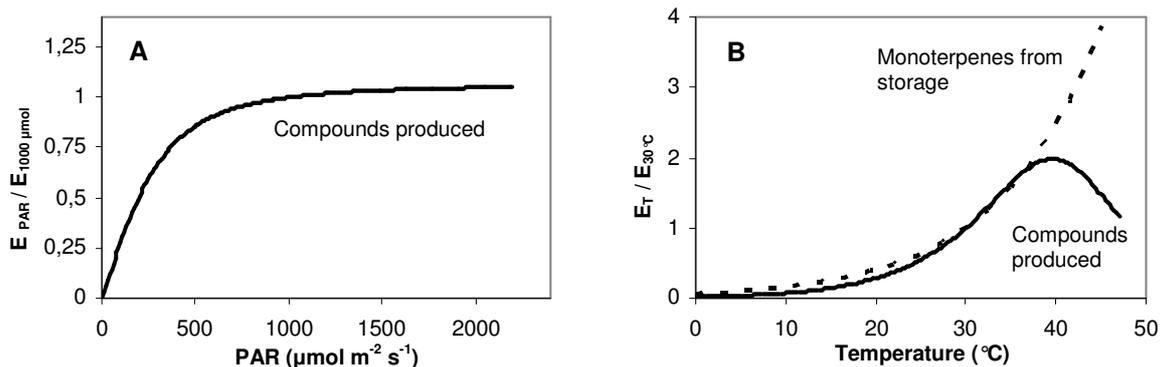


Figure 2. The theoretic relation of isoprene and monoterpene emissions to light (PAR), under constant temperature (a), and temperature, under constant PAR (b). Y-axis describes the emission according to the algorithms by Guenther *et al.* (1993), normalized by dividing by the emission at standard conditions. With high PAR and temperature, production of BVOCs will reach a saturation level or even decrease, depending on availability of photosynthetic products. Compounds that are already produced and stored in the plant will be emitted solely depending on temperature. Figures after Kesselmeier and Staudt, 1999.

2.3 INFLUENCES ON ATMOSPHERIC CHEMISTRY

BVOCs play an important role in tropospheric chemistry. A fairly large amount, typically 0-5% (Llusà and Peñuelas, 2000; Chopin *et al.*, 2002), of the carbon fixed by photosynthesis is released as VOCs, especially under stressful conditions, which influence atmospheric chemistry and indirectly, climate. Many of the BVOCs contain carbon-carbon double bonds that will readily react with NO_x and hydroxyl radicals to form ozone (Atkinson and Arey, 2003; Pacifico *et al.*, 2009; Atkinson, 2000), which have implications both for climate and plants. The influence of BVOCs on ozone pollution is significant, both in rural and urban areas (Bao *et al.*, 2010). If ozone concentrations are high and the air is relatively clean of anthropogenic NO_x emissions, the VOCs can also consume ozone, by reacting directly with the O_3 molecule or by the removal of hydroxyl radicals that are formed by products from the photodissociation of ozone (Atkinson and Arey, 2003; Matsunaga *et al.*, 2003; Laothawornkitkul *et al.*, 2009).

Isoprene and isoprenoids are the largest contributors to the formation of secondary organic aerosols (SOA), which can have an important role in the global radiation budget by absorbing and scattering sunlight or by acting as cloud-condensation nuclei (Henze and Seinfeld, 2006; IPCC, 2001). The oxidation of BVOCs lowers their volatility, thus leading to condensation and formation of aerosols. Goldstein *et al.* (2009) found that the spatial and temporal distribution of potentially cooling aerosol clouds over south eastern USA can not be explained by anthropogenic emissions alone, but is consistent with biogenic VOC emissions. They propose that the SOA formed by the combination of anthropogenic and biogenic emissions could be considered a negative radiative forcing caused by humans, regionally comparable with the effects of SO_2 , but there is not enough data to include the BVOC induced aerosols in larger models. Even with a low percentage of VOCs turning into aerosols, they must be considered in climatic models due to the substantial emissions.

Table 1. Chemical lifetimes of the most abundant BVOCs, estimated with regards to different atmospheric concentrations of NO₃ and OH during day and night (Kesselmeier and Staudt, 1999).

| Category | Chemical lifetimes | | Atmospheric concentrations |
|----------------|--------------------|-------------|---------------------------------------|
| | Day | Night | |
| Isoprene | 3 h | 1,5 h | ppt to several ppb |
| Monoterpenes | <5 min – 3 h | <1 – 30 min | ppt to several ppb |
| Sesquiterpenes | <4 min | <2 min | not detectable due to high reactivity |
| Other VOCs | varying | | 1-30 ppb |

2.4 EMISSION MAGNITUDES

BVOCs are emitted from above- and below-ground plant organs. Flowers and fruits have the greatest variety of compounds, but leaves have the largest mass emission rates (Laothawornkitkul *et al.*, 2009). Isoprene and monoterpene emissions from specific plants have been recorded at hundreds of $\mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$ (Kesselmeier and Staudt, 1999), but are generally much lower. Examples of emissions from different ecosystems are given in Table 2.

Total emission of BVOCs has been estimated by different models at 700-1150 Tg C per year, of which more than 50% consist of isoprene and monoterpenes (Lathièrè *et al.*, 2006; Guenther *et al.*, 1995). There are uncertainties to all models, and there are fairly large uncertainties concerning emission controls (Pacifico *et al.*, 2009; Kesselmeier and Staudt, 1999; Laothawornkitkul *et al.*, 2009). However, estimates on global isoprene emission have shown low variation in different reports, but this is possibly due to similarities in the models (Arneth *et al.*, 2008).

Sesquiterpenes often have very short chemical lifetime after release (Table 1), making it hard to measure emissions on a large scale. Duhl *et al.* (2008) compiled several measurements of sesquiterpenes and found a large span of emission rates, from 10s to 1000s of $\text{ng g}_{\text{dw}}^{-1} \text{h}^{-1}$.

Table 2. Examples of estimates on isoprene and monoterpene emission rates from different ecosystems (Guenther *et al.*, 1995). Actual emissions within an ecosystem may show large deviations.

| Ecosystem description | Emission rates ($\mu\text{g C g}_{\text{dw}}^{-1} \text{h}^{-1}$) | |
|--------------------------|--|--------------|
| | Isoprene | Monoterpenes |
| Boreal conifers | 8 | 2,4 |
| Temperate deciduous | 45 | 0,8 |
| Tropical seasonal forest | 16 | 0,8 |
| Tropical rain forest | 24 | 0,4 |
| Savanna | 16 | 0,8 |
| Dry evergreen | 45 | 2,4 |
| Tundra | 16 | 0,8 |

2.5 BIRCH VOC EMISSIONS

Birch species are not the largest BVOC emitters (Kesselmeier and Staudt, 1999), but is thought to increase its land cover in northern regions, at the expense of boreal forests, due to climate change (Kellomäki *et al.*, 2001). The most common birch species emit less isoprene and monoterpenes per leaf dry weight than the vaster Pine and Spruce forests (Table 3).

Isoprene is not emitted to any significant amount from Birches, but monoterpenes, sesquiterpenes and oxygenated VOCs can be substantial (Kesselmeier and Staudt, 1999; Hakola *et al.*, 1998; Haapanala *et al.*, 2009). Hakola *et al.* (1998) showed that the emitted compounds of Silver birch (*Betula pendula*) vary a lot during the course of a growing season, and among individual trees, and the same variations apply for the Downy birch (*Betula pubescens*) (Hakola *et al.*, 2001). Mountain birch (*Betula pubescens ssp. czerepanovii*), which is a subspecies of the Downy birch, have not been examined thoroughly regarding its VOC emissions. Haapanala *et al.* (2009), who did measurements at the same location this study was performed, recorded a large variation of monoterpenes and sesquiterpenes, with slightly higher emission potential than those of the Downy birch. Other VOCs, especially linalool, were also emitted at fairly large rates.

Vuorinen *et al.* (2005) analyzed the effect of elevated CO₂ and O₃, and a combination of these, on Silver birch VOC emissions, with no significant result.

Birches do not store terpenes to a significant amount, since they lack resin ducts or other long term storage compartments (Haapanala *et al.*, 2009). This property means that the emissions of all compounds should be closely related to the photosynthesis (i.e. light and temperature).

Table 3. Isoprene and monoterpene emission potentials at standard temperature (30°C) and PAR (1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$) of the most common tree species of Sweden, Norway spruce and Scots pine, as well as the most abundant birch species (Skogsdata 2010, www.slu.se), Silver birch. (Kesselmeier and Staudt, 1999)

| Tree species | Emission rates | |
|--|--|--------------|
| | ($\mu\text{g g}_{\text{dw}}^{-1} \text{h}^{-1}$) | |
| | Isoprene | Monoterpenes |
| Norway spruce (<i>Picea abies</i>) | 0,34-1,8 | 0,2-7,8 |
| Scots pine (<i>Pinus silvestris</i>) | - | 0,8-12,1 |
| Silver birch (<i>Betula pendula</i>) | 0 | 0,19-5,4 |

2.6 UNCERTAINTIES

Much of the BVOC research has been made during the last two decades, and understanding of the functions of these compounds and the mechanisms behind their emissions has increased, though uncertainties are still great (Laothawornkitkul *et al.*, 2009). Most measurements of BVOCs are short term experiments, and the algorithms used to describe emission potentials do not take into account any long term effects of e.g. elevated temperature or radiation (Kesselmeier and Staudt, 1999; Peñuelas and Staudt, 2010). A change in modelling algorithms is also needed since upscaling of leaf or canopy based emission measurements of monoterpenes have failed to describe seasonal variations (Kesselmeier and Staudt, 1999; Schurgers *et al.* 2009). Niinemets *et al.* (2004) argued that current models might not reflect the emissions, based on a

lack of physiochemical controls in the simulations. This is something which could be incorporated in various new emission algorithms that are not focusing solely on the environmental variables temperature and light, but rather consider processes within the plant (Grote and Niinemets, 2008).

It can be hard to compare results from different studies and models. There is a large variation in both magnitude and content of the emission from different plants (Kesselmeier and Staudt, 1999). Furthermore, the emission capacity may differ largely within a species, depending on the measurement site. Especially, laboratory studies, usually on young plants, have shown different behaviour compared to mature, wild growing plants. Even within a group of plants of the same species at the same site, emissions may differ largely, partly due to herbivore outbreaks (Haapanala *et al.*, 2009). The measurement technique used can also affect the results. Measurements on a single branch or leaf are hard to extrapolate to a forest or ecosystem, but might be able to capture compounds that can not be found in ecosystem-scale measurements.

With a lack of measurements and emission controls not fully understood, all modelling and conclusions are precarious.

2.7 BVOC EMISSIONS IN THE FUTURE

With a changing climate the processes involved in BVOC production and emission will also change. This possible climatic feedback has not been given much attention compared to the CO₂ budget in general (Peñuelas and Staudt, 2010). A simulated climate warming (1,9°C and 2,5°C) in a subarctic tundra doubled the BVOC emissions (Faubert *et al.*, 2010).

Future scenarios that might effect plant emissions include increases in temperature, atmospheric CO₂ levels and plant production rates, as well as a land-use change with more cropland and less tropic forests. There is a strong correlation between increased temperature and increased BVOC emission, given both by a higher synthesis rate of the compounds and by an increased vapour pressure (Guenther *et al.*, 1995; Peñuelas and Staudt, 2010). The climatic warming during the last 30 years may already have induced an increase in BVOC emissions by 10% (Peñuelas and Staudt, 2010), as calculated with the common emission algorithms. A model, based on the IPCC A1B scenario (IPCC, 2007), by Heald *et al.* (2008) estimates an increase in BVOC emissions of 22% and biogenic SOA of 26% by 2100. This however does not take into account a possible decrease in emissions due to higher concentrations of ambient CO₂, which is thought to inhibit isoprene emissions (Arneth *et al.*, 2007). Climate-driven changes in vegetation, mainly the recession of tropical forests, can also lead to less isoprene being emitted (IPCC, 2007). More research is needed to fully understand the mechanisms and feedbacks a changed climate might impose on BVOC emissions.

3. Materials and methods

3.1 STUDY AREA

The measurements took place during three days in July 2008 at Stordalen near the village of Abisko (68°21'N,18°49'E), northern Sweden, about 200 km north of the arctic circle (Figure 3). The mean annual temperature in Abisko between 1961-1990 (WMO reference period) is -0,8°C (data from Swedish meteorological institute, SMHI: www.smhi.se). Mean temperature during this period is below 0°C from November to

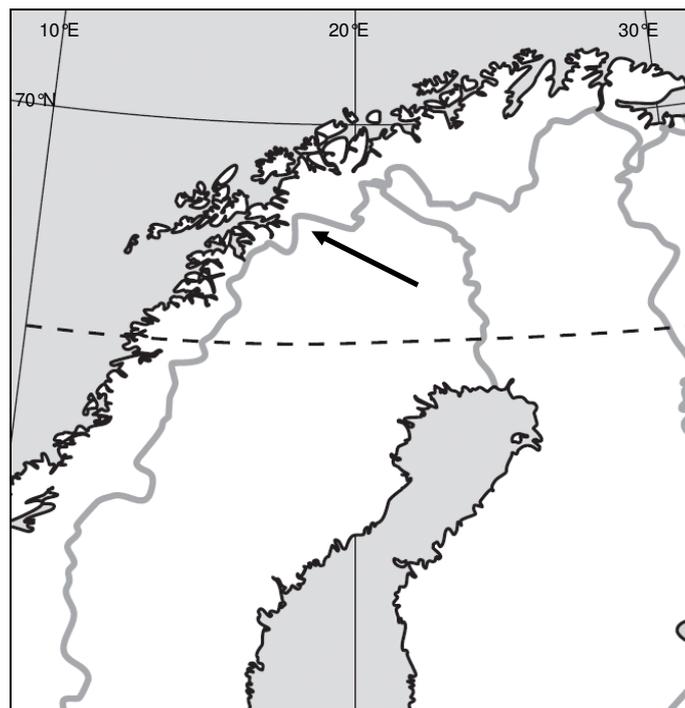


Figure 3. Map (scale roughly 1:13 000 000) showing northern Scandinavia from about 61-71°N. Dashed line is the arctic circle (66° 33' 44"). Arrow is roughly pointing at the Stordalen national park.

April, resulting in a very short growing season. The area is dry with an annual precipitation around 300 mm, of which a lot is snow. July is the warmest (11,0°C) and wettest (53,7 mm) month. Mean annual temperature in 2008 was 0,4°C (data from Abisko scientific research station, www.linnea.com/~ans/). The three days of measurements were all sunny and among the warmest of the year (Figure 17), but mean temperatures of July and preceding months were less than 1°C off the reference period's monthly average.

Today, birch forests account for 13 % of Sweden's total forest area (Skogsdata 2010, www.slu.se), but most of these consist of Silver birch, *Betula pendula*. The Mountain birches (*Betula pubescens ssp. czerepanovii*) growing in Stordalen are small, sometimes shrub like, trees. The canopy is at a height of about 4,5 m. This birch species is common in high-latitude ecosystems, often forming the tree line between the vast, boreal coniferous forests and bare mountains.

3.2 SAMPLING

3.2.1 BVOC emissions

Measurements were made between 28-30th of July 2008, using the approach described by Ortega *et al.* (2008), with a flow-through chamber technique. A branch of the Mountain birch was enclosed in a chamber, assembled at Lund university (Figures 4 and 5). The chamber is covered with a transparent Teflon film where BVOCs do not stick. Air, that was cleaned from hydrocarbons and ozone, was pumped into the system at a rate of approximately 5 l min⁻¹. Air from inside the chamber was pumped through tubes, which trap the BVOCs, at a rate of 220 ml min⁻¹. These tubes contain two adsorbing agents, Tenax TA, a porous organic polymer, and Carbograph ITD, graphitized carbon black, which are designed to trap volatile and semi-volatile

compounds (detailed descriptions of the tubes and manufacturer are available in Ekberg *et al.*, 2009). A reference tube, with the same flow rate, was also taken of the inflow air. The tubes were changed each hour and closed with long-term storage caps. Around ten sample tubes were collected each day.



Figure 4. Branch chamber, with inflow and outflow tubes. All components inside the chamber were covered with Teflon, on which surface BVOCs do not stick. The chamber was carefully set up at a height of about 1,5 m, facing south making sure it was sunlit during all of the day. Condensation (see picture) occurred inside the chamber during most measurements. Photo: Thomas Holst.

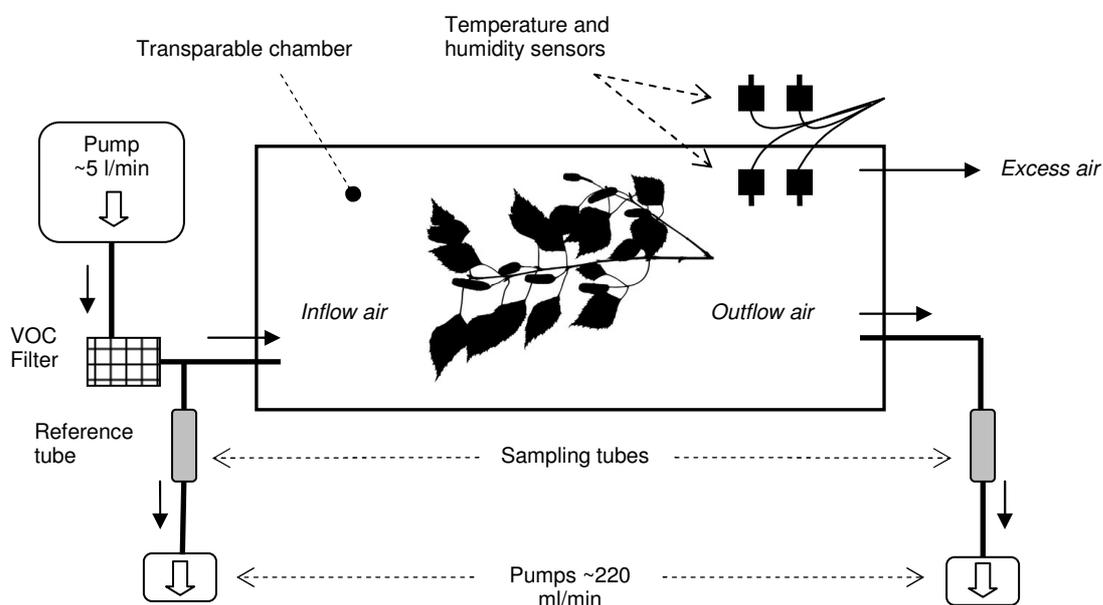


Figure 5. Schematic picture of the branch chamber measurements. The chamber is covered by a transparent, Teflon film. Excess air is flowing out of gaps in the chamber, which has a slight overpressure. Sampling tubes were exchanged after one hour. In addition to the above set-up, measurements of the flow rates into the chamber and into the tubes were taken in order to calculate concentrations of captured compounds.

A number of preventive actions were taken to inhibit unnatural emission patterns. The branch set up was made as gentle as possible, one day prior to measurements, so that induced emission, from tempering of the branch and leaves, was reduced. The chamber was open at all times except when measurements took place. It was also flushed with cleaned air during ten minutes prior to sampling initiation so that BVOCs emitted during other times of the day were not measured.

Due to lack of time, the tubes were stored in a refrigerator for one year, before the content was quantified and identified by gas chromatography-mass spectrometry (GC-MS) at the Finnish Meteorological Institute's air chemistry laboratory, giving a result in ng m^{-3} for twenty compounds that was found in the samples. GC-MS is an analysis method combining separation (chromatography) and identification (mass-spectrometry) of compounds in a sample. The samples were volatilized by heating of the tubes, and then condensed in a cold-trap. A secondary evaporation by heating leads the gases into the GC. Only compounds that were available as reference samples at the time of analysis could be identified.

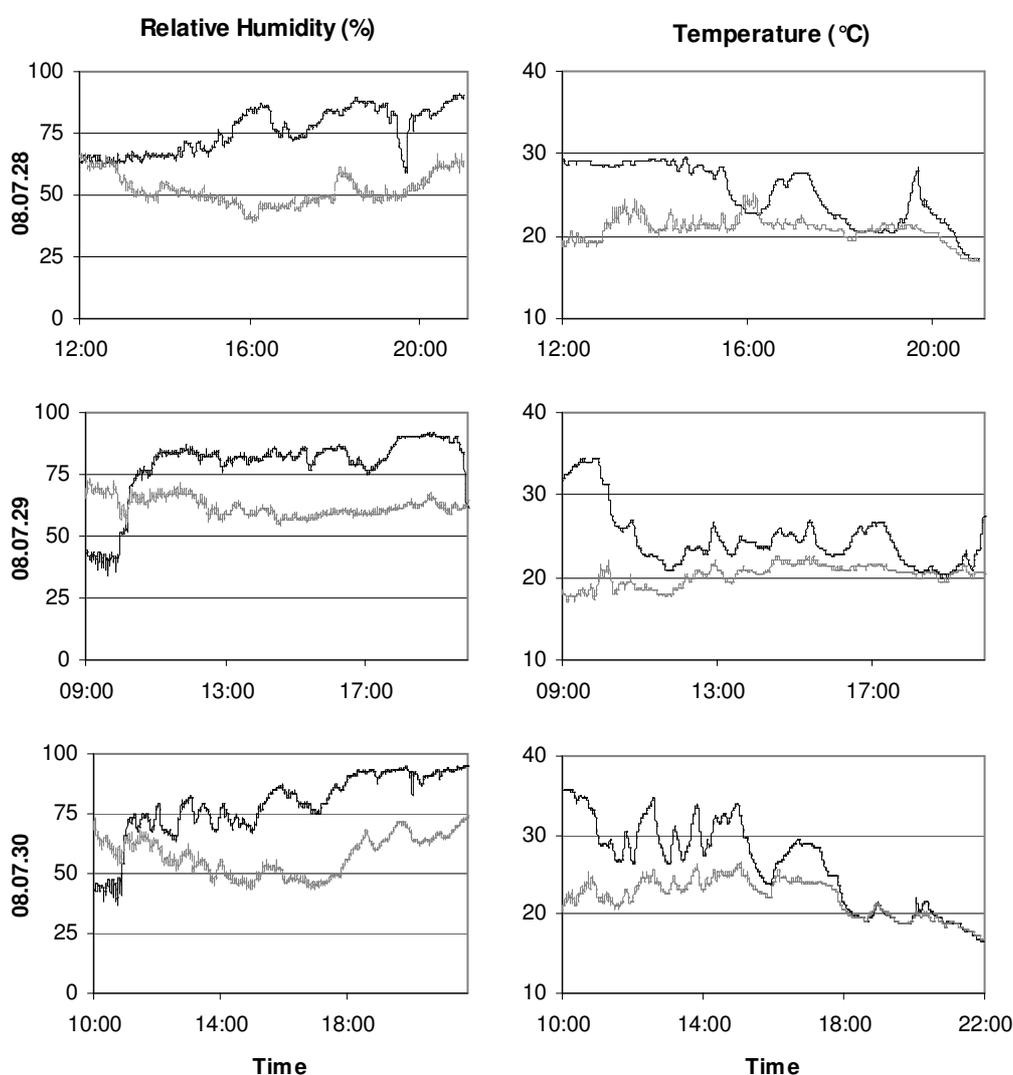


Figure 6. Daily variation of relative humidity and temperature inside the chamber (black) and in ambient air (grey) during measurements. The chamber was flushed before measurements but it is clear that the temperature did not reach ambient levels. As expected, the relative humidity increased within the chamber during measurement. The close relationship between the two variables is also shown, as rapid increases in temperature results in a dip in relative humidity.

Continuous measurements of temperature and humidity were taken inside the chamber and on ambient air, both showing significantly higher values inside the chamber (Figure 6), due to the relatively stationary air. Especially the elevated temperature affects VOC emissions. All leaves on the branch inside the chamber were collected after the last day of measurements and were later dried and weighed in order to convert the results from the GC-MS into emissions per gram leaf dry weight ($\text{g}_{\text{dw}}^{-1}$). The leaves' area was also measured. One leaf inside the chamber had turned yellow.

PAR was measured within a few meters of the chamber set up. The sensor was placed above the canopy so that it was only shadowed by clouds.

3.2.2 Photosynthesis

Photosynthesis was measured on leaf level by an infra-red gas analyzer, LI6400. This is a widely used portable system in which a single leaf is strapped onto a cuvette, in a closed environment. The leaf should cover the area of the cuvette so that fluxes can be measured directly per area unit. Humidity, temperature and CO_2 concentration of the inflow air is controlled. The PAR is also set manually, but was set to follow ambient variations. Photosynthesis is calculated directly, as $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$. This rate was transformed into $\mu\text{g (C)} \text{ g}_{\text{dw}}^{-1} \text{ h}^{-1}$ by multiplying by the mol weight of carbon (12) and dividing by the leaf dry weight per m^2 . During the first two days, temperature was locked at 25°C and 22°C respectively.

3.2.3 PAR

PAR was measured in a tower reaching above the canopy. Additionally to PAR, the tower was also mounted with a sensor measuring temperature. This series of measurement stretched from early June to late November 2008, and can be used to see how BVOC emissions correlate to long term changes in PAR and temperature (Figure 7).

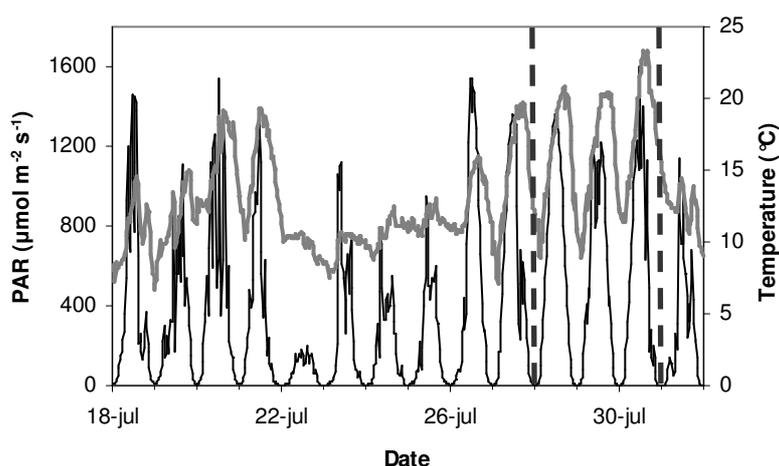


Figure 7. Variations in temperature (grey) and PAR (black) measured above the canopy during two weeks, including the days of measurement (28-30th of July, marked with dashed lines).

3.3 EMISSION POTENTIALS

To be able to compare the results to other measurements, a standardized emission potential was calculated. The most commonly used standard values are at a PAR of $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ and a temperature of 30°C . These values are unrealistic at subarctic sites and therefore an additional calculation using a temperature of 20°C was made, since this is more in accordance with realistic maximum temperatures of the growing season. This value was also used by Ekberg *et al.* (2009) and Haapanala *et al.* (2009), whose studies were also conducted near Abisko.

Calculations were made using the common algorithms describing the correlation of VOC emission to PAR and temperature developed by Guenther *et al.* (1993) and slightly modified by Guenther *et al.* (1997).

3.3.1 Fluxes

The results from the mass-spectrometry (ng m^{-3}) were transformed into fluxes after transformation of variables into appropriate units (Eq. 1);

$$E_{rate} = \frac{(C_{out} - C_{in}) \cdot V}{g_{dw} \cdot t} \quad (1)$$

where E_{rate} is the emission rate, C_{out} is the concentrations of VOCs in the sample tube taken off the outflow air, C_{in} is the concentrations of VOCs in the sample tube taken off the inflow air, V is the volume of air that passed through the chamber, g_{dw} is the leaf dry weight and t is the duration of the measurement. Resulting units are $\text{ng g}_{dw}^{-1} \text{h}^{-1}$.

The cleaned inflow air showed very low VOC concentrations, likely within the error margin of the GC-MS, but since some compounds were not emitted by the birch at any large rates the fluxes could show (very small) negative values. These values did not change the relative importance of any group of compounds, and were not used in further calculations.

3.3.2 Temperature and light dependent compounds

The model describing emissions that are dependent on both temperature and light, mostly used only for isoprene, is (Guenther *et al.* 1993):

$$I = I_s \cdot C_L \cdot C_T \quad (2)$$

where I is the isoprene emission rate from the chamber measurements, I_s is the isoprene emission rate at standard temperature and PAR (emission potential). C_L describes the light dependency (Figure 2) by

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{1 + \alpha^2 L^2}} \quad (3)$$

where L is PAR ($\mu\text{mol m}^{-2} \text{s}^{-1}$). α ($=0,0027$) and C_{L1} ($1,066$) are empirical coefficients.

C_T describes the temperature dependency (Figure 2) by

$$C_T = \frac{\exp\left(\frac{C_{T1}(T - T_S)}{RT_S T}\right)}{C_{T3} + \exp\left(\frac{C_{T2}(T - T_M)}{RT_S T}\right)} \quad (4)$$

where T and T_S (K) are measured and standard temperature, R ($=8,314 \text{ J K}^{-1}$) is the universal gas constant, T_M ($=314 \text{ K}$), C_{T1} ($=95000 \text{ J mol}^{-1}$), C_{T2} ($=230000 \text{ J mol}^{-1}$) and C_{T3} ($=0,961$) are all empirical coefficients.

To find the most accurate emission potential, a series of calculations and tests was completed. C_T and C_L was calculated at each sample point using the measurements of temperature and PAR. These were used to obtain a set of values for I_S for the measured emission rates, using Eq. 2. The mean value of I_S was then used to calculate modeled values for I . In order to get the best fit, values close to the mean (at an accuracy of $0,5 \text{ ng g}_{\text{dw}}^{-1} \text{ h}^{-1}$) were modeled and tested by calculating the root mean square error (RMSE, Eq. 5), which has the same units as the emission potential (Figure 8).

$$RMSE = \sqrt{\frac{\sum (E_i - E_{pot,i})^2}{n}} \quad (5)$$

$$NRMSE = \frac{RMSE}{E_{\max} - E_{\min}} \quad (6)$$

The emission potential value that yielded the smallest RMSE was chosen (Figure 8). This is a fairly good measure of the models but is complicated by the seemingly sensitive emission patterns, with violent variations that the models fail to describe. RMSE was normalized by division of the sample intervals in order to be able to compare different compounds (Eq. 6). Resulting NRMSE takes on values between 0-1 and can be viewed as a percentage of the measurement interval.

3.3.3 Temperature dependent compounds

VOCs that are thought to be stored inside the plant are best described by an algorithm which is only temperature dependent (Guenther *et al.*, 1993). This model is most often used for monoterpenes and sesquiterpenes:

$$M = M_S \cdot \exp(\beta(T - T_S)) \quad (7)$$

where M is the emission rate at temperature T (K), M_S is the emission rate at standard temperature T_S (K) and β (K^{-1}) is an empirical coefficient set to 0,09 for monoterpenes (Guenther *et al.*, 1993) and 0,18 for sesquiterpenes (Haapanala *et al.*, 2009; Duhl *et al.*, 2008). The most accurate emission potential is found using the same approach as for the temperature and light dependent algorithm (Eq. 2).

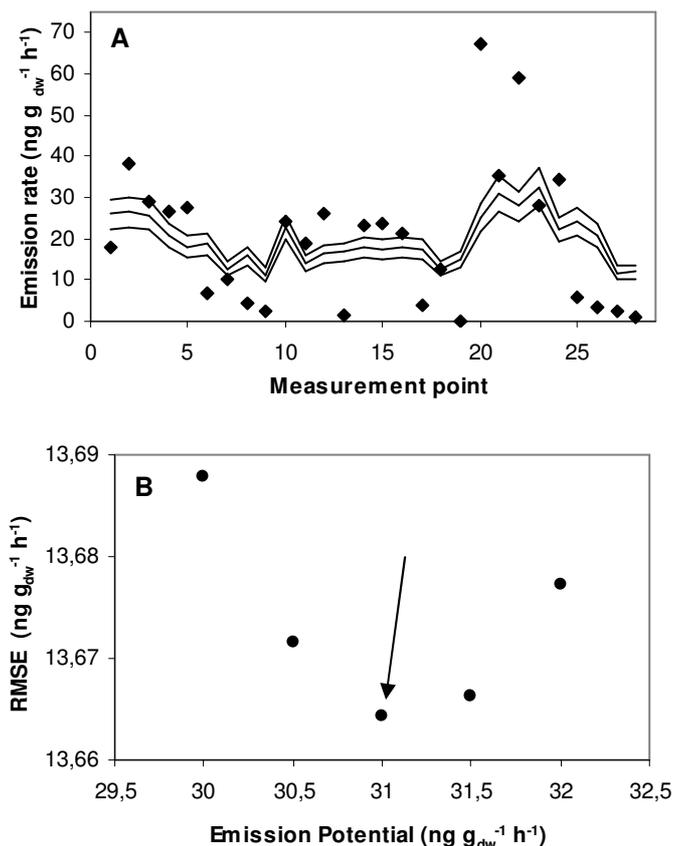


Figure 8. Emission potentials were chosen by minimizing the RMSE. The simulated emissions of three different emission potentials are plotted over the measurements (dots) in (a). The RMSE of the modeled data for different emission potentials were calculated, until a minimum (arrow) was found (b). Figures show emission potentials of monoterpenes calculated using the temperature dependent algorithm with a standard temperature of 30°C.

4. Results

4.1 EMISSIONS

The Mountain birch emitted a wide variety of compounds, with Linalool being the most substantial (Table 4, Figure 10). Linalool emissions accounted for half of all the mass emitted during the three days of measurements. Second to Linalool was an array of compounds at similar emission rates, with α -Humulene, β -Caryophyllene, Isoprene, Limonene, and α -Pinene at between 5-10% of total mass emitted. This emission pattern was kept throughout the experiment.

A test in near darkness was conducted at the end of one of the measurement days. Although emissions decreased quickly, the sesquiterpene isomers α -Humulene and β -Caryophyllene was released to some extent (between 10-40 ng m⁻³, which equals up to 2 ng g_{dw}⁻¹ h⁻¹), while all other BVOCs that were detected approached 0 ng m⁻³.

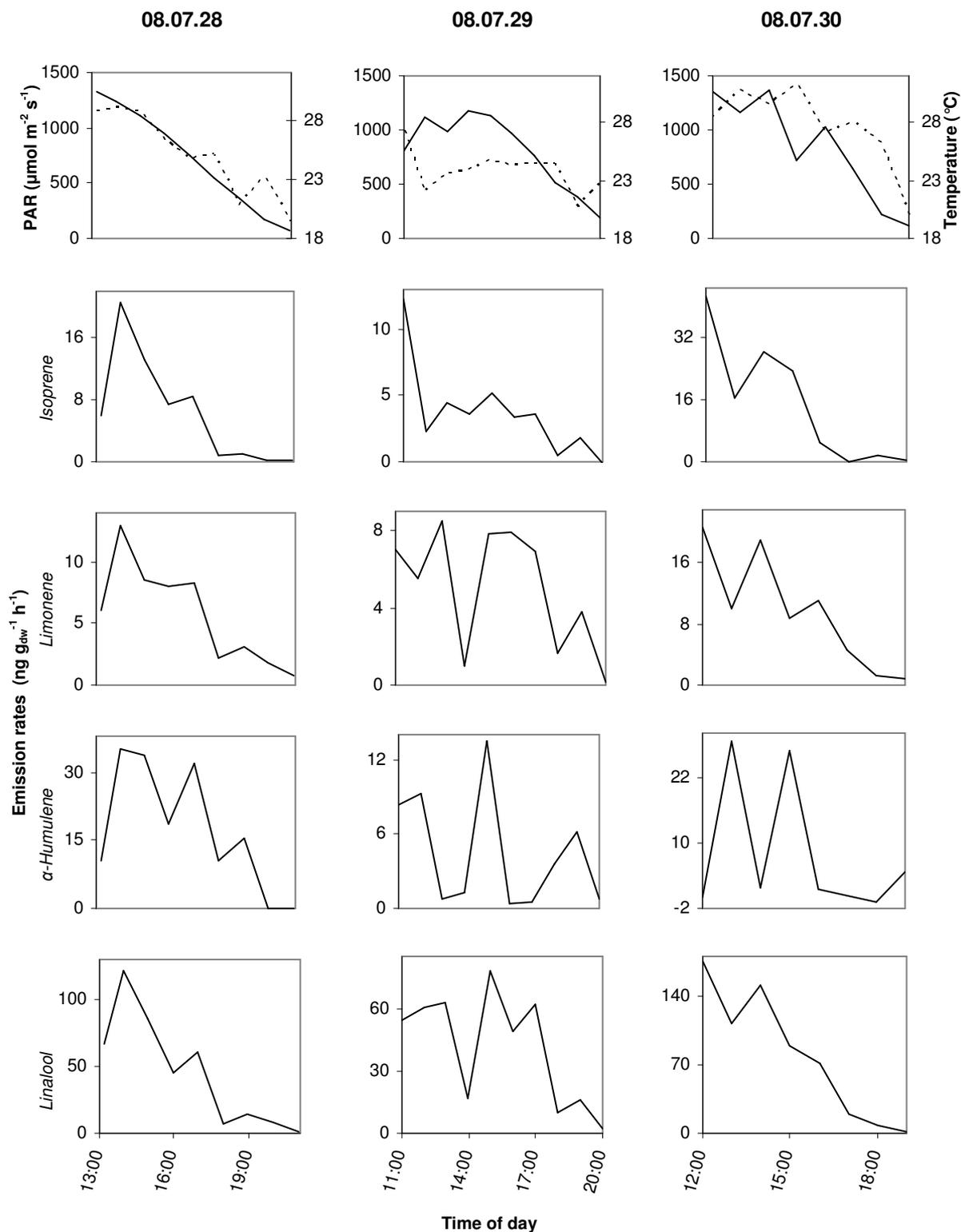


Figure 9. The daily variations of PAR and temperature (dashed line) during the three days of measurements are shown on the top row. The emissions of the compounds Isoprene, Limonene (Monoterpene), α -Humulene (Sesquiterpene) and Linalool (Monoterpenoid, alcohol), show variations that are mostly similar to each other, but much more violent than those of PAR and temperature.

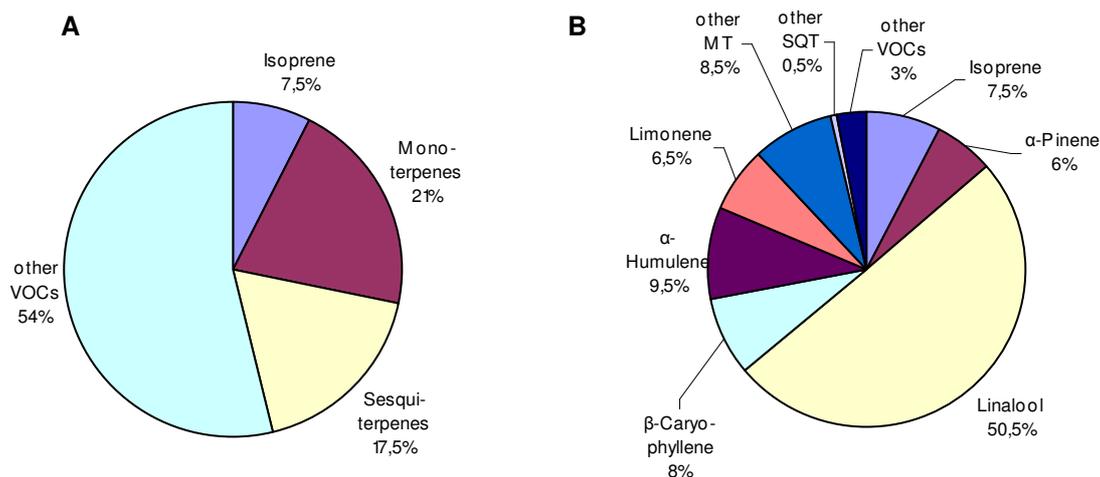


Figure 10. Relative mass importance of emissions for (a) groups of compounds and (b) specific compounds. These mutual magnitudes were not changed drastically from day to day.

Table 4. A list of all the compounds that were measured. The group “Other VOCs” include all compounds not sharing the molecular formula of monoterpenes or sesquiterpenes. The ones measured here are all terpenoids, including 3 monoterpene alcohols.

| Compound | % of total emission | Molecular Formula |
|-----------------------------|---------------------|-------------------|
| <i>Isoprene</i> | 7,6 | C_5H_8 |
| ----- | | |
| <i>Monoterpenes</i> | 20,8 | $C_{10}H_{16}$ |
| α-Pinene | 6,2 | |
| Camphene | 0,2 | |
| β-Pinene | 3,3 | |
| Carene | 2,1 | |
| Terpinolene | 2,6 | |
| Limonene | 6,3 | |
| ----- | | |
| <i>Sesquiterpenes</i> | 17,7 | $C_{15}H_{24}$ |
| Longicyclene | 0 | |
| Alloaromadendrene/Farnesene | 0,2 | |
| α-Humulene | 9,5 | |
| Aromadendrene | 0,1 | |
| β-caryophyllene | 7,9 | |
| Longifolene | 0 | |
| Iso-Longifolene | 0 | |
| ----- | | |
| <i>Other VOCs</i> | 53,9 | |
| P-Cymene | 1,8 | $C_{10}H_{14}$ |
| Linalool | 50,7 | $C_{10}H_{18}O$ |
| Bornylacetate | 0,2 | $C_{12}H_{20}O_2$ |
| 1,8-Cineol | 0,9 | $C_{10}H_{18}O$ |
| MBO (2-Methyl-3-buten-2-ol) | 0,4 | $C_5H_{10}O$ |

4.2 CORRELATION TO TEMPERATURE AND PAR

The emissions were clearly correlated to temperature and PAR (Figures 9 and 11), although it is hard to say which had the strongest influence, since the temperature is generally increased with higher irradiation. Both photosynthesis (production) and a high temperature (volatilization) are needed for emissions to take place. It was clear however that emission approached zero at night time measurements when light was scarce.

The different compound groups were tested individually by normalizing emission rates, both by dividing with the highest value and the average value, and plotting against PAR. A linear trend line was fitted to the values. All groups showed a similar strong response to PAR. Sesquiterpenes had a slightly lower response and more values that were not close to zero at a low PAR, but sample points were deemed too few, and with many outliers, to draw any conclusions on which groups had the strongest or weakest response to PAR.

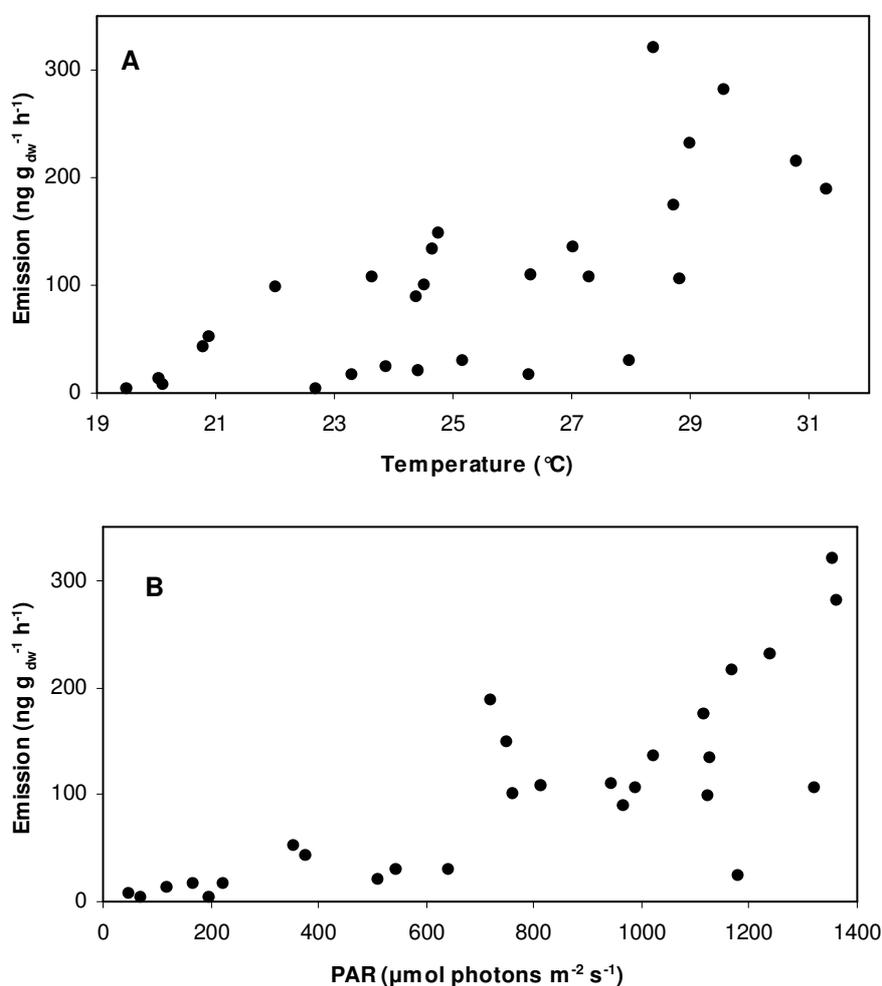


Figure 11. Emission rates of all compounds added together plotted against temperature (a) and PAR (b). Although the relationship seems clear with higher emissions at high PAR and temperature, the measurements are too few and spread out to establish a good curve fit. Furthermore, a clear saturation is not visible (compare to theoretic emissions of Figure 2).

4.3 PHOTOSYNTHESIS

The photosynthetic rate (Figure 12) at saturation level was around $10 \mu\text{mol m}^{-2} \text{s}^{-1}$, which corresponds to $5760 \mu\text{g (C) g}_{\text{dw}}^{-1} \text{h}^{-1}$, which is significantly larger than the maximum emission rates of BVOCs at $\sim 300 \text{ ng g}_{\text{dw}}^{-1} \text{h}^{-1}$ (Figure 11). Because different leaves were used each day, and the temperature was not set to ambient values during the first two days, the photosynthesis at saturation level is very spread out. During the first day, saturation was at $8 \mu\text{mol m}^{-2} \text{s}^{-1}$, which can be seen as a line in the figure. The leaf used this day did not cover the cuvette entirely, resulting in a lower measured photosynthetic rate. The lower saturation values (line at $\sim 6 \mu\text{mol m}^{-2} \text{s}^{-1}$), are from the third day when temperature was variable.

BVOC emission and Photosynthesis were not measured simultaneously at the same conditions. In order to control the correlation between emission and photosynthesis, all values needs to be linked to their corresponding PAR value. Since the PAR values were not measured by the same sensor (see Discussion), such a comparison would be precarious. A correlation is however expected (Figures 12 and 11b), especially at low PAR where neither photosynthesis nor emission have reached saturation levels.

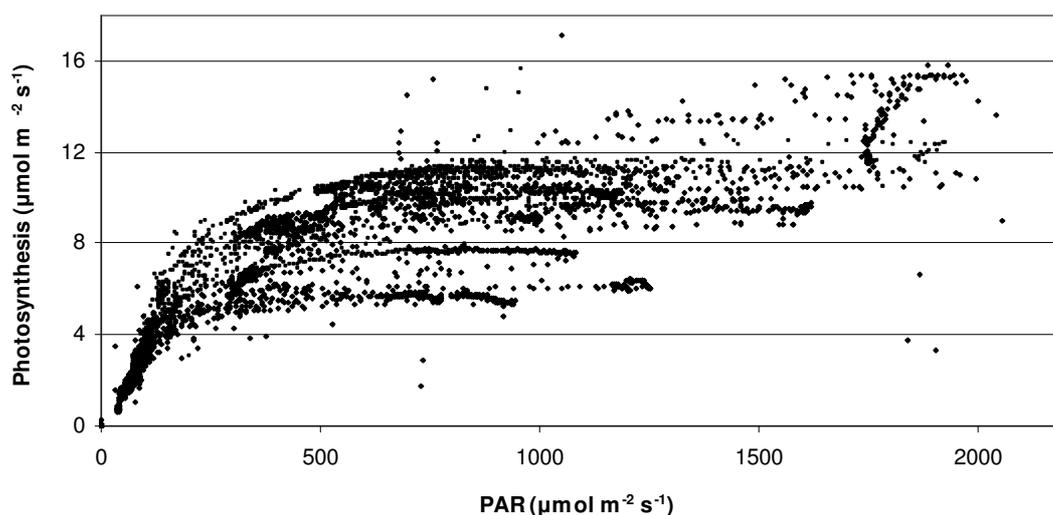


Figure 12. Photosynthesis during the three days of measurements plotted against PAR. Although the sampling points are well spread out, it is clear that the saturation level was reached at a relatively low PAR of $\sim 400 \mu\text{mol m}^{-2} \text{s}^{-1}$. The large variation of PAR at the saturation level is due to different temperatures, which also affect photosynthesis, but also partly because different leaves were used each day, one of which did not cover the area of the cuvette, resulting in lower photosynthesis, with saturation at around $8 \mu\text{mol m}^{-2} \text{s}^{-1}$.

4.4 EMISSION POTENTIALS

Emission potentials were calculated for isoprene, monoterpenes, sesquiterpenes and linalool. For comparative reasons, the emission potentials of monoterpenes and sesquiterpenes were calculated using both the temperature dependent algorithm (G_{TEMP}) and the temperature and light algorithm (G_{TL}) (Table 5). The emission potential of Linalool, the compound that by far was emitted at the largest rate, was calculated, using G_{TL} , at $28,5$ ($T_{\text{S}} 20^{\circ}\text{C}$) and 104 ($T_{\text{S}} 30^{\circ}\text{C}$) $\text{ng g}_{\text{dw}}^{-1} \text{h}^{-1}$ respectively, with a NRMSE of $0,166$.

Table 5. Emission potentials ($\text{ng g}_{\text{dw}}^{-1} \text{h}^{-1}$) for monoterpenes and sesquiterpenes, at different standard temperatures, using both the temperature dependent algorithm (G_{TEMP}) and the temperature and light dependent algorithm (G_{TL}). Normalized root mean square errors (NRMSE) are shown in parenthesis, and takes on values from 0-1.

| Compounds | G_{TEMP} | | G_{TL} | |
|----------------|---|-------------------------------------|-------------------------------------|-------------------------------------|
| | $\beta_{\text{MT}} = 0,09 \text{ K}^{-1}$ $\beta_{\text{SQT}} = 0,18 \text{ K}^{-1}$ | | | |
| | $T_{\text{S}} = 20^{\circ}\text{C}$ | $T_{\text{S}} = 30^{\circ}\text{C}$ | $T_{\text{S}} = 20^{\circ}\text{C}$ | $T_{\text{S}} = 30^{\circ}\text{C}$ |
| Monoterpenes | 12,5 (0,204) | 31,0 (0,204) | 10,5 (0,172) | 38,0 (0,172) |
| Sesquiterpenes | 5,5 (0,235) | 34,5 (0,235) | 9,0 (0,227) | 33,0 (0,227) |

Emission potentials of monoterpenes and sesquiterpenes are of similar magnitudes, as expected by the emission rates. There are differences in how the emission potentials change when using a different standard temperature as input in the G_{TEMP} , in that sesquiterpenes has a stronger response to high temperatures, which can be seen clearly in Figure 13. This property is a consequence of the different β -values and is hard to establish by looking at the measured emissions.

The emission rates did not change drastically for any of the compounds or their relative magnitudes during the three days. This was tested by calculation of daily emission potentials of monoterpenes and sesquiterpenes (Table 6, compare Figure 9). When grouping the compounds there are some differences between the days.

The emission potential values, yielded by the initial calculations, had large variations, depending on the measurement points, and therefore, the chosen values do not fit the measurement variations very well (Figure 15), which can be seen in the NRMSE values that are fairly high. The emissions seem to be much more sensitive to variations in temperature and PAR than the algorithms, although the reasons for emission variations could originate from other properties as well.

The models were compared to the measurements visually (as in Figure 15), but also by plotting estimated values against measured values (Figure 16). The G_{TEMP} algorithm fails to describe the low measured values, partly since the temperature never reached very low values but mostly because the algorithm assumes that all compounds emitted are stored. The G_{TL} algorithm model reaches zero emission with low PAR, which is clearly closer to real values. Both models fail to estimate the highest measured emission rates.

Table 6. A comparison of the emission potentials at $T_{\text{S}} = 30^{\circ}\text{C}$ (303 K), with the same β values as above, calculated per day. Although the days were not dramatically different in emission patterns regarding both magnitudes and composition, there are variations. Monoterpenes were emitted at the largest rate on the third day of measurement, while sesquiterpenes were emitted the most on day one.

| Compounds | G_{TEMP} | | |
|----------------|-------------------|-------|-------|
| | Day 1 | Day 2 | Day 3 |
| Monoterpenes | 28,5 | 27 | 35,5 |
| Sesquiterpenes | 46 | 27,5 | 30 |

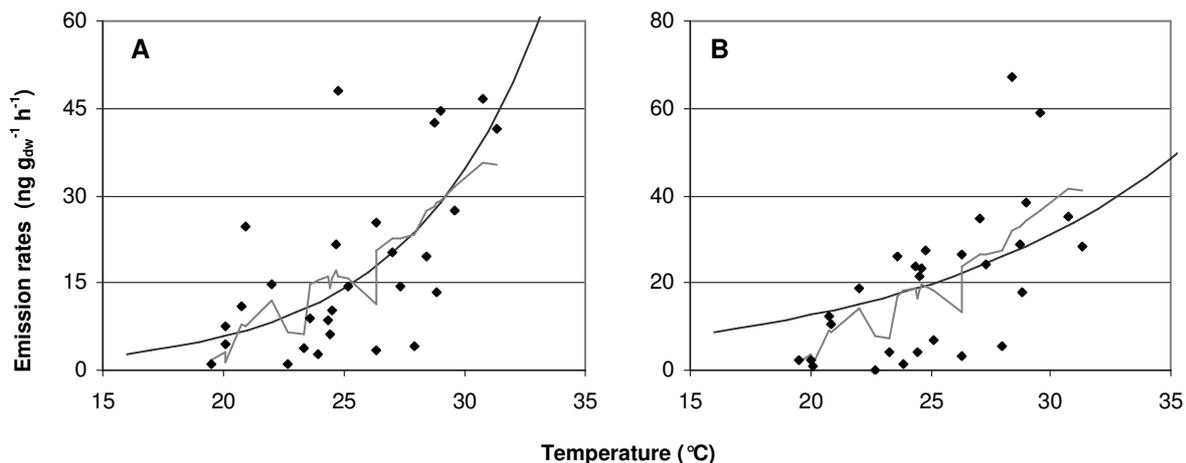


Figure 13. The emissions of sesquiterpenes (a) and monoterpenes (b) plotted against temperature. Solid black line shows the modelled emission according to the temperature dependent algorithm, G_{TEMP} , with a standard temperature of 20°C. Solid grey line shows the modelled emission when calculated with the G_{TL} algorithm at the underlying PAR value of the measurements, standard temperature 20°C. As shown in the graphs, the G_{TEMP} model strictly increases with temperature.

In order to see how emissions would change during the season, PAR and temperature data from above the canopy were used in a model describing linalool emissions according to the G_{TL} algorithm with a standard temperature of 20°C, from early June to early September (Figure 14). The emissions are much lower than those measured (Figure 9), since the three days in July were very warm and also since the temperature inside the chamber were higher than ambient values (Figure 6). Seasonal emissions are most likely very different from this model, since it only uses two variables, and do not take any seasonal emission patterns into account.

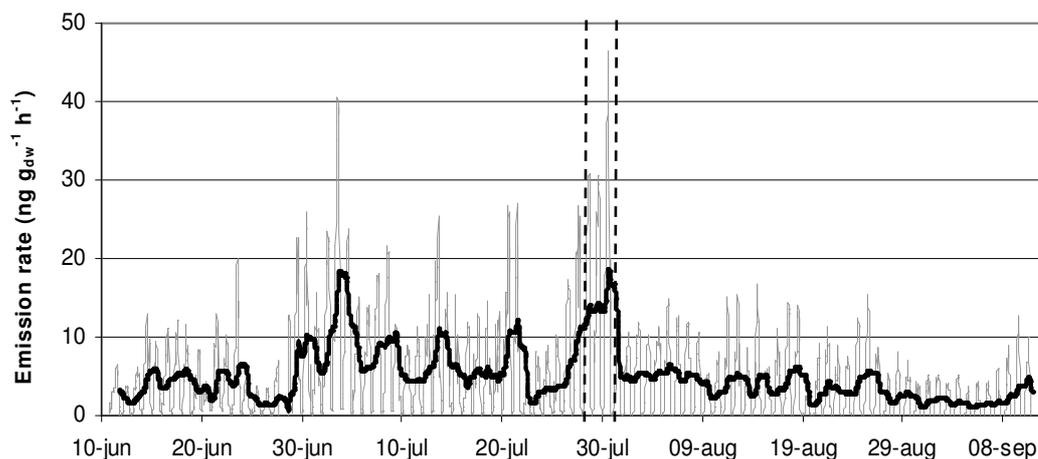


Figure 14. The seasonal pattern of linalool emission plotted with the G_{TL} model (grey line) and temperature data from a sensor above the forest canopy. Thick black line is a moving average of daily emissions. Dashed vertical lines marks the time measurements were made (compare figure 9). The above pattern is a model that do not account for the plants' growing patterns or compound regulation by gene expression. True seasonal emissions would most likely look very different.

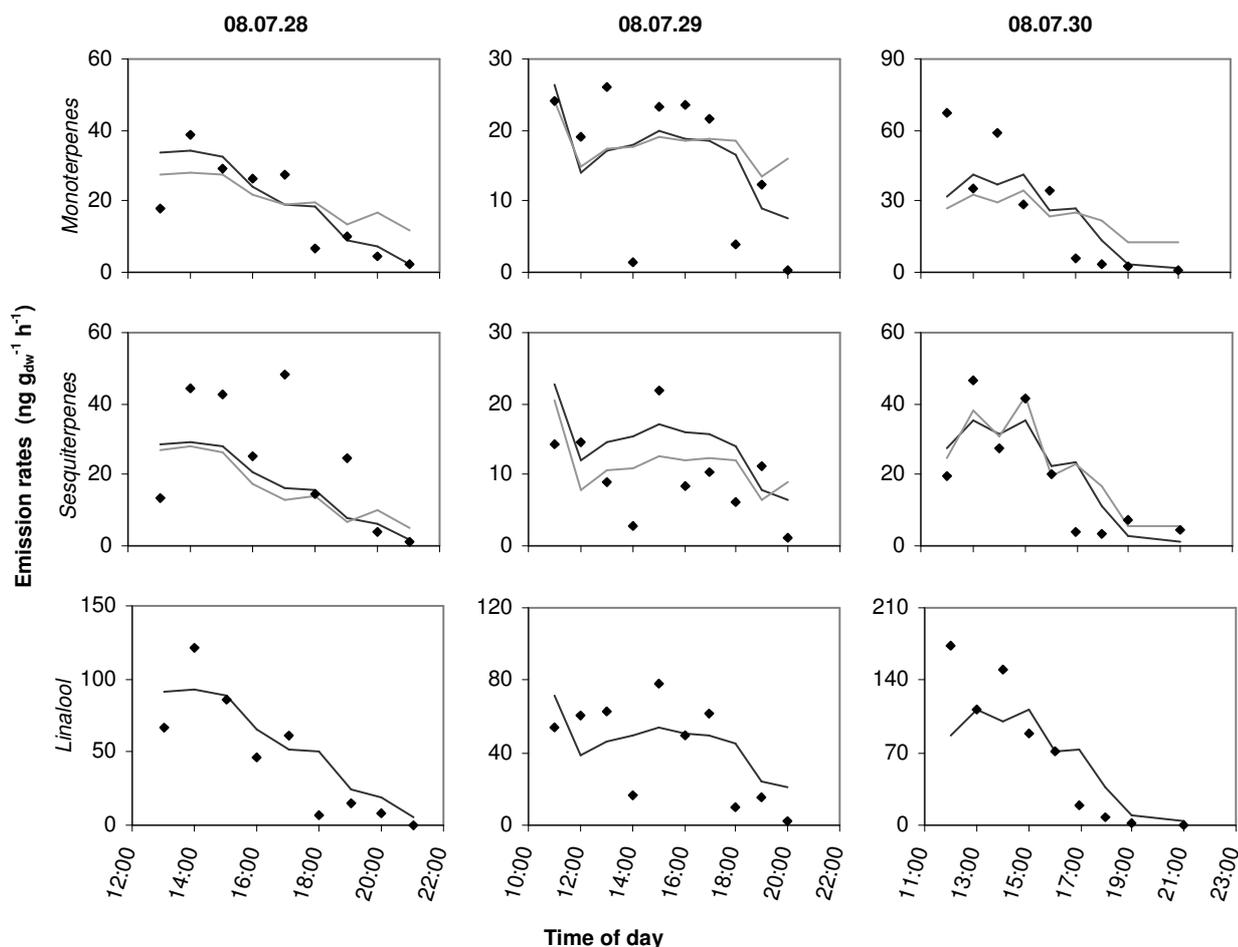


Figure 15. Emission rates (dots) plotted together with modelled emission (solid lines) for the two main BVOC groups; monoterpenes and sesquiterpenes, as well as the main compound emitted; linalool. Black lines show the G_{TL} model that is dependent on both temperature and PAR. Grey lines show the G_{TEMP} model (for monoterpenes and sesquiterpenes), which is only dependent on temperature. Standard temperature is 20°C and standard PAR is 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$.

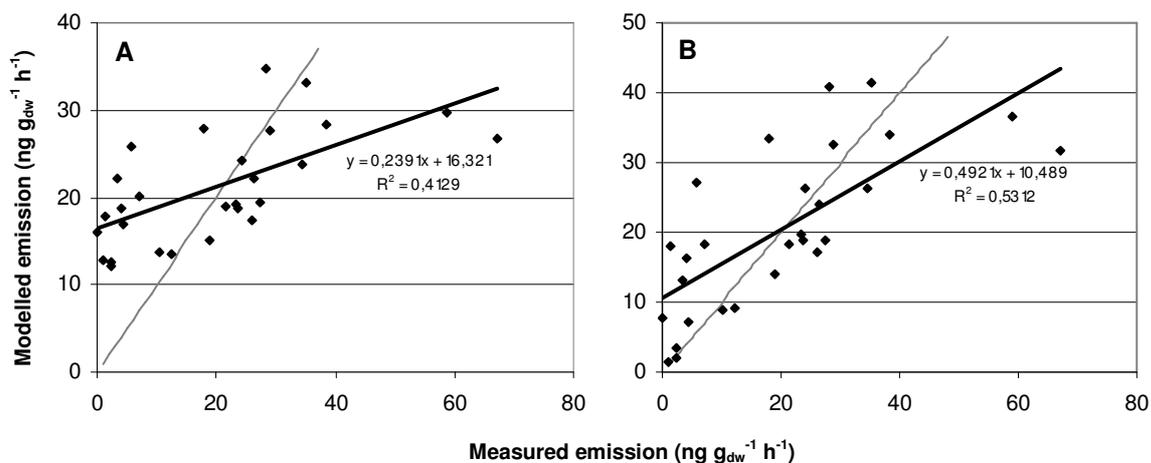


Figure 16. Modelled monoterpene values, from G_{TEMP} (a) and G_{TL} (b), are plotted against measured values at a standard temperature of 30°C. The ideal relationship between model and measurements is depicted by the grey line, $y = x$. No models were close to this value.

5. Discussion

5.1 SOURCES OF ERROR

5.1.1 Measurements

Making an experimental set up, that is to mimic natural conditions during measurements inside a chamber, can have several implications. Although relative humidity is thought not to affect VOC emissions to any large degree (Kesselmeier and Staudt, 1999), the condensation droplets that occurred inside the chamber during the measurements (Figure 4) might have caught any hydrophilic compounds that were emitted. Although the chambers were flushed prior to measurements, the temperature was significantly higher than that of ambient air, even during the first samples of the day. This implies that the branch inside the chamber did not experience natural variations in the environmental variables that affect BVOC emissions and that flushing the chamber for ten minutes was insufficient. Elevated temperatures inside the chamber can also volatilize compounds that would otherwise be stored inside the plant. All of those compounds are flushed out before measurements and, any emissions afterwards will be solely dependent on synthesis. At some points the temperature sensors were sunlit, probably accounting for some of the steep slopes in the temperature diagrams (Figure 6).

PAR was measured by two sensors nearby the chamber, with differing results. The LI6400 sensor was slightly tilted towards the south and recorded much higher values than the sensor at the top of the canopy that was placed horizontally (Figures 11 and 12). The values from the canopy measurement were deemed better since the other set of values were clearly disturbed, by shadowing of twigs or people, at some points and certain sample times were missing. Also, even if the sensor that was tilted towards the sun show a more accurate incident PAR, all leaves are not facing the same direction. The PAR used in the analysis should be thought of as an average for the leaves in the chamber, since it is impossible to obtain the true value of incident PAR on each leaf. This is also important to keep in mind when modeling emissions from a forest using measurements on sun leaves.

To be able to confidently say anything on BVOC emissions from Mountain birches in general, more samples are needed. Hapanala *et al.* (2009) investigated the emissions of several trees and found large variations, which might be a property of the Mountain birch, but can also be a result of the small scale and short-term experiments. A long term experiment on several trees would be ideal, but is costly and time-consuming.

5.1.2 Analysis and modelling

The sample tubes were stored refrigerated for a year before they were opened for analysis. This might not have had an impact on the results, but a shorter storage time would eliminate doubts.

The fact that all compounds emitted and caught in the sample tubes, might not have been found in the analysis have large implications for the results of the study. Identifying unknown substances in the GC-MS analysis is dependent on reference samples being available. The compounds that are found and analyzed in this study might therefore not be all of the compounds emitted. This makes the usual grouping of compounds (monoterpenes, sesquiterpenes) very risky, since it can not be said if a specific compound in a group is missing. The monoterpene Sabinene, which was emitted in large amounts (more than 50% of total emission mass from one tree) during the Mountain birch measurements made by Haapanala *et al.* (2009), is one of

the compounds that were not identified in the samples of this study, due to the lack of reference samples for the GC.

Although most compound emissions, except for isoprene, in most plants, are calculated using G_{TEMP} , slightly better fits, according to RMSE, were achieved using G_{TL} . The emission potentials and the modelled values derived from these, do not describe measured values very well, but it seems rather clear that all emissions are slightly better explained by a model that is dependent on PAR and temperature, rather than temperature alone (Figure 13, Figure 15, Table 5). This might be due to external impact, such as an elevated temperature during a long period of time that volatilized stored compounds, or because the production rate of terpenes were quite low, but can also be a feature in the Mountain birch's emission pattern. This is contradicted by Haapanala *et al.* (2009) who got slightly better fits using the G_{TEMP} algorithm, but also had much larger emissions. In their analysis a variable β -value was also tested, which further improved the results. This implies that the empirical constants of the algorithms used should be updated, and are perhaps unique to each species and ecosystem.

5.2 RESULTS

The emission rates of this study are much lower than expected. Monoterpene and Sesquiterpene emission potentials are only a fraction of those reported by Haapanala *et al.* (2009), which to my knowledge is the only recent study on Mountain birches that has been made. They did measurements on four trees in 2006 (two years prior to the measurements analyzed in this study) with monoterpene emission rates (G_{TEMP} , 20°C, $\beta=0,09$ °C⁻¹) from 188-4090 ng g_{dw}⁻¹ h⁻¹ and sesquiterpene emission rates (G_{TEMP} , 20°C, $\beta=0,18$ °C⁻¹) from 389-2720 ng g_{dw}⁻¹ h⁻¹. On one tree, they did measurements again in 2007 and found significantly lower emission rates (about 41% for MT and 5% for SQT, of those in 2006), which they discuss was due to the trees recuperating from an insect (autumnal moth) outbreak that peaked in 2004. Our measurements, done in 2008, could be further proof of a return to normal BVOC emission rates, which should then be lower than their report suggested. Insect outbreaks are, however, reoccurring events that affect the growing patterns of these forests to a large degree (Hoogesteger, 2006), and should therefore be included in long term models.

There are some factors that imply our calculated emission rates and emission potentials for monoterpenes and sesquiterpenes are lower than true values. Haapanala *et al.* (2009) also found large linalool emission, but the dominant compound was sabinene (between 43-66 % of mass emitted from the tree that was measured in 2006 and 2007). This compound was not analyzed in this study, and could theoretically have been present in the samples. Excluding sabinene from their results, linalool accounts for 62 % of the remaining mass emitted in 2007, which is in line with our measurements. Other compounds that they reported significant emissions of, such as ocimene, trans-ocimene and α -farnesene, were not analyzed either. This is clearly a problem and should be considered in the conclusions of the study.

During the course of a growing season, trees change their emission pattern. The studies in 2006-2007 were carried out earlier in the growing season, which is likely to affect the results. Weih and Karlsson (1999) reported a 12 week growing season for seedlings of the Mountain birch. Ekberg *et al.* (2009) reported a start of emissions from a high latitude wetland site after an accumulated diurnal mean temperature above 0°C of about 100 degree days (unit for accumulated daily temperatures). Hakola *et al.* (2001) measured BVOC emissions from Downy birch, which is a close relative to

the Mountain birch, and found emission peaks of monoterpenes, sesquiterpenes and linalool quite early in the season, after about 400 degree days of accumulated temperatures above 5°C. Our study was conducted in the end of July, after ~600 degree days (Figure 17), while the studies of 2006 and 2007 recorded samples mostly in early July. A few weeks difference in such a study makes a large difference, especially with a growing season of only 12 weeks.

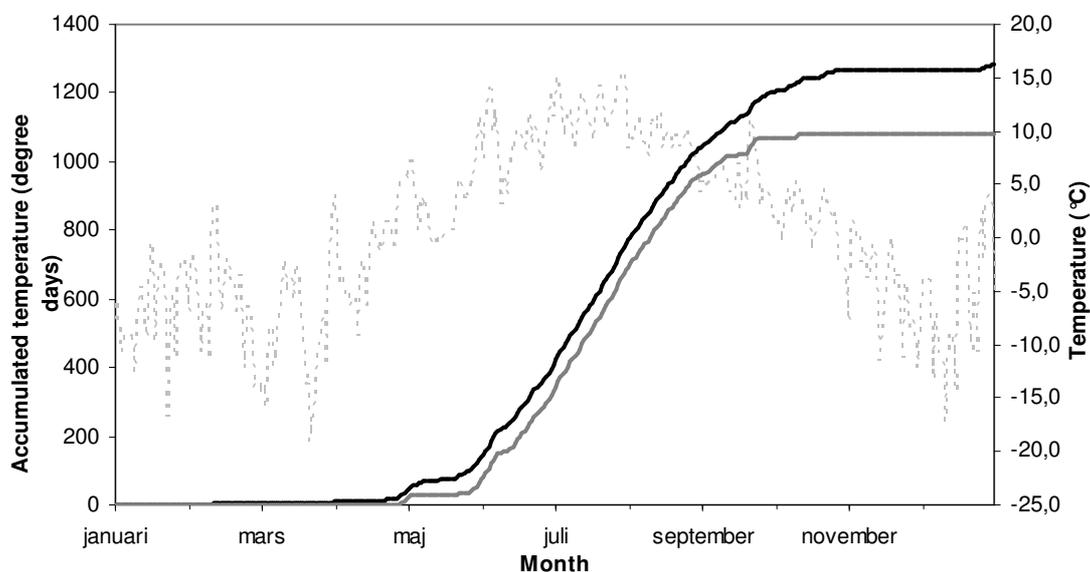


Figure 17. The temperature in Abisko during 2008 (www.linnea.com/~ans/). Dashed line show the daily mean temperature. Solid lines are accumulated temperatures above 0°C (black) and 5°C (grey).

The emission potentials that are calculated in this study fail to describe the emission peaks (Figures 15 and 16). Modelling of emissions during the course of a growing season is therefore bound to result in lower than true values. Comparing emission potentials obtained in a short term measurement on different trees, species or ecosystems will cause problems, unless the data is linked to seasonal emissions. Depending on what is sought after, annual emissions might be a better comparison, since the standardization variables of temperature and PAR is not static.

The long term influence on emission patterns from various environmental stresses can also be a factor that needs to be addressed in a small-scale experiment. A specific tree can be exposed to other temperatures than nearby trees. Prolonged elevated temperatures will change the emission patterns, but a harsh winter also affects the growing patterns. Weih and Karlsson (1999) exposed Mountain birch seedlings to different winter temperatures and found large differences in the summertime growth rate and nutrient uptake capacity, which will likely affect BVOC emissions.

6. Conclusions

There are many uncertainties in this study and more research is needed on Mountain birches to get a better understanding of its emission patterns. The results of this study should be used bearing in mind that the emission potentials of the VOC groups might be lower than actual values. Some facts that can be established when looking at the

measurements done in Abisko of 2006-2008 (Hakola *et al.*, 2009 and this study) is that Linalool is a compound emitted in large amounts by the Mountain birch, and emissions seem to decrease from year-to-year. Also, the emissions are closely related to the production, as low PAR gives lower or no emission.

Longer term measurements, during the whole growing season would be preferred. The obtained results from such a study could then be used as a pattern when doing short-term experiments. Also, more than one birch needs to be looked at since the variations from tree-to-tree are significant.

It is clear that photosynthesis, humidity, transpiration etc. that was measured by the LI6400 is something that is interesting to measure simultaneously to BVOC emissions. It would, however, be best to measure directly in the chamber if one is after general patterns of the plant, as opposed to the LI6400 device which only measure on one leaf. When a relationship between emissions and photosynthesis has been established, the LI6400 could be used to get a better understanding of the reactions to certain stresses, such as humidity, temperature and PAR, by using the refined machinery to lock all other variables. This is also something that needs to be done on a large-scale since photosynthesis is highly dependent on where on the tree the leaf is (sun and shade leaves), water access etc.

Some of the uncertainties in the results that are due to sampling methods could be reduced by small changes in the experimental set up and execution. With more than one chamber measuring on different trees, the result will be more trustworthy in describing the tree species, apart from the obvious benefit of more sampling points. With a stronger flushing of the chambers, a temperature that is closer to ambient conditions will be achieved at the start of measurements. Pumping air into the chamber at a higher rate could also be a solution to this problem, but leads to lower BVOC concentrations in the outflow air, and might cause other problems for the chamber structure.

Future studies of the Mountain birch as a BVOC emitter will surely be made. Emission inventories will be added to during the next decades, and should be considered when estimating the carbon budgets and climatic feedback systems of subarctic ecosystems.

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