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Effects of intra-genotypic variation, variance with height and time of season on BVOC emissions

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Abstract

Biogenic Volatile Organic Compounds (BVOCs) are trace gases other than CO₂ and CH₄ produced and emitted by the biosphere, where the amounts released depend on climatic factors such as temperature and solar irradiation. However, interpretation of leaf-level measurements is currently hampered by factors such as large within-genotypic variability, measurement height and time in the season. A campaign was performed between June and August in 2013 in Taastrup, Denmark to study these uncertainties. BVOC emissions were measured from leaves and needles at heights of 2 m, 5.5 m and 12.5 m in the canopy and for seven trees; four Norway spruces (*Picea abies*) of which two trees had a budburst approximately a week before the other two, two English oaks (*Quercus robur*) and one European beech (*Fagus sylvatica*). Differences in chemical composition and emission strength between June and August were observed between the different trees. English oak's main compound isoprene increased from 62–74 % of the total emission in June to approximately 97 % in August, which is linked to leaf development over the summer season. The total emission from all measured spruce trees decreased from July to August, but without a loss in the diversity of emitted compounds. The trees showed indications of drought stress as there was a period without precipitation lasting 21 days during the study. There were no differences in emission patterns within all of the measured Norway spruces. For measurement height, there was only a significant difference in emission pattern for European beech as the top of the canopy emitted 7–9 times more in relation to lower canopy levels. Our results suggest there was little within-genotype variability and the wide spacing between trees had an influence on the individual emission patterns. These results are important in order to understand the significance of within-genotypic variation, canopy height and seasonal development in relation to the emission patterns of the selected species. Furthermore, it will provide helpful insights for modelers who wish to improve their emission estimates.

Keywords: BVOC, isoprene, monoterpene, intra-genotypic variability, canopy height, time of season

1 Introduction

Biogenic Volatile Organic Compounds (BVOCs) are a large number of trace gases other than CO₂ and CH₄ which are involved in a range of environmental processes in the atmosphere (GUENTHER et al., 1993; KESSELMEIER and STAUDT, 1999; BEERLING et al., 2007). Some of the most prominent and studied BVOC groups are the isoprenoids, such as isoprene (C₅H₈), monoterpenes (C₁₀H₁₆) and sesquiterpenes (C₁₅H₂₄). From the naturally occurring trees in Europe, isoprene is mainly emitted by deciduous trees such as oak, aspen and willow whilst monoterpenes and sesquiterpenes are emitted mainly by coniferous species such as spruce and pine (KESSELMEIER and STAUDT, 1999). BVOCs are produced in various plant tissues. Some plant species are able to store BVOCs, whilst others release all compounds once they have been produced. The amount

and complexity of BVOCs produced and emitted by the vegetation are modulated by both internal (genetic and biochemical) and external (abiotic and biotic) factors (LERDAU et al., 1997; KESSELMEIER and STAUDT, 1999; PEÑUELAS and LLUSIA, 2001). Some compounds, like isoprene, are strongly affected by light and temperature (TINGEY et al., 1979; GUENTHER et al., 1993; KESSELMEIER and STAUDT, 1999), whilst other plants and compounds show no clear or uncertain responses to light variations (DEMENT et al., 1975; TINGEY et al., 1980; DUHL et al., 2008; LAOTHAWORNKITKUL et al., 2009 and references therein; STAUDT and LHOUTELLIER, 2011). BVOCs are used by plants either as a defence mechanism against herbivores and pathogens, to attract pollinators or alter flowering in other nearby plants or to protect plant tissues against stresses such as high temperatures or high irradiation (PEÑUELAS and LLUSIA, 2001 and references therein). BVOCs have also been shown to play an important role in atmospheric chemistry and the climate system, as they are much more reactive in comparison to CH₄ and N₂O (ARNETH et al.,

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2010). Once BVOCs are emitted, they either undergo oxidation into CO₂ (PARK et al., 2013), react with hydroxyl radicals (DI CARLO et al., 2004), contribute to the production and destruction of tropospheric ozone (ATKINSON, 2000) or influence the growth and formation of secondary organic aerosol (SOA) (CLAEYS et al., 2004; ARNETH et al., 2010). SOA is known to scatter and absorb radiation, act as cloud condensation nuclei and subsequently alter cloud formation which produces changes in weather events (ARNETH et al., 2010; PEÑUELAS and STAUDT, 2010).

Numerous field studies have been performed on a range of plant species and mixtures of species in order to quantify their emission rates, which in turn can be applied for emission estimates at a regional or a global scale (STEINBRECHER et al., 2009; ODERBOLZ et al., 2013). However, there are still high uncertainties regarding the influence of local growing conditions, seasonality and phenology and the effect of canopy structure on BVOC emission rates and compound composition (KESSELMEIER and STAUDT, 1999; HAKOLA et al., 2001; OWEN et al., 2001; STAUDT et al., 2001; THOSS et al., 2007; BÄCK et al., 2012; HAKOLA et al., 2012; NOE et al., 2012; POKORSKA et al., 2012; ŠIMPRAGA et al., 2013). Studying seasonal variation has shown that the emission rate and compound mixture may change with leaf or needle development. The usual patterns are low emission rates in the beginning of the growing season followed by an increase with the progression of summer (FUENTES et al., 1996; BERTIN et al., 1997; FUENTES and WANG, 1999; HAKOLA et al., 2003; THOSS et al., 2007; HAKOLA et al., 2012).

Little is known about the variability of BVOC emissions within individuals from the same species or provenance. There has been an increasing interest in studying the emission capacities within a genus, where some species can emit high amounts of BVOCs whilst others have lost this trait either by mutation or loss of its adaptive benefit (MONSON et al., 2013). Oak is often used as it has not only been shown to have significant differences in emission patterns between species, but also emission intensities between individuals (STEINBRECHER et al., 2013). In a study where monoterpene emissions were measured from 146 individual potted Holm oak trees, distinctly different proportions of monoterpene compounds were reported between individuals. Through cluster analysis, the individuals could be divided into three principal groups depending on the main emitted compound (STAUDT et al., 2001). BÄCK et al. (2012) made a similar field study for Scots pine, where they grouped 40 trees depending on their chemodiversity. They argued that a high variability in BVOC emission patterns exists due to genetic variation within a species and the authors recommended more comprehensive measurements involving chemotypes and population-level studies. Presently, there are only few studies that have investigated intra-specific variability caused by genetic differences. This might produce high uncertainties in model estimates of emissions when they are scaled

up to regional or global scales (ARNETH et al., 2010; SCHURGERS et al., 2011; BÄCK et al., 2012), which would have large implications for understanding both chemical processes in the atmosphere and the formation of SOA from BVOCs.

Some studies have shown that height within the canopy also affects BVOC emissions. Due to higher solar irradiation, temperatures and physiological differences in sunlit and shaded leaves, the top part of the canopy is often expected to have higher emission rates in comparison to lower parts of the canopy (HARLEY et al., 1996; SHARKEY et al., 1996; HARLEY et al., 1997). NOE et al. (2012) performed sampling of ambient air on six height levels for a spruce-dominated hemiboreal forest and reported no visible height profile pattern for isoprene, but a gradient in total monoterpene concentration from high concentration at the lower levels to low concentrations in the top of the canopy. ŠIMPRAGA et al. (2013) made a similar study on European beech at four height levels in the canopy from May to October and found that semi-shaded leaves had a higher monoterpene concentration in comparison to sunlit or shaded leaves. In order to get proper model simulations of the emission patterns from the vegetation, height must be taken into account to a larger degree than what it presently is (BERTIN et al., 1997; NIINEMETS et al., 2010).

In this study, we examine BVOC emission patterns from three common European tree species, using genetically identical individuals grown under natural conditions. The tree species that were chosen were English oak (*Quercus robur*), two provenances of Norway spruce (*Picea abies*), which were separated as they showed different budburst patterns, and European beech (*Fagus sylvatica*). We aim to (i) investigate the BVOC mixture and variation between identical trees grown outdoors, (ii) to establish the importance of height within the canopy for determining BVOC emission quantities and (iii) to investigate if there is a change with time in the emission patterns.

2 Materials and methods

2.1 Experimental site

The field study was carried out at Højbakkegård Experimental Station in Taastrup, Denmark (55°40'N, 12°18'E), run by the Faculty of Science at the University of Copenhagen. The region has an annual long-term (30 y) average precipitation of 583 mm and a mean air temperature of 7.5 °C, with monthly mean temperatures of -0.9 °C in February and 15.8 °C in July. The soil consists of a sandy loam soil, which contains approximately 13 % of clay in its dry matter (JENSEN et al., 1997). The experimental station is part of the International Phenological Gardens (IPG) network, a network of gardens distributed throughout Europe to achieve long-term phenological observations for the most common European species of trees and bushes. Currently, the network focuses on 21 species including different provenances and

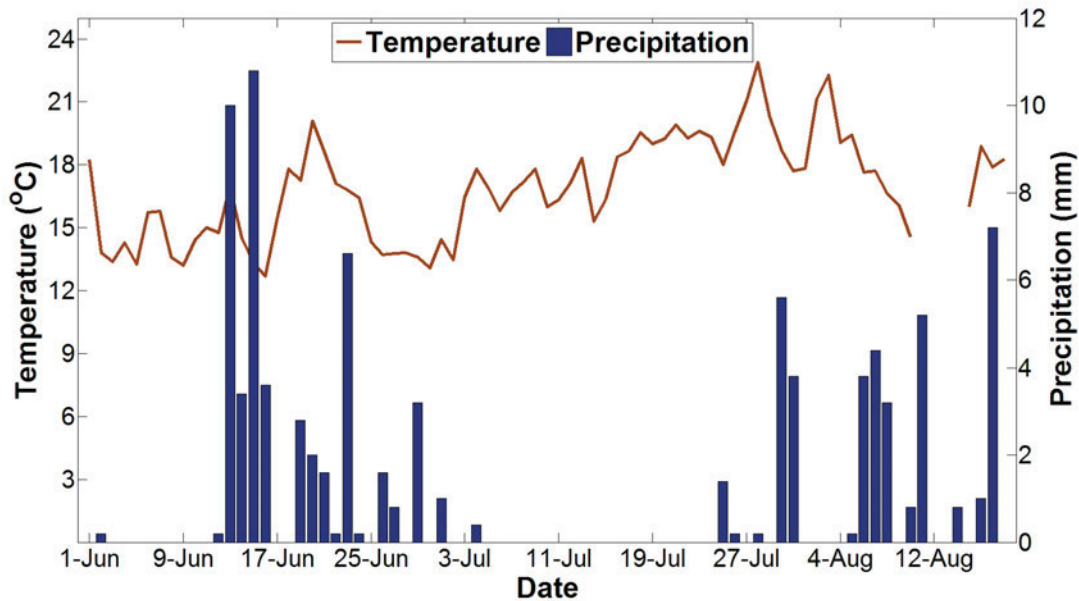


Figure 1: Daily average temperature and total daily precipitation for Taastrup, Denmark. The average daily temperature and total daily precipitation for Taastrup, Denmark between 1 June to 18 August 2013. The gap in the temperature pattern in August is due to instrumentation failure.

Table 1: Amount of samples taken from different leaves or needles, from different trees and heights (2 m, 5.5 m and 12.5 m in the canopy) at several dates during summer 2013. The first number represents all the samples taken at 2 m, the second at 5.5 m and the last at 12.5 m.

| Date | Number of samples taken per tree for different heights and months | | | | | | |
|----------------------|---|---------|----------------|----------------|---------------|---------------|-------|
| | Oak 1 | Oak 2 | Early spruce 1 | Early spruce 2 | Late spruce 1 | Late spruce 2 | Beech |
| 4th–27th June | 4/4/4 | 10/10/9 | – | – | – | – | – |
| 1st–15th July | – | – | 10/10/8 | 4/4/3 | – | – | – |
| 16th–23rd July | – | – | – | – | 4/4/3 | 4/4/4 | – |
| 24th, 29th–30th July | – | – | – | – | – | – | 4/4/4 |
| 1st–6th August | 4/3/4 | 4/3/3 | – | – | – | – | – |
| 7th–15th August | – | – | –/4/4 | 4/4/4 | – | – | – |
| Total | 23 | 39 | 36 | 22 | 11 | 12 | 12 |

each garden is provided with up to three individuals of the same species. All the plants used in the network are genetically identical, with the advantage that the genetic variation between sites is restricted (CHMIELEWSKI et al., 2013). The garden in Taastrup contains 21 trees from 13 different species and provenances, where the first trees were planted in 1971. The average daily temperature and total daily precipitation which was experienced during the field study (1 June to 18 August 2013) can be seen in Fig. 1.

2.2 Sampling and analytical method

Air samples using a chamber to quantify BVOC emissions have been collected from June to August 2013 from seven individual trees; two English oaks (*Quercus robur*), four Norway spruces (*Picea abies*) and one European beech (*Fagus sylvatica*) which all had an age of 42 years by the time of sampling. The Norway spruces have been classified into two different provenances as the time of budburst was about a week apart from each

other. Norway spruce with an early May shoot will henceforth be referred to as early spruce and Norway spruce with a late May shoot as late spruce. Emissions from each tree were measured at three different height levels within the canopy; at ground level (2 m), at an intermediate level (5.5 m) and in the higher canopy (12.5 m). Measurements on the English oak trees and early spruce individuals were repeated later in the season (August) at all three canopy layers, while late spruce and European beech were only measured once during the growing season (Table 1).

For each sample, measurements of leaf net C assimilation and BVOC emissions were made. Leaf net assimilation was measured with a portable infra-red gas analyser (IRGA; LI-6400, LI-COR, Lincoln, NE, USA), equipped with either a leaf chamber or a conifer chamber, which both allowed to control temperature, photosynthetic active radiation (PAR) and flow rates within the chamber, as well as CO₂-concentration entering the chamber. Undamaged leaves and needles were randomly

selected at the western side of all trees and enclosed in a leaf or conifer chamber (6400-22L lighted conifer chamber, LI-COR, Lincoln, NE, USA). The leaves always covered the 2×3 cm leaf chamber within and therefore a leaf area of 6 cm^2 was used for assimilation and BVOC emission calculations. The conifer chamber had an approximate volume of 270 cm^3 . The area of the needle branch which was put into the chamber was calculated by picking all the needles and measuring the total area, which ranged between 10 and 64 cm^2 for the samples. Chamber conditions were kept constant and were set to 400 ppm of CO_2 , PAR to $1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$ and an air flow rate of $500 \mu\text{mol s}^{-1}$. Leaf temperatures were held constant at anticipated ambient daily temperature, where the set temperature ranged between $17\text{--}25 \text{ }^\circ\text{C}$ over the summer season. At the end of each measurement cycle, the leaf or needle branch was picked, weighed, dried for at least two days and weighed again in order to scale the emissions with the enclosed biomass. The dry weight of the leaves (gdw) was used for calculating the BVOC emissions.

Air samples for subsequent analysis of BVOC emissions were taken following an acclimation period of approximately one hour after enclosure. The inlet air of the IRGA was filtered through a hydrocarbon trap to remove organic contaminants from the sample stream. A sub flow of air leaving the sample chamber was led through stainless steel cartridges (Markes International Limited, Pontyclun, UK) packed with adsorbents Tenax TA (porous organic polymer) and Carbograph 1TD (graphitized carbon black) using flow-controlled sampling pumps (Pocket Pump, SKC Ltd., Dorset, UK) with a sampling flow rate of 200 ml min^{-1} . The collected volume for each sample varied between 41 and 51. Empty chamber blanks, with air which circulated through the LI-6400 system without any leaves or needles in the chambers, were also collected under the same chamber conditions in order to acknowledge any background contamination. The sampled tubes were sealed, stored and kept at $2\text{--}3 \text{ }^\circ\text{C}$ until analysis, which took place within four weeks after sampling.

The samples were analysed with a Gas Chromatography-Mass Spectrometry system (GC-MS, Shimadzu QP2010 Plus, Shimadzu Corporation, Japan). The cartridges were initially heated to $280 \text{ }^\circ\text{C}$ in a flow of purified helium for 10 minutes. A Tenax TA cold trap maintained at $-30 \text{ }^\circ\text{C}$ cryo-focused the volatilised VOCs downstream. In the second stage, the cold trap was flash heated ($40 \text{ }^\circ\text{C s}^{-1}$) to $300 \text{ }^\circ\text{C}$ and desorption time was maintained for 6 minutes. The volatilised VOCs passed through a heated transfer line ($200 \text{ }^\circ\text{C}$) to a Gas Chromatograph (GC, Clarus 500, PerkinElmer, Waltham, MA, USA) equipped with a flame ionisation meter (FID). The compounds within the sample were identified by comparing the measured mass spectra for different compounds with the spectra in the NIST mass spectra library. Peak quantification was done using liquid standards in methanol solutions.

2.3 BVOC standardization

To analyse and compare measured leaf BVOC emission, the emission rates were normalised to standard light and temperature conditions ($1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$ and $30 \text{ }^\circ\text{C}$) by using the algorithms presented by GUENTHER et al. (1993, 1995):

$$I = I_S C_L C_T, \text{ where } C_L = \frac{\alpha C_{L1} \text{PAR}}{\sqrt{1 + \alpha^2 \text{PAR}^2}}, \quad (2.1)$$

$$\text{and } C_T = \frac{\exp \frac{C_T(T-T_S)}{RT_S T}}{1 + \exp \frac{C_T(T-T_M)}{RT_S T}}$$

where I is the emission rate at a measured leaf temperature T (K) and PAR flux ($\mu\text{mol m}^{-2} \text{ s}^{-1}$) and I_S isoprene emission rate at the specified standard temperature T_S (K) and a standard PAR flux ($1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$). The factor C_L is a hyperbolic response to light and C_T is a modified Arrhenius relationship with temperature. R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and α (0.0027), C_{L1} (1.066), C_{T1} ($95\,000 \text{ J mol}^{-1}$), C_{T2} ($230\,000 \text{ J mol}^{-1}$) and T_M (314 K) are empirical coefficients. The climatic conditions are relatively similar, where the same light conditions were used on all samples and the temperature varied between $17\text{--}25 \text{ }^\circ\text{C}$, which means there is little suspicion for high variation between samples. Since the measurements were performed at standard PAR, the standardization was effectively done for temperature only, which makes it unnecessary to have *a priori* information on the light dependence of the emission. Four samples from the Norway spruce trees with emissions over $19 \mu\text{g gdw}^{-1} \text{ h}^{-1}$, much higher than the amounts found in literature, were removed from the data set as they were believed to be caused by disturbance during chamber set-up.

3 Results

3.1 Intra-genotypic variability

To establish the emission pattern and the intra-genotype variability between genetically identical trees, we did measurements on seven trees of different species and provenances. All emission rates were standardized to a temperature of $30 \text{ }^\circ\text{C}$ and PAR of $1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$ according to GUENTHER et al. (1993), in order to make better comparisons between observed emission patterns. Table 2 shows the average standardized emission and standard deviation (std) for all of the measured samples between individuals of the same species, at different heights and time of measurement. English oak showed high isoprene emissions with an average standardized emission of $9.8 \mu\text{g gdw}^{-1} \text{ h}^{-1}$, but not as high as had been found in previous studies (ISODOROV et al., 1985; POKORSKA et al., 2012). Isoprene contributed to approximately 79 % of the total average BVOC emission, with a maximum emission of $51 \mu\text{g gdw}^{-1} \text{ h}^{-1}$

Table 2: Average standardized BVOC emission (per grams per dry weight of biomass (gdw)) at 30 °C temperature and a photosynthetic active radiation of 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ (GUENTHER et al., 1993), standard deviations (std) and the total number of samples (n) taken from English oak, Norway spruce with an early and late May shoot and European beech during a field campaign in June to August 2013. No data (n.d.) indicates that the compound was not detected within any sample from that tree. The hyphen indicates that there was only one sample where this compound was found.

| | Standardized emission rate (ng gdw ¹ h ¹) at 1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ and 30 °C | | | | | | | |
|------------------------|---|------|------------------|------|-----------------|------|--------------|-------|
| | Oak (2) | | Early spruce (2) | | Late spruce (2) | | Beech (1) | |
| | n=62 Mean | std | n=56 Mean | std | n=23 Mean | std | n=12 Mean | std |
| Isoprene | 9797 | 7643 | 201 | 1319 | 157 | 310 | n.d. | n.d. |
| α -Thujene | 0 | – | 6 | 33 | 18 | – | 225 | 364 |
| Tricyclene | n.d. | n.d. | 2 | – | n.d. | n.d. | n.d. | n.d. |
| α -Pinene | 593 | 679 | 630 | 579 | 2370 | 1125 | 492 | 336 |
| Camphene | 9 | 58 | 170 | 574 | 147 | 389 | 32 | – |
| β -Pinene | n.d. | n.d. | 9 | – | 4 | – | n.d. | n.d. |
| Sabinene | n.d. | n.d. | 13 | 83 | 51 | 84 | 8562 | 9949 |
| β -Myrcene | n.d. | n.d. | 92 | – | n.d. | n.d. | 28 | – |
| α -Phellandrene | 57 | 94 | 14 | 55 | 253 | 176 | 541 | 267 |
| α -Terpinene | n.d. | n.d. | n.d. | n.d. | 1 | – | 43 | – |
| 3-Carene | 835 | 966 | 277 | 465 | 172 | 307 | n.d. | n.d. |
| Limonene | 976 | 1146 | 1735 | 1571 | 1033 | 873 | 664 | 427 |
| β -Phellandrene | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 179 | 295 |
| Eucalyptol | 43 | – | 366 | 1252 | 63 | 146 | n.d. | n.d. |
| β -Ocimene | 49 | 178 | 9 | 36 | n.d. | n.d. | n.d. | n.d. |
| γ -Terpinene | n.d. | n.d. | n.d. | n.d. | 136 | 165 | 250 | 501 |
| Linalool | 8 | – | 122 | 301 | 1 | – | n.d. | n.d. |
| Sum monoterpenes | 2570 | 3121 | 3444 | 4950 | 4248 | 3265 | 11014 | 12139 |
| α -Farnesene | 0 | – | 182 | 408 | n.d. | n.d. | 4 | – |
| β -Farnesene | n.d. | n.d. | 264 | 767 | 12 | – | n.d. | n.d. |
| Sum sesquiterpenes | 0 | – | 446 | 1175 | 12 | – | 4 | – |

from oak 1 in August. On average over the field study, oak 1 emitted $10.9 \mu\text{g gdw}^{-1} \text{h}^{-1}$ whilst oak 2 emitted $7.9 \mu\text{g gdw}^{-1} \text{h}^{-1}$. The remaining 21 % of the emission were mainly from limonene, 3-carene and α -pinene. European beech emitted almost exclusively monoterpenes, of which an average of 78 % was from sabinene. Both provenances of Norway spruce emitted mainly monoterpenes, but isoprene and sesquiterpenes were also found within the samples. Isoprene contributed to approximately 4–5 % to the total average BVOC emission for both provenances (early and late spruce). The average sesquiterpene emission contribution was 11 % for early spruce in comparison to 0.2 % for late spruce. The most abundant sesquiterpene was β -farnesene, which when it was found formed either 40 % or 100 % of the total sesquiterpene emission (Table 2).

The average total standardized monoterpene emission for the two provenances ranged between 3.7 – $4.6 \mu\text{g gdw}^{-1} \text{h}^{-1}$ for early spruce and 3.4 – $5.0 \mu\text{g gdw}^{-1} \text{h}^{-1}$ for late spruce. The dominant compounds for all individuals were limonene and α -pinene. However, the emission ranged between 2.0 and 3.2 (limonene) and 0.4 and $0.6 \mu\text{g gdw}^{-1} \text{h}^{-1}$ (α -pinene) for early spruce and 1.0 and 1.1 (limonene) and 1.6 and $3.1 \mu\text{g gdw}^{-1} \text{h}^{-1}$ (α -pinene) for late spruce, indicating differences in emission patterns between these two

provenances. Other common compounds were 3-carene and camphene, where 3-carene contributed to approximately 0.5 – $1.0 \mu\text{g gdw}^{-1} \text{h}^{-1}$ (13–21 %) for early spruce and 0.0 – $0.6 \mu\text{g gdw}^{-1} \text{h}^{-1}$ (0–14 %) for late spruce and camphene contributed to 0.1 – $0.3 \mu\text{g gdw}^{-1} \text{h}^{-1}$ (2–7 %) for early spruce and 0.2 – $0.7 \mu\text{g gdw}^{-1} \text{h}^{-1}$ (4–16 %) for late spruce. Other measured monoterpenes contributed between 0.9 – $1.0 \mu\text{g gdw}^{-1} \text{h}^{-1}$ (18–19 % of the total monoterpene emission) for early spruce and 0.4 – $0.7 \mu\text{g gdw}^{-1} \text{h}^{-1}$ (8–14 % of the total monoterpene emission) for late spruce (Fig. 2).

3.2 Canopy height

Emission patterns and net assimilation rates at different heights within the trees were measured in order to study the emission variation within the canopy. The analysis below highlights vertical profiles of isoprene, limonene, α -pinene and sabinene since they were the most common compounds emitted and where found in almost all of the studied species. The remaining compounds identified were classified into other compounds.

The standardized emission of English oak showed a decreasing emission trend with increasing height for all of the measured compounds (Fig. 3). Isoprene had an average total emission of 10.9, 10.1

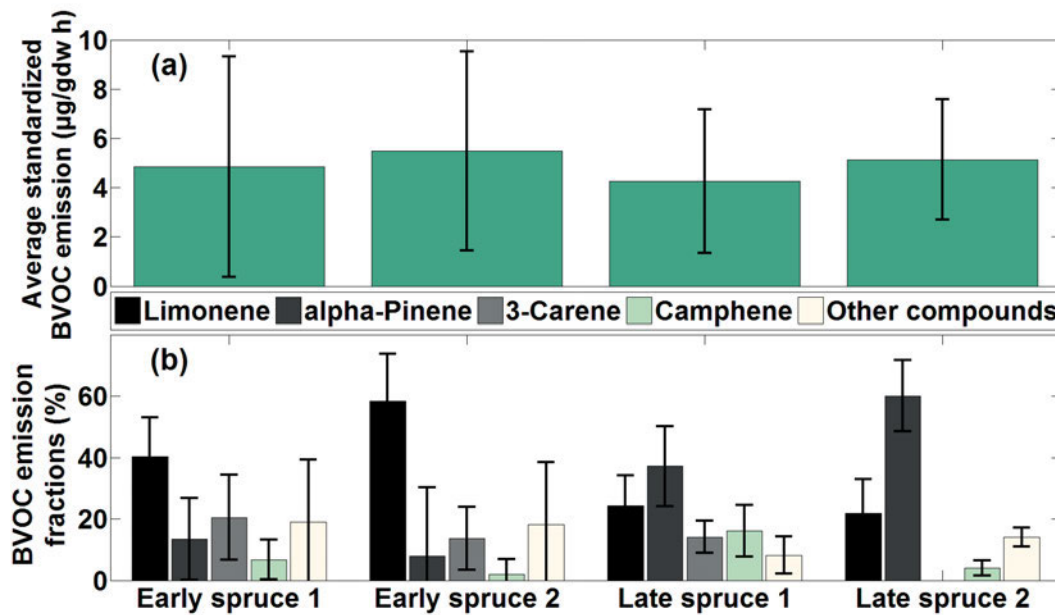


Figure 2: BVOC emission from different provenances of spruce. Standardized emission characteristics for the four individuals of Norway spruce: (a) Total standardized emissions of BVOC, (b) Emission fractions in % of the most dominant compounds. The first two individuals are Norway spruce with an early May shoot (early spruce) and the last two are the late May shoot individuals (late spruce). The error bars indicate the standard deviation for all the measured samples.

and $7.2 \mu\text{g gdw}^{-1} \text{h}^{-1}$ for 2 m, 5.5 m and 12.5 m, respectively. The total emission pattern were fairly similar between individuals for low and intermediate levels, ranging between $10.6\text{--}11.3 \mu\text{g gdw}^{-1} \text{h}^{-1}$ at 2 m and $8.4\text{--}11.9 \mu\text{g gdw}^{-1} \text{h}^{-1}$ at 5.5 m, but ranged between $4.1\text{--}11.3 \mu\text{g gdw}^{-1} \text{h}^{-1}$ at 12.5 m. However, even though emission pattern differences occurred between individuals, a decreasing trend with increasing canopy height was observed for both trees. The net assimilation rate had an opposite trend compared to the BVOC emission rates, where the average net assimilation increased with increasing height.

Early spruce showed a similar decreasing pattern with height as English oak, whilst late spruce showed an increase in emissions with height. The average total emission from the two provenances of spruce ranged between $3.8\text{--}5.1 \mu\text{g gdw}^{-1} \text{h}^{-1}$ for early spruce and $3.2\text{--}5.9 \mu\text{g gdw}^{-1} \text{h}^{-1}$ for late spruce. Net assimilation ranged between $7.0\text{--}9.2 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ for early spruce and between $10.0\text{--}11.5 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ for late spruce, indicating a slightly higher assimilation rate for late spruce. For late spruce the amount of other compounds increased from $0.3 \mu\text{g gdw}^{-1} \text{h}^{-1}$ at 2 m and $0.5 \mu\text{g gdw}^{-1} \text{h}^{-1}$ at 5.5 m in the canopy to $3 \mu\text{g gdw}^{-1} \text{h}^{-1}$ at 12.5 m. There was a higher amount of sesquiterpenes found in the samples from early spruce, where β -farnesene was only found in samples on low and intermediate levels within the tree. In the higher canopy, α -farnesene was the main sesquiterpene contributor.

European beech had an average total standardized emission of $3.6 \mu\text{g gdw}^{-1} \text{h}^{-1}$ at 2 m, $2.9 \mu\text{g gdw}^{-1} \text{h}^{-1}$ at 5.5 m and $26.5 \mu\text{g gdw}^{-1} \text{h}^{-1}$ at 12.5 m, indicating that the highest canopy level emitted 7–9 times more in comparison to lower levels. The largest source to the emission from the highest level was from sabinene, which contributed between 81–86 % of the total emission. Furthermore, the amount and compound complexity was higher at the higher canopy level, releasing between 6–9 different compounds in relation to 4–5 compounds at lower levels. The net assimilation rate followed a similar pattern in comparison to the total average BVOC emission, but does not fully explain the high increase of emission at 12.5 m (Fig. 3).

3.3 Seasonal variation

To determine if the emission patterns changed as the summer progressed, measurements were made twice for both individuals and for all heights within the canopy of the English oaks and the early spruces. The English oaks were measured in June and August. Standardized isoprene emissions increased from an average of 8.8 to $13.4 \mu\text{g gdw}^{-1} \text{h}^{-1}$ for oak 1 and 6.5 to $12.7 \mu\text{g gdw}^{-1} \text{h}^{-1}$ for oak 2. The proportion of isoprene out of the total BVOC emission increased from 62–74 % in June to approximately 97 % in August. In the same period, average monoterpene emission was lowered from 3.1 to $0.5 \mu\text{g gdw}^{-1} \text{h}^{-1}$ for oak 1 and from 3.9 to $0.4 \mu\text{g gdw}^{-1} \text{h}^{-1}$ for oak 2. In June, the leaves on both trees were influenced by a herbivorous attack of

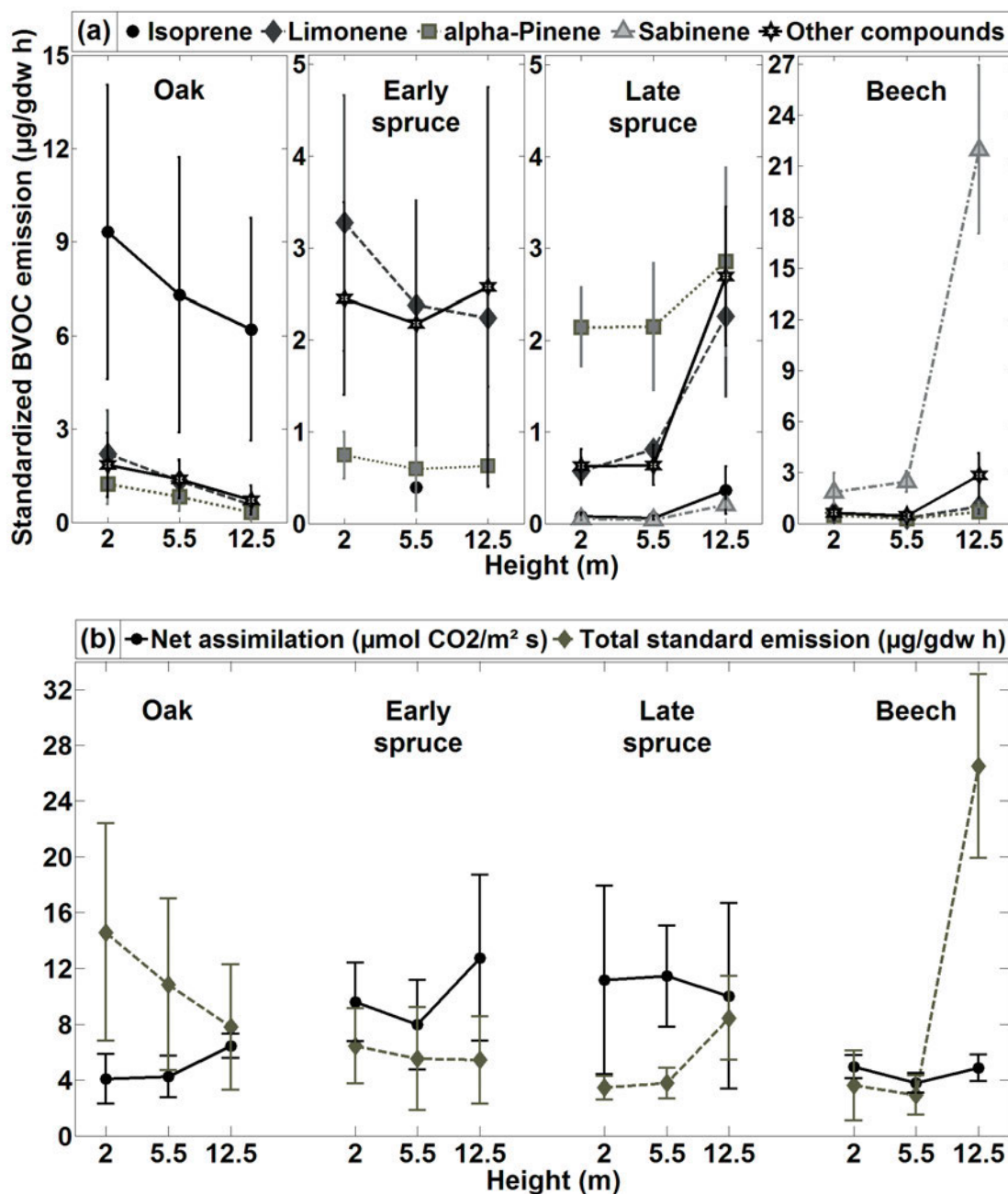


Figure 3: Compound emission and net assimilation at different heights. Standardized emission patterns per gram dry weight (gdw) for the most common compounds (a), the total emission ($\mu\text{g gdw}^{-1} \text{h}^{-1}$) and the net assimilation rate ($\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$) (b) for English oak, Norway spruce with an early and late May shoot (called early spruce and late spruce) and European beech at low (2 m), intermediate (5.5 m) and high (12.5 m) height levels within the canopy. The data used are between June to July. The error bars indicate the standard deviation.

winter moth caterpillars. These caterpillars were not observed by the time of measurement in August. Furthermore, the time of leaf unfolding started 4th of May and there was an average leaf weight increase from 0.79 g to 0.84 g per leaf from June and August, but with a standard deviation of 0.2 g the increase was not significant. However, the net assimilation showed an average increase from 4.9 to 6.8 $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ from June to August.

Early spruce was measured in July and August. For the early spruce trees, the average monoterpene emission decreased from 5.1 to 1.2 $\mu\text{g gdw}^{-1} \text{h}^{-1}$ for spruce 1

and 6.5 to 2.7 $\mu\text{g gdw}^{-1} \text{h}^{-1}$ for spruce 2 (Fig. 4). In July, a prolonged period without precipitation was observed which lasted for 21 days (Fig. 1). By the end of this period, the lowest measured canopy level for early spruce 1 was lost as all of the needles had fallen off. There was also an increase of sesquiterpene contribution to the total BVOC emission for almost all of the remaining levels, from 1–21 % to 30–45 % for spruce 1 and 0–16 % to 18–33 % for spruce 2. There was no sesquiterpene emission from spruce 2 at the highest level within the canopy. But even though the total emission decreased, the num-

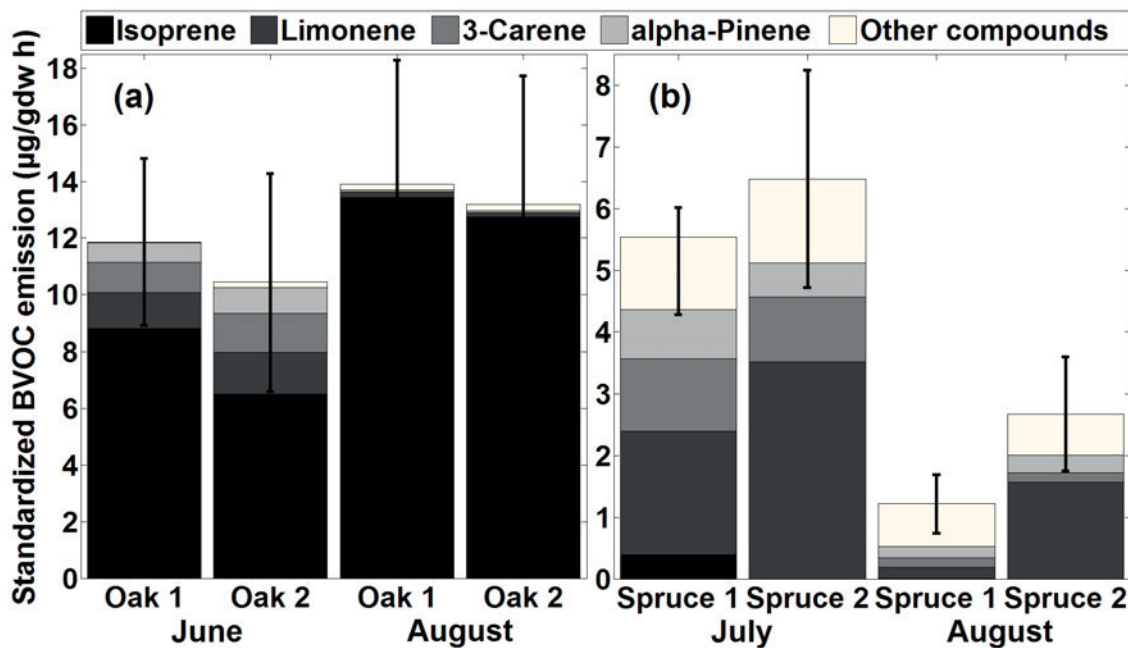


Figure 4: Compound emission from oak and early spruce at different times in the summer. Variation in standardized BVOC emission per gram dry weight (gdw) ($\mu\text{g gdw}^{-1} \text{h}^{-1}$) including all height measurements for (a) English oak between June to August and (b) Norway spruce with an early May shoot between July to August. The error bars indicate the standard deviation of the standardized total emissions.

ber of different detected compounds was fairly constant as 3–8 compounds could be found in all the collected samples in July, whilst 2–11 compounds could be found in the samples measured in August.

4 Discussion

Over the last decades, research on the short-term emission patterns of BVOCs has focused largely on the impact of meteorological variations (mostly temperature and radiation) on emissions. There is still little knowledge about the variability in emissions related to intra-genotypic variation, measurement height and seasonal development. Intra-genotype variation and genetic differences have earlier been estimated for some of the dominant trees growing in Europe, showing that the main differences in chemotypes between individuals in a stand were caused by genotypic differences within a species and less by the climatic conditions (STAUDT et al., 2001; BÄCK et al., 2012). Our findings demonstrate that the magnitude and compound composition of the BVOC emission for English oak, Norway spruce and European beech were consistent with previously performed studies (ISODOROV et al., 1985; TOLLSTEN and MÜLLER, 1996; DINDORF et al., 2006; HOLZKE et al., 2006; GRABMER et al., 2006; MENTEL et al., 2009; POKORSKA et al., 2012), but the experienced emission range was smaller between the studied genetically identical trees and the composition of BVOCs were similar for individuals within the same tree species, time of season and height for most of the individuals.

English oak, which is mainly an isoprene emitter, had an average standardized emission of $9.8 \mu\text{g gdw}^{-1} \text{h}^{-1}$,

contributing approximately 79% of its total average BVOC emission. This emission rate of isoprene was lower than what has previously been shown in most performed studies (ISODOROV et al., 1985; POKORSKA et al., 2012 and references within), but it should also be noted that most other studies performed have either taken place in central or southern Europe or in various lab settings. It is likely that these trees have adapted to a warmer climate in comparison to the trees measured in our study and are therefore able to produce higher isoprene emissions. Studies performed in Russia have reported isoprene emissions from European oaks in approximately similar amounts as the trees growing in Taastrup (ISODOROV et al., 1985). Oak 1 emitted approximately 28% more isoprene in comparison to oak 2, with the highest differences at 5.5 m and 12.5 m in the canopy. A possible explanation for the difference in emission intensity might be that oak 1 is planted on the edge of the southwest corner of the IPG garden, where it is exposed to sunlight for long periods of the day. Even though both trees are influenced by the same climatic settings during the field study, it is likely that oak 1 has a better capability for emission release due to adaptation to higher light conditions.

Our results further show that the isoprene and monoterpene emissions changed with time. Between June and August, isoprene emissions increased from 6.5–8.8 to 12.7–13.4 $\mu\text{g gdw}^{-1} \text{h}^{-1}$, whilst monoterpenes decreased from 3.1–3.9 to 0.4–0.5 $\mu\text{g gdw}^{-1} \text{h}^{-1}$ for oak 1 and 2. The composition of BVOCs has been shown to change as leaves or needles mature, usually with lower concentrations in the developing stages in comparison to the fully matured stage (FUENTES et al., 1996;

HAKOLA et al., 2003; THOSS et al., 2007). Leaf unfolding during 2013 started first in the beginning of May. Both the weight of the leaves and the net assimilation rate increased for both trees between June and August, even though the weight of the leaves did not increase significantly. From these data we hypothesize that the leaves were not yet fully developed by the time measurements began in early June and for those reasons gave lower isoprene emissions. For monoterpenes, it is known that stresses, such as attack by insect herbivores, might induce emissions (LERDAU et al., 1997; KESSELMEIER and STAUDT, 1999; PEÑUELAS and LLUSIA, 2001). In our study, the trees were subjected to visible damage from caterpillars in June, but with no clear occurrence in August. This indicates that the mechanical damage performed by the caterpillars might have triggered a response in the leaves and increased the monoterpene emissions in June in comparison to August, even if the leaves selected for measurements were undamaged.

The four Norway spruce trees separated into two provenances showed little variance in the amounts emitted and the emission capacities were consistent with other performed studies (CHRISTENSEN et al., 2000; GRABMER et al., 2006; RINNE et al., 2009). However, the two provenances could be distinguished by their differences in compound mixture, where early spruce had a higher proportion of limonene, whilst late spruce emitted more α -pinene. These findings are similar to the study on pine stands made by BÄCK et al. (2012), who argued that huge variation in emission intensities might exist, but that the main emitted compound remains the same within the season and that the emission patterns are more related to genetic differences rather than the climatic conditions. For this study, the number of individuals measured for each provenance is too few in order to fully acknowledge this difference in compound mixtures. However, the similarity in compound mixtures between the two individuals within each provenance seems to indicate a similarly strong dependence on the genotype.

There was little difference in emission between the sampling heights for the spruce trees. This is contradictory to a study on vertical gradients for a Norway spruce dominated forest made by NOE et al. (2012), who found for ambient air concentrations an accumulation of monoterpenes in the lower canopy with a dominance of α -pinene and a dominance of limonene in the upper part of the canopy. One of the early spruces measured in this study showed a higher emission from the lower levels together with an increased emission of α -pinene, whilst the late spruces showed higher amounts of limonene at 12.5 m. These patterns were not significant, but higher amounts of light-dependent compounds (STAUDT et al., 2000; DINDORF et al., 2006; MOUKHTAR et al., 2006), such as eucalyptol, linalool and myrcene, were measured in the upper canopy compared with the lower canopy. This lack of height dependence in our study can be related to the wide spacing in between rows applied in the garden, which results in high levels of ra-

diation even in lower layers, diminishing the difference in leaf adaptation to light levels.

When the BVOC emissions from early spruce between July and August were compared, the average total emission of BVOCs decreased from 5.1 to 1.2 $\mu\text{g gdw}^{-1} \text{h}^{-1}$ for spruce 1 and 6.5 to 2.7 $\mu\text{g gdw}^{-1} \text{h}^{-1}$ for spruce 2, but without a change in the number of detected compounds. The decreased emissions are likely related to a period without precipitation which lasted for 21 days between the two measurement campaigns. A significant drop in monoterpene emissions from Norway spruce has been reported by WU et al. (2015) during severe drought stress. In our study, the volumetric water content of the soil was not measured. However, there were several indications that the trees were water-stressed. One of the early spruces lost the lowest measured height level as the needles had dried and were shed whenever they were handled. There was also an increase in sesquiterpene emissions, which has been shown to act as an indicator for plant water stress (DUHL et al., 2008).

European beech is a *de novo* monoterpene emitter, and sabinene contributed to the highest proportion of the total emission of compounds. These results match those observed in earlier studies (TOLLSTEN and MÜLLER, 1996; DINDORF et al., 2006; HOLZKE et al., 2006). European beech had the most clear emission difference in regards to different heights within the canopy, where the highest level emitted 7–9 times more BVOCs in comparison to lower levels. There were also a higher number of emitted compounds, some of which could not be found at lower levels. This is in contradiction to a study made on European beech by ŠIMPRAGA et al. (2013), who found the highest emission from semi-shaded leaves. The reason was hypothesized to be a lower synthesis of carotenoids in comparison to the sunlit levels, which is used as a photo-protective agent, leaving fewer resources for the biosynthesis of monoterpenes. For our measurements, it should be noted that the top of the canopy could not be reached, but the highest performed measurements were only approximately two meters below the highest branches. We are therefore not able to determine whether the emission patterns were similar between the top of the canopy and the measurement level of 12.5 m. There was also a visual difference in colour between leaves growing on the sunlit side of the tree, which were more yellow, in comparison to leaves growing on the shaded side of the tree which were greener. How the colour might have affected the emission patterns is unclear, as the shaded leaves were not measured. It is also important to bear in mind that there was only one beech tree available at the site, hence prohibiting replicate measurements.

In this study, we have shown that the trees at the IPG site in Taastrup have little intra-genotype variability, but that different emission patterns occurred for different provenances (and hence genotypes) of Norway spruce. Moreover, the importance of measurement height and measurement time for different trees was addressed for English oak and early spruce. Some other influencing

factors which might have affected the results could not be excluded. As the measurements have been performed outdoors, the daily change in weather might have had some influence on the results. The emission capacities can be influenced by the average temperature over the past few days (EKBERG et al., 2009 and references therein). When measurements were performed at the top of the canopy for the English oaks in June, the daily temperature had dropped to an average of 15 °C in comparison to 19 °C for the whole study period. Furthermore, it is not possible to clearly give the seasonal change in BVOC emission by only using two occasions for the same tree during the period of June to August. More measurements during different parts of the season are therefore needed in order to specify the emission pattern change with the progression of the season, and our results clearly show that this should be addressed. There is also a necessity to do longer time-series of measurements over a multiple of years in order to verify that the emission that have been seen in the summer of 2013 is comparable for a longer period of time.

Further work is needed in order to understand the importance of genotypic variations, variability of emissions with canopy height and seasonal development and their impact on BVOC emission from different plant species. The work also shows that the IPG network, which has planted genetically identical individuals of tree species across Europe, can serve as an important tool in order to better understand the importance of genetic differences and climatic variations. The results shown here will be used in upcoming field measurement campaigns at other IPG sites in Europe to assess the emission patterns from genetically identical trees growing under different climatic conditions.

5 Conclusions

The study made in Taastrup, Denmark has used adult and genetically identical trees grown under natural conditions in order to measure the trees BVOC emissions. The study highlights some of the less understood factors influencing the BVOC emission from different tree species, namely intra-genotypic variation, height within the canopy and seasonal development. There was no clear intra-genotypic difference in the measured trees, except for an emission pattern difference between different provenances of Norway spruce. In accordance to previously performed studies, this highlights the importance of taking the genotypic differences into account when determining emission capacities for model estimates at large spatial scales. Moreover, the genetically identical trees in the IPG network can be used for a more robust estimate of the impact of growing conditions on BVOC emissions by excluding genotype-related variations in emissions. No difference in emission for different heights within the canopy was found for English oak and the two provenances of spruce, but there was a significant difference in height for European beech. The

lack of height dependence for most trees could be explained by the wide spacing between the different trees in the IPG garden, leading to more similar leaf adaptation to light at all levels of the tree. There are too few measurements performed to show clear seasonal changes in emission patterns for English oak and Norway spruce, but it was clear the emission patterns did change between the two measurement occasions. At the site, one or two trees per species were available, which is too few to confirm any emission pattern similarities. But despite the relatively small number of replicates of trees, the information provided can help to evaluate how the emission patterns for the measured trees are influenced by above mentioned variables. There is also a need to do more long-term studies in order to verify that observed emission patterns are consistent for the measured trees. Future research, which takes these variables into account, will need to be undertaken and the results found from this field study will be used for upcoming experiments.

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