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Is genetic diversity more important for terpene emissions than latitudinal adaptation?

Using genetically identical trees to better understand emission fluctuations across a European gradient

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2017

Document Version:
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Citation for published version (APA):

van Meeningen, Y. (2017). *Is genetic diversity more important for terpene emissions than latitudinal adaptation? Using genetically identical trees to better understand emission fluctuations across a European gradient*. Lund University, Faculty of Science, Department of Physical Geography and Ecosystem Science.

Total number of authors:
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Is genetic diversity more important for terpene emissions than latitudinal adaptation?

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Using genetically identical trees to better understand
emission fluctuations across a European latitudinal
gradient

Ylva van Meeningen



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DOCTORAL DISSERTATION

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To be defended at Pangea auditorium, Geocentrum II, Sölvegatan 12, Lund.
Thursday, June 1st 2017 at 10:00 am.

Faculty opponent
Professor Jaana Bäck

Organization LUND UNIVERSITY Department of Physical Geography and Ecosystem Science Sölvegatan 12, SE-223 62, Lund, Sweden Author: Ylva van Meeningen		Document name DOCTORAL DISSERTATION	
		Date of issue 2017-06-01	
		Sponsoring organization	
Title and subtitle Is genetic diversity more important for terpene emissions than latitudinal adaptation?: Using genetically identical trees to better understand emission fluctuations across a European latitudinal gradient			
Abstract <p>Biogenic volatile organic compounds (BVOCs) are trace gases other than CO₂ and CH₄ produced and emitted by the vegetation. The group consists of thousands of compounds in various shapes and sizes and with short atmospheric lifetimes. Some of the most common BVOC groups are called isoprene, monoterpenes and sesquiterpenes. For the plant, the emission of BVOCs is used for plant communication, attracting pollinators, to deter herbivores and to enhance abiotic stress defense against for example high temperatures, irradiation or oxidative stresses. But once released into the atmosphere, they might affect the atmospheric chemistry which in effect alters our climate. Depending on the atmospheric composition, BVOC emissions can either enhance tropospheric ozone and indirectly prolong the lifetimes of greenhouse gases such as methane by reducing the concentration of hydroxyl radicals, or increase the formation of aerosols and cloud condensation nuclei which may mitigate the effect of greenhouse gases on global warming.</p> <p>It is fairly well known that BVOCs have an impact on the climate. However, whether the BVOC emissions have a warming or cooling effect on the overall climate is difficult to determine, due to existing emission pattern variations both between individuals of the same species and between species. Some of the reasons which are often discussed to be influential and where there is relatively little data available are within-species genetic variation, stress response, adaptation to different weather and climatic conditions and seasonality. In this thesis, focus has been given to the importance of genetic diversity and adaptation to different growing conditions. Studies have been conducted on three European tree species with genetically identical individuals across a latitudinal gradient, stretching from Slovenia to southern Finland. The main results were that even though the emission amounts varied between sites due to differences in weather events, the progression of the growing season and insect outbreaks, the compound composition between individuals were similar both across latitudes and between measurement years. By showing compound composition stability for genetically identical trees, the results highlights the importance of taking genetic diversity into account in terms of observed emission pattern variations. The response to changing light conditions on the emission amount of different compounds was also investigated. The results uncovered that different compounds had different emission responses to changing light conditions, but that the response of the compounds were fairly similar across different species.</p>			
Key words: Biogenic Volatile Organic Compounds (BVOCs), English oak, European beech, Norway spruce, latitude, genetic diversity			
Classification system and/or index terms (if any)			
Supplementary bibliographical information		Language: English	
ISSN and key title		ISBN (print): 978-91-85793-81-5 ISBN (PDF): 978-91-85793-82-2	
Recipient's notes	Number of pages		Price
	Security classification		

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A doctoral thesis at the university in Sweden is produced either as a monograph or as a collection of papers. In the latter case the introductory part constitutes the formal thesis, which summarizes the accompanying papers already published or manuscripts at various stages (in press, submitted, or in preparation).

Coverphoto by Ylva van Meeningen: European beech tree in Taastrup, Denmark

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Faculty of Science, Lund University
Department of Physical Geography and Ecosystem Science

ISBN (print): 978-91-85793-81-5

ISBN (PDF): 978-91-85793-82-2

Printed in Sweden by Media-Tryck, Lund University
Lund 2017



There is a way that nature speaks. Most of the time we are simply not patient enough, quiet enough, to pay attention to the story.

-Linda Hogan

List of papers

Paper I: Persson, Y., Schurgers, G., Ekberg, A., Holst, T., (2016). Effects of intra-genotypic variation, variance with height and time of season on BVOC emissions. *Meteorologische Zeitschrift*, 25, 377-388.

Paper II: van Meeningen, Y., Schurgers, G., Rinnan, R., Holst, T., (2016). BVOC emissions from English oak (*Quercus robur*) and European beech (*Fagus sylvatica*) along a latitudinal gradient. *Biogeosciences*, 13, 6067-6080.

Paper III: van Meeningen, Y., Wang, M., Karlsson, T., Seifert, A., Schurgers, G., Rinnan, R., Holst, T. BVOC emission variation of Norway spruce across a European transect. *Submitted*.

Paper IV: van Meeningen, Y., Schurgers, G., Rinnan, R., Holst, T., (2017). Isoprenoid emission response to changing light conditions of English oak, European beech and Norway spruce. *Biogeosciences Discussions (in review)*.

List of contributions

Paper I: The author contributed to the study design, collected field data, performed the data analysis and led the writing.

Paper II: The author contributed to the study design, collected field data, performed the data analysis and led the writing.

Paper III: The author collected and provided field data, performed data analysis and led the writing.

Paper IV: The author contributed to the study design, collected field data, performed the data analysis and led the writing.

Abstract

Biogenic volatile organic compounds (BVOCs) are trace gases other than CO₂ and CH₄ produced and emitted by the vegetation. The group consists of thousands of compounds in various shapes and sizes and with short atmospheric lifetimes. Some of the most common BVOC groups are called isoprene, monoterpenes and sesquiterpenes. For the plant, the emission of BVOCs is used for plant communication, attracting pollinators, to deter herbivores and to enhance abiotic stress defense against for example high temperatures, irradiation or oxidative stresses. But once released into the atmosphere, they might affect the atmospheric chemistry which in effect alters our climate. Depending on the atmospheric composition, BVOC emissions can either enhance tropospheric ozone and indirectly prolong the lifetimes of greenhouse gases such as methane by reducing the concentration of hydroxyl radicals, or increase the formation of aerosols and cloud condensation nuclei which may mitigate the effect of greenhouse gases on global warming.

It is fairly well known that BVOCs have an impact on the climate. However, whether the BVOC emissions have a warming or cooling effect on the overall climate is difficult to determine due to existing emission pattern variations both between individuals of the same species and between species. Some of the reasons which are often discussed to be influential and where there is relatively little data available are within-species genetic variation, stress response, adaptation to different weather and climatic conditions and seasonality. In this thesis, focus has been given to the importance of genetic diversity and adaptation to different growing conditions. Studies have been conducted on three European tree species with genetically identical individuals across a latitudinal gradient, stretching from Slovenia to southern Finland. The main results were that even though the emission amounts varied between sites due to differences in weather events, the progression of the growing season and insect outbreaks, the compound composition between individuals were similar both across latitudes and between measurement years. By showing compound composition stability for genetically identical trees, the results highlights the importance of taking genetic diversity into account in terms of observed emission pattern variations. The response to changing light conditions on the emission amount of different compounds was also investigated. The results uncovered that different compounds had different emission responses to changing light conditions, but that the response of the compounds were fairly similar across different species.

Sammanfattning

Biologiskt flyktiga organiska ämnen (BVOCs) är spårämnen förutom CO_2 och CH_4 som produceras och släpps ut av växter. Termen innehåller tusentals olika ämnen i varierande former och storlekar och där ämnena har korta atmosfäriska livstider. Några av de vanligaste BVOC grupperna kallas isopren, monoterpener och sesquiterpener. Växterna använder sig av BVOCs för att kommunicera med varandra, attrahera pollinering, avskräcka växtätare eller för att öka sitt interna försvar mot abiotiska stressfaktorer så som höga temperaturer, hög solstrålning och oxidativ stress. Men när de väl släpps ut i atmosfären så påverkar de atmosfärens kemi och på så sätt förändrar de vårt klimat. Beroende på atmosfärens partikelsammansättning så kan utsläppen av BVOCs öka mängden troposfäriskt ozon och indirekt förlänga livslängden på olika växthusgaser, så som metan, genom att minska koncentrationen av hydroxylradikaler. Men de kan också öka antalet aerosoler och kondensationskärnor som bildar moln, vilket mildrar den effekt växthusgaserna har på den globala uppvärmningen.

Det är relativt välkänt att BVOCs påverkar vårt klimat, men på grund av existerande utsläppsvariationer, både mellan olika individer av samma art och mellan olika arter, så är det svårt att avgöra hur stor påverkan BVOCs har på vårt klimat. Orsaker som diskuterats och som det finns relativt lite information om är genetisk diversitet mellan individer inom samma art, stressrespons, anpassning till olika väder- och klimatförhållanden och variationer mellan olika säsonger. I den här avhandlingen har fokus legat på vikten av genetisk diversitet och potentiell anpassning till olika växtförhållanden. Genom att bedriva studier på tre europeiska trädarter med genetiskt identiska individer, men som växer längs en latitudinell gradient som sträcker sig från Slovenien och upp till södra Finland. Resultaten visade att trots att det fanns skillnader mellan de valda undersökningsområdena när det gällde mängden utsläpp, främst på grund av olika väderförhållanden, hur långt växtsäsongen hade fortlopit och insektsutbrott, så var sammansättningen av ämnen jämförbara mellan de studerade individerna och över både latitud och de år som undersökningarna genomfördes. Genom att visa stabilitet i ämneskomposition för genetiskt identiska träd, understryker resultaten vikten av att ta med genetisk variation i beräkningen när det gäller observerade variationer i ämnesutsläpp. Något som också har undersökts är hur mängden utsläpp av individuella ämnen reagerar vid förändringar i ljusförhållanden. Resultaten visade att olika ämnen reagerade på olika sätt vid

förändringar i mängden tillgängligt ljus, men att responsen av dessa ämnen var förhållandevis lik mellan de studerade trädarterna.

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Introduction

In the 1960's, a plant physiologist named F. Went investigated the blue haze which often can be seen over various mountain ranges across the world. He concluded that this blue haze must originate from plants releasing submicroscopic particles or, as they are also called, terpenes (Went, 1960). Since that time, more studies have been performed uncovering some of the complex interactions that these particles have, not only in biological communication and stress tolerance enhancement in plants but also in regards to the different chemical dynamics in the atmosphere (Atkinson and Arey, 2003; Peñuelas and Staudt, 2010). The compounds released may vary both in amounts and complexity due to genetic variation, variation in growing conditions or stress (Peñuelas and Staudt, 2010; Fineschi et al., 2012). These submicroscopic particles have later been termed as biogenic volatile organic compounds (BVOCs) and have also been recognized to play a role in atmospheric chemistry, secondary organic aerosol (SOA) formation and global warming (Laothawornkitkul et al., 2009). But due to their short atmospheric lifetimes and their large emission fluctuations between and within species (Kesselmeier and Staudt, 1999), it is difficult to quantify their importance on our climate seen on a global scale. In order to better understand how BVOC emissions affect our environment, it is important to investigate the effect of climate and genetic variation separately.

BVOCs - its production and influence

All organisms have the potential to emit BVOCs, where the main terrestrial proportion of the emissions originates from the vegetation (Fuentes et al., 2000; Possell and Loreto, 2013). The term BVOC consists of thousands of organic molecules that are released, both above- and below-ground, from different plant organs (Laothawornkitkul et al., 2009). It includes compounds such as terpenoids (isoprene, monoterpenes and sesquiterpenes), alcohols, alkanes, alkenes, aldehydes, esters, ethers and carboxylic acids. Within the terpenoid group, isoprene consists of one C₅ unit, monoterpenes of two C₅ units and sesquiterpenes of three C₅ units (Kesselmeier and Staudt, 1999; Possell and Loreto, 2013) and collectively they comprise the largest groups of BVOCs. Terpenoids are produced from the building blocks isopentenyl diphosphate (IPP) and its allylic isomer dimethylallyl diphosphate (DMAPP). These building blocks can be synthesized from two alternative pathways; the methyl-erythritol-phosphate (MEP) pathway in the plastids or the mevalonic acid (MVA) pathway in the cytosols (Dudareva et al., 2006; Li and Sharkey, 2013). Isoprene and most of the monoterpenes are produced via the MEP pathway whilst sesquiterpenes are produced via the MVA pathway (Li and Sharkey, 2013). BVOCs are either released directly after they have been produced or in some cases they can accumulate in non-specific or specialized storage organs, such as trichomes or resin ducts (Peñuelas and Llusià, 2003; Maffei, 2010; Niinemets et al., 2010).

From the perspective of the plant, BVOCs play an important role in regards to plant growth, survival and reproduction (Pierik et al., 2014). In order to insure the survival of the plant, it needs to find a balance between the investment in reproduction (e.g. flowers, nectar and fruit), growth and defense against herbivores (Trowbridge and Stoy, 2013). The specific emission rates from different plant species are therefore never stable, but the emission intensity changes depending on the local growing conditions, the developmental stage of the plant as well as genotype and age (Hewitt and Street, 1992; Laothawornkitkul et al., 2009; Trowbridge and Stoy, 2013). Furthermore, the plant also need to cope with various stresses, which are often divided into either abiotic or biotic stress (Vickers et al., 2009; Loreto and Schnitzler, 2010; Peñuelas and Staudt, 2010). Abiotic stress includes extremes of high or low temperatures, high light intensity, drought, air pollutants or tearing of the plant's tissues (Vickers et al., 2009; Loreto and Schnitzler, 2010). Biotic stress includes mechanical wounding caused by herbivore attack (Vickers et al., 2009). By releasing BVOCs, the plant can either directly deter herbivores from feeding (called direct biotic stress defense) or attract parasitoids or predators which attack the herbivores for them (called indirect biotic defense) (Vickers et al., 2009; Figure 1).

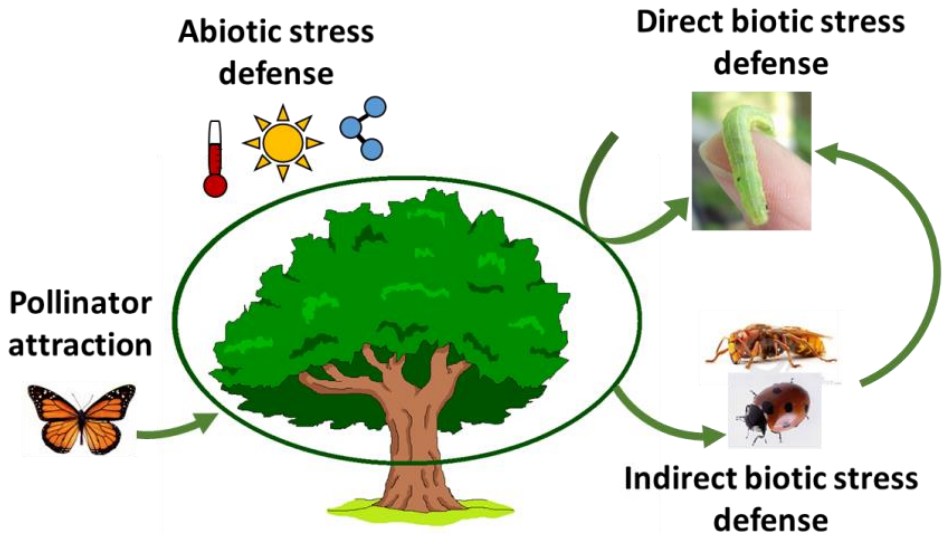


Figure 1: Some of the main reasons for plants to release BVOCs. BVOC emissions can be used for reproduction by attracting pollinators and to enhance the tolerance of the plant against abiotic stress factors, such as high temperatures, radiation or oxidative stress. They are also used to protect against herbivore and pathogen attacks, either by repelling the herbivores directly or indirectly by attracting natural enemies and carnivores. Redrawn from Fineschi and Loreto (2012).

Of the different plant tissues, leaves generally emit the highest mass rate of BVOCs, whilst flowers and fruits release the widest varieties (Laothawornkitkul et al., 2009 and references therein). Isoprene is the most commonly emitted BVOC compound, with a global estimated emission of $400\text{-}600 \times 10^{12}$ g C (Arneth et al., 2008; Laothawornkitkul et al., 2009; Guenther et al., 2012). Isoprene is emitted directly from *de novo* synthesis and contributes to the largest non-methane hydrocarbon flux into the atmosphere (Li and Sharkey, 2013). The distribution of species capable of emitting isoprene is broad and the trait to produce isoprene has in some cases been developed and lost repeatedly within plant lineages (Sharkey et al., 2008; Monson et al., 2013). High isoprene emitters are often found within woody plant species, such as poplars (*Populus* spp.), willows (*Salix* spp.) and some subspecies of oak (*Quercus* spp.) (Kesselmeier and Staudt, 1999; Loreto, 2002; Monson et al., 2013). Some of the advantages for the plant to release isoprene is that it has been experimentally confirmed to enhance thermotolerance (Sharkey and Singaas, 1995; Singaas et al., 1997; Hanson and Sharkey, 2001), protect against oxidative stress (Loreto and Velikova, 2001; Velikova et al., 2005) and has also been suggested to strengthen cellular membranes (Peñuelas and Llusà, 2003; Loreto and Schnitzler, 2010).

Monoterpenes are one of the most abundant groups of BVOCs and exists in a variety of different isomers. The emission of monoterpenes contributes to many of the characteristic smells of different vegetation species (Dudareva et al., 2006; Li and Sharkey, 2013). They have similar roles as isoprene and are both known to increase membrane stabilization and to enhance protection against abiotic stresses such as heat, drought or salt stress (Possell and Loreto, 2013 and references therein). Many vegetation species have also developed specialized organs where monoterpenes can accumulate and then be released in large amounts after wounding. Important reasons for this accumulation of monoterpenes are that they directly act as powerful deterrents for herbivores and pathogens (Dicke and Baldwin, 2010) or as an indirect defense by attracting parasitoids or predators of herbivores (Peñuelas and Llusà, 2003; Dicke and Baldwin, 2010; Trowbridge and Stoy, 2013). Monoterpene emitting species are often dominating in temperate and boreal areas, including species such as beech (*Fagus* spp.), birch (*Betula* spp.), spruce (*Picea* spp.) and pine (*Pinus* spp.) (Kesselmeier and Staudt, 1999; Rinne et al., 2009).

Sesquiterpenes are among the least studied of the terpenoid groups due to their high reactivity and low vapor pressures. But it is known that these compounds are important contributors for floral scents, pollinator attraction, enhanced seed production, deterring herbivore attacks and acting as stress markers (Caissard et al., 2004; Duhl et al., 2008; Unsicker et al., 2009; Schiestl, 2010). The emission of sesquiterpenes varies between species and due to factors such as temperature, light intensity, drought, plant developmental stage and seasonality (Duhl et al., 2008). Furthermore, disturbances such as foliar damage or infestation might provide additional short-term bursts of sesquiterpene emissions, which makes it even more difficult to categorize specific emission pattern for different vegetation species (Duhl et al., 2008 and references therein).

BVOC production and emission can be divided into constitutive and induced emissions (Possell and Loreto, 2013). Constitutive emissions can be observed throughout the plant's developmental stages and is biosynthetically controlled by factors such as light and/or temperature, atmospheric CO₂ or nutrition (Loreto and Schnitzler, 2010). The rate of constitutive BVOC production and release can be altered due to their sensitivity to high light or temperature regimes (Niinemets et al., 2004; Trowbridge and Stoy, 2013). Induced emissions are a response to mechanical wounding from e.g. wind or herbivore attack (Loreto and Schnitzler, 2010; Possell and Loreto, 2013). Typical BVOCs induced are specific monoterpenes, such as linalool, cis- and trans- β -ocimene, sesquiterpenes and oxygenated short-chained alcohols and aldehydes (Niinemets, 2010).

BVOCs and their impact on air chemistry

Terpenoids are some of the most reactive classes of BVOCs when released into the atmosphere, with chemical lifetimes ranging from seconds to days (Kesselmeier and Staudt, 1999; Monson and Baldocchi, 2014). Once the compounds are released, they are subject to a series of oxidative reactions which ultimately break them down into CO₂ and H₂O (Laothawornkitkul et al., 2009; Monson and Baldocchi, 2014). The gas-phase oxidation of BVOCs is mostly initiated by a reaction with hydroxyl radicals (OH), but they can also be oxidized with nitrogen oxides (NO_x) or ozone (O₃) (Laothawornkitkul et al., 2009).

Depending on the atmospheric composition, BVOC emissions might have a positive or negative effect on global warming (see Figure 2). As BVOCs react with OH radicals they indirectly prolong the lifetime of other greenhouse gases, such as methane (CH₄), in the atmosphere (Laothawornkitkul et al., 2009; Arneth et al., 2010; Monson and Baldocchi, 2014). When there are high NO_x levels due to e.g. fuel combustion, road transport and agricultural fertilization, BVOC oxidation products might also lead to increased tropospheric O₃ formation (Chameides et al., 1988; Curci et al., 2009; Laothawornkitkul et al., 2009; Arneth et al., 2010; Monson and Baldocchi, 2014). Not only is O₃ a potent greenhouse gas, but also a respiratory irritant, it is phytotoxic and a main component of smog formation (Karl et al., 2009; Arneth et al., 2010). Some compounds, like isoprene, have a higher quantitative capacity to form reactive compounds in comparison to other BVOCs, which potentially can raise the O₃ levels further. In many urban areas, where the amount of anthropogenic pollutants often is high, the choice of vegetative species can therefore have a significant effect on the surrounding air quality (Calfapietra et al., 2013). However, when there are low NO_x concentrations, BVOC oxidation may lead to a net consumption of O₃ instead (Laothawornkitkul et al., 2009). O₃ reacts by addition to C=C bonds and which lead to the formation of organic peroxy (HO₂ and RO₂) radicals (Atkinson, 2000; Atkinson and Arey, 2003). These radicals are an intermediate between OH and O₃ production or destruction. When NO_x levels are low, the radicals react with O₃ and produce OH and oxygen (Fleming et al., 2006). Some compounds which have been shown to react rapidly with O₃ are sesquiterpenes such as β-caryophyllene and α-humulene (Lee et al., 2006).

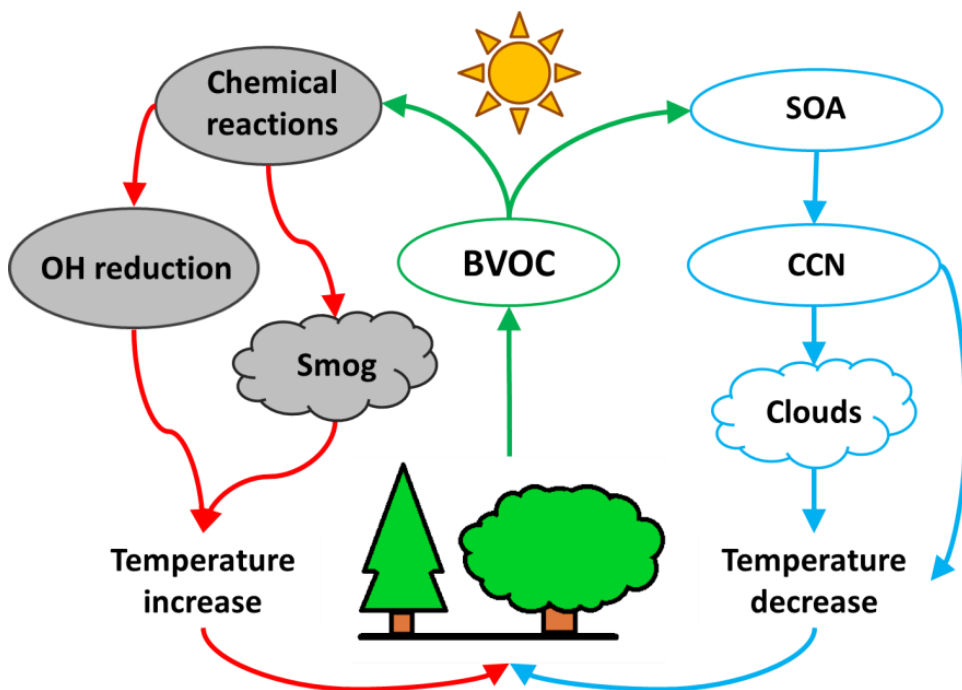


Figure 2: The effect of BVOC emission on some of the most important atmospheric processes. BVOC emissions can increase smog production, reduce the amount of available hydroxyl radicals (OH) or increase the production of Secondary Organic Aerosols (SOA) and Cloud Condensation Nuclei (CCN), which are important for cloud formation. When OH decrease and smog production increase there is generally an increase in air temperature, whilst an increase in cloud formation generally decreases air temperature. The change in air temperature will further influence the release of BVOC emission, with higher emissions with increasing temperatures. Redrawn from Paasonen et al., 2013.

BVOC emissions and their oxidation products are also important primary precursors for secondary organic aerosols (SOA) and cloud condensation nuclei (CCN) (Karl et al., 2009; Arneth et al., 2010; Paasonen et al., 2013). SOA and CCN impact Earth's radiative balance by scattering or absorbing incoming solar radiation or by modifying the properties of clouds (VanReken et al., 2006). Many sesquiterpenes have high SOA yields caused by a reactive external double bond. But even terpenes with internal double bonds, like limonene, 3-carene, α -pinene and terpinolene have the capacity to produce high SOA yields (Lee et al., 2006).

The CCN particle activity depends on the size of the particle and the hygroscopicity (Farmer et al., 2015), where higher hygroscopicity indicates a higher CCN activity of a given size (Zhao et al., 2017). As shown by Zhao et al (2017), as the emission of BVOCs can be altered due to biotic or abiotic stresses, changes in emission patterns would also influence cloud formation. It was found that biotic stresses, such as insect infestation, lead to induced VOC emissions which modified the hygroscopicity, whilst abiotic stresses, such as heat and drought, affected the particle size distribution. As the global temperature is increasing, changes in environmental factors could cause stresses to plants, which would influence their emission patterns and modify particle size and formation (Zhao et al., 2017).

Important environmental factors and their use in emission modeling

Some of the environmental factors which play a part in observed BVOC emission rates are temperature and light. Whilst temperature controls terpenoid synthesis and the diffusion rate of specific compounds, light determines the amount of terpenoid precursors produced by photosynthesis (Niinemets et al., 2004 and references therein; Lichtenthaler, 2007). However, it is difficult to study the effect of light and temperature separately *in situ*, as they are often dependent on each other. In emission models, standardized emission rates are often used to determine emission intensities, where many models either focus on plants grouped into functional types (Schurgers et al., 2011) or used to characterize geographic variations (Guenther, 2013).

Some of the algorithms used in models are implemented depending on if the emissions from plants are considered to be light dependent or light independent. The calculated emission from *de novo* emitters often use light dependent algorithms as the emitters are assumed to lack storage structures. Therefore, the emissions from these species are considered to be released directly into the air after its production. For the emission calculations of species possessing storage structures, temperature dependent algorithms have been used instead as the emission from storage structures are often assumed to originate from evaporation processes. But there are studies which have shown that the emissions can be both light dependent and independent simultaneously, making modeling of emission rates harder to perform (Guenther et al., 1993; Guenther et al., 1995; Niinemets and Reichstein, 2003; Niinemets et al., 2004; Ghirardo et al., 2010; Taipale et al., 2011). As most studies have focused on the emission from different types of plants and if they should be classified into light dependent or independent emitters, there has been less focus on if separate compounds are light or temperature dependent and if this is a consistent pattern across different species.

Genetic diversity versus environmental impact – what is more important?

Both abiotic and biotic factors have been shown to have an important influence on the observed BVOC emission amounts and mixtures among different plant species (Holopainen and Gershenson 2010 and references therein; Loreto and Schnitzler, 2010). But studies have also revealed that the genetic diversity that exists within the majority of all living species might cause large variations in emission concentrations, both within populations and between species. The combination of abiotic and biotic influences together with genetic variability makes it difficult to separate how the emission patterns have been influenced by different factors (Isebrands et al., 1999; Staudt et al., 2001; Thoss et al., 2007; Bäck et al., 2012; Genard-Zielinski et al., 2015; Hakola et al., 2017).

Several studies have tried to understand the variability in observed emission patterns and what might be the underlying causes (Kesselmeier and Staudt, 1999; Staudt et al., 2001; Funk et al., 2005; Genard-Zielinski et al., 2015). In a screening study on *Quercus ilex*, three main types could be distinguished in regards to the highest emitted compound. This pattern remained fairly stable in relation to season, leaf age and emission amounts (Staudt et al., 2001).

Bäck et al. (2012) collected needle branches from 40 Scots pine trees, where 25 branches were collected from the same pine stand and 15 branches from surrounding stands. They found that the tree samples could be divided into chemotypes depending on their main emitted compound and that the chemotypes remained fairly stable with the progression of time. This would suggest that even though there are influences due to different stresses, such as mechanical damage, changes in weather and phenological stages, the preferred chemotype is genetically determined and not as influenced by the local environment.

However, even genetically identical individuals may experience significant emission variations. Studies on poplar clones have found significant emission variation between identical individuals, suggesting that microclimate or plant history also have an effect on the emission patterns and that the BVOC emissions cannot be fully explained by only considering static factors (Isebrands et al., 1999; Funk et al., 2005).

Aims and objectives

BVOC emissions from plants can vary in both complexity and intensity, which makes it difficult to quantify their role and impact on atmospheric chemistry. The variation has been explained to be caused by different growing conditions, climate adaptations and genetic variation, but few studies have been able to separate the different processes. This thesis aims to analyze various sources of BVOC emission variability from some of the most common European tree species, namely English oak (*Quercus robur*), European beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*) (see Figure 3). The main objectives of this PhD thesis were to:

- Analyze various impacts on BVOC emissions for selected and genetically identical trees (paper I-IV)
- Investigate the emission variation between genetically identical trees growing at different locations (paper II, III)
- Investigate the impact of changing light conditions on the BVOC composition (paper IV)

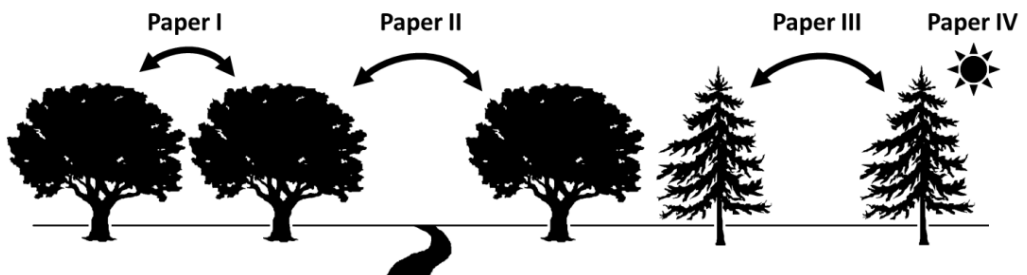


Figure 3: Schematic outline of the included papers, where paper I focus on the sources of the variation in BVOC emissions from genetically identical trees, paper II and III on the emission variation between identical trees grown at different locations and paper IV on the effect of changing light conditions.

Material and methods

Study sites

In situ foliar BVOC measurements from some of the most common European tree species were performed at four sites, stretching from 46° N to 60° N along a latitudinal transect across Europe. The chosen sites were Ljubljana in Slovenia, Grafrath in Germany, Taastrup in Denmark and Piikkiö in Finland (Figure 4; a more detailed description of the mentioned sites is given below). The study sites are part of a network called International Phenological Gardens (IPG) of Europe (Chmielewski et al., 2013). In 2017, the network consisted of 69 active sites in 36 European countries (F.-M. Chmielewski, personal communication). The observation program focuses on 21 coniferous and deciduous plant species with the inclusion of different provenances. Newly established IPG sites are provided with two to three saplings per available plant species. If the site is climatically restricted and therefore have unsuitable growing habitats for many of the plant species within their propagation program, the site may be provided with more plants of the species that can grow in that particular environment (Chmielewski et al., 2013). The aim of the IPG network is to study the long-term change of the phenological phases of European plants and how these phases might have changed due to global warming. The advantage of the IPG network is that the stations are provided with genetically identical plants, propagated from the same propagation site. This limits genetic diversity between sites and makes it possible to study the tree's phenological development and adaptation to different environments (Chmielewski et al., 2013).

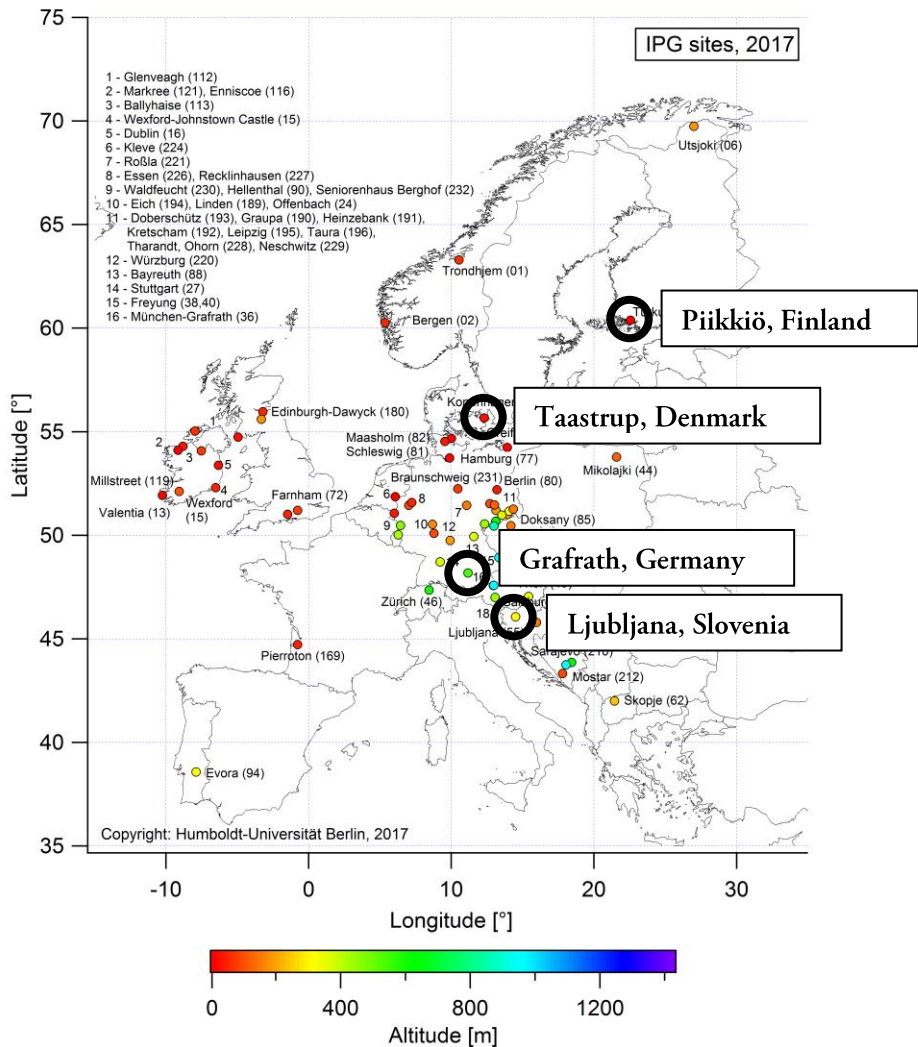


Figure 4: Map of the IPG sites active in 2017 and their position in Europe. The visited sites are marked with circles (with permission from Humboldt-University in Berlin).

Ljubljana

The IPG site in Ljubljana, Slovenia (46°04' N, 14°30' E, IPG 055) was established in 1962 and is run by the Slovenian Environment Agency. The site is situated in the eastern corner of a public park called Tivoli Park, located on the northern outskirts of the central town district. There are 26 different trees available at the site in a variety of ages and provenances. Between the years 1981-2010, the annual precipitation was 1362 mm and the mean annual air temperature was 10.9 °C, with a monthly mean temperature of 1.9 °C in February and 21.3 °C in July (Slovenian Environment Agency, 2014). For this project, five trees were measured, where one was an English oak tree, one was a European beech tree and three were Norway spruces.

Grafrath

Forstlicher Versuchsgarten in Grafrath, Germany (48°18' N, 11°17' E, IPG 036) was established in 1963 and is run by the Bavarian State Institute of Forestry. This site is the parental garden of the IPG network and is in charge of both propagating species from the IPG program and to provide with new seedlings to established and newly created sites. The site also serves as a botanical garden and was first established in 1881 as a test garden to study which types of exotic lumber they were capable of growing and breeding in southern Germany. The size of the garden is presently 34 ha with over 200 different species of trees and shrubs and has shifted more of its attention towards public relations and forest education (www.lfw.bayern.de). The annual precipitation was 875 mm and the mean annual air temperature for the site was 8.7 °C, with a monthly mean temperature of 0.5 °C in February and 17.8 °C in July between years 1995-2014 (Agrarmeteorologie Bayern). Measurements were performed on 10 trees, where two were English oaks, two were European beeches and six were Norway spruces.

Taastrup

Højbakkegård Experimental Station in Taastrup, Denmark (55°40' N, 12°18' E, IPG 010) became an established IPG site in 1971 and is run by the Faculty of Science at the University of Copenhagen (A. K. Nørgaard, personal communication). 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 (Jensen et al., 1997). The garden in Taastrup contains 21 trees from 13 different species and provenances. For this dissertation, measurements were made on seven of the trees, where two were English oaks, one was European beech and four were Norway spruce trees.

Piikkiö

The site Piikkiö in Finland (60°23' N, 22°30' E, IPG 008) became an established IPG site in 1965 and is since 2015 part of the Natural Resources Institute Finland. The site has an area of 25 ha and focuses on horticultural research and preservation of horticultural genetic resources (S. Juhanoja, personal communication). The annual precipitation for the site is 698 mm and the mean annual air temperature is 5.9 °C, with a monthly mean temperature of -5.9 °C in February and 18 °C in July between years 2005-2013 (Finnish Meteorological Institute). Measurements were performed on five Norway spruce trees which were available on site. Due to the restriction in climatic conditions, the site in Piikkiö is only able to grow Norway spruce out of the chosen European tree species. But due to their climatic restrictions, the Piikkiö site was instead provided with up to three clones of the same species.



Figure 5: The study sites Ljubljana (IPG 055), Grafrath (IPG 036), Taastrup (IPG 010) and Piikkiö (IPG 008).

Methods

Plant material

From the information provided by the IPG network, three common European tree species were chosen as they have the capacity to grow and thrive over a large area of Europe, have high emission capacities for BVOCs ($>1\mu\text{g gdw}^{-1} \text{h}^{-1}$) and are of importance for the overall European BVOC emission budget (Kesselmeier and Staudt, 1999; Skjøth et al., 2008). The tree species chosen were English oak (*Quercus robur*), European beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*). The Norway spruces were divided into two types of provenances according to the IPG framework. This division was implemented according to different budburst patterns, where one provenance experienced budburst approximately one week earlier than the other. Henceforth, these provenances are going to be called early spruce (SE) and late spruce (SL).

Both English oak and European beech are known to be *de novo* emitters (Holzke et al., 2006; Kleist et al., 2012; Steinbrecher et al., 2013). English oak mainly emits isoprene (Isidorov et al., 1985; Pérez-Rial et al., 2009; Pokorska et al., 2012; Steinbrecher et al., 2013), with an establishment range from Scandinavia and the Baltic countries to the north and through the rest of Europe to the south (Skjøth et al., 2008). European beech is mainly a monoterpene emitter, where sabinene is the main emitted compound (Moukhtar et al., 2005; Dindorf et al., 2006; Holzke et al., 2006; Demarcke et al., 2010; Kleist et al., 2012). European beech has a northern limit from southern Sweden and a southern limit in Spain and Portugal (Skjøth et al., 2008). Norway spruce is a monoterpene emitter and a major coniferous source of isoprene (Janson et al., 1999; Kesselmeier and Staudt; Grabmer et al., 2006). It has storing capacity in its resin ducts and is known to be both a *de novo* emitter and to simultaneously have emissions originating from storage structures (Ghirardo et al., 2010; Kleist et al., 2012). Norway spruce is one of the more dominant tree species in the northern Europe and has a southern limit in France, Italy and Turkey (Skjøth et al., 2008).

Leaf chamber measurements

Measurements of the plant's net assimilation rates (A_n) and stomatal conductance (G_s) were conducted on a leaf scale by using a portable photosynthesis system (LI-6400 and LI-6400XT, LICOR, NE, USA). This is an open system, meaning that photosynthesis and transpiration rates are calculated by measuring the differences in CO_2 and H_2O in the incoming and outgoing airstream that passes through the chamber cuvette. The calculations used to get photosynthetic measurements are according to the equations by von Caemmerer and Farquhar (1981). The gas analyzers are placed in the sensor head, which means measurements are quick and potential responses to changing leaf responses can be captured instantly. Another advantage with this type of system is that it enables the user to control the environmental conditions inside the chamber cuvette, minimizing the differences in setup conditions between samples.

The system is equipped with chemical tubes used to remove both CO_2 and water vapor from the ingoing air stream. Chemicals used for removing CO_2 are soda lime (consisting of calcium oxide and sodium hydroxide) and for removing water vapor Drierite (consisting of 97 % calcium sulfate and 3 % cobalt chloride). After CO_2 has been removed, a disposable 12 grams CO_2 cartridge can be used together with a 6400-01 CO_2 mixer in order to control the ingoing CO_2 level into the chamber cuvette.



Figure 6: LED source leaf (6400-02B) and lighted conifer chambers (6400-22L).

The system was equipped with a LED source leaf chamber (6400-02B) for measurements conducted on oak and beech and a lighted conifer chamber (6400-22L) for measurements on spruce. For each measurement, the subjected plant material got an acclimation time of one hour before measurements were taken in order to adjust to set chamber conditions. According to laboratory experiments performed on spruce saplings before the first campaign, this was seen as sufficient to reach fairly stable emission levels. All samples were conducted on the south or southwest side of the trees. The plant material was subjected to $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ Photosynthetically Active Radiation (PAR, except for the study investigating light response of different compounds) and $400 \mu\text{mol CO}_2 \text{mol}^{-1}$ air. Relative humidity inside the chamber was maintained between 50 and 65 % and an average daily temperature was set according to the anticipated daily average. The ingoing airstream into the instrument was filtered through a hydrocarbon trap in order to remove possible sample contamination. According to some controlled measurements done *in situ*, the removal of organic contaminants in the air did not cause stress emissions from the leaves or needle twigs. Air samples were taken directly from the chamber outlet by using flow-controlled pocket pumps (Pocket Pump, SKC Ltd., Dorset, UK). The sampling flow rate was 200 ml min^{-1} and for each sample the collected volume was between 5-6 liters. Samples were collected by using stainless steel cartridges (Markes International Limited, Llantrisant, UK) packed with adsorbents Tenax TA (a porous organic polymer) and Cartograph 1TD (graphitized carbon black). Empty chamber samples were also taken in order to acknowledge possible background contamination from the sampled tubes. After measurements had been conducted, the leaf or needle twig inside the chamber was collected, dried and weighed in order to get the dry weight of the material.

GC-MS

All samples were analyzed using a gas chromatograph-mass spectrometer (GC-MS), a method which has been used for detecting volatile compounds for more than 60 years (James and Martin, 1952). The GC volatilizes the compounds in the cartridge sample and those are separated by using a carrier gas, for example helium, whilst the MS ionize the compounds by electron impact. The charged fragments are detected by providing atomic mass generated spectra. The given spectra can then be compared to a spectrum library in order to confirm the compounds detected by the instrument setup and quantification was done by using pure liquid standards in methanol solution.

Two separate GC-MS systems have been used when analyzing collected BVOC samples. The data collected in 2013 were analyzed with a Shimadzu QP2010 Plus (Shimadzu Corporation, Japan) with a gas chromatograph (GC, Clarus 500, PerkinElmer, Waltham, MA, USA) equipped with a flame ionization meter (FID), whilst the data from 2014-2016 were analyzed with a 7890A Series GC coupled with a 5975C inert MSD/DS Performace Turbo EI system (Agilent Santa Clara, CA, USA) after thermal desorption (UNITY2 couples with an ULTRA autosampler, Markes, Llantrisant, UK).

Emission calculations

After peak quantification had been performed, the emissions were calculated by using the emission rate equation for dynamic enclosure techniques presented by Hakola et al.(2003):

$$E = (C_2 - C_1)Fm^{-1} \quad (1)$$

where C_2 and C_1 are the outlet and inlet compound concentrations ($\mu\text{g l}^{-1}$), F is the flow rate of the purge air (l min^{-1}) and m is the dried mass (g) of the leaves or needles which were inside the chamber. As the inlet air is scrubbed before entering the chamber, BVOC emissions were considered to be negligible (i.e. $C_1 = 0$).

Field campaigns

One of the main aims with this dissertation was to investigate how the emission patterns for some of the most common European tree species have been influenced by different environmental conditions in absence of genetic diversity. Table 1 gives an overview of what campaigns were performed at which sites and in which paper the results are presented.

Table 1. Overview of location, when a campaign was performed, the type of study and in which paper the results are presented.

Location/coordinates	Date of campaign	Study	Paper
Ljubljana, Slovenia 46°04' N / 14°30' E	26-31 May 2014	Latitude variation Spruce	II III
Grafrath, Germany 48°18' N / 11°17' E	2-16 June 2014	Latitude variation Spruce	II III
Taastrup, Denmark 55°40' N / 12°18' E	3-4, 10-19 and 24-27 June, 1-31 July and 1-14 August 2013 14-25 July 2014 10-31 July 2015	Canopy height Latitude variation Spruce Light	I II III IV
Piikkiö, Finland 60°23' N / 22°30' E	29-31 July and Q11-2 August 2014	Spruce	III

Emission variations with canopy height and time of season

At the Taastrup site in 2013, three levels within the canopy were measured on all of the investigated trees in order to study the potential differences in emission capacity (paper I). The levels chosen within the canopy were approximately at 1-2 meters, 5.5 meters and 12.5 meters above the ground. All heights were measured at the same side of the tree and the different levels were reached with the help of a portable scaffold or an electric lift. For the oak and early spruce trees, measurements were also performed twice within the measurement campaign to investigate possible emission changes with a change in time.

Latitudinal BVOC emission variations

A_n , G_S and BVOC measurements were conducted during May to August in 2014 at four IPG sites in Europe (paper II and paper III). The genetic diversity between sites and individuals were assumed to be absent, which made comparisons of different environmental conditions possible. The measurement campaigns started in Ljubljana and ended in Piikkiö in order to minimize the differences in leaf development and environmental conditions between sites. The aim of the performed studies was to investigate if genetically identical tree species had different emission patterns due to adaptation to site-specific conditions or if the emissions remained similar across different latitudes.

Light experiment

The effect of different light levels on the BVOC emission from the selected tree studies were performed in Taastrup in 2015 on both *de novo* and storing plant species (paper IV). Measurements at four light levels were taken on each leaf or needle twig, namely 0, 500, 1000 and 1500 $\mu\text{mol m}^{-2} \text{s}^{-1}$. The light levels and other influencing variables (such as temperature, humidity and CO_2 levels) were controlled within the LI-6400 in order to provide similar basic settings for each leaf or needle twig. All measurements started with 0 $\mu\text{mol m}^{-2} \text{s}^{-1}$ and increased in intensity with the progression of the day. At 0 $\mu\text{mol m}^{-2} \text{s}^{-1}$, each leaf or needle twig got an acclimation time of one hour before measurements were taken. For the remaining light levels, the acclimation time was 30 minutes as preliminary tests had shown this to be sufficient in order for the emissions to acclimatize to the new light level. The leaf or needle twig was collected after the last light level had been performed.

Results and discussion

Emission pattern variability between genetically identical trees and provenances

By using the IPG network, it was possible to study if genetically identical individuals of English oak, European beech and two provenances of Norway spruce were similar in their BVOC emission rates, both within the same site but also between sites. The genetically identical trees were first studied in Taastrup, Denmark in order to investigate possible emission pattern variations. The results showed there were no clear BVOC emission pattern differences between individuals of the same tree species. English oak was mainly emitting isoprene, European beech was a monoterpene emitter and Norway spruce emitted mainly monoterpenes with a slight emission of isoprene and sesquiterpenes (Persson et al., 2016). Similar emission patterns have also been confirmed by other earlier studies (Isidorov et al., 1985; Dindorf et al., 2006; Holzke et al., 2006; Demarcke et al., 2010; Kleist et al., 2012; Pokorska et al., 2012). However, there was a difference in the emission spectra for the two provenances of spruce. Whilst early spruce had a higher proportion of limonene in their emission samples, late spruce had a higher emission of α -pinene. Tree-to-tree variability has also been shown for genetically different trees, growing in the same area (Hakola et al., 2017). As compounds have variable reactivity rates in the atmosphere due to their molecular structure (Atkinson and Arey, 2003), it is important to get a better understanding of within-species emission diversities.

Similar compound compositions between individuals within the same site were also seen at the study sites Ljubljana, Grafrath and Piikkiö (see Figure 7 for English oak and European beech; Figure 8 for Norway spruce). These results highlight the importance of taking genetic variation into account in regards species-specific emission pattern variations for different species. The robustness of emission spectra from genetically identical trees can therefore serve as a tool to understand other impacts on BVOC emissions, such as growing conditions or age and could further improve emission modeling by improving emission parameterizations.

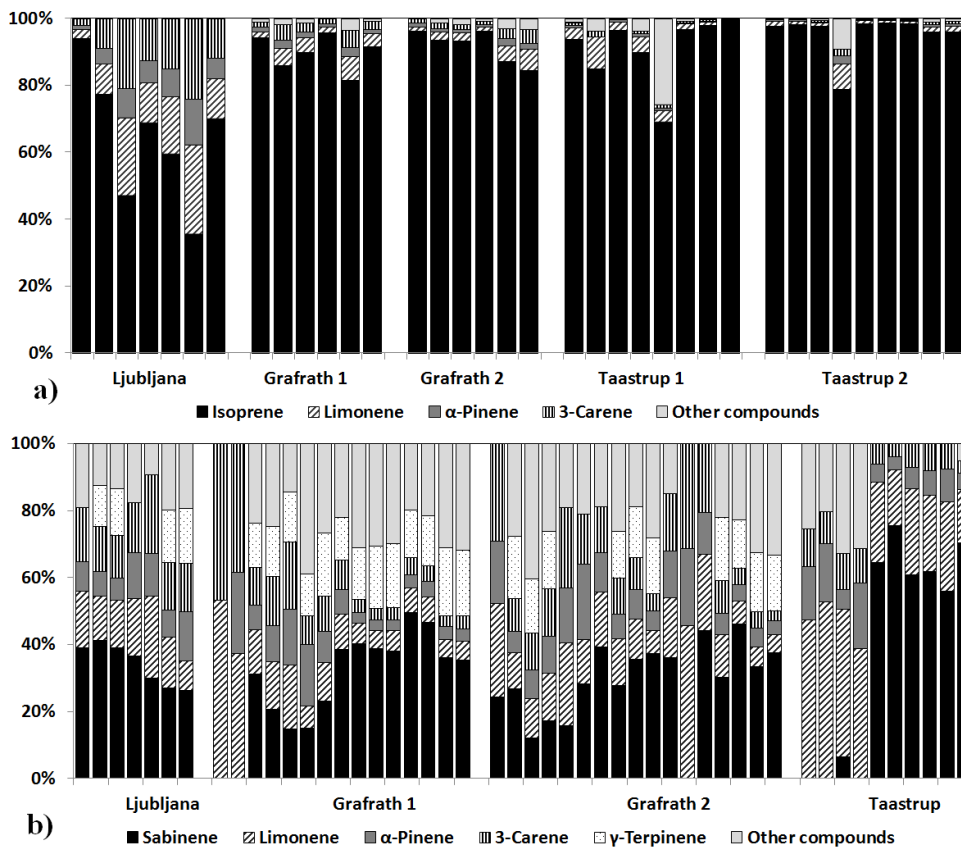


Figure 7: Relative compound contribution for individual samples from a) English oak ($n = 36$) and b) European beech ($n = 49$). The category “Other compounds” contains the compounds camphene and β -ocimene for oak and α -thujene, camphene, α -phellandrene, α -terpinene, β -phellandrene and terpinolene for beech. The figure is adapted from paper II.

The effect of latitudinal environmental differences

As the individual trees within the IPG network showed little emission pattern variation within the same site, it was possible to compare how different local growing conditions would affect the observed emission rates. For the change in latitude it was shown that the emission amounts differed between visited sites, but the relative compound contribution remained fairly similar across the entire transect. English oak mainly emitted isoprene, contributing with between 78-97 % of the total emission. The oak tree in Ljubljana had the lowest emission and contribution of isoprene in its samples in comparison to the other sites. The reason is believed to be due to a frost event prior to the measurement campaign and a third of the tree had to be cut, which most likely would have affected the tree's emission capacity (van Meeningen et al., 2016; Figure 7).

The emission from the European beech trees were generally low in comparison to other performed studies (Moukhtar et al., 2005; Dindorf et al., 2006; Demarcke et al., 2010), most likely because all measurements were taken at the lower part of the canopy. However, all trees had similar compound contributions even though the total emission differed, with sabinene as the highest emitted compound followed by limonene (van Meeningen et al., 2016; Figure 7).

The emission rates from the two provenances of Norway spruce were fairly similar in comparison to each other. Within the IPG network Taastrup was most different in comparison to the other sites, both in regards to almost twice as high emission rates measured in 2013 and due to the compound composition of the two provenances. Whilst early spruce had a higher emission of pinenes and late spruce emitted more isoprene and limonene at the other sites, the trees in Taastrup had the opposite emission pattern for monoterpenes. For the remaining sites, there were little compound composition differences with a change in latitude and the composition remained fairly stable between measurement years (Figure 8).

The similarity in compound contributions between measured trees suggests a potential stability in their compound production across the studied transect. Since the relative compound contribution did not change significantly with a change in latitude, it highlights the potential impact genetic diversity has on observed emission pattern variations between conducted studies. The results would suggest it is the genetics of the tree that determine the compound composition and that acclimation to local growing conditions do not change their relative compound composition considerably. But in order to confirm this, more studies need to be performed on a larger set of genetically identical trees and species.

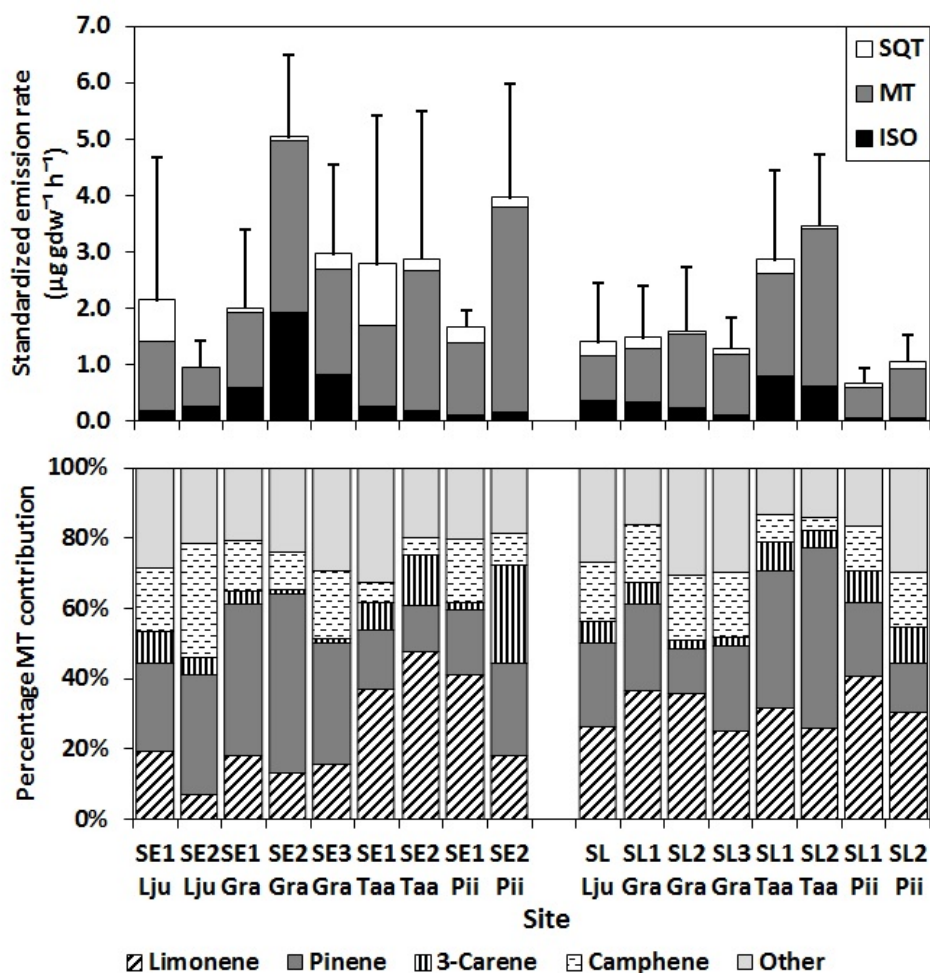


Figure 8: The standardized BVOC emission rate of isoprene (ISO), monoterpenes (MT) and sesquiterpene (SQT) and the relative compound contribution of MTs for the individuals of early spruce (SE; $n = 8-56$ samples) and late spruce (SL; $n = 6-34$ samples). Early spruce is defined by an early budburst, whilst late spruce begins its budburst approximately one week later. The error bars are the standard deviation of the data. The category “Other” contains the compounds tricyclene, α -thujene, sabinene, α -phellandrene, α -terpinene, β -phellandrene, eucalyptol, ocimene, γ -terpinene, terpinene and linalool. Figure adapted from paper III.

BVOC emission variation in regards to light, height within the canopy and time of season

Light is an important environmental factor which determines the amount of terpenoid precursors produced by photosynthesis and the BVOC amount which is released (Niinemets et al., 2004 and references within). Whilst some compounds are released upon production, other compounds can be stored in internal storage structures from which they are evaporated at another time (Kesselmeier and Staudt, 1999; Niinemets et al., 2004).

A light dependent fraction of the total compound emission was calculated to study the response of various compounds to changing light. The light dependent percentage was calculated as $100 \% \times (\text{light emission} - \text{dark emissions}) / \text{light emissions}$. Measurements were performed in Taastrup, where the relative contributions at a light level of $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ were similar between individuals of the same species. Some compounds were species specific, with high emissions of isoprene from the English oaks, sabinene from European beech and either α -pinene or limonene from the two provenances of Norway spruce (Figure 9). Five compounds were emitted by all of the measured trees, making it possible to study how individual compounds reacted to changes in light between different species. These were α -pinene, camphene, 3-carene, limonene and eucalyptol.

Isoprene from English oak and Norway spruce and sabinene from European beech were shown to be light-dependent for all of the measured tree species. For the remaining compounds emitted by English oak and European beech, there was no significant emission response with a change in light. The compound camphene showed no clear emission response from any of the tree species with an increase in light. An exception was for two individuals of spruce, but there was only a significant emission response from darkness to $500 \mu\text{mol m}^{-2} \text{s}^{-1}$.

Many of the individuals of the two provenances of Norway spruce showed high light-dependent fractions from the compounds α -pinene, 3-carene and eucalyptol, which remained fairly stable with an increase in light. This potential stability in light dependency could be used to further improve emission modeling and might potentially be valid over a larger set of tree species. But for some of the trees, there was a high internal variation which might have masked some of the emission responses. There is also a need to do emission studies on light levels below $500 \mu\text{mol m}^{-2} \text{s}^{-1}$, as the chosen levels did not fully cover the emission response of the chosen tree species.

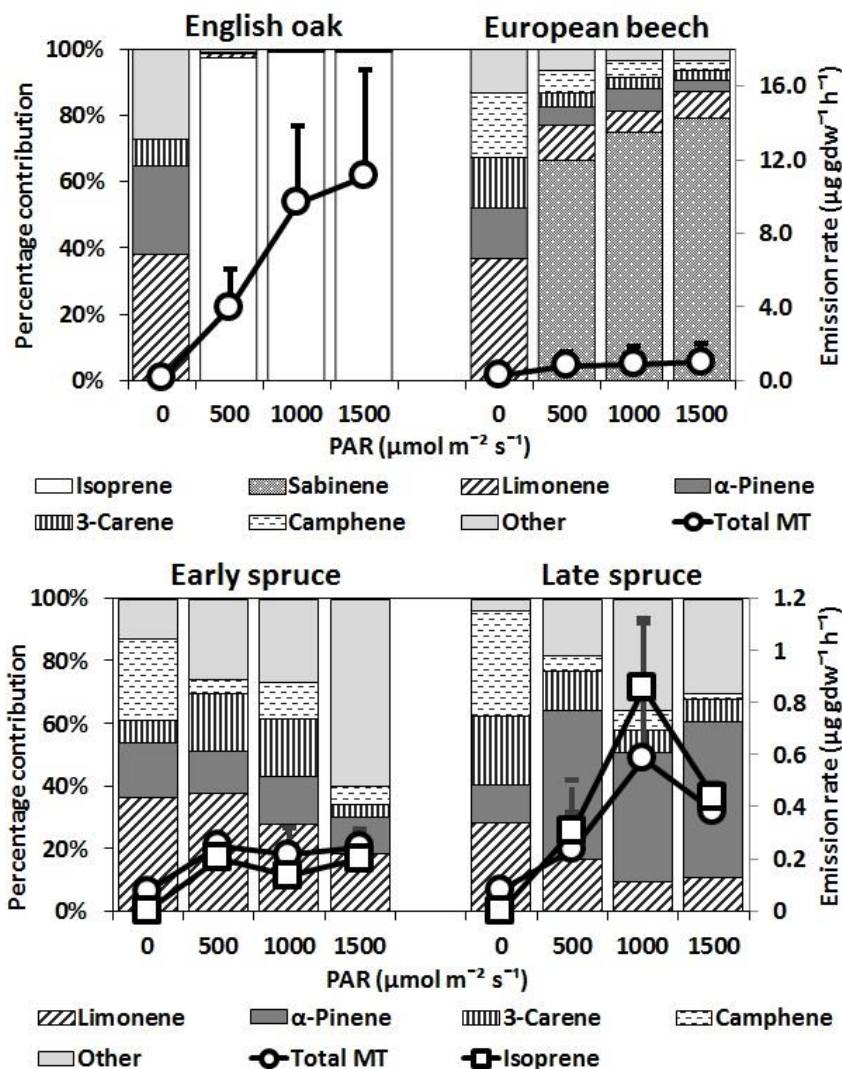


Figure 9: The average BVOC emission rate from individuals of English oak, European beech and two provenances of Norway spruce and the relative compound contribution at four photosynthetically active radiation (PAR) levels. Early spruce is defined by an early budburst, whilst late spruce begins its budburst approximately one week later. The open circles show the total monoterpene emission (MT), whilst the open squares show the isoprene emission ($n = 3-6$ samples). The error bars are the standard deviation of the data. “Other” contains the compounds tricyclene, camphene and eucalyptol for oak, tricyclene and eucalyptol for beech, tricyclene, β -pinene, eucalyptol and linalool for early spruce and tricyclene, β -pinene, α -terpinene eucalyptol and γ -terpinene for late spruce. Figure adapted from paper IV.

Some points to take into consideration are that all measurements were performed on the lowest positioned branches, which have previously been shown to be poorly acclimated to drastic increases in light (Harley et al., 1997; Šimpraga et al., 2013). The effect of measurement height on the observed emission rates was investigated at three canopy levels in the study conducted in Taastrup 2013. For English oak and the two provenances of spruce, there were no distinct differences in emission rates with the measurement height within the canopy. This lack of height dependence could be explained by similar light adaptations between different levels in the canopy as there was sufficient spacing between trees to provide light at lower canopy levels (Persson et al., 2016). The results from Norway spruce was compared with another spruce tree growing in a dense forest stand. The emission patterns from the tree growing in a dense forest stand showed significantly different emission patterns on all measured height levels, which would indicate that the lack of significant differences in Taastrup might be due to that more light is able to reach down to the ground.

However, for the European beech there were distinct emission rate differences between canopy levels. At the top of the canopy, the emissions were seven to nine times higher in comparison to lower levels in the tree. There was also a difference in leaf color between the upper and lower canopy levels, with leaves that were more yellow at lower heights. In comparison to the other studied trees, the European beech tree was standing in the northeast corner of the IPG site and was partly shaded by the surrounding trees. It is possible that the beech tree received less light at lower canopy levels in comparison to the remaining trees and therefore was less adapted to the light conditions provided by the instrumental setup (Persson et al., 2016).

Studies on emission pattern changes in regards to time of season have been shown to have a substantial effect on BVOC emission rates (Hakola et al., 2003; Tarvainen et al., 2005). The effect of seasonal development on the BVOC emission patterns was also investigated in Taastrup in 2013 and for Norway spruce in Ljubljana. In Taastrup, measurements were performed twice on English oak and early spruce in different parts of the season in order to study the possible change in emission spectra with the progression of summer. For oak, the total emission increased from June to August and the total proportion of isoprene increased from 62-74 % to approximately 97 %. It was believed that the increased emission rate was due to leaf maturation and that a higher monoterpene emission in the beginning of the season was due to stress from herbivore attack. The trees were visibly subjected to damage from caterpillars in June, but with no clear occurrence later in the season. For early spruce, the total emission decreased from July to August without a change in the number of detected compounds. This decrease is believed to be caused by water stress due to a 21 days long period without rainfall. The volumetric water content was not measured at the time, but the lowest branches were visibly affected as the needles dried and fell off by the end of the campaign (Persson et al., 2016). There was also an

increased emission of sesquiterpenes, which has been shown to be an indicator for plant water stress (Duhl et al., 2008).

Ljubljana was revisited in another measurement campaign between 2015 and 2016, where the provenances of spruce were measured both in October and in April to May. The standardized emission rates in October were less than a third in comparison to measurements performed in May and the compound composition changed for both provenance of spruce. There was not enough data to be able to compare differences in emission rates and compound composition with other studies, but the results show clear indications that there is a change in emissions with the progression of the season and that this change can only be encouraged to be studied further.



Figure 10: One of the measurement branches from late spruce growing in Taastrup, Denmark.

Conclusion and outlook

The main objective of this thesis was to analyze the impact of genetic diversity and latitudinal adaptation on BVOC emissions for English oak, European beech and Norway spruce by using the IPG network as its foundation. Emphasis has been on minimizing the within species variability caused by genetic differences in order to shed more information on the importance of local growing conditions and if the observed emission patterns adapt to site-specific climates. Most studies use seedlings or saplings in order to understand the effect of site specific growing conditions whilst excluding genetic diversity, with the disadvantage that the emission patterns can differ depending on the age of the plant. The advantage of using the IPG network is that studies can be done on genetically identical trees that are fully grown, which gives a much better representation of emission pattern responses for the chosen tree species as a whole. As the IPG network focuses on 21 different species in their observation program, it is possible and encouraged to study the emission pattern variation with a change in latitude for other common European tree species as well.

The similarity in relative compound composition for genetically identical trees across latitudes and time suggests that genetics have an important role in regards to the observed relative compound contribution across performed measurement campaigns. The largest emission variation between individuals was found for the provenances of spruce, but the variation was mainly found in the emission amounts of isoprene and sesquiterpenes. The compound composition for monoterpenes however was quite stable between provenances and across the latitudinal gradient. There was also an indication that the compound composition remained fairly stable over time, as similar compositions have been provided from the site Taastrup measured at approximately the same time in the growing season four years in a row. What these results would suggest is that the observed compound composition for these three types of trees is genetically determined and less prone to change with a change in local growing conditions. The stability in compound composition makes it possible to investigate how climatic differences might affect the emission amounts. Another suggestion would be to use these genetically identical trees and sites to find compounds that are more associated to various stresses and investigate if these patterns can be modeled over a larger spatial scale. However, in order to confirm this potential compound stability, more studies at different IPG sites would be recommended. To conduct more studies over a larger latitudinal range would give modelers an opportunity to

further improve their emission rate parameterization. It would also be possible to adjust the modeled emission patterns according to set regional conditions, which would hopefully provide with a better understanding how BVOC emissions might change with a changing climate.

However, even though the compound composition remained stable across different latitudes, the emission amount varied between sites. This result indicates that even though it is the genetics that determine the compound composition of a particular plant, the amount depends more on local growing conditions, including climate, and possible impacts of stress. Short-term stresses which were observed during some of the performed studies, such as extreme weather events, water shortage or insect outbreaks, had a clear impact on the emission patterns. But these impacts were in our cases only temporary and did not seem to influence the compound composition over a longer time perspective. Other effects which indicated influences on the emission amounts were measurements at different canopy heights and time within the growing season. These effects have not been studied in detail, but there were indications that they were influencing the emission rates and should be further investigated in order to fully understand their possible impacts.

By using the portable photosynthesis system LI-6400 and LI-6400XT, where the environmental conditions inside the chamber could be determined, it was possible to study the individual responses of the emitted BVOCs from oak, beech and spruce. Whilst some compounds were light-independent, others had high light-dependent fractions which remained stable with an increase in light. There were also some compounds which showed very little emission response with a change in light and which had similar emission responses across different tree species. However, when the light response study was performed it was assumed that all levels within the canopy had a similar light acclimation due to the wide spacing in between the individual trees. This was one of the results from the study done in 2013 in Denmark, where BVOC samples were taken at different heights within the canopy without a significant difference in emission amounts. However, this was not the case for the European beech tree, where the emission at the top of the canopy was seven to nine times higher in comparison to lower levels. It would therefore be important to study if this light response for different compounds is similar at the top of the canopy in comparison to lower levels.

Uncertainties which have emerged by using the IPG network is if the emission rates from individual trees are representable for the emissions from a forest. Most of the IPG sites have planted their trees with wide spacing in between, whilst a forest which the measured rates would be applied to usually grow in dense stands. Another uncertainty is that one to two individuals per site really is not enough to prove genetic similarities within a site. However, as the relative compound composition was shown to be similar between sites, there would still be indications that we would get similar

results if more trees were available. Lastly, there is an unknown effect from that some of these sites have been situated close by various agricultural practices and what the effect the nutrient availability at these sites might have had on the observed emission rates. However, despite these mentioned uncertainties, the IPG network has nevertheless provided with a unique opportunity to study how the emission patterns were affected by different climatic conditions.

More studies on more types of trees, in particular other important tree species such as pine, other subspecies of oak and birch, would be beneficial in terms of both model improvement but also to get a better understanding on how the emissions from these trees are affecting the atmospheric chemistry on a regional scale. Future studies could also aim at studying the effect of season at different IPG sites and if genetically identical individuals remain similar with the progression of time. Even though there were no clear emission adaptations in regards to compound composition between sites, it would be interesting to investigate if it is the same across different generations of genetically identical trees. Younger tree saplings have been measured in Grafrath, but their emission rates could either not be compared, due to that there was no mature trees available, or was not compared due to a lack of data. Another suggestion could be to study how tree species that are planted outside of their normal distribution range might have adapted to their conditions and what type of BVOCs they emit. These types of studies could potentially shed some additional light on how the emission patterns of our European tree species might change with global warming.

Acknowledgements

Trees can communicate! That has been my war cry at a number of different presentations and discussions regarding my work. My fascination for trees goes far back, from the time when I was 4 years old and had a pet spruce in my parent's garden. To get the opportunity to work with trees as an adult and learn about their secret ways, which is a whole unknown world for many of us, has been mind-numbingly fantastic! And all of this hard work has finally resulted in this thesis, which you now hold in your hands. I cannot take the whole credit though, for it has also taken immense amounts of dedication, encouragement and inspiration from a lot of wonderful people. I hope most of you already know what you have meant during this time, but just in case here comes some heartfelt appreciation. For this is the purpose of acknowledgements, is it not?

First of all, I would like to thank my supervisors Thomas Holst, Guy Schurgers and Riikka Rinnan for your support, for taking the time to discuss my questions and having patience with me when I got too impatient with the slow process of writing. All the freedom you have given me to develop my own set of skills, positive feedback whilst producing paper drafts and encouragement when things went wrong has turned me into what I am today. The amount of trust we have shared is something I have cherished and which I only can encourage you to withhold. To Thomas, I thank you for our long discussions about all aspects of work when I only intended to ask where we kept the screwdriver. Even at your most intense periods, you somehow managed to squeeze in a little room to discuss my ideas. To Guy, who is always quick to reply and to go through things with me that extra time, I thank you for your patience and passion. I never felt uncomfortable about bringing up my concerns and ideas to you, since you always had such good answers. And to Riikka, the powerhouse and my inspiration to do my fullest, I thank you for bringing that outside perspective to what I have done. Furthermore, I also want to send my gratitude to Anna Ekberg, who supervised me during my first year. Your expertise and knowledge about the LI-6400 was invaluable at the start of my studies. And you also helped me a lot when I tried to figure out what to do after my PhD defense party.

To my mentor Per Persson, who have followed me through half of my journey. To you, I just wanted to say you have been an excellent mentor and I believe we have both grown from this experience. By bringing your own personal perspective on

things, you have helped me to open my eyes for what I am capable of doing and to develop new skills which I did not think I had. I will always be grateful for that.

I am also very grateful to all the PhD students and staff at INES for making such a friendly and productive research environment. For all of the scrumptious cakes and lunches in the Botanical garden. For staying late watching movies or just talking about this and that in the corridor or the lunch room. I hope you never forget that what you do is amazing and mind blowing. And I encourage you to challenge yourselves as this will only help you to grow. To Kerstin and Florian, my office mates, we have faced so many stages of life and work together during our shared time. I can only wish you the best and thanks for all the talks and energy. Thank you Niklas, who I shared the LUCCI R3i leadership with, for always being positive and for all of the fun times that we shared during our planned activities. To David, Kristine and Aleksandra, who I worked together with during my brief time as a LDK vice president, I just wanted to say thank you. You believed in me and helped me grow into the president role more than you know. Thank you all of your hard work and for being who you are!

To the BVOC group in Copenhagen, what would I have done without our fruitful discussions? Frida, Michelle, Magnus and Jing, who I have talked to the most from the Copenhagen group, it has been a joy to join in on your biweekly journal groups (mostly via skype). And especially a big thanks to Michelle, Magnus and Gosha for helping me with GC-MS analysis in Copenhagen. Without you, less data, less publications, less of a thesis. So thank you for putting down so much effort.

When it comes to my own little BVOC group in Lund, thanks for all the wonderful times. To Tomas, I wish you the best and that you continue running towards your goal. Thanks for all the trips back and forth to Copenhagen, bringing home all the data. I am very grateful for that. To Min, my sister in arms, I cannot explain in words what you have meant to me during my PhD studies. We have shared office, taken courses together and gone to the other side of the world in the name of science. We were almost eaten by polar bears, got application grants in China and were star struck as Alex Guenther approached our posters. And even though I don't say it often, I will always admire your intelligence and positivity.

Last, but not least, I want to thank my family for the support and love they have always given me. To Kerstin, Lars and Viktor, you have helped me to think positive and to continue fighting when things looked rough. You remind me of the most important things in life and to not stop breathing whatever hits you. I would not have gotten this far without you. To Bodil, Ronald, Mimmi and Måns, thank you for your support and patience as I try to explain the complexity of my work. I am really happy to be part of your extended family and that I can be the sore loser in board games that I actually am. And to Max, my loving husband and best friend, what would I have done without your support, never ending encouragement and love? You always know

what to say to cheer me up. You keep me calm and happy and you make me laugh all the time. You have helped me grow so much during the progression of my PhD studies and you have always been there for me no matter what. And as a wise person once said to me, by just being yourself you help me be the person that I want to be. You and our joint future have inspired me to push my boundaries to the horizon and beyond.

-Jag älskar dig av hela mitt hjärta.

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