Scots pine resin and BVOC emissions in relation to tree water dynamics

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Trees have different mechanisms to avoid and mitigate biotic and abiotic stresses, among which resin is essential for conifer trees. Conifer resin is also a large pool of monoterpenes that – similarly to other volatile organic compounds (VOCs) produced by plants, e.g. methanol, acetone and acetaldehyde – have important roles in tree signalling and atmospheric chemistry once emitted to ambient air. The VOC emissions from different tree parts and resin dynamics depend on environmental variables, with intrinsic effects on conifer defence.

This thesis aims at clarifying the environmental and physiological drivers of resin dynamics and VOC emissions from shoots and stem of mature boreal Scots pines (*Pinus sylvestris*) in field conditions, with special attention to the effect of tree water relations. Resin pressure dynamics were studied using pressure transducers, and VOC emissions using online mass spectrometer and dynamic chamber system. Composition of resin and monoterpene emission was analysed based on gas-chromatograph measurements.

At a short term, resin pressures and VOC emissions both from shoots and stem of Scots pine were explained by temperature. Over a longer period, resin pressures and stem monoterpene emissions decreased with decreasing soil water availability and tree water potential. In addition, the emission dynamics of water-soluble acetaldehyde, methanol and acetone, from shoots and stem were connected to transpiration rate and soil water content, indicating an important effect of their transport in xylem sap.

These results show that although often overlooked, tree stems can be an important source of VOCs, and that even relatively small changes in water availability can alter the VOC and resin dynamics despite their strong short-term temperature control. This information could help to understand the potential susceptibility of conifer trees to biotic stresses in different environmental conditions and to improve VOC emission modelling by accounting for the stem emission dynamics.

Keywords: resin, monoterpene, methanol, acetaldehyde, acetone, Scots pine

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LIST OF ORIGINAL ARTICLES

The thesis includes the following publications, later referred to with their roman numerals.

I.   Rissanen, K., Hölttä, T., Vanhatalo, A., Aalto, J., Nikinmaa, E., Rita, H. & Bäck, J. (2016). Diurnal patterns in Scots pine stem oleoresin pressure in a boreal forest. *Plant, Cell and Environment* 39: 527–538.
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II.   Rissanen, K., Hölttä, T., Barreira, L.F.M., Hyytinen, N., Kurtén, T. & Bäck, J. (2019). Temporal and spatial variation in Scots pine resin pressure and composition. *Frontiers in Forests and Global Change* 2: 23.
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III.   Rissanen, K., Vanhatalo, A., Salmon, Y., Bäck, J. & Hölttä, T. (2019). Stem emissions of monoterpenes, acetaldehyde and methanol from Scots pine affected by tree water relations and cambial growth. Manuscript.

IV.   Rissanen, K., Hölttä, T. & Bäck, J. (2018). Transpiration directly regulated the emissions of water-soluble short-chained OVOCs. *Plant, Cell and Environment* 41: 2288–2298.
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1 INTRODUCTION

Trees stand still, living tens, hundreds, even thousands of years never moving from where they landed as seeds. Where they stand, they have to find all they need to sustain themselves, and where they stand, they have to resist all weathers and invasions from other organisms. Nevertheless, trees are among the most long-living individual creatures on our planet.

To survive and outlive the challenges in their habitat, trees have developed a multitude of fine mechanisms and processes to acquire water and nutrients, to transport substrates where they are needed, and to defend themselves against herbivores and pathogens. The functioning and fine-tuning of these processes have been – and still are – a great puzzle for researchers.

One successful survival mechanism has developed in conifer trees that are one of the most abundant groups of plants. To deter herbivores and pathogens, conifers produce resin. Resin is a viscous liquid that flows to cover wounds on stem surface, and it is toxic for many small organisms. It is also a large pool of monoterpenes, volatile molecules that create the distinct odour of resin and the odour of forest. While we detect these scents as a pleasant addition to the scape of scents, many organisms, plants and insects use them to receive information from their surroundings. They alert of possible hosts, prey or stress.

Alongside monoterpenes, trees produce a whole spectrum of different volatile compounds, the functions of which are not thoroughly understood at the tree level or in the ecosystem. It is known, however, that these compounds have an important role in the chemistry of atmosphere, affecting for example the quality of air and the formation of clouds. Instead of just surviving in their environment, trees actively affect the processes surrounding them.

Despite their fine mechanisms, despite resin, conifers are facing new challenges, including rapid shifts in their environment caused by land-use changes and global warming with its side effects. Thus, understanding the mechanisms of tree survival and their interactions with other organisms and atmosphere is increasingly important.

1.1 Resin

Resin, or oleoresin, is the sticky, gold-coloured liquid from conifer trees that embodies the odour of forest and freshly sawn wood. It has long been a valued raw material: fresh resin has been used to heal wounds and hardened resin chewed to clean teeth, but most importantly, resin has made its mark on history on the sides of sailing ships – pitch and tar that were used to coat the ships are products of slow burning of wood, high in resinous compounds. Nowadays, pine resin is used in the production of chemicals for different industrial and household uses, e.g. in adhesives, coatings, fragrances and flavours (Coppen and Hone 1995; Langenheim 2003). However, more than to human, resin is important for the trees. In conifer trees, resin is an essential part of the first-line of defence against herbivores and pathogens.

1.1.1 Resin composition and storage structures

Resin is found in most conifer species. For example, almost all genera of Pinaceae family, which is the largest conifer family, can produce resin. The composition of resin has been studied since 1930's and increasingly since 1960's (e.g. Kurth & Sherrard 1931; Smith 1964a b c), with varying intensities until present. During this time, the methods for resin component extraction and identification developed considerably, allowing increasingly reliable and comprehensive results on the resin composition.

Resin contains approximately 75% of resin acids that are non-volatile diterpene acids and 25% of volatile monoterpenes, as well as small amounts of volatile sesquiterpenes (Croteau and

Johnson 1985). Sometimes other wood extractives, such as phenolic compounds, are also classified as resins but in the following, resin includes only the terpene compounds. The mixture of the two types of terpenes enables resin functions: the volatile terpenes act as solvents that mobilise the non-volatile terpenes, whereas the non-volatile terpenes increase resin viscosity and cause its crystallisation. In *Pinus* species, the most common diterpenes are abietane- and pimarane-type diterpenic acids, such as abietic and pimaric acids (Langenheim 2003), and the most common monoterpenes are α-pinene, ß-pinene, Δ^3-carene, sabinene, myrcene, limonene and ß-phellandrene (Smith 2000) (Figure 1).

However, the composition of resin, and its monoterpene concentrations in particular, vary considerably between species, populations and even individuals of the same species (Smith 1964a; Zavarin and Cobb 1970; Marpeau et al. 1989; Latta et al. 2000, 2003; Fäldt et al. 2001; Thoss et al. 2007; Kännaste et al. 2013), and the composition seems to be under genetic control (Hanover 1966, 1992). Within one tree, resin composition may also vary between different tissues, especially when comparing needles, phloem and sapwood (Latta et al. 2000). However, within sapwood, resin composition is quite uniform (Smith 1964c). Despite the variation within and between trees, the temporal variation of resin composition should be limited in the absence of stresses: because resin production is small in comparison to the size of resin pool, the turnover is long, even in order of several years (Wilson et al. 1963; Gershenzon et al. 1993).

The structures for resin storage differ between species: resin can be stored in isolated resin cells scattered in stem (e.g. in *Thuja*), in resin blisters or glands that are round multicellular structures in sapwood and bark (e.g. in *Abies* and *Sequoia*), or within resin ducts that are long, intercellular cavities in sapwood, bark, roots, needles and buds (e.g. in *Pinus*, *Picea* and *Larix*). The resin duct system in pines (*Pinus*) is considered highly developed, forming a dense network of partially interconnected longitudinal and radial canals within the stem (Figure 2) (Werker and Fahn 1969; Bosshard and Hug 1980; Phillips and Croteau 1999; Zhang et al. 2008). The pine and spruce (*Picea*) resin ducts are enveloped by one or several layers of thin-walled epithelial cells that produce the resin acids and monoterpenes in their plastids, and the sesquiterpenes in their endoplasmic reticulum (Dell and McComb 1979; Langenheim 2003; Zulak and Bohlmann 2010). The epithelial cells are surrounded by layers of thick-walled sheath cells (Wu and Hu 1997). In pines, the epithelial cells can stay biologically active for several years, whereas the sheath cells can be dead (Wu and Hu 1997).
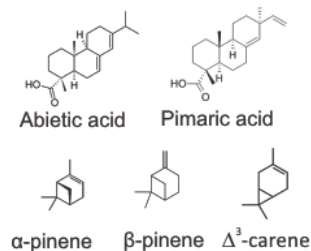

Figure 1. Crystallising resin and the most common components of resin in *Pinus* species (photo by Kaisa Rissanen).
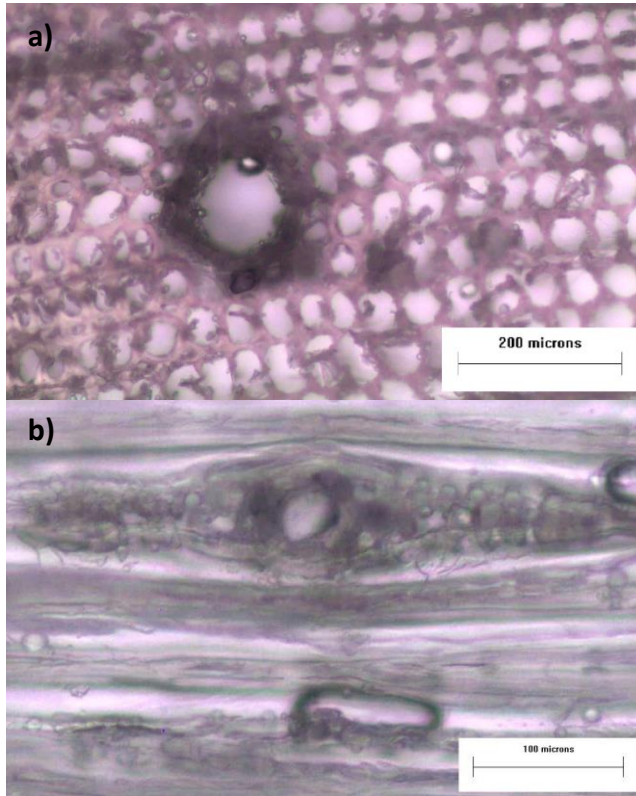
Figure 2. a) Axial (vertical) resin duct and b) smaller horizontal resin duct in ray of Scots pine (*Pinus sylvestris*) (photo: Study I, Rissanen et al. 2016).

1.1.2 Resin in conifer defence

Resin has been an important subject of research because of its commercial value but even more because of its central role in the defence of conifer trees. For example, during and after the outbreaks of southern pine beetle (*Dendroctonus frontalis*) in the southern USA in 1970's, researchers concentrated on identifying the traits that made the local pine species and individual trees either susceptible or resistant to the bark beetle infestations. These traits included among others, resin composition and flow, and the density of resin ducts.

Resin protects the tree against pathogens and pest insects, for example, herbivorous larvae and bark beetles, both mechanically and chemically. As the mechanical defence, resin pitches out intruders and seals wounds. In pines, resin in resin ducts is stored under a pressure that can exceed 10 bar (Bourdeau and Schopmeyer 1958; Vité 1961; Vité and Wood 1961), which enables a rapid release of resin after the duct has been injured. The flow of resin released from the wound can overwhelm and drown an invasive insect. After the flush of resin to the wounded site, the resin monoterpenes evaporate, and the resin acids crystallise to form a seal that protects the wound from further intruders (Figure 3). The chemical defence comprises resin compounds that are either harmful for herbivores or pest insects, such as monoterpenes limonene, Δ^3-carene and α- and β-pinene (Smith 1965, 1966; Phillips and Croteau 1999; Seybold et al. 2006; Reid et al. 2017), anti-fungal, such as resin acids abietic acid and isopimaric acid (Kopper et al. 2005), or anti-bacterial, such as monoterpenes thymol, carvacol, p-cymene and y-terpinene (Cristani et al. 2007). These compounds can affect the herbivore preferences, larvae development (Langenheim 1994), and fungal germination or growth (Kopper et al. 2005), but they can also be used as signals by the host-seeking insects (Phillips and Croteau 1999) or their predators and parasites

(Langenheim 1994). In addition, monoterpenes can transmit signals within plant and between plant individuals (Baldwin et al. 2006): high concentrations of stress-related monoterpenes in air can provoke the production of defensive compounds and prepare other plant parts or even other plants against potential herbivory (Baldwin et al. 2006).

However, even from the insect perspective, resin is not only harmful. Certain insects can tolerate the high concentrations of resin acids and monoterpenes and find protection within resinous tissues (Langenheim 1994). European sawfly larvae (*Neodiprion certifer*) can even sequester resin acids for their own defence and eject them on predators (Eisner et al. 1974). In addition, wood ants carry resin into their nest in order to protect it against pathogens (Chapuisat et al. 2007; Castella et al. 2008).

1.1.3 Resin dynamics

While studying the susceptibility and resistance of certain pines to a mass-attack of bark beetles, researchers found that not only the resin composition and certain toxic compounds, but also the production, flow and pressure of resin play a central role in the resistance. Although none of these variables explained the tree resistance alone (Lorio 1994), it was observed that the trees that were more resistant to bark beetles had, among other things, large and persistent resin flow (Smith 1966; Hodges et al. 1979; Strom et al. 2002) and high resin pressure (Vité and Wood 1961; Wood 1962).

Resin pressure is not a static feature of the tree, but it changes depending on water availability and tree water relations at different time scales. At a seasonal scale, decreasing availability of water causes a decreasing trend in the resin pressure, partly explaining the susceptibility of trees to bark beetles in dry conditions (Vité 1961; Barret and Bengtson 1964; Lorio and Hodges 1968a). At a daily scale, high resin pressures have been invariably measured at night when the water potential in stem is high and low resin pressures in day time when the water potential is low (Schopmeyer et al. 1954; Bourdeau and Schopmeyer 1958; Vité 1961; Hodges and Lorio 1968, 1971; Lorio and Hodges 1968b; Helseth and Brown 1970; Neher 1993). These dynamics have been explained by the changing xylem water tensions and turgor pressures within the stem. On the one hand, in day time, high transpiration decreases the water potential in xylem, which shrinks the xylem tracheids and creates more space for the intercellular resin ducts, decreasing the resin pressure (Helseth and Brown 1970; Neher 1993). On the other hand, low water potential also draws water from the epithelial cells lining the resin duct, decreasing their turgor pressure and thus the pressure they pose on the resin (Vité 1961).

The large body of knowledge on the pine resin dynamics has been collected in the drought-prone pine forests in southern USA, but similar understanding is lacking in the cool and moist boreal environment. In the boreal forests, the role of resin-base defence is crucial, since bark beetles pose a major threat to the conifer trees particularly after storms and during and after dry years (see Bakke, 1983). Storms and windfalls, as well as droughts or inundations may become more frequent because of climate change, favouring bark beetle epidemics. In addition, warmer and longer growing seasons in the north can allow bark beetles to produce two broods in one growing seasons, which also increases the risk of epidemics (Schlyter et al. 2006). Thus, to predict and prevent forest dieback it is important to understand the factors affecting tree defence in the boreal environment, as well.

Figure 3. Resin leaked from Aleppo pine (*Pinus halepensis*) stem where bark beetles have entered the stem (photo by Kaisa Rissanen).

1.2 Volatile organic compounds (VOCs)

The volatile constituents of resin, monoterpenes and sesquiterpenes belong to a group of compounds called volatile organic compounds (VOCs) and more specifically, biogenic volatile organic compounds (BVOCs). They are a variety of hydrocarbon molecules that plants produce and emit as a part of their secondary metabolism, meaning that these compounds are not directly necessary for normal growth and reproduction. However, they serve many purposes, such as the resistance against heat and high irradiation as well as the signalling and defence against biotic stresses, but they can also leak out as side products of other metabolic processes in plants. BVOCs have been of growing interest both because of new findings on the signalling within and between plants or between plant and insects, and because of their important role in the atmospheric chemistry.

Once emitted to ambient air, BVOC react with the atmospheric oxidants: hydroxyl radical (OH), ozone (O_3) and nitrate radical (NO_3) (Atkinson and Arey 2003). These reactions have different consequences in the atmospheric chemistry. First, BVOCs reacting with OH reduce the atmospheric sink for methane, meaning that high concentrations of BVOCs lengthen the methane life time (Kaplan et al. 2006). Second, BVOCs can react with nitrogen oxides (NO_x) that originate from anthropogenic sources, such as industry and transport, and produce ozone. Thus, high concentrations of BVOCs combined with high concentrations of NO_x increase ozone concentration in the troposphere, contributing to the poor air quality in already polluted areas (Atkinson 2000). In contrast, in the areas where NO_x concentrations are small, BVOCs remove ozone, contributing to the good air quality (Atkinson and Arey 2003). Third, BVOCs participate in processes that impact regional and global radiative budget. BVOC oxidation products initiate or participate in the growth of secondary organic aerosols (SOA) (Ziemann and Atkinson 2012). When large enough, SOA form cloud condensation nuclei that evolve into cloud droplets and form clouds, the properties of which depend on the quantity and size of the cloud droplets (Andreae and Rosenfeld 2008; Kazil 2010; Rosenfeld 2014). Together with SOA, clouds increase

albedo and scatter the radiation from sun, thus they have a net cooling effect on the climate (Kulmala et al. 2013; Paasonen et al. 2013; Kulmala 2014). The scattering of radiation also increases the ratio of diffuse to direct radiation which is advantageous for plant growth (Gu 2002) and further emissions of BVOCs, creating a cooling feedback loop (Kulmala et al. 2013).

The reactions of BVOCs in the atmosphere are important parts of climate modelling, and detailed information on BVOC emissions budgets from vegetation is necessary to represent the BVOC effects accurately. The remaining questions concerning the role of BVOCs include, for example, the contributions of different ecosystem sources to total BVOC budget and the dynamics of long-term BVOC pools in vegetation.

1.2.1 Terpenes

Terpenes are BVOCs formed of five-carbon isoprene units. Isoprene emissions from terrestrial vegetation are considerable, and it has the largest global annual budget of non-methane BVOCs, 516 Tg C (average of different models, Arneth et al. 2008). Monoterpenes consist of two isoprene units (10 carbon atoms) (Figure 1) whereas sesquiterpenes contain three of them (15 carbon atoms). Monoterpenes are among the second most emitted non-methane BVOCs, with the global annual budget of 91 Tg C (average of different models, Arneth et al. 2008). Monoterpene emissions are pronounced over conifer-dominated forests, such as boreal forests, because conifer trees can store monoterpenes in resin. Sesquiterpene emissions from terrestrial vegetation are also large, but sesquiterpene emission budgets and sources remain relatively uncertain because of their low volatility and high reactivity, and consequent difficulties in measuring them (Kim et al. 2009). The larger terpenes, such as resin acids that contain four isoprene units (Figure 1) have low volatility and are not commonly studied among VOCs.

This thesis discusses mainly monoterpenes, since they form a large part of resin and are an important part of the BVOC budget of boreal forests. Monoterpenes are mainly defence and signalling compounds, and in addition to the defence against biotic stresses described earlier (section 1.2.2), monoterpenes can increase plant resilience to abiotic stresses. For example, monoterpenes can help to reduce dangerous oxidation reactions in leaves that are exposed to heat (Loreto et al. 1998).

Monoterpenes are produced in the plastids of living cells, especially in the epithelial cells of resin-producing conifers (Turner et al. 2019). Monoterpene production is limited by enzymatic regulation and substrate availability controlled by temperature and light, and it also depends on phenology and tissue maturity, at least in leaves (Vanhatalo et al. 2018). Upon production, monoterpenes can be stored in long-term storages, such as resin in conifer trees or in temporary storages, such as cell membrane lipids (Niinemets and Reichstein 2002; Noe et al. 2006), or they can be emitted instantly (*de novo* emissions). The size and composition of monoterpene storage in a pine needle, for example, may vary either because of new production or emissions from the storage. The variation is often small (Llusià et al. 2006; Vanhatalo et al. 2018), probably due to the long storage turnover times, but during the needle development, larger changes in the monoterpene storage are possible (Thoss et al. 2007). Monoterpene production and storage affect the emissions of monoterpenes, but the emissions also depend on temperature and other fast changes in the environment. A large part of the monoterpene emissions from needles are *de novo* emissions (Ghirardo et al. 2010; Harley et al. 2014), and another part can originate from both long-term and temporary storages (Niinemets and Reichstein 2002; Noe et al. 2006), meaning that the total emissions are combined emissions of stored compounds and recently produced compounds. As a result, there may be considerable differences between the composition of monoterpenes that are produced, stored and emitted, and these interrelations are further complicated by the varying time lags in the different processes (Vanhatalo et al. 2018).

The monoterpene emissions may also diverge from the storage and production because of the different volatilities of the different monoterpene compounds (Table 1). Volatility describes how easily a substance vaporises and it is regulated by the vapour pressure of the compound. In the case of BVOCs, partitioning between water and air, described by Henry's law constant, and between water and lipid phases, described by octanol/water partition coefficient, also affect the overall volatility from plant structures to ambient air. The vapour pressures of different monoterpenes vary considerably (Hoskovec et al. 2005; Rumble et al. 2017; Kim et al. 2018). For example, α-pinene is highly volatile with vapour pressure of 663 Pa in 25°C whereas vapour pressure of terpinolene is smaller, 99 Pa in 25°C (Kim et al. 2018) (Table 1). Monoterpenes are generally not soluble in water, but certain oxygenated monoterpenes (monoterpenoids), such as linalool are moderately water-soluble (Copolovici and Niinemets 2005; Noe et al. 2006) (Table 1). These differences in vapour pressure and solubility affect the spectrum and dynamics of monoterpene emissions measured from plants so that compounds with higher vapour pressure may be pronounced in emissions compared to their proportions in storage. In addition, the emissions of compounds that are water-soluble are more controlled by stomatal conductance than emissions of compounds that are not water-soluble.

1.2.2 Resin effects on monoterpene emissions

Resin is a large pool of monoterpenes and sesquiterpenes in conifer trees, thus its composition can be expected to affect the emissions of these compounds. As discussed earlier (section 1.1.1), the tree-to-tree variation in resin composition even within the same species is considerable (e.g. Marpeau et al. 1989; Latta et al. 2000; Fäldt et al. 2001; Thoss et al. 2007; Kännaste et al. 2013). Similar tree-to-tree variation has been reported in monoterpene emissions from pine shoots (Komenda and Koppmann 2002; Semiz et al. 2012; Bäck et al. 2012), but whether the emitted monoterpenes correspond to the monoterpene spectrum in resin is unclear. If resin composition and monoterpene emissions correlate closely, resin sampling could be an easy and fast way to map the monoterpene emission variability within a population or species. For example, Flores & Doskey (2015) used information on resin composition and the different chemical characteristics of the resin compounds to estimate the emissions of terpenes and terpenoids from *Pinus strobus* shoots. This kind of information would be useful when the atmospheric chemistry models evolve to account for the diverse monoterpenes.

When modelling and quantifying the monoterpene emissions from conifers, even when considering the effects of resin composition (Flores and Doskey 2015), resin is often considered a passive pool from which the compounds evaporate in a temperature-dependent manner (e.g. Tingey 1980) also potentially affected by other variables, such as humidity (Tingey et al. 1991; Llusià and Peñuelas 1999). However, resin is not passive, on the contrary, its pressure and flow vary according to temperature and water potential in xylem, and the effects of these resin dynamics on the monoterpene emissions from foliage and stem are unknown.

In addition to the potential effects of resin dynamics inside the tree, resin that is exposed can temporarily alter the stand-level emissions of monoterpenes. On the one hand, cutting conifer trees expose the stored resin, thus forest management practices can have large, yet relatively short term effects on stand level monoterpene budgets (Schade and Goldstein 2003; Räisänen et al. 2008; Haapanala et al. 2012; Kivimäenpää et al. 2012). On the other hand, naturally exposed resin on developing cones, buds and the bases of needles may contribute up to 10% of the total ecosystem monoterpene flux while the resin is fresh (Eller et al. 2013). Extreme effect of resin can be observed in pine forests that are used for resin tapping, where emissions from resin can dominate the emissions from foliage (Pio and Valente 1998). Finally, bark beetles cause resin leakage, which probably contributes to the increased emissions of monoterpenes that have been detected over bark beetle infested forests (Berg et al. 2013).

Table 1. Chemical properties of some compounds studied in this thesis

	Molecular mass (g mol^{-1})	Henry's law coefficient (Pa m^3 mol^{-1}, at 25°C)	Octanol/ water partitioning coefficient (mol mol^{-1}, at 25°C)	Vapour pressure (Pa, at 25°C)
Monoterpenes				
α-pinene	136.24	13 600	30 900	663
β-pinene	136.24	6 830	26 300	391
Δ^3-carene	136.24	13 640	40 740	496
terpinolene	136.24	2 600	29 510	99
Monoterpenoids				
linalool	154.25	2.09	933	21
OVOCs				
methanol	32.04	0.461	0.170	16 900
acetaldehyde	44.05	7.00	0.457	120 300
acetone	58.08	3.88	0.575	30 900

Sources: https://pubchem.ncbi.nlm.nih.gov (visited in 22.6.2019), Niinemets and Reichstein 2002, 2003, Copolovici and Niinemets 2005, references therein

1.2.3 Water-soluble oxygenated VOCs

Among the most common oxygenated volatile organic compounds (OVOCs) measured from vegetation are methanol, acetaldehyde and acetone (Fall 2003). Estimates for global annual biogenic emissions range between 38–107 Tg C for methanol (Fall 2003; Messina et al. 2016), 44–88 Tg C for acetaldehyde (Fall 2003) and 25–59 Tg C for acetone (Fall 2003; Messina et al. 2016). These compounds are emitted as side products of plant metabolism, but all their sources and possible functions are not yet fully understood.

Methanol is mainly produced in plant growth: it is released in demethylation when the pectin of cell walls is formed or degraded during the growth and senescence of plant tissues (Nemecek-Marshall et al. 1995; Fall and Benson 1996; Galbally and Kirstine 2002; Hüve et al. 2007; Seco et al. 2007). Thus, it is produced in all growing plant parts. Some methanol is also released in the protein methyl transferase and protein repair processes, as well as in soil during the degradation of plant material (Fall and Benson 1996).

High emissions of methanol and acetaldehyde, in particular, occur when the soil is flooded and tree roots lack oxygen (Kreuzwieser et al. 2000; Holzinger et al. 2000; Karl et al. 2003; Copolovici and Niinemets 2010; Bracho-Nunez et al. 2012). The acetaldehyde emission peaks are explained by anoxic metabolism in plant roots that produces ethanol that is further oxidised into acetaldehyde (Seco et al. 2007). However, ethanol and acetaldehyde emissions have also been measured during low soil moisture (Schade 2002), indicating that other important sources exist. Ethanol formation and acetaldehyde emissions may also result from insufficient diffusion of oxygen and anoxia in stem especially during fast growth and high metabolic activity (Kimmerer and Stringer 1988). Like methanol, acetaldehyde is also produced in the plant material degradation in soil (Warneke et al. 1999). In addition, the decarboxylation of pyruvic acid in leaves that are exposed to fast light-dark transitions cause release of acetaldehyde and large emission bursts (Karl et al. 2002, 2003; Hayward et al. 2004; Karl 2004; Seco et al. 2007; Jardine et al. 2012).

The VOC emission bursts after light-dark transition also contain acetone (Jardine et al. 2012). Acetone has been proposed to be a side-product on hydrogen cyanide, and a product of the

acetoacetate carboxylation in soil bacteria (Fall 2003; Seco et al. 2007), but its main sources and its role in plants are not well known.

Methanol, acetaldehyde and acetone are all water-soluble with small Henry's law coefficients (Table 1). Thus, they can enter the water films in leaves and the xylem sap in roots and stem, and their emissions from shoots are considered to be controlled by stomatal conductance (Niinemets and Reichstein 2003; Niinemets et al. 2004; Harley et al. 2007). There is also evidence that methanol and acetaldehyde, along with its precursor ethanol, can be transported in the xylem sap from soil and stem to the leaves (Kreuzwieser et al. 2001; Grabmer et al. 2006; Folkers et al. 2008). Consequently, the emissions measured from the leaves could originate partly from soil, roots and stem due to the transport. However, the magnitude and importance of the OVOC transport in total shoot emissions is still unknown, and the transport mechanism has not been studied in field conditions.

1.2.4 VOC emissions from stem

The BVOC emissions from trees are most commonly measured from the foliage, because it is considered the most active part of the tree. When studying compounds such as isoprene that are tightly linked with metabolism that takes place only or mainly in leaves, this is reasonable. However, for example monoterpenes, methanol and acetaldehyde are also synthesised and transported in other parts of tree, and in the case of monoterpenes, even stored in other parts of tree in large amounts.

The relatively few studies on conifer stem BVOC emissions have measured the effects of fungal infection or insect damage on the emissions, and the volatile cues that the stem sends to bark beetles (Rhoades 1990; Gara et al. 1993; Heijari et al. 2011; Amin et al. 2012, 2013; Lusebrink et al. 2013; Kovalchuk et al. 2015; Ghimire et al. 2016). The emissions of ethanol and monoterpenes from stem have been reported to increase due to different biotic stresses (Gara et al. 1993; Amin et al. 2012, 2013; Lusebrink et al. 2013; Ghimire et al. 2016). When the stress is targeted to the stem, the stem emissions increase more than the emissions from foliage (Heijari et al. 2011; Amin et al. 2012). Abiotic stresses may also affect the emissions from stem: when subjected to drought, total monoterpene emissions from the stem of lodgepole x jack pine hybrids increased (Lusebrink et al. 2013). Including the stem BVOC emissions into the context of the whole stand BVOC emissions for the first time, Vanhatalo (2018) calculated that the unwounded stem of Scots pine (*Pinus sylvestris*) trees contributed approximately 2% of the total stand BVOC emissions, while the foliage made up the largest part. Although 2% is a small proportion, omitting it will cause a bias when calculating emission sums over longer periods. Furthermore, the proportion of stem emissions probably varies considerably depending on the basal area, tree species and age of the forest, and environmental conditions or stresses, but similar estimates from other forests are not yet available.

Measurements on the short and long-term VOC emission dynamics from tree stem are quite sparse. Temperature has been reported to drive the emissions of monoterpenes and methanol from pine stem at least at a daily scale (Vanhatalo 2018; Staudt et al. 2019). However, at a longer time scale the effect may be different: Staudt et al. (2019) reported largest monoterpene emissions from Maritime pine (*Pinus pinaster*) stem during humid rather than warm days. Stem monoterpene emissions also depend on phenology: the onset of transpiration and change from winter to summer state in the stem caused large peaks of monoterpene emissions from the stem (Vanhatalo et al. 2015). In addition, the different enantiomeric composition of α- and β-pinene emissions between shoots and stem indicate differences in their production between the different tree parts (Staudt et al. 2019). Thus, we can assume that the BVOC emissions from stem do not follow exactly the same patterns as the emissions from shoots, but in comparison to shoot emissions, the environmental or physiological factors that drive stem emissions are poorly understood.

2 MOTIVATION AND OBJECTIVES

Scots pine stem is both a considerable storage and source of VOCs, but our understanding on the stem VOC emission dynamics, drivers and spatial variability is too limited to include them into stand level modelling. In addition, the functioning of resin, the major monoterpene pool and important defence mechanism has been little studied in moist boreal environment. Considering the environmental changes, understanding on the drivers of resin dynamics is needed to predict the challenges for tree defence.

In this dissertation, I studied the effects of temperature and tree water relations and transport on the resin pressure dynamics and BVOC emissions from Scots pine. The overall aim was to clarify the relationships between tree physiology – with special attention to tree water relations – resin dynamics and composition, and BVOC emissions from mature tree stem and foliage, in field conditions.

The more specific objectives were to

1) describe the temporal dynamics and environmental and physiological drivers of resin pressure both at a diurnal and day-to-day scale (studies I, II)

2) compare the spatial patterns of resin pressure and composition with monoterpene emission patterns from foliage (study II)

3) analyse the dynamics of monoterpene emissions as a function of resin pressure (study I) and the dynamics of monoterpene and OVOC emissions as a function of soil moisture and tree water status (study III)

4) study the transport of water-soluble VOCs – methanol, acetone and acetaldehyde – in xylem sap and the role of transport in their emissions from foliage (study IV) and stem (study III)

3 METHODS

3.1 Study site

All field measurements took place between 2011 and 2017 at the SMEAR II station (Station for Measuring Ecosystem-Atmosphere Relation) located in Hyytiälä, Southern Finland. The measurement forest is dominated by mature Scots pines (*Pinus sylvestris*), regenerated by sowing after prescribed burning in 1962. The dominant trees during the measurements were approximately 18–20 meters tall. Other species of the stand include of Norway spruce (*Picea abies* (L.) Karst.), especially in the undergrowth, downy birch (*Betula pubescens* Ehrh.), silver birch (*Betula pendula* Roth) and trembling aspen (*Populus tremula* L.). The understorey vegetation contains mosses and dwarf shrubs: bilberry (*Vaccinuim myrtillus* L.) and lingonberry (*Vaccinium vitis-idaea* L.). The soil is of medium fertility haplic podzol. The long-term mean temperature in the forest is 3.5 °C and yearly rainfall 711 mm (Ilvesniemi et al. 2010; Pirinen et al. 2012).

SMEAR II is a station where the matter and energy fluxes between the different parts of ecosystem and between the ecosystem and the atmosphere have been studied since 1995 (Hari and Kulmala 2005). It consists of measurements on micrometeorology, and gas and trace gas fluxes using the eddy covariance techniques and enclosures dedicated to measure fluxes from soil, understorey vegetation, tree shoots and stem. In addition, continuous measurements are available on soil conditions, including moisture, temperature and water potential.

3.2 Resin measurements

3.2.1 Resin pressure

Scots pine resin pressure in studies I and II was measured with a system modified from Vité (1961). First, a 3 mm hole was drilled slightly tangentially to the tree stem, approximately 4 cm into the xylem. Then, a 3 mm metal tube was pushed into the hole, approximately 3 cm deep, and the other end of the tube was connected to a pressure gauge (Wika 111.16.40.16, Klingenberg, Germany) (studies I and II) or to a pressure transducer (Gems Sensors 3100, Plainville, USA) (study II) (Figure 4). The hole, the tube and the pressure gauge or transducer cavity were filled with glycerine to transmit the changes in resin pressure and to prevent resin flowing into the gauge or transducer. The connection between stem and the metal tube was sealed with silicone, but the small amount of spill over resin was also a good seal.

Because the resin tended to crystallise inside the hole and the metal tube, the pressure measurement needed to be reinstalled every two or three weeks. The crystallisation and the potential decreasing defence reaction following the wounding often caused a general, decreasing trend of the resin pressure over the two-to-three-week measurement periods. In study I, where mainly short-term dynamics were studied, this trend was corrected if necessary by using the residuals of a linear function of time. In study II, where long-term trends were also studied, data both with and without trend correction were used because the actual trends and the trend caused by the measurement could not be separated.
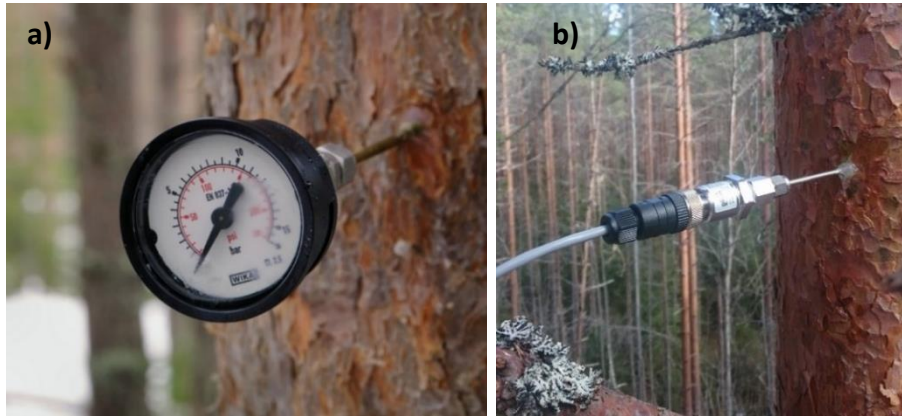
Figure 4. a) pressure gauge (used in studies I and II) (photo by Juho Aalto), and b) pressure transducer (used in study II) attached to Scots pine (*Pinus sylvestris*) stem (photo by Kaisa Rissanen)

3.2.2 Resin composition

In study II, the monoterpene composition of resin was measured using a gas-chromatograph mass-spectrometer (GC-MS) which composes of two phases of molecule separation: the capillary column of GC and the ionisation and fragmentation of MS, enabling separation of the compounds with similar ion mass and similar retention time in GC capillary. The monoterpene composition was analysed from approximately 3 mg resin samples that were collected from small wounds punched to xylem surface of 16 sample trees. The samples were collected rapidly after the first resin droplets appeared on the wound, and after weighting, they were dissolved in heptane to avoid loss of volatile components. The samples were analysed by Agilent 6890 N gas chromatograph connected with an Agilent 5975 mass selective detector (Agilent Technologies, Palo Alto, CA, USA). Each sample contained an internal standard Decane-d22 and standard solutions were used to calibrate for mass spectrums and retentions times. The quantification of the monoterpene concentrations was made by calculating the area of the ion chromatogram peak of the base ion of each compound.

3.3 Resin dynamics modelling

In study II, the temperature dependence of resin pressure was modelled using the information on resin monoterpene composition (see above section 3.2.2) and COSMOtherm software. The COSMOtherm calculates based on COSMO-RS (Conductor-like Screening Model for Real Solvents) theory the properties of liquids that consist of several compounds (Klamt et al. 1998) and it is generally used in predicting the characteristics of solvents used in industry. The COSMOtherm calculated the density of three resin mixtures – with high, intermediate and low monoterpene content – at different temperatures. Based on the density changes, the thermal expansion of resin and the resulting changes in pressure could be calculated. In addition, COSMOtherm calculated the solubility of CO_2, N_2 and O_2 in the three resin mixtures and at different temperatures. Based on this information, the volume and growth of potential gas bubbles within resin could be estimated, and consequently the change in total resin volume and resulting change in pressure. Finally, COSMOtherm calculated the vapour pressures of resin at different temperatures. These three temperature-related effects were combined to explain the diurnal temperature-dependency of resin pressure.

3.4 VOC emission measurements

3.4.1 Continuous VOC emission measurements

The continuous measurements of VOC emissions from both Scots pine shoots and stem were based on a chamber system where chambers attached around shoots, stem and soil are cyclically measured and flushed (Kolari et al. 2009, 2012; Aalto et al. 2014; Aalto 2015; Vanhatalo et al. 2015; Vanhatalo 2018). The chambers used in this study consisted of dynamic shoot chambers (study IV), steady state stem chambers (studies I, III and IV) and dynamic stem chambers (study III).

The dynamic shoot chambers (Figure 5 a) were built of FEP-coated (fluorinated ethylene propylene) acrylic plastic and they enclosed top-canopy pine shoots, the buds of which had been removed the previous year to remove the effect of growth on the emission dynamics. For measurement, one chamber at a time was automatically closed, and sample air was drawn from it to gas analysers. The sample air was replaced by ambient air that leaked through the small holes of the chamber. While the chamber was not measured, it remained open for flushing.

The steady-state stem chambers consisted of a polyethylene-coated aluminium spiral tube around the tree stem and FEP foil tightened around the stem and the spiral tube, closed from top and bottom with elastic bands (Figure 5 b). The only openings in these chambers were the openings for incoming replacement air and outgoing sample air. When the chamber was in measurement, a sample air flow of 1 l/min was drawn from the chamber to the analysers and replaced with a slightly larger flow of ambient air. When the chamber was not measured, a 0.4 l/min flow of ambient air was maintained through it for flushing.

The dynamic stem chambers (Figure 5 c) were built of aluminium pieces around the tree stem and a FEP foil tightened around the stem and the aluminium pieces, closed from top and bottom with elastic bands. Two of the pieces on opposite sides of the stem had automatic opening and closing lids and fans that helped to circulate air through the chamber during and between the measurements. For measurement, the chamber lids were automatically closed, 1 l/min of sample air was drawn from it to analysers, and the sample air was replaced with a slightly larger flow of ambient air. When the chamber was not measured, a 0.4 l/min flow of ambient air was maintained through the open chamber for flushing. In most chambers, the temperature within the chamber was recorded with copper-constantan thermocouples.

Figure 5. Chambers for measuring VOC emissions and H_2O and CO_2 exchange from different parts of Scots pine (*Pinus sylvestris*). a) Dynamic shoot chamber (photo by Juho Aalto), b) steady-state stem chamber (photo by Juho Aalto) and c) dynamics stem chamber (photo by Kaisa Rissanen).

The analyser used for measuring the concentration of VOCs in the sample air drawn from the chamber was a proton transfer reaction-mass spectrometer (PTR-MS, IONICON Analytic GmbH, Innsbruck, Austria) that is a commonly used instrument for high-frequency online VOC measurement. Sample air was drawn into the PTR-MS at a rate of 0.1 l/min. In high vacuum of the PTR-MS reaction chamber, H_3O^+ ions give their proton to the sample air molecules (proton-transfer reaction). This is a gentle ionisation method that causes relatively little fragmentation of the molecules, but it works only for compounds that have higher proton affinity than water. In the quadrupole PTR-MS used here, the ions are then separated by quadrupole and led to secondary electron multiplier and finally to detector. As the quadrupole filters the ions by their mass-to-charge ratio, different compounds with similar ionised mass cannot be separated in this system. Here, ionised masses (amu) 137, 33, 45 and 59 were measured, corresponding to monoterpenes, methanol, acetaldehyde and acetone.

Based on calibrations made with standard gas every two or three weeks, the instrument sensitivities to certain masses were known, and the concentrations in sample gas could be calculated from the measured detector counts (Taipale et al. 2008). The concentrations of enclosure air were calculated into emissions using a mass-balance equation (Equation 1) in case of the dynamics chambers.

$$C(t) = C_0 + \frac{E}{F}\left(1 - e^{-\frac{Ft}{v}}\right) \qquad \text{(Equation 1)}$$

C(t) is the concentration of the compound in the chamber as a function of time (t), C_0 is the concentration of the ambient air, F is the airflow through the chamber, v the chamber volume and E the emission rate that was found by fitting the equation to the concentration increase during the chamber closure (Hari et al. 1999; Kolari et al. 2012). For the steady-state chambers, the emissions were calculated as the difference between the chamber concentration in steady state and the ambient air concentration, multiplied by the air flow through the chamber.

In high relative humidity, water vapour can condense on the chamber walls, tubing and enclosed surfaces. Water-soluble OVOCs methanol, acetaldehyde and acetone can be adsorbed into the water films, thus in studies III and IV, OVOC data was omitted when the relative humidity in the chamber was above 70–75% (Altimir et al. 2006).

3.4.2 VOC emission potential

To achieve comparable values of VOC emissions from different environments, the emissions are often normalised to standardised conditions (for example, temperature 30°C and photosynthetic photon flux density 1000 µmol m^{-2} s^{-1}). If the measured compounds mainly originate from pools, like monoterpene emissions from conifers, the emissions are normalised only to temperature (Guenther et al. 1993; Guenther 1995) (Equation 2).

$$E = E_0 * e^{[\beta(T-T_s)]} \qquad \text{(Equation 2)}$$

E is the measured emissions, E_0 is the emission potential, β is an empirical parameter describing the temperature sensitivity of the emissions (often a global average 0.09 K^{-1} is used), T is the temperature in the chamber and T_S is the standard temperature (30°C or 303 K). This normalisation removes from the data the short-term effect of temperature on the vapour pressures and evaporation of the VOC compounds and gives a base line emission value called emission potential.

The emission potential of monoterpenes, methanol and acetaldehyde were calculated in study III to analyse the effects of different environmental variables, such as tree water relations on temperature normalised stem emissions. However, instead of using the β-parameter fixed at 0.09 K^{-1}, β-parameter was fitted in three-day windows. This aimed at accounting for the temperature sensitivity changes over the growing season and variation between different years, trees and compounds.

3.4.3 Point measurements of VOC emissions from shoots

In study II, the monoterpene composition of Scots pine shoot emissions was measured from cut branches of 16 sample trees similarly as described in Bäck et al. (2012). The branches were collected with a long pole branch cutter from the lower canopy. After approximately one week of storage in dark, at + 4°C, the cut shoots were taken to room temperature and after short acclimation installed for measurement into FEP foil bags. 0.2 l/min of air that was purified from VOCs and oxidants with an activated carbon trap and manganese dioxide-coated copper net was led into the bag and both incoming and outgoing air were sampled into Tenax TA - Carbopack B adsorbent tubes. In laboratory, the adsorbed VOCs were released by a thermal desorter (PerkinElmer TurboMatrix 650, Waltham, USA) and measured using a gas chromatograph (PerkinElmer Clarus 600, Waltham, USA) connected with a mass spectrometer (PerkinElmer Clarus 600T, Waltham, USA). Six standard samples with different concentrations of the studied analytes were used for calibrations. Emission values were calculated based on steady-state measurement: as difference between the incoming and outgoing sample concentration multiplied by the flow rate through the sample bag.

Table 2. Resin and BVOC measurements in each study of the thesis

Measurement	Method	Study I May-August 2013	Study II June-August 2017	Study III June-August 2013, 2015 & 2017	Study IV May-August 2010, 2011, 2013, 2014 & 2015
Resin pressure	Pressure gauge	5 trees	10 trees		
Resin composition	GC-MS		16 trees		
Monoterpene emissions from stem	PTR-MS	1 tree		3 trees	
Monoterpene composition in shoot emissions	GC-MS		16 trees		
OVOC emissions from shoots	PTR-MS				3 trees
OVOC emissions from stem	PTR-MS			3 trees	

3.5 Tree water status and CO₂ efflux measurements

To analyse the effects of tree physiology and especially tree water status on the resin dynamics and the emissions of VOCs, different measurements on water potential, transpiration and growth were used. In studies I and III, tree water status was observed using linear displacement transducers as point dendrometers (Solartron Inc., Model AX/5-0/5, Bognor Regis) (Figure 6). They measure changes in the whole stem or xylem diameter that are functions of growth (irreversible) or changes in the stem water status (reversible). Decreasing water potential reduces the stem diameter because it causes both shrinkage of the water conducting tracheids and decrease of turgor pressure in the living parenchyma cells in sapwood (Irvine and Grace 1997; Perämäki et al. 2001; Mencuccini et al. 2013; Lintunen et al. 2017). As the radial growth of stem takes place in the cambial zone, diameter variations measured from xylem beneath this zone reflect only changes in water status. Measuring the stem diameter both from xylem and on bark enables separating the growth signal (Chan et al. 2016).

In addition, measurements on transpiration were used to analyse the effect of transport on the emissions of OVOCs (studies III and IV) and measurements on carbon dioxide (CO_2) efflux from the stem were used to describe the metabolic activity in stem (study III). Transpiration was measured by the shoot chamber system described above (section 3.4.1) and by Kolari et al. (2012), and stem CO_2 flux using the stem chambers described above (section 3.4.1) and by Vanhatalo (2018). For analysis of water and CO_2 concentrations, the sample air from the chambers was drawn to a URAS 4 infrared light absorption gas analyser (Hartman and Braun, Frankfurt am Main, Germany) or to a Li-840 A gas analyser (Li-Cor, Lincoln, NE, USA). Like VOC emissions, the water and CO_2 fluxes were calculated using the mass-balance equation (Equation 1) or their steady-state concentrations, depending on the chamber type. Because of the condensation of water on the chamber surfaces in high relative humidity, the water and CO_2 flux measurements were unreliable when relative humidity exceeded 70-75% and these measurements were removed prior to analysis.

Figure 6. Linear displacement transducers for continuously measuring small changes in xylem and bark diameter

3.6 Path analysis as a tool to separate variable interactions

In studies I and IV, different path analysis approaches were used to compare and distinguish the simultaneous effects of different variables on the emissions of monoterpenes from the stem (study I) or the emissions of OVOCs from the shoots (study IV). In study I, the elaboration method EFRA (explanatory framework-based regression analysis) was employed to compare the effects of resin pressure and temperature on the stem emissions of monoterpenes. The method was based on simple regressions, so that first the coefficients of temperature and resin pressure effects on monoterpene emissions were calculated separately (Figure 7 a, line 1) and then their coefficients were calculated in a model where they both explained monoterpene emissions (Figure 7 a, line 2). The changes in their coefficients gave indications on the roles of the two variables in explaining the emissions and whether and how much the effect of temperature was mediated through resin pressure.

A simple form of structural equation model (SEM) was employed to clarify the interactions between temperature, stomatal conductance and transpiration in explaining the emissions of OVOCs from shoots. The calculations were made in R lavaan package (Rosseel 2012). The path analysis described the causal relations between independent variables (temperature and stomatal conductance) that explained the dependent variable (OVOC emissions) (Figure 7 b, line 1), possibly through another dependent variable (transpiration) (Figure 7 b, line 2). The interrelations between the variables and the importance of each variable were estimated by their coefficients in each regression and the significance (p-value) of each coefficient.
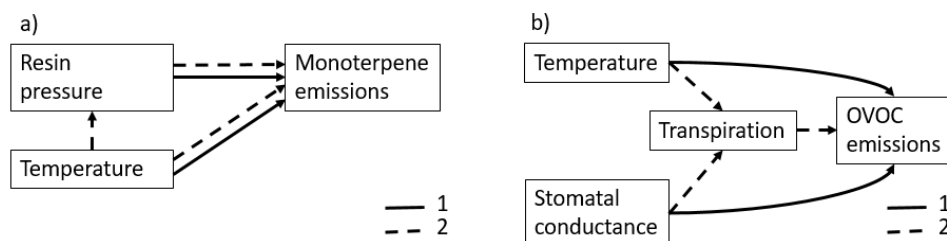

Figure 7. a) Framework of EFRA approach, where first the individual effects of resin pressure and temperature on monoterpene emissions were calculated (1) and then their effects when both variables were explaining monoterpene emissions (2) and b) framework of path analysis, where the effects of temperature and stomatal conductance on OVOC emissions were calculated (1) and then the transpiration was added to the model (2).

4 RESULTS AND DISCUSSION

4.1 Resin pressure dynamics

4.1.1 Resin pressure as a function of temperature and tree water status

Unlike expected based on the previous studies from dry environments, studies I and II showed that in the moist and cool boreal environment the diurnal resin pressure dynamics of Scots pine followed temperature (Figures 8 and 9). The resin pressures were highest in daytime, between 13 h and 15 h, whereas the lowest pressures occurred at dawn, between 3 h and 6 h. This pattern was similar regardless the measured tree or the phase of growing season.

The strong control of temperature on resin pressure was explained in study II by two processes: 1) thermal expansion increases resin pressure, and 2) increasing temperature decreases the solubility of gases (for example, N_2, O_2 and CO_2) in resin, which allows these gases to move to gas phase and enlarge bubbles in resin, increasing resin pressure. Although in study I, the monoterpene vapour pressure changes were suggested to be one reason for the strong temperature regulation, the changes in vapour pressures were too small to contribute to the daily dynamics of resin pressure. Correspondingly, Pio & Valente (1998) found that changes in vapour pressure could not alone explain the temperature dependence of monoterpene emissions from exposed resin.

Despite the strong temperature dependence at a daily scale, temperature did not explain all variation in resin pressure. In study I, resin pressure sometimes deviated from the diurnal temperature dynamics, especially when the ambient vapour pressure deficit (VPD) changed suddenly. In addition, over some of the 5–8-day measurement periods, the residuals of a temperature model explaining resin pressure correlated positively with xylem water potential inferred from the xylem diameter change measurements (study I) (Figure 9). Moreover, in study II, resin pressure trends over the growing season followed soil water potential whereas the long-term effect of temperature was negative (Figure 9). These diurnally small, but at a longer term important impacts of xylem and soil water potential on resin pressure showed that in the boreal environment there is also an effect of water relations on resin pressure, as shown in drier regions by Bourdeau and Schopmeyer (1958), Vité (1961), Lorio and Hodges (1968b) and Helseth and Brown (1970). However, this impact seems to be most of the time overshadowed by the strong impact of temperature.

4.1.2 Resin pressure dynamics in moist and dry environments

Based on the results presented above (section 4.1.1), resin pressure follows the diurnal patter of temperature in moist environment (Figure 8), but in dry environments it has been found to follow the diurnal changes in xylem water potential, and inversely the changes in transpiration rate and VPD (Bourdeau and Schopmeyer 1958; Vité 1961; Barret and Bengtson 1964; Lorio and Hodges 1968a; Neher 1993). This difference in the daily dynamics of resin pressure between dry and moist sites suggests either that the availability of water strongly shapes the resin pressure dynamics between these different environments, or that the measurement techniques for resin pressure were considerably different between the measurements.

Considering the first option, Vité, (1961) reported that the effect of VPD on resin pressure was weaker when the availability of water in soil was high and stronger when the soil was dry. In Hyytiälä, Finland, drought is very rare and during the measured years, the availability of water was high: in study I, soil water potential during the resin pressure measurements varied between 0 and -500 kPa, and in study II, between 0 and -25 kPa. Thus, the high water availability in these measurements should weaken the effect of VPD and water potential on resin pressure. Moreover, the daily range of resin pressure measured in drought-prone environment is considerably larger

(approximately 4 bar) (Lorio and Hodges 1968b) in comparison to moist environment (0.5–1 bar) (Figure 8). Thus, in moist conditions and at a short term, VPD, transpiration and water potential probably do not affect the tracheid sizes and turgor pressures of epithelial cells strongly enough to overcome the temperature effect on resin pressure. At a longer term, however, the slow changes of water status in the tracheids and epithelial cells can be large enough to impact the resin pressure. At an even longer time scale, acclimation and adaptation of the trees to a certain climate might affect even the resin duct responsiveness, rigidity and permeability.

Considering the second option about the different measurement techniques, the methods used in studies I and II were tested in a drought-prone Scots pine forest (Pfynwald) standing on sandy soil in Switzerland. In Pfynwald, resin pressures followed a diurnal pattern with maximum at dawn and minimum in the afternoon (unpublished data) (Figure 8), corresponding to the results from dry regions (Bourdeau and Schopmeyer 1958; Vité 1961; Lorio and Hodges 1968b; Helseth and Brown 1970; Neher 1993). Moreover, the long-term resin pressure dynamics in the Pfynwald forest followed the soil water potential trends, decreasing towards the end of the growing season. Based on these results from dry environment that corresponded to the earlier studies, the methods used in studies I and II were considered valid.
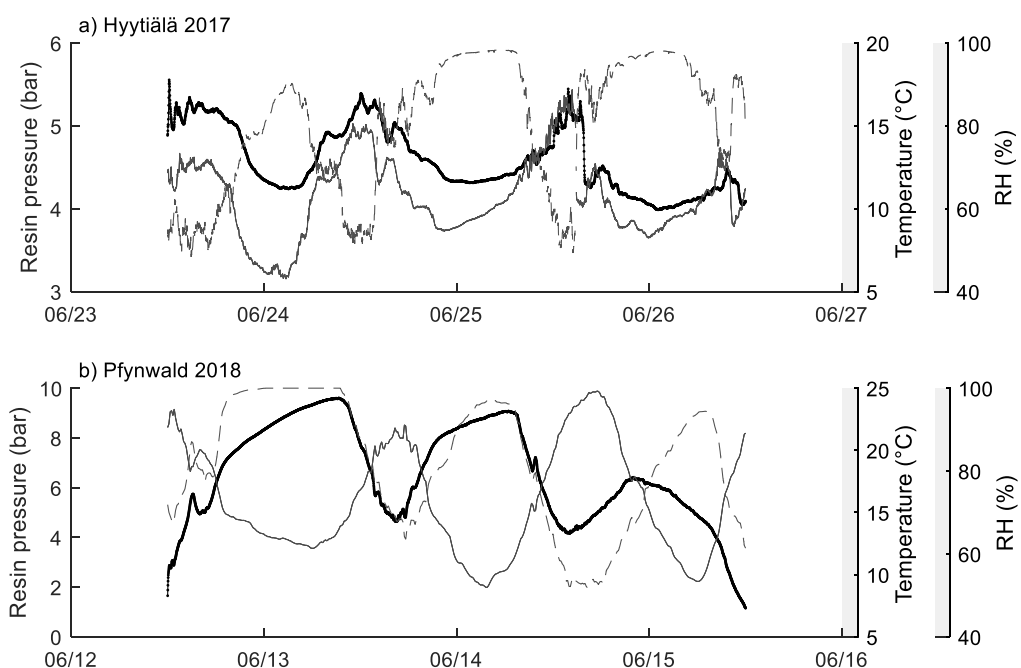

Figure 8. Variation in resin pressure (solid black), ambient temperature (solid grey) and relative humidity (dashed grey) a) in moist, boreal Scots pine (*Pinus sylvestris*) forest of Hyytiälä, Finland (study II) and b) in dry inner-alpine Scots pine forest of Pfynwald, Switzerland (unpublished data).
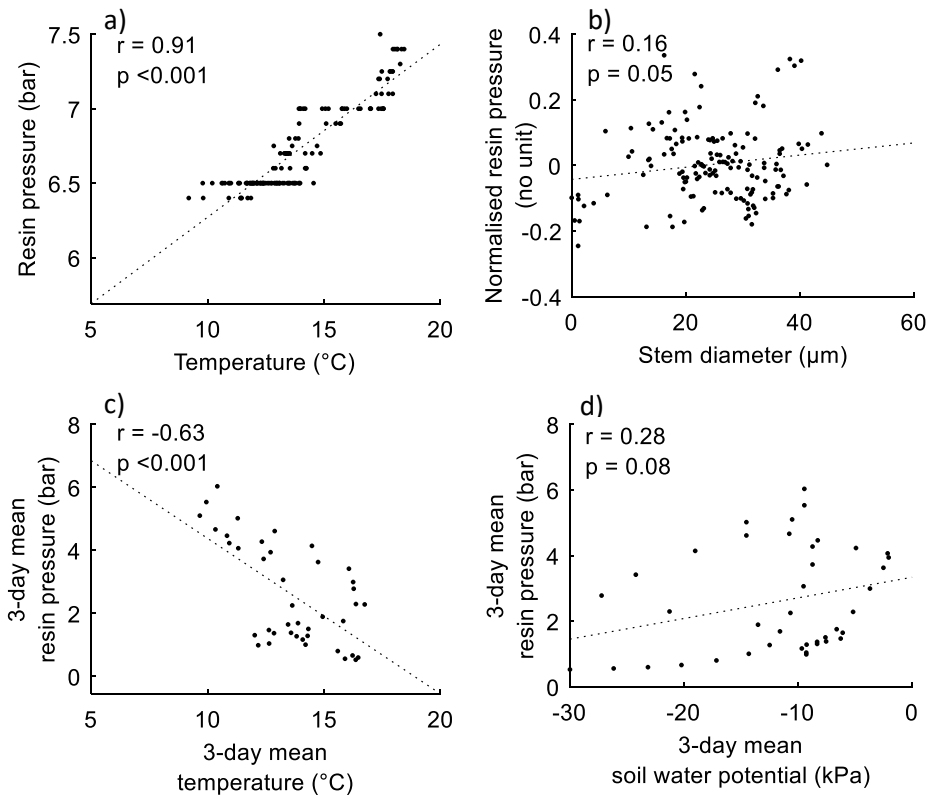
Figure 9. Correlations between a) trend-corrected resin pressure and temperature, b) temperature-normalized resin pressure and xylem diameter in Scots pine (*Pinus sylvestris*), in Hyytiälä, July 15–18, 2014 (study I), and c) 3-day mean of resin pressure and temperature and d) 3-day mean of resin pressure and soil water potential in Scots pine, in Hyytiälä, June–July 2017 (study II). Dashed lines present the least-square fit.

4.1.3 Resin pressure dynamics in different stem parts

Although the dynamics of resin pressure were corresponding between all measured trees, there were differences between the tree parts. Resin pressures were higher in the top part versus the bottom part of the stem in the beginning and in the end of growing season, but in mid-summer, resin pressure was higher in the bottom part of the stem (study II). The differences between the top and bottom part were largest when the water potential in xylem was below average and transpiration was high (study I). Transpiration decreases water potential proportionally more in the top part of the stem than in the bottom part, which could explain the lower resin pressure in the top part of stem during the periods of high transpiration.

4.2 Resin effects on monoterpene emissions

4.2.1 Resin pressure and monoterpene composition in comparison to monoterpene emissions from shoots

As resin is a large pool of monoterpenes in conifer stem and shoots, resin composition could be expected to affect the composition and tree-to-tree variation of emitted monoterpenes. Indeed, study II showed that the stem resin and shoot emissions of 16 measured Scots pines contained the same monoterpenes in roughly corresponding proportions (Figure 10). The most abundant compounds were α-pinene, Δ^3-carene and β-pinene, with smaller quantities of limonene, terpinolene, camphene, and p-cymene.
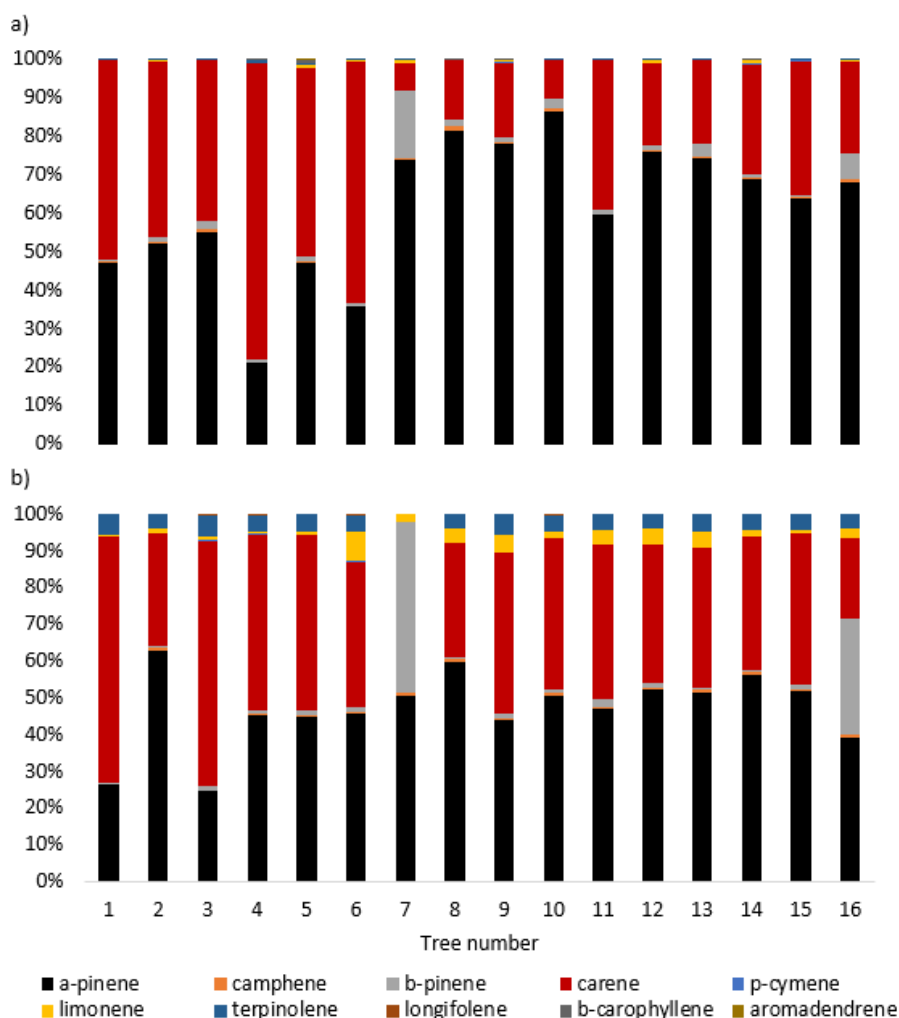

Figure 10. Monoterpene spectrum in a) shoot emissions and b) stem resin of 16 Scots pines (*Pinus sylvestris*) in Hyytiälä, August 2016

However, the monoterpene proportions in stem resin and shoot emissions within one tree were not identical and the tree-to-tree variation in shoot emissions was larger than in resin composition. In resin, the proportions of Δ^3-carene and α-pinene varied generally little between trees, whereas the shoot emissions of some trees were clearly dominated by either of the compounds (Figure 10). Moreover, α-pinene was generally more abundant in shoot emissions than in resin, probably because of its high volatility in comparison to the other monoterpenes. Interestingly, only in two trees the proportions of β-pinene were considerable, but in these trees, it was an important component of both the shoot monoterpene emissions and stem resin (Figure 10).

Mismatches between the stem resin composition and shoot emission spectrum can be expected (Vanhatalo et al. 2018): in addition to emission from storages, shoots emit monoterpenes directly upon synthesis (Ghirardo et al. 2010; Harley et al. 2014), the different monoterpenes have different volatilities and diffusion rates, and the resin composition can differ between stem and shoots (Latta et al. 2000). The resin composition difference between stem and shoots may strongly affect the emission patterns between these two tree parts according to data collected in the Pfynwald forest: comparing the monoterpene emissions and resin composition within the same tree part, stem or shoot, showed better matches (unpublished data).

Resin pressures also varied between trees. In general, the trees with higher resin pressure had higher content of monoterpenes, especially α-pinene in their resin and larger emissions of monoterpenes, especially Δ^3-carene and terpinolene from their shoots. These connections between resin pressure, resin composition and monoterpene emissions might reflect past stress events that have increased resin pressures and the production and emissions of certain monoterpenes.

4.2.2 Resin pressure and water availability effects on monoterpene emissions from stem

Study I showed that like the resin pressure dynamics, the daily monoterpene emission dynamics from Scots pine stem followed temperature (Figure 11). To separate the potential effects of temperature and resin pressure on the monoterpene emissions, the EFRA analysis was used (Figure 7). The analysis indicated that both temperature and resin pressure were important in explaining the monoterpene emissions. Temperature affects the monoterpene emissions by regulating their vapour pressures and diffusion rates, and resin pressure may increase the monoterpene emissions by facilitating their release from resin ducts and the stem. According to EFRA, a part of the temperature effect on monoterpene emissions was mediated through the temperature effect on resin pressure, but resin pressure also had an independent impact. The independent resin pressure impact could be connected to the subtle short-term changes and larger long-term changes in resin pressure, caused by slow changes in water availability and water potential in xylem.

Correspondingly, the daily mean stem monoterpene emission potential, normalised for the short-term effects of temperature, correlated with daily mean soil water content and xylem water potential (study III) (Figure 11). Anomalies of high monoterpene emission potential occurred when soil water content and xylem water potential were higher than average. This effect probably manifests the long-term variation in resin pressure, but at least a part of it could also result from more direct effects of humidity on monoterpene emissions. Abundant water availability might enhance the production of monoterpenes, and air humidity could provoke monoterpene release from short-term storages or resin ducts as a result of the uneven wetting and swelling of stem tissues as suggested by Staudt et al. (2019) or because of the changes in bark conductance as proposed for leaf cuticula (Croteau et al. 1977).

In the moist conditions of Hyytiälä, completely separating the effects of temperature and resin pressure on stem monoterpene emissions is impossible because temperature and resin pressure covary. Thus, it would be interesting to study the connections between resin pressure and stem monoterpene emissions in conditions where the resin pressure dynamics diverge from temperature dynamics. This could be achieved in a dry environment, where resin pressure is regulated by water potential more than temperature.

Another interesting question concerns the effect of resin pressure on the emissions of monoterpenes from pine shoots. Resin pressures or pressure variations within pine needles are not known, but if they follow the same dynamics as in stem, a part of the temperature effect on the shoot monoterpene emissions could be explained by resin pressure, as well. The effect of resin pressure could also partly explain the decrease in monoterpene emissions during drought (Staudt et al. 2002; Lüpke et al. 2016). However, these suggestions remain hypothetical until resin pressures can be measured within resin ducts of needles.
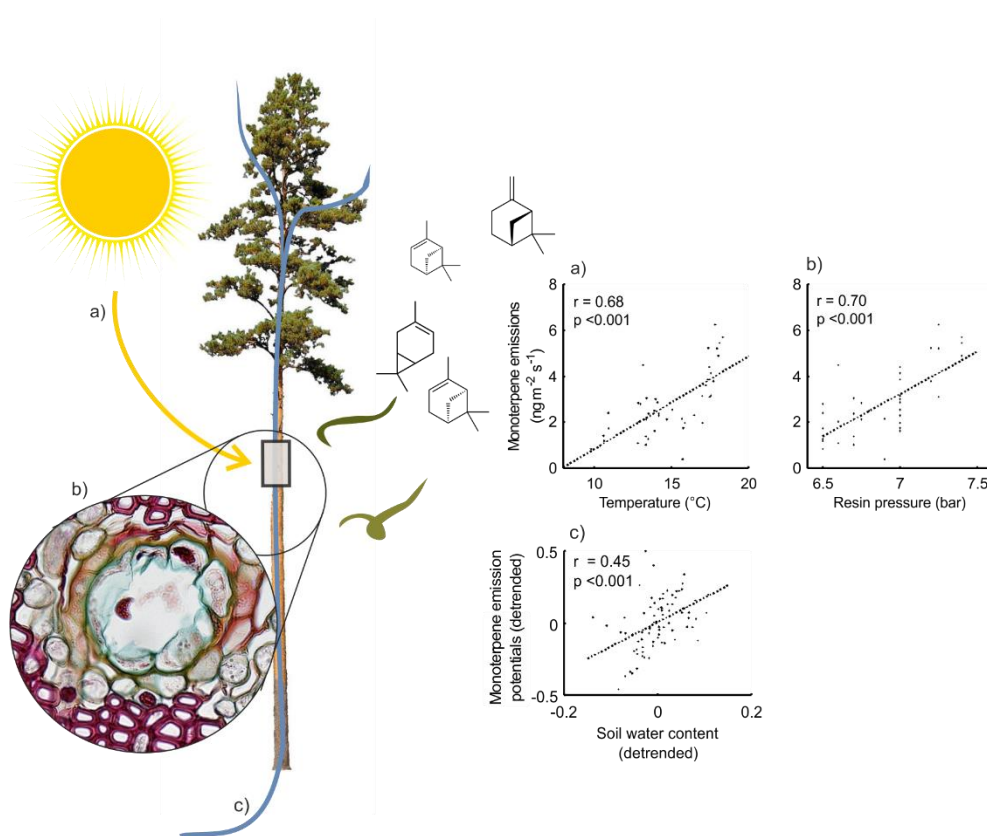

Figure 11. Monoterpene emissions from Scots pine (*Pinus sylvestris*) stem explained with a) temperature and b) resin pressure, 15.-18.7.2013 (study I), and c) soil water content in June-August 2015 (study III), in Hyytiälä, Finland.

4.3 Water transport effects on OVOC emissions

4.3.1 OVOC emissions from shoots

Like the emissions of most VOCs, the shoot emissions of water-soluble oxygenated VOCs (OVOCs) – methanol, acetone and acetaldehyde – depend on temperature. They are also considered dependent on stomatal conductance, in particular methanol and to a lower degree acetone and acetaldehyde. When stomatal conductance is small, the capacity of these compounds to dissolve in water inhibits the increase of their concentration inside the leaf air space, which can cause a momentary reduction of their emissions (Niinemets and Reichstein 2003).

Nevertheless, study IV showed that transpiration rather than stomatal conductance controlled the shoot OVOC emissions from Scots pine in field conditions. The emissions were best explained by temperature and transpiration, and according to the structural equation model, stomatal conductance affected the emissions only indirectly by regulating the transpiration. The strong coupling of OVOC emissions with transpiration suggests that a part of the OVOCs measured from shoots evaporate from transpired xylem sap (Figure 12). It also indicated that these OVOCs or their precursors can be transported within xylem sap from their sources in roots and stem up to shoots and to ambient air, as suggested in the case of methanol (Grabmer et al. 2006; Folkers et al. 2008) and acetaldehyde (Kreuzwieser et al. 2000; Fall 2003).

Due to the transport, a certain proportion of OVOC shoot emissions can originate from stem or roots. How large is this transported proportion in comparison to the proportion that originates from the shoot depends on 1) how much these compounds are produced in shoots versus stem and roots, and 2) where in stem or roots they are mainly produced. Methanol is produced in the cambial zone of the stem, near the stem surface, so it might more likely diffuse through bark to ambient air than dissolve in xylem sap. Thus, the proportion of transported methanol of total shoot emissions is probably small. In contrast, acetaldehyde mainly originates from roots and the anoxic parts of stem, so it might more likely dissolve in xylem sap than diffuse through sapwood and bark to ambient air. Thus, the proportion of transported acetaldehyde of total shoot emissions is probably larger. In line with this hypothesis, the stem OVOC emissions were dominated by methanol, although the methanol emissions from shoots were slightly smaller than the shoot emissions of acetone and acetaldehyde (study IV). Furthermore, the shoot emissions of methanol were generally better explained by temperature than by transpiration rate, indicating a larger proportion of locally produced methanol. The shoot emissions of acetone and acetaldehyde in particular were generally better explained by transpiration rate than temperature, indicating an important role of the transported portion.

4.3.2 OVOC emissions from stem

The daily emissions of methanol and acetaldehyde from stem of Scots pine were also temperature-dependent, but like their emission patterns from shoots, the emission patterns from stem reflected the effect of transport in xylem sap (study III). Increased acetaldehyde emission potential occurred after anomalies of high soil water content, with a lag of three to seven days (Figure 12). The lag times corresponded to the average xylem sap transport times, calculated from the average transpiration rates, from the base of the stem to the measurement location at the top of the stem (Figure 12). The lagged effect of soil water content indicates that acetaldehyde production in soil and roots follows water availability even when the soil is not flooded or anoxic and that the transport in xylem sap affects acetaldehyde emissions from stem, as well. In addition to the transported acetaldehyde, some stem acetaldehyde emissions might originate from the lack of oxygen near heartwood or in cambium during fast stem growth that could cause formation of ethanol and acetaldehyde (Kimmerer and Stringer 1988). This local production could explain the correlations found between stem acetaldehyde emissions and stem growth as well as stem CO_2 efflux (Study III), but its significance to total acetaldehyde emissions is unknown.

A weaker effect of soil water content was found on methanol emission potential (Figure 12). The fact that the effect of soil water content was smaller highlights the complexity of methanol sources in stem: a large part of methanol measured from the stem probably originates from the local production connected to stem growth, whereas another part can be transported from roots and the lower parts of the stem. In addition, a part of the local production can dissolve in xylem sap or be metabolised (Jardine et al. 2017). To describe the methanol emissions more accurately, the sources and sinks would need to be separated and the lag times between growth, methanol production and emissions estimated. The methanol emissions potential from stem also correlated with bark water conductance, indicating that the diffusion through bark could be an important constraint for the emissions.

The acetone emissions from stem followed temperature changes poorly and the emission dynamics were generally related to air humidity. Further studies would be necessary to first locate the main acetone sources in trees and then to understand its emission patterns from stem. Transport in xylem sap might have an important role, since the emission patters from shoots followed closely transpiration.

The spatial pattern of OVOC emissions from different stem heights corresponded to the stem CO_2 efflux pattern that is also affected by transport in xylem sap (study IV) (Hölttä & Kolari 2009). The emissions were low from the bottom part of the stem, where diffusion to ambient air is slow due to thick bark, and the compounds easily dissolve in xylem sap. The emissions were higher from the middle part of the stem and highest from the top. At the top, diffusion through thin bark is fast, and the xylem sap already may have high concentrations of OVOCs, enhancing their release. The top part of the stem is also more active (Vanhatalo 2018) and more exposed to the changes in temperature, contributing to higher emissions.
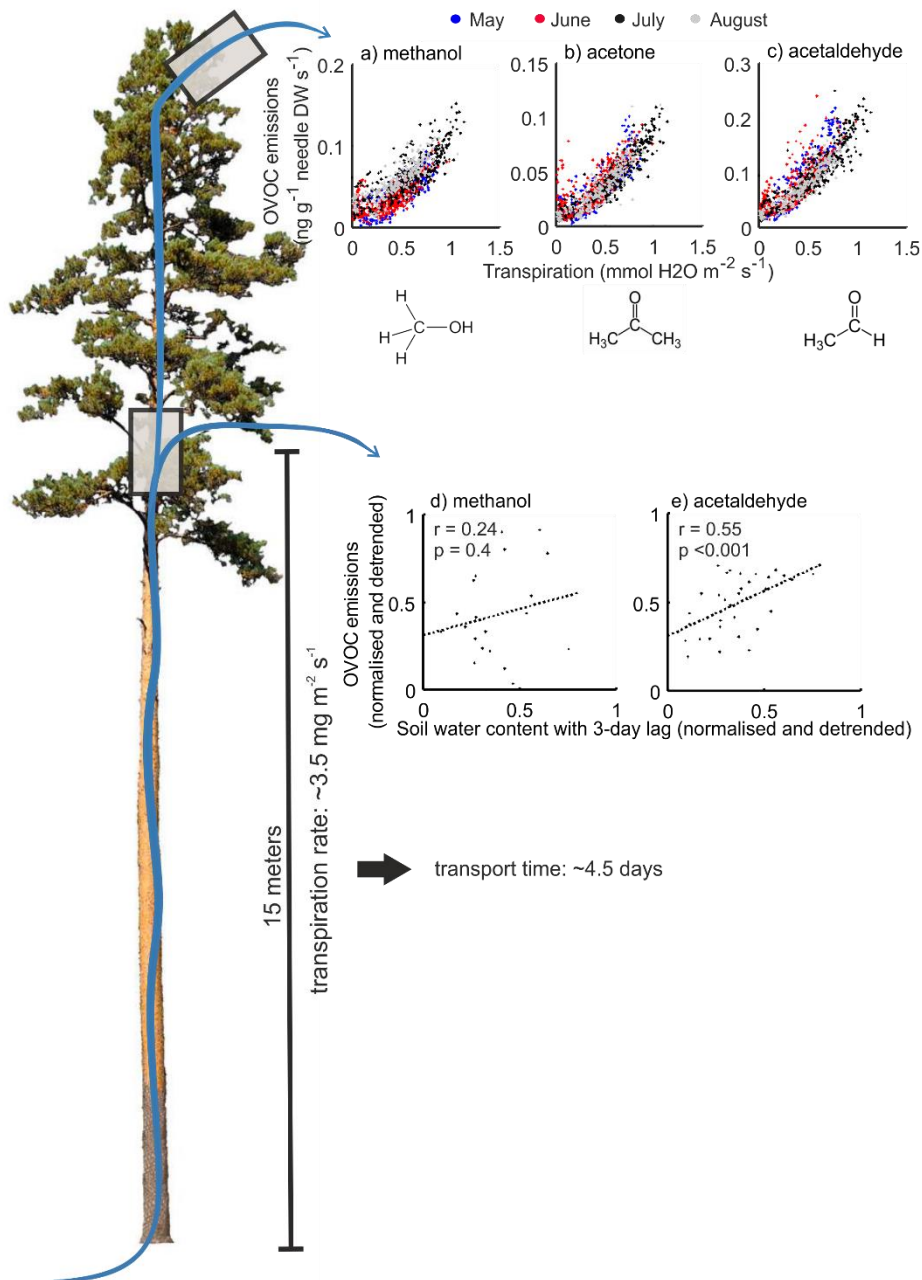
Figure 12. The framework of soil water and xylem sap transport on emissions of OVOCs (methanol, acetone and acetaldehyde) from Scots pine (*Pinus sylvestris*) shoots and stem. Effects of transpiration on shoot emissions of a) methanol, b) acetaldehyde and c) acetone in Hyytiälä, 2010. No lags were detected in the effect of transpiration on shoot OVOC emission. Effect of soil water content with a 3-day lag on stem emissions of d) methanol and e) acetaldehyde in Hyytiälä, 2017. The lag time of 3 days is in the same scale as the roughly estimated transport time of water from the tree base to the measurement location at 15 meters calculated based on average summer time transpiration rate.

5 CONCLUSIONS

In contrast to a dry environment, Scots pine resin pressure in a moist environment is controlled by temperature at a short term, most likely because of thermal expansion and the temperature dependent changes in solubility of gases in resin. At a longer term, the direct temperature effect is less important or even negative, and the resin pressure is affected by changes in water availability and tree water status. This impact of water status suggests that even in a moist environment, the defence capacity of Scots pine could be reduced during drought periods because of decreasing resin pressures.

In addition to tree defence, resin pressure along with temperature also affects the emissions of monoterpenes from Scots pine stem. A part of the resin pressure effect is caused by temperature, but it also has an independent effect on the emissions that is probably linked to the long-term trends of water availability and water potential in xylem. For example, high stem monoterpene emission potential can be observed when soil water content is higher than average. In addition to the temporal variation, resin pressure and composition are associated with the tree-to-tree variation of monoterpene emissions. On the one hand, the monoterpenes that are stored in resin can be emitted from stem and foliage, contributing to the spectrum and quantity of monoterpenes emitted from the tree. However, in foliage, the *de novo* emissions of monoterpenes cause some diversion of the emission spectrum from the resin composition. On the other hand, a tree with high resin pressure may have larger emissions of monoterpenes from shoots. Thus, the knowledge on resin dynamics and variability plays an important role in advancing the understanding on tree-to-tree variation and tree-level monoterpene emissions of conifers.

Apart from monoterpenes, conifer trees are large sources of OVOCs: methanol, acetone and acetaldehyde. Their emissions from Scots pine are not dependent on resin, but also strongly regulated by temperature and by tree water relations owing to their water solubility. Upon production, these compounds can dissolve in xylem sap and travel from their sources in soil, roots and stem up to foliage. Thus, a part of the OVOCs emitted from foliage originates from other tree parts and the OVOC emissions from foliage are strongly dependent on transpiration. Transpiration and soil water content also affect the stem emissions of acetaldehyde and, to a smaller degree, methanol. Their emission potential from stem increase after anomalies of high soil water content with a lag that corresponds to their transport time in xylem sap.

The results of this thesis highlight the strong impact of temperature on all the studied tree processes in a boreal environment that has moderate or minor limitations in water availability. However, while temperature can be used to predict the pressure of resin and the emissions of VOCs from stem and foliage at a short time scale, the interconnection between tree water relations and resin and VOC emissions dynamics may cause unpredicted dynamics at a longer time scale and especially in case of extreme events such as drought or flooding.

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