

## **Impact of sub-canopy removal on the stand-level volatile organic compounds exchange**

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Tiivistelmä – Referat – Abstract <p>Removal of sub-canopy trees is a type of forest management practice, mainly employed to minimize subsequent harvesting costs. Such management activities, however, are a source of disturbance in boreal forests, including those of Finland. The removal of understory trees causes mechanical damage to trees, with coniferous trees, such as Scots pine, being particularly susceptible. The resulting injuries significantly enhance emissions of biogenic volatile organic compounds (BVOCs) to the atmosphere, thereby modulating its gas composition. BVOCs are involved in plant growth, reproduction and defence, while functioning as communication media within and between plants. These plant-released compounds have high chemical reactivity with large mass emission rate from vegetation into the atmosphere; therefore, they are major determinants of atmospheric gas composition with important implications for the Earth's atmosphere and climate.</p> <p>Despite the wealth of knowledge on this topic, our understanding of how forest management activities affect BVOC emissions is limited. Uncertainty remains as what the impact of sub-canopy removal is on BVOC emissions from forest trees over a long timescale. This is important since such management activities are common, with equal or potentially even larger impact on BVOC emissions both in the short- and long-run. To address this knowledge gap, I test the impacts of sub-canopy removal on the emissions of BVOCs from a Scots pine stand in a boreal forest. In so doing, I also consider the effects of temperature, soil moisture, and photosynthetically active radiation on the concentrations of these compounds above the canopy. The research sheds light on the complex and intertwined effects of the sub-canopy removal and environmental variables on the stand-level BVOC emissions. The results have implications regarding how forest management practices, and more broadly anthropogenic activities, influence forest-atmosphere interactions. Finally, the research provides promising avenues for future research.</p>			
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## 1. Introduction

A common type of forest management practice is removal of sub-canopy trees, a practice in which a considerable number of small, below-canopy trees are felled. The primary reason to employ sub-canopy removal is to minimize subsequent harvesting costs. Such management activities, however, could be a source of forest disturbance (see e.g., Haapanala et al., 2012; Räsänen et al., 2008). Removal of forest trees may create establishment sites for colonizing species and alters understory vegetation, soil water and nutrient availability (Dodson et al., 2008). Soil compaction through machinery work, which limits root growth of a variety of tree species, could be another consequence of sub-canopy removal (Berger et al., 2004). Additionally, the removal of understory trees causes mechanical damage to trees, with coniferous trees, such as Scots pine, being particularly susceptible (Kari et al. 2019). The resulting injuries significantly enhance emissions of biogenic volatile organic compounds (BVOCs) to the atmosphere, thereby modulating its gas composition (Haapanala et al., 2012; Räsänen et al. 2008).

BVOCs are “any organic compound with vapour pressures high enough under normal conditions to be vaporized into the atmosphere” (Yuan et al., 2010, p. 323). BVOCs are involved in plant growth, development, reproduction and defence, while functioning as communication media within and between plants (Laothawornkitkul et al., 2009). These plant-released compounds have high chemical reactivity with large mass emission rates from vegetation into the atmosphere (Laothawornkitkul et al., 2009). Therefore, they are major determinants of atmospheric gas composition with important implications for the Earth’s climate (Koppmann, 2007). Volatile isoprenoids such as monoterpenes and isoprene are particularly important among BVOCs, because of their high reactivity in the atmosphere and their contribution to the total plant emission (Niinemets et al., 2010). They play an important role in atmospheric processes, for example by being the main biogenic precursors of ozone (Mu et al., 2018). Therefore, BVOCs have significant effects on the biosphere and the atmosphere, making them important research subjects.

We also know that environmental variables affect BVOC emission rates (Penuelas & Staudt, 2010). For example, numerous studies have hitherto analysed the effect of temperature on BVOC emissions from forests (e.g., Tarvainen et al., 2005; Schallhart et al., 2018). Temperature directly modulates BVOCs by influencing their biochemical reactions and volatility. Temperature also indirectly affects BVOC emission rates by lengthening of the growing season (Penuelas & Staudt, 2010). The extant research also shows that temperature in the short term increases plant BVOC emissions exponentially (Guenther, et al., 1995; Filella, et al., 2007). Light is the other environmental variable that affects BVOC emissions. Tree BVOC emissions in boreal forests (e.g., Bäck et al., 2005; Schurmann et al.,

1993) as well as temperate forests (Ghirardo et al., 2010) are light dependent. Soil moisture, ozone and herbivory are other climatic factors that modulate tree BVOC emissions (Holopainen et al., 2018; Niinemets, 2009).

Despite the current wealth of knowledge on BVOCs, our understanding of how forest management activities affect their emission rates is limited. Thus far, we know that management activities such as harvesting and thinning are sources of mechanical damage, inducing stress on trees, altering their BVOC emission rates (Haapanala et al., 2012; Kari et al., 2019). The few studies on this subject have analysed BVOC emissions either at a short timescale spanning merely some weeks (Räisänen et al., 2008) or one growing season (Haapanala et al., 2012). In addition, these studies have mainly looked into the effect of thinning and harvesting on forest tree emissions (e.g., Schade & Goldstein, 2003; Räisänen et al., 2008; Haapanala et al., 2012). Yet, much uncertainty remains as what the impact of sub-canopy removal is on BVOC emissions from forest trees over a long timescale. Our knowledge of the combined effect of sub-canopy removal and environmental variables such as temperature, light and soil moisture on tree BVOC emissions is even more limited. Addressing this literature gap is important, since BVOCs have significant effects on climate system and thereby forest-atmosphere interaction, potentially influencing climate change, too. Additionally, anthropogenic activities could have considerable impacts on BVOC emission rates both in the short- and long-run (see e.g., Haapanala et al., 2012; Schade and Goldstein 2003).

Against this background, I set out to test the impacts of sub-canopy removal on the emissions of BVOCs from a Scots pine stand in a boreal forest. I also consider the effects of temperature, soil moisture, and photosynthetically active radiation (PAR) on the concentrations of these compounds above the canopy. In addition to studying the data coming from the measurement of BVOCs during the sub-canopy removal in spring-summer 2019, I analyse the data from two previous years. This deems necessary for a comparison of the year in which the removal has occurred (i.e., 2019) with years (here, 2017 and 2018) in which the forest stand had remained intact. Accordingly, the following are the study hypotheses:

- 1) Compared to an intact stand, the concentrations of BVOCs above a forest stand during and after a mechanical disturbance (due to sub-canopy removal) is higher.
- 2) The main environmental drivers of BVOC concentrations above a Scots pine stand are air temperature, soil moisture and PAR level; and as such, they positively affect BVOC concentrations.

The rest of this thesis is structured as follows. First, I review the relevant literature on BVOC emissions from forests. Second, I present the material and methods used in this study. Third, I discuss the results of the data analysis. Finally, I conclude with a discussion of the research findings.

## 2. Literature

In this chapter, I review the ecological functions of BVOCs in forests; look into how they affect the atmosphere; discuss the most common BVOCs in boreal forests; review how abiotic factors influence these compounds; and finally discuss how forest management practices affect BVOC emission.

### 2.1. BVOCs and the interaction of forest organisms

BVOCs serve numerous ecological functions<sup>1</sup>, playing important roles in the interaction of forest organisms. BVOCs act as external signals in within-plant communication (intraspecific signals) carrying information from one part to distant parts of the plant (Frost et al., 2007). Frost et al. (2007) demonstrated that when hybrid poplar (*Populus deltoids*) is wounded by herbivores, it releases volatiles that prime defences in adjacent leaves that have little or no vascular connection to the wounded leaves. They exposed undamaged leaves to volatiles emitted by wounded leaves on the same stem, and showed that the undamaged leaves had elevated defensive responses to herbivory compared to those leaves that did not receive volatiles. Karban et al. (2006) also showed that vascular connections were insufficient for systemic induced resistance among branches on an individual plant. Their experiment revealed that an individual sagebrush plant (*Artemisia tridentata*) needed to release volatiles to induce resistance in its yet-unwounded branches. In a later study, Karban and Shiojiri (2009) demonstrated that BVOCs vary between individuals of even the same species. They argued that plants may have the ability to distinguish self from non-self by emitting self-specific BVOCs that function in self-communication among different parts of the individual plant.

In addition to inducing systemic resistance within an individual, trees emit BVOCs to attract natural predators of offensive herbivores. This is called 'indirect defence'. It is used when plants attract, nourish or house other organisms to defend themselves against enemies (Heil, 2008). In these tritrophic interactions, plants that are under attack release BVOCs, subsequently sensed by carnivore organisms. These organisms, typically predatory arthropods, are attracted by the BVOCs. They then locate the emitting plant, and once found the plant, begin feeding on the herbivores. Thus, they indirectly help the plant to defend itself against the herbivores' attack. Heil and Silva Bueno (2007),

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<sup>1</sup> For a thorough summary, see Holopainen (2004).

for example, showed that BVOCs released from damaged leaves of lima bean can induce secretion of extrafloral nectar—a nectar that attracts arthropods by yet-undamaged leaves.

Studies reviewed above reveal that plant signals sent via BVOCs enhance systemic responses within plants. This is the case even when the transmission of internal signals is constrained by vascular connectivity as demonstrated by Frost et al. (2007). These results indicate that within-plant signalling—that is, transmitting information from one part of the plant to the other parts and thereby enhanced protection against imminent threat—is *raison d'être* of these compounds. Moreover, according to the results, plants use BVOCs to defend themselves indirectly; through a tritrophic interaction, plant-released BVOCs attract predatory arthropods that feed on herbivores. True, now, backed by strong evidence, the primary reasons of the emitted BVOCs are intraspecific signalling and tritrophic interaction as a means of defence. Yet, in dense, natural conditions, BVOCs emitted upon wounding or attack could easily reach such concentration levels in the air that it becomes readily possible for the neighbouring trees to sense them (Kegge & Pierik, 2010). Do, then, the neighbouring trees prepare themselves for the incoming threat?

To answer this question, we need to be introduced to a phenomenon referred to as “talking trees”. In a renowned study in the 1980s, two plant scientists, using a chamber experiment, found that neighbours of a defoliated tree induced elevated resistance against herbivores (Baldwin & Schultz, 1983). A field study done in the same year led to the same result (Rhoades 1983). Later, Haukioja et al. (1985) set out to put these results to test by repeating similar field experiments. They also reached the same conclusion. Subsequent studies confirmed these results, too. For example, BVOCs induced by feeding of spider mites on lima beans led to secretion of extrafloral nectar by neighbouring, healthy plants (Heil, 2008; Blande et al., 2010a). Initially, ecologists considered that damaged trees were “talking” to their neighbours informing them of the imminent attack. However, as discussed above, trees emit BVOCs as external signals to transmit information to their undamaged parts. It is a way of communication between organs within the same tree. If this is the case, the question arises as how then do we explain Baldwin’s and Schultz’s (1983), and other researchers’, studies that neighbours of a damaged tree induce resistance against a possible attack before even being attacked.

We now know that as BVOCs are spread in the surrounding air, neighbouring trees sense them and thus prepare, say, for an imminent herbivory attack. Therefore, more recently, scientists, instead of using the term “talking trees”, believe that trees “eavesdrop” on their neighbours (Baldwin et al., 2006). In fact, communication among individual trees may be a by-product of BVOCs emitted to integrate trees’ own systemic physiological processes (Karban & shiojiri, 2009). Regardless of the primary reason, however, trees uses BVOCs in the air as a means to sense external cues in the

surrounding environment. Once a tree emits BVOCs, it has no control over the distance and direction they are spread. The dynamics of how these volatile compounds are transported are governed by factors such as temperature and wind (Baldwin et al., 2006). Neighbouring trees sense these BVOCs; then uptake them into their leaves via stomatal openings or cuticle diffusion (Baldwin et al., 2006). Once these BVOCs signals are received, a tree can activate defence mechanisms or prime defence-related genes for earlier and/or stronger induction on future defence acquisition within the tree (Penuelas et al., 1996). This ultimately serves as an evolutionary defence mechanism. Perhaps a term borrowed from Unsicker et al. (2009) can summarize the above discussion well: BVOCs are protective plant perfumes. The evolutionary functions of BVOCs, however, do not end here.

BVOCs play an important role in plant reproduction, too. To ensure reproduction success, plants emit an innumerable of BVOCs from their flowers helping them to attract pollinators (Wright et al., 2005). The BVOCs act as signals assisting pollinators to identify conspecific flowers while foraging (Andersson et al., 2002). Plants release BVOCs from their flowers with different mixtures and abundance. These differences make the scent bouquet specific to a particular flower (Knudsen & Tollsten, 1993; Knudsen et al., 2006). Floral blends of volatiles are similar to private communication channels between emitter plants and pollinator receivers (Raguso, 2008). Sensing the floral mixtures, pollinators identify the emitter plant species, and receive various information about the flowers, such as their developmental stage and the availability and quality of their rewards (see e.g., Farré-Armengol et al., 2014; Goodrich & Raguso, 2009; Proffit et al., 2008). Once they sense the floral scents, pollinators can then locate respective flowers (Carde & Willis, 2008). Given this and the preceding discussions, we can say that BVOCs evolve mainly as a defence mechanism and to serve reproduction purposes by attracting pollinators and seed dispersers—though which one is the main reason is still a matter of debate (Yuan et al., 2010).

Yet, not all BVOC molecules are absorbed by the leaves and other parts of the same or other plant(s). A myriad of BVOCs do not remain in the biosphere; they rise up to the atmosphere, modulating microclimate and changing the composition of the air above and beyond the forest canopy by reacting with other molecules therein. Thus, these carbon-based compounds have important implications for the Earth's atmosphere and climate system (see e.g., Penuelas et al., 2009), to which we now turn our attention.

## **2.2. BVOCs and the atmosphere**

There is now a consensus that biological processes in terrestrial ecosystems broadly influence the Earth's atmosphere and climate system (Penuelas et al., 2009; Penuelas & Staudt, 2010). Among



these biological processes, those related to BVOCs have gained substantial attention; in recent decades, atmospheric BVOCs have been among the most discussed topics in atmospheric chemistry (Matsumoto, 2014). This comes with good reasons. The global flux of BVOCs from the biosphere to the atmosphere is estimated at  $700\text{-}1000 \times 10^{12}$  g (C) year<sup>-1</sup>, far exceeding the global anthropogenic VOC flux (Guenther et al., 1995; Laothawornkitkul et al., 2009). In addition, BVOCs are highly reactive molecules with short atmospheric lifetimes. Whereas atmospheric lifetimes of trace gases such as nitrous oxide and methane are 114 and 8-12 years, those of acetone, methanol and monoterpenes are merely 15, 10 and 0.1-0.2 days, respectively (Bäck, 2019). The short lifetime of BVOCs and their deep concentration gradient around emission source may have evolved to maintain their high signaling value (Heil & Karban, 2010). Because of large emission rates and high chemical reactivity, BVOCs have a profound effect on the chemical composition and physical characteristics of the lower atmosphere (Laothawornkitkul et al., 2009).

An important implication of BVOCs for the Earth's atmosphere is their role in the formation of ozone (O<sub>3</sub>) in the troposphere. This is important as O<sub>3</sub> is the third most important greenhouse gas after CO<sub>2</sub> and methane (IPCC, 2007). BVOCs play a fundamental role in the formation of photochemical smog in the troposphere. Thus, they lead to the formation of tropospheric O<sub>3</sub> (Calfapietra et al., 2009). To do that, BVOCs react with nitrogen oxides (NO<sub>x</sub>), which are essentially derived from combustion processes in urban areas (Jenkin & Clemitshaw, 2000). Here, the ratio of non-methane BVOCs to NO<sub>x</sub> is of particular significance, as it is an important parameter to distinguish the efficiency of O<sub>3</sub> formation (Calfapietra et al., 2009). At high ratio of BVOC to NO<sub>x</sub>, O<sub>3</sub> formation is limited by availability of NO<sub>x</sub> rather than BVOCs, whereas this is opposite at BVOC-limited ratio. This can explain why O<sub>3</sub> concentration is higher in the countryside with high BVOC concentration than in urban areas where BVOC level is low (Calfapietra et al., 2009). When the urban air masses with high NO<sub>x</sub> concentrations are transported by air circulation to the countryside, the result will be high peaks of O<sub>3</sub>—though the countryside is usually far away from sources of NO<sub>x</sub> (Millan et al., 1997). Hence, O<sub>3</sub> in the troposphere is considered a direct product of BVOC degradation (Curci et al., 2009).

As BVOCs readily react with O<sub>3</sub>, they contribute to the destruction of O<sub>3</sub>, too (Penuelas & Staudt, 2010). The emission of BVOCs, particularly isoprene, from tropical forests plays an important role in recycling OH (hydroxyl) radicals, buffering the oxidative capacity of the climate above the tropical forests (Lelieveld et al. 2008; Taraborrelli et al., 2012). OH radicals are highly reactive oxidant that act as the primary cleansing agent for the atmosphere (Lelieveld et al., 2008). What BVOCs do in this case stands in contrast to their effect on an anthropogenically influenced troposphere above

polluted urban areas. Whether or not net O<sub>3</sub> formation happens is therefore strongly dependent on the presence of NO<sub>x</sub> in the troposphere (Penuelas & Staudt, 2010).

BVOCs could also indirectly change methane atmospheric lifetime. BVOCs affect the levels of OH radicals, which are the main sink of methane in the atmosphere (Poisson et al., 2000; Ortega et al., 2007). If OH radicals are reduced by BVOCs—which is likely as researchers show (e.g., Laothawornkitkul et al., 2009; Pacifico et al., 2009) and explained above—the oxidation capacity of atmosphere is also reduced. As a result, methane lifetime increases. Since methane is an important greenhouse gas, BVOCs could therefore indirectly enhance climate warming. However, as mentioned above, whether BVOCs decrease the atmospheric oxidation capacity largely depends on the presence of NO<sub>x</sub>, derived from anthropogenic activities in polluted areas. In pristine environments, such as those of remote Amazonian tropical forests, BVOCs can strengthen the oxidative capacity of the atmosphere (Lelieveld et al. 2008; Taraborrelli et al., 2012). Therefore, how BVOCs modulate methane atmospheric lifetime depends on a mix of anthropogenic and biogenic gas emission.

Another consequence of BVOCs is the formation of secondary organic aerosol (SOA) in the atmosphere. Atmospheric aerosols are liquid or solid particles suspended in air (Hallquist et al., 2009). Primary organic aerosols are emitted from both anthropogenic (e.g., fossil fuel combustion or biomass burning) and biogenic (e.g., fungal spores, plant debris and wildfires) sources (Holopainen et al., 2017). SOAs, on the other hand, consist of particulate particles in air produced by oxidation of biogenic and anthropogenic VOCs (Holopainen et al., 2017), through reacting with OH radicals (Andreae & Rosenfeld, 2008; Kirkby, 2016). The terpenoids are, for example, considered to lead to aerosol formation by rapid reaction with atmospheric oxidants such as O<sub>3</sub>, OH and nitrate (NO<sub>3</sub>) radicals (Kulmala et al., 2004). As a result of these reactions, low volatility products are formed (Hoffmann et al., 1998). The products take part in gas-to-particle conversion processes (Atkinson, 2000). With increasingly high concentration of O<sub>3</sub> and nitrate radicals in the troposphere due to anthropogenic activities these low-volatile products become more important (Kanakidou et al., 2000), as they are formed more rapidly currently than previous decades.

The SOA particles influence climate in two ways: either directly by reflecting or absorbing solar radiation or indirectly by acting as cloud condensation nuclei (CCN) increasing the optical thickness of individual clouds (Kulmala et al., 2004; Penuelas & Staudt, 2010). Either of these effects leads to a decrease in the amount of solar radiation reaching the biosphere (Kulmala et al., 2004), with a consequent cooling effect on the surface of Earth (Penuelas & Staudt, 2010). BVOC-induced changes in the concentration of cloud nuclei can modulate local radiative forcing by approximately  $-4 \pm 2.5$  W

m<sup>-2</sup> (Goldstein et al., 2009; Spracklen et al., 2008). Aerosols produced by BVOCs' reactions also increase the amount of diffused light (Niyogi et al., 2004). Compared with direct sunlight, diffused radiation can enhance CO<sub>2</sub> fixation by plants, expanding canopy-scale light use efficiency of photosynthesis (Niyogi et al., 2004). This is another indirect, potentially negative feedback to climate warming (Peneulas & Staudt, 2010). SOA, however, impacts human health negatively (Friedman & Farmer, 2018), and indirectly add to climate warming by potentially scavenging of OH radicals, increasing O<sub>3</sub> production, and the atmospheric lifetime of methane (Peneulas & Staudt, 2010).

The above discussion sheds light on the uncertainty and complexity of BVOCs' implications on the Earth's atmosphere and climate system. What we can conclude with relative certainty is that the products of BVOCs' reactions do influence the radiative forcing of the atmosphere (Richardson et al., 2013). How this occurs can be summarized as follows. Enhanced BVOCs emissions increase aerosol formation and CCN concentrations. Rise in aerosol and CCN concentrations, in turn, reduces temperature, as they reflect sunlight back to space. However, increased BVOCs emissions have also positive feedbacks on climate warming. BVOCs have indirect greenhouse effect through ozone formation and methane lengthening lifetime, CO<sub>2</sub> production and their latent heat due to water condensation (Peneulas & Staudt, 2010). In addition, climate warming, increasing likelihood of drought, rising atmospheric CO<sub>2</sub> concentrations and enhanced UV-B radiation are global changes—mainly due to anthropogenic activities—that also modulate BVOC emissions (Peneulas & Staudt, 2010). Given these complex processes, whether the likely enhanced emissions of BVOCs in the future mitigate or contribute to the current climate crisis is a complicated matter.

### **2.3. Common BVOCs in forests of Finland**

Though globally isoprene is the most abundant emitted BVOC (Guenther et al., 1995), most tree species in Eurasian boreal forests, including forests of Finland, predominantly emit monoterpenes (Rinne et al., 2009). In the forests of Finland, these species are evergreen Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*), and deciduous birch (*Betula spp.*), covering roughly 50%, 30% and 17% of the forest land area, respectively (Vaahtera et al., 2018). Different measurement techniques, both at branch and ecosystem scale, show that Scots pine is a monoterpene emitting species (Rinne et al., 2009). *Betula pendula*, a dominant birch species in Finland, also emit considerable amount of monoterpenes, releasing  $\alpha$ -pinene,  $\beta$ -pinene, subinene, ocimenes, and 3-carene as main volatiles (Hakola et al., 1998; Lindfors et al., 2000). Norway spruce is mainly a monoterpene emitter, too (Lindfors & Laurila, 2000). However, Norway spruce emits isoprene, too, though with lower potential than broadleaves trees; yet because of its large needle biomass density, Norway spruce is an important

contributor of atmospheric isoprene (Rinne et al., 2009; Tarvainen et al., 2007). Hakola et al. (2017), for instance, showed Norway spruce emit considerable amount of isoprene, particularly during late summer. Non-dominant trees, such as European aspen and willows, are also sources of isoprene in Eurasian taiga (Rinne et al., 2009).

In addition to isoprenoid, forest trees emit a number of low-molecule-weight BVOCs ( $C < 5$ ) (Laothawornkitkul et al., 2009). The most abundant of these compounds emitted from boreal forests are methanol, acetone, acetaldehyde and formaldehyde (e.g., Janson et al., 1999; Cojocariu et al., 2004). Ecosystem scale BVOCs emitted from Scots pine ecosystem shows that methanol, acetone, and acetaldehyde comprise half of the emitted BVOCs (Rinne et al., 2009 and references therein). Birch species, too, emit substantial amount of methanol, acetone, and acetaldehyde especially during spring and early summer when leaves are young (Hakola et al., 2001). Norway spruce also emits considerable amount of acetone and acetaldehyde, with some methanol and ethanol in its BVOC mix (Grabmer et al., 2006).

Overall, monoterpenes are the most common BVOCs emitted from boreal forests of Finland, contributing to 45% of total annual emission of the forests (Lindfors & Laurila, 2000). Due to the presence of Norway spruce, isoprene is also emitted from these ecosystems, comprising 7% of the total BVOC emission (Lindfors & Laurila, 2000). In addition, substantial amount of methanol and acetone are emitted from tree species in Finnish forests, as discussed above.

#### **2.4. Abiotic factors and BVOC emissions**

The mix of BVOCs produced and emitted by a single plant is specific, highly individual and strongly dependent on abiotic factors such as temperature, light, water availability and humidity (Holopainen et al., 2017; Yuan et al., 2009; Zhao et al., 2017). Plants synthesize terpenoids by two distinct pathways (Kulmala et al., 2004 and reference therein): the mevalonic acid and the 1-deoxy-D-xylulose-5-phosphate. Both these pathways are influenced by abiotic factors. Via the mevalonic acid pathway, production of terpenoids such as monoterpenes that are stored in specialized storage tissues occurs. The emission of these terpenoids is influenced by the ambient temperature (Fuentes et al., 2000). The synthesis of isoprene and  $\alpha$ -pinene happens through the 1-deoxy-D-xylulose-5-phosphate pathway, which is influenced by a number of environmental variables such as temperature or light intensity (Staudt & Bertin, 1998). Enzyme activities of foliar BVOCs synthesis are also dependent on ambient temperature and radiation in addition to the physiological status of the leaf (Mayrhofer et al., 2005).

Temperature is one of those important abiotic factors that directly increases tree BVOC emissions by increasing the BVOCs' vapour pressure thereby lowering the resistance of the diffusion pathway (Tingey et al., 1991). For example, while a 10 °C rise in temperature results in two- to threefold increase in photosynthetic carbon assimilation rate, the same degree of temperature increase results in 6 times rise in BVOCs emissions, showing that, in the short term, the relationship between BVOC emissions and temperature is exponential (Niinemets, 2004; Penuelas & Staudt 2010). Studies conducted in boreal forests show a similar pattern. In an open-field exposure in central Finland, Kivimäenpää et al. (2016) demonstrate that elevated ambient temperature increases total emissions of monoterpenes twofold to fourfold in Scots pine seedlings. Using online measurement with PTR-MS, Filella et al. (2007) also show that rise in temperature leads to exponential increase in the emission of most BVOCs from Norway spruce. Hartikainen et al. (2012) study the effect of rise in temperature by +0.8-1 °C on four silver birch clones over two growing seasons in an open-air exposure. They reveal that elevated temperature leads to significant increase in total emission of monoterpenes and sesquiterpenes. These studies highlight that temperature has a strong positive effect on BVOCs emission from tree species in boreal forests, including forests of Finland, in which Scots pine, Norway spruce and silver birch are common tree species.

Light is another important abiotic factor that influence tree BVOC emissions. Various studies show that monoterpene emissions from coniferous tree species such as Scots pine and Norway spruce is light dependent (Bäck et al., 2005; Tarvainen et al., 2005; Schurmann et al., 1993). Monoterpene emissions from silver birch is even more dependent on light. Using stable isotope <sup>13</sup>CO<sub>2</sub>-labelling technique, research shows that silver birch emits zero emission of monoterpenes overnight, indicating that the emission is completely light-dependent (Ghirardo et al., 2010). However, in situ measurements in boreal forests of Finland scientists reveal that trees continue to emit low rates of monoterpenes during the night; it is only isoprene that is completely light-dependent being produced and emitted only during the day (Hakola et al., 2012). Rapid decline of isoprene emission in darkness also occurs in other species less common in Eurasian boreal forests such as European larch and Holm oak (Ghirardo et al., 2010).

In addition to temperature and light, water availability plays an important role in tree production and emission of BVOCs (Bonn et al., 2019; Loreto & Schintzler, 2010). In a greenhouse study, Lüpke et al. (2016) examined the impact of soil water availability on gas exchange of Scots pine seedlings. They showed that the trees' isoprenoid emission decreased during a 6-week of water shortage in summer, though the emissions significantly recovered after rewetting. This was not the case for control trees, which did not experience any water shortage. Focusing particularly on monoterpene

emission of Scots pine, in a  $^{13}\text{C}$  labelling experiment, Lüpke et al. (2017) demonstrated that 11-day lack of sufficient soil moisture leads to reduction in monoterpene emission, confirming previous studies. Besides isoprenoids, oxygenated BVOCs such as methanol and acetone are influenced by water availability, too. A consequence of low water availability in plants is stomatal closure. Since the emission of oxygenated BVOCs is dependent on stomatal opening, then low water availability is particularly expected to reduce the emission of these compounds (Loreto & Schintzler, 2010).

According to these studies, BVOC emissions in trees strongly depend on water availability. However, due to the complexity of how trees respond to lack of water, we still need more studies to understand the dependency of emissions of higher terpenes and oxygenates on water availability in different environments (Bonn et al., 2019). In absence of such detailed studies, we still have uncertainties regarding the magnitude of the natural feedback processes of forests and ecosystems and especially how forest management activities affect them in natural conditions (Bonn et al., 2019). Forest management activities indeed induce direct and indirect changes to BVOC emissions from forest trees. One of the common forest management activities that could have significant impact on BVOC emissions from trees is the removal of understorey trees.

## **2.5. BVOCs and understorey removal**

Similar to other abiotic stresses (see e.g. Loreto & Schnitzler, 2010), mechanical damage enhances tree emissions of BVOCs (Haapanala et al., 2012). This is the case in coniferous trees (e.g., Loreto et al., 2000) as well as birch species (Hakola et al., 2001). Mechanical wounding of leaves in trembling aspen (*Populus tremula*) also leads to the emissions of different low-molecule-weight oxygenated compounds (Portillo-Estrada et al., 2015). Coniferous trees are particularly susceptible to mechanical injuries, since they store considerable amount of monoterpenes within their resin ducts (Haapanala et al., 2012). Kari et al. (2019), for instance, show that mechanical damage increases the emission of terpenes from Scots pine saplings, since the injured stem tissues expose the trees' terpene pools into the atmosphere.

Forest management activities such as commercial thinning, clear-cutting and sub-canopy removal are significant sources of forest disturbance and thus mechanical damage to the trees in boreal forests (Haapanala et al., 2012; Räisänen et al., 2008). Particularly during winter and spring, extensive forestry work is conducted in boreal forests (Haapanala et al., 2012). Studies on the effects of these activities are still relatively uncommon. Schade and Goldstein (2003) did one of the early works on the topic by examining how thinning influences the mixing ratio and emission rates of monoterpenes in a ponderosa pine plantation. They demonstrated that during the thinning, monoterpene fluxes rose

by a factor of 40, with the annual emissions at the site increasing by a factor of five due to higher basal emission rates. In a subsequent study, Räsänen et al. (2008) evaluated the effects of clear-cutting and thinning in a Scots pine forest on the ambient monoterpenes concentrations of air below the canopy layer. They showed that the monoterpene concentrations rose twofold-threefold seven weeks after the felling by clear-cutting compared to the control plot. Thinning also induced increase emission of monoterpenes, albeit at a smaller increment compared to clear-cutting, yet larger than the control plot.

The tree stumps that remain in the site after felling are residue woods with a root system that is still living. Since the root system is still functioning, resin flows from the roots to the stump surface to heal the wound. This leads to substantial monoterpene emissions from fresh and drying resin (Šimpraga et al., 2019). This indicates that mechanical damage leads to higher emissions of monoterpenes than isoprene in most boreal forest ecosystems, wherein dominant tree species are resin storing conifer trees such as Scots pine (Kivimäenpää et al., 2012). Measuring terpenoids in a boreal forest in Finland, Haapanala et al. (2012) also showed that monoterpene emissions increased noticeably from both single stump and from the whole felling area after timber felling. In their experiment, however, the emissions of sesquiterpenes were small, and those of isoprene were negligible. In temperate forests, the composition of emitted gases are likely to differ from boreal forests. Though studies are rare on this topic, Purves and his colleagues (2004) showed that in the forests of the Eastern US, wherein live a large number of broadleaf tree species, harvesting leads to increase in isoprene but reduction in monoterpene emissions.

### **3. Material and methods**

#### **3.1. Study site and sub-canopy removal**

I use measurements carried out in Hyytiälä at the SMEAR II site (Station for Measuring Forest Ecosystem–Atmosphere Relations; 61°51'N, 24°17'E, 180 m a.m.s.l., UTC + 2) located in southern Finland. Typical to Eurasia boreal forests, the dominant tree species in Hyytiälä is Scots pine, with Norway spruce covering approximately 15% of the forest (Schallhart et al., 2018). In addition to Scots pine and Norway spruce, juniper and some broadleaf tree species such as silver birch, rowan (*Sorbus aucuparia*), trembling aspen, goat willow (*Salix caprea*) and alder are also present at the study site. The forest was sown with seeds in 1962. The current canopy height is above 18 meters and the stand density is around 1300  $ha^{-1}$  (Schallhart et al., 2018). During the climatological normal period 1981-2010, the mean annual temperature and precipitation were 3.5 °C and 711 mm, respectively (Pirinen

et al., 2012). Hari et al. (2013) provide a detailed description of the station facilities and the surrounding forest.

During spring and early summer 2019, the forest at the SMEAR II station underwent a process of sub-canopy removal, in which most trees smaller than average were removed. According to the inventory results (Isotalo et al., 2019, unpublished results), the top three most occurring sub-canopy species were rowan, birch and spruce, which numbered 1453, 1395 and 1296, respectively. Willow (178), pine (80), juniper (49), aspen (43) and alder (18) were other sub-canopy tree species. The majority of these trees—particularly those three most occurring species—had been felled in the process, while a fraction had remained intact, especially this was the case among those less common sub-canopy species.

### 3.2. BVOC measurement

The measurement I use for the BVOC fluxes and concentrations is conducted by the proton transfer reaction quadrupole mass spectrometer (PTR-MS) instrument (manufactured by Ionicon Analytik GmbH, Innsbruck, Austria). The PTR-MS is an analytical technique enabling rapid and continuous monitoring of plant emissions (Hansel et al., 1995). PTR-MS can measure different masses from towers standing at different heights. The height used in this study for BVOC concentrations in the air is 33.6 m, which was above the forest canopy. To calculate the ecosystem scale BVOC fluxes, surface-layer profile method were employed, in which the measured BVOC concentrations data from several heights were utilized (see Rantala et al., 2014 for a thorough explanation on the calculations). The computational height for fluxes in this study was also 33.6 m.

Table 1. Information on the compounds studied in the research. The compound measured masses [m/z], names and formula shown in first, second and third column, respectively.

[m/z]	Compound	Chemical formula
33	methanol	CH <sub>4</sub> O
59	acetone	C <sub>3</sub> H <sub>6</sub> O
69	isoprene	C <sub>5</sub> H <sub>8</sub>
137	monoterpenes	C <sub>10</sub> H <sub>16</sub>

Out of 27 masses measured by PTR-MS, I analyse four masses in this research: monoterpenes, methanol, acetone, and isoprene. (See Table 1 for more information on these compounds.) As explained in section 2.3., these are the most common BVOCs emitted from boreal forests, including the tree species present in the forest at the SMEAR II. Here, it is worthwhile to note that PTR-MS



cannot distinguish different types of monoterpenes from each other (Grabmer et al., 2006). Therefore, in this study volume mixing ratio of monoterpenes always refer to the sum of all monoterpenes.

### 3.3. Data analysis

Since I aimed to study concentrations and fluxes of BVOCs before, during and after the removal, I chose the data on the concentrations and fluxes spanning from 2017 to 2019. This timeframe allowed comparison of BVOC emissions before, during and after the removal. To do the analysis, I used R programming language. The first step was to download data from Aavaa open research data portal website (available at <https://avaa.tdata.fi/web/smart/smear>). All the raw data on BVOCs from SMEAR II site were available in the web portal. Next, I sorted out and prepared the data for further analysis. In the process, several files containing data from different time periods were combined. Then, missing values analysis was done and time periods with large amount of missing data were specified and later eliminated. Out of 63368 observations, the number of missing data for the concentrations was 6755, 6746, 6857 and 7125 for methanol, acetone, isoprene and monoterpenes, respectively, amounting to approximately 10%. For fluxes, this was 1747, 1754, 1750 and 1777 out of 7050 observations, amounting to approximately 25% missing data. Regarding soil water content, there was about 98% missing data (1382275 out of 1399501 observations). This was particularly the case during spring 2018. Due to such large missing data, I decided to do the analysis on soil water content only during time period with available data. In the case of PAR and temperature, there were approximately 1% and 1.5% missing values (13309 out of 1316160 and 19021 out of 1316160 observations), respectively.

To examine soil moisture, I calculated soil moisture index (SMI; see e.g., Betts, 2004). To do so, I first calculated the average of the volumetric soil water content in B1 and B2 horizon, with the depths of 14-25 cm and 26-36 cm, respectively. I excluded the A horizon, with the depths of 2-6 cm, because as explained by Gao et al. (2017), it is strongly affected by other variables such as temperature and precipitation. Following previous literature (Gao et al., 2017; Seneviratne et al., 2010), I then used the following equation:

$$SMI = (\theta - \theta_{WILT}) / (\theta_{FC} - \theta_{WILT})$$

Where  $\theta$  is volumetric soil moisture ( $\text{m}^3 \text{H}_2\text{O m}^{-3}$ ),  $\theta_{FC}$  is the field capacity ( $\text{m}^3 \text{H}_2\text{O m}^{-3}$ ), and  $\theta_{WILT}$  is the permanent wilting point ( $\text{m}^3 \text{H}_2\text{O m}^{-3}$ ). When  $\theta$  exceeds  $\theta_{FC}$ , soil water will drain, whereas below  $\theta_{WILT}$ , soil water cannot be absorbed by plants (Hillel, 1998). Therefore, SMI indicates the ratio of available soil moisture to plants to the maximum available volume of water.

To examine whether the differences between monthly concentrations and fluxes are statistically significant across the three years under study, I performed a pairwise test of daily median values of the concentrations and fluxes during spring and summer (March-August) of the three years. I performed this to examine the differences between the year 2019 and the other two years. To examine the combined effects of temperature, PAR and soil moisture on BVOC emission rates, I performed multiple regression analysis on daily median values of these variables during summer (June-August) 2017, 2018 and 2019.

To simulate the temperature dependence of BVOC emission rates, I followed the algorithm suggested by Guenther et al. (1991, 1993), which assumes that BVOC emissions respond exponentially to temperature:

$$E = E_0 e^{\beta(T-T_0)}$$

Where E is the emission potential of the source,  $E_0$  is the standard emission potential under standard temperature (here,  $T_0 = 30$  °C) and  $\beta$  is an empirical coefficient for the temperature dependency of the compound under study. For monoterpene emission rates,  $\beta$  usually holds constant value of 0.09 (Guenther et al., 1993). In this study, I also considered 0.09 as initial value for  $\beta$ ; then using the equation above, I fitted a curve to the measured flux data. This was used to estimate a new  $\beta$  and  $E_0$ , which were then used to calculate the temperature normalized fluxes. The normalized fluxes allowed comparison of the BVOC emission rates amongst the years at a standard temperature, hence removing the effect of yearly variation in temperature.

## 4. Results

### 4.1. Annual BVOC concentrations and fluxes 2017-2019

First, it is worth examining the time series of the compounds under study. The three-year time series, as shown by Figure 1, provides important details on the annual, seasonal and monthly fluctuations of the compounds' concentrations above the canopy as well as fluxes. Such long-term canopy scale data demonstrate the dependencies of the concentrations and fluxes on environmental variables (Rantala et al., 2015). Figure 1A and B show the concentrations and fluxes of monoterpenes. Compared to other compounds, monoterpenes are more scattered with more fluctuations. In the case of isoprene (Fig.1C and D), methanol (Fig.1E and F) and acetone (Fig.1G and H), both concentrations and fluxes show clear seasonal pattern, increasing gradually during early spring, reaching a peak during summertime and decreasing during the colder months of the year. This pattern is more pronounced for the concentrations. This is in line with prior studies (e.g., Bäck et al., 2005) showing that

seasonality affects synthesis and storage of BVOCs and thereby actual emission rates. In addition, Figure 1F and H show high deposition (i.e., negative fluxes) for methanol and acetone, whereas Figure 1B demonstrates more positive fluxes (net emission) of monoterpenes.

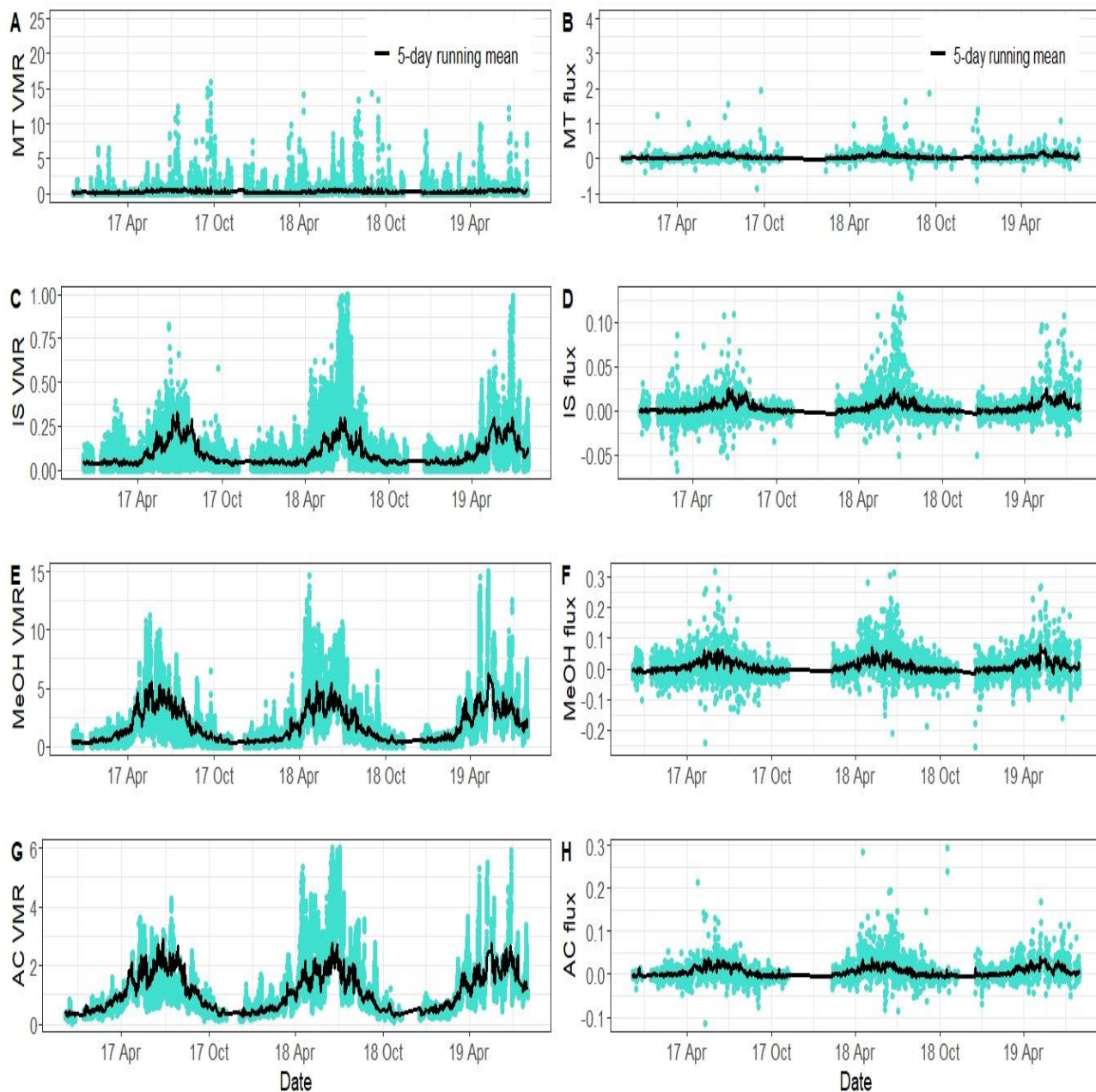


Figure 1. Concentrations and fluxes of BVOCs during 2017-2019. The left panel shows concentrations, and the right shows fluxes. Unit for concentrations is parts per billion and for fluxes is  $\mu\text{g m}^{-2}\text{s}^{-1}$ . MT, monoterpenes; IS, isoprene; MeOH, methanol; AC, acetone. VMR, volume mixing ratio. The solid black line shows 5-day running mean of the actual values demonstrated by the turquoise dots.

Table 2 shows some basic descriptive statistics of the BVOCs. Generally, the results, from Figure 1 and Table 2, reveal that fluxes and concentrations of methanol, acetone and monoterpenes are considerably high, whereas those of isoprene are relatively low. This is consistent with prior studies

that look into BVOC emissions from trees in boreal forests (e.g., Rantala et al., 2015; Rinne et al., 2007).

Table 2. Descriptive statistics of the selected BVOCs. Unit for the concentrations is part per billion and for the fluxes is  $\mu\text{g m}^{-2}\text{s}^{-1}$ .

		Mean	Median	Max	Min	Variance
Monoterpenes	Concentrations	0.29	0.13	15.95	2.63e-6	0.42
	Fluxes	0.047	0.02	1.96	-0.86	0.01
Isoprene	Concentrations	0.10	0.06	0.99	1.16e-6	0.014
	Fluxes	0.004	0.0009	0.13	-0.06	0.0002
Methanol	Concentrations	1.99	1.21	14.99	1.3e-4	4.12
	Fluxes	0.009	0.002	0.32	-0.25	0.002
Acetone	Concentrations	1.20	0.93	5.99	0.05	0.88
	Fluxes	0.005	0.0008	0.29	-0.11	0.0005

#### 4.2. Monthly BVOC concentrations and fluxes

Figure 2A reveals that monoterpene concentrations in 2018 are generally higher than those in 2017 and 2019. As expected, this holds for the fluxes, too (see Figure 2B). With regards to fluxes, however, we can see that they are generally higher in 2019 than 2017, though fluxes in 2018 still remain higher than those in the other years.

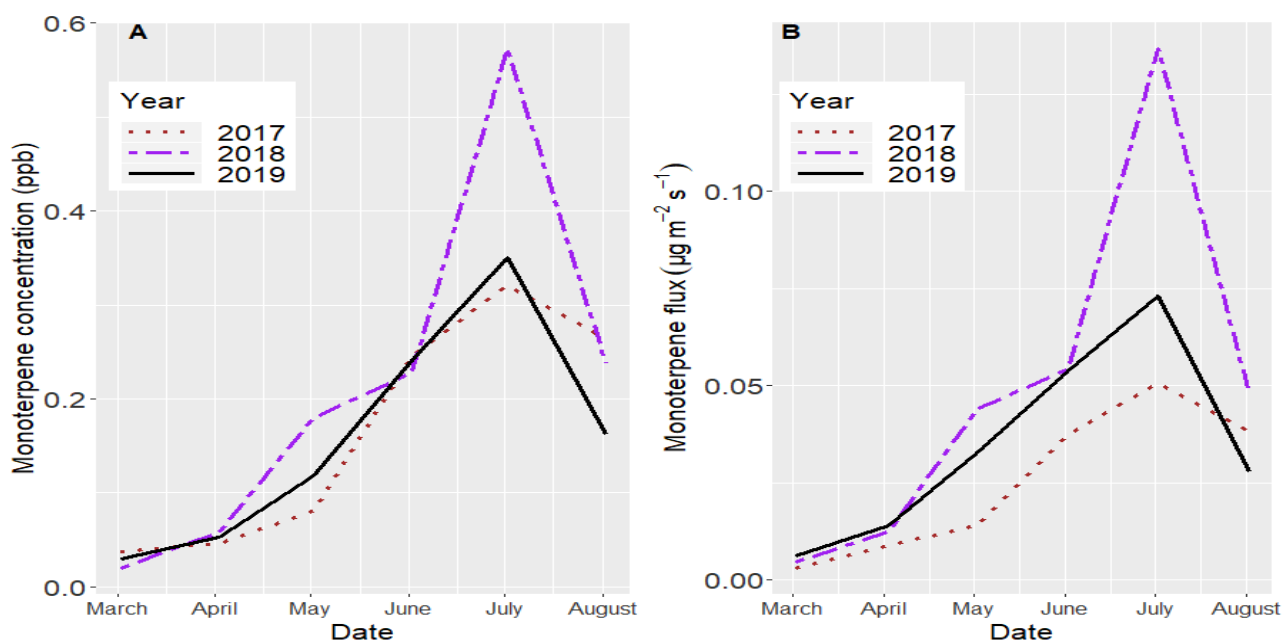


Figure 2. Monthly median monoterpenes (A) concentrations and (B) fluxes during spring and summer 2017 – 2019.

Figure 3 shows the results of the pairwise test of daily median values of monoterpene, which are similar for both concentrations and fluxes. The difference between 2019 and 2017 is not statistically significant, while concentrations and fluxes are lower in 2019 compared with 2018, and this is statistically significant.

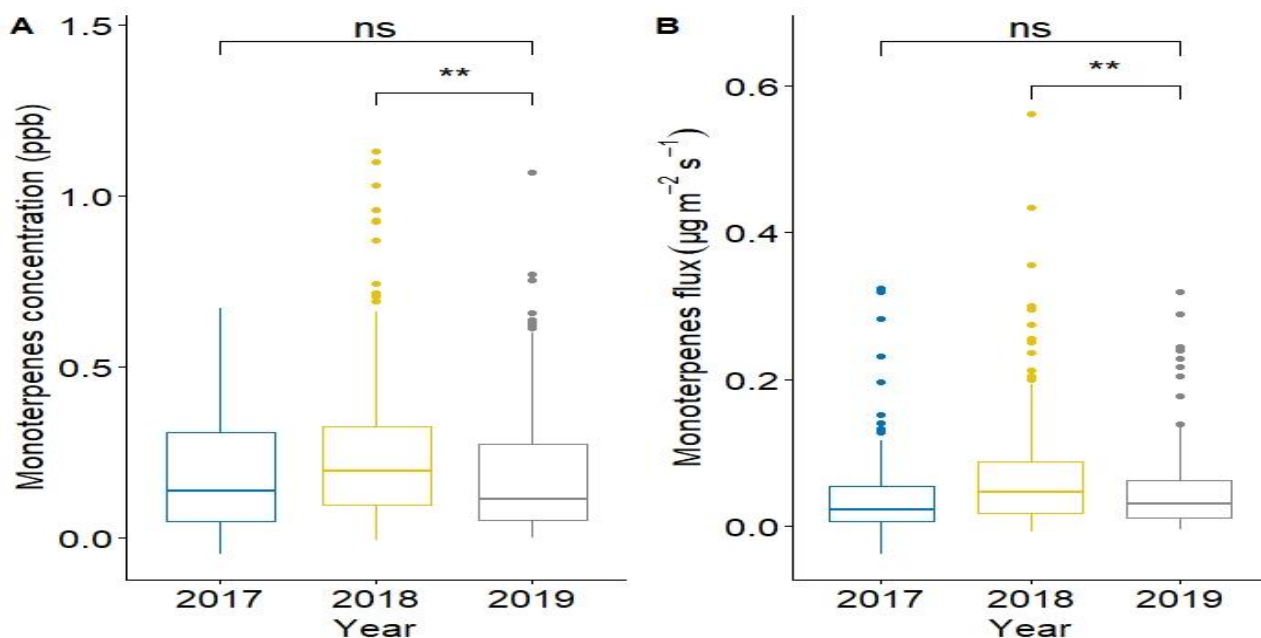


Figure 3. Pairwise test of daily median values of monoterpene (A) concentration and (B) fluxes during spring and summer (March-August) 2017 and 2018 against the same period in 2019. The boxes are divided at the median values. The first quartile is the bottom line of the box; the third is the top line. Whiskers extend to the minimum and maximum of each quartile. Significant differences between 2019 and other years are denoted by asterisks (t test); \*\*\*  $p < 0.001$ ; \*\*  $p < 0.01$ ; \*  $p < 0.05$ .; ns, not significant.

Figure 4 shows isoprene concentrations and fluxes. Similar to monoterpenes, isoprene concentrations and fluxes in 2018 are generally higher than those in 2017 and 2019, while in 2019 these values are higher than 2017.

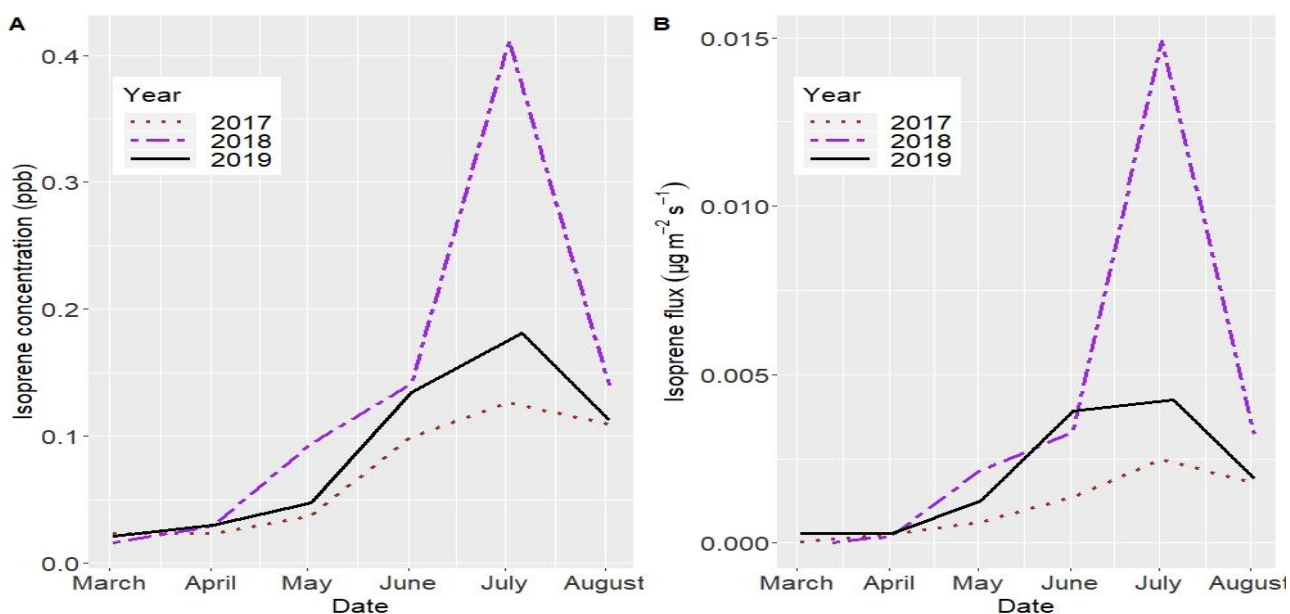


Figure 4. Monthly median isoprene (A) concentrations and (B) fluxes during spring and summer 2017 – 2019.

Figure 5 shows the results of the pairwise test of daily median values of isoprene concentrations and fluxes, revealing that the concentrations and fluxes during 2019 were lower than 2018 but higher than 2017, with both being statistically significant.

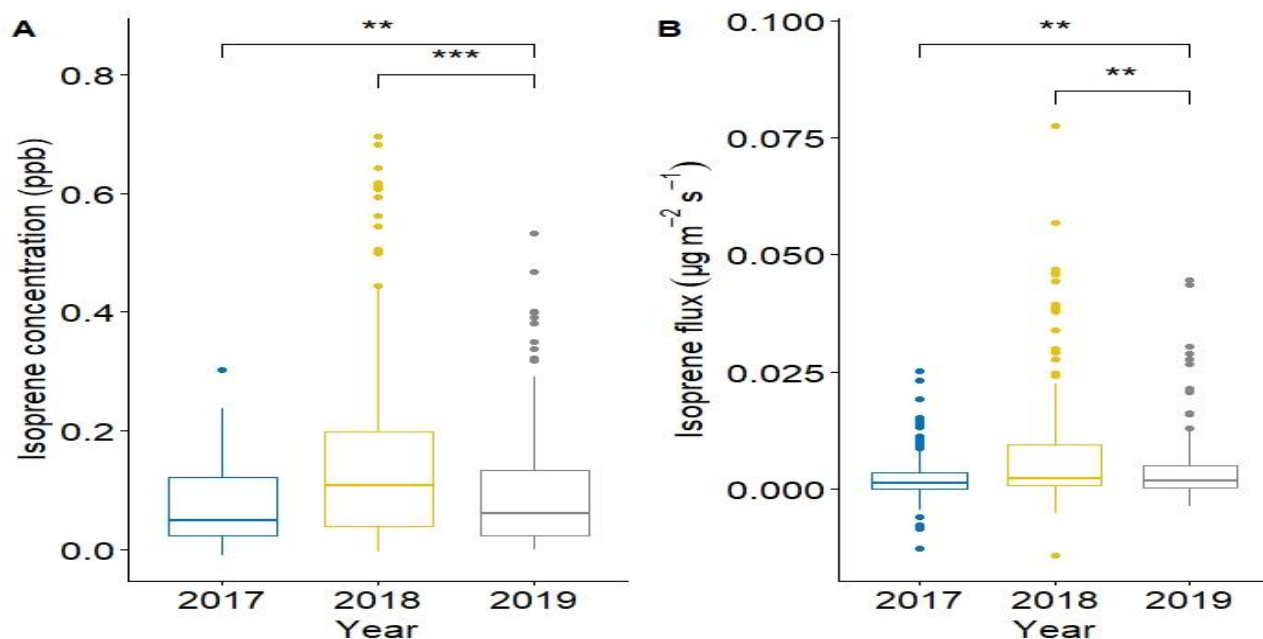


Figure 5. Pairwise test of daily median values of isoprene (A) concentration and (B) fluxes during spring and summer (March-August) 2017 and 2018 against the same period in 2019. Significant differences between 2019 and other years are denoted by an asterisk (t test). For explanations on the boxes and whiskers, see Fig 3.

The trend for both concentrations and fluxes in methanol seems to be different from other compounds studied so far. As can be seen from Figure 6, methanol concentrations and fluxes are clearly higher in 2019 than 2017. However, here, unlike the previous BVOCs, the concentrations and fluxes in 2018

are not higher than the two other years consistently. For example, concentrations during March and June seem to be higher in 2019 compared to 2018. Nevertheless, in general both concentrations and fluxes are comparably higher in 2018, following the same pattern as the previous BVOCs. To test this, however, we need to perform statistical analysis.

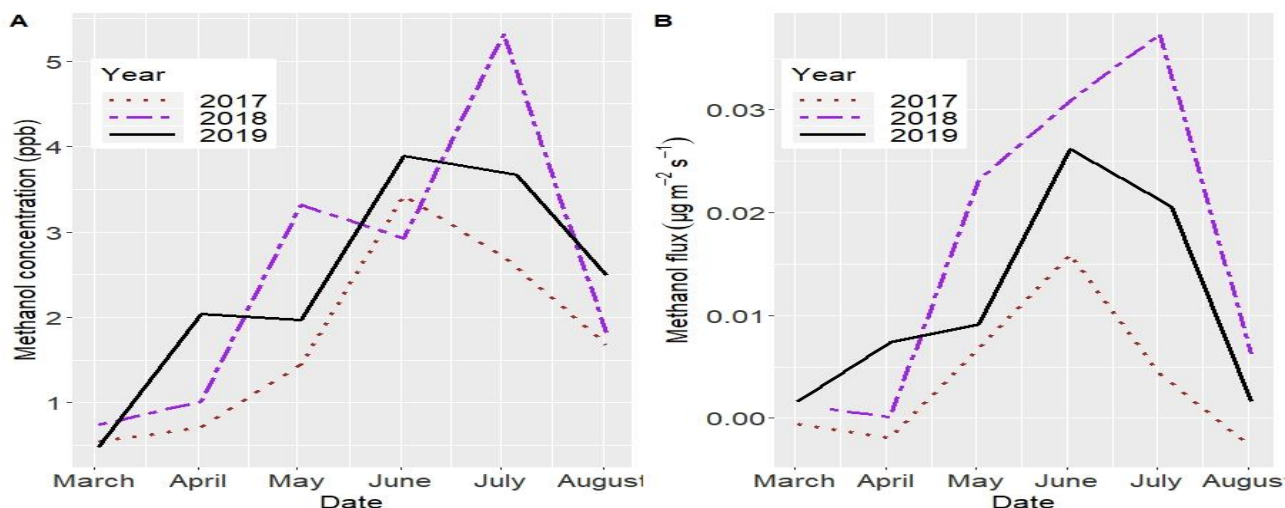


Figure 6. Monthly median methanol (A) concentrations and (B) fluxes during spring and summer 2017 – 2019.

Figure 7 shows that even though both concentrations and fluxes are slightly higher in 2018 compared with 2019, the difference is not statically significant. However, both concentrations and fluxes are higher in 2019 compared with 2017, and the difference is statically significant. The difference is more significant for the concentrations than for the fluxes.

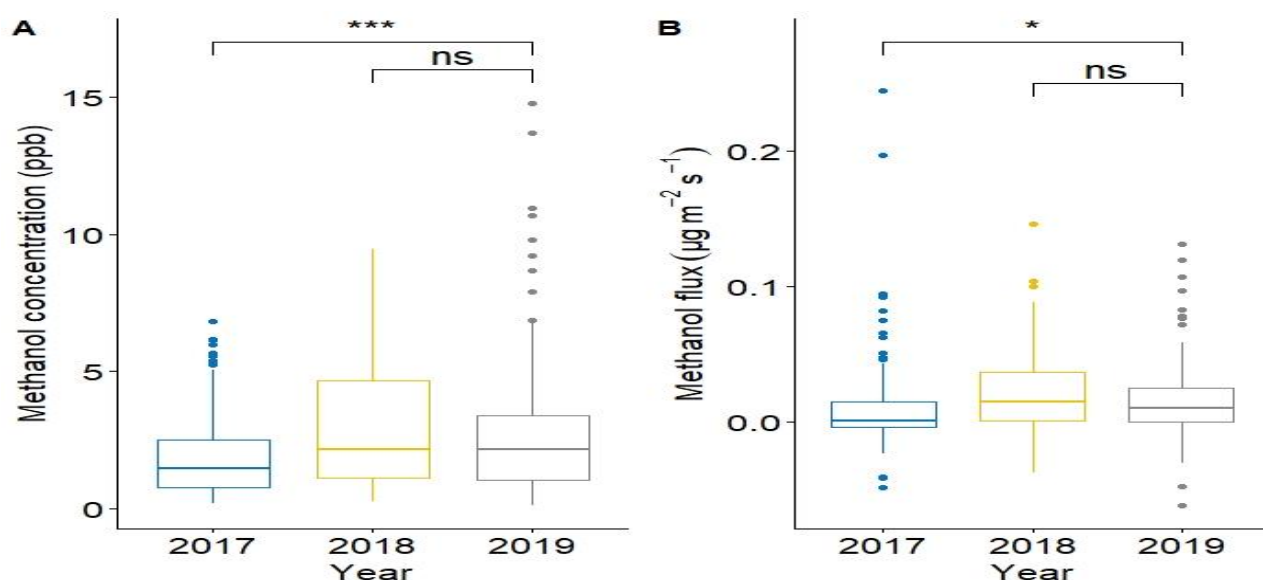


Figure 7. Pairwise test of daily median values of methanol (A) concentration and (B) fluxes during spring and summer (March-August) 2017 and 2018 against the same period in 2019. Significant differences between 2019 and other years are denoted by an asterisk (t test); ns, not significant. For explanations on the boxes and whiskers, see Fig 3.



Concentrations and fluxes of acetone resemble more those of methanol (see Figure 8). Though generally they are higher in 2018, the trend is not consistent, and this is particularly visible for fluxes (Fig. 8B).

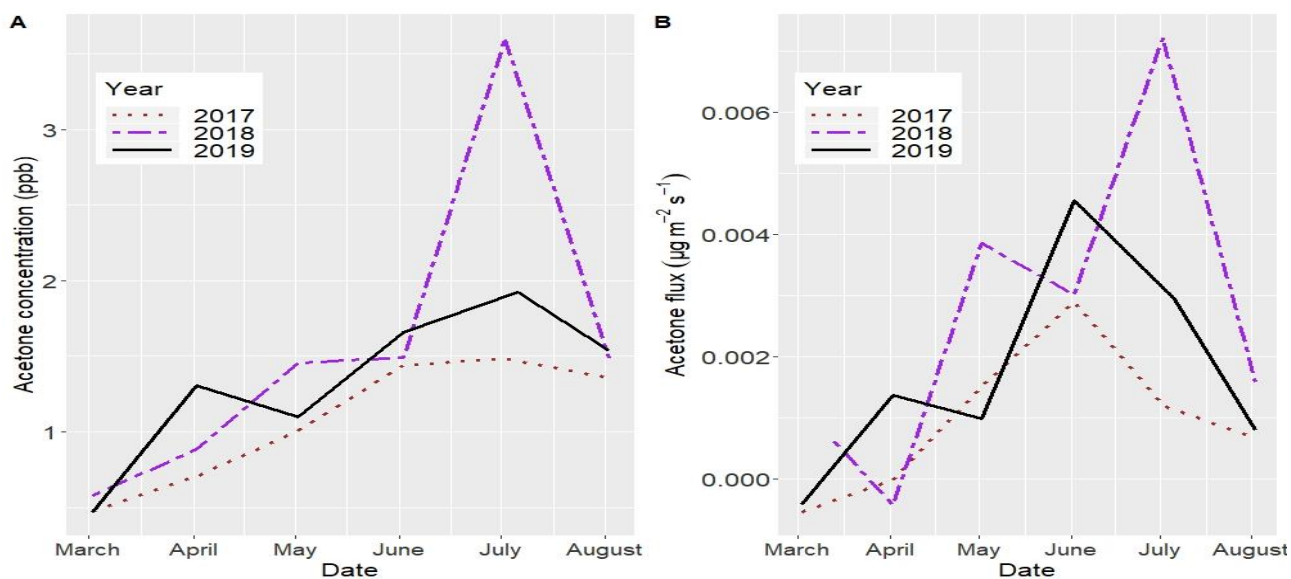


Figure 8. Monthly median acetone (A) concentrations and (B) fluxes during spring and summer 2017 – 2019.

Figure 9A demonstrates that acetone concentrations in 2019 are lower than 2018 but higher than 2017, both being statistically significant. With regards to the fluxes (Fig. 9B), the same relationship between 2019 and 2018 holds; however, the difference between the fluxes in 2019 and 2017 is not statistically significant, though they are slightly higher.

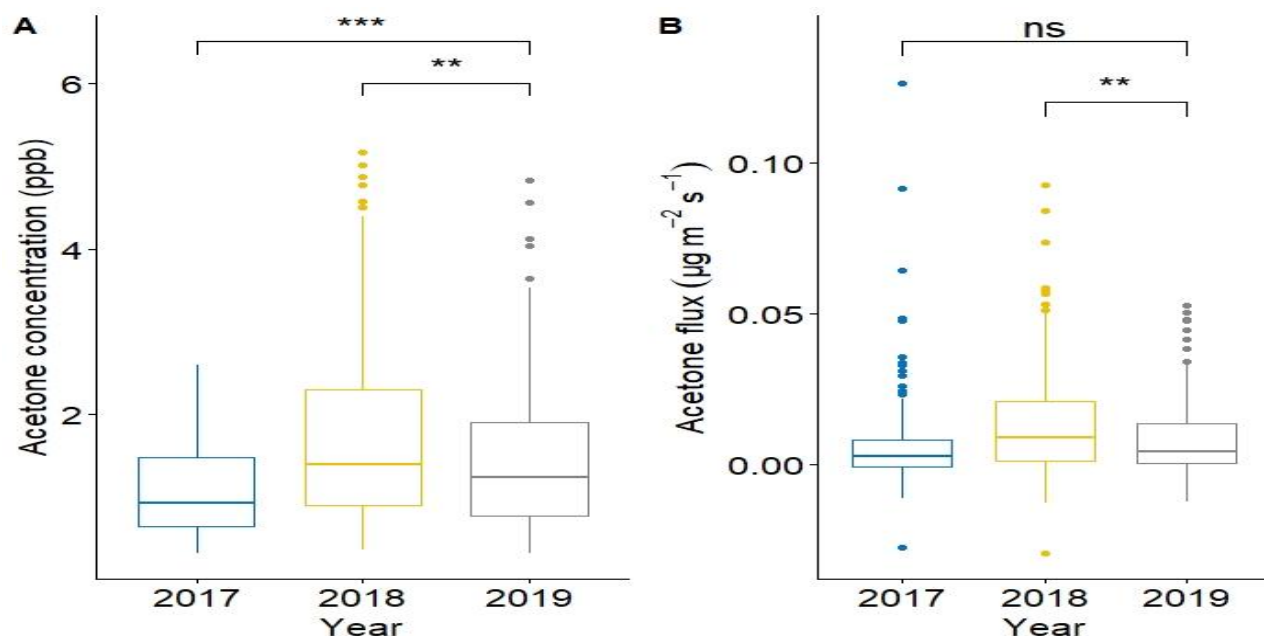


Figure 9. Pairwise test of daily median values of acetone (A) concentration and (B) fluxes during spring and summer (March-August) 2017 and 2018 against the same period in 2019. Significant differences between 2019



and the other years are denoted by an asterisk (t test); ns, not significant. For explanations on the boxes and whiskers, see Fig 3.

Generally, when comparing 2019 with 2018, monoterpene, isoprene and acetone concentrations and fluxes are lower, with the results being even statistically significant. When comparing 2019 with 2017, the results are inconsistent for different compounds: For monoterpenes, no statistically meaningful difference can be observed between 2019 and 2017; for isoprene, the concentrations and fluxes are higher in 2019 than 2017, and for acetone only concentrations are higher in 2019 than 2017. Considering only these results, one may conclude that sub-canopy removal increased concentrations and fluxes of monoterpenes, isoprene, methanol, and acetone in 2019 compared to 2017. However, in most cases, the concentrations and fluxes in 2019 were lower than 2018. Nonetheless, without analysing other environmental variables that explain BVOC emission rates, reaching any conclusions would be inconclusive. Therefore, I next examine how these variables have influenced the concentrations and fluxes.

#### **4.3. Effects of soil moisture, PAR, and temperature**

Before analysing the effects of soil moisture, PAR, and temperature on BVOC concentrations and fluxes, it is informative to examine how these variables change over the three years. Figure 10 shows the summer daily (including nighttime) median values, comparing the years on these environmental variables. The Figure reveals that in June 2019 temperature is higher than June 2017 and 2018, while during July and August, we can observe higher temperature in 2018 compared to the same months in 2017 and 2019. PAR follows the same trend as temperature, except for August, in which it is higher in 2019 than in the other years. The most noticeable differences come from SMI, which is clearly higher for 2017 than the other years.

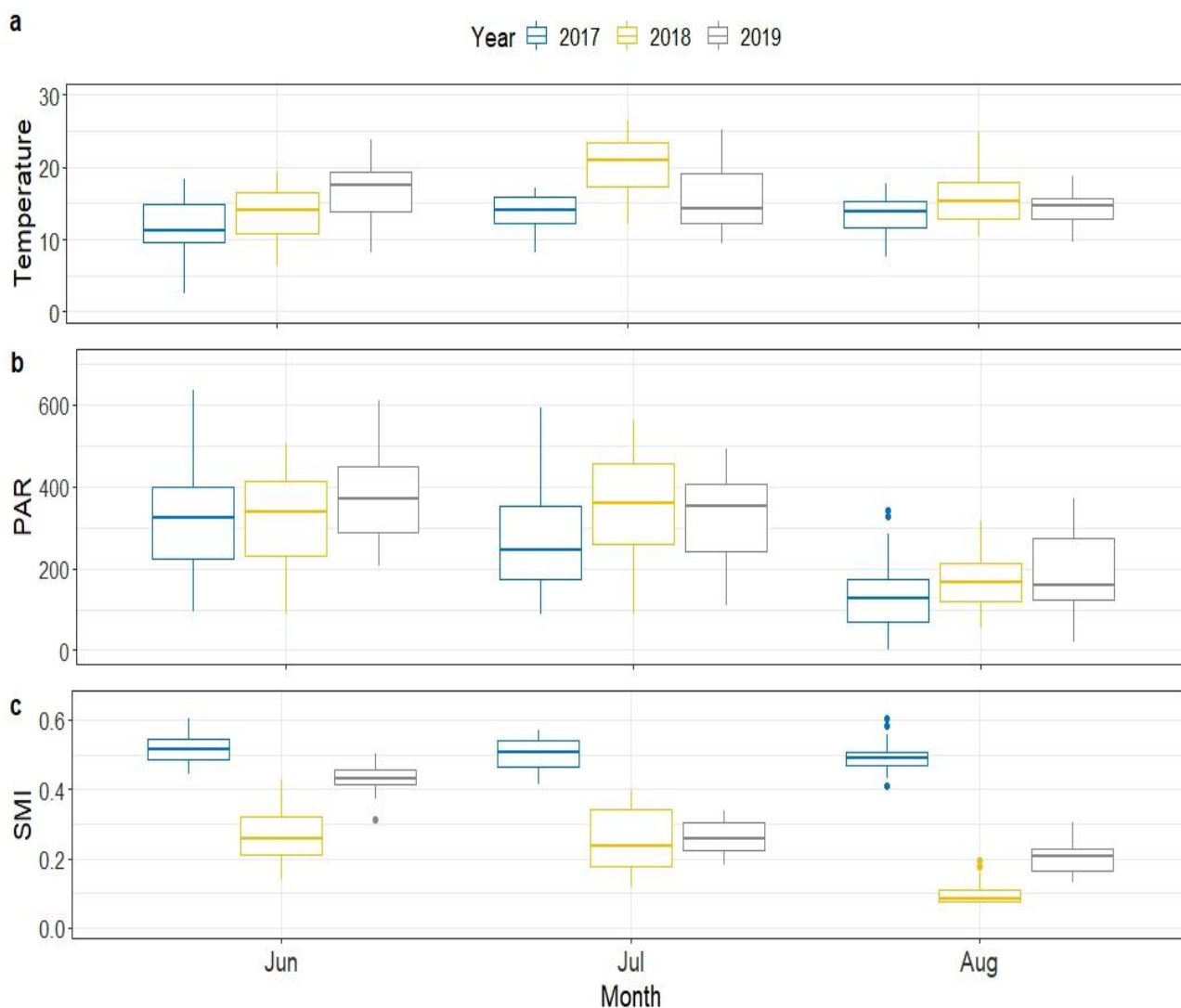


Figure 10. Daily median values of SMI, PAR, and temperature during summer 2017, 2018 and 2019. The unit for SMI is  $\text{m}^3\text{m}^{-3}$ , for PAR is  $\mu\text{mol m}^{-2}\text{s}^{-1}$ , and for temperature is  $^{\circ}\text{C}$ .

#### 4.3.1. Soil moisture index and BVOCs

Figure 11 shows that relationship between SMI and the BVOC concentrations and fluxes<sup>2</sup>. It is worthwhile to note that the relationship is negative for all BVOCs, and insignificant for most. For isoprene concentrations and fluxes, however, this relationship is relatively strong and statistically significant (see Fig. 11C and D). As soil moisture increases, isoprene concentrations and fluxes decrease. This is also the case for monoterpene fluxes (Fig. 11B) and acetone concentrations (Fig.

<sup>2</sup> Due to large missing data on soil moisture during most of spring 2018, here I chose to analyze only summer time. When considering the effect of sub-canopy removal, as the removal continued through the summer 2019, looking at the data only during summer should not be a problem.

11G). The negative relationship may be due to the effects of other variables such as air temperature. Particularly in boreal forests, when soil moisture gets high, air temperature may decrease.

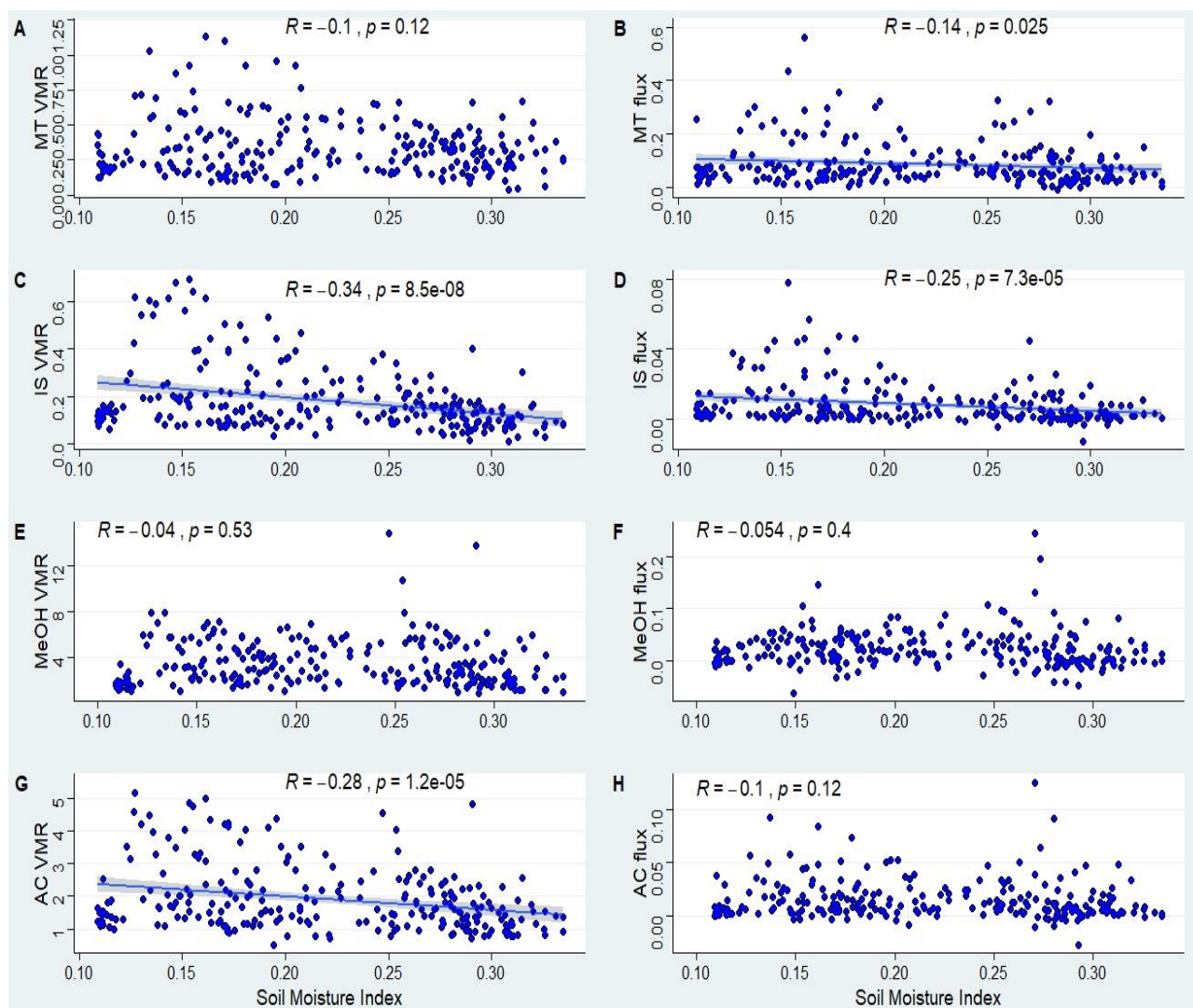


Figure 11. Daily median concentrations and fluxes of BVOCs during summer (June-August) 2017, 2018 and 2019 in relation to daily median SMI. The left panel shows concentrations, and the right shows fluxes. Unit for concentrations is parts per billion and for fluxes is  $\mu\text{g m}^{-2}\text{s}^{-1}$ . Unit for SMI is  $\text{m}^3\text{m}^{-3}$ . Where the relationship is significant, linear fit is displayed. MT, monoterpenes; IS, isoprene; MeOH, methanol; AC, acetone. VMR, volume mixing ratio.  $R$ , correlation coefficient;  $p$ , P-value; method: Pearson.

### 4.3.2. Temperature and BVOCs

Figure 12 shows that the relationship between temperature and BVOC concentrations and fluxes is exponential. While this is less visible in the case of methanol fluxes (Fig. 12F), for other BVOCs, the exponential relationship clearly holds. Previous research (e.g., Filella et al., 2007; Laothawornkitkul et al., 2009) confirms these results. Temperature affects BVOC emission rates exponentially, as it enhances the enzymatic activities of synthesis, increases the BVOCs vapour pressure and volatility, and reduces the resistance of the diffusion pathway (Peneulas & Staudt. 2010; Tingey et al., 1991).

The exponential relationship between temperature and BVOC emissions is more visible at ecosystems in cold biomes such as boreal forests than southern latitudes whereby water, compared to energy, is a more limited resource (Llusia et al., 2008; Peneulas & Staudt, 2010; Tiiva, et al., 2008). Figure 12 confirms this.

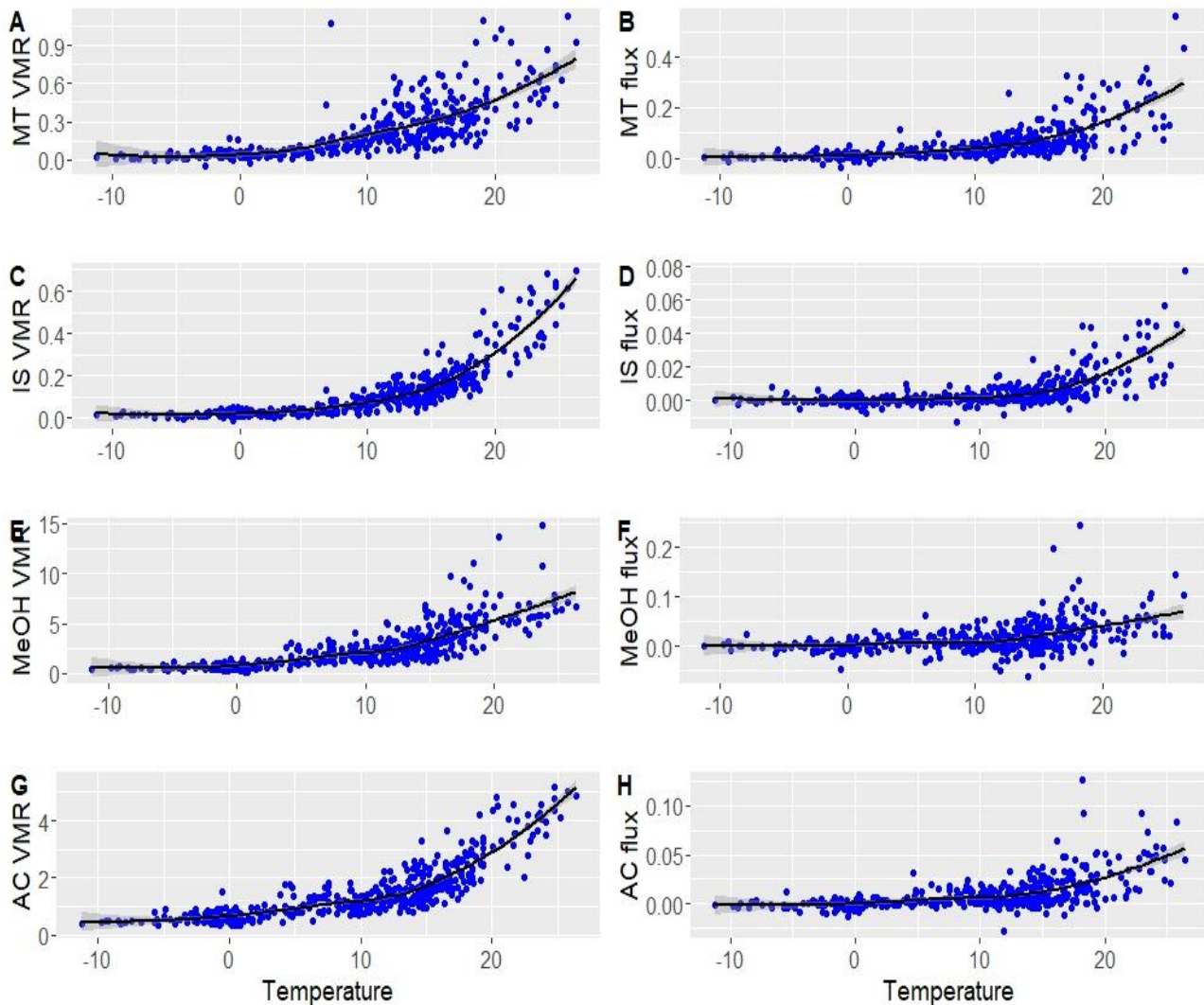


Figure 12. Daily median concentrations and fluxes of BVOCs during spring and summer (March-August) 2017, 2018 and 2019 in relation to temperature. The left panel shows concentrations, and the right shows fluxes. Unit for concentrations and fluxes is parts per billion and  $\mu\text{g m}^{-2}\text{s}^{-1}$ , respectively. Unit for temperature is  $^{\circ}\text{C}$ . The line shows fit between the two variables; method: loess. For the abbreviation, see Fig 11.

#### 4.3.3. PAR and BVOCs

Though not as visible as the exponential effect of temperature, PAR has a saturating effect on BVOC concentrations and fluxes (see Fig. 13). For most BVOCs, at PAR lower than  $200 \mu\text{mol m}^{-2}\text{s}^{-1}$ , we can detect linear relationship; however, as PAR rises, the concentrations and fluxes remain relatively constant. These results are confirmed by previous research (e.g., Staudt & Lhoutellier, 2011). The emission rates of some BVOCs, particularly those not stored in specialized storage compartments

(e.g., resin ducts in *Pinus* and *Abies*), depend on the photon flux density, and hence light (Laothawornkitkul et al., 2009).

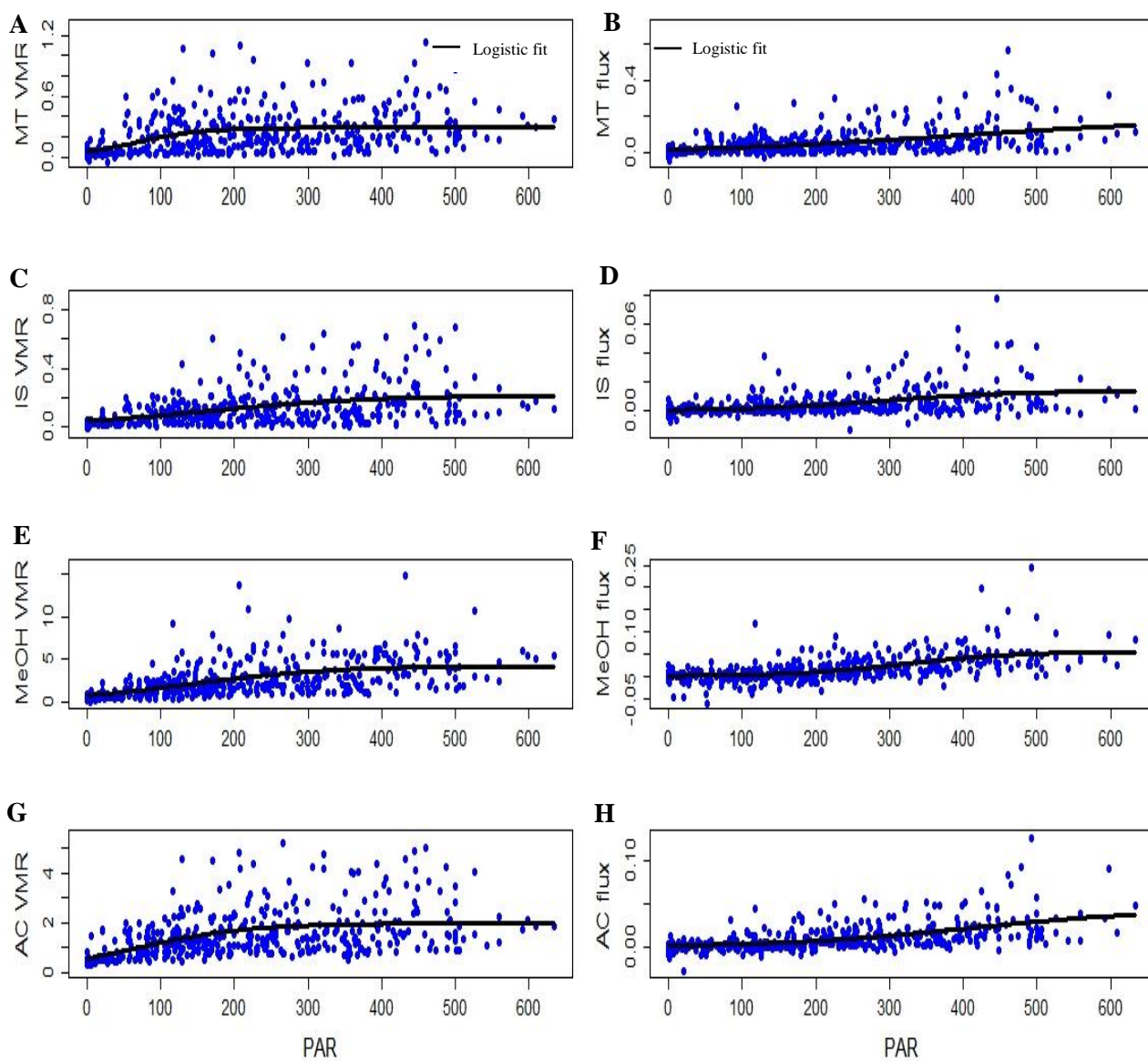


Figure 13. Daily median concentrations and fluxes of BVOCs during spring and summer (March-August) 2017, 2018 and 2019 in relation to PAR. The left panel shows concentrations, and the right shows fluxes. Unit for concentrations and fluxes is parts per billion and  $\mu\text{g m}^{-2}\text{s}^{-1}$ , respectively. Unit for PAR is  $\mu\text{mol m}^{-2}\text{s}^{-1}$ . For the abbreviation, see Fig 11. The line shows fit between the two variables; method: logistic growth. For the abbreviation, see Fig 11.

#### 4.3.4. Combined effect of temperature and soil moisture

In this section, I examine the combined effect of soil moisture and temperature on BVOC concentrations and fluxes during summer 2017, 2018 and 2019. Table 3 demonstrates the results. Temperature positively affects the concentrations and fluxes of all BVOCs, whereas soil moisture is significant—and positive—in monoterpenes and methanol concentrations as well as acetone fluxes.



It does not affect other compounds when combined with temperature. Figure 14 visualizes the results shown in Table 3, with monoterpenes and methanol as examples.

Table 3. Multiple regression analysis on the relationship between daily median values of BVOCs, temperature and soil moisture during summer (June-August) 2017, 2018 and 2019. Values in parenthesis indicate standard errors. For the abbreviations, see Fig 11.

	(Intercept)	Temperature	SMI	R <sup>2</sup>
MT VMR	-0.18*** (0.05)	0.03*** (0.00)	0.17* (0.07)	0.39
MT flux	-0.12 *** (0.02)	0.01 *** (0.00)	0.05 (0.03)	0.41
IS VMR	-0.19 *** (0.03)	0.03 *** (0.00)	-0.04 (0.03)	0.68
IS flux	-0.02 *** (0.00)	0.00 *** (0.00)	-0.00 (0.00)	0.43
MeOH VMR	-3.31 *** (0.44)	0.38 *** (0.02)	3.22 *** (0.59)	0.57
MeOH flux	-0.04 *** (0.01)	0.00 *** (0.00)	0.02 (0.01)	0.18
AC VMR	-1.11 *** (0.18)	0.20 *** (0.01)	0.19 (0.24)	0.71
AC flux	-0.03 *** (0.01)	0.00 *** (0.00)	0.01 * (0.01)	0.32

\*\*\* p < 0.001; \*\*p<0.01; \*p<0.05. N = 243

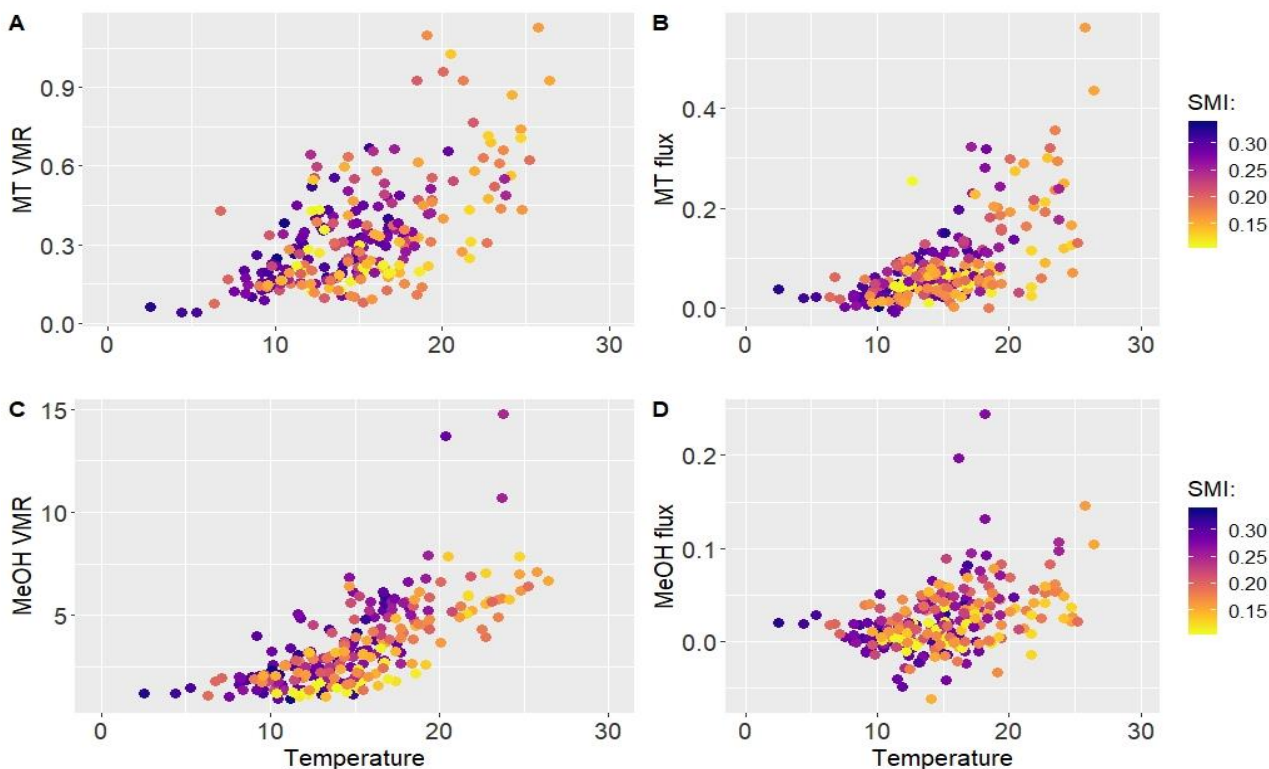


Figure 14. Effect of daily median values of temperature and SMI on monoterpenes and methanol during summer 2017, 2018 and 2019. The left panel shows concentrations, and the right shows fluxes. Unit for concentrations and fluxes is parts per billion and  $\mu\text{g m}^{-2}\text{s}^{-1}$ , respectively. Unit for temperature is  $^{\circ}\text{C}$ , and for SMI is  $\text{m}^3\text{m}^{-3}$ . For the abbreviations, see Fig. 11.

#### 4.3.5. Combined effect of PAR and soil moisture

As can be seen from Table 4, soil moisture has a negative relationship with fluxes and concentrations when combined with PAR. As regards to SMI, these results are highly similar to when it was considered individually, whereby it affected the concentrations and fluxes negatively. The results here are in contrast to when SMI was combined with temperature, wherein SMI had positive effects on the concentrations and fluxes for most compounds. How PAR affects BVOCs when combined with SMI is also similar to when PAR was considered individually; PAR positively affects both fluxes and concentrations in all BVOCs, and is statistically significant. Figure 15 visualizes the results presented in Table 4, with monoterpenes and methanol as examples.

Table 4. Multiple regression analysis on the relationship between daily median values of BVOCs, PAR and soil moisture during summer (June-August) 2017, 2018 and 2019. Values in parenthesis indicate standard errors. For the abbreviations, see Fig 11.

	(Intercept)	PAR	SMI	R <sup>2</sup>
MT VMR	0.32 *** (0.04)	0.00 * (0.00)	-0.14 (0.08)	0.03
MT flux	0.05 *** (0.01)	0.00 *** (0.00)	-0.09 ** (0.03)	0.17

IS VMR	0.20 *** (0.02)	0.00 *** (0.00)	-0.31 *** (0.05)	0.20
IS flux	0.01 ** (0.00)	0.00 *** (0.00)	-0.02 *** (0.00)	0.19
MeOH VMR	1.96 *** (0.35)	0.01 *** (0.00)	-0.86 (0.75)	0.20
MeOH flux	-0.01 * (0.01)	0.00 *** (0.00)	-0.02 (0.01)	0.37
AC VMR	2.01 *** (0.18)	0.00 *** (0.00)	-1.85 *** (0.38)	0.15
AC flux	0.00 (0.00)	0.00 *** (0.00)	-0.02 * (0.01)	0.30

\*\*\*  $p < 0.001$ ; \*\*  $p < 0.01$ ; \*  $p < 0.05$ . N = 243

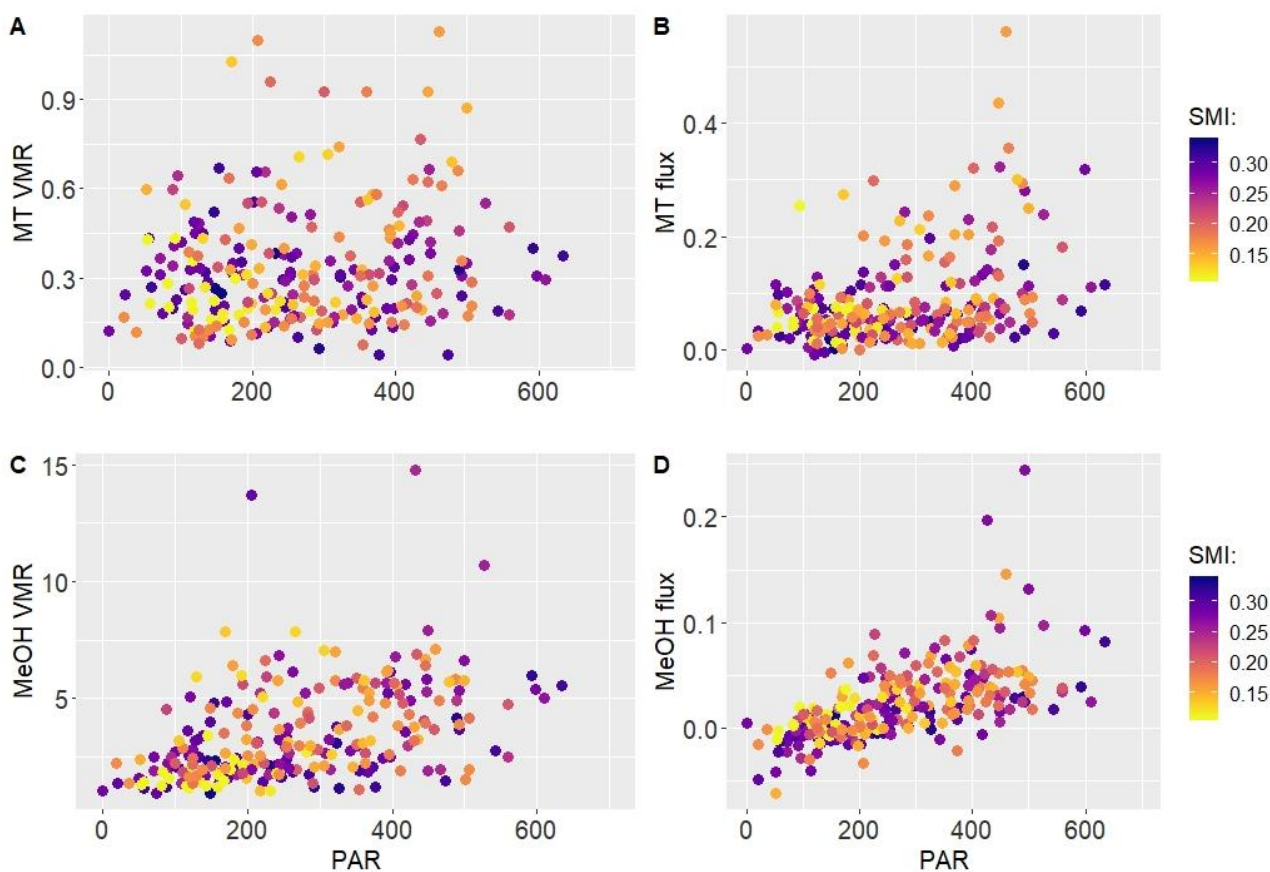


Figure 15. Effect of daily median values of PAR and SMI on monoterpenes and methanol during summer 2017, 2018 and 2019. The left panel shows concentrations, and the right shows fluxes. Unit for concentrations and fluxes is parts per billion and  $\mu\text{g m}^{-2}\text{s}^{-1}$ , respectively. Unit for PAR is  $\mu\text{mol m}^{-2}\text{s}^{-1}$ , and for SMI is  $\text{m}^3\text{m}^{-3}$ . For the axes abbreviations, see Fig 11.



### 4.3.6. Combined effect of temperature, soil moisture and PAR

A logical step forward is to look at the combined effect of all these variables on the concentrations and fluxes. Table 5 reveals the results, according to which temperature has the strongest effect on both concentrations and fluxes, being statistically significant in all the models. Unsurprisingly, PAR has the same effect as temperature in most cases, with the monoterpene and acetone concentrations as exceptions, in which cases PAR negatively affects the concentrations. Soil moisture does not have any strong effect on the concentrations and fluxes except for monoterpene and methanol concentrations. Generally, the results indicate that temperature plays a major role in BVOC concentrations and fluxes both when considering its individual effect and when combining it with other variables. Therefore, it is reasonable to remove the effect of temperature on emission. The common approach to do so is to normalize temperature, which allows one to estimate the emission potential of BVOCs at a standard temperature, as explained in Guenther et al. (1993; 1995).

Table 5. Multiple regression analysis on the relationship between daily median values of BVOCs, SMI, PAR and temperature during summer (June-August) 2017, 2018 and 2019. Values in parenthesis indicate standard errors. For the abbreviations, see Fig 11.

	(Intercept)	SMI	PAR	Temperature	R <sup>2</sup>
MT VMR	-0.18 *** (0.05)	0.21 ** (0.07)	-0.00 * (0.00)	0.03 *** (0.00)	0.40
MT flux	-0.12 *** (0.02)	0.03 (0.03)	0.00 * (0.00)	0.01 *** (0.00)	0.43
IS VMR	-0.19 *** (0.03)	-0.03 (0.03)	-0.00 (0.00)	0.03 *** (0.00)	0.68
IS flux	-0.02 *** (0.00)	-0.00 (0.00)	0.00 * (0.00)	0.00 *** (0.00)	0.44
MeOH VMR	-3.28 *** (0.43)	2.78 *** (0.59)	0.00 *** (0.00)	0.35 *** (0.02)	0.59
MeOH flux	-0.04 *** (0.01)	-0.00 (0.01)	0.00 *** (0.00)	0.00 *** (0.00)	0.40
AC VMR	-1.12 *** (0.18)	0.32 (0.24)	-0.00 * (0.00)	0.21 *** (0.01)	0.71
AC flux	-0.03 *** (0.00)	0.00 (0.01)	0.00 *** (0.00)	0.00 *** (0.00)	0.43

\*\*\* p < 0.001; \*\* p < 0.01; \* p < 0.05. N = 243

### 4.3.7. Temperature normalized fluxes

Figure 16 shows monthly median values of the temperature normalized emission rates of the BVOCs (the left panel) in comparison to the same values of the measured emission rates (the right panel). As expected, temperature normalized emission rates are higher than measured emission rates. Generally,

the normalized emission rates vary less between the years compared with measured emission rates. However, there are still some visible differences in normalized emission rates.

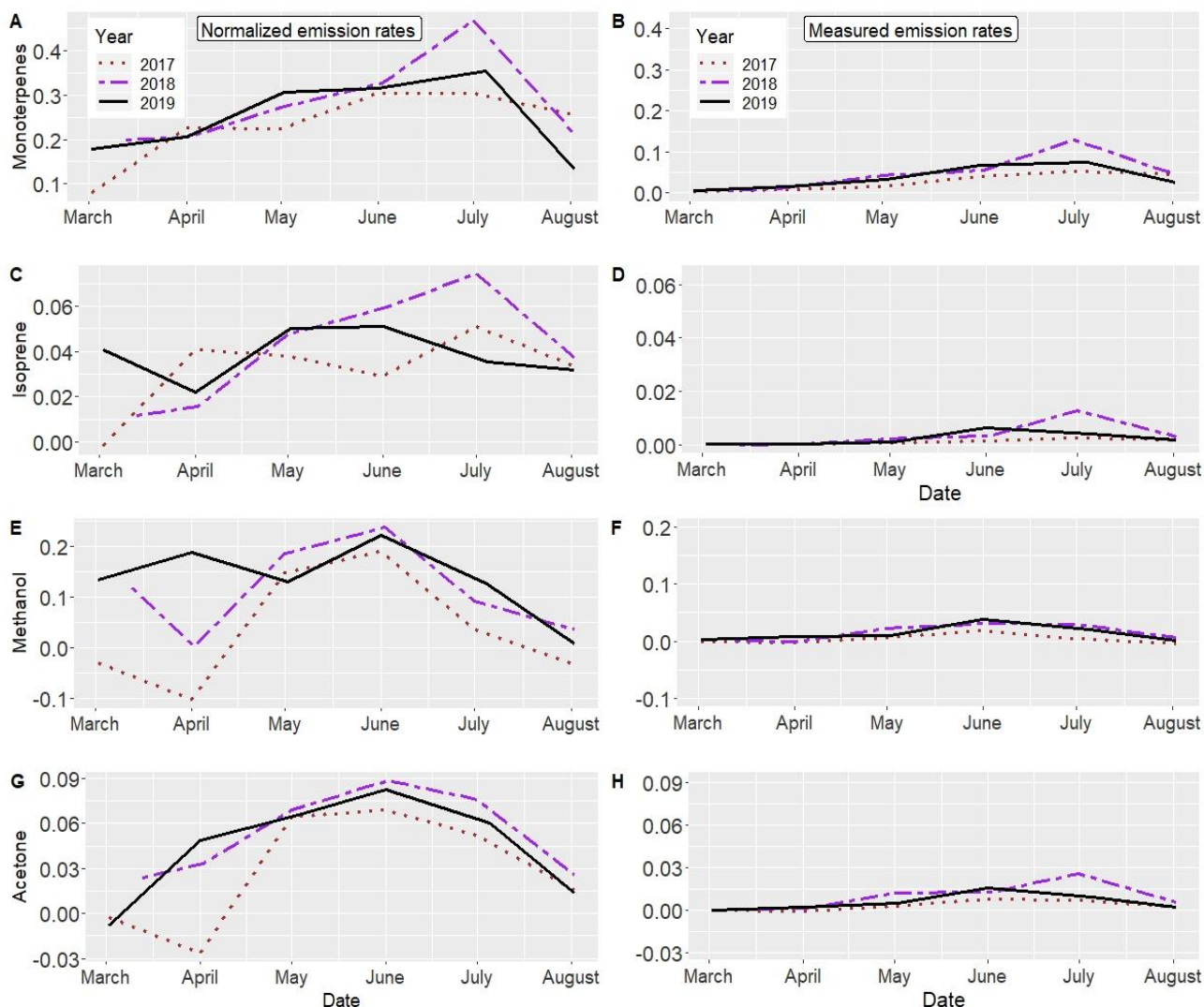


Figure 16. Monthly median BVOC emission rates during spring and summer 2017-2019. The left panel shows temperature normalized emission rates (emission potential), and the right shows measured emission rates. Unit for emission rates is  $\mu\text{g m}^{-2}\text{s}^{-1}$ .

To understand whether the BVOC concentrations and fluxes during 2019 differ from the other years when temperature is normalized, I compare the daily median values of the temperature normalized BVOCs in 2019 with similar values in 2018 and 2017. Figure 17 shows the results. In comparison to Figure 3, 5, 7 and 9 in section 4.2, in which yearly differences are visible, Figure 17 reveals that when emission rates are temperature normalized, there is no significant difference between the years. The only exception is methanol emission rates, in which case 2019 has higher emission rates than 2017, albeit with weakly significant difference ( $p < 0.05$ ).

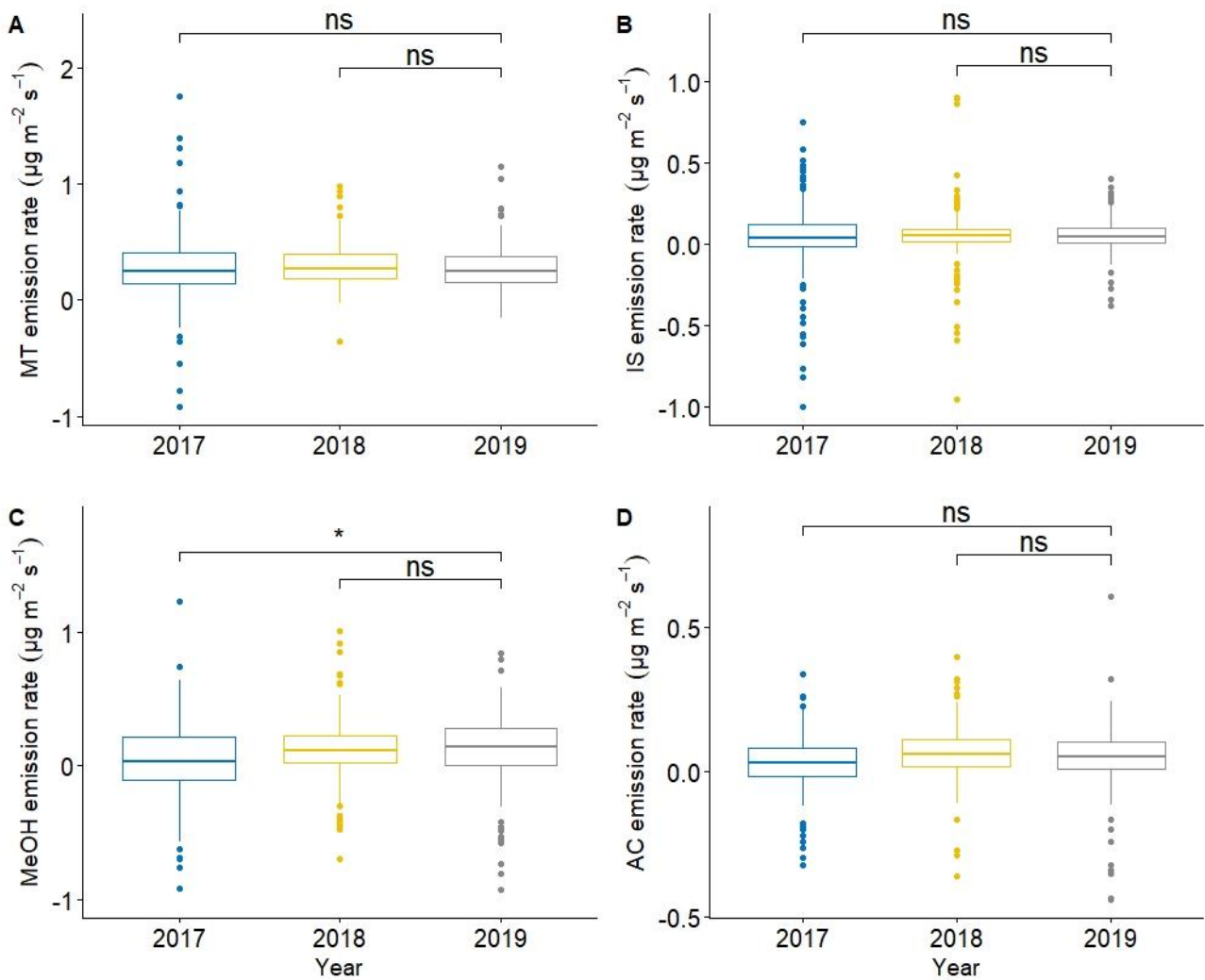


Figure 17. Pairwise test of daily median values of temperature normalized BVOC emission rates during spring and summer (March-August) 2017 and 2018 against the same period in 2019. Significant differences between 2019 and other years are denoted by asterisks (t test); \*\*\*  $p < 0.001$ ; \*\*  $p < 0.01$ ; \*  $p < 0.05$ .; ns, not significant. For explanations on the boxes and whiskers, see Fig 3. For the axes abbreviations, see Fig 11.

### 4.3. BVOC concentrations and fluxes during the night

At night, compared to daytime, the atmosphere is more stable and turbulence is lower and sporadic (Velasco et al., 2008). Therefore, BVOCs tend to accumulate during the night within the canopy, which are then released to the air in the early morning (Genzeveld et al., 2008). Thus, in forests, BVOC concentrations tend to be higher during the night. Due to the differences between BVOC concentrations and fluxes during daytime and nighttime, it deems important to look at nighttime values, too. To examine nighttime concentrations and fluxes, I choose PAR values equal or lower than  $2 \mu\text{mol m}^{-2} \text{s}^{-1}$ . Figure 18 shows the results regarding monoterpenes and isoprene, and Figure 18 regarding methanol and acetone.

Figure 18A and B show monoterpene concentrations and fluxes, respectively. As expected, the monthly changes of the concentrations and fluxes during the nights are similar to the daily values, beginning to rise in early spring until they reach a peak during July, henceforth they start decreasing. Since monoterpenes are stored in specialized compartments—for example, resin ducts in *Pinus* plants—their emissions are less coupled to incident light intensity and air temperature (Laothawornkitkul et al., 2009). Hence, the concentrations and fluxes of monoterpenes remain high during the night, too. Similar to monoterpenes, the concentrations of isoprene are relatively high at night, which can be attributed to the night lower turbulence (see Figure 18C). However, in contrast to monoterpene concentrations, Figure 18D shows that fluxes of isoprene are marginal at night, as isoprene is not stored in specialized storage compartments, and therefore its emission rate is strongly dependent on temperature and light (Laothawornkitkul et al., 2009).

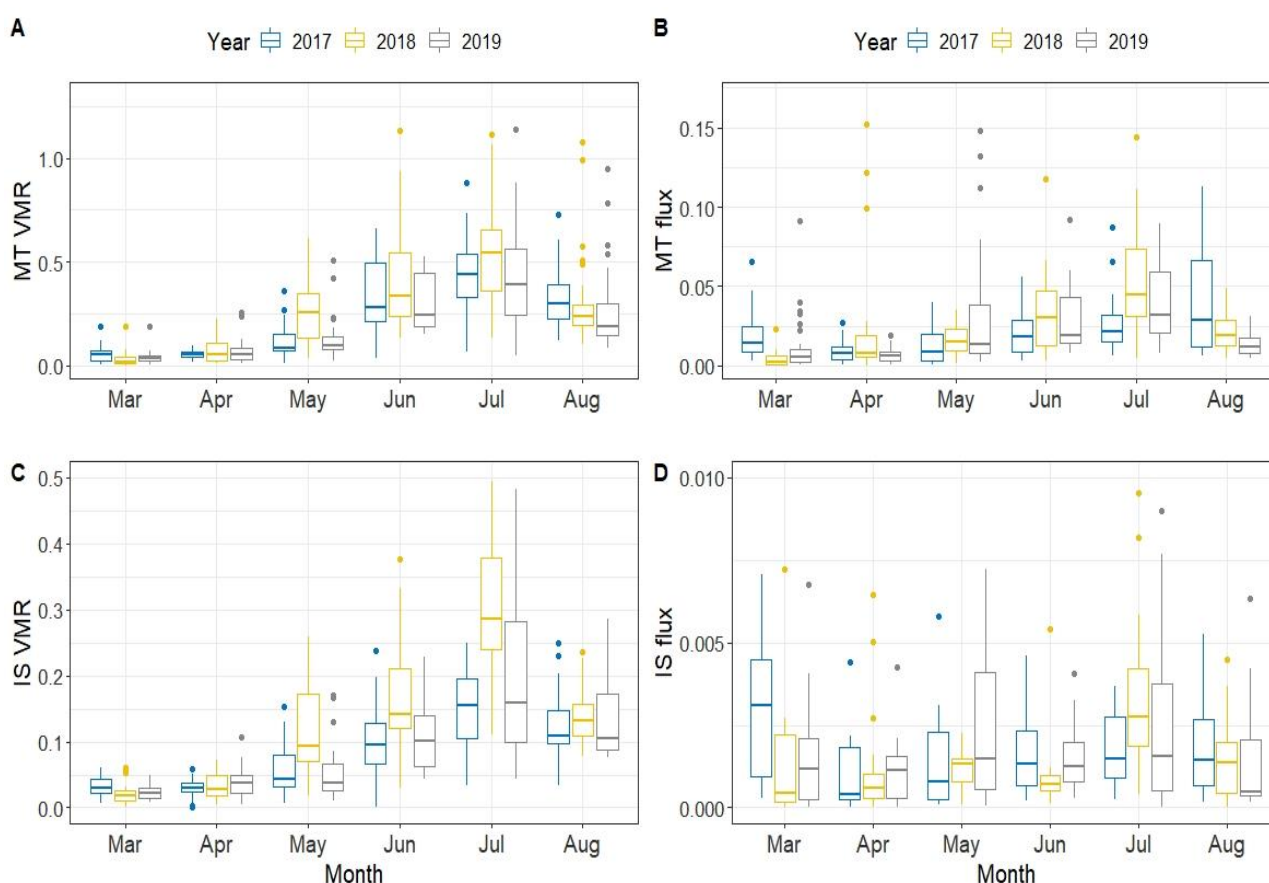


Figure 18. Median nighttime values of monoterpenes and isoprene concentration and flux during spring and summer 2017, 2018 and 2019. The left panel shows concentrations, and the right shows fluxes. Unit for concentrations and fluxes is parts per billion and  $\mu\text{g m}^{-2}\text{s}^{-1}$ , respectively. For the abbreviations, see Fig 11.

Figure 19A and 19C show that both methanol and acetone concentrations remain relatively high during the night, resembling the night concentrations of monoterpenes and isoprene (Fig. 18A and C). Yet, similar to isoprene, methanol and acetone fluxes are low at night as can be seen from Figure

19B and D. Methanol and acetone, in contrast to monoterpenes and isoprene, are water-soluble compounds, the emissions of which could be regulated by stomatal conductance (Harley et al., 2007; Rissanen et al., 2018). Because of low stomata conductance during the night, these water soluble compounds are accumulated at night, and released as the stomata open in the morning (Folkers et al., 2008; Rissanen et al., 2018). Therefore, fluxes of methanol and acetone are considerably lower at night than during the day.

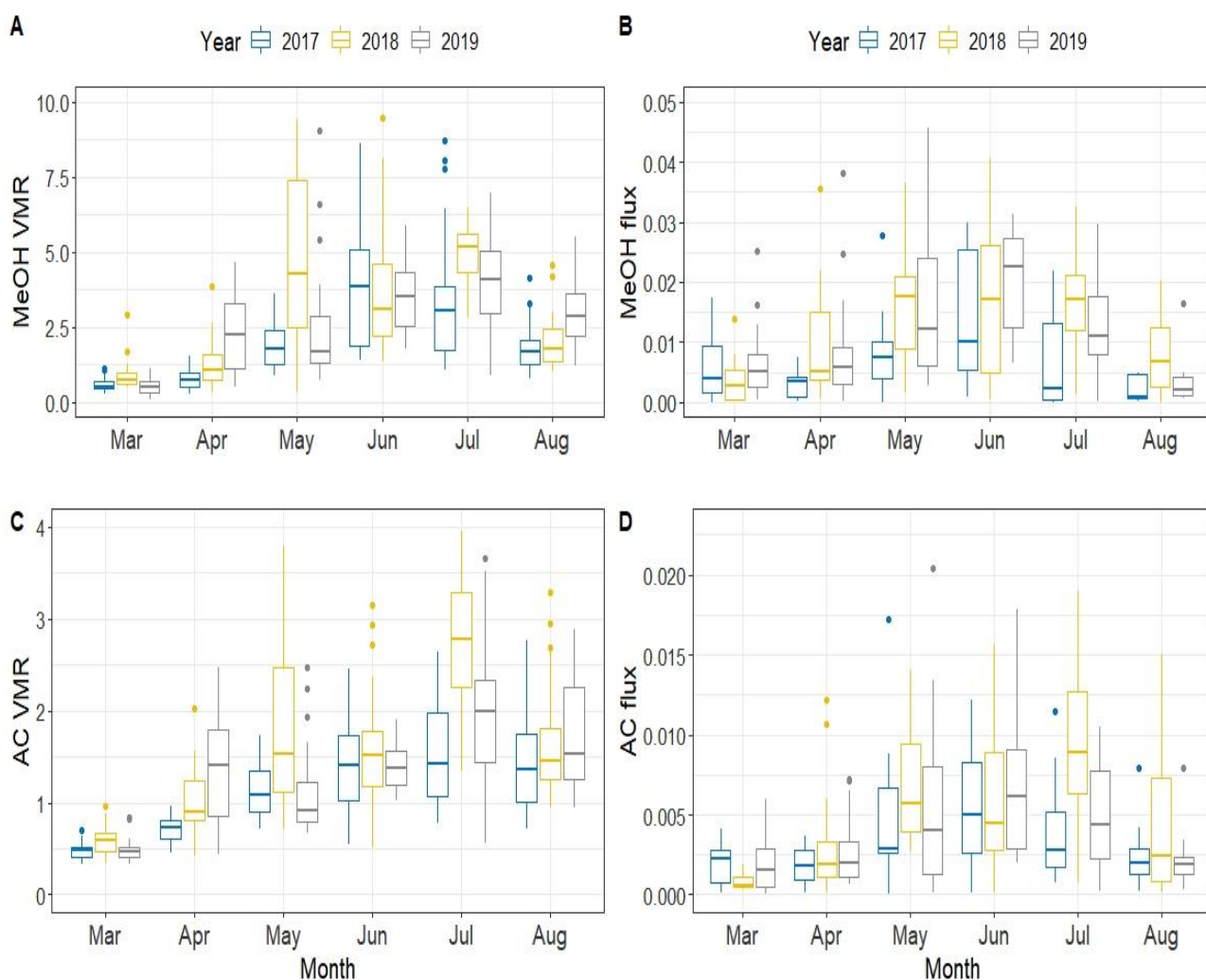


Figure 19. Nighttime median values of methanol and acetone concentrations and fluxes during spring and summer 2017, 2018 and 2019. The left panel shows concentrations, and the right shows fluxes. Unit for concentrations and fluxes is parts per billion and  $\mu\text{g m}^{-2}\text{s}^{-1}$ , respectively. For the abbreviations, see Fig 11.

Figure 20 shows the differences between the nighttime concentrations and fluxes in 2019 with 2017 and 2018 during spring and summer for monoterpenes and isoprene. Compared with daily median values (see section 4.2) examined earlier, the differences here are mainly statistically insignificant. Only in 2018, the concentrations—but not fluxes—of monoterpenes and isoprene are higher than

2019, while being statistically significant, too. However, nor for the concentrations, neither for the fluxes, there is no difference between 2019 and 2017.

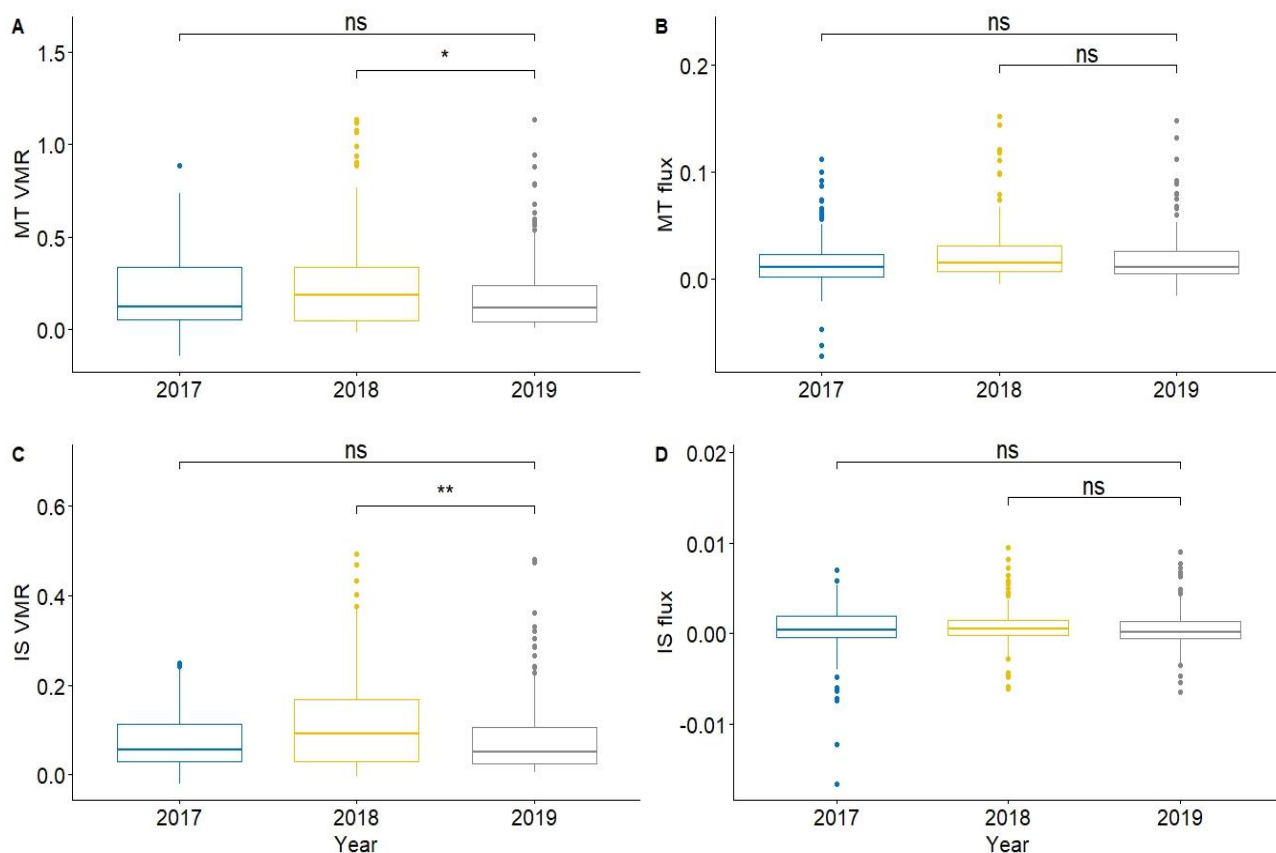


Figure 20. Pairwise test of nighttime median values of monoterpenes and isoprene during spring and summer (March-August) 2017 and 2018 against the same period in 2019. The left panel shows concentrations, and the right shows fluxes. Unit for concentrations and fluxes is parts per billion and  $\mu\text{g m}^{-2}\text{s}^{-1}$ , respectively. Significant differences between 2019 and other years are denoted by an asterisk (t test). For explanations on the boxes and whiskers, see Fig 3, and for the abbreviations, see Fig. 11.

Figure 21A and B reveal the differences of the night-time concentrations and fluxes of methanol in 2019 with 2017 and 2018 during spring and summer. Whereas there is no difference between 2019 and 2018, both the concentrations and fluxes in 2019 are higher than 2017. In regard with acetone, the concentrations follow the same pattern as methanol concentrations; in 2019 they are higher than in 2017, and this is statistically significant, while there is no difference between concentrations in 2019 and those in 2018 (see Fig. 21C). Concerning the acetone fluxes, Figure 21D shows that there is no significant difference between 2019 and 2017, whereas fluxes in 2018 are higher than 2019, being statistically significant, too. Additionally, it is worth noting that at night considerable negative fluxes (net deposition) are visible for these compounds (see Fig. 21B and D).

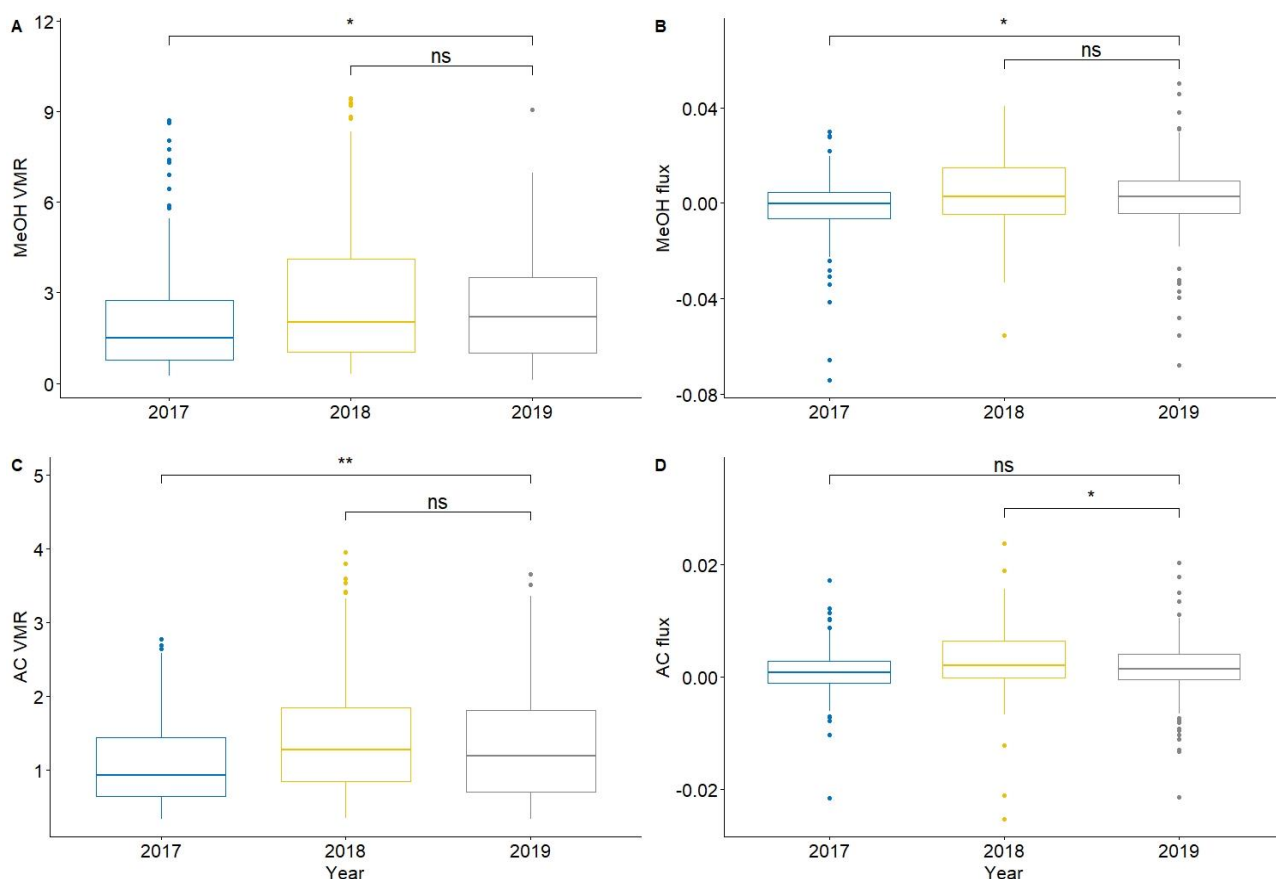


Figure 21. Pairwise test of nighttime median values of methanol and acetone during spring and summer (March-August) 2017 and 2018 against the same period in 2019. The left panel shows concentrations, and the right panel shows fluxes. Unit for concentrations and fluxes is parts per billion and  $\mu\text{g m}^{-2}\text{s}^{-1}$ , respectively. Significant differences between 2019 and other years are denoted by an asterisk (t test). For explanations on the boxes and whiskers, see Fig 3, and for the abbreviations, see Fig. 11.

Finally, I temperature normalized nighttime median values of the BVOCs, as demonstrated in Figure 22. According to the results, when nighttime values are temperature normalized, there is no difference between the years. This holds for all the BVOC emission rates. It is also worth noting that, as expected, temperature normalized nighttime emission rates (Fig. 22) are sharply higher than measured nighttime fluxes (Fig. 21 and 22).



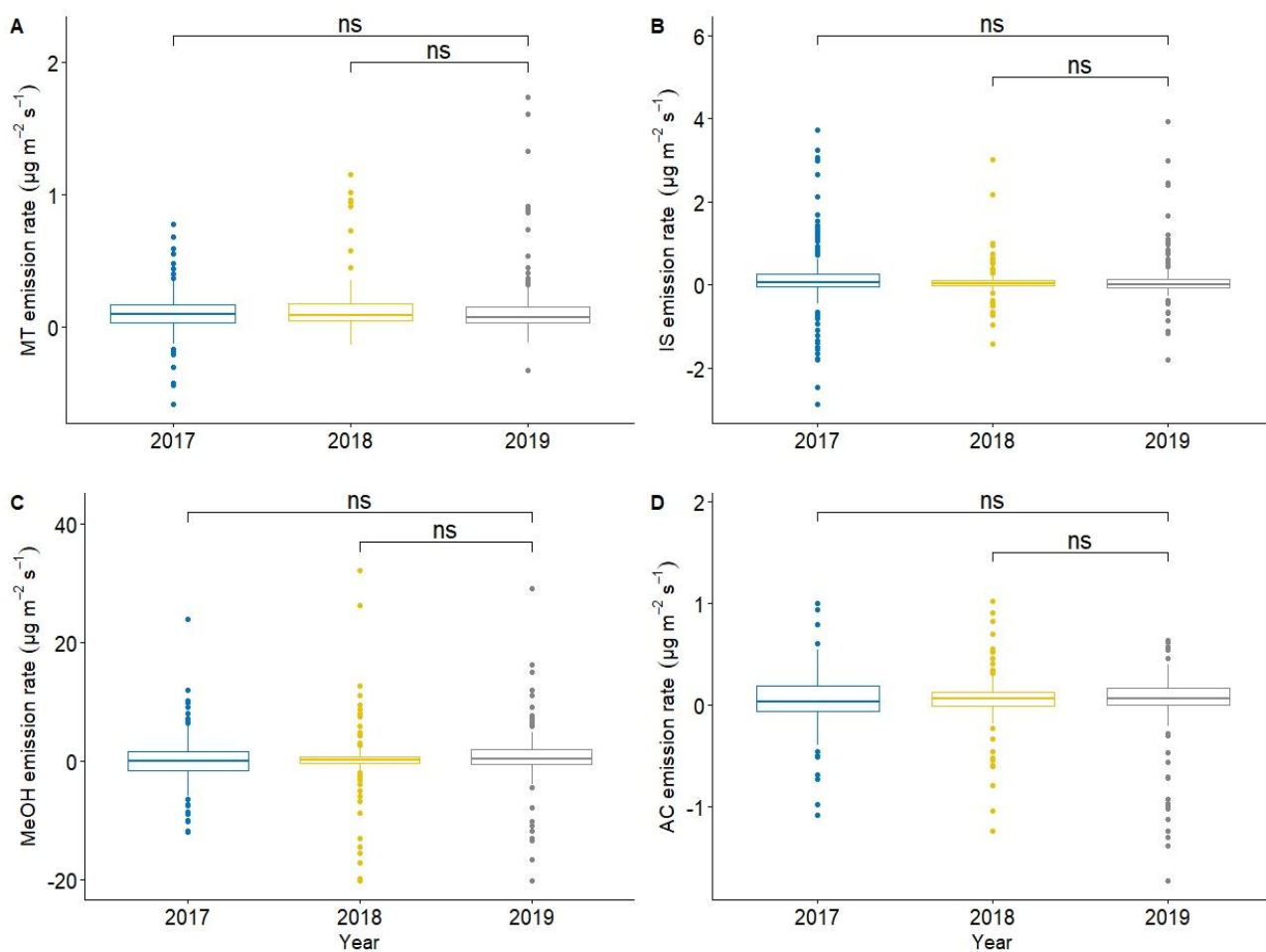


Figure 22. Pairwise test of temperature normalized nighttime median values of the BVOCs during spring and summer (March-August) 2017 and 2018 against the same period in 2019. For explanations on the boxes and whiskers, see Fig 3; for the abbreviations, see Fig. 11. ns, not significant.

## 5. Discussion

This research began to understand whether sub-canopy removal increases BVOC emissions from a boreal forest stand. In doing so, the concentrations as well as fluxes of three common BVOCs emitted from boreal forests, namely monoterpenes, methanol and acetone during the growing season in 2019 were compared with 2018 and 2017. Isoprene was also studied, as it is an important BVOC globally. The reason 2019 was selected was that a sub-canopy removal had occurred during spring and early summer of that year, whereas in 2018 and 2017 the stand had remained intact. Prior to conducting any analysis, the annual concentrations and fluxes of these compounds over a period of three years, from 2017 to 2019, were examined. The results showed that the concentrations and fluxes were dependent on seasonal changes, reaching a peak during summer, and decreasing as air temperature and light intensity fell. This revealed the important roles temperature and light played on the emissions of the compounds. This pattern was clearly visible for isoprene, methanol and acetone.



Based solely on the results of the comparison between 2019 and 2018 (section 4.2.), one may reject the initial research hypothesis that sub-canopy removal increases the concentrations of BVOCs above the forest stand. However, the differences observed between 2019 and 2017 (section 4.2) partially confirm the hypothesis. Accordingly, sub-canopy removal may have increased the concentrations during spring and summer 2019 compared to 2017. However, since the concentrations and fluxes in 2019 were either lower than or remained the same as 2018, more analysis deemed necessary. Other factors may have affected the concentrations. For example, climatic variables have an important role in forest BVOC emissions (Holopainen et al., 2017; Zhao et al., 2017). Accordingly, air temperature, light intensity and soil moisture were compared amongst the years under study.

A series of multiple regression analyses demonstrated that air temperature was the most significant driver of BVOC concentrations and fluxes. Though exhibiting milder effect, PAR also showed a significant effect on BVOC concentrations and fluxes. Soil moisture, however, had a different impact. When it was combined with temperature, soil moisture had a positive and statistically significant effect on monoterpene and methanol concentrations and acetone fluxes. Generally, these results confirmed the second research hypothesis that air temperature, soil moisture and PAR play a considerable role in BVOC concentrations above the forest stand. Higher temperature during better part of the growing season in 2018 coupled with relatively similar PAR levels as the other years could well be the reason for higher concentrations and fluxes during that year.

For most BVOCs, as opposed to daily values, the differences between nighttime concentrations and fluxes between the years were mainly statistically insignificant. These nighttime patterns differed from daily patterns because the atmosphere at night is more stable and there is less turbulence compared to daytime (Velasco et al., 2008). In addition, as isoprene is strongly light dependent, its emission patterns were different at night than in the day. Moreover, low stomata conductance during the night should cause the emission of water soluble compounds, such as methanol and acetone, to be low, with noticeable net deposition for both (Folkers et al., 2008; Rissanen et al., 2018). However, air temperature affects nighttime concentrations and fluxes, too.

To remove the effect of air temperature from the analyses both for daily and nighttime emissions, the BVOC fluxes were temperature normalized (Guenther et al., 1994, 1995). The results of the yearly comparison between temperature normalized BVOC emission rates yielded no statistically significant results; there was no difference between emission rates in spring and summer 2019 and the same period in the other years. This was the case for both the daily and nighttime emission rates. Once again, this confirmed the strong effect of temperature on BVOCs emission rates.

According to the results above, sub-canopy removal did not change BVOC emission rates neither during the entire day, nor during nighttime. Previous research, however, shows that mechanical disturbance, caused by different management activities such as thinning and harvesting, increases BVOC emission rates sharply during and after the disturbance (e.g., Räisänen et al. 2008; Haapanala et al. 2012). One reason the results of this study diverged from earlier research could be the long timescale—here, seasonal—used to do the analysis. This can be addressed by conducting further study of BVOC concentrations and fluxes in shorter timescale, for example comparing monthly, weekly and daily emission rates. This can also complement the results of this study.

Given the strong effect of environmental variables on BVOC emissions, of particular relevance here is that climate change is modulating temperature, atmospheric CO<sub>2</sub> and O<sub>3</sub> concentration and precipitation. For example, due to climate change, it is likely that global temperature will rise by 1.5 °C between 2030 and 2052 (IPCC, 2018). Such a rise in temperature leads to a general decrease of soil moisture and a negative water balance, hence drought in most areas of the world (Dai, 2012), with boreal forests being particularly sensitive (Vicente et al., 2013). In this research, relatively long-term responses of BVOC emissions to some of these environmental changes were studied. This is necessary to complement the extant studies (Penuelas and Staudt, 2010), particularly in predicting how these changes, resulting from global warming, could influence the forest BVOC emissions in the future, thereby future impacts on the Earth's biosphere, atmosphere and climate system. Furthermore, the continuous and relatively long-term measurements of BVOCs could be an important step in developing global models of BVOC exchange processes (Guenther et al., 2006).

The limitations of the research are also acknowledged here. The surface-layer-profile method could have had systematic error of up to 10% for the measurement (Rantala et al., 2014). In addition, it is likely that PTR-MS has had instrumental problems in the concentration measurements of the compound, though generally it is less sensitive to the instrumental noise and tube attenuation (Rantala et al., 2014). Overall, the profile method has shown several systematic error sources since it is an indirect method to measure fluxes, being based on parameterization of the surface layer turbulence (Rantala et al., 2015).

## **6. General discussion and conclusion**

According to the best of the author's knowledge, this research was the first attempt to respond to the question of whether sub-canopy removal increases the concentrations of BVOCs above a boreal forest canopy. While merely based on the results, one may not conclude definitively what the impact of the sub-canopy removal on the stand BVOC emissions is, the research shed light on the complex and

intertwined effects of the sub-canopy removal and environmental variables on the stand-level BVOC emissions. This has implications regarding how forest management practices, and more broadly anthropogenic activities, influence forest-atmosphere interactions.

More generally, the above-canopy concentrations and fluxes of the compounds studied in this research (see Figure 1 and Table 2) concur with prior studies. For example, monoterpene fluxes in a boreal forest in Hyytiälä, Finland reported by Rantala et al. (2015) are of the same magnitude as those reported in this research. The same can be noted regarding the temperature normalized values of methanol and isoprene fluxes. The magnitude of the BVOC fluxes reported by Schallhart et al. (2018) seem to agree with that of the fluxes reported in this study. This research also confirmed the extant research (e.g., Rinne et al., 2009 and references therein; Schallhart et al., 2018) that monoterpenes, methanol and acetone are among the most common BVOCs emitted from a boreal forest, with large concentrations above the canopy. Additionally, the study showed that trees in a boreal forests also emit considerable amount of isoprene, though with concentrations and fluxes lower than the other compounds studied.

Finally, this study provides promising future research avenues. Here, the likely changes in concentrations and fluxes due to sub-canopy removal over the entire growing season were compared. Future researchers are encouraged to do a narrower analysis focusing on the comparison of the daily, weekly and monthly concentrations and fluxes over the years. This could well complement the results of the current research, yielding novel findings. For example, as demonstrated earlier, air temperature was higher during June 2019 than June 2018. Also, weekly or daily temperature patterns might well differ from seasonal and monthly patterns. Furthermore, while some important environmental drivers of BVOC emissions have been considered in this research, other variables such as soil temperature, leaf temperature, atmospheric O<sub>3</sub> and CO<sub>2</sub> concentrations are missing. A fruitful future research avenue is to consider these, too. Future studies could also focus on a wider timespan by adding more years, and hence more data, to the analysis. This will provide greater variability, naturally increasing the reliability of the research results. Finally, analysing the extreme values of air temperature and soil moisture, when they are either high or low simultaneously, allows examining whether under those extremes, the concentrations and fluxes differ from other periods.

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