



Pro Gradu  
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# The Effect of Autumnal Moth Induced Volatile Organic Compound Emissions to Aerosol Load in Subarctic Region

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<p>Volatile organic compounds (VOCs) are hydrocarbons that are emitted to the atmosphere from biogenic or anthropogenic sources. Plants emit VOCs as a part of normal metabolism, but the emissions are significantly increased under stressed conditions. For example heat wave, drought and herbivory cause stress for the plants. Laboratory studies have shown that VOCs emitted by herbivory infested boreal forest trees have enhanced secondary organic aerosol (SOA) production. In this study, 25 years (1992–2016) of atmospheric data from measurement site in eastern Finnish Lapland was analyzed to understand whether the enhancement is atmospherically relevant. The knowledge is important, as aerosol particles cause changes in radiative forcing, and thus contribute to the climate change.</p> <p>At the study site autumnal moth (<i>Epirrita autumnata</i>) larvae are prominent defoliator of mountain birches (<i>Betula pubescens</i> spp. <i>czerepanovii</i>). Autumnal moths have cyclic population dynamics, and during the severe population outbreaks, they can consume all the leaves of mountain birches in vast regions. Despite the severity of the herbivory to the local ecosystem, the analysis did not show connection between the number of autumnal moths and aerosol processes. Also, no clear correlation between the total number concentration and temperature, and hence the basal VOC emissions from biogenic sources, was observed. Nor did sulfur dioxide or sulfuric acid concentration have strong correlation with total particle concentration which would have been expected. The results indicate that probably the total biomass of mountain birches is too small to cause detectable changes in atmospheric variables. Additionally, the study period had only one severe population outbreak during which the data availability of atmospheric variables was limited. However, climate change proceeds fast in the Arctic region. Hence, the basal VOC emissions from vegetation will increase. Also, both the mountain birches and new moth species will expand to the areas where they did not earlier succeed. In the future the enhancement of autumnal moth larvae feeding may be atmospherically relevant.</p>			
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# 1. Introduction

In Scandinavian subarctic area, the periodic defoliation of mountain birches and mortality of trees has received a lot of attention (Saalas, 1949; Lehtonen and Heikkinen, 1995; Tenow and Nilssen, 1990; Jepsen et al., 2008). The meaning of the mountain birches to the ecosystem is significant as they are the dominating species between coniferous forest zone and treeless areas (Figure 1.1) (Wielgolaski, 2005). The cause for the defoliation is autumnal moth larvae feeding on the leaves. The species has fairly regular, 9–11 years, periodic cycle in population density in northern and mountaineous Fennoscandinavia (Ruohomäki et al., 2000; Klemola et al., 2016).

For centuries, plants have developed ways to minimize the herbivory feeding. Some of the carbon they take up from the atmosphere in photosynthesis, is allocated to synthesis of defence compounds (Mithöfer and Boland, 2012). These organic compounds can be toxic or repellents for herbivores, but they can also be infochemicals. Volatile, gaseous compounds emitted by the plants to the surrounding air, can warn the neighboring plants of the presence of herbivores, or they can attract predators of herbivores, and hence diminish the damages (Dudareva et al., 2006; Holopainen and Gershenzon, 2010).

It has been shown that volatile organic compounds (VOCs) emitted by the mountain birches can enhance the formation of the secondary organic aerosol (SOA). SOA consists of particulate matter formed in the atmosphere from gas phase precursors, production (Yli-Pirilä et al., 2016). Aerosol particles contribute to the climate change as they can alter the Earth's radiative balance directly by scattering or ab-



**Figure 1.1:** Figure showing how coniferous ravine turns to mountain birch forest and finally to treeless summit in Finnish Lapland. © Ilona Ylivinkka, 2018.

sorbing incoming solar radiation and indirectly by changing the cloud properties (IPCC, 2013).

The aim of this thesis is to investigate, whether autumnal moth larvae feeding can enhance SOA formation observably in field conditions. Previously, only laboratory and model studies of the effects of biotic stresses have been conducted. They have, however, proved the connection between VOC emissions caused by biotic stresses and SOA production (Mentel et al., 2013; Bergström et al., 2014; Joutsensaari et al., 2015; Yli-Pirilä et al., 2016). Yet, the intriguing question, is the induction atmospherically relevant, has remained unanswered.



## 2. Theory

In this chapter, the theoretical bases of autumnal moths, mountain birches and aerosols are introduced. Also, the steps how herbivore feeding can enhance aerosol particle formation are explained.

### 2.1 Autumnal Moths

Autumnal moth, *Epirrita autumnata* (class *Insecta*, order *Lepidoptera*, family *Geometridae*), is a geometrid moth. The order *Lepidoptera* covers moths and butterflies. Moths whose larvae move in a looping way, like measuring the travelled distance, belong to the family of geometrid moths (*Geometridae*). The adult moth has pale gray coloring with darker cross sectional stripes in front wings. The larvae are light green with yellowish longitudinal stripes on sides (Figure 2.1) (Mikkola et al., 1985; Heliövaara and Mannerkoski, 1987). The wingspan of an adult moth is 31–40 mm, and the length of a larva varies between 22 and 26 mm (Saalas, 1949).

Autumnal moth is obligatorily univoltine, meaning that it can have only one new generation per year (Klemola et al., 2014). Females lay eggs to the branches of host plants where the eggs overwinter. In the spring, the larvae hatch from the eggs concurrently with the bud burst, and start feeding (Klemola et al., 2003). Bud burst usually takes place in early June in Finnish Lapland. When growing, larvae go through five development stages, instars, within 4–7 weeks (Klemola et al., 2016). After that they decent to the ground to pupate. The adult moths merge flying in mid-August to breed (Mikkola et al., 1985; Heliövaara and Mannerkoski, 1987).



**Figure 2.1:** Autumnal moth larva on a leaf of mountain birch. Photograph has been taken in early July in eastern Lapland, Finland. © Esko Karvinen, 2018.

The moth is distributed over the northern parts of the Holarctic region, restricting approximately to 45th latitude (Mikkola et al., 1985). In Finland the moth is very common everywhere where deciduous trees and shrubs grow, but mass outbreaks occur only in Lapland and elsewhere in northern and mountainous Fennoscandia (Saalas, 1949). In these areas the population density has statistically significant 9–11 years periodic cycle with or without severe outbreak levels (Klemola et al., 2016). Many theories have been proposed for the reason of the cyclicity, including changes in host plants caused by sunspots and cosmic rays, degraded food quality or quantity, diseases, parasitoids and predators (Myers and Cory, 2013). According to the latest knowledge, the major driver of the population cyclicity is the mortality caused by parasitism of moths in egg, larva and pupa stages (Klemola et al., 2014, 2016).

## 2.2 Mountain Birches

The main host plant for autumnal moths, in the areas where outbreak level population densities appear, is mountain birch (*Betula pubescens* spp. *czerepanovii*, Figures 1.1, 2.1 and 2.2) (Saalas, 1949). The trees are often polycormic, meaning that they consist of several below ground connected stems (Figure 2.2). Mountain



**Figure 2.2:** Typical polycormic mountain birches consisting of several below ground connected stems. © Ilona Ylivinkka, 2018.

birches can grow as bushes or up to 10 m high trees. The size of the leaves varies, but usually they are smaller than the leaves of downy birch (*Betula pubescens*) (Wielgolaski, 2005). Mountain birches form the tree line in northern Norway, Sweden and Finland and northwestern Russia. In their distribution area, they make up the major share of plant biomass, and thus have a significant role in northern ecosystem (Wielgolaski, 2005). Estimated average leaf area index (LAI) of mountain birch forest ranges about from  $0.76 \text{ m}^2 \text{ m}^{-2}$  to  $2.06 \text{ m}^2 \text{ m}^{-2}$  (Dahlberg et al., 2004 and references therein; Heiskanen, 2006). In mixed boreal forest in central Finland LAI values range from  $0.3 \text{ m}^2 \text{ m}^{-2}$  to  $4.5 \text{ m}^2 \text{ m}^{-2}$ . Larger than  $3 \text{ m}^2 \text{ m}^{-2}$  values were obtained from birch and spruce stands (Stenberg et al., 2008; Aalto et al., 2014). The average total biomass of subarctic mountain birch forest estimated by Dahlberg et al. (2004) is  $27\,493 \text{ kg ha}^{-1}$  and by Heiskanen (2006)  $8\,350 \text{ kg ha}^{-1}$ . The large difference is explained by the different locations, methods, and the large regional variability ( $0\text{--}33\,260 \text{ kg ha}^{-1}$ ) in the estimation by Heiskanen (2006). In North American boreal forest the estimated value is  $41\,800 \text{ kg ha}^{-1}$  and in northern Europe about  $45\,000 \text{ kg ha}^{-1}$ – $47\,000 \text{ kg ha}^{-1}$  (Botkin and Simpson, 1990; Häme et al., 1997).

During mass outbreak years, the autumnal moth larvae can consume the foliage of the trees completely in vast regions (Saalas, 1949; Lehtonen and Heikkinen, 1995; Tenow and Bylund, 2000). Usually trees can recover well even from total foliage loss, yet mortality of the trees have been observed (Lehtonen and Heikkinen, 1995; Tenow and Bylund, 2000; Tenow et al., 2005). It has also been discovered that herbivory influences to understorey vegetation, and causes slowly recovering changes to plant fungal communities (Jepsen et al., 2013; Saravesi et al., 2015).

## **2.3 Volatile Organic Compounds**

Volatile organic compounds comprises a large variety of different hydrocarbons that can additionally contain other atoms (Piccot et al., 1992; Guenther et al., 1995; Kansal, 2009). They are atmospheric trace gases with magnitude of mixing ratios ranging typically from ppt to ppb (Kansal, 2009). The main sources of primary emissions are vegetation and by-products of combustion and biomass burning (Kansal, 2009). Guenther et al. (2012) estimated that the global emissions of naturally emitted nonmethane VOCs is about 1 000 Tg/year, which dominates the estimated anthropogenic emissions by one order of magnitude (Kansal, 2009). VOCs are present continuously in everyday life as they can be found in the air, water, foods and drinks. For example many smells are caused by released VOCs, like the smell of forest, coffee or perfumes.

### **2.3.1 Biogenic VOCs**

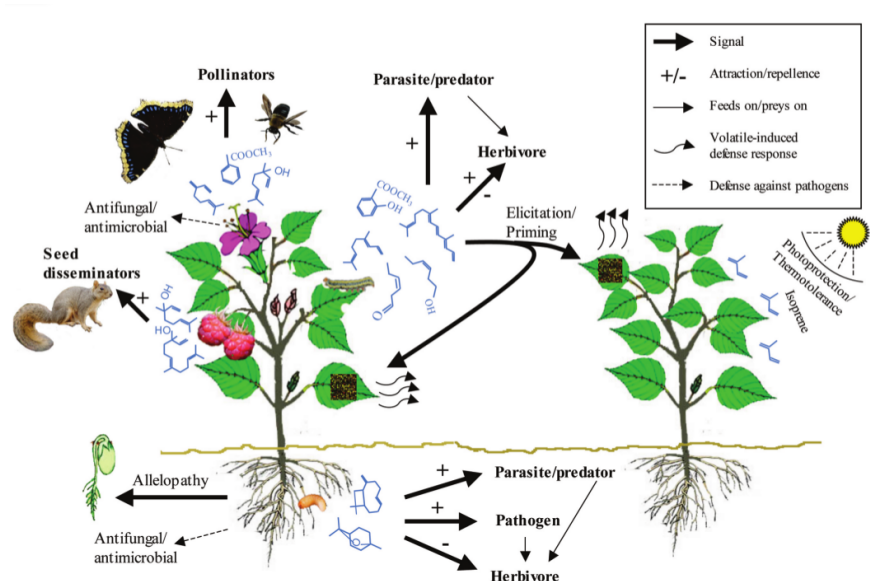
Naturally emitted VOCs, or biogenic VOCs (BVOCs), are compounds which plants synthesize and emit for various reasons to compensate their immobility, and to interact with the surrounding environment (Dudareva et al., 2006). All plants can release and receive VOCs during photosynthesis and respiration, and many of them can exchange VOCs with several plant parts (Dudareva et al., 2006; Tholl et al., 2006). More than 30 000 different compounds have been recognized (Trowbridge

and Stoy, 2013). Some compounds are emitted constitutively as a part of plant metabolism whereas some are induced by stresses, like herbivory attack, heat wave, drought or air pollution (Kesselmeier and Staudt, 1999; Possell and Loreto, 2013). Stresses may increase the emissions of constitutively emitted VOCs and alter their relative share, but also new compounds may be released (Holopainen, 2004; Niinemets, 2010; Fineschi and Loreto, 2012). The emission rates of the compounds depend on stresses and their severity (Niinemets, 2010; Holopainen and Gershenzon, 2010). Thus, the emitted VOC profile is species specific, but contains also information of plant physiology and growth conditions (Vuorinen et al., 2007; Mithöfer and Boland, 2012; Aalto et al., 2014). Under stressed conditions plants can use up to 10 % of assimilated carbon to BVOC synthesis (Peñuelas and Llusà, 2003). Even though the meaning of the VOCs for plants have been investigated vastly, all the functions are not fully understood (Dudareva et al., 2006; Vickers et al., 2009; Holopainen and Gershenzon, 2010). The crucial, known processes are introduced in next section.

### **Functions of Induced BVOCs**

Apart from phenological purposes, stress relief and defence are the main reasons for BVOC emissions (Holopainen and Gershenzon, 2010). For instance, plants can emit repellents or toxic compounds to defend against herbivores and pathogens (Mithöfer and Boland, 2012). Studies have also revealed that emitted BVOCs can increase the thermotolerance during the periods of excess heat and light, or to protect the plant from oxidative stress (Peñuelas and Llusà, 2003; Laothawornkitkul et al., 2009; Vickers et al., 2009).

Secondly, BVOCs enable plant-plant communication. For example, VOCs emitted from a wound inform other plant parts about it, or when a plant under herbivory attack release specific VOCs, the synthesis of the defend compounds is induced also in the neighbouring plants (Loreto et al., 2006; Holopainen and Ger-



**Figure 2.3:** Schematic figure of VOC mediated plant-environment interactions. Figure courtesy Dudareva et al. (2006).

shenzon, 2010). This helps them to diminish the damages, but additionally helps the originally attacked plant, as more and more defence compounds are emitted to surrounding air.

Earlier researches have even discovered multitrophic interactions when the released BVOCs from herbivory wounded plants attracted other insects and birds, parasiting or predatoring on herbivores (Dudareva et al., 2006; Mäntylä et al., 2008; Koski et al., 2015). The scents of flowes and fruits give also reproductional advantage as they attract pollinators and seed dispersers (Dudareva et al., 2006; Laothawornkitkul et al., 2009). Figure 2.3 illustrates the known BVOC mediated interactions between plants and surrounding environment.

### BVOC Emission Controls

The synthetized VOCs may not be emitted directly after the production. Emissions are controlled by physicochemical properties of the compounds (e.g. volatility and diffusion), physical conditions (e.g. ambient temperature and irradiation) and biological factors (e.g. phenological state and stress) (Guenther et al., 1995; Niinemets

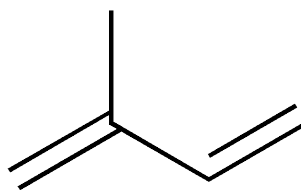
et al., 2004; Aalto et al., 2014). Besides, the factors may influence simultaneously; for instance increasing temperature accelerates evaporation of the compounds, but also enhances photosynthesis and production of the BVOCs. Then again, too high temperatures from the plant point of view, cause stress related BVOC emissions (Yuan et al., 2009; Holopainen and Gershenzon, 2010).

Furthermore, some plants have storage pools, e.g. resin ducts, where they store certain compounds, and release them directly after stress is experienced (Dudareva et al., 2006; Grote and Niinemets, 2008). In general, the induced stress response may be immediate, in which case the VOCs are emitted within seconds to one hour, or delayed, when effects occur only after several hours, days or months (Kesselmeier and Staudt, 1999).

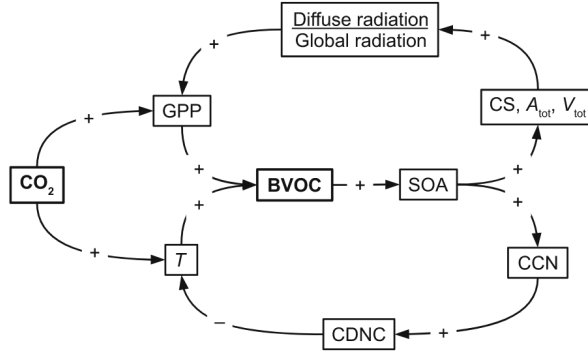
### Chemical and Physical Aspects of BVOCs

About half of the naturally emitted VOCs is isoprene. Group of monoterpenes (MT) and sesquiterpenes (SQT) sum up to 15 % and 3 %, respectively (Guenther et al., 2012). They belong to diverse and abundant group of terpenes. The basic structure of terpenes is isoprene unit (2-methyl-1,3-butadiene), consisting of five carbon atoms (Figure 2.4). Monoterpenes have two isoprene units (10 carbon atoms), and sesquiterpenes three (15 carbon atoms). Other important natural VOCs are methanol, ethanol, acetaldehyde and acetone (Guenther et al., 2012).

The chemical lifetime of many BVOCs, including isoprene and most monoterpenes and sesquiterpenes, varies from seconds to hours due to their high reactivity with atmospheric oxidants (Kesselmeier and Staudt, 1999). This has made their



**Figure 2.4:** Chemical structure of an isoprene unit.



**Figure 2.5:** Figure shows the biosphere and atmosphere connecting feedback loops. GPP (gross-primary production) represents a measure of photosynthesis; CS (condensation sink),  $A_{\text{tot}}$  (total aerosol surface area) and  $V_{\text{tot}}$  (total aerosol volume) describes the aerosol particle properties regarding the scattering of solar radiation, and CDNC is cloud droplet number concentration related to the cloudiness and albedo of the clouds. Figure courtesy Kulmala et al. (2014a).

measurements difficult, and the improvements in the measurement techniques have been needed to obtain their concentrations accurately (Rinne et al., 2005; Ruuskanen et al., 2005; Hellén et al., 2018). The high reactivity of VOCs affects also to the lifetime of a strong green house gas, methane, as there is less oxidants available for its oxidation (Voulgarakis et al., 2013). Additionally, when VOCs react with nitrogen oxide radicals, they produce tropospheric ozone which is an air pollutant (Sillman and He, 2002). Kulmala et al. (2014a) provided a quantitative estimates of a feedback loop connecting biosphere and atmosphere (Figure 2.5). The loop describes how elevated  $\text{CO}_2$  concentration enhances photosynthesis and BVOC emissions, leading to higher SOA formation and growth of aerosol particles (Laaksonen et al., 2008; Yuan et al., 2009). Particles scatter incoming solar radiation giving larger share of diffuse radiation (Charlson et al., 1992). Closing the loop, photosynthesis have shown to increase, when the share of diffuse radiation is higher (Gu et al., 2002). On the other hand, rising temperature also enhances BVOC emissions and thus, SOA formation (Peñuelas and Staudt, 2010). If aerosol particles can act as cloud condensation nuclei (CCN), they can increase the cloudiness and raise cloud albedo, when more solar radiation is scattered back to space cooling the climate (Rap et al.,

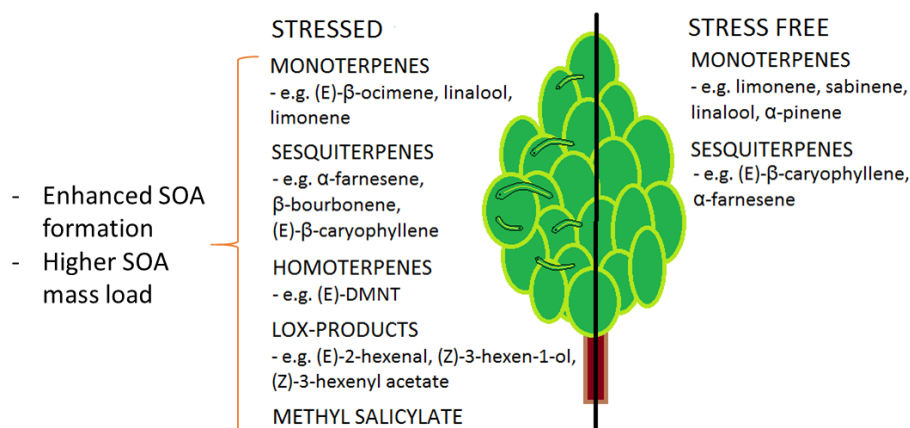


2013). The BVOC emissions related to biotic stresses have higher SOA formation potential, and lead to increased mass yield (Mentel et al., 2013; Bergström et al., 2014; Yli-Pirilä et al., 2016). Thus, BVOCs have a crucial contribution to the atmospheric chemistry and physics, and their emissions and effects on the atmospheric processes are important to understand.

### 2.3.2 VOCs from Mountain Birches

The main VOCs emitted constitutively from mountain birches are monoterpenes and sesquiterpenes. Emissions of isoprene are insignificant (Haapanala et al., 2009). When exposed to autumnal moth larvae, mountain birches have shown to induce production of compounds typically emitted by plants under herbivore attack. These compounds include several terpenes (e.g. (*E*)- $\beta$ -ocimene (MT), linalool (MT),  $\beta$ -bourbonene (SQT) and homoterpene (*E*)-4,8-dimethyl-1,3,7-nonatriene (DMNT)), lipogxygenase (LOX) pathway products (e.g. (*E*)-2-hexenal and (*Z*)-3-hexen-1-ol) and methyl salicylate (Kesselmeier and Staudt, 1999; Mäntylä et al., 2008; Yli-Pirilä et al., 2016). Emitted LOX products, mainly C<sub>6</sub> aldehydes and alcohols, are especially related to the mechanical damage caused by larval feeding. The BVOC emissions from infested trees include constitutively emitted compounds, yet the emission rates may be changed. Additionally, new stress related compounds are also emitted (Figure 2.6).

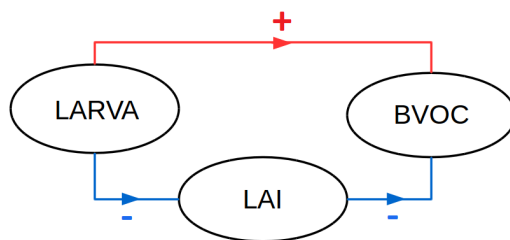
The emission rates of BVOCs depend on the level of consumption, and thus the number of larvae and their size. In early summer, when the larvae are small, they consume only little nutrition. Later on, when they are larger, they consume more due to their size, but also because the nutritive quality of the mature leaves is poor compared to young leaves, forcing to larger consumption (Haukioja, 2003). However, during outbreak years the larval feeding reduces the leaf biomass suppressing BVOC emissions (Figure 2.7). Usually, the level of defoliation is only less than 15 %, but during severe outbreak years, the BVOC emissions from defoliated trees may even



**Figure 2.6:** Figure illustrates the changes in BVOC emissions from mountain birches after they are exposed to autumnal moth larvae feeding. The emission rates of constitutively emitted BVOCs are changed, and emissions of new compounds are induced. The overall variety of different compounds is larger from the infested trees, and LOX-products are particularly related to mechanical damage. The quality and quantity of BVOCs from infested trees have larger potential to contribute to SOA formation, and lead to higher aerosol mass load (Mäntylä et al., 2008; Haapanala et al., 2009; Mentel et al., 2013; Bergström et al., 2014; Yli-Pirilä et al., 2016).

be less than the constitutive emissions from stress free mountain birches (Karlsson et al., 2005; Miresmailli et al., 2012; Yli-Pirilä et al., 2016).

In the future, the emission rates of BVOCs are predicted to increase with the increasing global temperature (Tiiva et al., 2008; Faubert et al., 2010; Peñuelas and Staudt, 2010). The main causes are more pronounced effects of the climate change in the Arctic region (Law and Stohl, 2007), the increasing number of mountain birches (Wielgolaski, 2005; Valolahti et al., 2015), and the expanding population of autumnal moths (Jepsen et al., 2008, 2013). Also, another geometrid moth, winter moth (*Operophtera brumata*), has recently reached cyclic outbreak dynamics in northern Fennoscandinavia (Hagen et al., 2007; Jepsen et al., 2008; Klemola et al., 2016). The outbreak cycle is similar to autumnal moths', but the peak densities occur 1–3 years after those of autumnal moths (Jepsen et al., 2013; Klemola et al., 2016). Yet, the population density of winter moth in Finnish Lapland is minor compared to autumnal moth (Hunter et al., 2014).



**Figure 2.7:** When the number of the larvae increases, also the BVOC emissions increase (red arrow). However, the limiting factor for BVOC emission increase is the decreasing leaf biomass (leaf area index, LAI) due to larval feeding (blue arrows).

## 2.4 Atmospheric Aerosol Particles

Atmospheric aerosols, the mixture of air and levitating liquid or solid particles, have been studied intensively due to their climate and health effects (IPCC, 2013). The size, number concentration and chemical composition of aerosol particles have large spatial and temporal variation, and are affected by the formation process and age of particles (Yu et al., 2010; Ng et al., 2011). The size range of an aerosol particle, from about 1 nm to 100  $\mu\text{m}$ , is limited by the size of a molecular cluster and a particle that still can levitate in the air despite the gravity effects. Typically, aerosol particles consist of sulfates, nitrates, organic compounds, various minerals, sea salt and soot (Jimenez et al., 2009).

The particles can either be primary particles from natural or anthropogenic sources, or form secondarily in the atmosphere from precursor gases (IPCC, 2013; Kulmala et al., 2014b). Primary particles from natural sources are e.g. sea salt, dust and pollen, whereas anthropogenic sources are for example different kinds of combustion processes and mining. New particle formation (NPF) in the atmosphere is a process where new aerosol particles are formed due to gas-to-particle conversion. First, oxidiced precursor gases form molecular clusters that, after nucleation, can activate and grow to larger sizes by condensation of vapors (Kulmala et al., 2014b). Even though primary particles contribute largely to mass loading of atmospheric aerosol particles, secondary particles are believed to dominate the aerosol number

concentration (Kerminen et al., 2018).

Despite the fact that the initial precursors and pathways of forming new particles may differ depending on location, time and surrounding conditions, NPF events have been reported to take place almost all over the world (Kulmala et al., 2014b). In boreal forest zone, a significant share of particulate mass is different organic compounds (Jimenez et al., 2009). The organic material originates from the oxidation products of BVOCs emitted by the surrounding vegetation (Laaksonen et al., 2008; Ehn et al., 2012, 2014). Laboratory studies have also confirmed that when exposed to foliage feeding herbivores, typical boreal forest trees emit such volatile vapors that boost secondary particle formation and their further growth (Joutsensaari et al., 2015; Yli-Pirilä et al., 2016).

The aerosol number concentration has increased from pre-industrialized era due to increasing number of combustion processes that produce both primary particles and precursor gases (IPCC, 2013). In polluted areas, the fine particles transported to respiratory and circulatory systems, increase the risk for airway infections, lung cancer and heart illnesses (Cohen et al., 2005; Hu and Rao, 2009; Laumbach and Kipen, 2012). In addition to health issues, atmospheric particles contribute to the climate change by affecting the radiative balance. Particles floating in the air can cool the climate by scattering solar radiation, or dark particles, like soot, can warm by absorbing incoming radiation. Aerosol particles can also affect the cloud properties when acting as CCN or ice nuclei (IPCC, 2013). In polluted areas, where the abundance of CCN is high, clouds tend to have more and smaller cloud droplets, which increases their albedo making them scatter more light back to space. Also, the lifetime of clouds in polluted areas is often longer as the water is distributed on high number of droplets. Both properties have a cooling climatic effect (IPCC, 2013). Yet, the interactions between aerosols and clouds are complex, and have large uncertainties (IPCC, 2013).

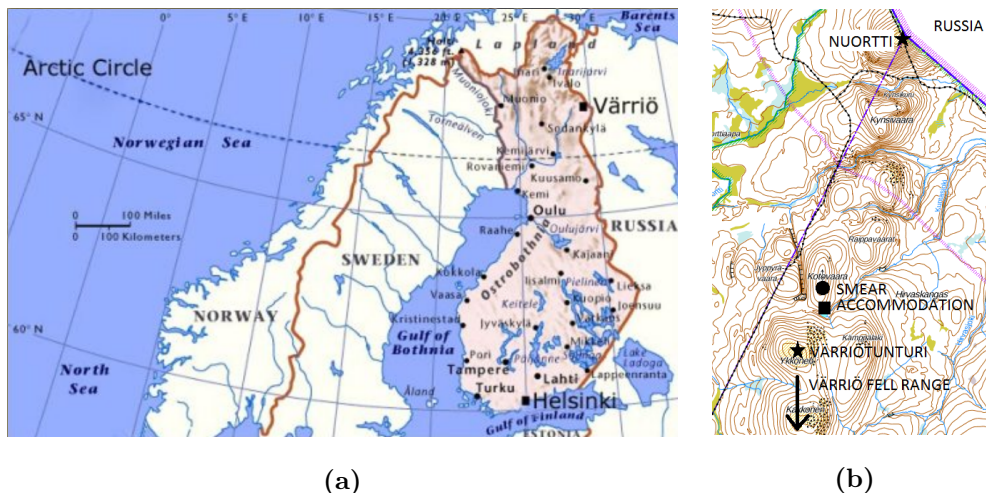
## 3. Materials and Methods

In this chapter the measurement site, used datasets and statistical methods will be introduced. The study covers fully years 1998–2016 and partially years 1992–1997. The time is limited by the launch of new continuous measurements at the study site. Outset of each measured variable is reported in the sections below. Figure 3.5 at the end of Section 3.3.3 contains a summarizing timeline of measurement data used in this study and data availability during the declared time periods. Due to the annual dynamics of autumnal moths, the analysis focuses on June and July — the time when moths are still in the larval stage and feed on the foliage (Section 2.1).

### 3.1 Measurement Site

The measurement site is located in Värriö Strict Nature Reserve (Värriön luonnonpuisto) in eastern Finnish Lapland (67°44' N, 29°37' E, 360 m a.s.l.). The area lies 250 km north from the Arctic Circle and 6 km from Finnish–Russian border (Figure 3.1a). There is no permanent residence nearby, and anthropogenic influence in the area is minor. However, occasional events of high concentrations of atmospheric trace gases and aerosols occur when wind advects them from the industrial area in Kola peninsula in Russia (east–northeast from the station) (Pirjola et al., 1998; Kyrö et al., 2014).

To the south from the study site stands Värriö fell range with fjelds peaking at 500–550 m a.s.l. Northwards from the station, the highest fjeld is Nuortti with peak reaching 482 m a.s.l. (Figure 3.1b). The average temperature in January (the



**Figure 3.1:** (a) Geographical location of the research station in Värriö. © <http://www.helsinki.fi/forestsciences/varrio/contact/location.html>, September 7, 2018. (b) Map representing the surroundings of the measurement site. © Paikkatietoikkuna.

coldest month) during the normal period (1981–2010) was  $-11.4^{\circ}\text{C}$ , and in July (the warmest month)  $13.1^{\circ}\text{C}$ . The region is free from snow approximately from end of May to mid-October. The Sun does not set between end of May and mid-July.

Värriö site is ideal for the study due to versatile continuous measurements of atmospheric variables (Hari et al., 2013). Also, the ecological parameters and phenological situation, such as the abundance of autumnal moths, have been observed for several decades (Hunter et al., 2014). Furthermore, it is a remote site where the possible effect of larvae feeding induced VOCs to aerosol load can be detected more easily.

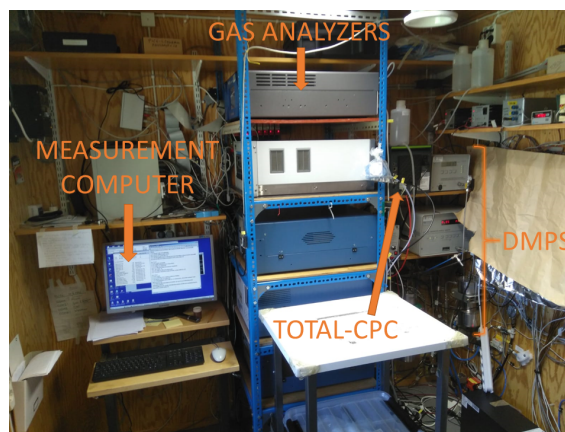
## 3.2 Atmospheric Data

The atmospheric data are provided from the SMEAR I (Station for Measuring Ecosystem-Atmosphere Relations) site. It is on top of Kotovaara hill ( $67^{\circ}45'31''\text{N}$ ,  $29^{\circ}36'41''\text{E}$ , 390 m a.s.l.), 800 m north from the accommodation building (Figure 3.1b). The station was established in 1991 to monitor air quality in Lapland due to advected pollutants from Kola peninsula (Hari et al., 1994). Nowadays, the

focus has shifted towards understanding the coupling of ecosystem and atmosphere (Hari et al., 2013).

### 3.2.1 Aerosols

The total number concentration ( $N_{\text{tot}}$ ) was obtained two ways: 1) from direct ambient air measurements with condensation particle counter (CPC). The measurement has been ongoing since 1991. Hereafter, this method is called “total-CPC”. 2) By integrating the concentrations in separate size classes in number size distribution data. At the SMEAR I site aerosol number size distribution has been measured with Differential Mobility Particle Sizer (DMPS) since 1997. It consists of two differential mobility analyser (DMA) and CPC pairs. DMA separates the particles according to their diameter depended electrical mobility (Aalto et al., 2001), and CPC counts the numebr of particles in each size bin. Two DMA-CPC pairs are needed to obtain measurements from wide size range. Before 2003 the lower cut-off size of DMPS was 8 nm and after that 3 nm. In 2005 the upper cut-off size was extended to 850 nm from 500 nm. Figure 3.2 shows the measurement set-up at SMEAR I.



**Figure 3.2:** The measurement set-up at SMEAR I. Gas analyzers are in the blue rack. Right from the rack is CPC measuring the total particle concentration and DMPS system consisting of two DMA-CPC pairs. On the left side, there is a computer that controls the measurement programs and data flow. © Esko Karvinen, 2018.

Two aerosol number concentration derived variables were also used in the analysis: 1) growth rate (GR) which describes how rapidly newly formed particles can grow to larger sizes (Equation (3.1)).

$$\text{GR} = \frac{\Delta D_p}{\Delta t}, \quad (3.1)$$

where  $\Delta D_p$  is the change in diameter and  $\Delta t$  is the considered time interval (Kulmala et al., 2012). In this study, the GR was obtained from the number size distribution measured with DMPS by fitting log-normal distribution modes, and calculating geometric mean diameters of the fits. The slope of linear fit to mean diameters represents GR (Hussein et al., 2005; Kulmala et al., 2012). 2) The formation rate,  $J$ , which quantifies the strength of an particle formation event. It is defined as time evolution of particle number concentration between certain size range

$$J_{D_p} = \frac{dN_{D_p}}{dt} + \text{Coag}S_{D_p} \cdot N_{D_p} + \frac{\text{GR}}{\Delta D_p} + S_{\text{losses}} \quad (3.2)$$

(Kulmala et al., 2012). In Equation (3.2) first term on the right hand side is the time evolution of number concentration in the certain size range,  $\text{Coag}S_{D_p} \cdot N_{D_p}$  describes the loss of particles due to coagulation and  $\text{GR}/\Delta D_p$  is the rate at which particles grow out of the defined size range.  $S_{\text{losses}}$  includes all the other loss terms, like losses in the sampling tubes or dilution of air mass due to boundary layer development. This term was not considered in this study. Although the cut-off size of the DMPS changes, the GR and  $J$  were always calculated for particles with diameter in the range 8–25 nm. The formation rate is then denoted as  $J_8$ .

Growth rates were also calculated using automatic method for all sizes from nucleation to accumulation mode. Basically, the growth rate was obtained as described above, but the growing modes were searched automatically from the whole DMPS size range. The method is explained more detailed in Paasonen et al. (2018).



The used NPF event classification analysis follows the procedure proposed by Dal Maso et al. (2005). The days were separated to event, class II event, non-event and undefined days visually by examining graph of aerosol size distribution data. If a new, growing mode was observed below 25 nm, the day was considered as an event day. If not, the day was non-event day. If new mode was observed, but particles were not growing, the day was classified as undefined. If the growth of the particles was fluctuating so that the growth rate could not be determined, the day was class II event.

### 3.2.2 Gases

Sulfur dioxide (SO<sub>2</sub>) has been measured with a pulsed fluorescence analyser since 1991 at SMEAR I (Figure 3.2). The measurement height is 9 m. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) concentration was calculated from a proxy developed by Petäjä et al. (2009)

$$[\text{H}_2\text{SO}_4] = k \cdot \frac{[\text{SO}_2] \cdot \text{UVB}}{\text{CS}}. \quad (3.3)$$

In the Equation (3.3) [SO<sub>2</sub>] is the concentration of SO<sub>2</sub>, UVB is the intensity of UV-B radiation, CS is condensation sink to pre-existing particles and  $k$  is empirically determined scaling factor:  $k = 1.4 \times 10^{-7} \cdot \text{UVB}^{-0.70} \text{ m}^2 \text{ W}^{-1} \text{ s}^{-1}$ . Even though the linearly parametrized proxy has a strong physical base, due to pseudo-steady H<sub>2</sub>SO<sub>4</sub> concentration assumption, it can be slightly biased as CS in Värriö is low.

### 3.2.3 Meteorological Variables

The temperature ( $T$ ) and relative humidity (RH) used in this study are measured at 2.2 m and 2 m altitude above ground, respectively. The temperature is measured with shielded and ventilated Pt-100 sensor (ongoing since 1991), and relative humidity with Vaisala HMI32 Humicap (July 1993 – January 2004) and Rotronic MP106A (from January 2004 onwards) sensors. UV-B radiation measurements started in July 1996 with Solar SL 501A pyranometer (wave length range 280–320 nm). Reemann

TP 3 pyranometer (May 1992 – May 2008) and Middleton SK08 pyranometer (from May 2008 onwards) has been used for global radiation ( $R_{\text{glob}}$ ) measurements (wave length range 300–4800 nm).

### **3.3 Autumnal Moth Population Estimates**

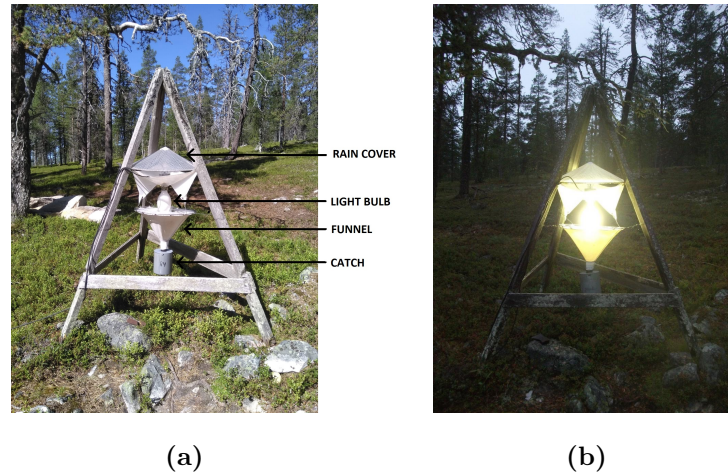
The population density of autumnal moths was estimated with three different collection methods: collection by hands in specified time-unit, catcing with light traps and sweeping with a net. The methods are explained below.

#### **3.3.1 Collection**

The population density of autumnal moths is estimated with once per year conducted time-unit specific method. One researcher (Kai Ruohomäki, University of Turku) counts all the larvae found from mountain birch branches in 10 minutes. When the population density is low, the collection is continued until 15 larvae are found, or until 1 h expires (Klemola et al., 2016). The method enables to calculate relative index of larval density per 10 min search. The data will be called here “larval index”. The collection is aimed to schedule so that larvae have moulted to fourth instar (Klemola et al., 2016). The collection method has been ongoing since 1987 (Klemola et al., 2016).

#### **3.3.2 Light Traps**

The light traps are meant for attracting and capturing nocturnal moths. Each trap has a 500 W light bulb which is switched on every night between 20:00 and 08:00 approximately from mid-May to mid-October (Hunter et al., 2014). Every morning the catches are emptied, and collected moths are stored to freezer. Later on, they are sent to Zoological museum of the University of Oulu where Juhani Itämies has identified the species and counted their number (Hunter et al., 2014).

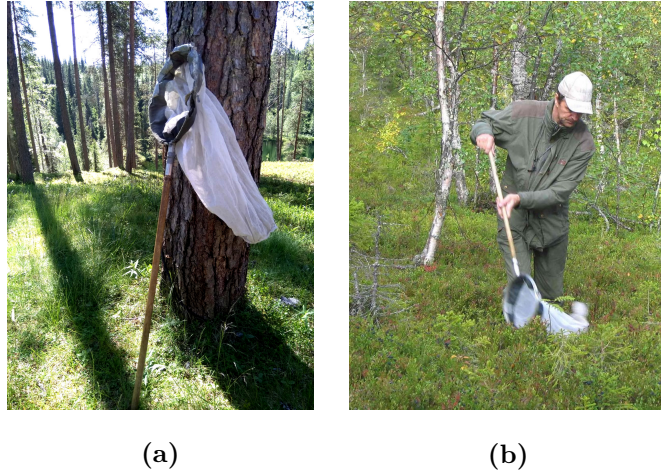


**Figure 3.3:** (a) Figure showing the light trap set-up in Värriö. The light-attracted moths are directed to catch which is emptied every morning. © Esko Karvinen, 2018. (b) Light trap switched on. © <http://www.atm.helsinki.fi/varrio/eng/?q=node/3#Y%C3%B6hy%C3%B6nteiset>, November 7, 2018.

From 1987 to 2012 there were 11 separate light traps, one of them shown in Figure 3.3. They formed a line from the proximity of the accommodation building to the northern slope of Värriötunturi fjeld, and all the way up to the treeless summit (Figure 3.1b). Three light traps were near the accommodation building where the forest is old-grown Scots pines (*Pinus sylvestris*), three traps in a ravine with spruce (*Picea abies*) dominated mixed forest, three on the northern slope in mountain birch forest, and two on the treeless summit (Hunter et al., 2014). After 2012 the number of light traps was reduced to two which locate close by to the accommodation building.

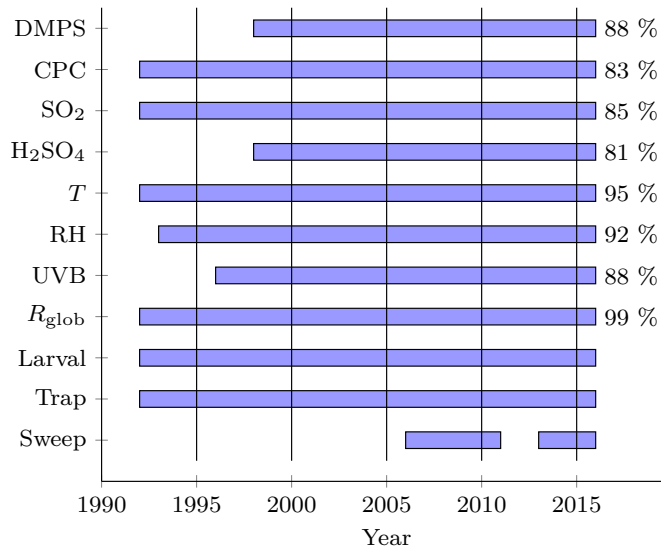
### 3.3.3 Sweeping

Sweeping is conducted approximately every fifth day from June to September. Collection is done by sweeping 100 times with the net shown in Figure 3.4a both from mountain birch branches and the bilberries (*Vaccinium myrtillus*, Figure 3.4b) on the northern slope of the Värriötunturi fjeld (Värriö, 2005). The exact spot, where the sweeping is conducted, is every time selected randomly. All the caught cater-



**Figure 3.4:** (a) Net used in sweeping of autumnal moth larvae from mountain birch branches and bilberries in Värriö. © Esko Karvinen, 2018. (b) Teuvo Hietajärvi shows how sweeping from bilberry bushes is conducted. © Veli Pohjonen, 2006.

pillars are counted and stored to ethanol filled tubes. Species are not separated, but the most abundant one by far in Värriö is autumnal moth (Hunter et al., 2014). The data are available from 2006 onwards, excluding the year 2012.



**Figure 3.5:** Timeline of ongoing measurements used in this thesis. The percentage value tells the data availability in June and July from the time period when the measurement was ongoing. Availability is calculated from 30 min averages. DMPS and CPC refer to total particle concentration calculated from DMPS and total-CPC data, respectively.

The data availability of variables used in the analysis are illustrated in the Figure 3.5.

## **3.4 Data Analysis**

In this section the beforehand data handling, filtering conditions and used statistical methods are introduced.

### **3.4.1 Treatment of Autumnal Moth Data**

Due to the changing number of light traps, the number of moths collected with light traps was normalized by the number of traps occupied during the considered year. Hence, the data from 1992–2012 were divided by 11, and data from 2013–2016 were divided by 2. The light trap method collects adult moths, but the larvae feeding cause the defoliation. Knowing the life cycle of autumnal moths (Section 2.1), could the number of adult moths be utilized in the analysis. As autumnal moths are univoltine, the number of adult moths collected in August and September with light traps must correlate with the number of larvae hatched from the eggs in June at the time of bud burst. Larval stage lasts about 4–7 weeks, so the data from light traps was shifted two months backwards from August–September to June–July.

As sweeping is conducted only about every fifth day, the number of caught larvae was interpolated linearly between the two consecutive collections. Interpolation helped to extend the analysis of daily values to days when the sweeping was not originally conducted. The interpolation was performed year by year between the first day when sweeping was conducted and July 31. In the analysis, sweeping data are presented as a sum of larvae found from mountain birch branches and bilberry bushes, because only few larvae were caught from the mountain birch branches.

### 3.4.2 Filtering

To ease the observation of enhancement in SOA formation, below described filtering conditions were set. In the outlining stage, larger perspective figures having all the data were always plotted first, to understand the behaviour of the variables and effects of the filtering. Besides the filtering conditions that will be introduced below, different limits of the filters were tested, and also filtering with respect to sulfuric acid concentration. Additionally, the data were separated with respect to event and non-event days, and different time averages and medians, including daily, monthly and yearly values, were used. All the draft figures had basically similar trends despite the data handling. The results will be discussed more detailed in corresponding sections.

#### Total Particle and SO<sub>2</sub> Concentration

H<sub>2</sub>SO<sub>4</sub>, which is a oxidation product of SO<sub>2</sub>, is known to contribute to the NPF (Kulmala et al., 2013). Thus, its effect was important to minimize when analyzing the data sets. The interest lay on the days when the total particle concentration was high but SO<sub>2</sub> concentration low. Hence, when mentioned, all the data sets were filtered according to SO<sub>2</sub> and total particle concentrations. The day was included to analysis if the 08:00–16:00 median SO<sub>2</sub> concentration was less than or equal to 0.7 ppb and total particle concentration higher than or equal to 500 cm<sup>-3</sup>. The magnitude of suitable filtering conditions were selected based on results reported by Pirjola et al. (1998) and Kyrö et al. (2014). As there was gaps in the dataset, also NaN (not a number) values were treated as to qualify the filtering conditions, to increase the number of data points in the analysis.

#### Temperature

In marked part of the analysis, the data were also filtered according to temperature. The idea was to filter out days, when the temperature was low or high. Thus, the

days, when the 08:00–16:00 median temperature was between 7 and 20 °C, were included to analysis. The set temperature interval was selected around the summer mean temperature in Värriö. In these conditions, the arctic plants have optimum temperature to grow and photosynthesize which, in turn, effect the BVOC emissions from the trees (Chapin, 1983; Aalto et al., 2014). NPF is also temperature depended, and it is unfavorable at low and high temperatures (Dada et al., 2017).

### 3.4.3 Statistical Methods

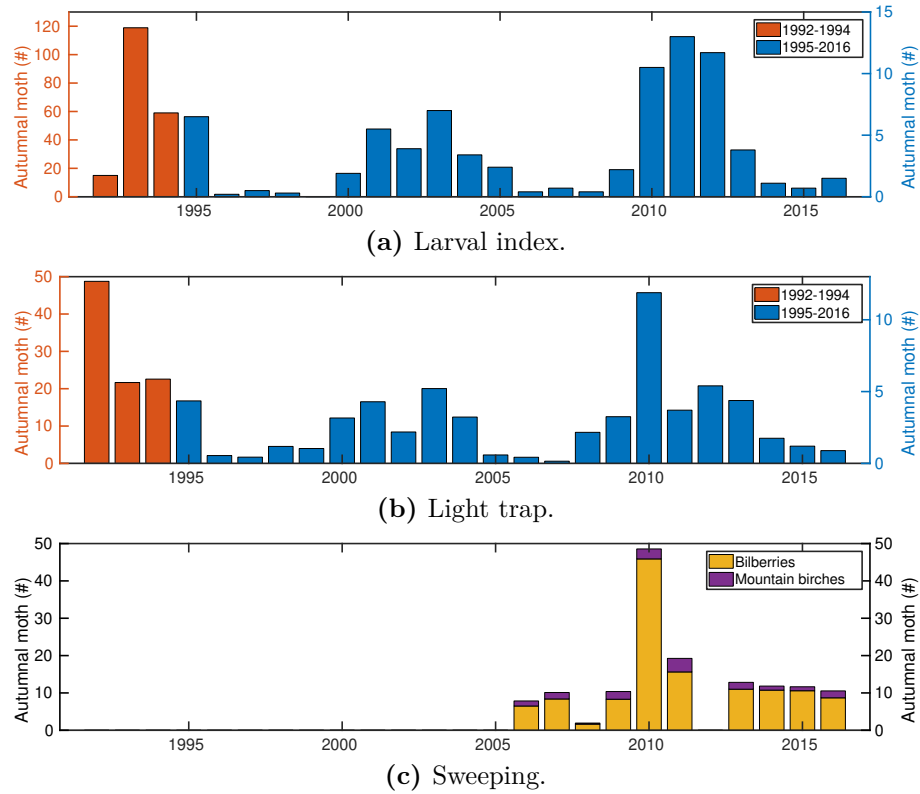
When examining the correlation between the variables, linear least squares fits were calculated to data points. Pearson’s correlation coefficient  $r$  was used for an estimate of dependency. Reported  $p$ -value describes how certain the relation is — or is the correlation caused only by coincidence. The smaller the  $p$ -value the more likely the actual dependency is. 5 % (meaning  $p$ -value 0.05) limit was applied to determine whether the correlation is statistically significant. Also, the slopes and number of data points per figure have been listed for clarification. Due to relatively low number of data points, the 95 % confidence intervals were plotted to figures. The confidence intervals show the limits in between the actual linear fit lies with 95 % confidence.

## 4. Results and Discussion

The aim of this thesis was to study whether larvae feeding on mountain birches can enhance SOA formation or growth detectably in field conditions. The research bases on long-term, continuous measurement data from research station in Finnish Lapland. The analysis was begun by investigating the outbreak dynamics of autumnal moths at the study site. Time series of the moth abundance estimated by the three methods introduced in Section 3.3, are presented in Figure 4.1. Larval index and light trap data (Figures 4.1a–4.1b) are presented so that the y-axis is different for the first three years (1992–1994) than the rest (1995–2016), due to the much higher moth densities in early 1990’s. The light trap and sweeping data are reported here as yearly averages of the original data, because the number of days when light traps were occupied and sweeping was conducted, varied between years (Hunter et al., 2014). The sweeping data are the original, non-interpolated data. Larval index is presented as such as it has only one value per year.

Figure 4.1c shows that more larvae are found from the bilberry bushes than from mountain birches. The cause may be that larvae fall down when swept with the net, and thus they would be more difficult to catch from tree branches than from bilberry bushes. The preferred host plant of autumnal moths is mountain birch, although they also feed on the leaves of other birch species, bilberries, alders and many fruit trees in the gardens (Saalas, 1949). Especially larval index and light trap data show clear cyclic population density dynamics. The same pattern is also seen in sweeping data, yet the available time series is shorter. Moreover, the estimates of the population density with different methods has similar cyclic pattern





**Figure 4.1:** Graph shows the number of autumnal moths in 1992–2016 collected with three methods: (a) larval index, (b) light trap and (c) sweeping. Light trap and sweeping data are presented as yearly averages of the original data. In (a) and (b) the y-axis is different for the first three years (1992–1994, left y-axis) than for the rest of the years (1995–2016, right y-axis). Sweeping data are presented as sum of larvae found from mountain birches and bilberry bushes.

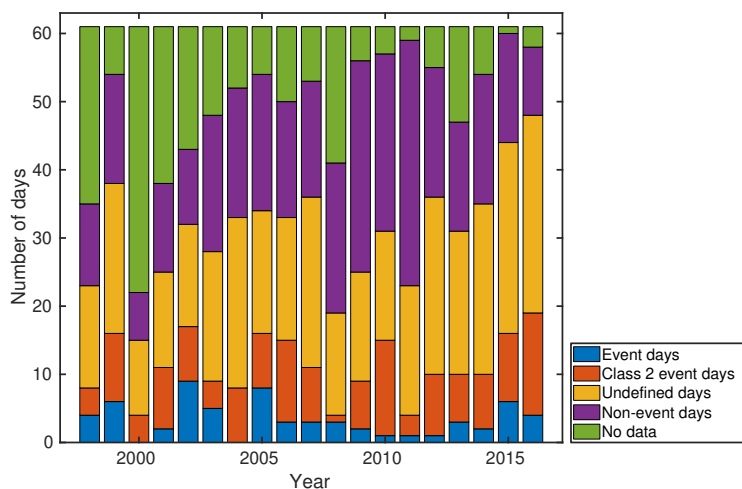
even though there is differences in details. The timing of the peak densities were also similar in other locations (Jepsen et al., 2013; Klemola et al., 2016). According to Klemola et al. (2016) the limit of severe outbreak is when the larval index is larger than 100 larvae per 10 minutes search. Hence, considering only larval index data, during 25 years period (from 1992 to 2016) there was only one year (1993) when the severe outbreak level was reached. Unfortunately, the data coverage of atmospheric variables was limited in 1993. Thus, in the analysis 2003, 2010, 2011 and 2012 were treated as years with high moth density and years 2006, 2007, 2008 and 2016 low moth density years. At some parts of the analysis, when data availability allowed, also years 1992 and 1993 were included to years with moth infestation and years 1996–1999 to stress free period. On the other hand, the fast reduce in leaf biomass

during severe moth outbreak years hinders the BVOC emissions, and thus SOA formation and growth. Hence, their meaning is diminished in the current analysis.

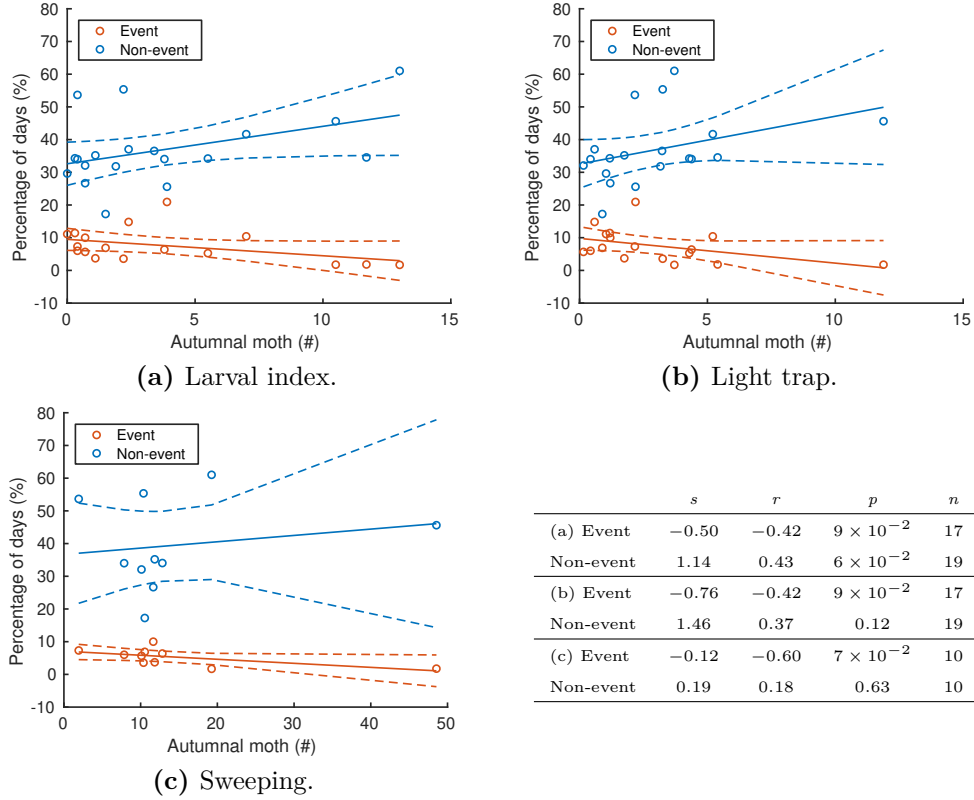
## 4.1 NPF Event Frequency Analysis

As the wounded and defoliated mountain birches emit BVOCs that may enhance the formation of new atmospheric particles, the frequency of NPF events in June and July was studied. Figure 4.2 shows the distribution of events (blue), class II events (red), undefined days (yellow), non-events (purple) and days when there was data missing (green). The number of days with missing data decrease over the years, due to improving maintenance techniques and practices at the station. The fraction of event and non-event days varies, but visually examined they do not follow the periodic pattern seen in autumnal moth data (Figure 4.1).

The correlation between event and non-event days and abundance of autumnal moths were further analyzed using scatter plots (Figure 4.3). The annual percentage of event and non-event days from June and July were plotted against the larval index data and yearly averaged number of autumnal moths caught with light traps and sweeping. When calculating the percentage of event and non-event days, the number of days with missing data were subtracted from the total number of days per year



**Figure 4.2:** Event classifications in June and July between 1998–2016.



**Figure 4.3:** Percentage of event (red) and non-event (blue) days in June and July as a function of (a) larval index and yearly averaged (b) light trap and (c) sweeping data. The number of days when DMPS data were missing have been excluded from the analysis. Solid lines are the linear least squares fits to the data points and dashed lines show the 95 % confidence intervals. Slopes of the fits  $s$ , correlation coefficients  $r$ ,  $p$ -values and number of data points  $n$  are presented in the table above for each subplot.

to eliminate the effect of data gaps to the percentage value of event or non-event days.

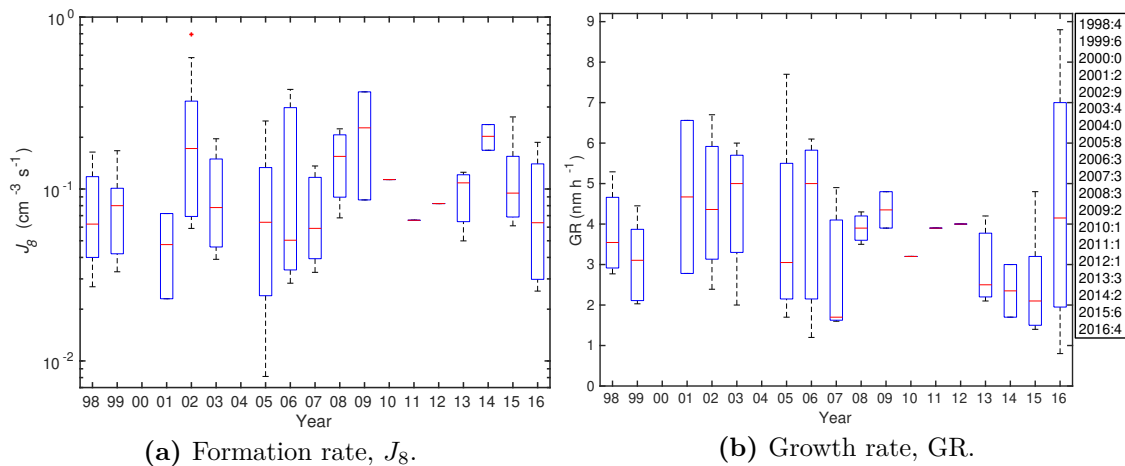
The correlation coefficients of event days show weak negative correlation, though the  $p$ -values exceed slightly the 5 % significance limit. The data from non-event days is more scattered. Only the subtle positive correlation between percentage of non-event days and larval index is statistically moderately significant. According to assumption that larval feeding contribute to SOA formation via emitted BVOCs, the number of event days should, on the contrary to the results, correlate positively with the amount of autumnal moths as long as the amount of photosynthesing biomass is not decreased essentially. During the years 1998–2016,

autumnal moth population outbreaks were not severe, and the population density was too low to cause BVOC emissions suppressing defoliation (Karlsson et al., 2005; Klemola et al., 2016).

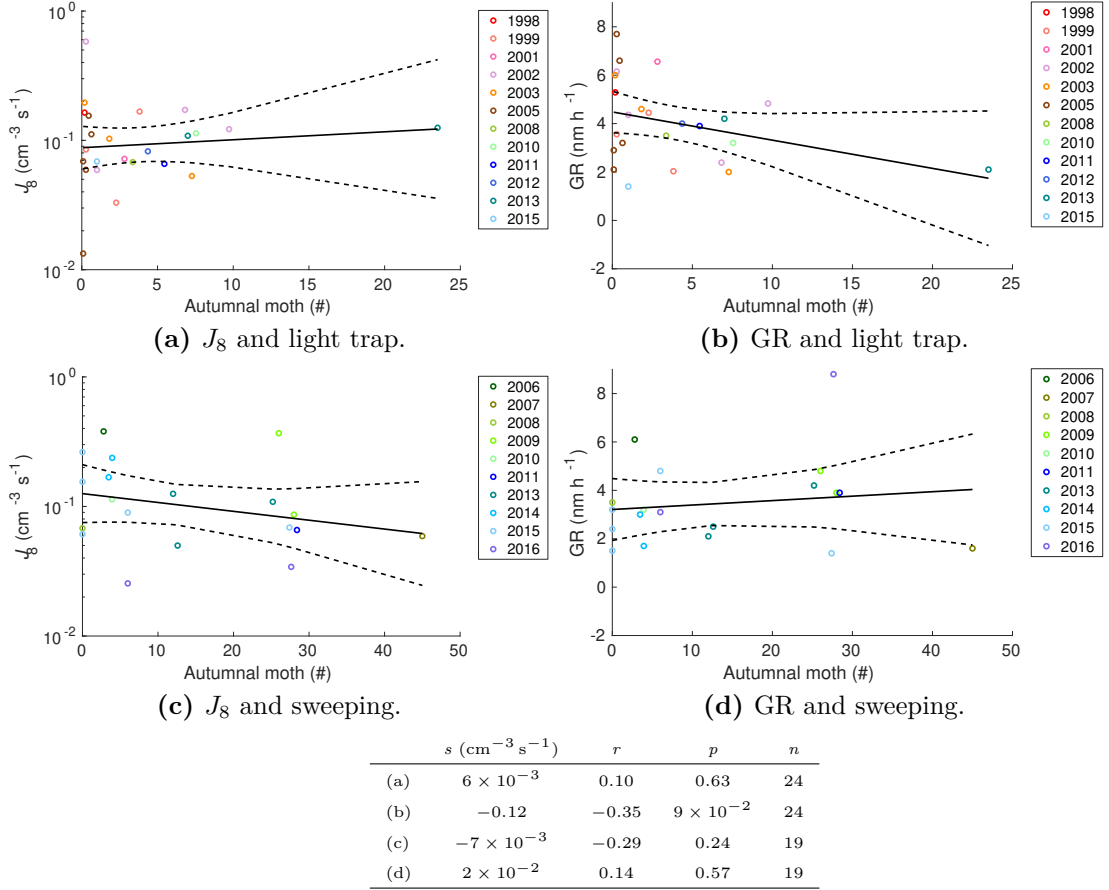
## 4.2 Formation and Growth Rates

Although there seem not to be correlation between autumnal moths and NPF events, in the field conditions the autumnal moth feeding induced BVOC emissions may affect rather to the growth of the newly formed particles than the initial nucleation. Thus, the behavior of formation and growth rates with respect to autumnal moths were examined. The first step of the analysis was to investigate yearly variation of growth and formation rates (Figure 4.4). It should be noted that there were years without or with only few data points.

Neither formation nor growth rate show clear correlation with the cyclic population dynamics of the autumnal moths. The analysis was continued by examining



**Figure 4.4:** Calculated (a) formation and (b) growth rates in June and July between 1998–2016. Both are obtained from the size range 8–25 nm. The number of data points per year are reported in table above. Note that there is years with no or only few data points. The red cross lines represent the median values and edges of the blue boxes are the 25th and 75th percentiles. Black dashed lines represent whiskers which extend approximately to  $\pm 2.7\sigma$  ( $\sigma =$  standard deviation). More extreme data points, called outliers, are plotted individually using red “+” symbol.



**Figure 4.5:** (a)  $J_8$  and (b) GR as a function of light trap data. (c)  $J_8$  and (d) GR as a function of sweeping data. Data are restricted to days when total particle concentration was high and  $\text{SO}_2$  concentration low. Coloring is the years when the observations were made. Meaning of the lines and statistical values same is as in Figure 4.3.

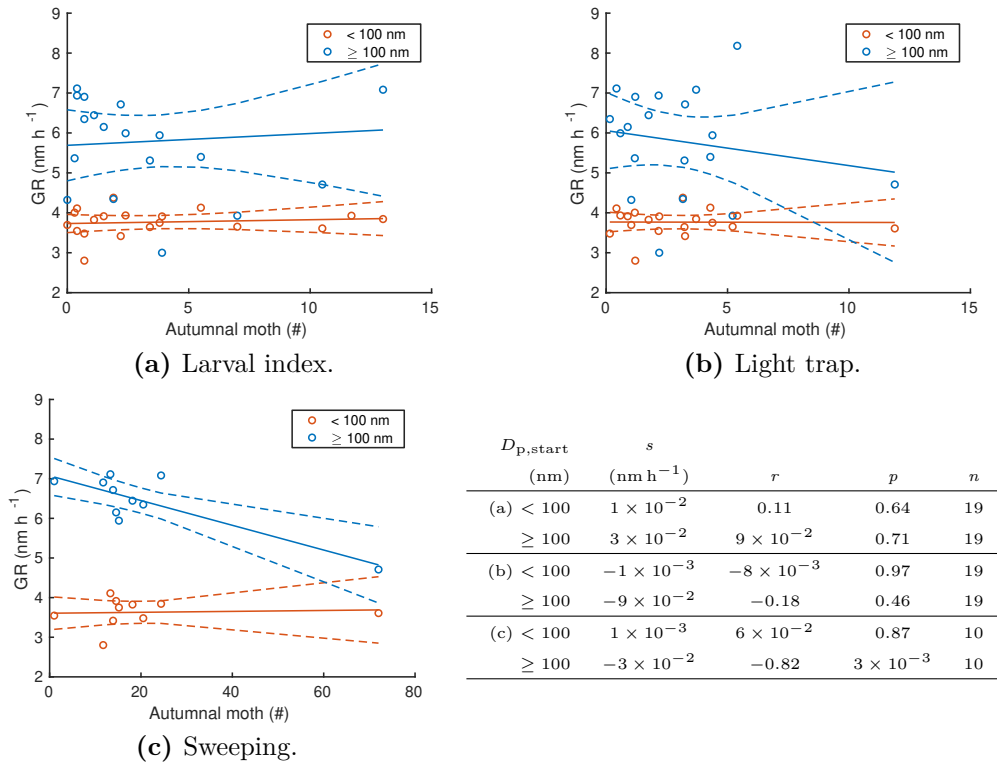
scatter plots that provide more comprehensive vision of the relations between variables. Hence, in Figure 4.5 the daily formation and growth rates were plotted against the caught number of autumnal moths. Coloring tells the year of observation. The data were filtered to consider only days when the total particle concentration was high and  $\text{SO}_2$  concentration low. Larval index data could not be used, as the analysis bases on daily values.

The examination of correlation coefficients and  $p$ -values reveal that there is not statistically significant dependence between the variables. There is few data points and they are scattered. Hence, nor can the opposite behavior of  $J_8$  and GR between

two different autumnal moth population density estimates be verified. Additionally, during the years when there is several data points, they are scattered and show no relation to the number of autumnal moths.

## 4.2.1 Automatical Growth Rates

The yearly averaged growth rates obtained with automatic method were plotted against all three autumnal moth population density estimates (Figure 4.6). The growth rate data were divided roughly to growing Aitken and accumulation modes by binning the data according to the size of the particles at the beginning of the growth. If the growing particles were initially below 100 nm in diameter they were considered as Aitken mode particles and if they were initially larger than or equal to 100 nm, they were considered as accumulation mode particles. The data were filtered with respect to total particle and SO<sub>2</sub> concentrations.



**Figure 4.6:** Yearly averaged growth rates calculated with automatic method as a function of (a) larval index and averaged (b) light trap and (c) sweeping data. Meaning of the lines and statistical values is same as in Figure 4.3.

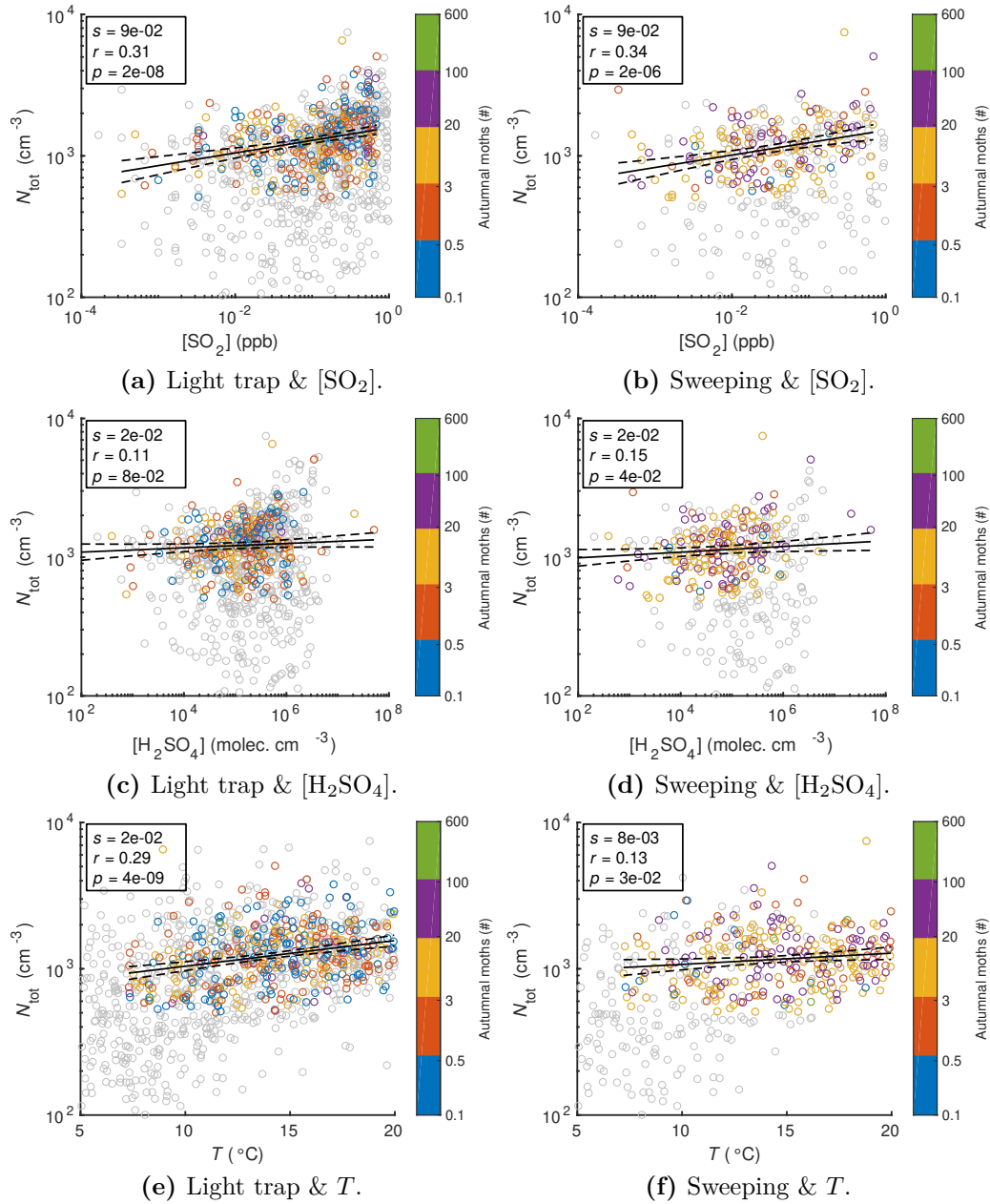
Growth rate of accumulation mode particles anticorrelate strongly with sweeping data. In other plots the scattered data points decrease the values of correlation coefficients and force  $p$ -values to exceed the 5 % significance limit by far. This investigation does not approve the enhancement by autumnal moth infestation to aerosol processes.

### 4.3 Effect of Atmospheric Variables to Aerosols

Next, the relations between total particle concentration and meteorological variables or gas concentrations were examined with respect to number of autumnal moths. The data in Figures 4.7 and 4.8 have been filtered according to temperature and total particle and SO<sub>2</sub> concentrations as introduced in Section 3.4.2. Here, the used total particle concentration was from direct ambient aerosol particle measurements, the total-CPC data, to extend the analysis to begin from 1992. In these figures, as much data were used as was available. Therefore, each subplot do not have the same amount of data, due to different launching times of the measurements (Figure 3.5). The available years and data coverage are listed in the Table 4.1. The interpolation of sweeping data cause larger data availability in plots using sweeping data compared to ones with light trap data (Section 3.4.1). In the figures, coloring is the number of autumnal moths, and gray dots show the non-filtered original data. The correlation coefficients  $r$  and  $p$ -values of the original data are presented in Table 4.2. The plotted graphs present daily values, and hence larval index data were not utilized.

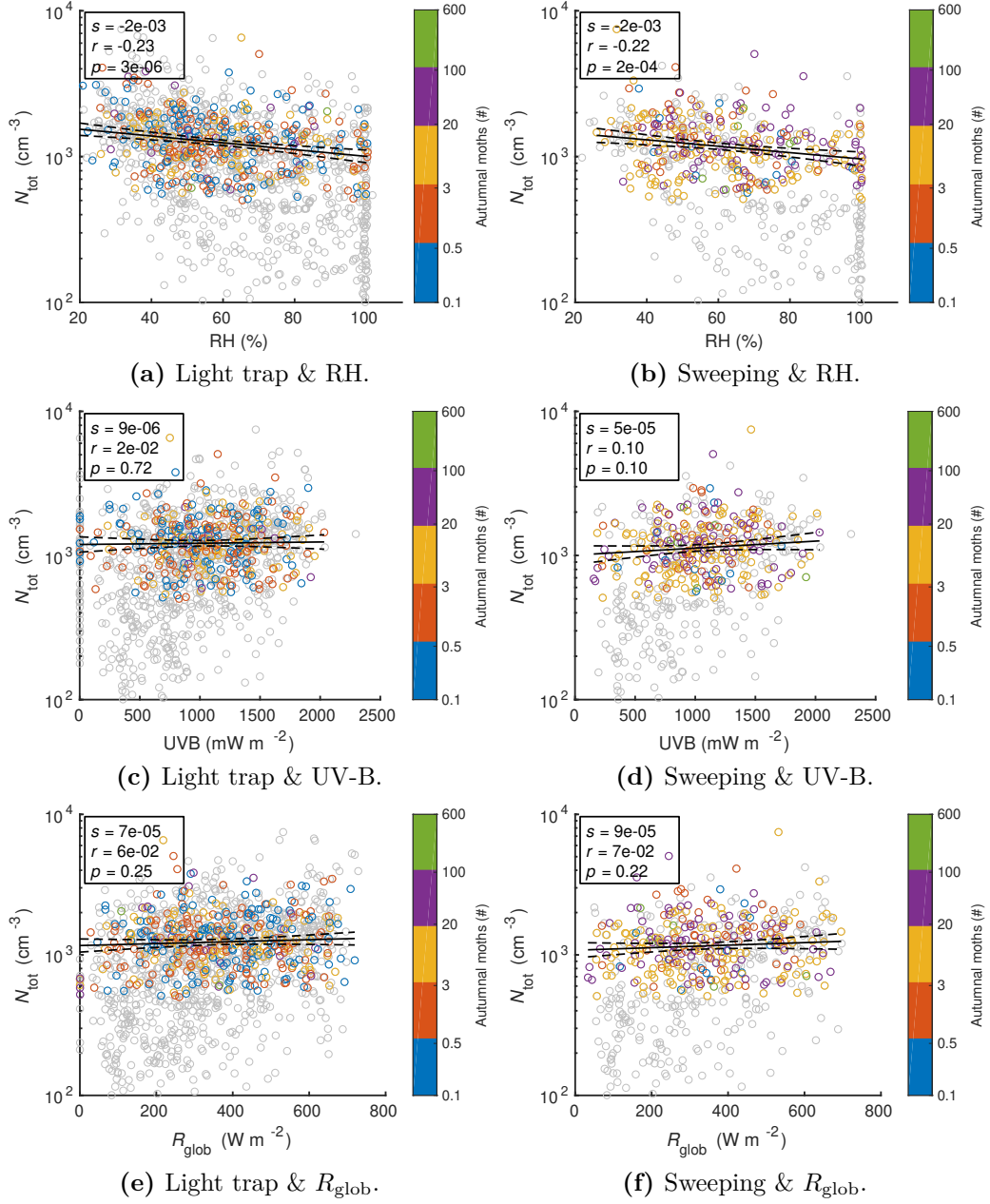
None of the presented variables show strong linear correlation with total particle concentration. Not even temperature, and hence the basal BVOC emissions. Nor SO<sub>2</sub> or H<sub>2</sub>SO<sub>4</sub> concentrations which would otherwise have been expected to correalate with the number of aerosol particles, due to the role of sulfuric acid in NPF. The differences are small between filtered and non-filtered data. Moreover, the number of autumnal moths (coloring) do not show relation to the measured variables. The results indicate that aerosol processes are more complex in the area,

and presumably the total leaf biomass is too small to lead strong temperature or infestation driven changes in aerosol load.



**Figure 4.7:** Scatter plots of total particle concentration (total-CPC) as a function of  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  concentrations and temperature (1992–2016). The data were filtered so that the considered days had high total particle and low  $\text{SO}_2$  concentrations and temperature was in the range 7–20 °C. Gray dots show the non-filtered data. The data coverage is presented in Table 4.1. Meaning of the lines and statistical values is same as in Figure 4.3.





**Figure 4.8:** Scatter plots of total particle concentration (total-CPC) as a function of RH and UV-B and gloral radiations (1992–2016). The data were filtered so that the considered days had high total particle and low  $\text{SO}_2$  concentrations and temperature was in the range 7–20 °C. Gray dots show the non-filtered data. The data coverage is presented in Table 4.1. Meaning of the lines and statistical values is same as in Figure 4.3.

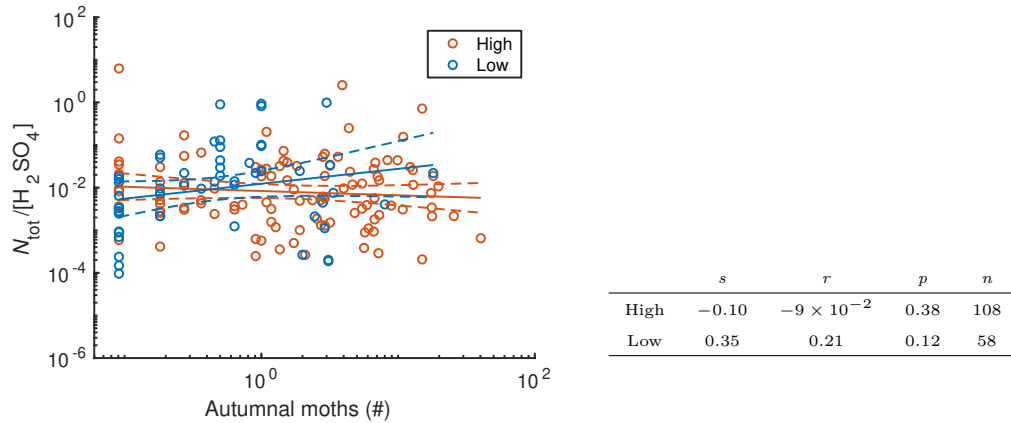
**Table 4.1:** The data availability in Figures 4.7 and 4.8. The table is constructed so that the data availability after filtering in light trap data plots is the first number, second number is the availability in sweeping method cases and last number tell the overall data availability without filtering. The maximum number of data points per year is 61 (one point per day from June and July). E.g. instrument break downs cause decrease in the available days from the maximum value.

Year	[SO <sub>2</sub> ]	[H <sub>2</sub> SO <sub>4</sub> ]	$T$	RH	UV-B	$R_{\text{glob}}$
1992	-/-/6	-/-/-	5/-/13	-/-/-	-/-/-	5/-/14
1993	-/-/9	-/-/-	-/-/9	-/-/-	-/-/-	-/-/9
1994	23/-/58	-/-/-	23/-/55	23/-/58	-/-/-	23/-/55
1995	21/-/61	-/-/-	21/-/61	21/-/61	-/-/-	21/-/61
1996	13/-/60	-/-/-	13/-/59	13/-/60	11/-/29	13/-/59
1997	7/-/55	-/-/-	7/-/56	6/-/53	7/-/56	7/-/56
1998	9/-/58	9/-/58	9/-/58	9/-/58	9/-/58	9/-/58
1999	19/-/60	19/-/60	19/-/61	19/-/61	19/-/61	19/-/61
2000	23/-/41	23/-/41	23/-/41	23/-/41	23/-/41	23/-/41
2001	21/-/60	21/-/60	21/-/60	21/-/60	21/-/60	21/-/60
2002	22/-/59	22/-/59	23/-/61	23/-/60	23/-/61	23/-/61
2003	17/-/57	17/-/57	17/-/57	17/-/57	17/-/57	17/-/57
2004	25/-/54	25/-/54	25/-/60	25/-/60	25/-/60	25/-/60
2005	20/-/44	20/-/44	22/-/47	22/-/47	22/-/47	22/-/47
2006	-/1/12	-/1/12	16/28/54	16/28/54	-/1/13	16/28/54
2007	3/13/43	3/13/43	3/13/43	3/13/43	3/13/43	3/13/43
2008	18/26/56	18/26/56	18/26/61	18/26/61	18/26/61	18/26/61
2009	22/35/57	22/35/57	23/36/58	22/35/57	23/36/58	23/36/58
2010	4/6/17	4/6/17	24/31/55	24/31/60	24/31/55	23/29/53
2011	22/27/60	22/27/60	22/27/60	22/27/60	22/27/60	22/27/60
2012	25/-/61	25/-/61	25/-/61	25/-/61	25/-/61	25/-/61
2013	26/36/60	26/36/60	26/36/61	26/36/61	26/36/61	26/36/61
2014	6/17/59	6/17/59	6/18/61	6/18/61	6/18/61	6/18/61
2015	4/35/61	4/35/61	4/35/61	4/35/61	4/35/61	4/35/61
2016	11/37/61	11/37/61	11/37/61	11/37/61	11/37/61	11/37/61

**Table 4.2:** Correlation coefficients  $r$  and  $p$ -values of non-filtered data in Figures 4.7 and 4.8.

	[SO <sub>2</sub> ]	[H <sub>2</sub> SO <sub>4</sub> ]	$T$	RH	UV-B	$R_{\text{glob}}$
$r$	0.31	$9 \times 10^{-2}$	0.51	-0.43	0.31	0.32
$p$	$8 \times 10^{-25}$	$7 \times 10^{-3}$	$2 \times 10^{-87}$	$3 \times 10^{-59}$	$7 \times 10^{-27}$	$1 \times 10^{-32}$

### 4.3.1 Normalized Aerosol Number Concentration

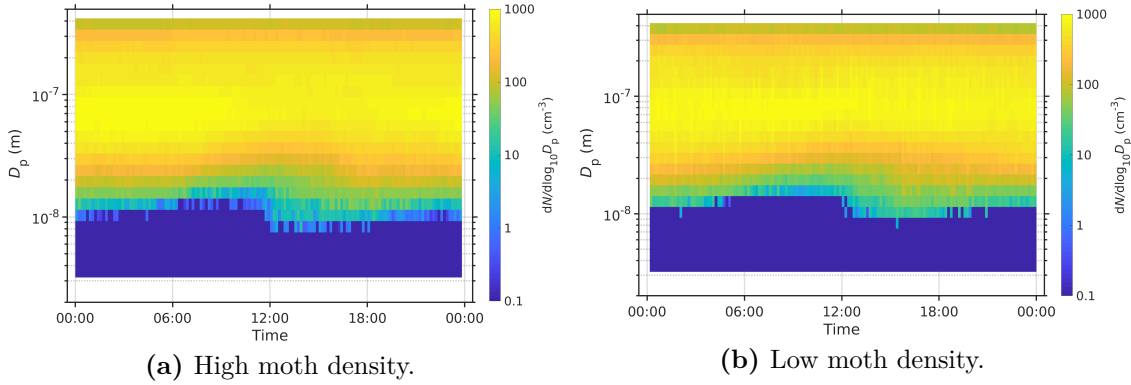


**Figure 4.9:** 08:00–16:00 median total particle concentration (from DMPS) normalized by corresponding  $\text{H}_2\text{SO}_4$  concentration from high (2003, 2010, 2011 and 2012; red) and low (2006, 2007, 2008 and 2016; blue) autumnal moth density years. The estimate of moth density is from light trap measurements. Meaning of the lines and statistical values is same as in Figure 4.3.

To emphasize the effect of autumnal moths to total particle concentration, several types of normalizations were tested. The analyses included total particle concentration normalized by  $\text{H}_2\text{SO}_4$  concentration, UV-B radiation, the product of UV-B radiation, temperature and  $\text{H}_2\text{SO}_4$  concentration and also formula of the linear fit of total particle concentration as a function of UV-B radiation. Besides total particle concentration, also concentration of particles with diameter below 25 nm was investigated. Different time averages and event–non-event day separation as discussed in Section 3.4.2 were also implied to normalized data. In all the cases the variables did not correlate linearly ( $|r| < 0.25$ ).

Figure 4.9 presents an example of total particle concentration (from DMPS) normalization by corresponding  $\text{H}_2\text{SO}_4$  concentration. The figure has values only from especially high (2003, 2010, 2011 and 2012) and low (2006, 2007, 2008 and 2016) autumnal moth density years. The moth density in the figure is from light trap measurements. The data points from different years overlap each other, and there is not differences nor correlation between the variables. This analysis did not show positive effect of larval feeding induced volatiles to aerosol load.

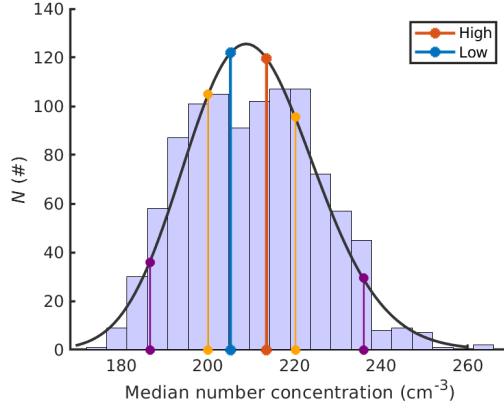
## 4.4 DMPS Size Distribution



**Figure 4.10:** Median diurnal evolution of DMPS size distribution from (a) years with high moth density (2003, 2010, 2011 and 2012) and (b) with low moth density (2006, 2007, 2008 and 2016) years.

The years with highest and lowest autumnal moth densities were compared with each other by plotting the median DMPS size distribution from June and July of high (2003, 2010, 2011 and 2012) and low (2006, 2007, 2008 and 2016) autumnal moth density years. The results are shown in Figure 4.10. The differences are minor, and statistical examination is needed. However, the statistical testing of two time series is not trivial. Hence, the testing was conducted by taking first daily medians of the aerosol number concentration from June and July days between 2003–2016. The range covers all the years when the lower limit of the DMPS system was 3 nm. Daily median of the number concentration was taken to simplify the analysis. After that, 4 random years from the range were selected, and median of the daily median number concentrations was calculated. By repeating the procedure as many times as there are different combinations of sets of 4 years ( $\binom{14}{4} = 1001$  different combinations), a distribution of median values was reached. When comparing the median number concentration from lowest and highest moth density years to the distribution, the significance of the differences could be estimated (Figure 4.11).

When reducing daily number size distribution to single median number concentration value, the information of diurnal variation is lost. Yet, the value represents

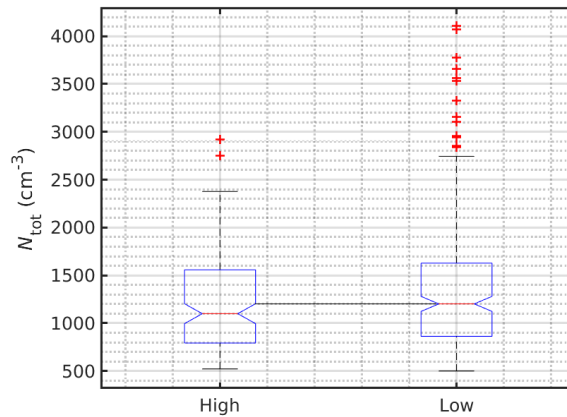


**Figure 4.11:** Lognormal distribution fitted to median values of daily median number concentrations from different sets of 4 years between 2003 and 2016. The red and blue lines show the positions of the medians from the years of high and low moth density, respectively. Yellow lines show the positions of 25 % and 75 % fractiles, and purple lines the 5 % and 95 % fractiles.

the overall aerosol particle concentration which is also affected by NPF. The procedure simplifies the analysis significantly, and allows to conclude the difference of the Figures 4.10a and 4.10b. The meteorology driven autocorrelation of subsequent days should be taken into account, if the median values in the Figures 4.10a and 4.10b were compared directly. Also, it should be noted that the data are not normally distributed, and hence many statistical tests cannot be used. When dividing the data to random combinations of sets of 4 years, the years can be assumed to be independent, and the autocorrelation can be neglected. Hence, Figure 4.11 gives a rough estimate of the statistical significance of the differences between lowest and highest autumnal moth density years.

Figure 4.11 shows that the medians of the daily median number concentrations from the highest and lowest moth density years do not stand out from the distribution of medians from random 4 years sets. Rather, they both lie within 25 % and 75 % fractiles. The plots lead to conclusion that autumnal moths do not significantly affect aerosol processes at the study site.

## 4.5 Sorting Aerosol Data



**Figure 4.12:** Notched box plots of total particle concentration (total-CPC) from high moth density years (1992, 1993, 2003, 2010, 2011 and 2012) and low moth density years (1996, 1997, 1998, 1999, 2006, 2007, 2008 and 2016). The data have been filtered to consider only high total particle and low  $\text{SO}_2$  concentration days with temperature within 7–20 °C range. Because the notches overlap, the values do not differ from each other at the 5 % significance level. Black line helps to visualize the overlapping. Otherwise the meaning of the signs are similar than in Figure 4.4.

Finally, the aerosol data were separated between the years with high and low moth densities and the results were compared. Using notched box plots, the conclusion of statistically significant differences could be made easily. If the notches do not overlap, the values are different with 95 % confidence. In Figure 4.12 the years 1992, 1993, 2003, 2010, 2011 and 2012 were considered as years with moth infestation and years 1996, 1997, 1998, 1999, 2006, 2007, 2008 and 2016 as stress free. The total particle concentration data are from total-CPC measurements. The introduced total particle and  $\text{SO}_2$  concentration and temperature filters were applied to the data. Several drafts were also made: using more and less years, filtering the data using  $\text{H}_2\text{SO}_4$  interval, or using no filtering at all. Additionally, the total particle concentration from total-CPC data were replaced with the formation and growth rates, total particle concentration from DMPS, and concentration of nucleation mode

particles (3–25 nm) integrated from the DMPS number size distribution data. The same filtering procedures were implied for these data sets yet, all the figures gave the similar results: the median values do not differ statistically significantly at 5 % significance level.

## 5. Conclusions

The aim of the study was to investigate whether the larvae of autumnal moths feeding on mountain birches have atmospherically relevant effect to aerosol load. The study is the first one trying to evaluate the enhancement of secondary aerosol production due to herbivory caused biotic stress in field conditions. It bases on the analysis of long-term field data from study site in eastern Finnish Lapland. At the study site, autumnal moths show clear about 10 years periodic outbreak cycle in population density. Considering that the site is remote with only minor human impact, and that autumnal moths are by far the most abundant defoliator in the area, the site is ideal for the evaluation.

Despite the laboratory studies reporting of emissions of such volatile organic compounds that can participate to aerosol production and growth, the present study show no correlation of aerosol related variables and the number of autumnal moths. Nor does the temperature, and hence the basal BVOC emissions via varying ambient temperature, effect clearly to particle formation or growth. The leaf biomass of mountain birches is probably too small to be able to cause detectable changes, particularly as the defoliation degree is usually less than 15 % (Karlsson et al., 2005). The average estimated biomass in subarctic region is considerable smaller, up to one order of magnitude, than that of the North European boreal forests (Häme et al., 1997; Dahlberg et al., 2004; Heiskanen, 2006). Unexpectedly, the  $\text{SO}_2$  and  $\text{H}_2\text{SO}_4$  concentrations, known to contribute to formation of new aerosol particles, do not have strong correlation with the number of atmospheric aerosols.



It should be noted that regardless of the long (25 years) period of data, the data have only two complete population density cycles which did not include severe outbreaks. The analysis of the results was complicated due to small number of data points and the scattering of the data. The time averaging and filtering decreased the number of data points. Yet, the procedure was important considering the nature of the study, as then the seasonal variation, and conditions where the enhancement due to biotic factors was more likely, could be investigated.

Ruuhola et al. (2007) found that the immunological memory of mountain birches exposed to autumnal moth feeding was at least 5 years. Hence, in addition to the direct BVOC emissions, the trees may emit stress related compounds for several years after the feeding (Haapanala et al., 2009). This could cause a time delay between the autumnal moth outbreaks and enhanced SOA formation. However, the analyzed draft figures and Figure 4.5 in the thesis show that the differences between the years are small. The time delay could be indicated by a pattern of higher values of the aerosol related variables during the years of maximum BVOC emissions. Thus, although the emission level may remain high for several years after the infestation, it is unlikely to influence significantly to the given results.

Moreover, another geometrid moth, winter moth, reached cyclic population dynamics in northern Fennoscandinavia during the measurement period. The peaks of the winter moth population occur 1–3 years after autumnal moth's. Although the population of autumnal moths at the measurement site is significantly larger, the defoliation by winter moths might still discriminate the analysis. Also, Tarvainen et al. (2005) also reported that sesquiterpene emissions in June were high from Scots pines growing in northern Finland compared to emissions from Scots pines growing in southern Finland. Needle rust by fungal infection (mainly on Norway spruce) is also common at the site. The rust cause similarly biotic stress to the infested trees. However, the rust usually appears during late summer or autumn, and thus the stress is not simultaneous with the one caused by herbivory (Tillman-Sutela

et al., 2004). Taipale et al. (2017) used a model to simulate the effects of biotic stresses to aerosol population. They found that neither constitutive nor autumnal moth feeding induced BVOCs from mountain birches led to new particle formation. Hence, VOC measurements from the study site would give valuable information on whether the local stresses and phenological states could be detected and separated.

As a consequence of climate change, the abundance of many moth species have predicted to increase and spread to regions where they did not succeed earlier (Hagen et al., 2007; Jepsen et al., 2013; Hunter et al., 2014). The overwintering eggs of autumnal moths will die if the ambient temperature decreases below  $-36\text{ }^{\circ}\text{C}$  (Tenow and Nilssen, 1990). Hence, besides the expanding living conditions, also the rise in minimum winter temperature, will increase the population density of autumnal moths. Mountain birches also respond to the warming, and treeline will extend to areas that used to be treeless (Tenow et al., 2005). Even the basal BVOC emissions are temperature dependent, and because of much faster warming of the Arctic region, these changes may be so radical that the enhancement of the aerosol processes due to biotic stresses could be observed from the atmospheric data in the future.

# Bibliography

- J. Aalto, P. Kolari, P. Hari, V.-M. Kerminen, P. Schiestl-Aalto, H. Aaltonen, J. Levula, E. Siivola, M. Kulmala, and J. Bäck. New foliage growth is a significant, unaccounted source for volatiles in boreal evergreen forests. *Biogeosciences*, 11(5):1331–1344, 2014.
- P. Aalto, K. Hämeri, E. Becker, R. Weber, J. Salm, J. M. Mäkelä, C. Hoell, C. D. O’dowd, H.-C. Hansson, M. Väkevä, et al. Physical characterization of aerosol particles during nucleation events. *Tellus B: Chemical and Physical Meteorology*, 53(4):344–358, 2001.
- R. Bergström, M. Hallquist, D. Simpson, J. Wildt, and T. F. Mentel. Biotic stress: a significant contributor to organic aerosol in Europe? *Atmospheric chemistry and physics*, 14(24):13643–13660, 2014.
- D. B. Botkin and L. G. Simpson. Biomass of the North American boreal forest: A step toward accurate global measures. *Biogeochemistry*, pages 161–174, 1990.
- F. Chapin. Direct and indirect effects of temperature on arctic plants. *Polar Biology*, 2(1):47–52, 1983.
- R. J. Charlson, S. Schwartz, J. Hales, R. D. Cess, J. J. Coakley, J. Hansen, and D. Hofmann. Climate forcing by anthropogenic aerosols. *Science*, 255(5043):423–430, 1992.
- A. J. Cohen, H. Ross Anderson, B. Ostro, K. D. Pandey, M. Krzyzanowski, N. Künzli, K. Gutschmidt, A. Pope, I. Romieu, J. M. Samet, et al. The global burden

- of disease due to outdoor air pollution. *Journal of Toxicology and Environmental Health, Part A*, 68(13-14):1301–1307, 2005.
- L. Dada, P. Paasonen, T. Nieminen, S. Buenrostro Mazon, J. Kontkanen, O. Peräkylä, K. Lehtipalo, T. Hussein, T. Petäjä, V.-M. Kerminen, et al. Long-term analysis of clear-sky new particle formation events and nonevents in Hyytiälä. *Atmospheric Chemistry and Physics*, 17(10):6227–6241, 2017.
- U. Dahlberg, T. W. Berge, H. Petersson, and C. P. Vencatasawmy. Modelling biomass and leaf area index in a sub-arctic Scandinavian mountain area. *Scandinavian Journal of Forest Research*, 19(1):60–71, 2004.
- M. Dal Maso, M. Kulmala, I. Riipinen, R. Wagner, T. Hussein, P. P. Aalto, and K. E. Lehtinen. Formation and growth of fresh atmospheric aerosols: eight years of aerosol size distribution data from SMEAR II, Hyytiälä, Finland. *Boreal Environment Research*, 10(5):323, 2005.
- N. Dudareva, F. Negre, D. A. Nagegowda, and I. Orlova. Plant volatiles: recent advances and future perspectives. *Critical reviews in plant sciences*, 25(5):417–440, 2006.
- M. Ehn, E. Kleist, H. Junninen, T. Petäjä, G. Lönn, S. Schobesberger, M. Dal Maso, A. Trimborn, M. Kulmala, D. Worsnop, et al. Gas phase formation of extremely oxidized pinene reaction products in chamber and ambient air. *Atmospheric chemistry and physics*, 12(11):5113–5127, 2012.
- M. Ehn, J. A. Thornton, E. Kleist, M. Sipilä, H. Junninen, I. Pullinen, M. Springer, F. Rubach, R. Tillmann, B. Lee, et al. A large source of low-volatility secondary organic aerosol. *Nature*, 506(7489):476, 2014.
- P. Faubert, P. Tiiva, Å. Rinnan, A. Michelsen, J. K. Holopainen, and R. Rinnan. Doubled volatile organic compound emissions from subarctic tundra under simulated climate warming. *New Phytologist*, 187(1):199–208, 2010.

- S. Fineschi and F. Loreto. Leaf volatile isoprenoids: an important defensive armament in forest tree species. *Iforest-Biogeosciences and Forestry*, 5(1):13, 2012.
- R. Grote and Ü. Niinemets. Modeling volatile isoprenoid emissions—a story with split ends. *Plant Biology*, 10(1):8–28, 2008.
- L. Gu, D. Baldocchi, S. B. Verma, T. Black, T. Vesala, E. M. Falge, and P. R. Dowty. Advantages of diffuse radiation for terrestrial ecosystem productivity. *Journal of Geophysical Research: Atmospheres*, 107(D6):ACL–2, 2002.
- A. Guenther, C. N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W. McKay, et al. A global model of natural volatile organic compound emissions. *Journal of Geophysical Research: Atmospheres*, 100(D5):8873–8892, 1995.
- A. Guenther, X. Jiang, C. Heald, T. Sakulyanontvittaya, T. Duhl, L. Emmons, and X. Wang. The model of emissions of gases and aerosols from nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions. 2012.
- S. Haapanala, A. Ekberg, H. Hakola, V. Tarvainen, J. Rinne, H. Hellén, and A. Arneeth. Mountain birch – potentially large source of sesquiterpenes into high latitude atmosphere. *Biogeosciences*, 6(11):2709–2718, 2009.
- S. B. Hagen, J. U. Jepsen, R. A. Ims, and N. G. Yoccoz. Shifting altitudinal distribution of outbreak zones of winter moth *Operophtera brumata* in sub-arctic birch forest: a response to recent climate warming? *Ecography*, 30(2):299–307, 2007.
- T. Häme, A. Salli, K. Andersson, and A. Lohi. A new methodology for the estimation of biomass of coniferdominated boreal forest using NOAA AVHRR data. *International Journal of Remote Sensing*, 18(15):3211–3243, 1997.
- P. Hari, M. Kulmala, T. Pohja, T. Lahti, E. Siivola, L. Palva, P. Aalto, K. Hämeri,

- T. Vesala, S. Luoma, et al. Air pollution in eastern Lapland: challenge for an environmental measurement station. 1994.
- P. Hari, E. Nikinmaa, T. Pohja, E. Siivola, J. Bäck, T. Vesala, and M. Kulmala. Station for measuring ecosystem-atmosphere relations: SMEAR. In *Physical and Physiological Forest Ecology*, pages 471–487. Springer, 2013.
- E. Haukioja. Putting the insect into the birch–insect interaction. *Oecologia*, 136(2): 161–168, 2003.
- J. Heiskanen. Estimating aboveground tree biomass and leaf area index in a mountain birch forest using ASTER satellite data. *International Journal of Remote Sensing*, 27(6):1135–1158, 2006.
- K. Heliövaara and I. Mannerkoski. *Metsähyönteiset: Lajintuntemus*. Helsingin yliopisto, 1987.
- H. Hellén, A. P. Praplan, T. Tykkä, I. Ylivinkka, V. Vakkari, J. Bäck, T. Petäjä, M. Kulmala, and H. Hakola. Long-term measurements of volatile organic compounds highlight the importance of sesquiterpenes for the atmospheric chemistry of a boreal forest. *Atmospheric Chemistry and Physics*, 18(19):13839–13863, 2018.
- J. K. Holopainen. Multiple functions of inducible plant volatiles. *Trends in plant science*, 9(11):529–533, 2004.
- J. K. Holopainen and J. Gershenzon. Multiple stress factors and the emission of plant VOCs. *Trends in plant science*, 15(3):176–184, 2010.
- Z. Hu and K. R. Rao. Particulate air pollution and chronic ischemic heart disease in the eastern United States: a county level ecological study using satellite aerosol data. *Environmental Health*, 8(1):26, 2009.
- M. D. Hunter, M. V. Kozlov, J. Itämies, E. Pulliainen, J. Bäck, E.-M. Kyrö, and P. Niemelä. Current temporal trends in moth abundance are counter to predicted

- effects of climate change in an assemblage of subarctic forest moths. *Global change biology*, 20(6):1723–1737, 2014.
- T. Hussein, M. Dal Maso, T. Petaja, I. K. Koponen, P. Paatero, P. P. Aalto, K. Hameri, and M. Kulmala. Evaluation of an automatic algorithm for fitting the particle number size distributions. *Boreal environment research*, 10(5):337, 2005.
- IPCC. *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2013.
- J. U. Jepsen, S. B. Hagen, R. A. Ims, and N. G. Yoccoz. Climate change and outbreaks of the geometrids *Operophtera brumata* and *Epirrita autumnata* in subarctic birch forest: evidence of a recent outbreak range expansion. *Journal of Animal Ecology*, 77(2):257–264, 2008.
- J. U. Jepsen, M. Biuw, R. A. Ims, L. Kapari, T. Schott, O. P. L. Vindstad, and S. B. Hagen. Ecosystem impacts of a range expanding forest defoliator at the forest-tundra ecotone. *Ecosystems*, 16(4):561–575, 2013.
- J. L. Jimenez, M. Canagaratna, N. Donahue, A. Prevot, Q. Zhang, J. H. Kroll, P. F. DeCarlo, J. D. Allan, H. Coe, N. Ng, et al. Evolution of organic aerosols in the atmosphere. *Science*, 326(5959):1525–1529, 2009.
- J. Joutsensaari, P. Yli-Pirilä, H. Korhonen, A. Arola, J. D. Blande, J. Heijari, M. Kivimäenpää, S. Mikkonen, L. Hao, P. Miettinen, et al. Biotic stress accelerates formation of climate-relevant aerosols in boreal forests. *Atmospheric Chemistry and Physics*, 15(21):12139–12157, 2015.
- A. Kansal. Sources and reactivity of NMHCs and VOCs in the atmosphere: A review. *Journal of Hazardous Materials*, 166(1):17–26, 2009.

- P. S. Karlsson, M. Weih, and C. Borg. Mountain birch growth in relation to climate and herbivores. In *Plant ecology, herbivory, and human impact in Nordic mountain birch forests*, pages 71–86. Springer, 2005.
- V.-M. Kerminen, X. Chen, V. Vakkari, T. Petäjä, M. Kulmala, and F. Bianchi. Atmospheric new particle formation and growth: review of field observations. *Environmental Research Letters*, 13(10):103003, 2018.
- J. Kesselmeier and M. Staudt. Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology. *Journal of atmospheric chemistry*, 33(1):23–88, 1999.
- T. Klemola, K. Ruohomäki, M. Tanhuanpää, and P. Kaitaniemi. Performance of a spring-feeding moth in relation to time of oviposition and bud-burst phenology of different host species. *Ecological Entomology*, 28(3):319–327, 2003.
- T. Klemola, T. Andersson, and K. Ruohomäki. Delayed density-dependent parasitism of eggs and pupae as a contributor to the cyclic population dynamics of the autumnal moth. *Oecologia*, 175(4):1211–1225, 2014.
- T. Klemola, T. Andersson, and K. Ruohomäki. No regulatory role for adult predation in cyclic population dynamics of the autumnal moth, *Epirrita autumnata*. *Ecological entomology*, 41(5):582–589, 2016.
- T.-M. Koski, T. Laaksonen, E. Mäntylä, S. Ruuskanen, T. Li, P. S. Girón-Calva, L. Huttunen, J. D. Blande, J. K. Holopainen, and T. Klemola. Do insectivorous birds use volatile organic compounds from plants as olfactory foraging cues? Three experimental tests. *Ethology*, 121(12):1131–1144, 2015.
- M. Kulmala, T. Petäjä, T. Nieminen, M. Sipilä, H. E. Manninen, K. Lehtipalo, M. Dal Maso, P. P. Aalto, H. Junninen, P. Paasonen, et al. Measurement of the nucleation of atmospheric aerosol particles. *Nature protocols*, 7(9):1651, 2012.



- M. Kulmala, J. Kontkanen, H. Junninen, K. Lehtipalo, H. E. Manninen, T. Nieminen, T. Petäjä, M. Sipilä, S. Schobesberger, P. Rantala, et al. Direct observations of atmospheric aerosol nucleation. *Science*, 339(6122):943–946, 2013.
- M. Kulmala, T. Nieminen, A. Nikandrova, K. Lehtipalo, H. E. Manninen, M. K. Kajos, P. Kolari, A. Lauri, T. Petäjä, R. Krejci, et al. CO<sub>2</sub>-induced terrestrial climate feedback mechanism: From carbon sink to aerosol source and back. 2014a.
- M. Kulmala, T. Petäjä, M. Ehn, J. Thornton, M. Sipilä, D. Worsnop, and V.-M. Kerminen. Chemistry of atmospheric nucleation: on the recent advances on precursor characterization and atmospheric cluster composition in connection with atmospheric new particle formation. *Annual review of physical chemistry*, 65:21–37, 2014b.
- E.-M. Kyrö, R. Väänänen, V.-M. Kerminen, A. Virkkula, T. Petäjä, A. Asmi, M. Dal Maso, T. Nieminen, S. Juhola, A. Shcherbinin, et al. Trends in new particle formation in eastern Lapland, Finland: effect of decreasing sulfur emissions from Kola Peninsula. *Atmospheric Chemistry and Physics*, 14(9):4383–4396, 2014.
- A. Laaksonen, M. Kulmala, C. O’Dowd, J. Joutsensaari, P. Vaattovaara, S. Mikkonen, K. Lehtinen, L. Sogacheva, M. Dal Maso, P. Aalto, et al. The role of VOC oxidation products in continental new particle formation. *Atmospheric Chemistry and Physics*, 8(10):2657–2665, 2008.
- J. Laothawornkitkul, J. E. Taylor, N. D. Paul, and C. N. Hewitt. Biogenic volatile organic compounds in the Earth system. *New Phytologist*, 183(1):27–51, 2009.
- R. J. Laumbach and H. M. Kipen. Respiratory health effects of air pollution: update on biomass smoke and traffic pollution. *Journal of allergy and clinical immunology*, 129(1):3–11, 2012.

- K. S. Law and A. Stohl. Arctic air pollution: Origins and impacts. *Science*, 315 (5818):1537–1540, 2007.
- J. Lehtonen and R. K. Heikkinen. On the recovery of mountain birch after Epirita damage in Finnish Lapland, with a particular emphasis on reindeer grazing. *Ecoscience*, 2(4):349–356, 1995.
- F. Loreto, C. Barta, F. Brillì, and I. Nogues. On the induction of volatile organic compound emissions by plants as consequence of wounding or fluctuations of light and temperature. *Plant, cell & environment*, 29(9):1820–1828, 2006.
- E. Mäntylä, G. A. Alessio, J. D. Blande, J. Heijari, J. K. Holopainen, T. Laaksonen, P. Piirtola, and T. Klemola. From plants to birds: higher avian predation rates in trees responding to insect herbivory. *PLoS One*, 3(7):e2832, 2008.
- T. F. Mentel, E. Kleist, S. Andres, M. Dal Maso, T. Hohaus, A. Kiendler-Scharr, Y. Rudich, M. Springer, R. Tillmann, R. Uerlings, et al. Secondary aerosol formation from stress-induced biogenic emissions and possible climate feedbacks. *Atmospheric Chemistry and Physics*, 13(17):8755–8770, 2013.
- K. Mikkola, I. Jalas, and O. Peltonen. *Suomen perhoseet: Mittarit 1*. Tampereen Kirjapaino Oy Tamprint, 1985.
- S. Miresmailli, R. Gries, G. Gries, R. H. Zamar, and M. B. Isman. Population density and feeding duration of cabbage looper larvae on tomato plants alter the levels of plant volatile emissions. *Pest management science*, 68(1):101–107, 2012.
- A. Mithöfer and W. Boland. Plant defense against herbivores: chemical aspects. *Annual review of plant biology*, 63:431–450, 2012.
- J. H. Myers and J. S. Cory. Population cycles in forest Lepidoptera revisited. *Annual Review of Ecology, Evolution, and Systematics*, 44:565–592, 2013.

- N. Ng, M. Canagaratna, J. Jimenez, P. Chhabra, J. Seinfeld, and D. Worsnop. Changes in organic aerosol composition with aging inferred from aerosol mass spectra. *Atmospheric Chemistry and Physics*, 11(13):6465–6474, 2011.
- Ü. Niinemets. Mild versus severe stress and BVOCs: thresholds, priming and consequences. *Trends in plant science*, 15(3):145–153, 2010.
- Ü. Niinemets, F. Loreto, and M. Reichstein. Physiological and physicochemical controls on foliar volatile organic compound emissions. *Trends in plant science*, 9(4):180–186, 2004.
- P. Paasonen, M. Peltola, J. Kontkanen, H. Junninen, V.-M. Kerminen, and M. Kulmala. Comprehensive analysis of particle growth rates from nucleation mode to cloud condensation nuclei in boreal forest. *Atmospheric Chemistry and Physics*, 18(16):12085–12103, 2018.
- J. Peñuelas and J. Llusià. BVOCs: plant defense against climate warming? *Trends in Plant Science*, 8(3):105–109, 2003.
- J. Peñuelas and M. Staudt. BVOCs and global change. *Trends in plant science*, 15(3):133–144, 2010.
- T. Petäjä, R. Mauldin III, E. Kosciuch, J. McGrath, T. Nieminen, P. Paasonen, M. Boy, A. Adamov, T. Kotiaho, and M. Kulmala. Sulfuric acid and OH concentrations in a boreal forest site. *Atmospheric Chemistry and Physics*, 9(19):7435–7448, 2009.
- S. D. Piccot, J. J. Watson, and J. W. Jones. A global inventory of volatile organic compound emissions from anthropogenic sources. *Journal of Geophysical Research: Atmospheres*, 97(D9):9897–9912, 1992.
- L. Pirjola, A. Laaksonen, P. Aalto, and M. Kulmala. Sulfate aerosol formation in the Arctic boundary layer. *Journal of Geophysical Research: Atmospheres*, 103(D7):8309–8321, 1998.

- M. Possell and F. Loreto. The role of volatile organic compounds in plant resistance to abiotic stresses: responses and mechanisms. In *Biology, controls and models of tree volatile organic compound emissions*, pages 209–235. Springer, 2013.
- A. Rap, C. E. Scott, D. V. Spracklen, N. Bellouin, P. M. Forster, K. S. Carslaw, A. Schmidt, and G. Mann. Natural aerosol direct and indirect radiative effects. *Geophysical Research Letters*, 40(12):3297–3301, 2013.
- J. Rinne, T. M. Ruuskanen, A. Reissell, R. Taipale, H. Hakola, and M. Kulmala. On-line PTR-MS measurements of atmospheric concentrations of volatile organic compounds in a European boreal forest ecosystem. *Boreal environment research*, 10(5):425–436, 2005.
- K. Ruohomäki, M. Tanhuanpää, M. P. Ayres, P. Kaitaniemi, T. Tammaru, and E. Haukioja. Causes of cyclicity of *Epirrita autumnata* (Lepidoptera, Geometridae): grandiose theory and tedious practice. *Population Ecology*, 42(3):211–223, 2000.
- T. Ruuhola, J.-P. Salminen, S. Haviola, S. Yang, and M. J. Rantala. Immunological memory of mountain birches: effects of phenolics on performance of the autumnal moth depend on herbivory history of trees. *Journal of chemical ecology*, 33(6):1160–1176, 2007.
- T. M. Ruuskanen, P. Kolari, J. Bäck, M. Kulmala, J. Rinne, H. Hakola, R. Taipale, M. Raivonen, N. Altimir, and P. Hari. On-line field measurements of monoterpene emissions from Scots pine by proton-transfer-reaction mass spectrometry. *Boreal Environment Research*, 10(6):553–567, 2005.
- U. Saalas. *Suomen metsähyönteiset sekä muut metsälle vahingolliset ja hyödylliset eläimet*. Suomen tiedettä. Werner Söderström Osakeyhtiö, 1949.
- K. Saravesi, S. Aikio, P. R. Wäli, A. L. Ruotsalainen, M. Kaukonen, K. Huusko, M. Suokas, S. P. Brown, A. Jumpponen, J. Tuomi, et al. Moth outbreaks alter

- root-associated fungal communities in subarctic mountain birch forests. *Microbial ecology*, 69(4):788–797, 2015.
- S. Sillman and D. He. Some theoretical results concerning O<sub>3</sub>-NO<sub>x</sub>-VOC chemistry and NO<sub>x</sub>-VOC indicators. *Journal of Geophysical Research: Atmospheres*, 107(D22):ACH-26, 2002.
- P. Stenberg, M. Rautiainen, T. Manninen, P. Voipio, and M. Mottus. Boreal forest leaf area index from optical satellite images: model simulations and empirical analyses using data from central Finland. 2008.
- D. Taipale, V.-M. Kerminen, M. Kulmala, and Ü. Niinemets. Do biotic plant stresses induce formation and growth of new particles? In *Proceedings of ‘The Centre of Excellence in Atmospheric Science (CoE ATM) – From Molecular and Biological processes to The Global Climate’ Annual Meeting 2017*, Report Series in Aerosol Science, pages 533–536. Aerosolitutkimusseura ry – Finnish Association for Aerosol Research FAAR, 2017.
- V. Tarvainen, H. Hakola, H. Hellén, J. Bäck, P. Hari, and M. Kulmala. Temperature and light dependence of the VOC emissions of Scots pine. *Atmospheric Chemistry and Physics*, 5(4):989–998, 2005.
- O. Tenow and H. Bylund. Recovery of a *Betula pubescens* forest in northern Sweden after severe defoliation by *Epirrita autumnata*. *Journal of Vegetation Science*, 11(6):855–862, 2000.
- O. Tenow and A. Nilssen. Egg cold hardiness and topoclimatic limitations to outbreaks of *Epirrita autumnata* in northern Fennoscandia. *Journal of applied Ecology*, pages 723–734, 1990.
- O. Tenow, H. Bylund, A. Nilssen, and P. S. Karlsson. Long-term influence of herbivores on northern birch forests. In *Plant ecology, herbivory, and human impact in nordic mountain birch forests*, pages 165–181. Springer, 2005.

- D. Tholl, W. Boland, A. Hansel, F. Loreto, U. S. Röse, and J.-P. Schnitzler. Practical approaches to plant volatile analysis. *The Plant Journal*, 45(4):540–560, 2006.
- P. Tiiva, P. Faubert, A. Michelsen, T. Holopainen, J. K. Holopainen, and R. Rinna. Climatic warming increases isoprene emission from a subarctic heath. *New Phytologist*, 180(4):853–863, 2008.
- E. Tillman-Sutela, A. Kauppi, A. Hilli, and J. Kaitera. Fungal injury to seed tissues of Norway spruce, *Picea abies* (L.) Karst. *Trees*, 18(2):151–156, 2004.
- A. M. Trowbridge and P. C. Stoy. BVOC-mediated plant-herbivore interactions. In *Biology, controls and models of tree volatile organic compound emissions*, pages 21–46. Springer, 2013.
- H. Valolahti, M. Kivimäenpää, P. Faubert, A. Michelsen, and R. Rinna. Climate change-induced vegetation change as a driver of increased subarctic biogenic volatile organic compound emissions. *Global change biology*, 21(9):3478–3488, 2015.
- Värriö. Värriö subarctic research station. <http://www.atm.helsinki.fi/varrio/eng/?q=node/3#Y%C3%B6hy%C3%B6nteiset>, 2005. [Online; accessed 10-July-2018].
- C. E. Vickers, J. Gershenzon, M. T. Lerdau, and F. Loreto. A unified mechanism of action for volatile isoprenoids in plant abiotic stress. *Nature chemical biology*, 5(5):283, 2009.
- A. Voulgarakis, V. Naik, J.-F. Lamarque, D. T. Shindell, P. Young, M. J. Prather, O. Wild, R. Field, D. Bergmann, P. Cameron-Smith, et al. Analysis of present day and future OH and methane lifetime in the ACCMIP simulations. *Atmospheric Chemistry and Physics*, 13(5):2563–2587, 2013.
- T. Vuorinen, A.-M. Nerg, L. Syrjälä, P. Peltonen, and J. K. Holopainen. Epirrita

- autumnata induced VOC emission of silver birch differ from emission induced by leaf fungal pathogen. *Arthropod-Plant Interactions*, 1(3):159, 2007.
- F. Wielgolaski. History and environment of the Nordic mountain birch. In *Plant ecology, herbivory, and human impact in nordic mountain birch forests*, pages 3–18. Springer, 2005.
- P. Yli-Pirilä, L. Copolovici, A. Kannaste, S. Noe, J. D. Blande, S. Mikkonen, T. Klemola, J. Pulkkinen, A. Virtanen, A. Laaksonen, et al. Herbivory by an outbreaking moth increases emissions of biogenic volatiles and leads to enhanced secondary organic aerosol formation capacity. *Environmental science & technology*, 50(21): 11501–11510, 2016.
- F. Yu, G. Luo, T. S. Bates, B. Anderson, A. Clarke, V. Kapustin, R. M. Yantosca, Y. Wang, and S. Wu. Spatial distributions of particle number concentrations in the global troposphere: Simulations, observations, and implications for nucleation mechanisms. *Journal of Geophysical Research: Atmospheres*, 115(D17), 2010.
- J. S. Yuan, S. J. Himanen, J. K. Holopainen, F. Chen, and C. N. Stewart Jr. Smelling global climate change: mitigation of function for plant volatile organic compounds. *Trends in Ecology & Evolution*, 24(6):323–331, 2009.