

Student thesis series INES nr 410

# The link between secondary organic aerosol and monoterpenes at a boreal forest site

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2016  
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Master degree thesis, 30 credits in Physical Geography and Ecosystem Analysis

Department of Physical Geography and Ecosystems Science, Lund University

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## Abstract

Secondary organic aerosol (SOA) plays a significant role in climate change by altering the global atmospheric radiation budget. Biogenic volatile organic compounds (BVOCs) are major sources for the formation of SOA. Their relationship is critical to understand the continental biosphere-aerosol-cloud-climate (COBACC) feedback mechanism but receives less attention in previous studies. In this study, a long time-series dataset (2008-2014) of SOA and monoterpene (the dominant biogenic precursor at the site) concentrations measured at the SMEAR II station in Hyytiälä, Finland, was analyzed to quantify the correlation between SOA and monoterpene concentrations. Climate factors including wind direction, temperature and relative humidity are studied to investigate their effects on the correlation.

Overall, there was a significant and moderate linear correlation between SOA and monoterpene concentration with the Pearson correlation coefficient  $R$  of 0.66. To rule out the anthropogenic influence, the dataset was filtered by selecting the data at the wind direction  $270\text{-}360^\circ$ , based on the air trajectory analysis. The correlation coefficient was improved from 0.66 to 0.68. Temperature has been found not only to affect monoterpene emission but also their oxidation and partition processes. Therefore, the correlation between SOA and monoterpene concentration was scrutinized from a number of temperature windows to study the temperature influence. The linear regression slopes at different temperature windows showed a strong temperature dependence ( $R=0.75$ ), indicating an increasing SOA yield with temperature. Following the same method, a negative correlation was found between the regression slopes and relative humidity ( $R=-0.88$ ), suggesting a decreasing SOA yield as relative humidity increased. However, this might be due to the anti-correlation between temperature and relative humidity.

Finally, the correlations between the SOA concentration increase rates and the monoterpenes oxidation rates by  $O_3$  ( $R=0.78$ ) and OH ( $R=0.36$ ) were compared, suggesting BVOC- $O_3$  was the dominant oxidation path in the night, comparing with OH. The general monoterpene oxidation level was also intense in the evening for the site.

Keywords: Physical Geography, Ecosystem Analysis, BVOC, Monoterpenes, SOA, Temperature, Relative humidity, Wind

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## List of Abbreviations

AMS: aerosol mass spectrometer

BVOC: biogenic volatile organic compound

CCN: cloud condensation nuclei

GPP: gross primary production

OH: hydroxyl radical

POA: primary organic aerosol

PTR-MS: proton transfer reaction mass spectrometer

SOA: secondary organic aerosol

VOC: volatile organic compound



# 1 Introduction

Aerosols are a mixture of solid particles, liquid or both, suspending in the air. They influence the earth's climate by altering the global radiation budget directly through scattering and absorbing solar and terrestrial radiations. They also affect the climate indirectly by taking part in the cloud condensation nuclei (CCN) and cloud droplets formation process to change the cloud properties and hydrological cycle (Tegen et al., 1996; Gouw and Jimenez, 2009).

A notable fraction of the aerosols is secondary organic aerosols (SOAs) (Merikanto et al., 2009), which are predominantly from biogenic volatile organic compounds (BVOCs) emitted by plants (Kanakidou et al., 2005). Despite the progresses made in recent years, there is still a knowledge gap in understanding the mechanisms behind the BVOC-to-SOA transformation process due to its complexity. This in turn has contributed to the the large uncertainty of aerosol-cloud radiative forcing for climate change estimation, according to IPCC (2013).

Many studies have tried to understand the mechanisms in the transformation from monoterpenes to SOA using lab and chamber experiments under a controlled environment, e.g influence from temperature and humidity (Takekawa et al., 2003; Jonsson et al., 2008; Hessberg et al., 2009). Due to the scarce measurement data, it is difficult to explore the direct link between SOA and BVOC from in situ measurements.

This thesis will serve as an ambient study based on a long term measurement data from 2008 to 2014 at a boreal forest site in Hyytiälä, Finland, with the purpose of understanding connections between SOA and monoterpenes (the dominant BVOC at the site).

## 1.1 Research objectives and questions

The aim of this study is to find out if there is any correlation between SOA and monoterpene concentrations based on the measurement data, and how different factors affect such correlations. To be more specific, the following questions will be addressed in this study:

- a) What does the measurement data (monoterpenes and SOA) look like, in terms of diurnal and seasonal variability?
- b) What is the correlation between monoterpene volume concentration and SOA mass concentration? Is there any positive correlation between the two?

- c) Is the correlation influenced by factors like wind, temperature, and relative humidity?  
And how?
- d) What is the temporal variation of monoterpene oxidation? Which monoterpene oxidation path is more dominant?

## **2 Background**

### **2.1 Atmospheric aerosols and secondary organic aerosols**

Atmospheric aerosols are a complex mixture of airborne liquid or solid particles or both in a size range from nanometer to micrometer. Study of atmospheric aerosols is among the central topics in the current environmental research, because of their significant effects on the atmospheric chemistry, climate and public health.

At a local level, aerosols are linked to air pollutions and adverse health effects, such as asthma and cardio-respiratory disease (Gouw and Jimenez, 2009). On the global scale, aerosols can influence the atmosphere and climate by altering the atmospheric energy balance (Tegen et al., 1996; Gouw and Jimenez, 2009). The feedback loops between atmospheric aerosols and the climate system will further be elaborated in section 2.4. In addition, atmospheric aerosols also affect the abundance and distribution of atmospheric trace gases by complex chemical reactions (IPCC, 2013).

The origins of atmospheric aerosols are diverse. Natural resources include ocean, vegetation, soil, fires and volcano eruptions, while anthropogenic resources comprise of fossil fuel combustion, biofuel burning, human activities like transportation heating and cooking (Boucher, 2015)

About 50% of the submicron aerosol mass is organic (Gouw and Jimenez, 2009). According to the pathway they enter the particulate phase, organic aerosols are divided into two categories. Primary organic aerosols (POA) are particles that are directly emitted to the atmosphere. The major sources of POA include fossil fuel and biomass combustion, viruses, bacteria, fungal spores and plant debris etc. (Kanakidou et al., 2005). Apart from direct emission, about 70% of the organic aerosols are secondary organic aerosols (SOA), which are produced from the oxidation of many volatile organic compounds (VOCs) (Hallquist et al., 2009). These VOCs are emitted from both natural sources (marine and terrestrial environment) and anthropogenic sources (fossil fuel, biomass burning etc.). Because of their high reactivity, VOCs tend to be oxidized in the atmosphere by oxidants like ozone (O<sub>3</sub>),

hydroxyl radical (hereafter OH), and nitrate radical (hereafter NO<sub>3</sub>) into semi- or non-volatile organic compounds with low vapor pressure, so that they will partition themselves between the gas and aerosol phases and contribute to the formation and growth of SOA (Hallquist et al., 2009) The main sources and processes of SOA formation mentioned above are summarized in Fig. 1.

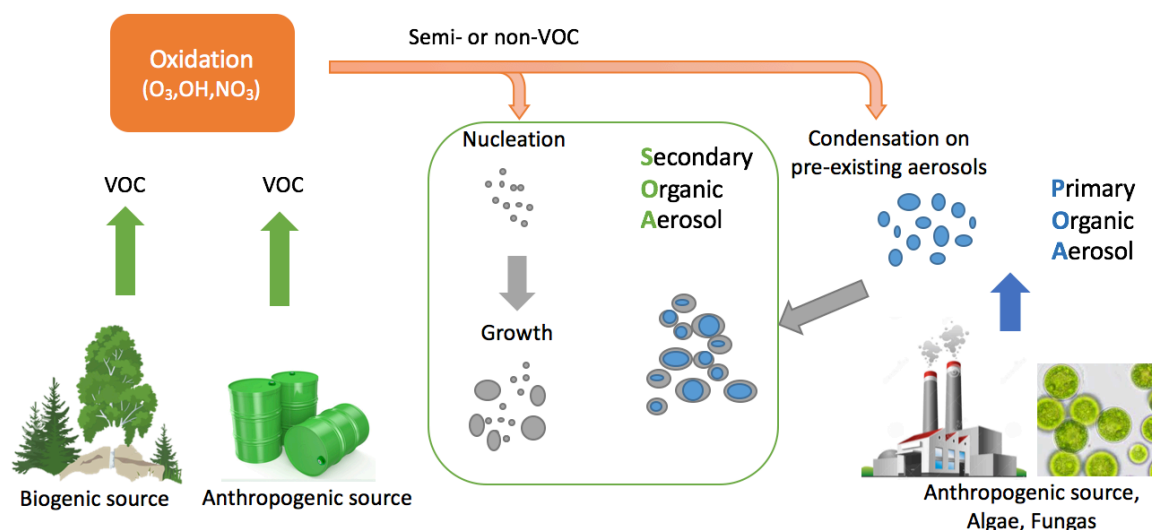


Figure 1. The major sources and formation processes of secondary organic aerosols.

However, there are still knowledge gaps in understanding relevant SOA processes and how they are related to the uncertainty on climate change. The uncertainties contributed by radiative forcing caused by aerosol particles and their interaction with clouds are the largest, comparing with other forcings (IPCC, 2013).

## 2.2 Biogenic volatile organic compounds (BVOCs)

### 2.2.1 Nature and functions of BVOC

BVOCs are a highly heterogeneous suite of organic trace gases, synthesized and emitted mostly by plants, including the terpenoids (isoprene, monoterpenes, sesquiterpenes and homoterpenes), alkanes, alkenes, alcohols, ketones, aldehydes, ethers, esters and carboxylic acids (Kesselmeier and Staudt, 1999; Fiore et al., 2012).

Some of the main BVOCs, their characters and an estimation of their global annual emissions are listed in table 1.

Table 1. Some of the BVOCs, their characters and estimated global annual emissions (Guenther et al., 1995, Kesselmeier and Staudt, 1999, Sindelarova et al., 2014)

Name	Chemical Formula	Chemical lifetimes <sup>1</sup>		Example	Atmospheric concentrations	Global emissions <sup>2</sup> Tg yr <sup>-1</sup>
		Day	Night			
Isoprene	$C_5H_8$	3 h	1.5 h	<i>isoprene</i>	ppt to several ppb	594±34
Monoterpenes	$C_{10}H_x$	2-3 h	5-30 min	<i>α-terpinene</i>	ppt to several ppb	95±3
		40-80 min	5-20 min	<i>limonene</i>		
		15-20 min	<1 min	<i>terpinolene</i>		
		<5 min	<2 min	<i>α-terpinene</i>		
Sesquiterpenes	$C_{15}H_x$	<4 min	<2 min	<i>β-caryophyllene</i>	not detectable due to high reactivity	20±1

<sup>1</sup> Lifetimes were estimated based on the oxidant condition, where  $[NO_3] = 10$  ppt,  $[O_3] = 20$  ppb during nighttime; and  $[OH] = 10^6$  molecules  $cm^{-3} \approx 0.04$  ppt,  $[O_3] = 20$  ppb during daytime. Both ppt and ppb are mol fractions, where ppt = nmol mol<sup>-1</sup> and ppb = μmol mol<sup>-1</sup>.

<sup>2</sup> The global annual emission from 1980 to 2010 estimated by MEGAN model (Sindelarova et al., 2014)

BVOCs play critical roles in plants' ecological functions. Plants release BVOCs to defend themselves against pathogens or herbivores (Paré and Tumlinson, 1999; Peñuelas and Llusà, 2004). These volatiles can either attract natural enemies of the pest insects or be toxic, indigestive or undesirable to them (Kessler and Baldwin, 2002). They may also function as a communication medium to trigger defense response in neighboring plants (Paré and Tumlinson, 1999). Some of the BVOCs are emitted to protect the plants under extreme conditions, such as high temperature and pollution (Sharkey and Singsaas, 1995; Peñuelas and Llusà, 2003).

### 2.2.2 BVOC emissions

Almost all plant organs can emit volatile isoprenoids, such as leaves, bark, flowers, fruits as well as roots (Loreto and Schnitzler, 2010). Some of the BVOCs (e.g. isoprene) are emitted directly after synthesis (e.g. Ghirardo et al., 2010), while others (e.g. monoterpenes) can also

be emitted from storage structures like resin ducts or glandular trichomes (e.g. Grote and Niinemets, 2008; Niinemets and Monson, 2013).

Because of BVOCs' various functions, their emissions are usually influenced by a number of factors, including internal factors such as plant species and gene, and external factors like temperature, light, air composition, foliar moisture, mechanical stress and injury (Kesselmeier and Staudt, 1999).

Monoterpene emissions, for instance, are mostly dependent on the factor of temperature. Their emission would increase exponentially with temperature up to an optimum, based on the monoterpene emission approximation models (Guenther et al., 1993). It is because that higher temperature favors BVOC synthesis through higher enzyme activity, and stimulates the emission process by enhancing the BVOC vapor pressure and decreasing the resistance of the diffusion pathway (Holopainen and Gershenzon, 2010). Variations of isoprene emissions are mainly attributed to the change of light and temperature (Guenther et al., 1993)

On a global scale, the annual BVOC emission is estimated to be about 1000 Tg C yr<sup>-1</sup> (Guenther et al., 2012), which exceeds the total anthropogenic VOC emissions (about 150 Tg yr<sup>-1</sup>) by an order of magnitude (Müller, 1992). About 50% of them is isoprene and 15% are monoterpenes (Guenther et al., 2012).

### **2.2.3 Boreal forest and BVOC emissions**

Boreal forests cover a vast land area (approximately 15 million square kilometer), which is about one-third of the global forested land. The dominant flora of boreal forests are pines and spruces (Tunved et al., 2006).

About half of the natural VOC emissions are originated from tropical woodlands (tropical rain forest, tropical seasonal, drought-deciduous and savanna woods), which cover about 15% of the global land surface (Guenther et al., 1995). Comparing with tropical forests, boreal forests are suggested to much less effective when it comes to BVOC emissions.

Nevertheless, the volatiles from boreal forests become increasingly important under the climate change context. It is especially true in the northern high latitude where much of the landscape is covered by boreal forests and a rapid climate change has taken place. BVOC emissions are very likely to change as a result of longer growing season and change of

species composition (e.g. more evergreen vegetation because of the warming) (Peñuelas and Staudt, 2010).

### **2.3 BVOC-to-SOA transformation**

SOA formation was briefly described in section 2.1. Biogenic VOCs are easily oxidized in the atmosphere by O<sub>3</sub>, OH and NO<sub>3</sub> into semi- or non-volatile organic compounds with very low vapor pressure. They will partition themselves between the gas and aerosol phases and form SOA (Hallquist et al., 2009). It is a very complicated process and mechanisms behind still remain uncertain.

Oxidants plays an important role in the transformation process. Different oxidation paths would affect the volatility of the condensable oxidation products and hence influence the SOA yield (Hao et al., 2011). The differences between the oxidation paths also affect the particle nucleation and growth rate in a varying way (Hao et al., 2009).

Temperature influences the SOA formation as well but its impact is quite uncertain. A chamber study by Takekawa et al. (2003) showed that temperature had a negative impact on SOA yield and the SOA concentration generated. However, Hessberg et al. (2009) found a positive temperature impact on SOA formation under a dry condition and negative impact under humid condition. Consequently, humidity might affect the SOA formation together with temperature, but the mechanisms behind it was unclear.

### **2.4 The role of BVOC and SOA in the aerosol-cloud climate feedback loop**

The continental biosphere-aerosol-cloud-climate (COBACC) feedback mechanism is linking BVOCs, SOA and cloud together to show a potential negative feedback on the climate (Fig. 2). The COBACC mechanism is comprised of two feedback loops. The upper loop is a negative climate feedback mechanism suggested by Kulmala et al. (2004a). Increased temperatures and atmospheric CO<sub>2</sub> concentration will boost continental BVOC emissions. Through oxidation and gas-particle partition, these BVOCs will lead to the formation and growth of SOA, resulting in higher concentrations of CCN and cloud droplet formation. More clouds will further induce a cooling effect. This feedback mechanism is similar to the CLAW-hypothesis (Charlson et al., 1987), which suggested that the increase of CCN

production can be triggered by sulfur emissions from plankton and hence forming a negative feedback between the climates and the ocean ecosystems.

Kulmala et al. (2013) extended the idea of COBACC mechanism by adding the lower positive feedback loop connecting aerosols with radiation and eventually the gross primary production (GPP). An increasing aerosol load tends to generate more diffusive radiation by scattering more light (e.g. Anton et al., 2012). This in turn can enhance the photosynthesis and GPP since more radiation could reach lower canopy where the light use efficiency for photosynthesis is higher (Mercado et al., 2009).

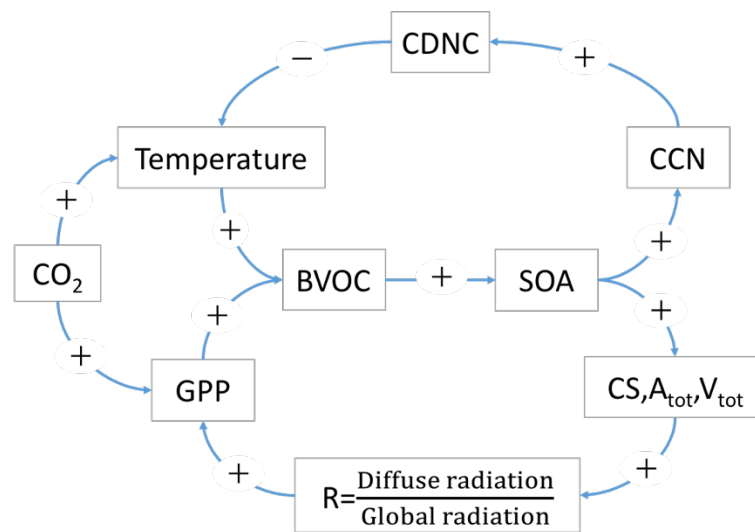


Figure 2. The two feedback loops associated with the COBACC feedback. GPP refers to the gross primary production, BVOC to the biogenic volatile organic compounds, SOA is the secondary organic aerosol, CCN is the cloud condensation nuclei, CDNC refers to the cloud droplet number concentration, CS is the condensation sink,  $A_{tot}$  is the total aerosol surfaced area and  $V_{tot}$  is the total aerosol volume. (modified from Kulmala et al., 2014).

Studies have already provided the support for the existence of the COBACC negative aerosol cloud feedback. An observation based study by Tunved et al. (2006) showed a substantial SOA formation from BVOC in the boreal forest in northern Europe. They further estimated that about 1000-2000 climatically active aerosol particles per cubic centimeter were provided by the forest during the late spring to early fall period. Paasonen et al. (2013) also discovered an exponential increase of CCN number concentration with temperature at different sites in the continental mid- and high-latitude environment.

Anthropogenic emissions of GHGs have increased substantially during the past century. Elevated concentrations of  $CO_2$  and methane are the most important forcing agents causing global warming (IPCC, 2007). However, it is not straightforward to attribute or predict the

climate change in detail and there are many feedback mechanisms that are difficult to quantify.

### 3 Material and methods

#### 3.1 Site description

All measurement data are obtained from the online database for the SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations) in Hyytiälä, Finland (Junninen et al., 2009) ( $61^{\circ}51'N$ ,  $24^{\circ}17'E$ ). The station provides services for multidisciplinary researches on forests, peat lands and atmosphere during the past decade.

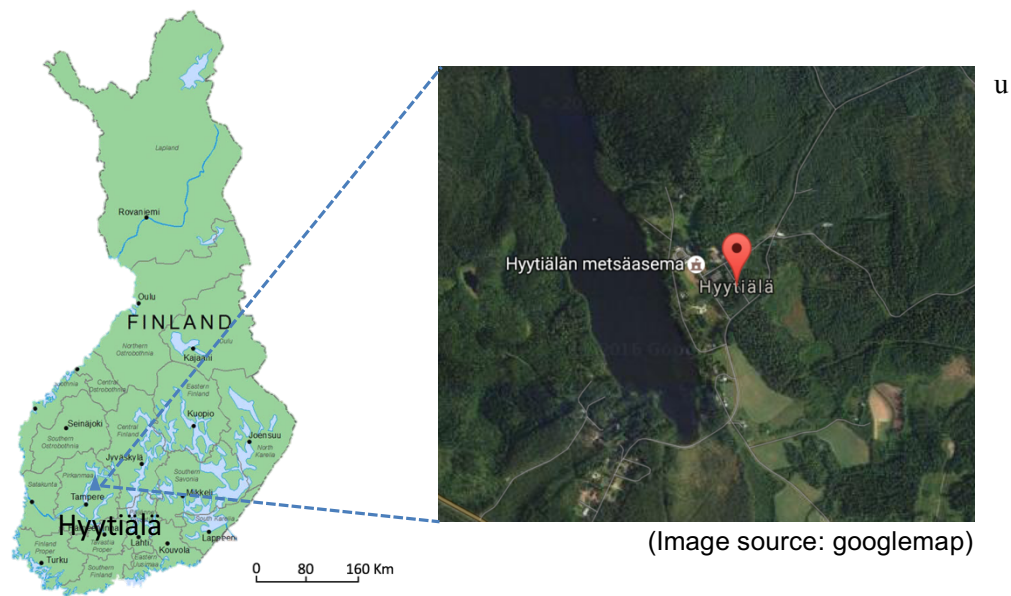


Figure 3. Location of the Hyytiälä SMEAR II measurement site.

The SMEAR II site consists of a managed forest stand, two open oligotrophic fen sites and a humic lake with forested catchment. The forest site is a homogeneous Scots pine (*Pinus sylvestris*) forest sown in 1962 (Hari and Kulmala, 2005). The annual mean temperature is  $3^{\circ}C$  and precipitation is 700 mm (Kulmala et al., 2001).

The study site is situated in a rural area with a relatively clean environment, but air masses from nearby cities (e.g. Tampere about 60 km to the south-west and Jyväskylä about 100 km to the north-east), as well as the pellet factory and sawmills nearby (e.g. Korkeakoski sawmill



about 12 km to the south-east) can sometimes leave anthropogenic influences in the data measurements.

Since 1996 the forest measurements have been conducted continuously, which include leaf, stand and ecosystem scale measurements of green-house gases, volatile organic compounds, pollutants (e.g. O<sub>3</sub>, SO<sub>2</sub>, NO<sub>x</sub>) and aerosols, as well as a full suite of meteorological measurements. The site has full carbon, water and nitrogen budgets made over 10 years, and it is a full Integrated Carbon Observation System (ICOS) ecosystem station (ExpeER, 2016).

A more detailed description about the site and instrumentations was given by Hari and Kulmala (2005), available at <http://www.atm.helsinki.fi/SMEAR/>.

### **3.2 Data and measurement**

SOA concentration was measured by the aerosol mass spectrometer (AMS) every five minutes at the ground level from 2008 to 2011, and from 2013 to 2014, mainly during spring and summer seasons. The measured SOA was the mass concentration of organic aerosols with the size range between 60nm and 1000nm and therefore it should be noted that it is not a direct measurement of SOA but rather total organic aerosol, irrespective of origin or age of aerosol. Monoterpene concentrations was measured at the height of 14 m from 2006 to 2008 and at 8.4m from 2010 to 2014 by the proton transfer reaction mass spectrometer (PTR-MS; Taipale et al., 2008) every six minutes in an hour and with two hours' interval in between. Prior to analysis, these data gaps for monoterpenes (less than two hours, the rotation time of sampling cycle) were filled by linear interpolation. All negative values of monoterpene and SOA concentrations were also removed from the datasets.

O<sub>3</sub> concentration we used was measured at 4.2m every six minutes with an ultraviolet light absorption gas analyzer (TEI 49C Ozone analyzer, Thermo Fisher Scientific, Inc., Waltham, MA, USA). Ultraviolet B radiation in wavelength range 280-320 nm was measured at 18 m height in the radiation tower with Solar Light SL501A radiometer. Air temperature was measured at 4.2m. Wind direction is an average of above-canopy records, measured from the height from 16.8 to 67.2 m.

Most of the data were averaged to 30-min mean values before the analysis, including SOA concentration, monoterpene concentration, O<sub>3</sub> concentration, UVB radiation, air temperature. Wind direction data was selected from the 1-minute interval data according to the time stamp. An important assumption with regard to the measurements is that the data measured at a specific point in the station would represent the average level of the bigger area because of the homogeneity. A brief summary of data descriptions could be seen in Table 2.

Table 2. A summary of data from Hyytiälä SMEAR II station used for this study.

	Unit	Measurement period	Sampling frequency	Sampling height
Monoterpene volume concentration	ppb	2006-2008 2010-2014	6 min	14m (2006-2008) 8.4m(2010-2014)
SOA mass concentration	µgm <sup>-3</sup>	2008-2011 2013-1014	5 min	ground level
O <sub>3</sub>	ppb	2008-2014	6 min	4.2m
UVB radiation	wm <sup>-2</sup>	2008-2014	1 min	18m
Air temperature	°C	2008-2014	1 min	4.2m
Wind direction	°	2008-2014	1 min	16.8-67.2m
Relative humidity	%	2008-2014	6 min	4.2m

Reference: Junninen et al., 2009

### 3.3 Correlation analysis and Pearson correlation coefficient

To quantify the link between SOA and monoterpene concentration and study the impact from temperature, wind direction and relative humidity, a correlation analysis was carried out for multiple times using a long time series data from Hyytiälä SMEAR II station.

The statistical correlation is the Pearson correlation coefficient based on the Equation 1.

$$R = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2} \sqrt{\sum_{i=1}^n (y_i - \bar{y})^2}} \quad (1)$$

N is the size of dataset x and y,  $\bar{x}$  and  $\bar{y}$  are the mean values.

### 3.4 Temporal variation of monoterpene oxidation

To find out the temporal variations of monoterpene oxidation, the diurnal and seasonal pattern was plotted based on the number concentration data of monoterpene oxidation products, provided by Jenni Kontkanen from University of Helsinki. Kontkanen et al. (2016) developed a monoterpene proxy to estimate number concentration of monoterpene oxidation products by O<sub>3</sub>, OH and NO<sub>3</sub> for Hyytiälä (Equation 2). More details of the method and the equations are available in Kontkanen et al. (2016).

$$[Oxorg] = \frac{(K_{OH+MT}[OH]+K_{O_3+MT}[O_3]+K_{NO_3+MT}[NO_3]) \times MT_{proxy}}{CS} \quad (2)$$

K<sub>OH+MT</sub>, K<sub>O<sub>3</sub>+MT</sub> and K<sub>NO<sub>3</sub>+MT</sub> are reaction rate coefficients between monoterpenes and different oxidants, MT<sub>proxy</sub> is the concentration of monoterpenes based on monoterpene proxy, [oxorg] is the number concentration of monoterpene oxidized products.

### 3.5 The dominant monoterpene oxidation path

To find out which monoterpene oxidation path contributes more to the SOA formation, monoterpene oxidation rate by OH/O<sub>3</sub> and the increase rate of SOA concentration were compared.

The following equations were used in order to estimate the monoterpene oxidation rate by OH and O<sub>3</sub> respectively.

$$[OR]_{OH} = K_{OH} \times [OH] \times [MT] \quad (3)$$

$$[OR]_{O_3} = K_{O_3} \times [O_3] \times [MT] \quad (4)$$

[OR]<sub>OH</sub> refers to oxidation rate with OH and [OR]<sub>O<sub>3</sub></sub> to oxidation rate with O<sub>3</sub>. [OH] is OH concentration and [MT] is monoterpene concentration. [O<sub>3</sub>] is O<sub>3</sub> concentration.

OH concentration in Eq.3 has no direct measurement at Hyytiälä station. It was therefore estimated from the intensity of UVB radiation as in Eq.5 (Petäjä et al., 2009), because of the high correlation between UVB radiation and OH concentration (Rohrer and Berresheim, 2006).

$$[\text{OH}]_{\text{proxy}} = 5.62 \times 10^5 \times \text{UVB}^{0.62} \quad (5)$$

Both  $K_{\text{OH}}$  ( $7.5 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ) and  $K_{\text{O}_3}$  ( $1.4 \times 10^{-17} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ) are constants derived from weighted averages of the reaction coefficients of individual monoterpenes particularly for SMEAR II according to Hakola et al. (2012).

For SOA, we used the average SOA concentration increase rate on a daily basis. By linearly fitting the SOA concentration data with time for each day, we could retrieve the slope, which tells us the average rate at which SOA increases during a day. In my calculation, only data from April-October were included because there were more available data during these months. Data from 00:00 and 02:00 were also selected because the previous diurnal analysis showed that SOA had a general trend of increase (Fig. 5) during this time. In addition, only results from relatively good linear fit ( $R > 0.7$ ) were kept for the later analysis. These three conditions will allow us to get a more reliable SOA concentration increase rate.

To keep a consistency, both monoterpene oxidation rate by  $\text{O}_3$  and OH were calculated using data between 00:00 and 02:00 for April-October, and then averaged to a daily value.

## 4 Results

### 4.1 Diurnal and seasonal variations of monoterpenes and SOA

The monoterpene concentration averaged for the period 2006-2014 showed distinct diurnal variations between growing seasons (May to October) and non-growing seasons (November to April) (Fig. 4). For instance, in the months of June July and August, the monoterpene concentrations had the highest values (i.e. 0.7-0.85 ppb) at night, and the lowest values (i.e. 0.2-0.4 ppb) at noon. From November to April, the diurnal variations were much smaller. In August and September, there was a tendency for the data to demonstrate dual peaks, one of which occurring in the late evening around 21:00-23:00 and the other occurring before dawn around 01:00-03:00.

The highest monoterpene concentrations (i.e.0.85 ppb) in a year were reached in June and July during nighttime when atmospheric boundary layer depth was low and emitted monoterpenes could stay in a more stable surface layer. In winter months (November, December, January, February and March), the average monoterpene concentrations were much lower, almost just one-third of the concentration level in summer months (June, July, and August). The number of measurement data points in each month for calculating the average monoterpene concentration are listed in Fig. 4.

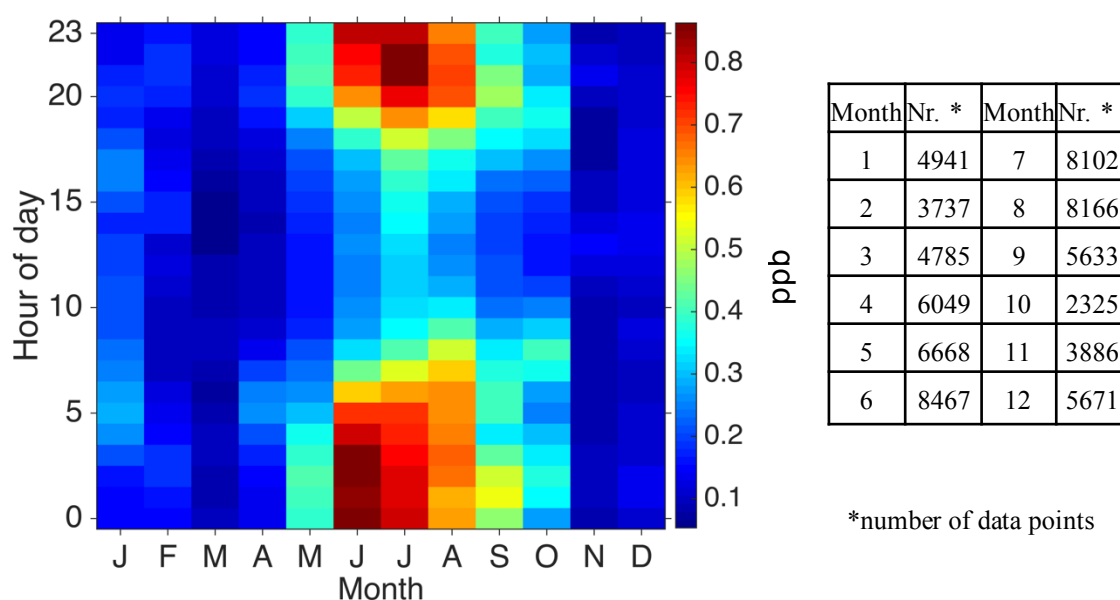


Figure 4. Diurnal and seasonal variations of average monoterpene concentration from 2006 to 2014, and the number of data points used for the calculation.

The diurnal pattern of average SOA concentrations are shown in Fig. 5. Similarly, for most of the months, such as May, June, July, September and October, the diurnal variations of the average SOA concentration showed similar patterns, with the daily maximum occurring between 02:00-05:00 and the daily minimum occurring between 11:00 to 20:00. For August and September, two peaks were observed during a day. In August, these two peak values occurred at about 05:00 and 14:00, while in September they appeared at about 03:00 and 20:00 (Fig. 6).

The SOA concentrations in summer (June, July and August) were higher in a year with the highest level in July (Fig. 5). The number of measurement data points in each month for calculating the average was also given in Fig. 5. There were no measurement data in January, February, November and December, and hence the concentration values in these months were not comparable with other months.

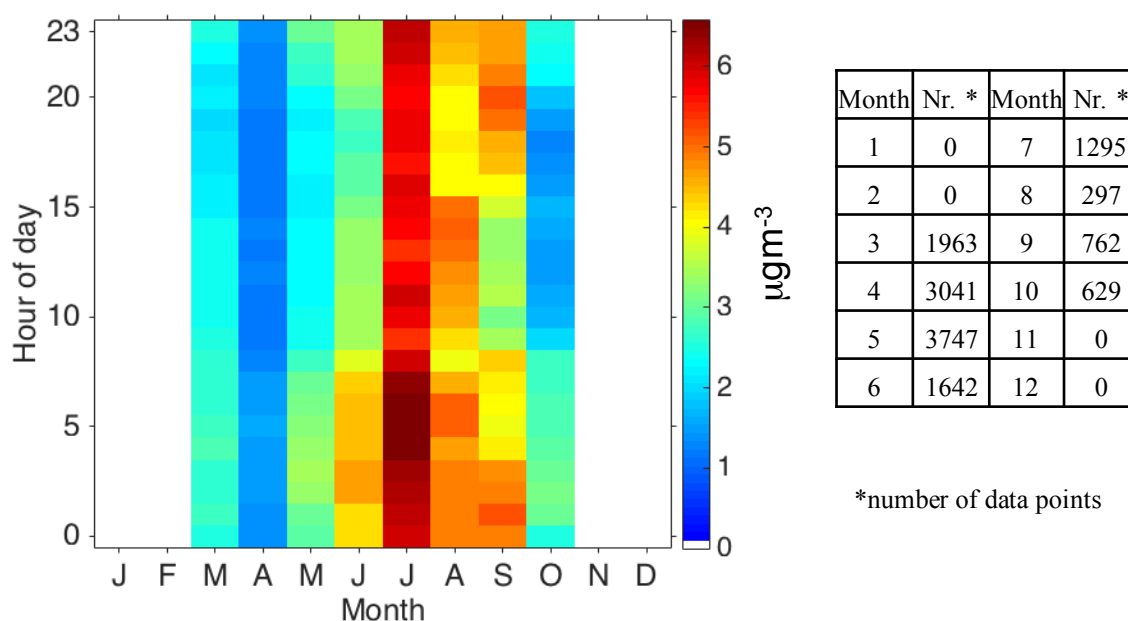


Figure 5. Diurnal and seasonal variations of average SOA concentration from 2008 to 2011, and 2013 to 2014, as well as the number of data points used for the calculation.

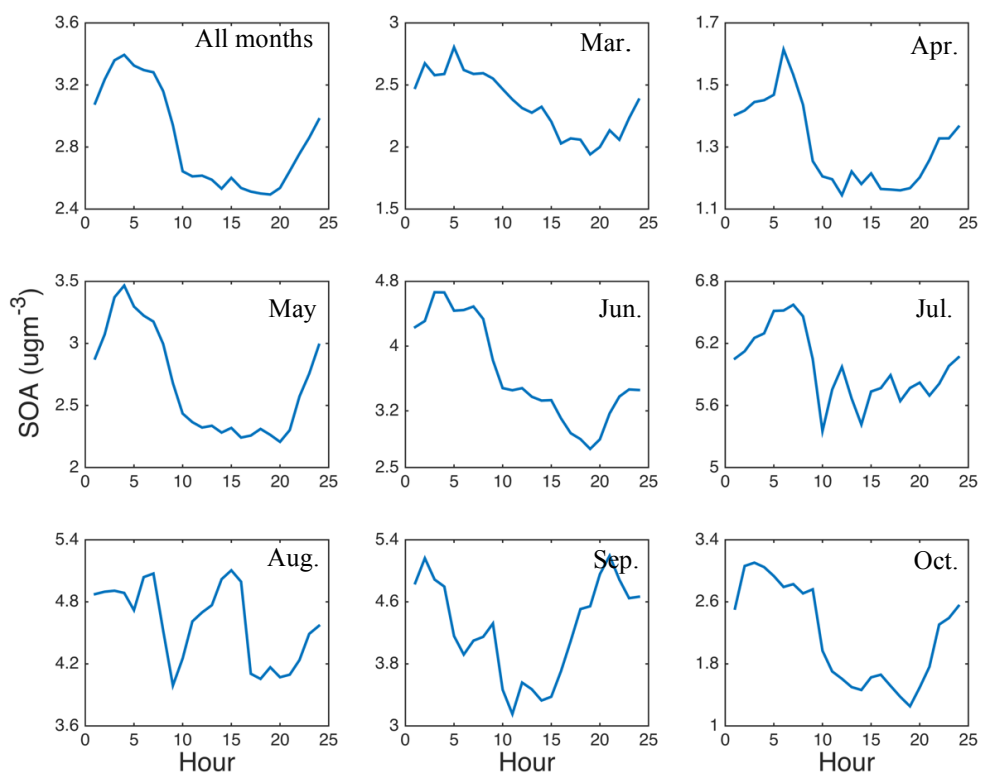


Figure 6. Average SOA concentration in individual month from Mar. to Oct as well as for all months for years 2008 to 2011 and 2013 to 2014.

## 4.2 Correlation analyses between SOA and monoterpene concentration

### 4.2.1 Overall correlation between SOA and monoterpene concentration

In general, SOA concentration data showed a large variation at a given monoterpene concentration (Fig. 7). When monoterpene concentration increased, SOA concentration tended to increase as well.

There was a significant and moderate linear correlation between SOA and monoterpene concentration on a logarithmic scale (Fig. 7), where the Pearson correlation coefficient  $R$  is 0.66.

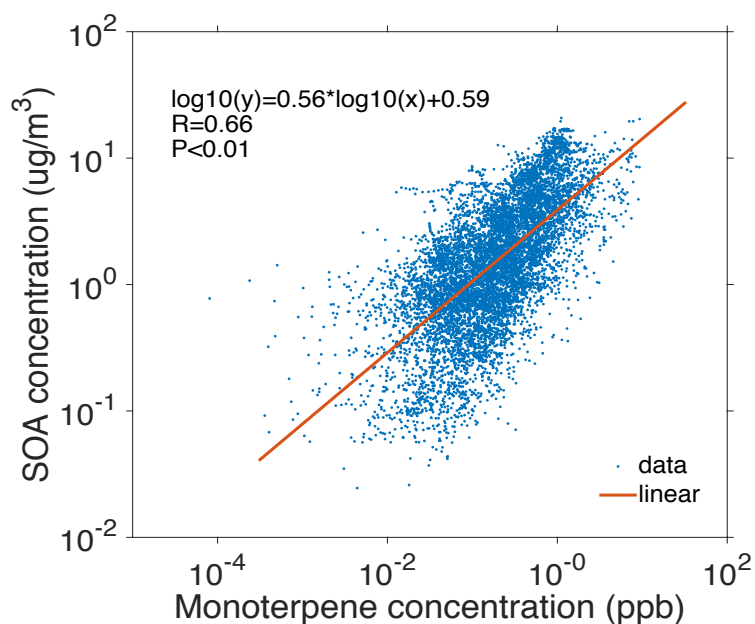


Figure 7. Correlation between observed SOA and monoterpene concentrations on a logarithmic scale. The red line is the linear regression line. The Pearson correlation coefficient R is 0.66, P<0.01.

#### 4.2.2 Time lag effect

The correlation analysis between SOA and monoterpenes shown in the previous section is based on the simultaneous measurement data without considering the time lag effect. However, once emitted, monoterpenes will go through oxidation and gas-to-particle partition processes to form SOA. Both processes take time and hence there should be a time delay between monoterpene emission and the observed increase of SOA concentration.

The oxidation of monoterpenes usually takes one hour to several hours depending on the time of year and day (Peräkylä et al., 2014). The growth rates of aerosols typically range from 1-20 nm h<sup>-1</sup> based on observations (Kulmala et al., 2004b). Therefore, a time difference of 0 to 24 hours was put between SOA and monoterpene data to test if there is a time lag effect from our data with any improvement of the correlation.

Figure 8 showed the correlation coefficients R between SOA and monoterpenes at a given time lag from 0 to 24 hours with 1 hour's time step. The Pearson correlation coefficient for the first 3 hours, number of data points and P values are listed in Table 3. The correlation between SOA and monoterpenes slightly increased after about 1-2 hours' time lag (Table 3), and after that the correlation coefficient R continued to decrease as the time lag increased.



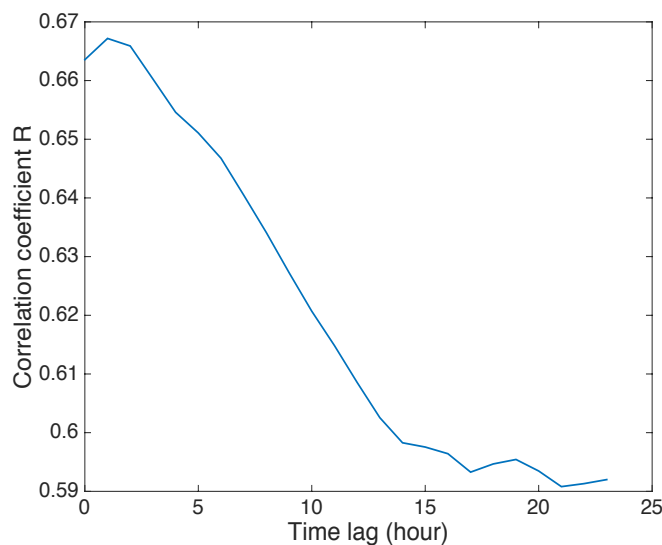


Figure 8. Variations of Pearson's correlation coefficient R between SOA and monoterpene concentration at a logarithmic scale considering different length of time lag.

Table 3. Pearson's correlation coefficient R between the SOA concentration and monoterpene concentration on a logarithmic scale when the time lag is between 0 to 3 hours, along with the number of observations (n) and the p values.

Time lag(hour)	0	1	2	3
R	0.6632	0.6672	0.6659	0.6603
n	8662	8661	8653	8645
P	<0.01	<0.01	<0.01	<0.01

The improvement of the correlation was very slight and hence the we will keep using the simultaneously measured data when conducting the correlation analyses between SOA and monoterpenes in the rest of the study.

### 4.3 Influence of wind direction

Another factor that may affect the correlation between SOA and monoterpenes is wind. When winds come from inhabited areas in the south, it is more likely to be associated with aerosols of anthropogenic origin, which can result in higher values of SOA measurements at the station.

Figure 9 showed how the accumulated SOA concentrations distributed at each wind direction (with a step of 20°) according to the measurement data. High SOA concentrations were more often associated with south and southeast winds. In the daytime, south winds were more related with high SOA concentrations while in the evening/night, south and southeast winds were more closely linked with high SOA concentration. As we know, south winds are often associated with high temperature, when monoterpene emission will be high, resulting in high SOA concentration. Therefore, this high SOA concentration we observed from south could be a combined result of both pollution and temperature effect.

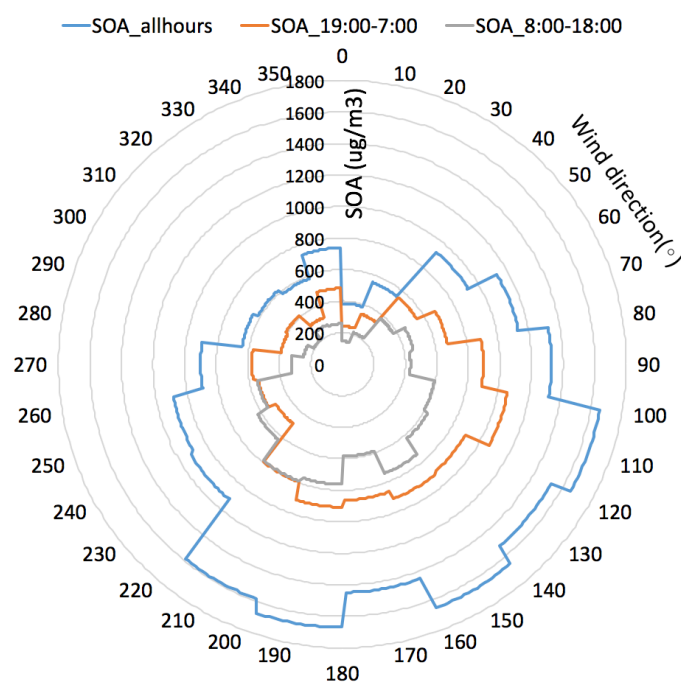


Figure 9. Accumulated SOA concentrations at each wind directions with a step of 20° for years 2008 to 2011 and 2013 to 2014. The blue line represents the whole dataset, while the orange line and grey line indicate SOA concentration at night and daytime respectively.

Tunved et al. (2006) modelled the trajectories of air masses in Hyytiälä and concluded that the clean air masses mainly come from northwest direction, approx. 270°-360°. In order to exclude any potential anthropogenic influence, we filtered SOA and monoterpene concentration data according to the study, leaving wind directions only from 270° to 360°. The new correlation between monoterpene and SOA concentration could be seen in Fig. 10. The Pearson's correlation coefficient R on a logarithmic scale was 0.68, which was slightly higher than the original one before filtering (R=0.66), suggesting anthropogenic influence in this study is minor.

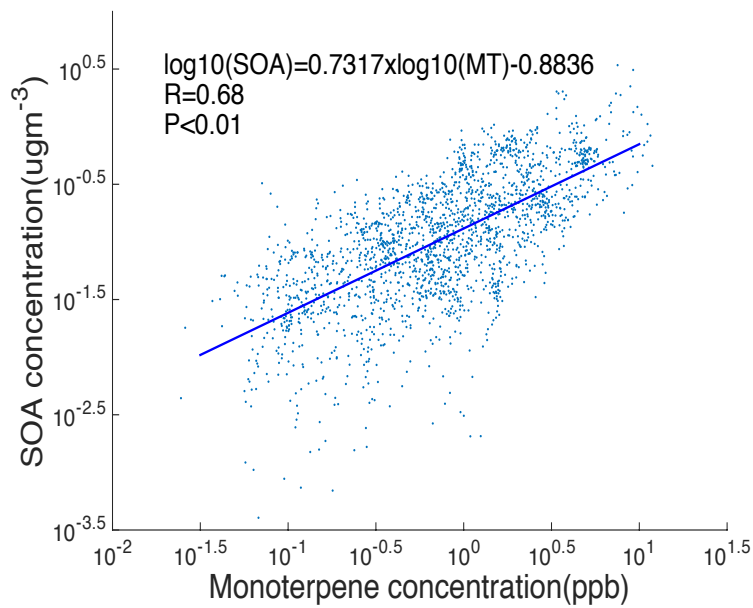


Figure 10. Correlation between SOA and monoterpene concentration with wind directions between 270° and 360°. The blue line is the linear regression line. The Pearson's correlation coefficient R is 0.68.

#### 4.4 Influence of temperature

To identify how temperature plays a role in the correlation between SOA and monoterpenes, we analyzed data based on a number of temperature windows, namely above 20°C, 10°C to 20°C, 0°C to 10°C, -10°C to 0°C and below -10°C. Both SOA and monoterpenes data were divided into 5 datasets accordingly and the correlation analysis was conducted within each sub-dataset.

Both the correlation coefficient and regression slope became higher as temperature increased (Fig. 11). The regression slope increased from -0.22 to 0.53 as temperature increases from below -10 to 20 °C. In the meanwhile, the Pearson correlation coefficient R increases from -0.45 to 0.57. When temperature is below -10°C, SOA data is very scattered and the correlation shifts from positive to negative.

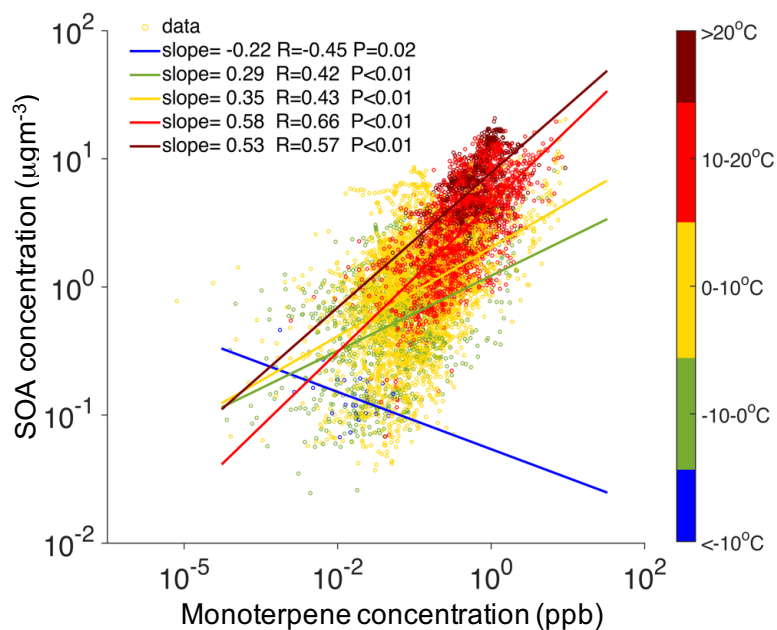


Figure 11. Correlation between observed SOA and monoterpene concentrations at different temperature windows for year 2008, 2010-2011, 2013-2014. The colored lines are linear regression lines at each temperature window.

This initial result suggested a potential positive temperature dependence of both the slope and the correlation coefficient. To further quantify such dependence, we re-defined the temperature windows with a smaller step of 5°C instead of 10°C and carried out a similar correlation analysis (Table 4).

Table 4. Correlation between SOA and monoterpene concentration at different temperature windows. The linear regression slopes, Pearson correlation coefficients R and P are given for each temperature window.

	Temperature window (°C)							
	<-10	-10~-5	-5~0	0~5	5~10	10~15	15~20	>20
Mean Temp.(°C)	-11.19	-7.14	-1.85	2.68	7.48	12.60	17.21	23.11
Slope	-0.22	0.42	0.25	0.27	0.42	0.60	0.48	0.53
R	-0.45	0.54	0.38	0.32	0.52	0.66	0.64	0.57
P	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

A linear correlation has been found between the regression slope and temperature (using the mean temperature of each temperature group) with the R of 0.75 (Fig. 12 and Table 4). When breaking down the data into day and night by time (09:00 to 16:00 for day and 21:00 to 04:00 for night), it showed a much stronger dependency during the day than the night.

However, no significant linear relation could be found between the correlation coefficient and temperature from the same data ( $R=0.68$ ,  $P=0.06$ ). If only considering summer months (May to September), the temperature dependence is quite strong (Fig. 13), especially during daytime. It means the higher the temperature, the higher the correlation coefficient between SOA and monoterpenes.

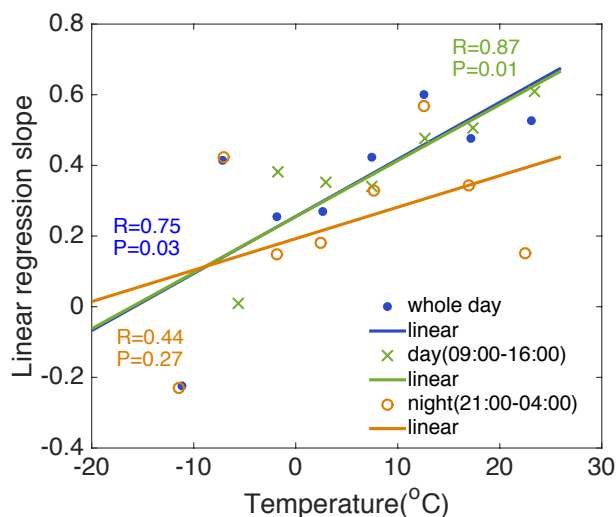


Figure 12. Correlation between the linear regression slope at different temperature windows and the temperature for year 2008, 2010-2011, 2013-2014. The blue line is the linear regression line for the whole day data. The green line and yellow line are the linear regression lines for daytime and nighttime data respectively.

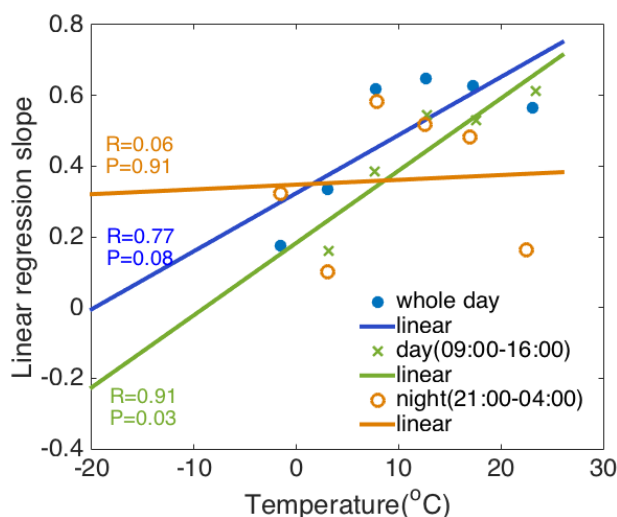


Figure 13. Correlation between the correlation coefficient at different temperature windows and the temperature for summer months (May to September) in year 2008, 2010-2011, 2013-2014. The blue line is the linear regression line for the whole day data. The green line and yellow line are the linear regression lines for daytime and nighttime data respectively.

#### 4.5 Influence of relative humidity

Following the same procedure by dividing relative humidity into 9 sub groups, namely 20-30%, 30-40%, 40-50%, 50-60%, 60-70%, 70-80%, 80-90%, 90-100% and >100%, we looked at SOA and monoterpenes correlation through these windows.

Results in Fig. 14 showed that there was a strong negative linear correlation between the slope and relative humidity ( $R=-0.88$ ,  $P<0.01$ ) in general, and this correlation was even stronger in nighttime ( $R=-0.92$ ,  $P<0.01$ ). Since slope is a rough estimation of the SOA yield from monoterpenes, this negative relation suggested a decrease tendency of SOA yield when relative humidity is higher.

However, relative humidity and temperature are often closely related to each other. We divided the relative humidity data to 8 sub-datasets by different temperature windows, and calculated the average relative humidity value for each dataset. Meanwhile, we calculated the average temperature value within each temperature window. It showed that there was a significant and strong negative correlation between the relative humidity and temperature (Fig. 15). As a result, the negative relative humidity dependence of slope could be a result of the anti-correlation between temperature and relative humidity.

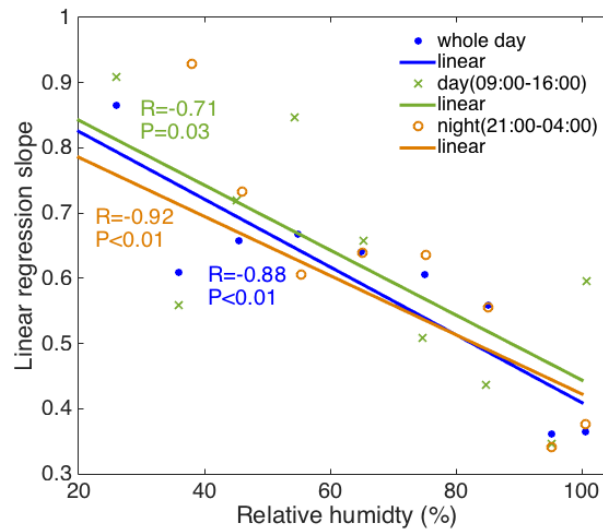


Figure 14. Correlation between the linear regression slope at different temperature windows and the relative humidity for year 2008, 2010-2011, 2013-2014. The blue line is the linear regression line for the whole day data. The green and yellow lines are the linear regression lines for daytime and nighttime data respectively.

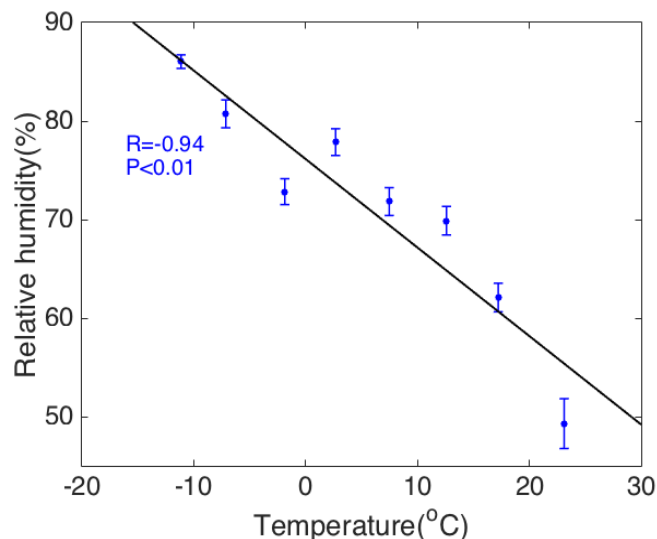


Figure 15. Correlation between the average relative humidity within each temperature group and the average temperature for each temperature group for year 2008, 2010-2011, 2013-2014. The error bar shows one standard deviation of each humidity dataset.

## 4.6 Monoterpene oxidation

### 4.6.1 Temporal variation of monoterpene oxidation

The temporal variation of the oxidation products concentration (Fig. 16), estimated by the monoterpene proxy from Kontkanen et al. (2016), showed that the maximum value was obtained in the afternoon and evening. This diurnal pattern was very similar to SOA diurnal variation as well. As for the seasonality, more intense oxidation happened in summer months like July and August.

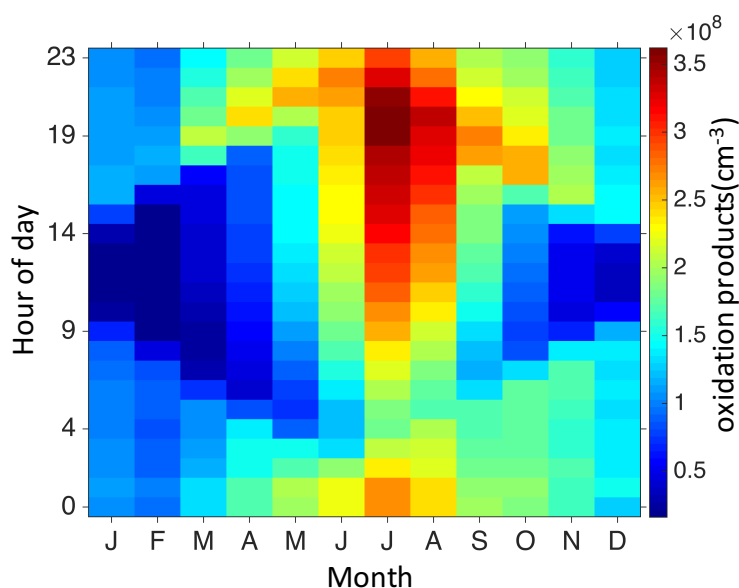


Figure 16. Diurnal and seasonal variations of average number concentration of monoterpene oxidation products from 2006 to 2014.

### 4.6.2 Dominant monoterpene oxidation path

Monoterpenes, once emitted, will be oxidized into less volatile organics by OH, O<sub>3</sub> and NO<sub>3</sub>, and then form SOA through gas-to-particle partition. The oxidation rate, which is essentially the production rate of less volatile organics, can directly affect formation process of SOA, and therefore the change of SOA concentration.

In order to find out which oxidant/oxidation path contributed more to the SOA concentration, we analyzed the relation between SOA concentration increase rates and monoterpene oxidation rates by OH and O<sub>3</sub> respectively. NO<sub>3</sub> oxidation was not included in the study, because of lack of measurements in Hyytiälä.

The results of the correlation analysis between SOA increase rates and monoterpene oxidation rates (Table 5) indicated that O<sub>3</sub> is the dominant oxidant in Hyytiälä in terms of monoterpene oxidation, comparing with OH.

Table 5. Correlation between SOA concentration increase rate and monoterpenes oxidation rate by OH and O<sub>3</sub>. R is the Pearson correlation coefficient, and n is the number of data points. Note that only days with good linear SOA increase rate (R>0.7) are included in the analysis.

	Oxidation rate by OH	Oxidation rate by O <sub>3</sub>
SOA increase rate	R=0.36	R=0.78
(only R>0.7, good linear fit )	P<0.01	P<0.01
	n=70	n=78

Both O<sub>3</sub> and OH are the major oxidants for monoterpenes during daytime, but for most of the year, the daytime oxidation was dominated by O<sub>3</sub> (Peräkylä, 2014). During nighttime, O<sub>3</sub> concentration is almost as stable as in daytime and hence oxidation can take place all day round. On the contrary, OH concentration is rather low (our estimation in this study is zero because UVB is zero), because they are mainly formed during the day via the radiation from the sun. Besides, monoterpene concentration (Fig. 4) peaks in the evening/night, which will favor the oxidation process with O<sub>3</sub>.



## **5. Discussion**

### **5.1 Temporal variations of monoterpene and SOA concentration**

Monoterpenes' diurnal pattern was consistent with previous BVOC emission studies (e.g. Hakola et al., 2012; Peräkylä et al., 2014) by having the daily maximum in the night and daily minimum during the day. The seasonal variation was similar with the study by Peräkylä et al. (2014) by having the highest values in summer months.

SOA concentration also showed a daily maximum at night time (Fig. 5 and Fig. 6), which could be resulted from many factors. Firstly, the changing atmospheric boundary layer depth (with a higher depth during daytime and a lower depth during nighttime) will trap the SOA near the surface and favor the build up of the SOA concentration. Secondly, the night time monoterpene oxidation was quite strong (Fig. 16), which supported the formation and growth of SOA. Thirdly, the lower nighttime temperature can increase the condensation rate of oxidized products (Claeys et al., 2004).

### **5.2 Time lag effect**

Based on the average monoterpene oxidation time (Peräkylä et al., 2014) and normal SOA growth rate (Kulmala et al., 2004b), it might take several to tens of hours for freshly emitted monoterpenes to grow into SOA larger than 60 nm and be captured by our measurement instruments.

The time lag also depends on the background aerosol concentration. If the air is clean and SOA is formed through new particle formation, the time lag from monoterpenes emission to SOA detection would be longer. However, if there are already existing background aerosols, the oxidized products of monoterpenes could directly condense onto them and be detected by our instrument in a much shorter time.

The 1-2 hours' short time lag (Fig. 8) implied that the monoterpene oxidation products very likely condensed directly upon the already existing background aerosols, which took shorter time for the changes of SOA concentration to be noticed by our instrument. In this way, SOA concentration data we observed was able to show a faster response to the change of monoterpene concentration. Interestingly, this time lag of 1-2 hours also falls into the typical range of monoterpene oxidation time (Peräkylä et al., 2014).

### **5.3 The temperature dependence of regression slope**

Our data suggested a positive temperature dependence of the regression slope between SOA and monoterpenes. The slope means how much SOA is changed in response to the change of monoterpenes and hence could roughly represent the SOA yield from monoterpenes. As a result, our finding suggested a positive temperature dependence of SOA yield.

What could be the responsible mechanisms/processes behind the positive temperature influence on SOA yield?

First of all, monoterpene emission has an exponential relation with temperature until an optimum level is reached (Guenther et al., 1993). As the major SOA precursor in Hyytiälä, it will provide more parent hydrocarbon at higher temperatures and directly contribute to an increasing SOA formation.

Besides, temperature may also affect SOA yield via oxidation and partition processes. When monoterpenes are oxidized to less volatile organics, they will partition themselves into the gas phase and particle phase. The vapor pressures of organics in general will increase as temperature increases. According to Seinfeld et al. (2001), vapor pressure will double when temperature increases every 10 K. In this case, monoterpenes in higher temperature will favor to be in the gas phase and lead to a negative effect on SOA yield, which was in line with some chamber experiments (e.g. Takekawa et al., 2003). Meanwhile, other chamber experiments have found an overall positive temperature effect for SOA formation (e.g. Jonsson et al., 2008; Hessberg et al., 2009), suggesting that the positive temperature influence on the reaction mechanisms probably outweighed its negative effect in the partition process. It should be noted that these experiments focused only on certain type(s) of monoterpenes in a controlled reaction environment, so that the results are not fully comparable with our ambient study using actual measurement data.

In general, the positive temperature effect on SOA formation we observed might be due to a combination of temperature influence in various processes from monoterpenes to SOA. It is likely that the positive temperature effects on monoterpene emission and oxidation process dominated over the negative effect on the partition process, which led to an overall positive impact.

#### **5.4 The temperature dependence of correlation coefficient**

The data indicated a positive temperature impact on the correlation coefficient between SOA and monoterpene (Fig. 13). It could be the case that both SOA and monoterpene concentration values are high at high temperature, making the data measurement more reliable. As a result, the correlation between SOA and monoterpenes was improved because of a better data quality. On the other hand, the exponential increase of monoterpenes emission at higher temperature (Guenther et al., 1993) would make monoterpenes more dominant in terms of SOA precursor, and hence bond the change of SOA more closely to it.

#### **5.5 Implication of the temperature dependence in the climate change context**

The average global temperature has increased since 1861 and it will continue to rise for decades to come (IPCC, 2013). Monoterpene emission is very likely to increase in a warming climate due to its highly dependence on temperature (Guenther et al., 1993). The positive temperature dependence of SOA yield from monoterpenes (Fig.12) we found in this study suggests that SOA concentration will increase significantly in the future.

This significant and positive correlation we found between monoterpene and SOA concentrations are to some extent in line with Tunved et al. (2006) and Paasonen et al. (2013). Our results provided a support for the existence of the COBACC feedback mechanism as described in the introduction. Such a negative aerosol cloud feedback will likely mitigate the climate change by cooling the earth in the future.

#### **5.6 Limitations of the study**

The main limitation of the study arises from data uncertainty. SOA concentration data used in this analysis is in fact total organic aerosols with size range of 60-1000nm. It means that the data cannot distinguish the age or origin of the aerosols, which will lead to uncertainties in SOA concentration. When temperature level was very low, SOA data exhibited a large scattering (Fig. 11). It is probably because the SOA concentration level are normally quite low at cold season due to the lack of precursor emission, which makes the SOA measurement

easier to be influenced by nearby anthropogenic aerosol pollutions, like wood mills and saunas etc.

Both OH and NO<sub>3</sub> are very important oxidants in Hyytiälä, but neither of them have direct measurements. We used Eq.3 to estimate OH concentrations, and it has to be noted that this approximation has its own limit, especially for night oxidation rate. OH concentration was estimated to be 0 in the night because UVB radiation is 0. However, according to the study by Petäjä et al. (2009), the measured OH concentrations in the night was not 0 and it was about an order of magnitude lower than the measured daytime concentrations. Hyytiälä is located in the rural area and is considered to be a forest site with very little anthropogenic influence and low NO<sub>3</sub> concentration. However, NO<sub>3</sub> may still be an important oxidant to react with monoterpenes in the night (e.g. Peräkylä et al., 2014) and it will be interesting to look at it in future studies.

When calculating the average SOA increase rate, a specific night time period of the data was selected because an increase of SOA concentration was observed at night. Since no day time data was included, this method could only identify the dominant oxidation path of monoterpenes at night, not during the day.

One important assumption of this study is that the measurement of SOA and monoterpenes we obtained could represent an average level for the forest area because of the homogeneity. However, the varying atmospheric boundary layer depth and mixing level will affect the transport and dispersion of any atmospheric constituents (Stull, 1988), including monoterpenes and SOA. It thus causes uncertainty of the of SOA and monoterpene concentration measurement, challenges the assumption and further impact the correlation analysis between the them.

## 6. Conclusion

Both monoterpene and SOA concentration exhibited a strong diurnal and seasonal cycle. Their daily minimum values were obtained around noon while the daily maximum occurred in the evening/night. Summer seasons had much higher values than other seasons.

There was a significant and moderate positive linear correlation between the observed SOA mass concentration and monoterpene volume concentration on a logarithmic scale ( $R=0.66$ ) for year 2008, 2010-2011 and 2013-2014.

Temperature and relative humidity showed stronger influences on the SOA and monoterpenes correlation, while wind direction exhibited a very weak impact. The correlation coefficient  $R$  between SOA and monoterpenes was slightly improved from 0.66 to 0.68 after filtering the data by wind direction ( $270-360^\circ$ ) to exclude potential anthropogenic influences. Temperature showed a strong and positive influence ( $R=0.75$ ,  $P=0.03$ ) on the SOA yield from monoterpenes. Relative humidity, however, showed a strong and negative impact ( $R=-0.88$ ,  $P<0.01$ ) on the SOA yield, which is likely due to the anti-correlation between temperature and relative humidity ( $R=-0.94$ ,  $P<0.01$ ).

Monoterpene oxidation level with all three oxidants, including OH,  $O_3$  and  $NO_3$ , were quite strong in the evening. Comparing with OH, the nighttime increase of SOA concentration was largely driven by  $O_3$  oxidation. The dominant oxidation path during daytime was unknown due to the limitation of the method, which was only applicable at night.

The positive correlation between SOA and monoterpenes and the positive temperature dependence of SOA yield found in this study provided the support for the existence of the negative aerosol-climate feedback mechanism as described in the COBACC feedback loops. It implied that under the future warming, the increasing SOA and its associated negative SOA-cloud feedback might induce a cooling effect to mitigate the climate change. However, the process-based mechanisms to explain the temperature dependence between monoterpenes and SOA yield need to further studied.

## **7. Acknowledgments**

I would like to extend my sincere gratitude to my supervisor, Prof. Janne Rinne for his guidance, patience, and support throughout the thesis work.

My sincere appreciations are also extended to Markku Kulmala, Risto Makkonen and Juan Hong for their insightful comments and suggestions at the 2016 winter school programme in Hyytiälä station, Finland, where my thesis topic was inspired. Moreover, I would like to thank Jenni Kontkanen from University of Helsinki for providing me with the data from her study for my analysis.

Finally, I would like to express my deep gratitude to my family for their unconditional love and support. A special thanks goes to my husband for believing in me and being there for me every step of the way.

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