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**HIGHLY OXYGENATED ORGANIC MOLECULES IN THE
ATMOSPHERE: SOURCES AND ROLES IN NEW-PARTICLE
FORMATION**

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Academic dissertation

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On the flight from Beijing to Helsinki,
Chao Yan

Highly oxygenated organic molecules in the atmosphere: sources and roles in new-particle formation

Chao Yan

University of Helsinki, 2018

Abstract

New-particle formation (NPF) can contribute to a large fraction of particle number concentration in the atmosphere. It is a world-wide phenomenon and can be driven by different precursors under various atmospheric conditions. Until now, molecule-level understanding of new-particle formation remains incomplete, which hampers our ability to simulate the aerosol budget, and in turn to predict the future climate.

Very recently, highly oxygenated organic molecules (HOMs) have been discovered in the atmosphere and due to their low volatilities, they may be involved at early stages of NPF. This thesis focuses on understanding how HOMs are involved in the NPF and their sources in the atmosphere. Data from both ambient measurement in a boreal forest and from the CLOUD chamber at CERN are analyzed and inter-compared.

We firstly produce HOMs from monoterpene oxidation by ozone in the CLOUD chamber, and they can drive NPF in the absence of sulfuric acid (H_2SO_4), in which the ion-induced nucleation (IIN) pathway plays a dominant role. Due to the Kelvin effect, HOMs start to contribute to particle growth at different sizes, depending on their volatility. As HOMs dominating the particle growth and in turn the particle survival probability, estimation of cloud condensation nuclei (CCN) concentration is highly sensitive to the volatility of HOMs.

HOMs are also key species in the ambient NPF. In the daytime, HOMs play major roles in more than half of ion-induced nucleation (IIN) events, when their total concentration exceeds the concentration of H_2SO_4 by 30 times. Nighttime IIN events are purely driven by HOMs, more specifically, by HOM dimers. This is the first atmospheric observation that provides direct evidence for the HOM-driven nucleation. It also demonstrates that chemical properties of HOMs is highly relevant to their capacity for forming new particles.

Since the roles of HOMs in particle nucleation and growth show high dependency on volatility and composition, which are determined by their sources, we investigate the HOM sources in the boreal forest using positive matrix factorization (PMF). Five monoterpene-related HOM factors are retrieved, representing ozonolysis, oxidation by NO_3 , $\text{RO}_2 + \text{NO}$ reaction, OH-limiting chemical processes, temperature-influenced processes. Most previous laboratory experiments only reproduce the ozonolysis of monoterpene factor, which is not fully representative to all HOMs in the atmosphere. This urges more investigations on HOM formed from other (especially daytime) pathways, including the role of NO_x , the yield, and volatility distribution.

By comparing HOM concentration at the ground level and above the canopy, we find that HOMs are homogeneously mixed during the daytime, whereas the ground-level HOMs were often significantly less abundant than above the canopy when stratified nocturnal boundary layer is formed. Thus, ground-level HOMs need to be used with caution when simulating atmospheric processes in the nighttime.

Altogether, this thesis demonstrates the crucial role of HOMs in NPF, both in the laboratory and in ambient atmosphere. However, this thesis also points out that current chamber experiments has only partly reproduced HOM-related processes in the atmosphere, for which further investigations are needed.

Keywords: NPF, IIN, HOMs, CLOUD chamber, PMF

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List of publications

This thesis consists of an introductory review, followed by six research articles. In the introduction part, they are cited according to their roman numbers. **Paper I, II, and V** are reprinted with the approval of all co-authors. **Paper III, IV, and VI** are reprinted under the Creative Commons Attribution 4.0 International license.

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1 Introduction

Since the industrialization, the constituents of the atmosphere have been changed by intensive human activities, which in turn profoundly influence the Earth's atmosphere systems. For instance, the emission of chlorofluorocarbons (CFCs) has destroyed the stratospheric ozone layer inside the polar vortex and enlarged the risk of ultraviolet exposure (Haas, 1992). Another widely concerned environmental issue is the emission of large amounts of greenhouse gases (GHG) into the atmosphere, such as carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), and hydrofluorocarbons (HFCs), which causes global warming (IPCC 2013). Although international consensus has been achieved about the hazardous influence of global warming and concrete action has been made, the overall abundance of GHG is still rising.

In addition to GHG, human activities have also been raising the number concentration of aerosol particles in the atmosphere. Aerosol particles are nanometer- to micrometer-sized solid or liquid substances that are suspended in air. The concentration of aerosol particles around the globe spans over several orders of magnitude, from only a few per cubic centimeter in the arctic region (Kyrö et al., 2013) to about a million per cubic centimeter in polluted urban environments. If aerosol particles are big enough, usually larger than a few tens of nanometers, they can exert an impact on climate. They can influence the radiative forcing by directly scattering or absorbing the sunlight, or indirectly acting as cloud condensation nuclei (CCN) to initiate the formation of a cloud, which can reflect the solar radiation back to space. Although a constituent of aerosol particles called black carbon can absorb solar radiation, aerosol particles have a net cooling effect, which counteract the warming effect by GHG and slow down the temperature increase (Stocker et al., 2013). From climate point of view, lives on Earth benefit from aerosol particles.

However, in some fast-developing countries such as China and India, where the emission control is usually poor, the concentration of aerosol particles may become too high, causing severe pollution and harming our health. In China, the premature mortality due to outdoor and indoor air pollution is estimated to be more than 2 million per year (Kulmala, 2015). Moreover, the pollution can be transported outside the original polluted area, causing approximately 12 % of global premature death (Zhang et al., 2017).

Aerosol particles may come from a variety of sources. They can be primary, i.e., being emitted directly into the atmosphere by natural sources, such as volcanoes, sea spray, dust, pollen, and by anthropogenic sources such as combustion processes. Aerosol particles can also come from secondary sources, meaning that they are formed in the atmosphere via gas-to-particle conversion (Kulmala et al., 2014). Phenomenologically, gas-to-particle conversion leading to an increase of particle number concentration is called new-particle formation (NPF). NPF has been observed round the globe since more than a decade ago (Kulmala et al., 2004a), in clean forest environment (Dal Maso et al., 2005), in marine environment (O'Dowd et al., 2002), and in polluted urban environment (McMurry et al., 2005). It has been estimated that NPF can potentially contribute to about half of the global

CCN concentration (Merikanto et al., 2009). Figure 1 give an overview of how NPF affects the CCN concentration and climate according to the current best understanding.

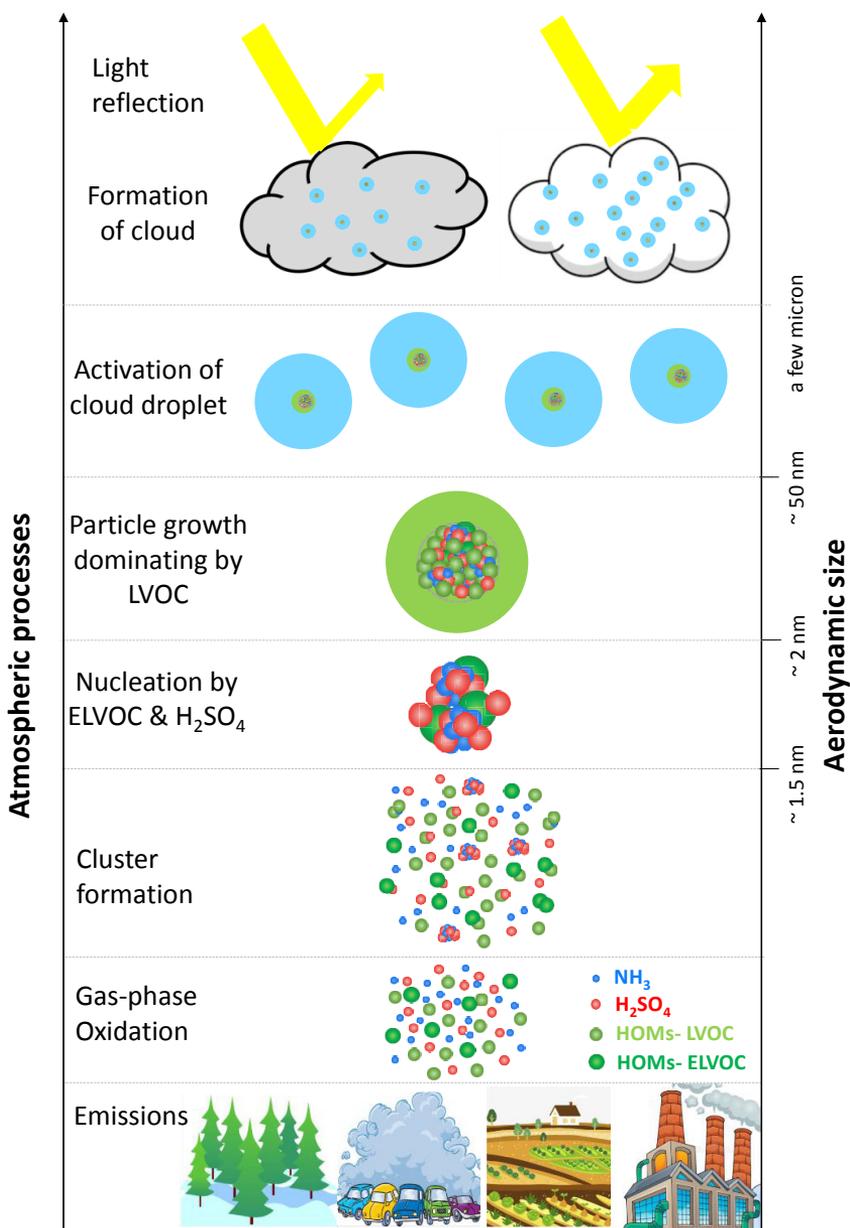


Figure 1. Schematic drawing illustrating the current understanding of most crucial steps from NPF to CCN and climate.

Although the exact NPF mechanisms are complicated in the atmosphere, NPF is generally thought to take place in two implicitly separated steps, i.e. the particle nucleation and their further growth to larger sizes. Particle nucleation refers to the process when gas-phase molecules form thermodynamically stable clusters, whose formation can outcompete evaporation. Based on various atmospheric observations, this process is conventionally believed to be driven by inorganic acids, for instance, sulfuric acid (H_2SO_4) and iodic acid (HIO_3) are the driving species in continental (Weber et al., 1996; Sihto et al., 2006; Kulmala et al., 2006; Kerminen et al., 2010; Wang et al., 2011) and marine atmosphere (O'Dowd et al., 2002; Mcfiggans et al., 2010; Sipilä et al., 2016), respectively. In addition, it has also been known for a long time that sulfuric acid is inefficient in nucleation by itself, and other species such as water and basic molecules like NH_3 (Ball et al., 1999) and/or amines are involved (Kurtén et al., 2008, Zhao et al., 2011).

In addition to various basic molecules, ions can also assist nucleation by making embryonic clusters more stable (Yu and Turco, 2001), which is usually called ion-induced nucleation (IIN). Ions in the atmosphere mainly come from galactic cosmic rays and the decay of radon. IIN has been observed frequently in the atmosphere (Hirsikko et al., 2011 and references therein), although in the planetary boundary layer, IIN may only contribute a relatively small fraction of total nucleation, comparing to particle formation from neutral pathways (Gagné et al., 2008; Manninen et al., 2009; Manninen et al., 2010; Kulmala et al., 2010; Kulmala et al., 2013). However, laboratory experiments have indicated that IIN might have a bigger contribution in cold environment, such as upper troposphere (Lovejoy et al., 2004).

A breakthrough in understanding how initial clusters are formed has been made recently when embryonic clusters can be directly observed on molecular scale with high resolution mass spectrometers (see Sect. 3.2). For instance, the HIO_3 -driven particle nucleation was directly observed in the atmosphere, and HIO_3 nucleation route has been depicted (Sipilä et al., 2016). In addition, the mechanisms of sulfuric acid nucleating with NH_3 or amines have also been studied at the CERN CLOUD chamber (see Sect. 3.1.2) and resolved in detail (Kirkby et al., 2011; Almeida et al., 2013). Besides, even a new nucleation mechanism, the pure biogenic nucleation, has been discovered (**Paper I**). This is the starting point of this thesis, and one main goal of this thesis is to examine to what extent these nucleation mechanisms can represent the NPF in the atmosphere (**Papers III, IV**).

After the nucleation step, small clusters/particles need grow to larger sizes to avoid being scavenged by other pre-existing particles. The competition of these two processes defines the survival probability of newly formed particles: the faster particles grow beyond the most scavenging-sensitive size range (e.g., 1 – 10 nm) the more likely they survive (Lehtinen et al., 2007). Observations in the continental boundary layer showed that the ambient concentration of sulfuric acid is not enough to explain the particle growth, leaving the organic vapors the most possible contributor (Nieminen et al., 2010; Paasonen et al., 2010; Riccobono et al., 2012; Riipinen et al., 2012; Donahue et al., 2013). Understanding of physicochemical properties of these organic vapors and how they are involved in particle growth is the key to link the NPF to the formation of CCN.

Although the existence of these organic vapors has been hypothesized for a decade (Weber et al., 1997; Kulmala et al., 1998), it had not been possible to measure their exact composition until the recent development of high resolution mass spectrometers (see Sect. 3.2). It was found that these low-volatility organic vapors are usually highly oxygenated molecules, in short, HOMs. The volatility of HOMs is expected to be extremely low owing to their multiple functional groups, and they proved the former hypothesis of the existence of effectively non-volatile organic vapors (Riipinen et al., 2012). As their supersaturation ratio is exceedingly high to overcome the Kelvin effect (i.e., the vapor pressure over a convex interface always exceeds that of the same substances over a flat surface), they may contribute to the particle condensational growth at very small sizes (Donahue et al., 2011; Donahue et al., 2013).

The exact volatility of HOMs is determined by their structures, which, in turn, are determined by the VOC precursors and the oxidation processes. The formation of HOMs usually involves three fundamental steps: 1) the initial oxidation of VOCs by OH, O₃, or NO₃, 2) the auto-oxidation, and 3) the termination reaction. The large variety of HOMs result from different reaction branches in the three stages, which will be described in more details in Sect. 2. Although we have successfully linked the particle growth to the HOM volatility using an aerosol dynamic model, the experiment in **Paper II** was done with only ozone and alpha-pinene, such HOMs and the respective volatility distribution can significantly deviate from those in the atmosphere. The conclusion on the impact of HOMs on CCN concentration is only conceptual and preliminary.

HOM formation pathway has remained largely uncertain under atmospheric conditions, and thus it is still difficult to precisely predict the HOM structure and volatility. It is therefore crucial to understand the HOM chemistry based on the measurement, which may also provide suggestive feedback for further laboratory experiments. In addition, the short lifetime of HOMs is likely to lead to inhomogeneous concentration profiles in the atmosphere even at smaller scales, which needs to be examined in future studies.

Overall, the formation of the highly oxygenated organic molecules and their involvement in NPF are important atmospheric processes that remain open. Therefore, the aims of this thesis are:

- i. to investigate the role of HOMs in particle nucleation and growth at the CERN CLOUD chamber (**Papers I, II**)
- ii. to improve the understanding about the role of HOMs in IIN in the boreal forest environment (**Papers III, IV**)
- iii. to characterize sources and other processes that influence HOMs in the boreal forest (**Paper V, VI**)

2 Theory and definitions

2.1 Definition of HOMs

Originally, HOMs stood for highly oxidized multifunction compounds (Ehn et al., 2012), to emphasize their high oxidation states. As the understanding of HOM formation improved, we realized that the oxygen atoms in the molecules not necessarily rise the molecular oxidation state due to the existence of peroxide, nitrate, nitro, and other functional groups. And for such a reason, we suggest to use “oxygenated” instead of “oxidized” to reduce the subjectivity in the terminology, because the former one is based on the direct observation.

In **Paper I**, we stated that “*HOMs are implicitly defined as oxidized organic compounds that can be detected by a nitrate CI-API-TOF*” to separate them from undetected less oxidized organic molecules. Later on, we understood that the detection of nitrate CI-API-TOF is mostly determined by the hydroxyl and hydroperoxyl functional groups (Hytinen et al., 2015), so that not all HOMs are able to be detected by nitrate- CI-API-TOF (Berndt et al., 2016). In more recent works, researchers tend to explicitly define HOMs as products from auto-oxidation of peroxy radicals in the atmosphere (personal communication). Thus, organic species that are detected by nitrate-CI-API-TOF are not necessarily HOMs either. For instance, nitrophenol as one prominent peak in the mass spectra (**Paper V**) should not be defined as a HOM, as it has large primary source, such as the biomass burning (Mohr et al., 2013).

In some early papers, extremely low-volatility organic compounds (ELVOC) has also been used to refer to these same vapors (Ehn et al., 2014; Jokinen et al., 2015), to highlight their key role in early particle growth, thus CCN number and in turn climate. However, it is realized later that the volatility of HOMs may span over many orders of magnitudes, from ELVOC ($C^* < 10^{-4.5} \mu\text{g m}^{-3}$; $N^* < 5 \times 10^4 \text{ cm}^{-3}$) to low-volatility (LVOC, $10^{-4.5} \leq C^* \leq 10^{-0.5} \mu\text{g m}^{-3}$; $5 \times 10^4 \leq N^* \leq 5 \times 10^8 \text{ cm}^{-3}$), to semi-volatile (SVOC $10^{-0.5} \leq C^* \leq 10^{2.5} \mu\text{g m}^{-3}$; $5 \times 10^8 \leq N^* \leq 5 \times 10^{11} \text{ cm}^{-3}$) organic compounds (Donahue et al., 2012, **Paper II**). Here, C^* and N^* denote the saturation vapor pressure of HOMs in mass and number concentrations, respectively.

In short, the term “HOMs” is more widely used to refer to these compounds, whereas terms such as ELVOC, LVOC, SVOC are often used in particular to describe their capacity of contributing to gas-to-particle conversion.

2.2 HOM formation pathways

The volatility of HOMs is mostly determined by the structure, including both the carbon backbone and functional groups, and in this regard, the VOC precursors as well as the oxidation processes are both important. In the past five years, laboratory experiments have

been extensively conducted to understand the HOM oxidation pathways and their corresponding yields using different VOC precursors under various conditions (e.g. Ehn et al., 2014; Jokinen et al., 2014; Jokinen et al., 2015; Rissanen et al., 2014; Mentel et al., 2015; Berndt et al., 2015; Berndt et al., 2016; Boyd et al., 2015; Wang et al., 2017; Molteni et al., 2018; Berndt et al., 2018). Although the HOM formation pathways and yields significantly differ from case to case, there are three general steps that the formation of HOMs follows, and the variety of HOMs in the atmosphere essentially result from diverged reactions in the three steps.

- i. VOC oxidized by main atmospheric oxidants, i.e., hydroxyl radical (OH), ozone (O₃), and nitrate radical (NO₃), which leads to the formation of carbon-centered radical and then the first generation of peroxy radical (RO₂) after a rapid addition of O₂. The limiting parameter of this step is usually the reactivity of VOC to these oxidants. For instance, biogenic VOCs, such as isoprene, monoterpenes and sesquiterpenes are reactive to all oxidants because of the double bond between carbon atoms, whereas aromatic species from anthropogenic sources are considered highly reactive with OH. Reaction rates of these initial oxidation have been well measured and incorporated in models like master chemical mechanism (MCM) (Saunders et al., 1997).
- ii. The first-generation RO₂ can further undergo a few steps of auto-oxidation to form highly oxygenated RO₂. Auto-oxidation occurs when hydrogen on a neighboring carbon is abstracted by RO₂ (also called H-shift), forming a new carbon-centered radical and then a new RO₂ by addition of another O₂ (Crouse et al., 2013; Rissanen et al., 2014; Ehn et al., 2014). This is the main reason for the high number of oxygen atoms of HOMs. The rate constant of the auto-oxidation drastically diverges, as it is highly structure-dependent, more specifically relying on how many loosely bonded hydrogens are available for H-shift. For instance, Mentel et al., (2015) has demonstrated that the aldehyde group significantly favors the H-shift, which explains the high HOM yield when O₃ initiates the oxidation of endocyclic alkenes, such as alpha-pinene, limonene, and beta-caryophyllene (Jokinen et al., 2015). Also, the alkyl-substitution can favor the auto-oxidation of aromatics (Wang et al., 2017). In contrast, the carbon ring structure suppresses the auto-oxidation by making the molecule too rigid for H-shift (Kurtén et al., 2015). This might be another important reason for the higher HOM yield of O₃-initiated oxidation than OH- or NO₃-initiated oxidation for endocyclic alkenes, as the former oxidation leads to a ring break-up.
- iii. The termination reaction that stops the auto-oxidation by converting RO₂ into closed-shell molecules. This is a competing step against the auto-oxidation, and they together regulate the yield of HOMs. Termination reaction can be bi-molecular between the RO₂ and terminators such as NO_x, RO₂, and HO₂, or sometimes can be also uni-molecular by self-decomposition (Orlando and Tyndall, 2012). The termination reaction by RO₂ can lead to formation of HOM dimers (Ehn et al., 2014; Berndt et al., 2018), all of which are ELVOCs and important for the initial stage of NPF (**Papers II, III**, Mohr et al., 2017). Termination reaction with NO_x can lead to

the formation with various organic nitrates, which are usually dominating products in the daytime atmosphere owing to the higher NO_x concentration than other terminators (RO_2 and HO_2). On the other hand, these bi-molecular reactions can also go through other branching reactions leading to the formation of alkoxy radical (RO), which may further undergo auto-oxidation, C-C bond scission, or self-decomposition (Atkinson, 2007, Kurtén et al., 2017). The rate coefficients and branching ratios of these reactions remain largely unknown and are crucial on-going research topics.

Overall, although most of classic understanding about gas-phase oxidation of organic molecules still hold in the formation of HOMs, the multifunctional groups in such molecules may lead to significant changes in the reaction rate coefficients and branching ratios, as well as the stability of products, as briefly mentioned in step ii and iii. It remains a major task to further investigate into the chemistry using various techniques, including quantum chemical calculation and direct measurements.

3 Methods

3.1 Measurement facilities

3.1.1 Station for Measuring Ecosystem – Atmosphere Relations (SMEAR II)

The main subjective of this thesis is to improve the understanding of NPF precursors in the boreal forest environment. **Papers III, IV, V and VI** are directly based on the ambient measurements at the SMEAR II (Station for Measuring Ecosystem – Atmosphere Relations), and the experimental design in **Paper I and II** is also relevant to atmospheric conditions in boreal forest environment.

The SMEAR II is located in Hyytiälä (61°51'N, 24°17'E), southern Finland (Hari and Kulmala, 2005). This station is surrounded by conifer forest and the closest city (Tampere; 213 000 inhabitants) is about 60km away. Due to the scarce anthropogenic emissions, this station is usually considered as a rural continental site, although it can be also influenced by polluted air masses from nearby cities, Russia, and Eastern Europe (e.g., Ulevicius et al., 2015).

SMEAR II is one of the most famous atmospheric measurement station in the world. Since mid-1990s, comprehensive measurements of ambient meteorological conditions and atmospheric constituents have been continuously conducted, such as temperature, relative humidity (RH), solar radiation, wind speed and direction, particle number concentration and number size distribution, and concentrations of aerosol particles and several trace gases, e.g., carbon dioxide (CO₂), carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen oxides (NO_x), and ozone (O₃). More recently, advanced instruments, such as proton-transfer-reaction mass spectrometer (PTR-MS, Rantala et al., 2014), Aerosol Chemical Speciation Monitor (ACSM, Ng et al., 2011), and atmospheric-pressure-interface time-of-flight mass spectrometer with and without a chemical ionization inlet (CI-API-TOF, Jokinen et al., 2012; API-TOF, Junninen et al., 2010; Ehn et al., 2010) have also been deployed for the continuous measurement.

3.1.2 CLOUD (Cosmics Leaving Outdoor Droplets) chamber

The CLOUD chamber is a stainless-steel cylinder with a volume of ca. 26.1 m³, located at CERN, Geneva, Switzerland (Kirkby et al., 2011; Duplissy et al., 2016). The most important feature of this chamber is its ultra-cleanliness, which allows studying the new particle formation phenomenon under carefully controlled and atmospherically relevant conditions, i.e., with precursors of similar concentrations to those in the atmosphere. Dedicated efforts are made to ensure a low contamination level in the chamber; besides the electro-polished inner surfaces of the chamber, vigorous rinsing with ultrapure water at 373K is done before each campaign, and ultra-clean, synthetic air produced by mixing cryogenic liquid nitrogen and oxygen is used throughout the experiments. The background total VOC concentration

of is at sub-ppbv level (Schnitzhofer et al., 2014), and the total condensable vapour concentration is sub-pptv. In **Papers I** and **II**, atmospherically relevant concentrations of α – *pinene* (~ 150 – 1200 ppt) and ozone (~ 40 ppb) were added into the chamber.

Ion concentrations in chamber can be controlled with a high voltage clearing field. By turning on the high voltage field (20 kV m^{-1}), all ions and charged particles are removed; we refer to this as the neutral condition (N). When the high voltage is switched off, ions are produced by the galactic cosmic rays (GCR) in the chamber; we refer to this as the GCR conditions. The chamber has several UV light systems to mimic the photochemistry in the atmosphere, including a Krypton-Fluoride (KrF) excimer UV-laser (3 W, $\lambda = 248 \text{ nm}$) to produce OH via O_3 photolysis, two UV LEDs (16.5W, $\lambda = 370\text{-}390 \text{ nm}$) to photolyze NO_2 into NO, and four Hamamatsu Xenon arc lamps (200W, $\lambda = 250\text{-}580 \text{ nm}$) to provide broad range UV light and bring the overall UV spectrum closer to atmospheric levels. The chamber temperature and relative humidity can be precisely controlled, in **Papers I** and **II**, the chamber was operated in constant conditions at 278 K and 38 % RH.

3.2 Instruments

3.2.1 Measurement of gas-phase sulfuric acid and HOMs

The nitrate-ion based chemical ionization atmospheric pressure interface time-of-flight mass spectrometer (CI-API-TOF) is one key instrument for this thesis, as it selectively measures sulfuric acid (H_2SO_4) and highly oxygenated molecules (HOMs) (Jokinen et al., 2012, Ehn et al., 2014), both of which are considered to be most important contributors to NPF.

The working principle of this instruments has been well described in previous works (e.g., Jokinen et al., 2012, Ehn et al., 2014), so we only briefly repeat it here. The nitrate ions are produced by exposing nitric acid (HNO_3)-containing sheath flow to soft x-ray radiation. These nitrate ions charge the analyte (e.g., H_2SO_4 or HOMs) in the drift tube, with a reaction time of ca. 200 ms. After that, the sample flow enters the mass spectrometer, where it is focused in the API module and analyzed in the TOF chamber based on the ion mass-to-charge ratio. The deployment of this instrument in CLOUD experiments and at SMEAR II has been described in details by Kürten et al., (2014) and Jokinen et al., (2012), respectively.

Recent quantum chemical calculation suggest that nitrate ion can selectively bond to molecules that contain two or more suitably located hydroxyl (-OH) or hydroperoxyl (-OOH) groups (Hytinen et al., 2015). And such groups are largely formed during the production of HOMs via auto-oxidation (Rissanen et al., 2014, Mentel et al., 2015, Jokinen et al., 2014). There are also some HOMs containing carboxylic acid groups ($\text{C}(\text{=O})\text{OH}$), and sometimes if acidity of HOMs exceeds that of nitric acid, they are charged by donating the hydrogen to nitrate ion and become deprotonated. For instance, malonic acid ($\text{C}_3\text{H}_4\text{O}_4$) is charged both in the cluster form $(\text{C}_3\text{H}_4\text{O}_4)\cdot\text{NO}_3^-$ and in bare ion form $\text{C}_3\text{H}_3\text{O}_4^-$. The case of H_2SO_4 is similar to malonic acid that it can be charged by deprotonation (HSO_4^-) or by clustering with

nitrate ion. Proton transfer is likely to happen as well in the latter case, and the cluster is more likely in the form of $(\text{HNO}_3) \cdot \text{HSO}_4^-$.

H_2SO_4 and HOMs are quantified based on Eq.1 or 2 and Eq.3 or 4, respectively.

$$[\text{H}_2\text{SO}_4] = \frac{\text{HSO}_4^- + \text{HNO}_3 \cdot \text{HSO}_4^-}{\text{NO}_3^- + \text{HNO}_3 \cdot \text{NO}_3^- + (\text{HNO}_3)_2 \cdot \text{NO}_3^-} \times C \times f_{inlet} \quad (1)$$

$$[\text{H}_2\text{SO}_4] = \ln\left(1 + \frac{\text{HSO}_4^- + \text{HNO}_3 \cdot \text{HSO}_4^-}{\text{NO}_3^- + \text{HNO}_3 \cdot \text{NO}_3^- + (\text{HNO}_3)_2 \cdot \text{NO}_3^-}\right) \times C \times f_{inlet} \quad (2)$$

$$[\text{HOMs}] = \frac{\sum \text{HOMs}}{\text{NO}_3^- + \text{HNO}_3 \cdot \text{NO}_3^- + (\text{HNO}_3)_2 \cdot \text{NO}_3^-} \times C \times f_{inlet} \times f_{trans} \quad (3)$$

$$[\text{HOMs}] = \ln\left(1 + \frac{\sum \text{HOMs}}{\text{NO}_3^- + \text{HNO}_3 \cdot \text{NO}_3^- + (\text{HNO}_3)_2 \cdot \text{NO}_3^-}\right) \times C \times f_{inlet} \times f_{trans} \quad (4)$$

Here, C is the calibration coefficient that is obtained from H_2SO_4 calibration, f_{inlet} is the inlet loss correction factor, and f_{trans} is the transmission correction factor. In practice, the signal of analytes is much smaller than that of reagent ions, making the term $\frac{\text{HSO}_4^- + \text{HNO}_3 \cdot \text{HSO}_4^-}{\text{NO}_3^- + \text{HNO}_3 \cdot \text{NO}_3^- + (\text{HNO}_3)_2 \cdot \text{NO}_3^-}$ is much smaller than 1, and thus Eq. 1 and 2 (and Eq.3 and 4) are roughly equal according to Taylor's Formula.

The general calibration approach includes:

- 1) Calibrate H_2SO_4 by relating the instrument signal to a known amount of sulfuric acid. This can be done either by using a H_2SO_4 calibration unit (Kürten et al., 2012) (**Paper I – II**), or by comparing to a reference instrument (Jokinen et al., 2012) (**Paper III – VI**). The overall quantification uncertainty when using a H_2SO_4 calibration unit is +50%/–33%, whereas the uncertainty when using a reference instrument is difficult to estimate.
- 2) For HOMs, as there is no appropriate standard for a direct calibration, the calibration coefficient for H_2SO_4 is adopted, assuming that the overall charging efficiency of H_2SO_4 and HOMs is similar, both of which has been demonstrated to be equal to collision limit (Viggiano et al., 1997; Ehn et al., 2014). However, Recent studies have shown that the charging of certain HOMs by nitrate may vary considerably (Berndt et al., 2016). Therefore, this method gives the lower limit of the HOM concentration. The uncertainty for least oxidized HOMs needs further investigation.
- 3) The diffusional loss during the sampling process for H_2SO_4 and HOMs is corrected assuming diffusional loss in a laminar flow (Gormley and Kennedy, 1948).
- 4) The mass-dependent transmission correction is applied on HOM quantification. The mass discrimination is instrument-specific, which results from different sources, such as the tunings of instrument voltage, pressure, and inlet flow. This mass-dependence correction factor is obtained using the method proposed by (Heinritzi et al., 2016).

3.2.2 Measurement of atmospheric ion composition

In this thesis, the composition of atmospheric ions is measured using the atmospheric-pressure-interface time-of-flight mass spectrometer (APi-TOF, Junninen et al., 2010). It is so far the most sensitive instrument for directly measuring chemical composition of atmospheric ion clusters, and a well-suited instrument for looking at IIN from molecular level.

The ion composition in the atmosphere is affected by both the quantity and the proton affinity of the species. For instance, although N₂ is the most abundant gas in the atmosphere, no signal in APi-TOF can be seen, because it is incapable of holding a charge. Thus, it is important to note that the signal strength of an ion in APi-TOF does not necessarily mean high concentration of its respective neutral species. On the other hand, APi-TOF measurement can be interpreted as a (semi-)quantitative way, when referring only to the quantity of ions. In **Paper I, III, and IV**, we use APi-TOF to observe qualitatively “what compounds are nucleating”. If the transmission efficiency of the instrument is known, APi-TOF directly measures the quantity of atmospheric ions. For instance, in **Paper IV**, the total count of charged HOM clusters in APi-TOF show a good correlation with the total ion counts observed in NAIS, indicating that same ions are detected by both instruments. Sometimes, the time evolution of ion clusters can be tracked. In **Paper III and IV**, APi-TOF tracks the time evolution of clusters, and then growth rate at the cluster-size can be estimated using the appearance time method presented by Lehtipalo et al., (2014).

3.3 Positive matrix factorization (PMF)

3.3.1 Working principle of PMF

Positive matrix factorization is a well-established receptor model that has been firstly developed by Dr. Paatero and his colleagues (Paatero and Tapper, 1994, Paatero, 1997, Paatero and Hopke, 2003). Mathematically, it expresses an overall matrix by a linear combination of a finite number of factors, who have varied weights and distinct profiles. Such an algorithm suits perfectly the analysis of mass spectrometry data, and in the past decades, PMF has been widely used on aerosol mass spectrometer (AMS) data to retrieve factors that represent different aerosol sources, such as hydrocarbon-like organic aerosol from vehicle emission, cooking organic aerosol, biomass burning organic aerosol and different secondary organic sources (Lanz et al., 2007; Ulbrich et al., 2009; Jimenez et al., 2009; Ng et al., 2010; Zhang et al., 2011).

When applying PMF on mass spectral data, the time-resolved mass spectra can be expressed by a linear combination of different sources (Eq.3), assuming the source profiles are constant and unique (Ulbrich et al., 2009).

$$X = TS \cdot MS + E \quad (\text{Eq.3})$$

X is a time-resolved mass spectral data in a size of $m \times n$, containing m time points and n masses. TS is an $m \times p$ matrix that represents the time series of p factors, and MS is a $p \times n$ matrix that gives the mass profiles of the p factors. Matrix E (in size $m \times n$) is the residual unexplained by the p factors.

One important virtue of this model is that it takes the measurement uncertainty into account by weighting the model residuals (Eq.4).

$$Q = \sum_{i=1}^m \sum_{j=1}^n \left(\frac{E_{ij}}{S_{ij}} \right)^2 \quad (\text{Eq.4})$$

Here, S_{ij} is the estimated uncertainty providing the weights of each data points in the algorithm and E_{ij} is the model residuals from Eq.3. The PMF works to find the minimum of Q . Even if measurement quality of some data points is poor, they will have big uncertainties (S_{ij}) and thus reduced weights in the algorithm. A proper estimation of measurement uncertainty is therefore a key step in PMF analysis.

3.3.2 Estimation of measurement uncertainty (S_{ij})

As PMF is for the first time applied on HOMs data in **Paper V**, we needed to develop a proper way to estimate the measurement uncertainty. Using unit-mass-resolution data, the overall uncertainty comprises the noise of the instrument σ_{noise} , the uncertainty caused by counting statistics σ_{ij} , as shown in Eq.5.

$$S_{ij} = \sigma_{ij} + \sigma_{noise} \quad (\text{Eq.5})$$

In **Paper V**, we applied a constant value of 0.035 the uncertainty due to instrumental noise σ_{noise} , which is determined as the standard deviation (3σ) of “blank masses”, where no real signal should be observed. σ_{ij} was estimated based on the counting statistical error proposed by (Allan et al., 2003) that has a square root dependence on the raw signal strength (in counts per second) divided by the counting time (in second), shown as the first term on the right side of the Eq.6:

$$S_{ij} = a \frac{\sqrt{I}}{\sqrt{t_s}} + \sigma_{noise} \quad (\text{Eq.6})$$

In addition, an empirical parameter a was used incorporate any unaccounted contributions to the uncertainty, and a was determined as 1.3 for our instrument. It should be noted that, for instruments that use an analog-to-digital converter as the data acquisition card, the empirical parameter a might be further enlarged by the variability in the size of pulses generated when single ions impact the detector.

3.3.3 Factor validation

The most important work in PMF analysis is validating the retrieved factors based on the “meaningfulness” or “interpretability”. There are multiple considerations when verifying the PMF solutions, including:

1. Directly comparing the spectral profile of the retrieved factors to reference spectra from laboratory experiments. This is the most robust way to interpret the retrieved factors. However, as HOM measurement has been emerged very recently, there are only very limited reference spectra that have been reported (Ehn et al., 2014; Jokinen et al., 2014; Mutzel et al., 2015; Wang et al., 2017; Molteni et al., 2018)
2. In the cases that reference spectral are not available, identification of fingerprint molecules is also helpful. As most molecular information is retained in the CI-APi-TOF spectra, fingerprint molecules can be used to deduce the source, e.g., the fingerprint molecules may be the products from a unique chemical reaction, or tracers for known sources.
3. Temporal correlation of factors with other tracers that present specific HOM sources or atmospheric processes.
4. Other available information, such as meteorology or air mass trajectories.

4 HOM-driven particle nucleation and growth in the CLOUD chamber

Sulfuric acid is believed to play a dominant role in the early stage of atmospheric new-particle formation (Kulmala et al., 2000; Kulmala, 2003). However, the binary nucleation (sulfuric acid – water) and ternary nucleation (sulfuric acid – ammonia – water) are not able to explain the observed tropospheric nucleation rates (Kirkby et al., 2011), unless amines are present (Almeida et al., 2013). On the other hand, a few recent studies have suggested that low-volatility organics are needed in very early stage of NPF (Riipinen et al., 2012, Donahue et al., 2013, Zhao et al., 2013, Ehn et al., 2014, Riccobono et al., 2014) to better explain the observed NPF.

The contribution of HOMs to new-particle formation, both in particle nucleation and further growth, was investigated in laboratory using the CERN CLOUD chamber. The role of HOMs in triggering particle nucleation (**Paper I**) and in contributing to particle growth (**Paper II**) were both studied in detail.

Alpha-pinene was chosen as the HOM precursor, as it is the most abundant biogenic VOC in boreal forest environment (Guenther et al., 1995, Rinne et al., 2000). Alpha-pinene was oxidized by ozone and also by hydroxyl radical (OH) that was produced via the ozonolysis of alpha-pinene. These experiments have been done under atmospherically relevant conditions, i.e., $\sim 150 - 1300$ ppt alpha-pinene, ~ 35 ppb ozone, at 38% RH and 278 K. In addition, the experiments were made in both neutral and GCR conditions, to study the role of ions in such conditions.

4.1 Nucleation purely driven by HOMs

Concentration of HOMs and sulfuric acid were quantified using CI-API-TOF as described in Sect. 3.1.1. During the experiment, total HOM concentration varied from $\sim 2 \times 10^6 - 3 \times 10^8$ cm⁻³ and sulfuric acid concentration ranged from below the detection limit to a typical concentration in the planetary boundary layer (5×10^4 to 6×10^6 cm⁻³). Figure 2 presents the nucleation rate of 1.7 nm particles ($J_{1.7}$) as a function HOM concentration in both neutral (J_n) and GCR (J_{gcr}) conditions, both of which increased at higher HOM concentrations. The presence of ions enhanced the nucleation by 1 – 2 orders of magnitude at low HOM concentrations (e.g., $[HOM] < 2 \times 10^7$). However, the maximum ion-induced effect was limited by the ion production rate (about 3 cm⁻³ s⁻¹), and when neutral nucleation rate was higher than this value at high HOM concentration, J_n and J_{gcr} converged. The magnitude of ion enhancement by negative and positive ions was rather equal, although the API-TOF observed clearly different patterns of cluster formation.

The strong nucleation enhancement by ions indicated that the embryonic HOM clusters were relatively unstable unless ions are attached. When increasing the sulfuric acid concentration, we shifted the major negative charge carriers from nitrate ion (NO₃⁻) to bisulfate (HSO₄⁻)

and other sulfur-containing ions (SO_4^- , SO_5^-), but the nucleation rate seemed to be unaffected, indicating that the exact composition of ions was not important as long as they can efficiently cluster with HOMs. The fact that such nucleation is almost independent from sulfuric acid is totally distinct from the acid-base nucleation mechanism, (i.e., sulfuric acid, water, with ammonia, amines), which shows a steep dependency on sulfuric acid concentration.

Although comparison between the chamber results with the observations in the atmosphere is rather preliminary due to the simplicity of chamber conditions, our newly discovered nucleation mechanism may help explain several nucleation phenomena associated with low sulfuric acid levels, such as the nighttime nucleation in temperate and boreal forest environment (Suni et al., 2008; Lee et al., 2008; Junninen et al., 2008; Lehtipalo et al., 2011), in Amazonian upper troposphere (Martin et al., 2010; Ekman et al., 2008). To verify its relevance to the atmosphere, we revisited the measurement using a similar set of instruments at SMEAR II, which will be discussed in details Sect.5 (**Paper III** and **IV**).

Moreover, this nucleation mechanism might have dominated the particle formation in pre-industrial era when anthropogenic vapors such as SO_2 and NO_x were much lower in the atmosphere. Thus, incorporating this mechanism in global aerosol model is important for improve the estimated anthropogenic radiative forcing by refining the aerosol baseline in pristine pre-industrial atmosphere. Our follow-up study has estimated that this mechanism increases CCN concentrations by 20 – 100 % over a large fraction of the pre-industrial lower troposphere, thus the cooling effect by anthropogenic aerosols is reduced (Gordon et al., 2016).

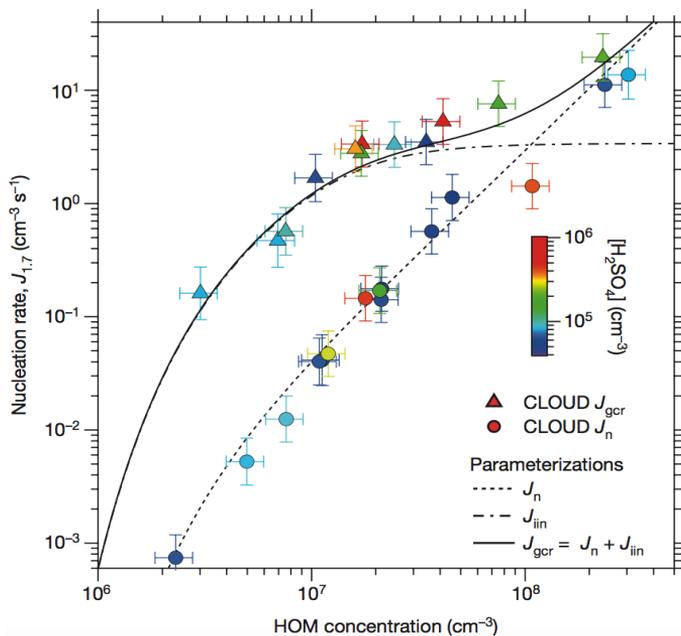


Figure 2. Nucleation rates ($J_{1,7}$) as a function of HOM concentration colour-scaled by sulfuric acid concentration. Circles represents the nucleation rates under neutral conditions (J_n), and triangles denotes those in GCR conditions (J_{gcr}). The uncertainty bars represent 1σ total errors. The figure is adopted from **Paper I**.

4.2 Contribution of HOMs in particle growth

It has been widely accepted that various low-volatility organic compounds are needed to explain the particle growth rate determined from the ambient observations (Riipinen et al., 2012, Ehn et al., 2014). However, finer details remain largely unclear. Riipinen et al., (2011) found that assuming 50 – 100 % of the organic vapors are effectively non-volatile gave the most comparable model results to the ambient measurement, which however, cannot reproduce the observed acceleration in particle growth, as reported by Kulmala et al., (2013). Donahue et al., (2011) further discussed that the volatility of organics may span over orders of magnitude so that they would behave differently in contributing to condensation growth due to their respective concentrations and Kelvin effect. However, extremely low-volatility organic compounds (ELVOC) have not been considered existing in the atmosphere, until more recently been discovered by Ehn and coworkers (Ehn et al., 2014). In **Paper II**, using the same dataset as in **Paper I**, we focused on understanding the yield and volatility distribution of HOMs, and examined the contribution of HOMs with different volatilities to particle growth at different sizes.

Particle growth rates were measured in a set of experiments as described before, and plotted as a function of concentration sulfuric acid (Figure 3 a,b) or HOMs (Figure 3 c,d). The derived growth rate cannot be explained by the sulfuric acid (Figure 3 a,c), but show a good correlation with HOMs (Figure 3 b,d), indicating that the particle growth was driven by HOM condensation. In addition, in contrast to the enhancement of nucleation rate by ions, the growth showed no dependence on ions.

Another important observation was that larger particles grew faster, which contrasted the model simulation assuming all HOMs are effectively non-volatile or ELVOC. Based on the SIMPOL model and estimation of chemical structure of major HOMs, we estimated the volatility distribution and found that the volatility of HOMs produced from ozonolysis of monoterpene spans about 20 orders of magnitude, from ELVOC to LVOC and to SVOC. The observed ratios for ELVOC, LVOC, and SVOC were 20:34:46.

To further understand the link between HOM volatility and particle growth, we used a dynamic volatility-distribution model to simulate the growth rate. However, the model did not give satisfactory results unless two modifications were made. First, we multiplied the four LVOC bins by 2, 2.5, 3.3, and 10, respectively. We observed in Figure 3d that even assuming non-volatile growth, the model predicted lower growth rate at particles larger than 5 nm, giving an evidence that the nitrate CIMS underestimated the HOM concentration. Meanwhile, the growth rate at smaller sizes were estimated correctly (Figure 3c), suggesting the measurement for ELVOCs was pretty good, in other words, the underestimation was likely for LVOCs. The need for scaling LVOC concentration was also supported by quantum chemical calculation (Hytinen et al., 2015) and inter-comparison between nitrate-CIMS and acetate-CIMS (Berndt et al., 2016). Recently, the inter-comparison between nitrate-CI-APi-TOF and a novel proton-transfer-reaction time-of-flight mass spectrometer has suggested similar scaling factors (Breitenlechner et al., 2017). Secondly, Kelvin effect needs to be incorporated in order to reproduce the particle growth at very small sizes.

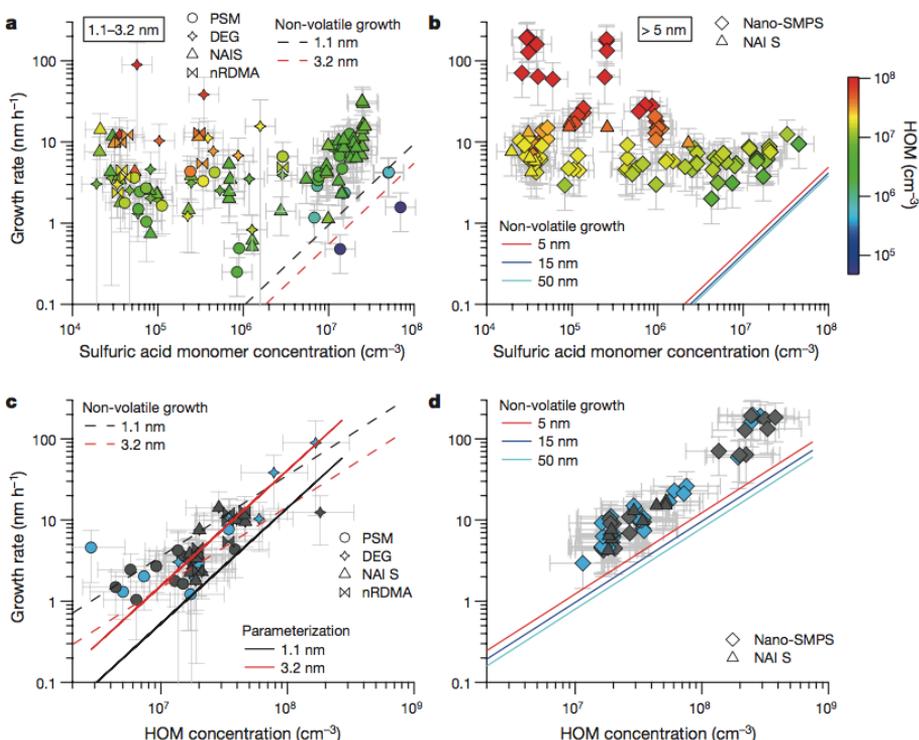


Figure 3. Measured particle growth rates at different sizes as a function of sulfuric acid (**a**, **b**) and HOM (**c**, **d**) concentrations. Growth rate determined from different instruments are marked using different symbols. Symbol colours in **a** and **b** are scaled to HOM concentration, and in **c** and **d** denote different chamber conditions, neutral in blue and GCR in gray. The uncertainty bars represent 1σ total errors. The figure is adopted from **Paper II**.

Our model results suggested that ELVOCs dominate the growth below 2 nm, and above that size, the Kelvin effect becomes weaker that allows more significant contribution from LVOC. As HOMs dominate particle growth from early stage (below 2 nm) to CCN size, the particle survival and thus the CCN budget is highly sensitive to the HOM concentration and volatility distribution. Indeed, such insight has pronounced influence on the simulation of CCN number in a global aerosol model: it gives a maximum 100 % higher CCN number concentration than assuming growth of 1 – 3 nm particles is solely by sulfuric acid and gives about one third lower CCN number concentration than what has been predicted by all HOMs can contribute to particle growth below 2.5 nm (D'Andrea et al., 2013).

5 Ion-induced nucleation at SMEAR II

Following the simulated ion-induced nucleation (IIN) purely driven by HOMs at the CLOUD chamber (Sect. 3.1, **Paper I**), we examined its applicability to the atmosphere. As the former CLOUD experiment used alpha-pinene as the VOC precursor, the remote boreal forest is the most similar environment, although the concentrations of NO_x and NH₃ are higher than in CLOUD.

As introduced before, the SMEAR II is a rural station located inside the boreal forest. New particle formation events have been observed and recorded continuously since 1996 (Mäkelä et al., 1997), and ion size distribution have been observed since 2003 (Kulmala et al., 2004b). Based on 4-month comprehensive measurement in spring 2007, Manninen et al., (2009) studied the importance of IIN and concluded that the median contribution of IIN to total nucleation is about 10 %, which agrees with a few other studies (Gagné et al., 2008; Kulmala et al., 2010). However, the contribution also exhibited high case-to-case variation (Manninen et al., 2009), and in general showed a decreasing tendency along with the increasing total nucleation rate (Kulmala et al., 2010), which could be explained by that IIN provide a relatively small but stable source of nucleated particles. Actually, this is similar to the observation in **Paper I**, that the contribution of IIN is regulated by the ion production, but the ion concentration was much higher in CLOUD chamber than in Hyytiälä (Wagner et al., 2017). Gagné et al., (2010) further investigated the relationship between the fractional contribution of IIN and other atmospheric parameters and found that the IIN contribution is evidently correlated with temperature and anti-correlated with sulfuric acid concentration, but the explanation for such dependencies was ambiguous due to instrumental limitations.

In addition to the rich literatures focusing on daytime IIN, nighttime IIN events at SMEAR II have also been reported in a few previous works (Junninen et al., 2008, Lehtipalo et al., 2011). As concentrations of sulfuric acid and nitrogen monoxide (NO) are very low in the nighttime, such environment may be the most representative to the conditions in the CLOUD chamber in **papers I and II**.

In this section, we will discuss the detailed IIN mechanisms at SMEAR II based on measurement using state-of-the-art instruments, including API-TOF, CI-API-TOF, NAIS, and other relevant instruments. API-TOF was operated only in negative mode at SMEAR II, thus our further discussion is only based on the negative ions. As the atmospheric conditions in the daytime and nighttime are clearly distinct, we divide this section into two parts, which focus on daytime IIN (**Paper III**) and nighttime cluster formation (**Paper IV**), respectively.

5.1 Ion-induced nucleation in the daytime at SMEAR II

5.1.1 The role of H₂SO₄-NH₃ clusters

Previous studies have demonstrated the diurnal variation of ion composition at SMEAR II (Ehn et al., 2010, Bianchi et al., 2017). Generally speaking, H₂SO₄ clusters ((H₂SO₄)_mHSO₄⁻, m≤3), H₂SO₄-NH₃ clusters ((H₂SO₄)_m(NH₃)_nHSO₄⁻, m≥3, n>0), as well as HOM clusters (HOM·NO₃⁻ and HOM·HSO₄⁻) are the main charge carriers in the daytime. Consistent with the observation in CLOUD experiment (Kirkby et al., 2011, Schobesberger et al., 2015), NH₃ molecules were observed only when clusters contain no less than 4 H₂SO₄ molecules including the HSO₄⁻.

Strong variations of cluster composition and intensity can be observed on a daily basis. As shown in Figure 4, daytime H₂SO₄ clusters can be NH₃-free (Figure 4A) or consist of different number of NH₃ and H₂SO₄ molecules (Figure 4 B – D). Over the 134 measurement days in three consecutive springs of 2011 – 2013, NH₃-free H₂SO₄ clusters were observed on 118 days, and bigger clusters that contained NH₃ were observed on 39 days. We further relate the appearance of these clusters in different sizes to the occurrence of IIN events that are identified using data from Neutral cluster and Air Ion Spectrometer (NAIS, Mirme and Mirme, 2013) when a distinct rise in the 1.5 – 2.5 nm ion concentration is observed. A strong connection is found between the maximum cluster size and the probability of IIN: IIN occurred at almost 100 % probability (24 out of 25 days) when clusters containing more than 5 H₂SO₄ molecules were observed; the probability dropped to 50 – 60 % when clusters contained 3 – 5 H₂SO₄ molecules, and to 0 % when H₂SO₄ clusters had less than 3 H₂SO₄ molecules. This may indicate that the formation of 6-H₂SO₄ clusters is a critical step in IIN triggered by H₂SO₄-NH₃ clusters. The mobility equivalent size of such clusters is about 1.4 nm using the conversion mentioned by Ehn et al., (2011) and assuming a density of 1770 kg/m³. Such a diameter is consistent with our previous understanding of the size of thermodynamically stable clusters (Kulmala et al., 2013).

There are always some other atmospheric processes that compete with the formation of (H₂SO₄)_m(NH₃)_nHSO₄⁻ clusters, such as larger particles capturing ions, or HSO₄⁻ ion clustering with HOMs instead of with H₂SO₄, and sometimes these processes may become dominating. We have examined the relevance between the formation of (H₂SO₄)_m(NH₃)_nHSO₄⁻ clusters and other environmental parameters, including the gas-phase concentrations of H₂SO₄, NH₃, and HOMs, condensation sink (CS), as well as other meteorological parameters, such as temperature, RH, wind speed and direction. We found that the ratio between the concentrations of H₂SO₄ and HOMs had the decisive influence on the appearance of (H₂SO₄)_m(NH₃)_nHSO₄⁻ clusters. A plausible explanation could be that most H₂SO₄ forming clusters with HOMs inhibited the formation of big-enough pure H₂SO₄ clusters to accommodate NH₃. As shown in Figure 5, days with and without the appearance of (H₂SO₄)_m(NH₃)_nHSO₄⁻ clusters separate from each other depending on the concentration of H₂SO₄ and HOMs, and a value of 30 for [HOMs]/[H₂SO₄] seem to be the threshold, above which (H₂SO₄)_m(NH₃)_nHSO₄⁻ clusters were not detected.

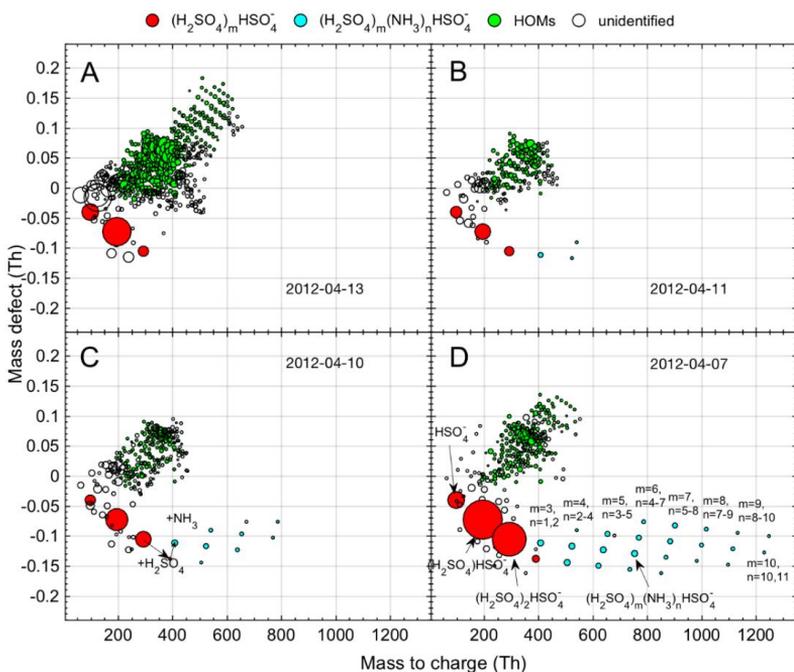


Figure 4. Mass defect plot showing the composition of ion clusters on four separate days. Colors denote different composition of ion clusters. The circle size is linearly proportional to the logarithm of the signal intensity. The figure is adopted from **Paper III**.

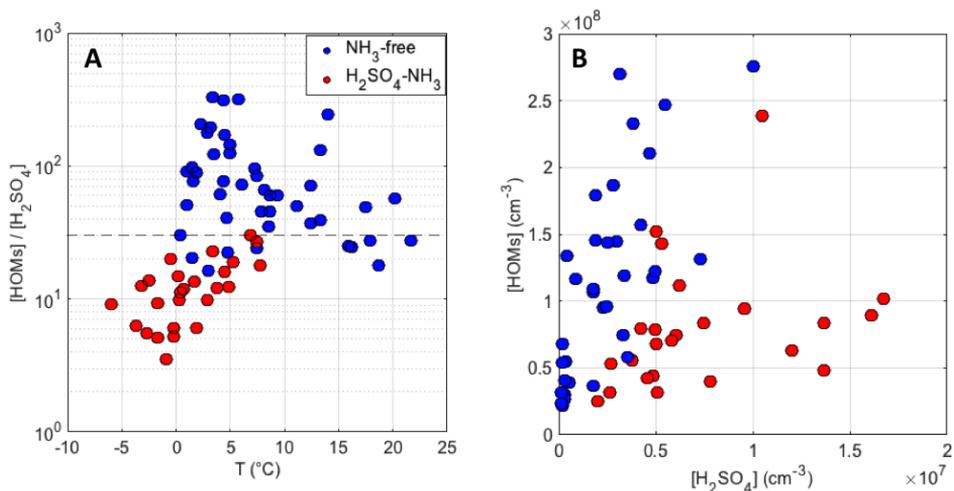


Figure 5. The dependence of $\text{H}_2\text{SO}_4\text{-NH}_3$ clusters formation on concentrations of HOMs, H_2SO_4 , their ratio ($[\text{HOM}]/[\text{H}_2\text{SO}_4]$), and temperature. The figure is adopted from **Paper III**.

5.1.2 Plausible contribution of HOM clusters to IIN

Interestingly, among the 67 IIN events over the 134 measurement days in **Paper III**, there were 35 IIN events occurring without the detection of $\text{H}_2\text{SO}_4\text{-NH}_3$ clusters, suggesting that these IIN events were driven by different mechanisms. Further statistical analysis suggested that HOMs were the most likely responsible species in such IIN events. In some cases, HOM clusters in API-TOF can reach a mass range of 500 – 600 Th (e.g., Figure 4A), which corresponds to a mobility equivalent diameter of about 1.4 nm, assuming a density of 1400 kg/m^3 . This size shows a remarkable agreement with the critical size in $\text{H}_2\text{SO}_4\text{-NH}_3$ cases. However, in these events, we did not observe how clusters grew even larger, for example to 1000 Th as shown in Figure 4D. Given the fact that HOMs and H_2SO_4 are also competing for charges, these two mechanisms, are likely alternately driving the IIN in daytime Hyytiälä. Moreover, it can be reasonably expected that the contributions of these two mechanisms vary seasonally, as higher temperature can promote the biogenic VOC emission and the HOM formation and in turn favor the HOM-driven mechanism.

Existence of two different IIN mechanisms provides possible explanations for the dependence of IIN contribution on sulfuric acid concentration and temperature, which has been reported by Gagné et al., (2010). When sulfuric acid is low, or temperature is high, the HOM-driven nucleation probably dominates, and such nucleation has a stronger reliance on ions than the $\text{H}_2\text{SO}_4\text{-NH}_3$ -driven nucleation does, as ions are likely the only stabilizer agents for HOM clusters. It is also important to note that, unlike the CLOUD experiment (**Paper I**), the contribution of H_2SO_4 in these HOM-driven IIN events cannot be excluded. Whether there is interaction between H_2SO_4 , NH_3 , and HOMs needs further investigation.

5.2 Nighttime ion-induced cluster formation driven by HOMs

After the HOM-driven ion-induced nucleation was detected in the CLOUD chamber, one important task is to verify this mechanism in the atmosphere. As mentioned in the beginning of this section, the chamber condition might be quite similar to the nighttime atmosphere at the SMEAR II. In the following part of this section, we will discuss to what extent the CLOUD results (**Paper I**) represent the nighttime atmosphere at SMEAR II.

Although not as well-known as the daytime observations, ion-induced cluster formation has been observed in the nighttime at SMEAR II (Junninen et al., 2008; Lehtipalo et al., 2011). For simplicity, in the following part of this section, we use “nocturnal events” or “nighttime events” to refer to this kind of nocturnal ion-induced cluster formation. By finding high frequency of nighttime events occurring right after a daytime event, Junninen et al., (2008) suggested that the precursors for nocturnal events is largely the same as those for daytime events. However, due to the limitation of instruments, direct observation of such nocturnal clustering processes was lacking at that moment. And Lehtipalo et al., (2011) further pointed out that oxidize organic vapors might be the most plausible contributor. Later on, Bianchi et al., (2017) have shown that the HOMs can form large clusters up to tetramer (~ 1000 Th), but their link with the nighttime events have not been demonstrated.

Following these observations, we further investigated how these HOM clusters are involved in the nighttime events (**Paper IV**). Data collected in spring (9th April to 15th May) of 2013 were analyzed. The occurrence of nighttime events was classified based on NAIS data in the same way as for the daytime IIN events. During the period, nighttime events were observed in 25 out of 32 nights. Concurrent with the occurrence of night events, we observed a build-up of HOM clusters from monomers to dimers, then to trimers and tetramers at an average speed of 181.8 amu h⁻¹ (Figure 6A). The presence of HOM monomers, dimers and trimers is also clearly illustrated in the mass defect plot, as well as their evolution from 19:30 to 21:30 (Figure 6B). The build-up of HOM clusters that started from the formation of HOM dimers due to the reduction of NO (**Paper V**), indicating that HOM monomers were not the main responsible vapors for the nighttime events. In contrast, total HOM dimer signal was evidently higher in the nights when cluster growth was the most pronounced than in those nights with weaker growth and in non-event nights, suggesting the formation of HOM dimer was the key step towards further cluster formation. These observations highlighted a negative effect of NO_x on cluster formation by inhibiting dimer formations, which is in line with a former chamber study (Wildt et al., 2014).

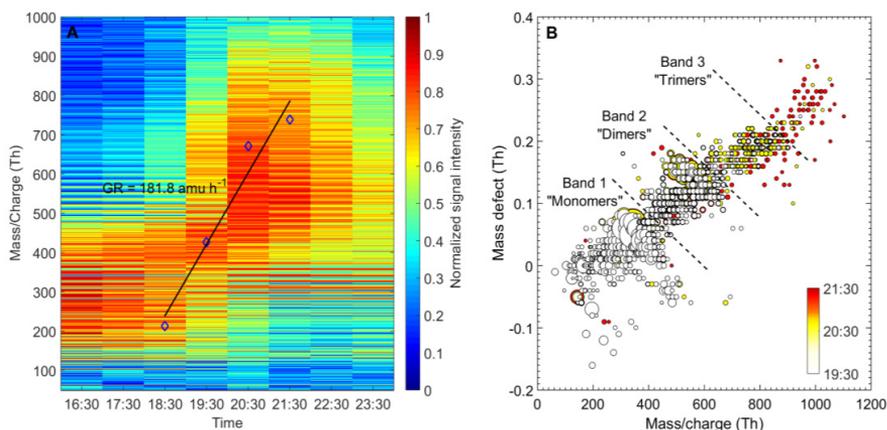


Figure 6. Build-up natural HOM anions. (A) Time evolution of the mass spectra between 16:00 and 00:00. (B) Mass defect plot showing the cluster formation event detected on 20th April. The size of the dots is proportional to the signal intensity the colour scale indicates the times at which the three mass spectra were measured. The figure is adopted from **Paper IV**.

In these nighttime events, the role of H₂SO₄ is insignificant. First, H₂SO₄-NH₃ clusters that are frequently observed in the daytime are not present, indicating their minor contribution to nighttime events. Second, the median concentration of neutral H₂SO₄ is $8.4 \times 10^5 \text{ cm}^{-3}$ as measurement by CI-APi-TOF, in the range that should not efficiently contribute to the IIN without the presence of NH₃, according to the results from CLOUD chamber experiment (**Paper I**).

Overall, our observation of nighttime events driven by HOMs qualitatively verifies the HOM-driven nucleation mechanism. The main responsible vapors, HOM dimers that were efficiently produced in the CLOUD chamber, are indeed able to nucleate also in the atmosphere. However, it remains not well understood why these nighttime clusters were very rarely able to grow beyond 6 nm in size at SMEAR II, whereas they could reach 100 nm in CLOUD chamber. One plausible explanation is lacking of photochemistry related LVOCs, which is decisive for particle/cluster growth, as also suggested in **Paper II**. It is important to note that the concentration of OH radical in CLOUD chamber was higher than in the nighttime SMEAR II due to the clearly lower OH sink. In this regard, the dark experiments in CLOUD also produced significant amount of “photochemical products”. This phenomenon needs to be understood in order to properly address the importance of the nighttime events in regard to the climate.

6 Source characterization of HOMs using PMF

6.1 Why do we need PMF?

As demonstrated in **Papers I – IV** and many other previous studies, HOMs are the key species in determining the atmospheric new-particle formation, CCN budget, and aerosol loading (Tunved et al., 2006; Jimenez et al., 2009; Riipinen et al., 2012; Kulmala et al., 2013; Paasonen et al., 2013; Jokinen et al., 2015). Since the recent development of instruments allows for direct measurement of HOMs, investigations on underlying chemistry of HOM formation emerged quickly. Extensive insights of HOM formation mechanism have been obtained based on laboratory experiments and/or quantum chemical calculations (e.g., Ehn et al., 2014; Jokinen et al., 2014; Jokinen et al., 2015; Rissanen et al., 2014; Mentel et al., 2015; Boyd et al., 2015; Berndt et al., 2015; Berndt et al., 2016; Kurtén et al., 2017; Wang et al., 2017; Molteni et al., 2018; Berndt et al., 2018). As we have shown before, the ways that HOMs are involved in the particle nucleation and growth are rather sensitivity to their volatility (**Paper II**) and chemical composition (**Paper IV**), for both of which the oxidation chemistry is crucial. Thus, one important task is to identify the HOM chemistry in the ambient, and to further link laboratory or theoretical studies to the atmosphere.

One challenge in extracting detailed chemistry of HOM formation from the complex atmospheric system is that many components are directly or indirectly interacting. For instance, increasing NO_x will certainly lift the importance of $\text{RO}_2 + \text{NO}_x$ channel in forming HOMs, but may also affect the O_3 -related channel by regulating the O_3 concentration; or increasing VOC can elevate all HOM production chemistry, but it may also cause a reduction of NO_x and in turn lower the contribution from these relevant reactions. Another degree of complexity is that the same peak (i.e., the same elemental formula) in CI-API-TOF spectra usually comprise several conformers that may form through different chemical pathways. This, together with the complicated chemistry, make it close to impossible to get a broader picture of HOM formation pathway without proper statistical analyses. As discussed in Sect. 3.3.1, PMF is a well-suited model to deal with such complexity. In this section, we will present the first successful application of PMF on HOMs data, which link the ambient measurement to previous chamber results and identify needs for future research efforts.

6.2 Verification of PMF results

This work uses unit-mass-resolution (UMR) data that were measured in spring 2012 (4th April – 7th May). Data were averaged into 5min time intervals, and mass-to-charge range from 201 to 650 Th were used to cover most of the low-volatility HOMs. This results a total input consisting of 9084 samples and 450 variables. PMF optimally found six factors to best explain the overall spectra, including five HOM factors and one transported pollution factor, each of which has distinct spectral profile (Figure 7) and temporal variation (Figure 8). Based on the peaking time-of-day, we firstly name the six factors as nighttime type 1,2,

daytime type 1,2,3, and a transported factor. Further verification based on the criteria mentioned in Sect. 3.3.3 is discussed below.

Nighttime factors

The nighttime type-1 is interpreted as the ozonolysis of monoterpene factor as the profile is almost the same as the reference spectrum reported by Ehn et al., (2014) when only mixing ozone and alpha-pinene. It should be noted that other endocyclic monoterpene as such delta-3-carene or limonene may generate similar products via the ozonolysis pathway, thus multiple monoterpene precursors could be involved.

The nighttime type-2 factor contains totally different HOM dimers that more than 80 % of dimers are nitrogen-containing. As the formation of dimer is most likely via the association reaction between two RO₂ radicals (Berndt et al., 2018), the nitrogen must from the parent RO₂ radical(s), leading to the only possibility that the parent RO₂ is formed from NO₃-initiated oxidation. Thus, this factor is assigned the NO₃-initiated oxidation of monoterpenes. Previous studies have suggested that NO₃-initiated oxidation is very inefficient in forming low-volatility vapors for alpha-pinene but highly efficient for delta-3-carene (Fry et al., 2014). Thus, it is highly possible that the nitrogen-containing RO₂ comes from delta-3-carene, the second most abundant monoterpene at SMEAR II (Rinne et al., 2000).

As the SMEAR II is a rural station, the NO_x and NO₃ concentrations are not high and the nighttime type-1 factor is the major HOM contributor in most nights. However, when polluted air masses containing high NO_x were transported to this location, the NO₃-initiated factor was enhanced and became dominant (Figure 8a). Although both factors are peaking at nighttime, the ozonolysis of monoterpene factor also has some contribution in the daytime, whilst the NO₃-initiated factor totally disappears and no longer contributes to HOM formation.

Daytime factors

In the early morning (around 4am), the daytime type-1 factor starts to increase concurrently with the decrease of both nighttime factors, indicating that NO might be directly involved in this factor. Three most prominent peaks are used as the fingerprint molecules, which are C₁₀H₁₅O₉N, C₁₀H₁₅O₁₁N, and C₁₀H₁₆O₉N₂, respectively. The former two peaks most likely come from the reaction between NO and two most abundant RO₂ radicals in CI-APi-TOF via ozonolysis of monoterpene (C₁₀H₁₅O₈• and C₁₀H₁₅O₁₀•), indicating the decrease of the ozonolysis of monoterpene factor (nighttime type-1) is at least partly due to that the chemical pathway has been shifted from RO₂ + RO₂ reactions to RO + NO reactions. Similarly, the third peak is likely formed via RO₂ + NO reaction, in which the RO₂ (C₁₀H₁₆O₈N•) is NO₃-initiated. This deduced chemistry is consistent with the observation in two aspects: 1) the two nitrogen atoms were introduced by NO₃ oxidation and NO termination, respectively, and 2) there was no hydrogen gain or loss as these products retained 16 hydrogen atoms, the same as in monoterpene precursors. This NO₃-initiated radical contains 8 oxygens, which indicates one intermediate step of alkoxy radical formation, which is also consistent with a recent quantum chemical calculation result

(Kurtén et al., 2017). In addition, a good covariation between this factor and NO concentration can be seen in Figure 8b.

The daytime type-2 factor starts to increase concurrently with the sunrise and becomes the major HOM contributor in the mid-day. It correlates well with UVB ($R = 0.84$) and sulfuric acid ($R = 0.76$), indicating its relevance to photochemical process. For this reason, we attribute this factor to OH-limiting HOM formation. Most peaks in this factor are organic nitrates, indicating the involvement of NO. The most prominent peak is $C_{10}H_{15}O_8N$, which was found to strongly connected with NPF events (Kulmala et al., 2013; Jokinen et al., 2017). However, the formation of this peak is still a puzzle, as to our best knowledge, all chamber studies using monoterpene as the VOC precursor failed to efficiently produce this peak. Since OH radical is very reactive in the atmosphere, we cannot tell if the OH oxidation occurs at the beginning or secondarily on the first-generation products, and neither do we know how many different VOC precursors are involved.

The last daytime factor type-3 shows maximum intensity in the afternoon. Fingerprint peaks in this factor are also organic nitrates but with lower molecule weight, such as $C_3H_5O_6N$, $C_4H_5O_7N$, $C_5H_7O_7N$, $C_6H_9O_7N$, and $C_7H_9O_7N$. The corresponding atmospheric process is not clear, but correlation analysis shows the highest coefficient with temperature ($R = 0.8$), suggesting that the process is influenced by temperature. One plausible explanation is that these molecules are rather volatile so that they tend to stay in the gas phase at higher temperature.

Transported factor

In addition to the five HOM factors, the last factor is assigned to transported pollution. The only prominent peak in this factor is $C_6H_5O_3N$, most likely nitrophenol, which has been reported as a tracer for anthropogenic pollution such as biomass burning (Mohr et al., 2013). It shows an elevated intensity when the measurement location was clearly affected by polluted air masses. The measurement of nitrophenol with nitrate CI-API-TOF has not been reported before, but our latest measurement in Chinese megacities (Beijing, Shanghai, and Hong Kong, unpublished data) indeed shows that the nitrophenol is the single highest peak in nitrate-CI-API-TOF spectra. Therefore, nitrophenol could be used as an important tracer for pollution transport from urban environment in future works.

6.3 Atmospheric implications

At SMEAR II, six factors were found to best explain the mass spectra, including five HOM factors and one factor representing the transported pollution. O_3 and NO_3 are main oxidation initiators and RO_2 radicals are main terminators responsible for nighttime HOM formation. These two channels can produce HOM dimers, most of which are ELVOC. As suggested in **Papers II**, and **IV**, HOM dimers are believed to play a major role in the early stage of NPF. As shown in this paper, formation of these dimers is suppressed by NO, leading to the formation of various organic nitrate HOM monomers that are mostly LVOC. In the context of NPF, this shift in HOM formation pathway has profound influence that the majority of

HOMs in the daytime may not efficiently contribute to very early stage of NPF (below about 2 nm) according to **Paper II**. Thus, future studies on HOM-driven NPF need to well simulate the formation of organic nitrates in the first place.

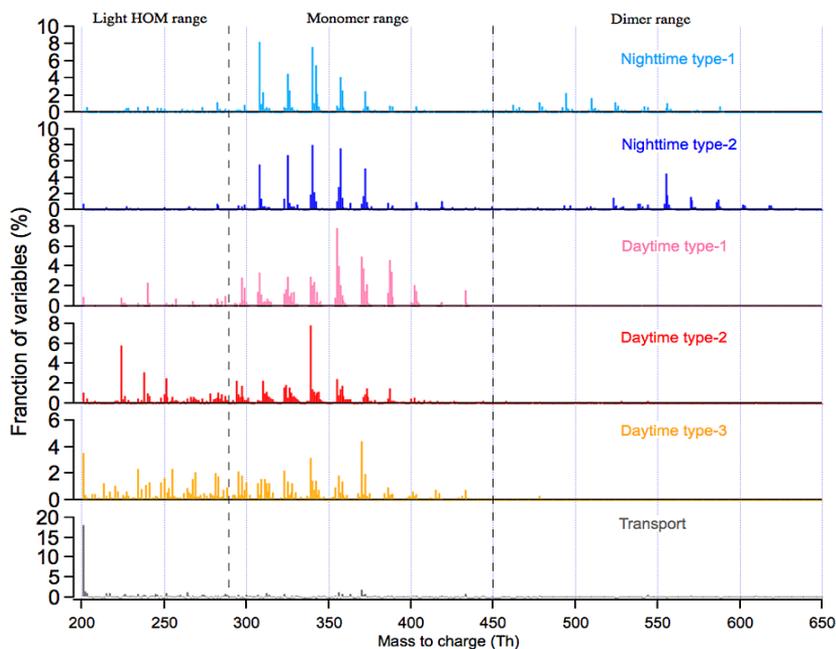


Figure 7. Profiles of the six factors retrieved by PMF. The figure is adopted from **Paper V**.

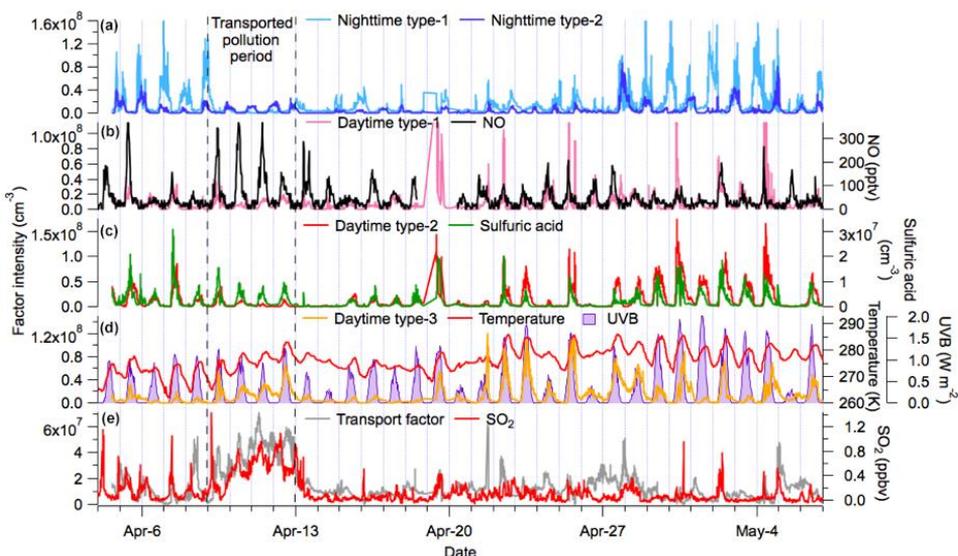


Figure 8. Temporal behaviors of PMF factors and relevant tracer gases as well as meteorological conditions. The figure is adopted from **Paper V**.

7 Vertical characterization of HOMs above and below the canopy

In addition to chemical processes, PMF also retrieved a factor representing temperature-related process, suggesting meteorological conditions may also play a role in HOM formation. For instance, the monoterpene concentration showed clearly different concentration at different heights (Rantala et al., 2014) and large variation of O₃ concentrations at different heights were observed as well (Chen et al., 2018). Despite the important atmospheric implications, HOM vertical characteristics have not been explored, mostly due to the practical difficulties in deploying two CI-API-TOF at different heights simultaneously. In the upcoming section, we are going to present the first concurrent measurement of HOMs in September 2016 at two different heights, ground level (1.5 m) and above the canopy (36 m).

Before the measurement, we injected trinitrotriazinane (C₃H₆N₆O₆) as a HOM surrogate with the same concentration into both instruments (e.g., perfluoro acids) using a temperature-controlled permeation tube, by which we evaluated the relative difference of transmission efficiency of the two instruments. This is also validated by directly comparing the HOM measurement at the two heights during a clear sunny day when the air was presumably well mixed (Figure 9). After correcting the data for the transmission efficiency, we are able to see the real change of HOMs due to the atmospheric conditions.

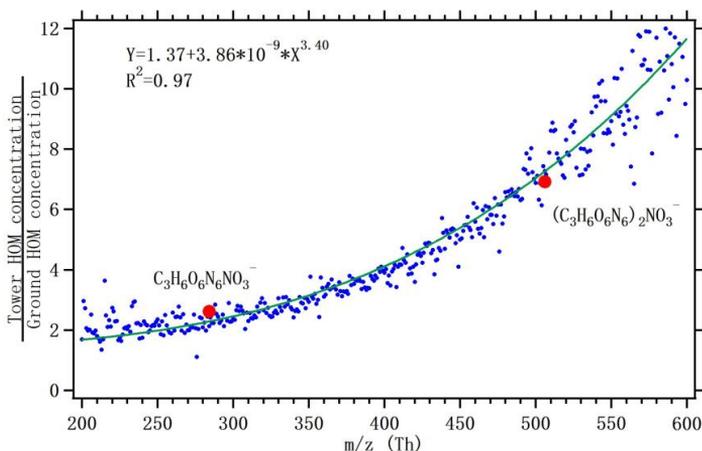


Figure 9. Relative transmission efficiency between the two CI-API-TOFs. This figure is adopted from **Paper VI**.

A data overview is shown in Figure 10. As anticipated, HOMs measured at two different height matched very well in the daytime, but sometimes show big deviations in the nighttime, especially during the nights associated with ozone depletion, increase of monoterpene concentration, and temperature inversion. Statistical analysis shows that the decrease of O₃ in these nights was in average a factor of two but the increase of monoterpene was about the similar magnitude, which led to rather similar HOM production so that its influence on HOM concentration should be minor.

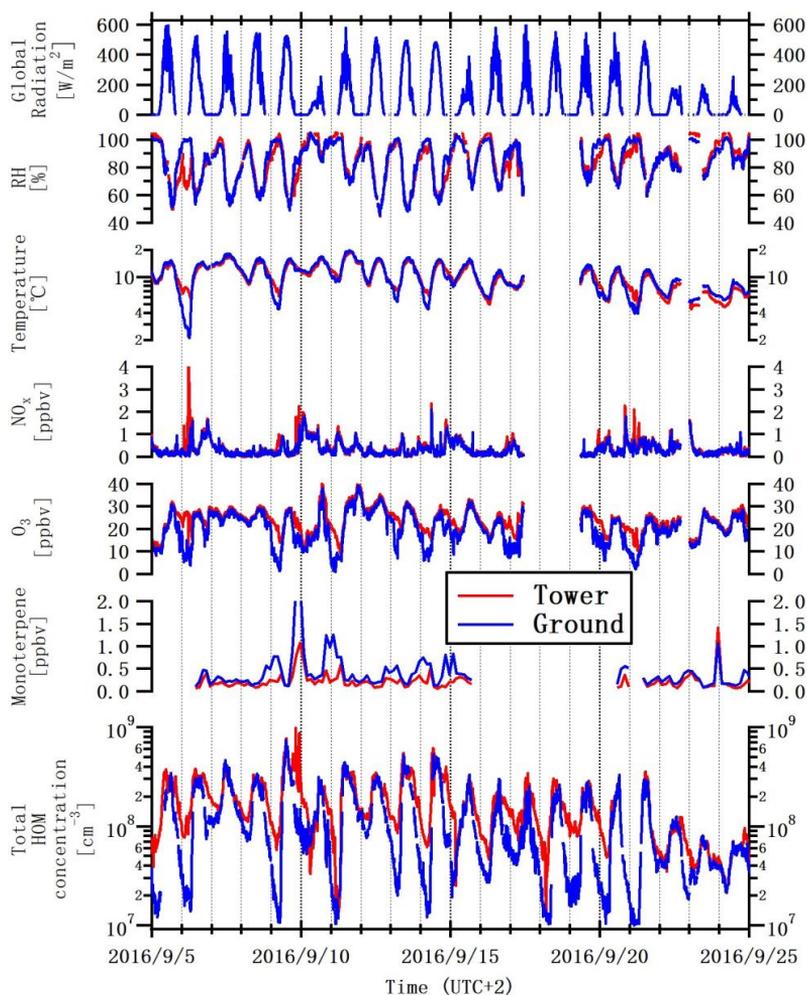


Figure 10. Time series of the measured trace gases, meteorological parameters and total HOM concentrations at the tower (red) and ground (blue) levels. This figure is adopted from **Paper VI**.

Further study on the meteorological conditions shows high air stability in these nights. Shallow and stable stratified nocturnal layer was formed, decoupling the near-ground air from the canopy top. This will further influence HOMs by two ways: Firstly, by enhancing the HOM surface loss due to the increased surface/volume ratio when the shallow layer formed; Secondly, by weakening the mass exchange via turbulent mixing and advection so that the layer with low HOM concentration was isolated. Although we cannot quantify the relative contribution of the two ways, the overall influence on HOM abundance by micrometeorology is obviously important in these nights. Thus, we conclude that HOMs measured at ground level HOM measurement should be used with caution when representing the HOM status in the local atmosphere, at least the micrometeorology needs to be considered.

8 Review of papers and the author's contribution

Paper I is the starting point of this thesis. It investigated the new-particle formation purely driven by HOMs, which complemented the traditional thought that the sulfuric acid is the main responsible vapor that triggers the nucleation in continental atmosphere and HOMs will only contribute in later steps. The strong ion effect in enhancing the nucleation is also reported and explained. This paper may help to explain the NPF observed in pristine environment with low sulfuric acid concentration, such as temperate and boreal forest, and Amazonian upper troposphere. It also refines the baseline of aerosol state in pre-industrial era, and thus improve our estimation of the anthropogenic radiative forcing. I collected and analyzed the HOM data, involved in the scientific discussion and commented on the draft.

Paper II demonstrated the role of HOMs in all stages of particle growth. It estimated the volatility distribution of products from the ozonolysis of alpha-pinene. By using an aerosol dynamic model to simulate the measured growth rate, this paper illustrated that ELVOC is dominating the particle growth below ~ 1.5 nm while LVOC has larger contribution to the growth rate at bigger sizes. The observed acceleration of particle growth is a result of both Kelvin effect and higher concentration of LVOC than ELVOC. This paper uses the same set of experiments as used in Paper I. I participated in the experiments and analyzed the HOM data from CI-APi-TOF and commented on the draft.

Paper III illustrated the mechanism of ion-induced nucleation at daytime Hyytiälä. It firstly demonstrated the role of $\text{H}_2\text{SO}_4\text{-NH}_3$ clusters in IIN in terms of both IIN probability and cluster growth rate. This study found that clusters containing 6 H_2SO_4 molecules (about 1.4 nm in aerodynamic diameter) could be at critical size in IIN. In addition to $\text{H}_2\text{SO}_4\text{-NH}_3$ clusters, clear evidence for HOM-driven IIN was shown, although the detailed nucleation agents were not clear. They could well be the HOM dimer, which are also suggested by **Paper I** and other studies. I generated the idea, processed and interpreted the data, and wrote most of the paper.

Paper IV presents direct observation of IIN purely driven by HOMs at nighttime at Hyytiälä. This is the first atmospheric evidence that supports the newly discovered nucleation mechanism in Paper I. By further analyzing the chemical specificities, we found that only the HOM non-nitrate dimers are the most likely nucleation agents, whereas nitrate dimers that have a similar molecular weight (or size) are not. The exact reason is unknown, but this shows that the HOM nucleation capacity is very sensitivity to their physicochemical properties. I analyzed part of the HOM data, contributed to the key ideas, and commented on the draft.

Paper V characterize the sources or relevant processes of HOMs in the real atmosphere using positive matrix factorization (PMF). Six retrieved factors include ozonolysis of monoterpene, NO_3 -initiated oxidation of monoterpene, $\text{RO}_2 + \text{NO}$ reaction, OH-limiting oxidation, temperature-influenced processes and transported species. Among the six retrieved factors, only the ozonolysis of monoterpene factor has been reproduced in the laboratory. Putting this in the context of NPF, more focus is needed to understand the daytime factors. As the first paper demonstrating the success of applying PMF on HOM data, this paper also provides detailed guidance of how to prepare the input data. I conducted a lab experiment to estimate the error matrix, performed the PMF analysis on HOM data, interpreted the retrieved factors and wrote the paper.

Paper VI presents the concurrent measurement of HOMs at ground and above the canopy and focuses on understanding the impact on HOMs by micrometeorology. We found that HOMs at these two heights were similar during the daytime, suggesting a rather homogeneous mixing layer. However, HOMs at ground level were very often much lower than above the canopy, which cannot be explained by the HOM production but can be attribute to the effect of micrometeorology. Therefore, we suggest to examine the meteorological conditions before using the ground-level measurement to represent the whole local atmosphere. I participated in the measurement, data analysis, scientific discussion, and commenting the manuscript.

9 Conclusions and outlook

New-particle formation may exert crucial impact on climate via contributing to a large fraction of CCN concentration. It is a world-wide phenomenon that has been observed in a variety of environments since the past decades, but molecular scale observations have been lacking due to the limitation of measurement techniques. And without such detailed information, it is not possible to accurately simulate the particle concentration in the whole atmosphere, leading to a large uncertainty on their climate impact (IPCC2013). Taking the advantages of recently developed instruments, this thesis attempts to improve our understanding of NPF mechanisms by conducting molecule-level observations.

Based on observations of NPF in the continental atmosphere, it is generally believed that H₂SO₄, with the help of stabilizing agents, forms the embryonic clusters and highly oxygenated organic molecules (HOMs) dominates the further growth to larger sizes. Prior to this thesis, molecular details of H₂SO₄ nucleation with water, ammonia, and/or amines has been depicted (Kirkby et al., 2011, Almeida et al., 2013, Kürten et al., 2014, Schobesberger et al., 2013) based on experiments in the CERN CLOUD chamber. However, the physicochemical properties of organic vapors and their plausible role in NPF remain largely unclear, and they became the main research goals of this thesis.

To evaluate the roles of HOMs in particle nucleation and growth, we conducted experiments in the CERN CLOUD chamber using HOMs produced from a mixture of alpha-pinene and O₃ (**Paper I, II**; *objective i*). Alpha-pinene was chosen as the precursor because it is one of the most emitted biogenic VOCs, especially in boreal forest environment (Hakola et al., 2012), and it can produce HOMs with a decent yield (Ehn et al., 2014, Jokinen et al., 2015). In such experiments, as presented in **Paper I**, particle nucleation purely driven by biogenic HOMs has been observed under atmospherically relevant precursor concentrations. Ions play an important role in this nucleation mechanism (also called ion-induced nucleation, IIN), enhancing the nucleation rate ($J_{1.7}$) by up to one order of magnitude (Figure 2). This nucleation mechanism might dominate the particle formation in pre-industrial era, thus it refines the baseline of particle states in pre-industrial atmosphere and decreases the estimated anthropogenic radiative forcing (Gordon et al., 2016). Furthermore, the nucleation mechanism might also be important in low-sulfuric acid environment, such as in the nocturnal boundary layer of forest environment.

Paper II focuses on understanding the role of HOMs in particle growth (*objective i*). The volatility of HOMs was estimated using SIMPOL model based on presumptions of certain structures, which spans over the volatility range of ELVOC, LVOC, and SVOC. We were able to further use an aerosol dynamic model to reproduce the size-segregated particle growth from the measurement. The model indicated that ELVOC dominates the particle growth below 1.5 nm due to the strong Kelvin effect, the more abundant LVOC take over the particle growth from 2 nm, and the contribution of SVOC via non-reactive condensation is negligible for particle growth up to 20 nm. The CCN concentration is very sensitive to

HOM volatility, which shows a +/- 50% change in CCN concentration in a global aerosol model if assuming the HOMs are entirely non-volatile or entirely volatile.

To further verify the existence of such nucleation mechanism in the present-day atmosphere, and understand its contribution to NPF, we revisited the IIN at SMEAR II and its plausible connection to the ion cluster compositions. As the ion composition are different between day and night (Ehn et al., 2010; Bianchi et al., 2017), IIN events are found to be driven by different cluster. **Paper III** focuses on the IIN events in the daytime (*objective ii*). We found about half of the IIN events involved sulfuric acid-ammonia ($\text{H}_2\text{SO}_4\text{-NH}_3$) clusters, and when such clusters were big enough (i.e., contain at least six H_2SO_4 molecules), IIN could occur at almost 100% probability. Observation showed that $\text{H}_2\text{SO}_4\text{-NH}_3$ clusters would not exist if HOM concentration was higher than H_2SO_4 by a factor of 30. However, about half of the IIN events were observed under such conditions, in which HOMs were the most plausible contributor. These results predicted a bigger contribution to IIN by HOMs in warmer seasons, which could not be fully verified using the spring data, and thus similar measurement in summer time is needed.

The ion clusters that caused the nocturnal IIN events (Junninen et al., 2008) have been investigated in **Paper IV** (*objective ii*), which presented the first direct atmospheric evidence of pure biogenic nucleation in **Paper I**. We demonstrated that the formation of HOM dimers was the key step to trigger further cluster formation. This also indicated that the capacity of nucleating is sensitive to HOM chemistry. Moreover, it was also found that these clusters barely grew beyond 6 nm, and thus probably had no actual impact on concentration of CCN-size particles. The reason of limited cluster growth is unclear, but probably related to the lacking of photochemical products.

Paper I, II, and IV showed that the roles of HOMs in both particle nucleation and growth are sensitive to their functional group or volatility, which are fundamentally determined by HOM formation chemistry. This urges a better understanding of the dominating HOM formation processes in the atmosphere (*objective iii*). We, for the first time, applied PMF to distinguish different HOM sources at SMEAR II on ambient HOM data (**Paper V**). Detailed descriptions on how to generate data matrix and error matrix were also provided. Five factors were found to explain HOMs at SMEAR II, including ozonolysis of monoterpene factor, NO_3 oxidation of monoterpene factor, $\text{RO}_2 + \text{NO}$ reaction factor, OH-limiting oxidation factor, and temperature-influenced factor. And one factor was defined as a good tracer for transported pollution. Out of these five HOM factors, our former CLOUD experiments (**Paper I, II**) only simulated the ozonolysis of monoterpene factor, and thus their results should be considered as preliminary and not directly applicable on present-day atmosphere.

Besides the chemistry, the micrometeorology may also influence the concentration and chemical composition of HOMs (**Paper VI**, *objective iii*). This challenges the use of ground-level measurement in understanding HOMs in the whole boundary layer. The shallow and stable stratified nocturnal boundary layer caused enormous reduction in near-ground HOMs. Therefore, HOMs measured at ground level HOM measurement should be used with caution

when representing the HOM status in the local atmosphere, at least the micrometeorology needs to be considered.

These six papers demonstrated the important role of HOMs in NPF and inspired a few new important research directions. Most NPF events occur in the daytime, when $\text{RO}_2 + \text{NO}$ reaction factor and OH-limiting factor (also NO_x termination) are dominant, it is therefore of extreme importance to better quantify these reaction channels in the laboratory. To understand this, new experiments aiming for better simulating daytime NPF at SMEAR II have been conducted at the CERN CLOUD chamber (Lehtipalo et al., 2018; Yan et al., 2018, manuscripts under review).

Another aim for this new chamber experiment is to simulate the retrieved PMF factors in **Paper V**. However, we were incapable of reproducing the OH-limiting factor no matter what OH level was conditioned. Thus, we suspect other VOC precursors, other than monoterpene, might contribute to HOMs. We found that p-cymene (p-Isopropyltoluene, $\text{C}_{10}\text{H}_{14}$) is a good candidate (Hakola et al., 2012). Our following flow tube experiment did show that p-cymene when oxidized by OH in the presence of NO_x , can efficiently form organic nitrates that have the same elemental formulae as monoterpene oxidation products, e.g., $\text{C}_{10}\text{H}_{15}\text{O}_8\text{N}$ (Yan et al., in preparation).

There is also room for improving the PMF. First, ambiguity of factor interpretations can be reduced by using high-resolution data as the model input. However, this requires a better understanding of measurement uncertainties associated with peak fitting (Cubison and Jimenez, 2015) and a proper way to introduce such an error term into the overall error estimation. Second, longer data set should be analyzed by PMF. As **Paper V** only applied PMF on spring HOM data, some important factors in HOM production might be too weak to be retrieved. For example, the sesquiterpene oxidation has been recently found to be important at SMEAR II at summer time (Hellén et al., 2018).

The majority of HOMs in this study are all from oxidation of monoterpene, thus the new insights provided in this thesis are mainly for improving the understanding about HOMs in boreal forest environment. In other typical environments, such as in the rainforest environment where high concentration of isoprene is also present in addition to monoterpenes, or the urban environment where aromatics are dominant, the HOM chemistry and their roles in NPF remain largely unknown and need future exploration. Nevertheless, the study route presented in this thesis is still useful to be applied on understanding the role of HOMs in other environments:

Measurement $\xrightarrow{\text{e.g., PMF}}$ *Chemistry* \rightarrow *Functional groups* \rightarrow *Volatility* \rightarrow *NPF*

For a final remark, current data shows that HOMs play a key role in determining the CCN concentration by participating in the particle nucleation and dominating the further growth in the environments studied until now. Only by fully characterizing their formation and physicochemical properties, can we accurately simulate the aerosol formation in the atmosphere and predict the future climate.

10 References

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