REPORT SERIES IN AEROSOL SCIENCE

N:o 172 (2015)

FORMATION OF LOW-VOLATILITY AEROSOL PRECURSOR MOLECULES AND CLUSTERS IN THE ATMOSPHERE

TUIJA JOKINEN

Division of Atmospheric Sciences
Department of Physics
Faculty of Science
University of Helsinki
Helsinki, Finland

Academic dissertation

To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public criticism in auditorium CK112, Gustaf Hällströmin katu 2 B, Exactum, on September 16th, 2015, at 10 o'clock before noon.

Helsinki 2015

Author's address: Department of Physics
P.O. Box 64
FI-00014 University of Helsinki
tuija.jokinen@helsinki.fi

Supervisors: Professor Markku Kulmala, Ph.D.
Department of Physics
University of Helsinki

Professor Tuukka Petäjä, Ph.D.
Department of Physics
University of Helsinki

Mikko Sipilä, Ph.D.
Department of Physics
University of Helsinki

Pre-examiners: Professor Kari Lehtinen, Ph.D.
Department of Applied Physics
University of Eastern Finland

Associate Professor Jesse H. Kroll, Ph.D.
Department of Civil and Environmental Engineering
Massachusetts Institute of Technology

Opponent: Doctor Karine Sellegri, Ph.D.
Université Blaise Pascal - Clermont-Ferrand II
France

ISBN 978-952-7091-30-2 (printed version)
ISSN 0784-3496
Helsinki 2015
Unigrafia

ISBN 978-952-7091-31-9 (pdf vesion)
http://ethesis.helsinki.fi
Helsinki 2015
Helsingin Yliopiston verkkopalvelut

Acknowledgements

The work behind this Ph.D. thesis was done at the Department of Physics, University of Helsinki and Department of Chemistry, Institute for Tropospheric Research in Leipzig, Germany. I thank the heads of the departments for providing me the working facilities. I thank my pre-examiners for reviewing this thesis. I thank my supervisors for their help and guidance that was always available regardless how busy things got at work. I thank all my co-authors for taking the time to comment our work and making paper drafts turn into cited articles in high impact journals.

I would like to express my deepest gratitude to Prof. Markku Kulmala for open-mindedly hiring me after two years of travelling around the world, utterly happy but unemployed. I'm still amazed to be part of the multidisciplinary work environment you created over the years, little by little.

From the moment I started working at the Division of Atmospheric Sciences, I felt like home. That's because of the wonderful people I share my office and work assignments with. I would like to thank Heikki, Sigi and Matti for being the best office mates ever. Even with the heavy traffic during the office hours, I wouldn't change it for the world. I would like to thank my friend and colleague Nina, it has been such a pleasure to have a partner in crime in the mass spectrometry group. In other words, thanks for being a girl and a chemist! I would also like to thank Juha, Jenni, Jani, Mikael, Nonne, Jyri, Hanna and the new kids on the block; Liine and Otso for being invaluable co-workers and friends.

I wouldn't be here today, defending my dissertation, if it wasn't for my dear friend and supervisor Dr. Mikko Sipilä. Thank you for sharing (often crazy) ideas, new innovations, work trips all over Europe and countless beer pints, twisted sense of humour and thus, lots of laughter with me. I sincerely appreciate the time you had for short coffee breaks and the time you spend advising me during my Ph.D. studies, manuscript writing, career planning and more often, life in general. Your friendship is priceless to me.

I have had the opportunity work in measurement campaigns and thus travel to various countries with many people and I would like to thank all of you for the wonderful experiences. Most of all I thank the personnel in Hyytiälä for their understanding, patience and collaboration during the years. International collaboration is nowadays crucial and I have had the privilege to work with the most motivated people in science from day one. I thank Prof. Doug Worsnop for his enthusiasm and ability to motivate people to work harder and find those ELVOC peaks in the mass spectrum. I thank Dr. Torsten Berndt for teaching me a lot about air chemistry during my pre-doc months in Leipzig. Working in the basement lab gave me the much needed insight into laboratory experiments. I would like to thank the students in CLOUD7 for your company and keeping the wheels turning during the long campaign.

Thanks for my friend outside of academia for understanding during the time I spend long periods of time away from home because I really wanted to find a neutral sulphuric acid containing cluster from the ambient air of Hyytiälä/Ireland/Antarctica. Thanks for dragging me to the gym or for a beer to get some valuable detox from science. Finally I would like to thank my family for saving my ass countless times when I was packing to move my home and possessions to yet another country. I don't know what I would do without you.

Tuija Beatta Aurora Jokinen
University of Helsinki, 2015

Abstract

We live in a world full of aerosols and witness their existence constantly. Changes in visibility, road dust and pollen filling the air in the spring time and even dosing some medicines are all related to aerosols. The most important aspect for this thesis is however, the formation of aerosol precursor molecules and clusters and their possible effects on aerosol properties. Different types of aerosols e. g. organic and inorganic, ice and pollen, biogenic and anthropogenic, when acting as cloud condensation nuclei (CCN), can change the optical properties of clouds and thus have different climate effects via changes in precipitation or cloud cover. Also the mechanism how the small cloud seeds are formed can have a major effect on the cloud properties. Clouds reflect and scatter radiation cooling the atmosphere but to this day aerosol effects still form the largest uncertainty in estimates of the climate of the future.

Low-volatility compounds in the ambient air are the most important components in both aerosol formation and their growth to sizes that can affect cloud properties such as their reflectivity. The vapours in the atmosphere form around half of the first precursors of aerosol particles via nucleation, still molecular in size. The rest is released directly into the air e.g. by the traffic or from the oceans as sea salt. Neutral molecular size precursor substituents are difficult to detect because they lack electric charge and their concentrations rarely exceed the detection limits of the used measurement instruments. This is one of the reasons why the first steps of nucleation process are still partly unsolved after decades of research.

This thesis concentrates first in development of selective methods and ultrasensitive instrumentation for the detection of acidic aerosol precursor molecules and clusters. These compounds include sulphuric acid, which is known to be highly important precursor for new particle formation. This thesis presents the first ambient measurements with the new instrumentation and even though sulphuric acid was detected in relative high concentrations during a particle formation event, no ambient cluster formation was yet observed. The same instrumentation was further used in an ultraclean chamber experiment were sulphuric acid and dimethyl amine formed growing clusters and they were detected from the smallest clusters all the way up to ~2 nm size. These compounds are likely to dominate the new particle formation with low-volatility organic compounds.

Tens of thousands of volatile organic compounds (VOC) are emitted in the atmosphere by terrestrial vegetation, marine environments and anthropogenic sources, making the search for the meaningful compounds for new particle formation extremely difficult. In this thesis a new group of extremely low-volatility organic compounds (ELVOC) from terpene oxidation are introduced. They form a large source of secondary organic aerosol (SOA) and might help explaining the former big gap between the measured and the modelled SOA loads in the atmosphere. Formation of these compounds from RO_2 radicals via rapid autoxidation process to stable molecules is also studied in details in laboratory experiments. This thesis also utilizes a global modelling framework, where the measurement results are applied. According to this thesis, ELVOC in particular are in crucial role when estimating SOA and CCN formation in the air. All together this thesis is a comprehensive study of both organic and inorganic low-volatility precursor molecules and clusters in the atmosphere, from their origin, formation mechanisms, and measurement techniques to their possible effects on climate now and in the future.

Keywords: mass spectrometry, clusters, sulphuric acid, dimethyl amine, ELVOC, new particle formation, secondary organic aerosol, field measurements, RO_2 radical chemistry, oxidation.

Contents

List of publications

This thesis is an introductory review of the following five research articles and they will be referred from here after according to their roman numbers. **Paper I** and **III** are reproduced under the Creative Commons Licence. **Papers II** and **V** are reprinted with permission from all the co-authors. **Paper IV** is reproduced under the John Wiley and Sons Licence.

I **Jokinen T.**, Sipilä M., Junninen H., Ehn M., Lönn G., Hakala J., Petäjä T., Mauldin III R. L., Kulmala M. and Worsnop D. R. (2012) Atmospheric sulphuric acid and neutral cluster measurements using CI-APi-TOF, *Atmos. Chem. Phys.*, 12(9): 4117 – 4125.

II Kürten A., **Jokinen T.**, Simon M., Sipilä M., Sarnela N., Junninen H., Adamov A., Almeida J., Amorim A., Bianchi F., Breitenlechner M., Dommen J., Donahue N. M., Duplissy J., Ehrhart S., Flagan R. C., Franchin A., Hakala J., Hansel A., Heinritzi M., Hutterli M., Kangasluoma J., Kirkby J., Laaksonen A., Lehtipalo K., Leiminger M., Makhmutov V., Mathot S., Onnela A., Petäjä T., Praplan A. P., Riccobono F., Rissanen M. P., Rondo L., Schobesberger S., Seinfeld J. S., Steiner G., Tomé A., Tröstl P., Winkler P. M., Williamson C., Wimmer D., Ye P., Baltensperger U., Carslaw K. S., Kulmala M., Worsnop D. R., and Curtius J. (2014) Neutral molecular cluster formation of sulfuric acid-dimethylamine observed in real time under atmospheric conditions, *Proc. Natl. Acad. Sci.*, 111(42):15019–15024.

III Ehn M., Thornton J. A., Kleist E., Sipilä M., Junninen H., Pullinen I., Springer M., Rubach F., Tillmann R., Lee B., Lopez-Hilfiker F., Andres S., Acir I.-H., Rissanen M., **Jokinen T.**, Schobesberger S., Kangasluoma J., Kontkanen J., Nieminen T., Kurtén T., Nielsen L. B., Jørgensen S., Kjaergaard H. G., Canagaratna M., Dal Maso M., Berndt T., Petäjä T., Wahner A., Kerminen V.-M., Kulmala M., Worsnop D. R., Wildt J. and Mentel T. (2014) A large source of low – volatility secondary organic aerosol, *Nature*, 506(7489):476-479.

IV **Jokinen T.**, Sipilä M., Richters S., Kerminen V.-M., Paasonen P., Stratmann F., Worsnop D., Kulmala M., Ehn M., Herrmann H. and Berndt T. (2014) Rapid autoxidation forms highly oxidizes RO_2 radicals in the atmosphere, *Angew. Chem. Inter. Ed.* 53(52):14596-14600.

V **Jokinen T.**, Berndt T., Makkonen R., Kerminen V.-M. Junninen H., Paasonen P., Startmann F., Herrmann H., Guenther A., Worsnop D. R., Kulmala M., Ehn M. and Sipilä M. (2015) Production of extremely low-volatile organic compounds from biogenic emissions: measured yields and atmospheric implications, *Proc. Natl. Acad. Sci.*, 112(23): 7123-7128

1. Introduction

Liquid or solid particles suspended in air are by definition called aerosols. The air surrounding us is thus an aerosol and it contains thousands of different chemical components, both liquid and solid, from various origins. Concentrations of these particles vary from up to a million particles per cc in polluted cities to the clean air of Antarctica where measured concentrations rarely exceed a few hundred particles (Kyrö et al. 2013). Aerosol particles cause changes in visibility, health problems when inhaled and they are estimated to be involved in half a million deaths globally (Saikawa et al., 2009). For example in polluted cities in China, dramatic increase of air pollution events has led to large enhancement in the incidence of lung cancer (Tie et al., 2009). In the changing and warming planet we live in, climate change is one of the existential 21st century issues and it is possible that by the end of the century Earth will be several degrees warmer than at the beginning (IPCC report). This is largely due to the massive increase in greenhouse gas emissions, such as CO_2 and methane, which affect the Earth's energy balance creating a positive forcing by absorbing more incoming energy. On the other hand, aerosols are suggested to have a net cooling effect (negative forcing) but the processes forming aerosols and their effect on cloud properties and thus their effect in the Earth's energy balance are highly uncertain (Haywood et al., 2005, Paasonen et al. 2013). Due to the lack of understanding in aerosol formation and properties, aerosols still remain the biggest contributor to the uncertainty of the radiative forcing by aerosol-cloud interactions reported by the International Panel of Climate Change (IPCC 2013).

Aerosol research is often reporting the number concentration of aerosol particles as well as different distributions such as mass, volume, number or surface size distributions. Today more and more efforts are put into recovering the chemical composition of the precursor vapours and molecules of aerosol particles (You et al., 2014, Taipale et al., 2014, Kulmala et al., 2013). These precursors are formed when low volatility vapours start condensing and forming clusters. This phenomenon is called gas-to-particle conversion (Kulmala et al., 2014). When a freshly formed sub-nanometer sized aerosol particle further grows by condensation of precursor vapours to a ~50-100 nm particle, it can already act as a cloud condensation nucleus (CCN). How and from which chemical components the CCN are formed and how they grow to meaningful sizes will finally influence the optical properties of clouds such as the cloud albedo effect (Lohmann et al. 2005). This thesis concentrates in studying the smallest precursor molecules and clusters, and their chemical compositions, concentrations and other properties to shed light into some these subjects mentioned before.

The particles that float in the air can be primary or secondary particles, in other words they can be emitted or released directly from the source into the air or they can be formed in the atmosphere. The most common primary aerosol particles are anthropogenic combustion products, sea salt, dust, sand and pollen. Secondary particles are formed from the vapours in the atmosphere and it has been estimated that up to 50 % of the particles can be formed via new particle formation (NPF) or as loosely referred as nucleation (Merikanto et al. 2009). NPF is a frequent phenomenon and it is observed ~30 % of the days in the boreal forest region in Hyytiälä, Southern Finland (Dal Maso et al., 2005, Nieminen et al., 2014) and often reported also in coastal areas of Ireland (O'Dowd et al. 2002a) and also in more polluted environments such as big cities in the USA (McMurry et al. 2005). The most prominent precursors of new particles are inorganic species such as SO_2, NO_x and NH_3. In the other hand, organic mass fraction of aerosol particles is observed to be significant or even dominant in some locations (Jimenez et al., 2009, Riipinen et al., 2012). Thus, both inorganic and organic species have important role in NPF (Kulmala et al., 1998, Metzger et al., 2009, Sipilä et al., 2010, Schobesberger et al., 2013).

Nucleation is suggested to follow ion assisted or neutral pathways (Lovejoy et al., 2004, Gagné et al., 2010). Recent studies find neutral pathway dominant in the boundary layer in the boreal forest region (Manninen et al., 2010, Kulmala et al., 2007). Compounds involved in ion induced nucleation can nowadays be studied using the latest mass spectrometric methods developed for ion detection (Junninen et al., 2010, Ehn et al., 2012), and ions are found to increase nucleation rates by two to ten-fold in laboratory experiments but it's suggested to be negligible in boundary layer condition (Kirkby et al., 2011). Instead of investigating ion species in the air, objectives of this thesis are in understanding the neutral nucleation pathway and the chemical composition of molecules and growing clusters involved. The reason for poor understanding of neutral nucleation pathway is mainly due to technological limitations as the detection of freshly formed neutral clusters is extremely challenging. Even though instruments capable of counting the number concentrations of newly formed sub-3 nm particles have been developed (Sipilä et al. 2008, Iida et al. 2009, Vanhanen et al., 2011, Wimmer et al., 2013), resolving the chemical nature of these newly formed clusters often require high resolution mass spectrometric techniques (see chapter 2 for methods).

The observed NPF in coastal or marine regions with strong tidal movements is often related to the presence of halogens (O'Dowd et al. 2002a). Most commonly iodic species such as iodine oxide and organic iodine compounds are suggested to contribute to NPF in coastal environments (Alicke et al., 1999, Hoffmann et al., 2001). Hotspots for iodide containing emissions are reported from Mace Head in Ireland (O'Dowd et al. 2002a), Weddel Sea in Antarctica (Atkinson et al. 2012) and west coast of Europe (McFiggans et al. 2010). According to several field studies the initial step of nucleation in continental areas is strongly connected to the presence of sulphuric acid (H_2SO_4, SA) (e.g. Paasonen et al. 2010, Sipilä et al., 2010, Weber et al., 1996). Sulphuric acid is formed in the atmosphere when sulphur dioxide (SO_2) is oxidised by the OH radical and it has a very prominent diurnal cycle. Thus, new particle formation including the growth of newly formed particles is commonly observed during the daytime over continental areas. However, SA does not nucleate by itself even at its highest atmospheric concentrations measured (some 10^7 molec cm^{-3}, e.g. in Hyytiälä boreal forest) or in a binary two component system with water under regular atmospheric conditions in the lower troposphere. The evaporation of water-SA clusters is restricting the cluster growth and thus other stabilizing or low-volatility compounds are needed to explain the observations in the ambient air (Petäjä et al. 2011, Kirkby et al. 2011).

SA is suggested to form stable clusters with ammonia, amines and highly oxidised organics (Kurtén et al., 2008, Riccobono et al., 2014). Concentration of ammonia is often an order of magnitude higher than concentrations of the most abundant amines but amines as strong bases will bind more likely to SA and thus enhance nucleation rates even in sub parts per trillion (ppt) levels (Freshour et al., 2014). Ion clusters containing SA and ammonia, SA and dimethyl amine and SA and oxidised organics have been detected from both laboratory systems and in ambient air (Kirkby et al 2011 Ehn et al. 2012, Schobesberger et al. 2013). These compounds present in ionic clusters are plausible candidates for stabilizing neutral clusters too and have been studied in this thesis (along with several other publications). The difficulties of detecting neutral species from the ambient air are i) the charging of molecules and clusters where some information is very likely lost, ii) extremely low concentrations (often sub-ppt levels) and iii) tens of thousands of chemical compositions to separate and detect. Nevertheless, such measurements still yield significant new information on the mechanisms relevant to neutral nucleation.

New high resolution mass spectrometric methods, especially the time-of-flight spectrometers are still rarely used for ambient neutral cluster detection with suitable charging mechanisms. These instruments are developed to be highly selective and sensitive to low-volatility compounds that are crucial for NPF and subsequent aerosol particle growth processes. In places that are clean and relatively free from anthropogenic influences, no neutral SA cluster measurements have been reported so far. Very few observations related to the molecules involved in neutral NPF events, other than molecular sulphuric acid concentration, are still missing when these events are reported in the literature. In a more polluted environment near to a big city in the USA some studies have reported neutral SA clusters up to SA tetramers in ambient air (Zhao et al. 2011, Jiang et al. 2011). For these reasons the focus of this thesis is neutral SA cluster measurements both in the laboratory and in ambient air and understanding their contribution to NPF. The role of sulphuric acid in new particle formation is discussed in detail within chapter 3 of this thesis.

Even though sulphuric acid is probably very important precursor for particle formation in the air, NPF is not solely connected to the presence of sulphuric acid and its clusters. Several studies show that the CCN production associated with atmospheric NPF is connected to the oxidation of biogenic volatile organic compounds (BVOC). BVOC are emitted by terrestrial ecosystems all around the planet. The most abundant BVOC are isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$), but the associated oxidation pathways to low-volatility products have remained unsolved. Also the emissions patterns of several terpenes, their magnitude and variability, are not well understood. In the boreal forest which has only a few dominant tree species, complex emission patterns of BVOC are observed with strong seasonal cycles. Large differences are also measured between the same tree species that dominantly emit monoterpenes but with different chemical structures e.g. some emit significantly more myrcene and some emit more α-pinene (Bäck et al. 2012).

When temperature in the atmosphere increases, also the emission rates of BVOC are expected to increase (Guenther et al., 1993). These BVOC will be removed from the air by oxidation processes and subsequent uptake onto pre-existing aerosol particles or other surfaces. This can further increase the number concentration of particles big enough to act as CCN. More CCN means more cloud droplets, denser clouds and thus suppression of solar radiation arriving in the atmosphere. The resent studies are thus more and more concentrating in detecting and quantifying the composition and concentrations of oxidised organics and estimating their contribution in NPF and especially in the growth of newly formed nanoparticles. The observations so far are scarce and most of the quantitative impacts are relaying in climate models. However, very recently a few studies have suggested that α-pinene oxidation products directly influence nucleation rates and not only participate in particle growth (Riccobono et al., 2012; Kulmala et al., 2013). The new mass spectrometric instrumentation, suitable for low-volatility gas phase compounds such as SA, is also able to detect low-volatility organic compounds very effectively (Ehn et al., 2012, Schobesberger et al., 2013).

BVOC and other volatile organic compounds are oxidised in the atmosphere by several oxidants. The most important oxidants include OH and NO_3 radicals and ozone. Very recently also the oxidative force of the stabilised Criegee radicals (sCI) is been discussed widely (Mauldin et al. 2012, Berndt et al. 2012, Sipilä et al., 2014). The most important daytime oxidant is the OH radical but all the OH radical reactivity (inverse of OH lifetime) cannot be explained by all the observed VOC or inorganic compounds (Di Carlo et al., 2004). This indicates that there must exist groups of compounds yet to be identified. It has been suggested that highly reactive biogenic precursors could explain a part of the missing reactivity. Nevertheless, there is still a big discrepancy between the measured and modelled secondary organic aerosol (SOA) burden from known precursor BVOC (Hallquist et al., 2009, Kroll and Seinfield 2008) indicating that there must be some unidentified reactivity of organic compounds in the air that are capable of producing SOA. In order to explain the atmospheric observations, large-scale model simulations demonstrate a need for a mechanism by which atmospheric BVOC oxidation produces extremely low-volatility organic vapours with molar formation yields of at least a few percent per reacted precursor compound.

The formation mechanisms of essentially non-volatile organic vapours in the ambient air have puzzled scientists for a while now (Riipinen et al., 2012, Kulmala et al., 1998, Donahue et al., 2012). Such extremely low-volatility organic compounds (ELVOC) were recently detected by Ehn et al. (2012) when investigating the naturally charged ions in both in the laboratory and ambient air. However, typical atmospheric oxidation chemistry schemes did not yet explain ELVOC produced on a time scale of minutes or even hours (Donahue et al., 2011). The amount of different ELVOC and also a little more volatile oxidized organics produced from BVOC may be extremely important to both local and global CCN budgets. The relative yields of ELVOC from different oxidants will also be important knowledge since all these quantities influence not only atmospheric NPF and subsequent growth but also the efficiency by which both newly-formed particles and sub-CCN sized primary particles produce new CCN.

The most important processes related to aerosol precursor molecules and clusters investigated in this thesis are depicted in figure 1 (marked with orange boxes) and the objectives of this research are depicted in here:

i) Develop a selective and sensitive method for neutral sulphuric acid and sulphuric acid containing cluster detection.
ii) Detect and understand the first steps of neutral acid – base nucleation including sulphuric acid and amines and/or ammonia from ambient air samples and quantify their concentrations in different environments using the developed instrumentation.
iii) Understand ELVOC formation mechanism from terpene oxidation and estimate their contribution in nucleation and growth of nanoparticles, SOA formation and cloud condensation nuclei concentrations globally.

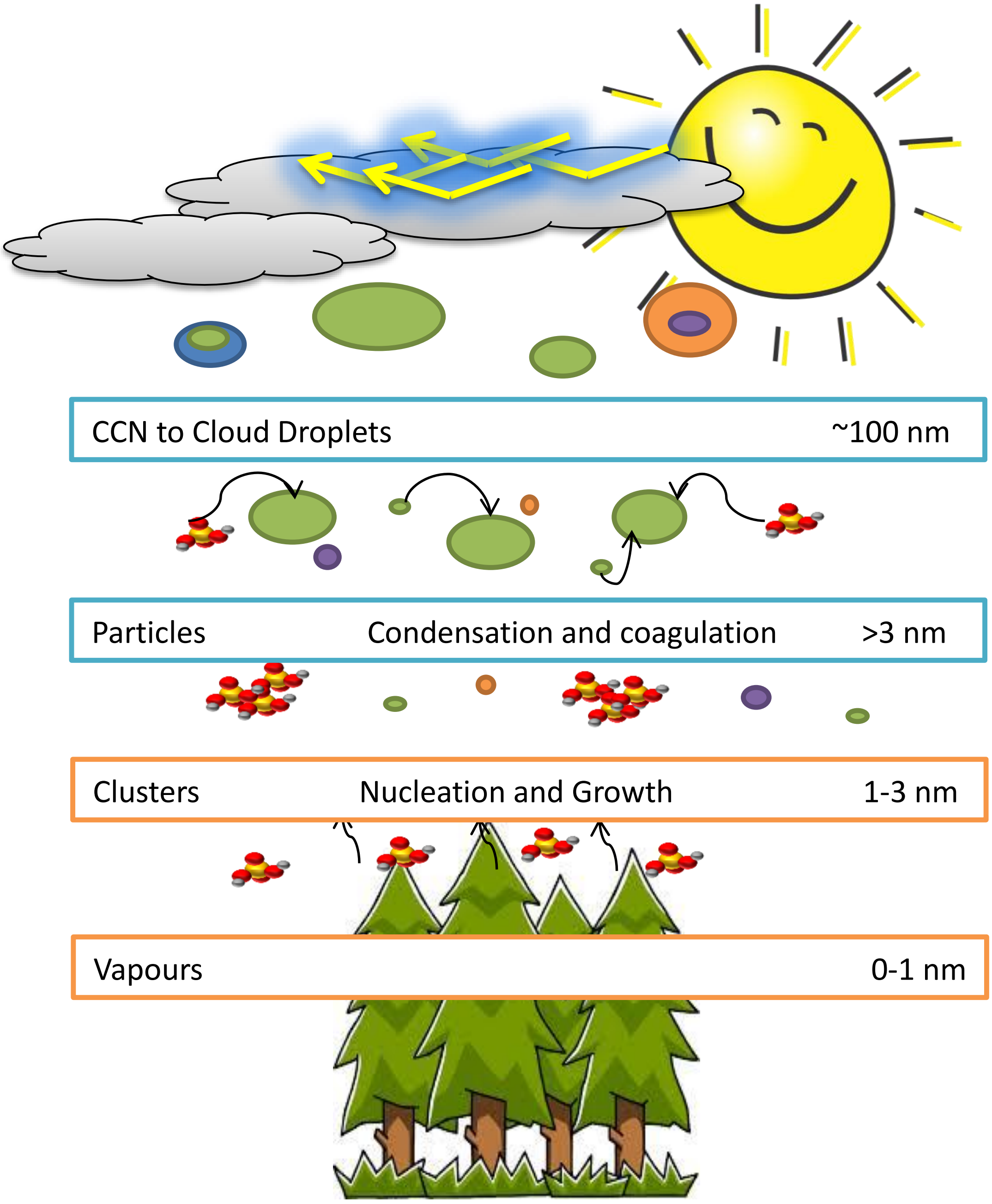

Figure 1. Formation of atmospheric aerosols and some of their most important processes. Size of given molecular clusters or particles are given on the right and it grows toward the upper end. When the particles reach CCN or cloud droplet size they can affect the optical properties of cloud and help reflect radiation back into space. Vapours and clusters are studied in detail in this thesis (boxes marked in orange) but all size ranges and atmospheric implications are also discussed.

2. Methods

2.1 Detecting low-volatility molecules in the atmosphere

The development of mass spectroscopic methods from popular quadrupole instruments to the high resolution time-of-flight mass spectrometers has helped atmospheric research tremendously. Sulphuric acid has been measured almost routinely since the 90s using chemical ionization mass spectrometers (CIMS) with very low detection limits (Eisele and Tanner, 1993, Mauldin et al., 1998, Petäjä et al., 2009). CIMS technique is also used to measure other atmospherically relevant precursor molecules such as ammonia (Nowak et al., 2007), organic acids (Veres et al., 2008) and nitric acid (Mauldin et al., 1998). The benefit of utilizing the high resolution mass spectrometers is that one can measure the whole selected mass-to-charge (m/z) range instead of single integer masses continuously after sample ionization. The benefits using chemical ionization coupled with mass spectrometers are the high collision rates of sample and reagent ions that increase the probability of neutral precursor molecules to get charged and detected. Detecting growing precursor molecules and clusters in such a way is becoming available in real time and with extremely low detection limits (sub-ppt levels).

The first objective of this thesis was to develop an instrument for neutral NPF precursor molecule and cluster detection. Requirements for a good field instrument are high sensitivity for the studied compounds and a low limit of detection (LOD). The best methods are operated in atmospheric pressure to minimize any sample modification prior to detection. Since the ambient air is full of molecules with various different origins and thousands of chemical formulas, some selectivity is most of the time preferred. All the articles in this thesis make use of the Chemical Ionization Atmospheric Pressure interface Time-of-Flight mass spectrometer (CI-APi-TOF) that is to this day the most suitable and possibly the most sensitive instrument for selective atmospheric neutral molecule and cluster detection (**Paper I**). In the following I present a summary of the used methods and development of the chemical ionization technique for ambient and laboratory measurements.

2.2 Chemical Ionization Atmospheric Pressure interface Time-of-Flight mass spectrometer (CI-APi-TOF)

In this thesis the goal was to first detect sulphuric acid and its clusters in ambient air. Previous ion measurements already show these compounds existing in small quantities in the canopy air of boreal forests. Sulphuric acid has been studied for years because it is the most prominent molecule in the air before and during new particle formation events, making it the best precursor for this phenomenon. This is the reason that guided us to develop a method that would be highly selective toward highly acidic compounds. The method was adopted from previous studies were chemical ionization was successively used to detect very low quantities of sulphuric acid (Eisele and Tanner 1993). During this thesis a new CI inlet was designed and built to fit the APi-TOF. The design was adopted from NCAR CIMS instrument because the coaxial sample and sheath flows will minimize sample losses to the walls. This is highly desirable since the atmospheric SA and low-volatility vapours are extremely low in concentration ($<10^4$ – some 10^7 molecule cm^{-3}). The CI inlet schematics are depicted in more detail in figure 2.

Chemical ionization is often described as a soft ionization method where the sample experiences only minimal and mostly chemically natural forces when ionized. The sample molecules are not impacted with electrons or fragmented on purpose in chemical ionization. Instead the sample is ionized using a proton transfer reaction or clustering the sample molecule to the reagent ion (=some type of derivatisation) and the loss of information of the whole unbroken compound is thus minimized. However, there are some problems related to all measurements using chemical ionization that are discussed within the chapters handling the measurements with the CI-APi-TOF.

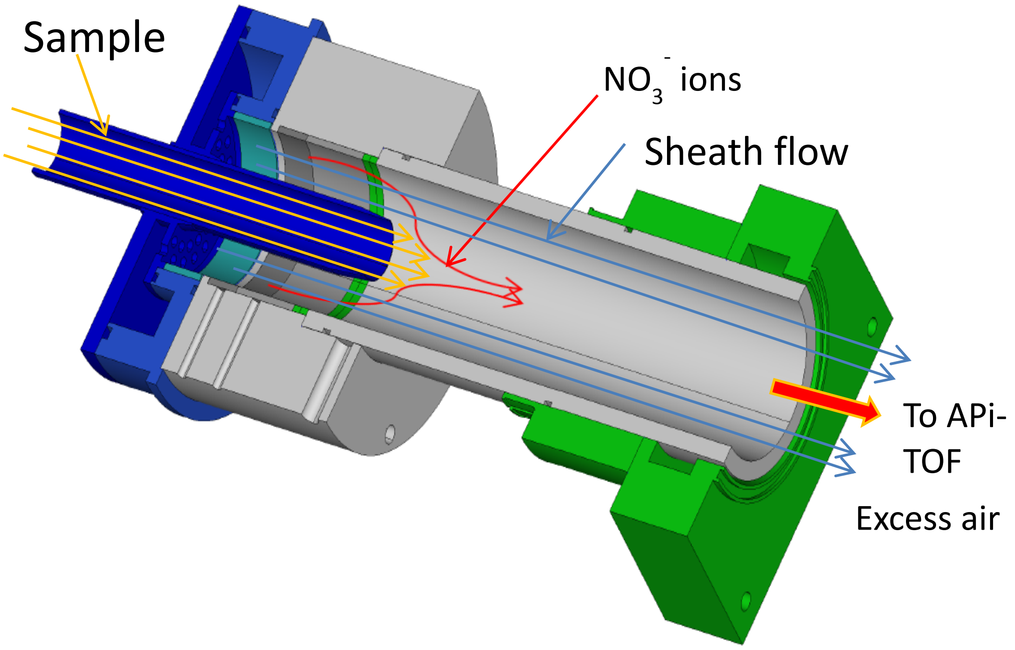

Figure 2. The Chemical Ionization inlet schematic. The arrows show the trajectories of the neutral sample air, sheath gas, NO_3^- ions (reagent ions) and excess air.

Chemical ionization is based on the proton affinities of the analyte and the reagent compounds. Acid (A) is by definition a compound that donates a proton and a base (B) is compound that accepts the proton.

$AH + B^+ \rightarrow A^- + BH$

Proton affinity describes the basicity of a compound in the air, in other words how strongly it is bound to a proton. For a highly selective chemical ionization one needs to choose a reagent ion close enough to the end or desired group. In this thesis we exclusively concentrate on detecting acids in the negative polarity, and thus the reagent ion was chosen to be an acid with a little stronger proton affinity than sulphuric acid. The perfect candidate to this purpose was nitric acid, which has been used in other studies before this thesis (e. g. Eisele and Tanner 1993). When nitric acid is ionized and it meets neutral sulphuric acid in the sample air, sulphuric acid acts as a proton donator because of its lower proton affinity and nitric acid accepts the proton and is this way neutralized in the process. Nitric acid can be ionized using several methods and the following chapter will be dedicated to different methods of producing the reagent ions, NO_3^-, tested during this thesis.

During the research for this thesis, three different ionization methods for the reagent ion production have been studied. The first method utilized was an alpha radiator, ^{241}Am (**Paper I**). The hypothesis behind the ionization process is that energetic particles hit nitrogen atoms in the air and rip off an electron. This free electron is then possibly adopted by oxygen to create O_2^-. When O_2^- meets the reagent nitric acid, the proton will be exchanged between these two to make NO_3^-. The notable benefit of using a radioactive source is the stability of ion production. A radioactive source is also more or less maintenance free for years. Utilizing an alpha radiating source is also relatively safe and precise to the ionization of sheath air solely since only a small obstacle blocks the radiation completely. The drawback of using this source is that the ion production cannot be turned off during e. g. transportation to the field site. Transportation brings in more disadvantages and legal issues if the source needs to be transported to another country or put on an aircraft.

The second option tested in this thesis was ionization using a corona discharge (partly in **Paper II**). This method utilizes a high electric voltage applied in the tip of a sharp needle where the current flows into air, causing ionization of the air molecules nearby. The disadvantages of a corona charger are production of ozone and NO_x (Rehbein and Cooray 2001). The production of oxidising agents is a problem since they can react with the sample air prior ionization.

The third reagent ion production was done using a soft x-ray source. The CI inlet had to be modified drastically to fit the new ionizer but the same time a stable ion source was again gained. The x-ray source is easily transportable to any location wanted and it is easily turned on and off, shutting down the radiation. The main issue with using the soft x-ray is to point the more energetic and permeating γ-radiation only to the ion production region. If directed incorrectly, the sample air itself might be ionized as well and this is highly undesirable because it causes uncertainty in the measurement.

After choosing the best and most suitable reagent ion production method, the ions need to get in touch with the neutral sample molecules that will be chemically ionized. The reagent ions travel in the sheath air that is coaxial with the sample flow that travels in the middle. Using a specific electric field the ions are mixed with the sample air without causing any unnecessary turbulence. These two flows interact in the drift tube region for ~200 ms and are then sucked into the mass spectrometer (see Figure 2). If the electric field is turned off, the reagent ions only mix with the sample flow by diffusion and most of them exit the system with the excess flow. The collision limited charging efficiency is approximately 0.1 % in this system.

The CI inlet part is connected to an APi-TOF mass spectrometer that is capable of high resolution mass-to-charge separation of the sample ions (Junninen et al., 2010). The mass spectrometer is sampling from atmospheric pressure via an interface and with a flow rate of ~0.8 litre min^{-1}. The APi-TOF is built by Tofwerk and University of Helsinki has contributed to the development. It offers a resolution of ~3000 Th/Th in so called “V-mode” and mass accuracy of <20 ppm. The measured mass range can be tuned by the user but for atmospheric research and relatively small cluster detection a mass range up to 2000 Th is preferred. The TOF-part mass spectrometer is kept in high vacuum (10^{-6} mbar) and the two quadrupoles in front of it are separately pumped gently toward the higher vacuum regions. Some cluster may evaporate or decompose in high vacuum but it is necessary for the detector to work. The applications and results of laboratory and atmospheric samples will be discussed after the study sites section.

2.3 Study sites

All the papers in this thesis utilize measurements from different environments. Both laboratory and ambient observation were made in the papers presented in this thesis. Environments vary from flow tube measurements to ultra clean chamber experiments and from boreal forest sites to agricultural surroundings and deciduous forests.

Most of the instrument development was done at the laboratory in University of Helsinki, Finland. All measurements reported in **Paper I** and all ambient measurements in **Paper II** were done at the SMEAR II (Station for Measuring Ecosystem – Atmosphere Relations) station in Hyytiälä (61°51’N, 24°17’E), southern Finland (Hari and Kulmala 2005). Also **Paper III** and **IV** utilize SMEAR II station data sets. SMEAR II station has been operational since the mid-90s and it offers the most comprehensive research facilities atmosphere-biosphere interactions, including a 127 m high mast for flux, meteorological and trace gas measurements. For the annual spring campaign, Hyytiälä accommodates hundreds of instruments in the small container village nest to the main station cottage. SMEAR II station is located around 60 km from the third biggest city in Finland, Tampere, which is located South-West from Hyytiälä. The closest surroundings are rather homogenous 50-year-old Scots Pine forest in the north and north-east and some small lakes and wetlands on the opposite direction.

Experiments in **Paper II** were all done in one of the cleanest laboratory facility available in CLOUD (Cosmic Leaving Outdoors Droplets) chamber at CERN, Switzerland (CLOUD collaboration 2000). The CLOUD chamber itself is a 26.1 m^3 stainless steel reaction chamber and it provides a well-defined and exceptionally clean environment for nucleation studies. In the chamber both neutral and ion induced processes can be studied. A pion beam from the CERN proton synchrotron can be used for ion production or the chamber can be used with high voltage clearing field for fast ion removal, ensuring neutral experimental conditions. The chamber is filled with synthetic air that is produced from cryogenic liquid oxygen and nitrogen. During experiments the CLOUD chamber can be controlled with very low concentrations of atmospherically relevant reagents such as sulphuric acid, amines, ammonia or volatile organic compounds. In **Paper II** atmospherically relevant concentrations of sulphuric acid were kept between 10^6 and 10^7 molecule cm^{-3} while dimethyl amine ($(CH_3)_2NH$, DMA) was present at mixing ratios between 5 and 40 pptv. All the experiments were conducted at 278 K and 38% relative humidity.

The majority of the results presented in **Paper III** were measured at the Jülich Plant Atmosphere Chamber facility (JPAC9) in Germany. The chamber is a 1450 litre borosilicate chamber that was kept in constant temperature of 16±1°C and relative humidity of 63±3% during the experiments. The JPAC measurements were mainly carried out in a continuously stirred tank reactor under steady-state conditions, contrary to many other chamber studies. This means that a constant flow of reactants and oxidants (including VOCs, ELVOCs and particles) to the chamber until steady-state is reached. The average residence time was ca. 45 min.

The laboratory experiments in **Paper IV** and **Paper V** were all done in Germany in Leibniz Institute for Tropospheric research (TROPOS) facilities. Most of the observations are measured in a glass flow tube. The IfT-LFT is laminar flow tube, 505 cm in length and inner diameter of 8 cm (Berndt et al., 2005). The flow tube is temperature and relative humidity controlled and various gases such as ozone or VOCs can be introduced in the carrier gas flow from the top of the flow tube. Carrier gas was produced from clean nitrogen and oxygen (79:21 v:v) but the relative amounts of the gases can be changed. Flow rate is usually kept in constant value of 30 litre min^{-1} but reaction times in the tube can be varied from the regular 39.5 s all the way down to ~8 s. UV-lights are assembled around the flow tube for enabling OH production for the experiments. Instruments were set up to measure the center flow from the flow tube outlet. Ambient measurements in **Paper IV** were done at the TROPOS field measurement station in Melpitz (51°54'N, 12°93'E). Melpitz is located approximately 50 km east from Leipzig. The station is surrounded by agricultural pasture and it is locate close to a deciduous forest area. Observation in Melpitz can be regarded as representative to Central European regional conditions (Spindler et al., 2010).

3. Role of sulphuric acid in new particle formation

During the recent years it has been first proposed theoretically and later on confirmed with ambient observations that atmospheric new particle formation is dependent sulphuric acid concentration (Weber et al., 1996, 1997, Kulmala et al. 2004, 2006, Sipilä et al., 2010). Known sources of gas phase sulphuric acid are sulphur dioxide (SO_2) emission from anthropogenic combustion processes. Natural sources include e.g. volcanic eruption and dimethyl sulphite (DMS) emissions from the oceans that oxidise to either methyl sulphonic acid (MSA) or SO_2 (). These compounds are then oxidized further by the OH radical or, as more recently suggested, by stabilised Criegee Intermediates (sCI), into sulphuric acid (Mauldin et al. 2012). OH radical is still considered the main oxidant for atmospheric sulphuric acid formation. The formation pathway of sulphuric acid in the gas phase from SO_2 can be depicted with the following reactions:

$$SO_2 + OH + M \rightarrow HSO_3 + M \qquad (1)$$

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \qquad (2)$$

$$SO_3 + 2\,H_2O + M \rightarrow \mathbf{H_2SO_4} + H_2O + M \qquad (3)$$

OH radical needed for SO_2 oxidation is formed in the atmosphere via photolysis of ozone by solar radiation (UV-B range of 280-320 nm) and thus sulphuric acid concentration very often reaches its maximum during sunny middays.

Molecular sulphuric acid (bold text in reaction 3) has been measured from ambient air for decades. The development of chemical ionization mass spectrometer (CIMS) by Eisele and Tanner (1993) has led to low detection limit for atmospheric SA research. Since the 90s sulphuric acid concentrations have been reported from various environments in several publications (e.g. Petäjä et al., 2009, Mauldin et al., 2004, Hanson and Eisele 2002, Hanson and Lovejoy 2006 and Zhao et al. 2010). Since sulphuric acid is produced mainly in the reaction with OH radical, it has a strong diurnal pattern and the concentration of neutral gas phase sulphuric acid varies significantly between NPF event and non-event days. In Hyytiälä, the maximum concentration reaches some 10^7 molecules cm^{-3} during event days and stays in low levels, $<10^6$ molecules cm^{-3}, during the days when no NPF is observed. The more important property of the CI method is the low detection limit that allows detailed measurements of the first steps of NPF where SA plays a crucial role.

Neutral clusters or nanoparticles in 1-3 nm size range can be nowadays detected with a new sensitive particle counter called the particle size magnifier (PSM, Vanhanen et al., 2011). Yet particle counters, such as PSM, do not provide information on the chemical composition of the growing neutral clusters and the CIMS usually only provides molecular SA concentration. The chemical information gap between these two instruments is now reachable with the use of the CI-APi-TOF. The CI-APi-TOF offers the equal or better sensitivity for molecular sulphuric acid measurements and the vast measurement range, usually up to 2000 Th is suitable for sulphuric acid cluster detection (**Paper I and Paper II**) as well as larger oxidised organic molecules (e .g. Schobesberger et al., 2013). Ambient ion measurement report sulphuric acid clustering to sulphuric acid multimers during several NPF events (Junninen et al., 2010). Field observations have reported a negligible contribution of ion clusters to new particle formation and growth (Iida et al. 2006, Manninen et al. 2010). Hence neutral nucleation pathway must be the dominating process, indicating the existence of corresponding neutral clusters.

The formation rate of stable 1 nm clusters (J_1, cm^{-3} s^{-1}) has been approximated by a power law relationship of the sulphuric acid concentration to explain atmospheric observations:

$$J_1 = K[H_2SO_4]^P \tag{4}$$

where K and P are empirically determined parameters. Field measurements have determined the value for P to be $1 \leq P \leq 2$ (Kulmala et al., 2006, Sihto et al., 2006, Riipinen et al., 2007, Kuang et al., 2008). The lower limit of the exponent corresponds to the activation model (Kulmala et al., 2006) and the maximum value corresponds to kinetic model for particle formation (McMurry and Friedlander 1979, McMurry 1980 and 1983). In the activation model only one sulphuric acid is present in the activated thermodynamically stable cluster during nucleation and in the kinetic model two sulphuric acid molecules are responsible for forming the critical cluster. The prefactor, K, has been reported to vary by several orders of magnitude in the case of kinetic nucleation model (i.e. P = 2) among different measurement environments for the given sulphuric acid concentration (Riipinen et al., 2007, Kuang et al., 2008). This large variability in the K-value from location to another indicates that nucleation is a multicomponent process that involves sulphuric acid with additional species other than just water (Paasonen et al., 2012). Several species more or less abundant in the atmosphere have been suggested to form stable clusters with SA. The most studied from the atmospheric compounds are strong bases such as dimethyl amine (Loukonen et al., 2010, Zhao et al. 2010, Almeida et al., 2013, **Paper II**), other bases such as ammonia (Merikanto et al., 2007, Kirkby et al., 2011, Ehn et al., 2010) organic acids (Zhang et al. 2004) and oxidised organic compounds (Ehn et al., 2012, Riccobono et al., 2013, Schobesberger et al. 2014, **Paper IV and V**).

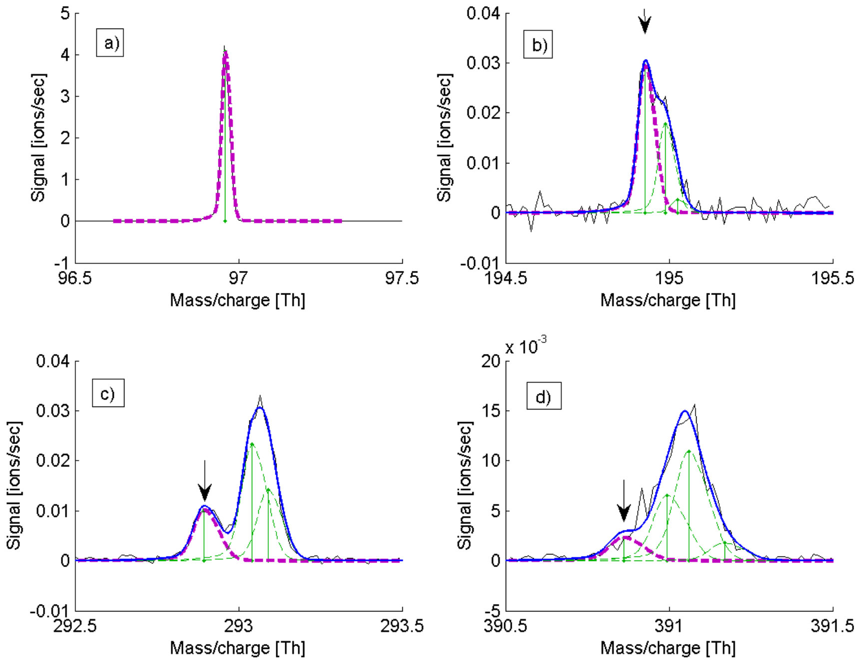

Figure 3. The detected sulphuric acid containing signals with the CI-APi-TOF in the spring 2011 at the Hyytiälä SMEAR II station. Sulphuric acid signals are depicted with purple dashed lines. The signals correspond to sulphuric acid monomer (a), dimer (b), trimer (c), and tetramer (d). Also interfering signals are included in the figures and the sum of peak areas fitted is depicted in blue. Figure adopted from **Paper I**.

3.1 Sulphuric acid containing clusters measurements

The first two papers in this thesis concentrated on the observation of neutral clusters containing sulphuric acid in the atmosphere and laboratory experiments. The new CI-APi-TOF, which is described in the previous chapters, was used for the first time for ambient measurements in the boreal forest region (**Paper I**). Measurements of neutral sulphuric acid clusters were done during the spring time, from March to April, when NFP is occurring frequently (Dal Maso et al, 2005, Nieminen et al., 2014). With the help of high resolution of the TOF and peak fitting according to the exact mass of the molecules or clusters, sulphuric acid containing molecules were separated from interfering peaks at the same integer masses. During the campaign the whole mass range up to 2000 Th was recorded and thus we were able to follow both pure SA clusters and possible ammonia and other base signals clustered with SA molecules or clusters.

In late March many consecutive days of strong new particle events were observed. In **Paper I** we reported two of these days when sulphuric acid concentration was the highest and the possible SA cluster observation was most likely. Sulphuric acid concentration reached a maximum value of 6 x 10^6 molecules cm^{-3} during both days. In the CI-APi-TOF the most abundant SA signal was the monomer (96.9601 Th) followed by cluster signals corresponding to the dimer, trimer and tetramer (194.9275 Th, 292.8949 Th, 390.8622 Th), respectively. Since CIMS measurements report sulphuric acid cluster measurements in unit mass resolution instead of exact mass peak fits, we evaluated the importance of high resolution peak fitting by comparing the difference between the results of unit mass resolution and exact mass peak fitting. Even with the high selectivity of the CI-APi-TOF instrument, only the monomer was detected without other interfering compounds at the same integer mass (Figure 3. The interfering compounds were identified to originate from the fluorinated tubing material used to carry sheath air and from other atmospheric compounds. **Paper I** concludes that without high resolution data the cluster concentrations can be overestimated even with the most selective methods and thus high resolution peak fitting is crucial for neutral sulphuric acid containing cluster measurements.

In **Paper I** the instrument did not have an ion precipitator and thus also naturally charged ions in the air were able to contribute to the detected SA and cluster signals. For this reason we had to confirm that the signals depicted in Figure 3 were neutral clusters. The americium source was removed to prevent neutral molecule chemical ionization and only ion clusters were measured for a period of two weeks. After comparison of these two methods, the only signal that was affected by the chemical ionization was the SA monomer. All SA cluster signals did not increase when chemical ionization was utilised for neutral cluster detection and thus they were not separable from naturally charged ion signals. Next we wanted to quantify the concentrations of the measured signals and compared the dataset to the calibrated CIMS instrument sulphuric acid concentration. The inter-comparison yielded a linear response with an additional factor of 3.78 to the used calibration factor of the CIMS (Mauldin et al., 1999). Calibration coefficient (*C*) of 1.89 x 10^{10} molecules cm^{-3} was applied when sulphuric acid concentration was calculated according to:

$$[H_2SO_4]_{neutral} = \frac{HSO_4^- + H_2SO_4 \cdot NO_3^-}{\sum \text{reagent ions}} x\ C \qquad (5)$$

This result of no neutral cluster detection in this study is contradictory with previous reports by Zhao et al. (2010) and Jiang et al., (2011) who detected neutral sulphuric acid clusters up to the tetramer with concentrations ~10^4 molecules cm^{-3} during NPF events. Possible reason for this discrepancy might be that if the naturally charged ion signal observed was converted to concentration (Eq. 5), the concentrations would be in the range of a few 10^4 molecules cm^{-3}. If the neutral cluster concentrations were lower, the CI-APi-TOF would not be able to detect them reliably because the limit of detection (LOD) in **Paper I** was determined to be 3.6 x 10^4 molecules cm^{-3} for the monomer and it was applied for all the cluster signals as well. If the sulphuric acid dimers during these NPF days would form close to collision limit, with negligible evaporation of the dimers and in the presence of stabilizing compounds as suggested in a laboratory experiment by Petäjä et al. (2011), concentration of neutral dimers in Hyytiälä should've been around 5 x 10^6 molecules cm^3. Since the dimer concentration in Hyytiälä was detected to be lower than LOD, we can speculate that either the evaporation rate of the dimers was higher than in the laboratory system or the presence of stabilising ternary species in Hyytiälä is inadequate to promote/allow dimer formation. Other possibility is that other abundant low-volatility compounds would rapidly condense on the dimers, changing their properties so that the new cluster would not get ionised with the nitrate chemical ionization. To conclude the results from **Paper I**, no neutral sulphuric acid clusters over the detection limit of the CI-APi-TOF were detected during the new particle formation events in Hyytiälä SMEAR II station in the spring of 2011.

Sulphuric acid cluster formation is further investigated in **Paper II**. During the CLOUD7 campaign the CI-APi-TOF was operated in an ultraclean environment and nucleation studies were performed using one of the suggested SA cluster stabilising agent, dimethyl amine (DMA). DMA was used for the experiments because only some parts per trillion (*ppt*) levels can explain the formation rates observed in the boundary layer (Petäjä et al., 2011). However, as demonstrated in the previous chapters, the composition or concentrations of neutral nucleating clusters have remained mostly open questions. The first unambiguous detection of neutral clusters, including sulphuric acid and dimethyl amine, during NPF is reported in **Paper II**. The CI-APi-TOF detected SA-DMA clusters containing up to 14 SA and 16 DMA molecules. The clusters are classified from here on by the number of sulphuric acid in the cluster (trimer corresponds to the sum of signal containing three SA molecules and so on). The clusters from the SA trimer onward were observed to grow step-by-step addition of one SA and one DMA molecule. This same mechanism of cluster growth of SA-DMA system has been recently observed in charged clusters (Almeida et al., 2013). Figure X depicts the detected nucleated clusters when sulphuric acid concentration was set close to the maximum concentration observed in e. g. Hyytiälä (3 x 10^7 molecules cm^{-3}) and 10 ppt of DMA was present.

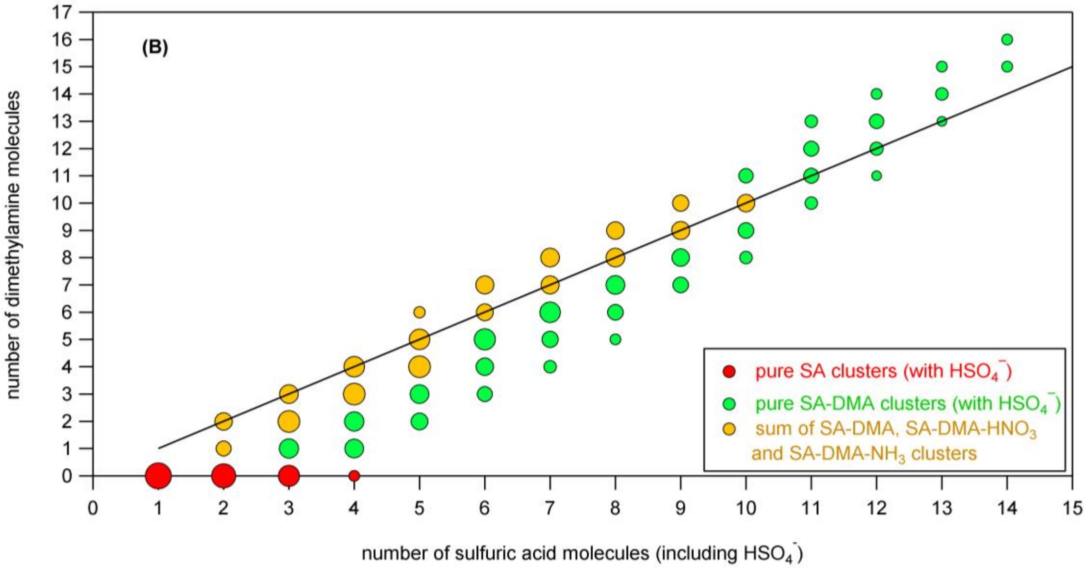

Figure 4. SA-DMA clusters detected in the laboratory experiments during CLOUD7 using the CI-APi-TOF.

As seen from Figure 4, the smallest SA clusters were not detected bound with DMA, but the first pure SA-DMA clusters detected by the CI-APi-TOF were detected from the SA trimer onward. It is likely that the DMA evaporates or fragmentises upon the charging of the smallest neutral clusters (monomer, dimer) as quantum chemical calculations support that all sulphuric acid clusters and molecules would be bound to DMA in these conditions (Ortega et al., 2012). Evidence of this clustering was not yet proven but indication of the SA dimer stabilisation with DMA and NO_3^- was observed in high dimer concentrations during the experiment (Figure 4). In binary system of water and sulphuric acid, the dimer concentration would have been approximately six orders of magnitude lower than in the experiments with DMA (Hanson and Lovejoy, 2006). Only the stabilising effect of the base used can explain the high SA dimer concentration observed (Almeida et al., 2013, Petäjä et al., 2011). This observation may also be linked to confirm the results of **Paper I**, where no neutral dimers were observed since cluster stabilising molecules were possibly present in extremely low concentrations (or missing).

Temporal behaviour of the formed SA-DMA clusters where studied in close detail using two CI-APi-TOF instruments. The formation of sulphuric acid and subsequent larger clusters are followed until they reach a steady-state. At steady-state the formation of the clusters and their loss rate are equal. The experimental results from the two CI-APi-TOF's were compared to a kinetic model (McMurry et al., 1980) that predicts SA-DMA cluster concentration when the sticking efficiency is unity and the only free parameter was the production rate of SA monomers. SA monomer parameter was set to represent the measured SA monomer concentration. The kinetic model describes the experimentally observed SA dimer signal within the measurement uncertainty (factor of 1.5). In the model calculation larger clusters show systematically increasing concentrations (with systematic increase in measurement error) and thus the formation of the large SA-DMA clusters can be explained to occur at or very close to the kinetic limit. In the model calculations, selected evaporate rates are considered for the cluster formation, the large cluster concentration show compatible slopes with the kinetic-limit curves instead of the finite evaporation rate curves. The finite evaporation rate would steepen the slopes in the case of increasing evaporation rate. To reproduce such data, the dimer evaporation rate would have increase to unphysical values. Also the evaporation of all the larger clusters should be consequently smaller than the dimers and thus all these clusters must have been stable at least in these laboratory conditions. Nonetheless, the data set measured in the ultraclean CLOUD chamber in **Paper II** indicates that the formation of SA-DMA clusters in the system was very close to be kinetic controlled and evaporation of these clusters are effectively zero even with some discrepancy with the model and experimental results.

However, even when the measurements within **Paper II** were done carefully mimicking the atmospheric conditions the results are not yet confirmed from atmospheric observations. The issue here may be in the sub-ppt levels of needed stabilising bases such as DMA in the atmosphere (Hanson et al., 2011). The measured DMA concentrations rarely exceed 10 ppt with the exception of e.g. cattle farms or piggeries. Quantification of DMA concentration in ambient air was done very recently by Sipilä et al. (2014) who reported lower than detection limit concentrations (< 30 ppq, parts per quadrillion) of DMA in the boreal forest in Hyytiälä. The laboratory investigation in **Paper II** and ambient measurements by Chen et al. (2012) both report a threshold value of DMA:SA ratio for the stable dimer production. Since the rate of DMA arrival and the SA-DMA cluster evaporation rate are compatible and thus the level of stabilising base determines the fraction of stable clusters. This threshold in both papers is in the factor of ~100:1 for DMA:SA ratio. Thus, the observation of neutral SA dimers in the atmosphere remains a challenge in clean environments such as the boreal forest region.

4 Extremely low-volatility organic compounds (ELVOC)

If the SO_2 emission leading to the formation of a known NPF precursor, atmospheric sulphuric acid, is mostly anthropogenic origin, volatile organic compounds (VOC) from vegetation play the most important role in the biogenic route to aerosol formation. A large fraction, 20-90%, of the small particulate matter is comprised of organic species (Guenther et al., 1995, Griffin et al., 1999, Jimenez et al., 2009, Kroll et al., 2008). Forests emit thousands of different biogenic VOC, such as isoprene and monoterpenes, and they make up approximately half of all VOC emissions globally (~55 %, ~600 Tg C, Guenther et al., 1995) and are equivalent to the global emissions of methane (~500-600 Tg CH_4, IPCC 2007 and references within). Since it is likely that all these individual BVOC chemically evolve over their lifetime in the atmosphere, a detailed understanding of their sources, transformation and fates are of crucial importance to modern climate models (Kroll et al., 2011, Paasonen et al., 2013).

The BVOC are removed from the atmosphere by oxidation processes and deposition of these reaction products. The OH radical is acknowledged to be the main oxidising compound of BVOC but they also react with NO_3 radical and olefinic (alkenic) BVOC react with ozone further producing OH radicals (Paulson et al., 1997, Donahue et al., 1998). Some these species are considered lower volatility reaction products since their O:C ratio increases with oxidation process (Donahue et al., 2011 and 2012, Kroll et al., 2011). Since aerosol samples are constantly detected with a high organic fraction, these oxidised organic molecules are possibly condensing even on the smallest aerosol particles, perhaps onto sulphuric acid clusters, growing them to bigger sizes and are thus contributing to secondary organic aerosol burden (Jimenez et al., 2009). Contribution of BVOC to aerosol formation has been studied intensively for decades. During the beginning of the 21st century indirect evidence of reactive BVOC emission was found and suggested to be a group of terpenes (O'Dowd et al., 2002b, Faloona et al., 2001, DiCarlo et al., 2004). The paper by Faloona et al. reported unexpected high nocturnal OH radical concentrations after late evening NPF event. They also pointed out that nocturnal HO_2 and OH radicals had dependence on ozone concentration. A few years after these results a significant decrease in ozone concentration was observed during similar conditions, indicating that the reactive terpene group might be olefinic (alkenic) (Kurpius et al., 2003). These results might be due to the Criegee radical, which are formed in monoterpene ozonolysis, decomposition (Vereecken et al., 2014). Ever since these results the contribution of monoterpenes to new particle formation and especially to nanoparticle growth has been suggested in various publications (e.g. Kulmala et al., 1998, Hirsikko et al., 2005, Tunved et al., 2006, Laaksonen et al., 2008, Riipinen et al., 2012 Kulmala et al., 2013). OH radical has kept its place as the main oxidant during the initial steps of NPF but ozonolysis becomes more important when the aerosol size exceeds a 5 nm diameter (Hao et al., 2009).

However, the exact sources, oxidation mechanisms or known chemical compositions of condensable low-volatility organic compounds needed to explain the growth rates of nanoparticles and the organic aerosol burden observed in various locations were not solved until very recently (Ehn et al., 2012, Zhao et al., 2013, Rissanen et al. 2014, **Paper III, Paper IV, Paper V**). Highly oxidised multifunctional organic compounds were first identified in the naturally charged ion measurements in the forest of Hyytiälä first by Ehn et al. (2012) and the compounds were mostly observed to be nocturnal, clustered with the nitrate ion (NO_3^-) and formed in α-pinene ozonolysis. In **Paper III** we demonstrate the first evidence of a direct pathway to from the forest emissions of monoterpenes and more precisely α-pinene to extremely low-volatility organic compounds (ELVOC) (formerly referred as highly oxidised multifunctional organic compounds). This neutral pathway of terpene oxidation via ozonolysis and OH radical reactions associated to the secondary organic aerosol formation and their possible impacts on total number concentration and CCN have been investigated in the second part of this thesis (**Paper III**, **Paper IV** and **Paper V**).

4.1. General ELVOC features

The first major breakthrough was that formerly unidentified neutral gas phase compounds were detected in α-pinene ozonolysis and OH radical reactions (**Paper III**). They appeared as nitrate ion clusters and had very high oxygen-to-carbon ratios indicating that the compounds must be close to or virtually non-volatile species with effective saturation concentration $C^* < -3.5\ \mu g\ m^{-3}$ (see definition in Donahue et al., 2012). Other terpenes such as β-pinene, myrcene, limonene and isoprene also produced the same type of reaction products from ozonolysis as well as in OH radical initiated oxidation (**Paper III, Paper V**). Major fraction of ELVOC signals detected had a chemical composition that corresponded to either C_{10} (referred hereafter as monomers) or C_{20} hydrocarbons (referred hereafter as dimers). In the case of isoprene monomers and dimers consist of C_5 and C_{10} hydrocarbons from OH radical initiated oxidation, respectively. Other signals contributed to the mass spectra as well but with less intensity. The signature ELVOC spectrum from α-pinene with both monomer and dimer features is depicted in Figure 5.

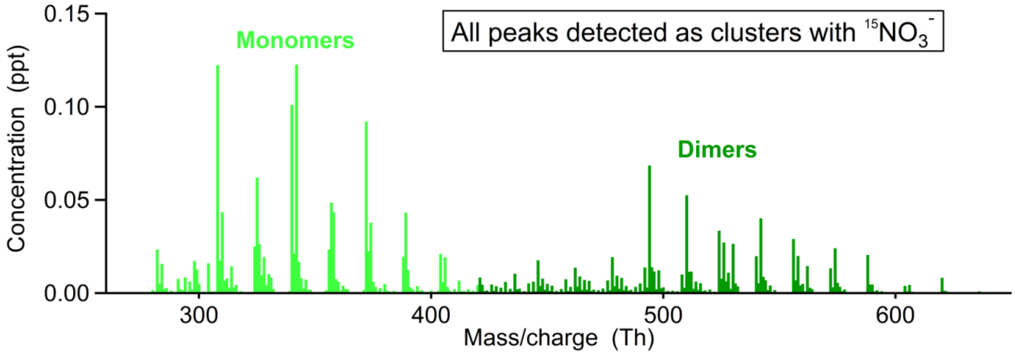

Figure 5. Typical α-pinene ELVOC spectrum measured the means of the CI-APi-TOF. The light green peak are monomers (C_{10} compounds) and darker green are dimers (C_{20} compounds) Figure adopted from **Paper III.**

Determining the yields of ELVOC is of great importance for climate models that have systematically failed to reproduce atmospheric observations of total SOA mass because a significant load of low-volatility products have been missing or poorly described. One possibility for this discrepancy is not considering the wall losses during chamber experiments (Zhang et al., 2014). The molar yields of ELVOC from ozonolysis of selected terpenes were quantified to be ~1-7 % per monoterpene (**Paper III, Paper V**) and marginal ELVOC formation yield for isoprene (~0.2 %). The monoterpenes with an endocyclic double bond produced more ELVOC quantitatively than monoterpenes with exo- or non-cyclic double bonds. We also determined the yield of OH radical initiated ELVOC formation and found out that exo- and non-cyclic double bonded monoterpenes yielded relatively higher amounts of ELVOC from OH radical initiated oxidation than from ozonolysis. Altogether, this thesis describes ELVOC formation from all the studied monoterpenes and isoprene and provide better parameterisation for the climate models that usually use <5 % mass yield of low-volatility reaction products from BVOC. Also isoprene formed some ELVOC and even when the formation yield stayed marginal, it may indicate relatively high loads of ELVOC globally and particularly over tropical forests where isoprene is the dominant BVOC.

The mass yield of α-pinene ELVOC was determined to according to the molar masses of ELVOC products (14-19 %). Thus a seed aerosol experiment was conducted to investigate if ELVOC would condense onto the pre-existing aerosol and increase the SOA mass. The results during low aerosol loadings were remarkable since ELVOC didn't just irreversible condense to form SOA but also were able to explain the whole mass increase and O:C ratio of the observed SOA. At higher aerosol loadings ELVOC were still able to explain a dominant fraction of the SOA mass but there was an apparent contribution of semivolatile reaction products such as pinic and pinonic acid, also formed in the ozonolysis of α-pinene.

Irreversible condensation onto surfaces and high mass yield of ELVOC make them a fine candidate for the vapours that grow newly formed nanoparticles. In **Paper III** the concentration of particles larger than 3 nm was affected by both sulphuric acid and ELVOC concentrations ($\sim[\text{ELVOC}]^2 \times [\text{SA}]$). This indicates that even when sulphuric acid is highly important in initial formation of aerosol particles of a few nanometres, a strong contribution of ELVOC is already observed in the formation of 3 nm particles. This thesis concludes that ELVOC can help to explain the fast growth of new particles observed over forested regions (Kulmala et al., 2013, Riipinen et al., 2011). The results also give a possible answer to the missing link between the VOC emissions and aerosol formation and growth. The further climate relevance and atmospheric implications of ELVOC are further discussed in chapter 4.3.

4.2. Formation mechanism of ELVOC

How these ELVOC are formed in the atmosphere are investigated in details in **Paper III - V**. The investigation of reaction mechanism of ELVOC formation started from the ozonolysis experiments with unsaturated α-pinene, which only has one reactive endocyclic double bond site for the ozone to attack. Since ozonolysis inevitably forms OH radicals, the contribution of the reaction products from OH radical oxidation were investigated using OH-scavengers. Ozonolysis products were unambiguously identified utilizing "heavy ozone" (isotopic labelled $^{18}O_3$). This way the ozonolysis and OH-oxidation signals could be separated and both ELVOC formation yields from ozonolysis and OH-oxidation could be determined.

In **Paper III** the formation mechanism of stable closed shell ELVOC is suggested to propagate via peroxy radical (RO_2) chemistry and this suggestion is further studied in **Paper IV**. The CI-APi-TOF spectra indicate that uneven mass-to-charge ratios (and uneven H-atoms) correspond to highly oxygenated radical species. These radical signals response to NO addition, producing a high yield of organic nitrates and peroxynitrates as described in the literature from the reaction of RO_2 with NO_x ($NO + NO_2$), thus confirming RO_2 radical driven ELVOC formation. The formation yields from $RO_2 + NO \rightarrow RONO_2$ and $RO_2 + NO_2 \rightarrow RO_2NO_2$ reaction were determined to be 32% and 27% for the most abundant RO_2 radicals $C_{10}H_{15}O_8$ and $C_{10}H_{15}O_{10}$ respectively. The process allowing high amounts of oxygen added in the RO_2 was firstly hypothesized to involve intramolecular H-atom abstraction and subsequent O_2 addition in the formed alkyl radical site (**Paper III**, Figure 6). This process of autoxidation was not formerly known to proceed fast enough in the atmosphere and only in 2013 it was proposed to have relevance in atmospheric oxidation processes (Crounse et al., 2013). Crounse et al., (2013) applied laboratory and ab-initio calculations with 3-pentanone and concluded that autoxidation did indeed increase the oxygen content of this organic compound fast enough to be important under atmospheric conditions.

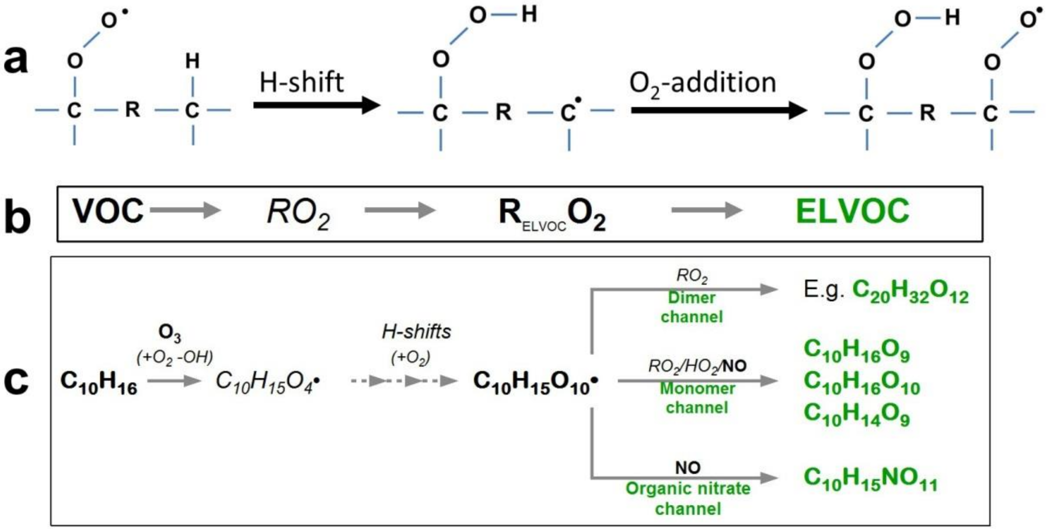

Figure 6. Illustration of RO_2 ELVOC formation from autoxidation (a), VOC oxidation route to ELVOC (b) and different RO2 reaction pathways for closed shell ELVOC formation. Adopted from **Paper III**.

Autoxidation of limonene and α-pinene was investigated in flow tube measurements described in **Paper IV** since monoterpenes with an endocyclic double bond appeared to produce ELVOC most efficiently. The flow tube allows changing the reaction time and this way the temporal behaviour of both RO_2 radicals and this way also closed shell ELVOC was determined. The relative concentration ratio between the detected RO_2 radicals reached a constant value only after ~10s. The RO_2 radical concentration increased throughout the experiment (8.3 – 39.5 s reaction time) demonstrating the fast conversion of molecules with increasing oxygen content to another even more oxygenated RO_2 molecules. The production of closed shell ELVOC, both monomer and dimer species, increased over time as well. The monomers appeared immediately after RO_2 concentration reached high enough concentration level and the same pattern is seen with dimer formation, indicating RO_2 + RO_2 dimer formation pathway. The dimer producing channel is also supported by the NO addition experiments when dimer formation is suppressed when RO_2 radicals react more rapidly with NO_x. If the oxygen content of the carrier gas was decreased, ELVOC formation was suppressed significantly further confirming that atmospheric O_2 is connected to ELVOC formation.

Closed shell monomer formation can be explained when an O and H-atom are lost from a highly oxygenated RO_2 radical. The reaction can proceed via two possible ways i) a unimolecular OH radical loss from the corresponding RO_2 or ii) via reaction with other RO_2 radicals forming an alkoxy radical. With O_2 this alkoxy radical forms HO_2 and a carbonyl compound, corresponding to the detected ELVOC monomer products. Unfortunately it is difficult to confirm the exact formation mechanism from these two possibilities and other processes such as decomposition and isomerization of the alkoxy radical may also occur. However, from **Paper III** and **Paper IV** in this thesis we may conclude that autoxidation of monoterpenes and isoprene is a very important oxidation pathway and confirms the formation of ELVOC from terrestrial forest emission and their impact on SOA formation (see also Rissanen et al., 2014). This thesis also demonstrates the importance of ozone in the atmospheric oxidation system that might have been underestimated before. High yields of highly oxygenated and also low-volatility organonitrates and peroxynitrates indicates possible high concentrations in the air as well. The future measurements focusing in organic nitrates and peroxynitrates should be studied with estimations if they could play a role in NPF since at least one indication of high organonitrates concentration has been published during NPF (Kulmala et al., 2013).

4.3. Atmospheric implications of ELVOC

Warming climate promotes BVOC emission rates in the future. Increasing CO_2 concentration and changes in vegetation cover will also affect the amount of BVOC released in the air. The distribution and characteristics of atmospherically relevant oxidants are also expected to change. Since the importance of ELVOC has been described in previous chapters, the last part of this thesis handles the atmospheric implications and possible future climate effects of ELVOC using a global modelling framework (**Paper V**). In here the different chemical structure and ELVOC yields of different types of terpenes associated with cloud condensation nuclei (CCN) production with different cloud super saturations (0.2% and 1.0 %) are estimated. Also the changes in total aerosol number concentration (CN) are investigated. With these parameters we are able to estimate the effect of ELVOC to particle formation and growth and the overall SOA effect on CCN production on a global scale.

The model used the ELVOC yields determined for isoprene and monoterpenes in **Paper V** and also the classification of monoterpenes to endocyclic or all other monoterpenes. ELVOC were assumed to condense according to the pre-existing aerosol surface area and the rest, semi-volatile organic compounds (SVOC), was partitioned according to the aerosol mass distribution. This is the first time that a hybrid type global model (kinetic and mass-based mechanism) with experimentally determined ELVOC yields has been used to study SOA formation, but it should be noted that the model excludes several important parameters (e.g. the model omits anthropogenic SOA precursors) and uses anthropogenic aerosol size distribution.

In the simulations isoprene emissions exceeded the monoterpene emissions by a factor of ~5 but monoterpene emissions dominated BVOC in the higher latitudes of the northern hemisphere (total annual emissions were 595 Tg a^{-1}). The total SOA yield was set to 20 % (15 % from MT and 5 % from isoprene) but the SOA and ELVOC forming compounds were varied. With these yields we obtained an annual total SOA formation of 37 Tg a^{-1}. The result of this paper is that SOA formation is still underestimated with these parameters if compared to aerosol mass spectrometer (AMS) observations but is twice as much compared to AeroCom models (Hallquist et al., 2009, Spacklen et al., 2011).

The importance of SOA to CN and CCN concentrations in general was estimated comparing the control (“CTRL”) and the no SOA formation (“NOSOA”) simulations. SOA formation from both isoprene and monoterpenes increased CN and CCN concentration over continental areas up to a few tens of percent (see Figure 7). There is an indication of decreasing concentrations of total particle and CCN(1.0%) number concentrations over marine areas and in the northern mid-latitudes and southern Australia, Africa and South-America. This effect is probably connected to the increase of condensation sink associated with SOA formation. Increasing condensation sink leads to the decrease in new particle formation and growth rates. However, SOA formation seems to be an essential link to CCN formation over continental areas.

The ELVOC contribution to CN and CCN was also tested. This time we compared the control simulation to the case where no ELVOC was formed at all. ELVOC enhanced new particle formation and growth and thus also the total number concentrations up to a few percent excluding marine areas and Northern Africa (Figure 7 lower panel). If the ELVOC producing monoterpenes were handled according to their speciation yields, meaning that all experimental yields for different monoterpenes were used separately and not treated as α-pinene, the effect on aerosol particles concentrations stayed moderate, <10 % in all our simulations.

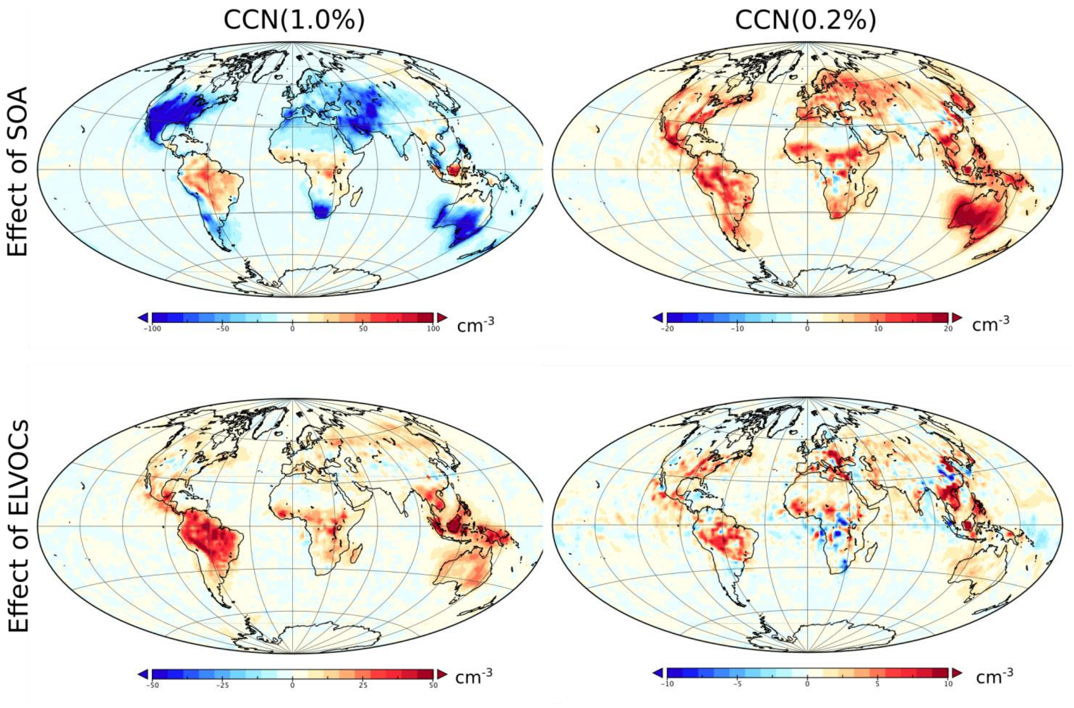

Figure 7. Global model simulation on the effect of SOA and ELVOC to CCN concentration using two different supersaturation values, 0.2% and 1.0%.

Formerly it was generally accepted that known oxidation product of isoprene did not contribute to atmospheric SOA since the known oxidation products e.g. methacrolein, methyl vinyl ketone and formaldehyde are all volatile (Pandis et al,. 1991). The annual emissions of isoprene are sufficiently that large that even a very small yield of ELVOC could result in substantial SOA production (Carlton et al., 2009). Since we found a small ELVOC production route from isoprene, the effect to SOA formation was also estimated in our simulations. However, only a fraction of SOA produced from isoprene is assigned to ELVOC formation and thus it is likely that isoprene could supress NPF and growth because the semivolatile oxidation products from isoprene are likely to condense and grow existing, already bigger in size, aerosol particles. When Isoprene SOA was omitted completely from the simulation, the CN and CCN(1.0%) were decreased up to 20 % over continental areas because of NPF and subsequent growth was suppressed. However, we found that SOA produced from isoprene enhances the growth of pre-existing small particles that can be observed in increased in the CCN(0.2%) concentrations in several regions.

In our simulations the effects of SOA and especially ELVOC on cloud condensation nuclei concentration are most sensitive to the aerosol size distribution, the fraction of monoterpenes with endocyclic double bond and also the ratio of monoterpene to isoprene emissions. The findings in Paper V demonstrate that both SOA and ELVOC formation from biogenic precursors are crucial for the production of CCN in the atmosphere. A large fraction of ELVOC is formed in ozonolysis of monoterpenes with an endocyclic double bond and they enhance NPF and growth over continental areas. This further increases CCN concentrations especially when the cloud super saturation is high. The marginal ELVOC formation from isoprene is indeed suppressing new particle formation and growth as hypothesised in previous studies (Kiendler-Scharr et al., 2009) but at the same time they assist sub-CCN sized particles to grow to CCN. The global scale model still needs a lot of specialised information about emission patterns of oxidants and terpenes, also other than monoterpenes and isoprene. The oxidation also does not dependent on the reactions only but also meteorology that should be included in the future investigations (Ervens et al., 2008) to describe SOA formation more accurately. Anthropogenic sources of ELVOC are to this day almost completely unknown (Rissanen et al., 2014) and should be studied and implemented in future models. These modelling results, even with lacking some parametrisations, provides significant new information related to BVOC emissions leading to a direct importance to the climate system via formation of ELVOC, SOA and subsequent CCN.

5 Review of papers and the author's contribution

Paper I is the base of this thesis and all research articles presented used the method developed and described in this paper. This paper introduces the new chemical ionization inlet coupled with the APi-TOF for neutral cluster and molecule detection. It describes the first molecular level detector for neutral highly acidic compounds such as sulphuric acid, which is proven to be the main precursor for new particle formation events. We performed measurements in Hyytiälä to identify sulphuric acid containing clusters in the ambient air. The result did not show any indication of neutral sulphuric acid or sulphuric acid – ammonia clusters. In this paper I was developing the instrumentation, performed the measurements in Hyytiälä, did the data analysis and wrote most of the paper.

Paper II presents the first measured neutral cluster measurements in the laboratory. This paper shows dimethyl amine – sulphuric acid nucleation step by step, starting from sulphuric acid formation in the gas phase and then clustering of sulphuric acid to its multimers. DMA is seen in the clusters with sulphuric acid trimer and bigger and the clusters grew by adding one acid and one base all the way to ~2000 amu or ~2 nm in size. SA_DMA clusters were observed to form close to the kinetic limit (within the experimental uncertainty). The evaporation of these clusters was suggested to be very small and that the loss process is concentrated in the growth of new particles instead of evaporation. In this paper I did the measurements in CERN, analysed most of the data and contributed by drafting and commenting the paper.

Paper III describes the discovery of a new extremely low-volatility organic compound group (ELVOC) from α-pinene ozonolysis that were first detected in naturally charged ions in the boreal forest. These neutral compounds were highly oxygenated and thus their volatilities are extremely low. They are able to condense onto even the smallest aerosol particles or molecules forming a large source of secondary organic aerosol. These compounds are produced in high molar yield (~7 %) and can explain the discrepancy between modelled and observed secondary organic aerosol burden in the atmosphere. This paper also gives the principle idea of their formation mechanism that was studied further in Paper IV. For this paper I contributed in the CI-APi-TOF measurements in Hyytiälä SMEAR II station and did all the experiments in TROPOS with data analysis. I contributed by commenting the paper.

Paper IV continues to study low-volatility organic compounds but concentrates more in the details how they are formed. This paper is mostly a laboratory experiment where a well-known liquid phase process autoxidation is proven to happen fast in the gas phase also. This paper describes the formation of highly oxidized RO_2 radicals and reaction pathways how they can further form closed shell monomers, e. g. most ELVOC described in Paper III. This paper also has a short section about ambient measurements of highly oxidized RO_2 radicals. I did the laboratory experiments and most of the field measurements, processed the data and participated in writing this paper.

Paper V reports the molar yields of ELVOC from several different monoterpenes from both ozonolysis and OH radical initiated oxidation. This paper describes the formation of low volatility products from isoprene, the most emitted VOC from vegetation. This information is then used in a modelling framework, from where we can detect changes in the CCN numbers globally. Knowledge of the chemical structure of terpenes and relevant oxidant levels were observed to play a crucial role when SOA formation is assessed in global frameworks. I wrote most of the paper except the global model section, did the measurements and analysed the data.

6 Conclusions and outlook

Both anthropogenic and biogenic emissions play a vital role in the atmospheric system and affect the weather and in the long run also our climate in several variable ways. To this PhD thesis, the most important gas-phase molecules floating in the air are anthropogenic emissions of sulphur dioxide and biogenic volatile compounds, more precisely a few monoterpenes and isoprene. The detection of the reaction products from these vapours, sulphuric acid and extremely low-volatility organic compounds will act as the core of this thesis (*objective i*). It may seem that only a tiny fraction of the possible compounds and their reactions were considered when the precursor molecules and clusters for atmospheric new particle formation were studied, but as described in this introductory review, you only need tiny molecules (**Paper I-IV**) to initiate big, even global, changes (**Paper V**). For example, the secondary new particle formation events create up to half of the aerosol particles over continental Europe. The focus of this thesis is in the understanding of the initial steps of particle formation and their subsequent growth, connected to the presence of low-volatility compounds in the ambient air (*objectives ii and iii*). Better understanding of the formation, reactions and also deposition processes will help with to estimate the atmospherically relevant processes that in future may affect the climate.

The role of sulphuric acid and its multimer clusters to new particle formation is investigated in **Paper I** further with strong base molecules in **Paper II**. The first *objective (i)* was to develop a sensitive and selective method for the acidic cluster measurements. This was done highly successfully as demonstrated with the lowest limit of detection (3.6×10^4 molecules cm^{-3} using the developed CI-APi-TOF) yet reported for chemical ionization method used with mass spectrometer and applicability to cluster measurements was also established (**Paper I-II**). High sensitivity from acidic monomer species to large molecular acid-base clusters was obtained during extensive laboratory studies as well as in field measurements (**Paper I-II**). The laboratory experiments utilizing ultra clean chamber at CERN gained tremendous amount of information on neutral SA-DMA cluster formation that had never observed in molecular level before reported in **Paper II** (*objective ii*). The formation of the SA-DMA clusters from the dimer onward was suggested to be kinetically limited or very close to that rate (when DMA:SA was ≥35 (Paper II figure 2)). Also the hypothesis that sulphuric acid cluster formation needs a stabilizing component to form stable clusters and to grow in the existing laboratory conditions was concluded to be valid. Unfortunately, neutral sulphuric acid clustered with strong bases have not been detected during regular spring time new particle formation events in the boreal forest region in Finland. Even when the hunt for neutral sulphuric acid clusters and the corresponding stabilizing agents from ambient air with the development of even better instrumentation will continue in the future, today the role of molecular sulphuric acid in initiating new particle formation can be considered solid and widely acknowledged by the research community.

Since the development of new techniques to detect newly formed molecules or clusters from sulphuric acid only explains about <10 % the growth rates of new particles in Hyytiälä Finland (Paasonen et al., 2010), something else in the air must be able to further react or condense on these precursors. The introduction of new group of extremely low-volatility compounds in this thesis takes a big leap toward a better understanding of new particle formation and the following particle growth at least in the forested continental areas (**Paper III**). These condensable vapours are formed in monoterpene and isoprene oxidation processes, and this thesis describes how secondary organic aerosol formation is dependent on these irreversibly condensing vapours under certain conditions.

Objective iii) is fulfilled with comprehensive studies describing the formation, reactions and fate of these extremely low-volatility vapours in the atmosphere. The gas-phase oxidation pathway is initiated by the ozone or OH radical reaction. In the reaction, RO_2 radicals and closed shell monomer molecules with C_{10} carbon chains are rapidly formed (in seconds) in further autoxidation by atmospheric O_2 molecules (**Paper IV**). Bigger C_{20} molecules and other signal were also detected that may even act as nano-CN if estimated by their probable size (~1-3 nm). The yields from these reactions varies between marginal <<1 % for isoprene and significant values of 3-7 % for monoterpenes with endocyclic double bonds and the yield is dependent on which oxidant initiated the reaction. This thesis underlines the importance of high formation yields of extremely low-volatility compounds from ozonolysis, leaving the role of OH radical reactions of less importance in this particulate matter. The future investigations will focus on gaining more knowledge of the formation mechanism of ELVOC, determining their functional groups and exact chemical compositions and detection of ELVOC in the often collected particulate matter samples. Another focus is to investigate ELVOC formation from semivolatile compounds and anthropogenic VOC's. Reaction products of highly oxidised RO_2 radicals with other atmospheric compounds e.g. RO_2 radicals, HO_2 and NO_x forming e.g. organic nitrates should be further investigated and their role in aerosol formation should be estimated.

Implementing these new results from **Paper III-V** in to a global model and using both kinetic and mass-based secondary organic aerosol formation mechanism lead us in conclusion that biogenic ELVOC in particular and SOA in general are both crucial for the observed rapid new particle formation and growth to cloud condensation nuclei sizes. Isoprene derived SVOC tends to suppress new particle formation but also grow larger pre-existing particles bigger in size and this way promoting CCN formation. These very special observations presented in this thesis are made possible by the instrumentation developed in **Paper I** and for the first time we can bridge the gap that links both anthropogenic SO_2 and biogenic emissions to aerosol formation influencing the climate system (**Paper V**). Since this thesis gives only the opening to sulphuric acid cluster detection and especially to ELVOC research a lot of open questions remain to be answered. For example the contribution and detection of low- or semi volatile organic compounds are not assessed in the scope of this thesis and should be studied in detailed manner. This thesis also focuses on monoterpenes and isoprene, which together make up around 55 % of BVOC emission, but ignores the impact of all other possibly thousands of BVOC compounds emitted by the terrestrial vegetation. For example highly reactive sesquiterpenes might be responsible for ELVOC formation in similar autoxidation reactions.

The world and its atmosphere are facing constant changes concerning e.g. population, land use, extreme weather conditions and warming atmosphere (IPCC 2013). Regulations to cut the anthropogenic emissions because of vast damages done to old buildings and boreal forests by the acidic rain falls in the 80s are decreasing the SO_2 levels in the atmosphere in the Western World. Therefore also the number new particle formation days observed to be decreasing in Northern Finland (Kyrö et al., 2014). The emissions of biogenic volatile organic compounds controlled e.g. by the type of vegetation, seasonal cycles, temperature, radiation and precipitation (Constable et al., 1999, Peñuelas and Staudt, 2010, Paasonen et al, 2013) are also bound to adapt to the changes. Negative feedback mechanism between the continental biosphere, aerosols and climate has been suggested (Kulmala et al., 2004, 2014; Paasonen et al., 2013) but the effect of aerosols and its precursors remain the most uncertain and poorly described part in the approximation of the radiating forcing of the Earth (IPCC reports). It will be a huge challenge to estimate how the changes in emissions will affect new particle formation and CCN and thus the future cloud properties and cover that absorbs infrared radiation heating up the atmosphere and scatters incoming radiation back to space cooling down the planet. Even when only a fraction of the processes influencing the feedback mechanisms related to the biosphere-atmosphere interactions are covered in this thesis, it provides a comprehensive study of both organic and inorganic low-volatility precursor molecules and clusters in the atmosphere. The subject has been investigated all the way from their origin, formation mechanisms and measurement techniques to their possible effects on cloud condensation nuclei concentrations that can be further utilized in global models predicting weather now and climate in the future.

7 References

Alicke B., Hebestreit K., Stutz J. and Platt U. (1999) Iodine oxide in the marine boundary layer, *Nature*, 397, 572-573, doi:10.1038/17508

Almeida J., Schobesberger S., Kurten A., Ortega I. K., Kupiainen-Määttä O., Praplan A. P., Adamov A., Amorim A., Bianchi F., Breitenlechner M., David A., Dommen J., Donahue N. M., Downard A., Dunne E., Duplissy J., Ehrhart S., Flagan R. C., Franchin A., Guida R., Hakala J., Hansel A., Heinritzi M., Henschel H., Jokinen T., Junninen H., Kajos M., Kangasluoma J., Keskinen H., Kupc A., Kurtén T., Kvashin A. N., Laaksonen A., Lehtipalo K., Leiminger M., Leppä J., Loukonen V., Makhmutov V., Mathot S., McGrath M. J., Nieminen T., Olenius T., Onnela A., Petäjä T., Riccobono F., Riipinen I., Rissanen M., Rondo L., Ruuskanen T., Santos F. D., Sarnela N., Schallhart S., Schnitzhofer R., Seinfeld J. H., Simon M., Sipilä M., Stozhkov Y., Stratmann F., Tome A., Trostl J., Tsagkogeorgas G., Vaattovaara P., Viisanen Y., Virtanen A., Vrtala A., Wagner P. E., Weingartner E., Wex H., Williamson C., Wimmer D., Ye P., Yli-Juuti T., Carslaw K. S., Kulmala M., Curtius J., Baltensperger U., Worsnop D. R., Vehkamäki H. and Kirkby J. (2013) Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, *Nature*, 502, 359–363, doi:10.1038/nature12663.

Atkinson H. M., Huang R.-J., Chance R., Roscoe H. K., Hughes C., Davison B., Schönhardt A., Mahajan A. S., Saiz-Lopez A., Hoffmann T. and Liss P. S. (2012) Iodine emissions from the sea ice of the Weddell Sea, *Atmos. Chem. Phys.*, 12, 11229-11244, doi:10.5194/acp-12-11229-2012.

Berndt T., Boge O., Stratmann F., Heintzenberg J. and Kulmala M. (2005) Rapid formation of sulfuric acid particles at near-atmospheric conditions, *Science*, 307(5710):698–700, doi:10.1126/science.1104054.

Berndt T., Jokinen T., Mauldin III R. L., Petäjä T., Herrmann H., Junninen H., Paasonen P., Worsnop D. R. and Mikko Sipilä (2012) Gas-Phase Ozonolysis of Selected Olefins: The Yield of Stabilized Criegee Intermediate and the Reactivity toward SO_2, *J. Phys. Chem. Lett.*, 3 (19): 2892–2896, doi: 10.1021/jz301158u

Bäck J., Aalto J., Henriksson M., Hakola H., He Q., Boy M. (2012) Chemodiversity of a Scots pine stand and implications for terpene air concentrations, Biogeosciences, 9, 689–702, doi:10.5194/bg-9-689-2012.

Carlton A. G., Wiedinmyer C. and Kroll J. H. (2009) A review of Secondary Organic Aerosol (SOA) formation from isoprene, *Atmos. Chem. Phys.*, 9, 4987–5005, doi:10.5194/acp-9-4987-2009, 2009.

Chen M., Titcombe M., Jiang J., Jen C., Kuang C., Fischer M. L., Eisele F. L., Siepmann J. I., Hanson D. R., Zhao J. and McMurry P. H. (2012) Acid-base chemical reaction model for nucleation rates in the polluted atmospheric boundary layer, *Proc. Natl. Acad. Sci. USA*, 109(46):18713–18718, doi: 10.1073/pnas.1210285109.

CLOUD Collaboration (2000), A study of the link between cosmic rays and clouds with a cloud chamber at the CERN PS, Rep. CERN/SPSC 2000-021, SPSC/P317, *Eur. Organ. for Nucl. Res.*, Geneva, Switzerland. Available at http://cloud.web.cern.ch/cloud. 1.5.2015

Constable J. V. H., Litvak M. E, Greenberg J. P., Monson RK (1999) Monoterpene emission from coniferous trees in response to elevated CO2 and climate warming, *Glob. Change Biol.*, 5: 255-267.

Crounse J. D., Nielsen L. B., Jorgensen S., Kjaergaard H. G. and Wennberg P. O. (2013) Autoxidation of Organic Compounds in the Atmosphere, *J. Phys. Chem. Lett.*, 4, 3513–3520, doi:10.1021/jz4019207.

Dal Maso M., Kulmala M., Riipinen I., Wagner R., Hussein T., Aalto P. P. and Lehtinen K. E. J. (2005) Formation and growth of fresh atmospheric aerosols: eight years of aerosol size distribution data from SMEAR II, Hyytiälä, Finland, *Boreal Env. Res.*, 10: 323–336.

Di Carlo P., Brune W. H., Martinez M., Harder H., Lesher R., Ren X. R., Thornberry T., Carroll M. A., Young V., Shepson P. B., Riemer D., Apel E. and Campbell C. (2004) Missing OH reactivity in a forest: evidence for unknown reactive biogenic VOC, *Science*, 304, 722–725, doi: 10.1126/science.1094392.

Donahue N. M., Kroll J. H., Anderson J. G. and Demerjian K. L. (1998) Direct observation of OH production from the ozonolysis of olefins, *Geophys. Res. Lett.*, 25(1), 59–62, doi: 10.1029/97GL53560.

Donahue N. M., Epstein S. A., Pandis S. N. and Robinson A. L. (2011) A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics, *Atmos. Chem. Phys.*, 11, 3303-3318, doi:10.5194/acp-11-3303-2011.

Donahue N. M., Kroll J. H., Pandis S. N. and Robinson A. L. (2012) A two-dimensional volatility basis set – Part 2: Diagnostics of organic-aerosol evolution, *Atmos. Chem. Phys.*, 12, 615-634, doi:10.5194/acp-12-615-2012.

Ehn M., Junninen H., Petäjä T., Kurtén T., Kerminen V.-M., Schobesberger S., Manninen H. E., Ortega I. K., Vehkamäki H., Kulmala M. and Worsnop D. R. (2010)

Composition and temporal behavior of ambient ions in the boreal forest, *Atmos. Chem. Phys.*, 10, 8513-8530, doi:10.5194/acp-10-8513-2010.

Ehn M., Kleist E., Junninen H., Petäjä T., Lönn G., Schobesberger S., Dal Maso M., Trimborn A., Kulmala M., Worsnop D. R., Wahner A., Wildt J. and Mentel, T. F. (2012) Gas phase formation of extremely oxidized pinene reaction products in chamber and ambient air, *Atmos. Chem. Phys.*, 12, 5113-5127, doi:10.5194/acp-12-5113-2012.

Eisele F. L. and Tanner D. J. (1993) Measurement of the gas phase concentration of H_2SO_4 and methane sulfonic acid and estimates of H_2SO_4 production and loss in the atmosphere, *J. Geophys. Res.*, 98(D5), 9001–9010, doi:10.1029/93JD00031.

Ervens B., Carlton A. G., Turpin B. J., Altieri K. E., Kreidenweis S. M. and Feingold, G. (2008) Secondary organic aerosol yields from cloud-processing of isoprene oxidation products, *Geophys. Res. Lett.*, 35, doi:10.1029/2007GL031828.

Faloona I., Tan D., Brune W., Hurst J., Barket D., Couch T. L., Shepson P., Apel E., Riemer D., Thornberry T., Carroll M. A., Sillman S., Keeler G. J., Sagady J., Hooper D. and Paterson K. (2001) Nighttime observations of anomalously high levels of hydroxyl radicals above a deciduous forest canopy, *J. Geophys. Res.*, 106, 24315–24333, doi: 10.1029/2000JD900691.

Freshour N. A., Carlson K. K., Melka Y. A., Hinz S., Panta B. and Hanson D. R. (2014) Amine permeation sources characterized with acid neutralization and sensitivities of an amine mass spectrometer, *Atmos. Meas. Tech.*, 7, 3611-3621, doi:10.5194/amt-7-3611-2014.

Gagné S., Nieminen T., Kurtén T., Manninen H. E., Petäjä T., Laakso L., Kerminen V.-M., Boy M. and Kulmala M. (2010) Factors influencing the contribution of ion-induced nucleation in a boreal forest, Finland, *Atmos. Chem. Phys.*, 10, 3743–3757, doi:10.5194/acp-10-3743-2010.

Griffin R. J., Dabdub D. and Seinfeld J. H. (1999) Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons, *Geophys. Res. Lett.*, 26, 2721–2724.

Guenther A. B., Zimmerman P. R., Harley P. C., Monson R. K. and Fall R. (1993), Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses, *J. Geophys. Res.*, 98(D7), 12609–12617, doi:10.1029/93JD00527.

Guenther A., Hewitt C. N., Erickson D., Fall R., Geron C., Graedel T., Harley P., Klinger L., Lerdau M., McKay W. A., Pierce T., Scholes B., Steinbrecher R., Tallamraju R., Taylor J. and Zimmerman P. (1995) A Global Model of Natural Volatile Organic Compound Emissions, *J. Geophys. Res.*, 100, 8873–8892, doi:10.1029/94JD02950.

Hallquist M., Wenger J. C., Baltensperger U., Rudich Y., Simpson D., Claeys M., Dommen J., Donahue N. M., George C., Goldstein A. H., Hamilton J. F., Herrmann H., Hoffmann T., Iinuma Y., Jang M., Jenkin M. E., Jimenez J. L., Kiendler-Scharr A., Maenhaut W., McFiggans G., Mentel Th. F., Monod A., Prévôt A. S. H., Seinfeld J. H., Surratt J. D., Szmigielski R. and Wildt J. (2009) The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155-5236, doi:10.5194/acp-9-5155-2009.

Hanson D. R. and Eisele F. L. (2002) Measurement of prenucleation molecular clusters in the NH_3, H_2SO_4, H_2O system, *J. Geophys. Res.*, 107, 4158, doi:10.1029/2001jd001100.

Hanson D. R. and Lovejoy E. R. (2006) Measurement of the Thermodynamics of the Hydrated Dimer and Trimer of Sulfuric Acid, *J. Phys. Chem. A.*, 110 (31): 9525–9528, doi: 10.1021/jp062844w.

Hanson D. R., McMurry P. H., Jiang J., Tanner D. and Huey L. G. (2011) Ambient pressure proton transfer mass spectrometry: detection of amines and ammonia, *Environ. Sci. Technol.*, 45, 8881–8888, doi: 10.1021/es201819a.

Hao L. Q., Yli-Pirilä P., Tiitta P., Romakkaniemi S., Vaattovaara P., Kajos M. K., Rinne J., Heijari J., Kortelainen A., Miettinen P., Kroll J. H., Holopainen J. K., Smith J. N., Joutsensaari J., Kulmala M., Worsnop D. R. and Laaksonen A. (2009) New particle formation from the oxidation of direct emissions of pine seedlings, *Atmos. Chem. Phys.*, 9, 8121–8137, doi:10.5194/acp- 9-8121-2009.

Hari P. and Kulmala M. (2005): Station for Measuring Ecosystem–Atmosphere Relations (SMEAR II). *Boreal Env. Res.*, 10, 315–322.

Haywood J. and Boucher O. (2000) Estimates of the direct and indirect radiative forcing due to tropospheric aerosols: A review, *Rev. Geophys.*, 38(4): 513-543, doi 10.1029/1999RG000078.

Hirsikko A., Laakso L., Hõrrak U., Aalto P., Kerminen V.-M. and Kulmala M. (2005) Annual and size dependent variation of growth rates and ion concentrations in boreal forest, *Boreal Environ. Res.*, 10, 357–369.

Hoffmann T., O’Dowd C. and Seinfeld J. (2001) Iodine oxide homogeneous nucleation: an explanation for coastal new particle production, *J. Geophys. Res.*, 28(10): 1949-1952, doi: 10.1029/2000GL012399.

Iida K., Stolzenburg M., McMurry P., Dunn M. J., Smith J. N., Eisele F. and Keady P. (2006), Contribution of ion-induced nucleation to new particle formation: Methodology and its application to atmospheric observations in Boulder, Colorado, *J. Geophys. Res.*, 111, D23201, doi:10.1029/2006JD007167.

Iida K., Stolzenburg M. R. and McMurry P. H. (2009) Effect of Working Fluid on Sub-2 nm Particle Detection with a Laminar Flow Ultrafine Condensation Particle Counter, *Aerosol Sci. Technol.*, 43, 81-96. doi: 10.1080/02786820802488194

IPCC 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

IPCC 2007: Contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, 2007 , M.L. Parry, O.F. Canziani, J.P. Palutikof, P.J. van der Linden and C.E. Hanson (eds) Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Jiang J. K., Zhao J., Chen M. D., Eisele F. L., Scheckman J., Williams B. J., Kuang C. A. and McMurry P. H. (2011) First Measurements of Neutral Atmospheric Cluster and 1–2 nm Particle Number Size Distributions During Nucleation Events, *Aerosol Sci. Tech.*, 45, II–V, doi: 10.1080/02786826.2010.546817.

Jimenez J. L., Canagaratna M. R., Donahue N. M., Prevot A. S. H., Zhang Q., Kroll J. H., DeCarlo P. F., Allan J. D., Coe H., Ng N. L., Aiken A. C., Docherty K. S., Ulbrich I. M., Grieshop A. P., Robinson A. L., Duplissy J., Smith J. D., Wilson K. R., Lanz V. A., Hueglin C., Sun Y. L., Tian J., Laaksonen A., Raatikainen T., Rautiainen J., Vaattovaara P., Ehn M., Kulmala M., Tomlinson J. M., Collins D. R., Cubison M. J., Dunlea E. J., Huffman J. A., Onasch T. B., Alfarra M. R., Williams P. I., Bower K., Kondo Y., Schneider J., Drewnick F., Borrmann S., Weimer S., Demerjian K., Salcedo D., Cottrell L., Griffin R., Takami A., Miyoshi T., Hatakeyama S., Shimono A., Sun J. Y., Zhang Y. M., Dzepina K., Kimmel J. R., Sueper D., Jayne J. T., Herndon S. C., Trimborn A. M., Williams L. R., Wood E. C., Middlebrook A. M., Kolb C. E., Baltensperger U. and Worsnop D. R. (2009) Evolution of organic
aerosols in the atmosphere, Evolution of Organic Aerosols in the Atmosphere, *Science*, 326(5959): 1525-1529, doi: 10.1126/science.1180353

Junninen H., Ehn M., Petäjä T., Luosujärvi L., Kotiaho T., Kostiainen R., Rohner U., Gonin M., Fuhrer K., Kulmala M. and Worsnop, D. R. (2010) A high-resolution mass spectrometer to measure atmospheric ion composition, *Atmos. Meas. Tech.*, 3, 1039-1053, doi:10.5194/amt-3-1039-2010.

Kiendler-Scharr A.,Wildt J., Dal Maso M., Hohaus T., Kleist E., Mentel T. F., Tillmann R., Uerlings R., Schurr U., and Wahner A. (2009) New particle formation in forests inhibited by isoprene emissions, *Nature*, 461, 381–384, doi:10.1038/nature08292.

Kirkby J., Curtius J., Almeida J., Dunne E., Duplissy J., Ehrhart S., Franchin A., Gagné S., Ickes L., Kürten A., Kupc A., Metzger A., Riccobono F., Rondo L., Schobesberger S., Tsagkogeorgas G., Wimmer D., Amorim A., Bianchi F., Breitenlechner M., David A., Dommen J., Downard A., Ehn M., Flagan R. C., Haider S., Hansel A., Hauser D., Jud W., Junninen H., Kreissl F., Kvashin A., Laaksonen A., Lehtipalo K., Lima J., Lovejoy E. R., Makhmutov V., Mathot S., Mikkilä J., Minginette P., Mogo S., Nieminen T., Onnela A., Pereira P., Petäjä T., Schnitzhofer R., Seinfeld J. H., Sipilä M., Stozhkov Y., Stratmann F., Tome A., Vanhanen J., Viisanen Y., Vrtala A., Wagner P. E., Walther H., Weingartner E., Wex H., Winkler P. M., Carslaw K. S., Worsnop D. R., Baltensperger U. and Kulmala M. (2011) Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, *Nature*, 476, 429–433, doi:10.1038/nature10343.

Kroll J. H. and Seinfeld J. H. (2008) Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, *Atmos. Environ.*, 42, 3593–3624, doi:10.1016/j.atmosenv.2008.01.003.

Kroll J. H., Donahue N. M., Jimenez J. L., Kessler S. H., Canagaratna M. R., Wilson K. R., Altieri K. E., Mazzoleni L. R., Wozniak A. S., Bluhm H., Mysak E. R., Smith J. D., Kolb C. E. and Worsnop D. R. (2011) Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol, *Nat. Chem.*, 3, 133–139, doi:10.1038/nchem.948.

Kurpius M.R. and Goldstein A.H. (2003) Gas-phase chemistry dominates O_3 loss to a forest, implying a source of aerosols and hydroxyl radicals to the atmosphere, *Geophys. Res. Lett.*, 30: 10.1029/2002GL016785.

Kroll J. H. and Seinfeld J. H. (2008), Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, *Atmos. Environ.* , 42(16): 3593–3624, doi: 10.1016/j.atmosenv.2008.01.003.

Kuang C., McMurry P. H., McCormick A. V. and Eisele F. R. (2008) Dependence of nucleation rates on sulfuric acid vapor concentration in diverse atmospheric locations, *J. Geophys. Res.*, 113(D10209) doi:10.1029/2007JD009253.

Kulmala M., Toivonen A., Mäkelä J. M., Laaksonen A. (1998) Analysis of the growth of nucleation mode particles observed in Boreal forest, *Tellus B*, 50(5), 449–462.

Kulmala M., Vehkamäki H., Petäjä T., Dal Maso M., Lauri A., Kerminen V.-M., Birmili W. and McMurry P. H. (2004) Formation and growth rates of ultrafine atmospheric particles: a review of observations. J. Aerosol Sci. 35, 143–176, doi:10.1016/j.jaerosci.2003.10.003.

Kulmala M., Lehtinen, K. E. J. and Laaksonen A. (2006) Cluster activation theory as an explanation of the linear dependence between formation rate of 3nm particles and sulphuric acid concentration, *Atmos. Chem. Phys.*, 6, 787-793, doi:10.5194/acp-6-787-2006.

Kulmala M., Riipinen I., Sipilä M., Manninen H. E., Petäjä t., Junninen H., Dal Maso M., Mordas G., Mirme A., Vana M., Hirsikko A., Laakso L., Harrison R. M., Hanson I., Leung C., Lehtinen K. E. J. and Kerminen V.-M. (2007) Toward Direct Measurement of Atmospheric Nucleation, *Science*, 318(5847): 89-92, doi: 10.1126/science.1144124

Kulmala M., Kontkanen J., Junninen H., Lehtipalo K., Manninen H. E., Nieminen T., Petäjä T., Sipilä M., Schobesberger S., Rantala P., Franchin A., Jokinen T., Järvinen E., Äijälä M., Kangasluoma J., Hakala J., Aalto P. P., Paasonen P., Mikkilä, J., Vanhanen J., Aalto J., Hakola H., Makkonen U., Ruuskanen T., Mauldin III R. L., Duplissy J., Vehkamäki H., Bäck J., Kortelainen A., Riipinen I., Kurtén T., Johnston M. V, Smith J. N., Ehn M., Mentel T. F., Lehtinen K. E. J., Laaksonen A., Kerminen V.-M. and Worsnop, D. R. (2013) Direct observations of atmospheric aerosol nucleation, *Science*, 339(6122), 943-946, doi: 10.1126/science.1227385.

Kulmala M., Nieminen T., Nikandrova A., Lehtipalo K., Manninen H. E., Kajos M. K., Kolari P., Lauri A., Petäjä T., Krejci R., Hansson H.-C., Swietlicki E., Lindroth A., Christensen T. R., Arneth A., Hari P., Bäck J., Vesala T. and Kerminen V.-M. (2014) CO2-induced terrestrial climate feedback mechanism: From carbon sink to aerosol source and back, *Boreal Env. Res.*, 19 (suppl. B): 122–131.

Kurtén T., Loukonen V., Vehkamäki H. and Kulmala M. (2008) Amines are likely to enhance neutral and ion- induced sulfuric acid-water nucleation in the atmosphere more effectively than ammonia, *Atmos. Chem. Phys.*, 8, 4095–4103, doi:10.5194/acp-8-4095-2008.

Kyrö E.-M., Kerminen V.-M., Virkkula A., Dal Maso M., Parshintsev J., Ruíz-Jimenez J., Forsström L., Manninen H. E., Riekkola M.-L., Heinonen P. and Kulmala M. (2013) Antarctic new particle formation from continental biogenic precursors, *Atmos. Chem. Phys.*, 13, 3527-3546, doi:10.5194/acp-13-3527-2013.

Laaksonen A., Kulmala M., O’Dowd C. D., Joutsensaari J., Vaattovaara P., Mikkonen S., Lehtinen K. E. J., Sogacheva L., Dal Maso M., Aalto P., Petäjä T., Sogachev A., Yoon Y. J., Lihavainen H., Nilsson D., Facchini M. C., Cavalli F., Fuzzi S., Hoffmann T., Arnold F., Hanke M., Sellegri K., Umann B., Junkermann W., Coe H., Allan J. D., Alfarra M. R., Worsnop D. R., Riekkola M.-L., Hyötyläinen T. and Viisanen Y. (2008) The role of VOC oxidation products in continental new particle formation, Atmos. Chem. Phys., 8, 2657–2665, doi:10.5194/acp-8-2657-2008.

Lohmann U. and Feichter J. (2005) Global indirect aerosol effects: a review, *Atmos. Chem. Phys.*, 5, 715–737, SRef ID: 1680-7324/acp/2005-5-715.

Loukonen V., Kurtén T., Ortega I. K., Vehkamäki H., Pádua A. A. H., Sellegri K. and Kulmala M. (2010) Enhancing effect of dimethylamine in sulfuric acid nucleation in the presence of water – a computational study, *Atmos. Chem. Phys.*, 10, 4961-4974, doi:10.5194/acp-10-4961-2010.

Lovejoy E. R., Curtius J. and Froyd K. D. (2004) Atmospheric ion-induced nucleation of sulfuric acid and water, *J. Geophys. Res.*, 109(D08204), doi:10.1029/2003JD004460.

Mauldin III, R. L., Tanner D., Heath J., Huebert B. and Eisele, F. (1999) Observations of H_2SO_4 and MSA during PEM-Tropics-A, J. Geophys. Res., 104, 5801–5816.

Mauldin III R. L., Kosciuch E., Henry B., Eisele F. L., Shetter R., Lefer B., Chen G., Davis D., Huey G. and Tanner D. (2004) Measurements of OH, HO_2 + RO_2, H_2SO_4, and MSA at the South Pole during ISCAT 2000, *Atmos. Environ.*, 38, 5423–5437, doi:10.1016/j.atmosenv.2009.07.058.

Manninen H. E., Nieminen T., Asmi E., Gagné S., Häkkinen S., Lehtipalo K., Aalto P., Vana M., Mirme A., Mirme S., Hõrrak U., Plass-Dülmer C., Stange G., Kiss G., Hoffer A., Törő N., Moerman M., Henzing B., de Leeuw G., Brinkenberg M., Kouvarakis G. N., Bougiatioti A., Mihalopoulos N., O'Dowd C., Ceburnis D., Arneth A., Svenningsson B., Swietlicki E., Tarozzi L., Decesari S., Facchini M. C., Birmili W., Sonntag A., Wiedensohler A., Boulon J., Sellegri K., Laj P., Gysel M., Bukowiecki N., Weingartner E., Wehrle G., Laaksonen A., Hamed A., Joutsensaari J., Petäjä T., Kerminen V.-M. and Kulmala M (2010) EUCAARI ion spectrometer measurements at 12 European sites – analysis of new particle formation events, *Atmos. Chem. Phys.*, 10, 7907–7927, doi:10.5194/acp-10-7907-2010.

Mauldin III, R. L., Tanner D. J. and Eisele F. L. (1998) A new chemical ionization mass spectrometer technique for the fast measurement of gas phase nitric acid in the atmosphere, *J. Geophys. Res.*, 103(D3), 3361–3367, doi:10.1029/97JD02212.

Mauldin III R. L., Berndt T., Sipilä M., Paasonen P., Petäjä T., Kim S., Kurtén T., Stratmann F., Kerminen V.-M., and Kulmala M. (2012) A new atmospherically relevant oxidant of sulphur dioxide, *Nature*, 488, 193–196, doi:10.1038/nature11278

McFiggans G., Bale C. S. E., Ball S. M., Beames J. M., Bloss W. J., Carpenter L. J., Dorsey J., Dunk R., Flynn M. J., Furneaux K. L., Gallagher M. W., Heard D. E., Hollingsworth A. M., Hornsby K., Ingham T., Jones C. E., Jones R. L., Kramer L. J., Langridge J. M., Leblanc C., LeCrane J.-P., Lee J. D., Leigh R. J., Longley I., Mahajan A. S., Monks P. S., Oetjen H., Orr-Ewing A. J., Plane J. M. C., Potin P., Shillings A. J. L., Thomas F., von Glasow R., Wada R., Whalley L. K. and Whitehead J. D. (2010) Iodine-mediated coastal particle formation: an overview of the Reactive Halogens in the Marine Boundary Layer (RHaMBLe) Roscoff coastal study, *Atmos. Chem. Phys.*, 10, 2975-2999, doi:10.5194/acp-10-2975-2010.

McMurry P.H. and Friedlander S.K., 1979, Atmospheric Environment, 13, 1635-1651

McMurry, P. (1983), New particle formation in the presence of an aerosol: Rates, time scales, and sub 0.01 mm size distributions, *J. Colloid Interface Sci.*, 95(1), 72–80.

McMurry, P. H. (1980). Photochemical aerosol formation from SO_2: A theoretical analysis of smog chamber
data, *J. Colloid Interface Sci.*, 78, 513-527.

McMurry P. H., Fink M., Sakurai H., Stolzenburg M. R., Mauldin R. L. III, Smith J., Eisele F., Moore K., Sjosted S., Tanner D,. Huey L. G., Nowak J. B., Edgerton E., Voisin D. (2005), A criterion for new particle formation in the sulfur-rich Atlanta atmosphere, *J. Geophys. Res.*, 110(D22S02), doi:10.1029/2005JD005901.

Merikanto J., I. Napari H. Vehkamäki T. Anttila and M. Kulmala (2007) New parameterization of sulfuric acid-ammonia-water ternary nucleation rates at tropospheric conditions, *J. Geophys. Res.*, 112, D15207, doi:10.1029/2006JD007977.

Merikanto, J., Spracklen, D. V., Mann, G. W., Pickering, S. J., and Carslaw, K. S. (2009) Impact of nucleation on global CCN, *Atmos. Chem. Phys*., 9, 8601–8616, doi:10.5194/acp-9-8601-2009.

Metzger A., Verheggen B., Dommen J., Duplissy J., Prevot A. S. H., Weingartner E., Riipinen I., Kulmala M., Spracklen D. V., Carslaw K. S. and Baltensperger U. (2010) Evidence for the role of organics in aerosol particle formation under atmospheric conditions, *P. Natl. Acad. Sci. USA*, 107, 6646–6651, doi: 10.1073/pnas.0911330107

Nieminen T., Asmi A., Dal Maso M., Aalto P. P., Keronen P., Petäjä T., Kulmala M. and Kerminen V.-M. (2014) Trends in atmospheric new-particle formation: 16 years of observations in a boreal-forest environment. *Boreal Env. Res.*, 19 (suppl. B): 191–214.

Nowak J. B., Newman J. A., Kozai K., Huey L. G., Tanner D., Holloway J. S., Ryerson T. B., Frost G. L., McKeen S. A. and Fehsenfeld F. C. (2007) A chemical ionization mass spectrometry technique for airborne measurements of ammonia, *J. Geophys. Res.*, 112, D10S02, 10.1029/2006JD007589.

O’Dowd C. D., Jimenez J. L., Bahreini R., Flagan R. C., Seinfeld J. H., Hämeri K., Pirjola L., Kulmala M., Jennings S. G., Hoffmann T (2002a) Marine Aerosol Formation From Biogenic Iodine Emissions, *Nature*, 417, 632-636.

O’Dowd C. D., Aalto P., Hämeri K., Kulmala M. and Hoffmann T. (2002b) Aerosol formation-Atmospheric particles from organic vapours, *Nature*, 416, 497–498.

Ortega I. K., Kupiainen O., Kurtén T., Olenius T., Wilkman O., McGrath M. J., Loukonen V. and Vehkamäki H. (2012) From quantum chemical formation free energies to evaporation rates, Atmos. Chem. Phys., 12, 225-235, doi:10.5194/acp-12-225-2012.

Paasonen P., Nieminen T., Asmi E., Manninen H. E., Petäjä T., Plass-Dülmer C., Flentje H., Birmili W., Wiedensohler A., Hõrrak U., Metzger, A. Hamed, A. Laaksonen A., Facchini M. C., Kerminen V.-M. and Kulmala M. (2010) On the roles of sulphuric acid and low-volatility organic vapours in the initial steps of atmospheric new particle formation, *Atmos. Chem. Phys.*, 10, 11223-11242, doi:10.5194/acp-10-11223-2010.

Paasonen P., Olenius T., Kupiainen O., Kurtén T., Petäjä T., Birmili W., Hamed A., Hu M., Huey L. G., Plass-Dülmer C., Smith J. N., Loukonen V., McGrath M. J., Ortega I. K., Laaksonen A., Vehkamäki H., Kerminen V.-M. and Kulmala M. (2012) On the formation of sulphuric acid – amine clusters in varying atmospheric conditions and its influence on atmospheric new particle formation, *Atmos. Chem. Phys.*, 12, 9113-9133.

Paasonen P., Asmi A., Petäjä T., Kajos M. K., Äijälä M., Junninen H., Holst T., Abbatt J. P. D., Arneth A., Birmili W., van der Gon H. D., Hamed A., Hoffer A., Laakso L., Laaksonen A., Leaitch W. R., Plass-Duelmer C., Pryor S. C., Räisänen P., Swietlicki E., Wiedensohler A., Worsnop D. R., Kerminen V.-M.and Kulmala M. (2013) Warming-induced increase in aerosol number concentration likely to moderate climate change, *Nature Geoscience*, 6, 438–442, doi:10.1038/ngeo1800.

Pandis S. N., Paulson S. E., Seinfeld J. H. and Flagan R. C. (1991) Aerosol formation in the photooxidation of isoprene and β-pinene, *Atmos. Environ.*, 25, 997–1008.

Paulson S. E., Sen A. D., Liu P., Fenske J. D. and Fox M. J. (1997) Evidence for formation of OH radicals from the reaction of O_3 with alkenes in the gas phase, Geophys. Res. Lett., 24(24), 3193–3196.

Petäjä T., Mauldin III R. L., Kosciuch E., McGrath J., Nieminen T., Paasonen P., Boy M., Adamov A., Kotiaho T., and Kulmala M. (2009) Sulfuric acid and OH concentrations in a boreal forest site, *Atmos. Chem. Phys.*, 9, 7435-7448, doi:10.5194/acp-9-7435-2009.

Peñuelas J., Staudt M. (2010) BVOCs and global change. *Trends in Plant Science* 15(3): 133-144.

Petäjä T., Sipilä M., Paasonen P., Nieminen T., Kurtén T., Ortega I. K., Stratmann F., Vehkamäki H., Berndt T., and Kulmala M. (2011) Experimental Observation of Strongly Bound Dimers of Sulfuric Acid: Application to Nucleation in the Atmosphere, *Phys. Rev. Lett.*, 106, 228302(1-4), DOI: http://dx.doi.org/10.1103/PhysRevLett.106.228302

Saikawa E., Naik V., Horowitz L. W. Liu J. F. and Mauzerall D. L. (2009) Present and potential future contributions of sulfate, black and organic carbon aerosols from China to global air quality, premature mortality and radiative forcing, *Atmos. Environ.*, 43, 2814–2822.

Schobesberger S., Junninen H., Bianchi F., Lönn G., Ehn M., Lehtipal, K., Dommen J., Ehrhart S., Ortega I. K., Franchin A., Nieminen T., Riccobono F., Hutterli M., Duplissy J., Almeida J., Amorim A., Breitenlechner M., Downard A. J., Dunne E. M., Flagan R. C., Kajos M., Keskinen H., Kirkby J., Kupc A., Kuerten A., Kurten T., Laaksonen A., Mathot S., Onnela A., Praplan A. P., Rondo L., Santos F. D., Schallhart S., Schnitzhofer R., Sipilä M., Tome A., Tsagkogeorgas G., Vehkamäki H., Wimmer D., Baltensperger U., Carslaw K. S., Curtius J., Hansel A., Petäjä T., Kulmala M., Donahue N. M. and Worsnop, D. R. (2013) Molecular understanding of atmospheric particle formation from sulfuric acid and large oxidized organic molecules, *Proc. Natl. Acad. Sci. U.S.A.*, 110(43), 17,223–17,228, doi:10.1073/pnas.1306973110.

Sihto, S.-L., Kulmala, M., Kerminen, V.-M., Dal Maso, M., Petäjä, T., Riipinen, I., Korhonen, H., Arnold, F., Janson, R., Boy, M., Laaksonen, A., and Lehtinen, K. E. J. (2006) Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms, *Atmos. Chem. Phys.*, 6, 4079-4091, doi:10.5194/acp-6-4079-2006.

Sipilä, M., Lehtipalo, K., Kulmala, M., Petäjä, T., Junninen, H., Aalto, P. P., Manninen, H. E., Kyrö, E.-M., Asmi, E., Riipinen, I., Curtius, J., Kürten, A., Borrmann, S., and O'Dowd, C. D. (2008) Applicability of condensation particle counters to measure atmospheric clusters, *Atmos. Chem. Phys.*, 8, 4049-4060, doi:10.5194/acp-8-4049-2008.

Sipilä M., Berndt T., Petäjä T., Brus D., Vanhanen J., Stratmann F., Patokoski J., Mauldin III R. L., Hyvärinen A.-P., Lihavainen H., Kulmala M. (2010) The role of sulphuric acid in atmospheric nucleation, *Science*, 327(5970): 1243-1246, DOI: 10.1126/science.1180315.

Sipilä, M., Jokinen, T., Berndt, T., Richters, S., Makkonen, R., Donahue, N. M., Mauldin III, R. L., Kurtén, T., Paasonen, P., Sarnela, N., Ehn, M., Junninen, H., Rissanen, M. P., Thornton, J., Stratmann, F., Herrmann, H., Worsnop, D. R., Kulmala, M., Kerminen, V.-M., and Petäjä, T. (2014) Reactivity of stabilized Criegee intermediates (sCIs) from isoprene and monoterpene ozonolysis toward SO_2 and organic acids, *Atmos. Chem. Phys.*, 14, 12143-12153, doi:10.5194/acp-14-12143-2014.

Sipilä, M., Sarnela, N., Jokinen, T., Junninen, H., Hakala, J., Rissanen, M. P., Petäjä, T., and Worsnop, D. R. (2015) Bisulphate-cluster based atmospheric pressure chemical ionization mass spectrometer for ultra-high sensitivity (10 ppq) detection of atmospheric amines: proof-of-concept and first ambient data from boreal forest, *Atmos. Meas. Tech. Discuss.*, 8, 3667-3696, doi:10.5194/amtd-8-3667-2015.

Spindler, G., Brüggemann, E., Gnauk, T., Grüner, A., Müller, K., Herrmann, H. (2010) A four-year size-segregated characterization study of particles PM10, PM2.5 and PM1 depending on air mass origin at Melpitz, *Atmos. Environ.*, 44, 164-173.

Spracklen D. V., Jimenez J. L., Carslaw K. S., Worsnop D. R., Evans M. J., Mann G. W., Zhang Q., Canagaratna M. R., Allan J., Coe H., McFiggans G., Rap A. and Forster P. (2011) Aerosol mass spectrometer constraint on the global secondary organic aerosol budget, *Atmos. Chem. Phys.*, 11, 12109-12136, doi:10.5194/acp-11-12109-2011.

Rehbein N. and Cooray V. (2001) NOx production in spark and corona discharges, *J. Electrostat.*, 51–52, 333–339

Riccobono F., Schobesberger S., Scott C. E., Dommen J., Ortega I. K., Rondo L., Almeida J., Amorim A., Bianchi F., Breitenlechner M., David A., Downard A., Dunne E. M., Duplissy J., Ehrhart S., Flagan R. C., Franchin A., Hansel A., Junninen H., Kajos M., Keskinen H., Kupc A., Kürten A., Kvashin A. N., Laaksonen A., Lehtipalo K., Makhmutov V., Mathot S., Nieminen T., Onnela A., Petäjä T., Praplan A. P., Santos F. D., Schallhart S., Seinfeld J. H., Sipilä M., Spracklen D. V., Stozhkov Y., Stratmann F., Tomé A., Tsagkogeorgas G., Vaattovaara P., Viisanen Y., Vrtala A., Wagner P. E., Weingartner E., Wex H., Wimmer D., Carslaw K. S., Curtius J., Donahue N. M., Kirkby J., Kulmala M., Worsnop D. R., and Baltensperger U. (2014) Oxidation Products of Biogenic Emissions Contribute to Nucleation of Atmospheric Particles, *Science*, 344, 717–721.

Rissanen, M. P., Kurtén, T., Sipilä, M., Thornton, J. A., Kangasluoma J., Sarnela N., Junninen H., Jørgensen S., Schallhart S., Kajos M. K., Taipale R., Springer M., Mentel T. F., Ruuskanen T., Petäjä T., Worsnop D. R., Kjærgaard H. G. and Ehn M. (2014) The formation of highly oxidized multifunctional products in the ozonolysis of cyclohexene, *J. Am. Chem.l Soc.*, 136(44):15596-15606., doi:10.1021/ja507146s.

Riipinen, I., Sihto, S.-L., Kulmala, M., Arnold, F., Dal Maso, M., Birmili, W., Saarnio, K., Teinilä, K., Kerminen, V.-M., Laaksonen, A., and Lehtinen, K. E. J. (2007) Connections between atmospheric sulphuric acid and new particle formation during QUEST III–IV campaigns in Heidelberg and Hyytiälä, *Atmos. Chem. Phys.*, 7, 1899-1914, doi:10.5194/acp-7-1899-2007.

Riipinen, I., Pierce, J. R., Yli-Juuti, T., Nieminen, T., Häkkinen, S., Ehn, M., Junninen, H., Lehtipalo, K., Petäjä, T., Slowik, J., Chang, R., Shantz, N. C., Abbatt, J., Leaitch, W. R., Kerminen, V.-M., Worsnop, D. R., Pandis, S. N., Donahue, N. M., and Kulmala, M. (2011) Organic condensation: a vital link connecting aerosol formation to cloud condensation nuclei (CCN) concentrations, *Atmos. Chem. Phys.*, 11, 3865-3878, doi:10.5194/acp-11-3865-2011.

Riipinen, I., Yli-Juuti, T., Pierce, J. R., Petäjä, T., Worsnop, D. R., Kulmala, M., and Donahue, N. M. (2012) The contribution of organics to atmospheric nanoparticle growth, *Nat. Geosci.*, 5, 453–458, doi:10.1038/ngeo1499.

Taipale, R., Sarnela, N., Rissanen, M., Junninen, H., Rantala, P., Korhonen, F., Siivola, E., Berndt, T., Kulmala, M., Mauldin, R. L. III, Petäjä, T. & Sipilä, M. (2014) New instrument for measuring atmospheric concentrations of non-OH oxidants of SO2, *Boreal Env. Res.*,19 (suppl. B): 55–70.

Tie, X. X., Wu, D., and Brasseur, G. (2009) Lung cancer mortality and exposure to atmospheric aerosol particles in Guangzhou, China, *Atmos. Environ.*, 43, 2375–2377

Tunved, P., Hansson, H.-C., Kerminen, V.-M., Ström, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P. P., Komppula, M., and Kulmala, M. (2006) High natural aerosol loading over boreal forests, *Science*, 312, 261–263.

Vanhanen, J., Mikkilä, J., Lehtipalo, K. , Sipilä, M. , Manninen, H. E. , Siivola, E. , Petäjä, T. and Kulmala, M. (2011) Particle Size Magnifier for Nano-CN Detection, *Aerosol Sci. Technol.*, 45: 4, 533-542.

Vereecken, L., Nguyen, T. L., Hermans, I. & Peeters, J. (2004) Computational study of the stability of α-hydroperoxyl-α-alkylperoxyl substituted alkyl radicals. *Chem. Phys. Lett.*, 393, 432–436

Veres, P., J.M. Roberts, I.R. Burling, C. Warneke, J. de Gouw, R.J. Yokelson (2008) Development of negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) for the measurement of gas-phase organic acids in the atmosphere, *Int. J. Mass Spectrom.*, 274(1–3), 48–55, doi:10.1016/j.ijms.2008.04.032.

Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, D. J., and Jefferson, A. (1996) Measured atmospheric new particle formation rates: Implications for nucleation mechanisms, *Chemical Engineering Communications*, 151, 53–64.

Wimmer, D., Lehtipalo, K., Franchin, A., Kangasluoma, J., Kreissl, F., Kürten, A., Kupc, A., Metzger, A., Mikkilä, J., Petäjä, T., Riccobono, F., Vanhanen, J., Kulmala, M., and Curtius, J. (2013) Performance of diethylene glycol-based particle counters in the sub-3 nm size range, *Atmos. Meas. Tech.*, 6, 1793-1804, doi:10.5194/amt-6-1793-2013.

Weber, R. J., J. J. Marti, P. H. McMurry, F. L. Eisele, D. J. Tanner, and A. Jefferson (1997), Measurements of new particle formation and ultrafine particle growth rates at a clean continental site, *J. Geophys. Res.*, 102(D4), 4375–4385, doi:10.1029/96JD03656.

You, Y., Kanawade, V. P., de Gouw, J. A., Guenther, A. B., Madronich, S., Sierra-Hernández, M. R., Lawler, M., Smith, J. N., Takahama, S., Ruggeri, G., Koss, A., Olson, K., Baumann, K., Weber, R. J., Nenes, A., Guo, H., Edgerton, E. S., Porcelli, L., Brune, W. H., Goldstein, A. H., and Lee, S.-H. (2014) Atmospheric amines and ammonia measured with a chemical ionization mass spectrometer (CIMS), *Atmos. Chem. Phys.*, 14, 12181-12194, doi:10.5194/acp-14-12181-2014.

Zhang, R., Suh, I., Zhao, J., Zhang, D., Fortner, E. C., Tie, X., Molina, L. T., and Molina, M. J. (2004) Atmospheric new particle formation enhanced by organic acids, *Science*, 304, 1487–1490.

Zhang X., Cappa C. D., Jathar S. H., McVay R. C., Ensberg J. J., Kleeman J. K., Seinfeld J. H. (2014) Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, *Proc. Natl. Acad. Sci.,* 111(16), 5802–5807, doi: 10.1073/pnas.1404727111.

Zhao, J., Eisele, F. L., Titcombe, M., Kuang, C., and McMurry, P. H. (2010) Chemical ionization mass spectrometric measurements of atmospheric neutral clusters using the cluster-CIMS, *J. Geophys. Res.*, 115, D08205, doi:10.1029/2009JD012606.

Zhao, J., Smith, J. N., Eisele, F. L., Chen, M., Kuang, C., and McMurry, P. H. (2011) Observation of neutral sulfuric acid-amine containing clusters in laboratory and ambient measurements, *Atmos. Chem. Phys.*, 11, 10823-10836, doi:10.5194/acp-11-10823-2011.

Zhao, J., J. Ortega, M. Chen, P. H. McMurry, and J. N. Smith (2013), Dependence of particle nucleation and growth on high-molecular-weight gas-phase products during ozonolysis of alpha-pinene, *Atmos. Chem. Phys.*, 13(15), 7631–7644, doi:10.5194/acp-13-7631-2013.