THE ORGANIC TANDEM DIFFERENTIAL MOBILITY ANALYZER: INSTRUMENT DEVELOPMENT AND STUDIES OF FRESHLY NUCLEATED AND AITKEN MODE SIZE ATMOSPHERIC NANOPARTICLE COMPOSITIONS AT MARINE AND FOREST ENVIRONMENTS

PETRI VAATTOVAARA

Department of Physics

Faculty of Natural and Environmental Sciences

University of Kuopio

Kuopio, Finland

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Author's address: Department of Physics
University of Kuopio
P.O.Box 1627
FI-70211 Kuopio
Finland
Petri.Vaattovaara at uku.fi

Supervisors: Professor Ari Laaksonen, Ph.D.
Department of Physics
University of Kuopio
Finland
and
Finnish Meteorological Institute
Helsinki
Finland

Docent Jorma Joutsensaari, D.Sc. (Tech.)
Department of Physics
University of Kuopio
Finland

Reviewers: Professor Erik Swietlicki, Ph.D.
Department of Physics
Division of Nuclear Physics
Lund Institute of Technology
Sweden

Associate professor Zoran Ristovski, Ph.D.
School of Physical and Chemical Sciences
Queensland University of Technology
Australia

Opponent: Professor Hans-Christen Hansson, Ph.D.
Department of Applied Environmental Science
Stockholm University
Sweden

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Petri Vaattovaara

The Organic Tandem Differential Mobility Analyzer: Instrument development and studies of freshly nucleated and Aitken mode size atmospheric nanoparticle compositions at marine and forest environments

Petri Olavi Vaattovaara

University of Kuopio, 2009

Abstract

Secondary organic aerosol (SOA) accounts for a large fraction of the organic aerosol burden and a significant fraction of ambient tropospheric aerosol. They are of significant importance from viewpoint of climate and health issues. In order to evaluate their impact on climate and human health, a detailed knowledge of the formation, growth, transformation, composition and properties of SOA and secondary organic gases is required. The chemical and physical processes associated with SOA formation and properties are complex and varied, and therefore represent a major research challenge in atmospheric science. Atmospheric nanoparticle formation is known to occur worldwide and thus it is also important to understand from the viewpoint of climate issues. However, its SOA related properties and processes have been poorly known, because they are very difficult to investigate especially in freshly nucleated nucleation mode size (d>20 nm) and larger Aitken mode (20 nm<d <100 nm) size particles.

Therefore, a novel TDMA method has been developed in this thesis in order to study the presence, fraction and transformation of secondary organic compounds in the nucleation and Aitken mode particle compositions during new particle formation events. This method was applied in two major natural environments which together cover over 80% of the Earth's surface. The results indicate a significant marine secondary organic fraction in newly-formed particles from a biologically active marine environment and a strongly dominating secondary organic fraction in newly-formed particles from a forest environment. On the other hand, secondary inorganic compounds were very likely necessary for nucleation. The results also reveal that anthropogenic secondary inorganics can play a role even for new particle formation and nanoparticle composition in virgin natural environments. Furthermore, these real atmosphere studies show that secondary organic compounds and their aging affect the size, composition and thus properties of ultrafine particles. Additionally, the results support the ideas that those secondary organic and inorganic compounds chemically interact and thus affect the composition and properties of the particles in atmospheric conditions.

Keywords: organic TDMA, nanoparticles, nucleation, SOA, nature, composition, properties, evolution, aging, marine, forest, pollution, health, climate

Contents

List of Publications

This thesis consists of an introductory review, followed by five research articles which are cited according to their roman numerals. The papers are reproduced with the kind permission of the journals concerned.

I Jorma Joutsensaari, **Petri Vaattovaara**, Milko Vesterinen, Kaarle Hämeri, and Ari Laaksonen. A novel tandem differential mobility analyzer with organic vapor treatment of aerosol particles. *Atmospheric Chemistry and Physics*, 1, 51-60, 2001.

II Jorma Joutsensaari, Teemu Toivonen, **Petri Vaattovaara**, Milko Vesterinen, Jouko Vepsäläinen, and Ari Laaksonen. Time-resolved growth behavior of acid aerosols in ethanol vapor with a tandem-DMA technique. *Journal of Aerosol Science*, 35, 851-867, 2004.

III Petri Vaattovaara, Markus Räsänen, Thorsten Kühn, Jorma Joutsensaari, and Ari Laaksonen. A method for detecting the presence of organic fraction in nucleation mode sized particles. *Atmospheric Chemistry and Physics*, 5, 3277-3287, 2005.

IV Petri Vaattovaara, Piia E. Huttunen, Young Jun Yoon, Jorma Joutsensaari, Kari E.J. Lehtinen, Colin D. O'Dowd, and Ari Laaksonen. The composition of nucleation and Aitken modes particles during coastal nucleation events: evidence for marine secondary organic contribution. *Atmospheric Chemistry and Physics*, 6, 4601-4616, 2006.

V Petri Vaattovaara, Tuukka Petäjä, Jorma Joutsensaari, Pasi Miettinen, Boris Zaprudin, Aki Kortelainen, Juha Heijari, Pasi Yli-Pirilä, Pasi Aalto, Doug R. Worsnop, and Ari Laaksonen. The evolution of nucleation- and Aitken-mode particle compositions in a boreal forest environment during clean and pollution-affected new particle formation events. *Boreal Environment Research*, 14, 662-682, 2009.

1 Introduction

The Earth's atmosphere is fundamental for our life. From the viewpoint of climate (e.g., IPCC 2007) and health issues (e.g., Nel 2005; Löndahl 2009), and thus of our living conditions, it is crucial what are the atmospheric gas and particle phase compositions. Gases and particles are tightly connected via physical, chemical and meteorological processes occurring in the atmosphere and at the atmosphere-biosphere interface (e.g., Kulmala and Kerminen 2008).

In regards to climate change, one of the largest uncertainties is related to aerosols and their direct and indirect (via clouds) connections to the Earth's radiative balance and climate (IPCC 2007). An important phenomenon associated with the climatically important direct and indirect aerosol effects is the formation of new nanometer-size particles. This phenomena consists of a set of processes that include the production of nanometer-size clusters from gaseous vapours, the growth of these clusters to detectable sizes (see e.g., Kulmala and Kerminen 2008), and their growth to potential cloud condensation nuclei (CCN) and larger radiatively active sizes.

The aerosols typically consist of both organic and inorganic compounds whose relative ratios strongly depend on the environmental conditions where the interaction and the ratio of anthropogenic and biogenic gases and particles define the overall compositions and properties. In order to more fully understand the effects of atmospheric aerosols, the formation, growth, transformation and composition of freshly nucleated nucleation mode particles and Aitken mode size particles need to be properly understood in changing conditions and various environments as a function of time and size.

However, the composition and especially the organic content of particles smaller than 50 nm in diameter are very difficult to experimentally study due to the requirements of instrumental methods with high sensitivity and near online time resolution. These challenges arise from the small sizes and low mass of the particles, the brevity of particle forming nucleation events and the rapid changes that may occur in particle composition.

Around the start of the third millennium when this work began, a known method (see McMurry 2000) to fill a part of the requirements was the hygroscopicity tandem differential mobility analyzer (H-TDMA; Rader and McMurry 1986). The H-TDMA was applied to different field, laboratory and chamber measurements (e.g., McMurry and Stolzenburg 1989; Hansson et al. 1990; Covert et al. 1991; Svenningson et al 1992; Hansson et al. 1998; Virkkula et al.1999; see Swietlicki et al. 2008). Especially ultrafine version, namely ultrafine hygroscopicity TDMA (UFH-TDMA; Hämeri et al. 2000), was also applied to virgin natural environments (e.g., Väkevä 2002). However, while the importance of organic aerosols was recognized, the development of methods was needed to further understand the presence, properties and effects of organics (Jacobson et al. 2000).

Therefore, the aim of this PhD work was to acquire additional information about the presence of organics and their properties and effects on atmospheric aerosols in various environments. A novel TDMA, using subsaturated ethanol vapour, was consequently successfully planned, built, tested and developed (**Papers I, II and III**), and applied with further developed analysis methods to different environments (**Papers IV and V**). In order to study the contribution and the role of secondary organics to freshly nucleated ultrafine (d < 20 nm) and Aitken mode size (d < 100 nm) particle properties in different natural environments, the novel TDMA measurements were carried out at a

marine (**Paper IV**) and a forest environment (**Paper V**). These sites represent two major natural environments, where the relations of organics and inorganics were not properly understood. In addition to those objectives, the original research plan included hygroscopicity TDMA studies (**Papers I and V**) and theoretical studies of measured particle composition (**Papers I, II, III, and V**). As a result of the objectives, the role of anthropogenic inorganics to ultrafine particle formation, composition, transformation and properties (**Paper V**), and the connections of inorganic and organic chemistry (**Papers IV and V**) were also studied.

In Chapters 2 and 3, the development of the first O-TDMA (organic TDMA) versions and the development of the UFO-TDMA (ultrafine organic TDMA) method are described. In Chapters 4 and 5, the results of the UFO-TDMA applications to a marine environment and to a forest environment are provided. In Chapters 6 and 7, the publications that describe this compiled work are briefly reviewed and the Author's contribution is presented. Finally, overall conclusions are drawn and references are provided in Chapters 8 and 9.

2 The OTDMA: Instrument development and laboratory studies

Liu et al. (1978) were the first to introduce the tandem differential mobility analyzer (TDMA) technique to study the change in particle diameter via electrical mobility due to aerosol processing. Since then different types of TDMAs have been developed and widely used. The most common used have been the H-TDMAs (hygroscopicity TDMA) and the V-TDMAs (volatility TDMA). As regards DMAs and CPCs (condensation particle counters), a good review of the history of the mobility analyzers is provided by Flagan (1998) and a good historical review of CPCs is shown by McMurry (2000). A review of mobility techniques with extensions is presented in Park et al. (2008). For organic aerosols, good reviews of organic aerosols (Kanakidou et al. 2005) and the formation, properties and impact of secondary organic aerosols (Hallquist et al. 2009) can be found in recent literature.

In order to obtain information about the organic content of atmospheric aerosol particles (20nm<d<150nm), a novel instrument, the O-TDMA (Organic tandem differential mobility analyzer; **Papers I and II**) was built and developed during the years 2000-2002. The main difference between a traditional hygroscopicity TDMA and O-TDMA is that in the latter device, particles are grown in subsaturated ethanol vapour instead of subsaturated water vapour. In the first phase of the building of the TDMA, the goal was to construct an H-TDMA (**Paper I**) in order to test the proper functioning of the basic system and to acquire reference information for the H-TDMA field measurements (e.g., Anttila et al. 2009; Kivekäs et al. 2009) and for the O-TDMA measurements. The H-TDMA was built following the guidelines of Liu et al. (1978), Sekigawa (1983), Rader and McMurry (1986), McMurry and Stolzenburg (1989), Svenningson et al. (1992), and Hämeri et al. (2000). After the H-TDMA was successfully built and verified, the O-TDMA was built and the working principle tested in an aerosol laboratory at Kuopio University (**Paper I**).

One of the most important decisions made during the assembly of the O-TDMA, was the selection of an organic solvent. The chosen solvent was ethanol. The advantages of ethanol as the organic solvent in an OTDMA are at least as follows (**Paper III**): Solubility information for different organic and inorganic compounds is readily available. This information reveals that various

oxidized organic compounds are soluble or very soluble in ethanol whereas typical atmospheric inorganic species are not soluble or are only slightly soluble. In addition, ethanol solubility properties differ sufficiently from those of water. Ethanol is not too harmful, toxic, corrosive, explosive or reactive. The reaction products of ethanol with OH radicals are not expected to nucleate (i.e. acetaldehyde, see Carter 1990), the odour is bearable, a high enough amount of very pure ethanol is usually easy to supply and store, and it is not too expensive. One disadvantage is that ethanol may burn if a spark is present inside a DMA.

The saturation ratio of the ethanol vapour was measured by a dew point monitor (General Eastern, Hygro M4 with Model D-2 Chilled Mirror Sensor). For example, Vaisala Humicap 180, which is used for the H-TDMA, cannot measure the ethanol vapour. The final selection of the General Eastern dew point monitor for ethanol vapour measurements was mainly based on my communications with Mr. Gerald Schultz from General Eastern (e.g. 29 February 2000 he stated: "if one excludes water or ethanol, one can measure the other"). Thus, dried (water saturation ratio below 0.03) and purified sheath air is needed for ethanol measurements. The saturation ratio of the solvent is controlled by a flow meter, preferably located in front of the ethanol saturator system (see Fig. 1). This is necessary as the flow meter function (e.g. Brooks Instrument, Model 5850S) could otherwise be disturbed by the ethanol.

A schematic presentation of the O-TDMA is shown in Figure 1 (**Paper I**). In the O-TDMA, which has the safe measurement range for the particles of 20-150 nm in diameter, the first differential mobility analyzer (DMA-1, Hauke type, length 28 cm; Winklmayr et al., 1991) is used to classify a monodisperse fraction of the aerosol particles based on their electrical mobility. The particles are passed to DMA-1 through a neutralizer ([63]Ni radioactive β-source, half-life over 90 years). A sample flow of 1 l/min is used. A dry (relative humidity, RH < 3%) and clean air flow of 10 l/min is used as sheath and excess flow in the DMA-1 (aerosol-sheath flow ratio 1:10). The sheath and excess flows are controlled by critical orifices. The selected particle sizes for the DMA-1 are typically 20 nm, 30nm, 50 nm, 80 nm, 100 nm, and 150 nm. A good review about H-TDMA instruments operation, data inversion and sources of errors, generally also applicable to an O-TDMA, are found in Swietlicki et al. (2008).
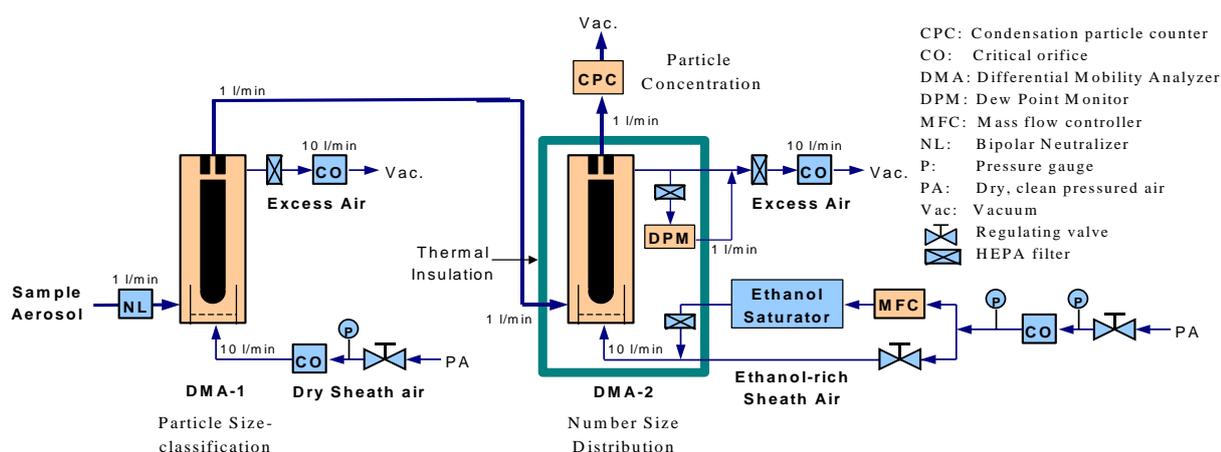

Figure 1. A schematic presentation about the O-TDMA system.

The change in particle size due to interaction with the ethanol vapour is determined with the second DMA (DMA-2, similar to DMA-1) by measuring the particle number size distribution. The DMA-2 is also operated with aerosol and sheath flows of 1 and 10 l/min, respectively (aerosol-sheath flow ratio 1:10), and the flows are controlled by critical orifices. The particle number concentrations after DMA-2 are determined with TSI 3010 condensation particle counter, which provides the sample flow of 1 l/min through the O-TDMA. The number size distributions are calculated using a standard DMA data inversion algorithm (Reischl 1991; Knutson and Whitby 1975). To determine growth factors (GFs, diameter at certain saturation ratio/selected diameter) of the particles, the geometric number mean diameter (GMD) of the size distribution is used as an averaged particle size in the calculations. If bimodal distributions are present, the GMDs and growth factors (GFs) are determined for both modes. A controlled concentration of ethanol vapour is set to the sheath air flow of DMA-2 in order to treat particles with ethanol vapour and to avoid also ethanol evaporation from the particles inside DMA-2 during the measurements (**Paper I**).

The working principle of the O-TDMA without (Figure 1) or with (Figure 2) an external aerosol treatment unit was successfully tested for 100 nm particles using typical atmospheric inorganic compounds sodium chloride and ammonium sulfate and model organic compounds citric acid and adipic acid. The measured GFs and model results indicated that the measured compounds mainly behaved like expected based on the solubility and growth information in the literature (**Paper I**). Importantly, the ethanol insoluble or slightly soluble inorganics did not grow but the oxidized organics grew in subsaturated ethanol vapour, thus making possible to apply the method to study the organic content of atmospheric particles. Furthermore, the growth behaviour of the measured compounds was such that the O-TDMA and H-TDMA produce complementary information for each other when they are operated parallel.

| Experiments | GF | | | Independency | | Organic volume |
	AS+org	org	AS	factor ξ	S	fraction (DMPS)
Toluene, O$_3$ and DMB with	1.23	-	1.01	0.88	0.87	0.61
and without AS seed	-	1.37		-	0.87	1.00
Toluene, H$_2$O$_2$ and hv with	1.22		1.01	1.05	0.86	0.64
and without AS seed	-	1.30		-	0.86	1.00
Pure AS in the laboratory experiment	-	-	1.01	-	0.0-0.9	0.00

Table 1. An example of the O-TDMA 100 nm particle measurements in the smog chamber.

The working principle of the O-TDMA with an external aerosol treatment unit (i.e. reactivity organic TDMA, RO-TDMA; Figure 2) was also tested with secondary organic compounds in the EUPHORE (European Photoreactor) smog chamber in Valencia, Spain (Vaattovaara et al. 2004a; **Paper V**). Table 1 (Vaattovaara et al. 2004a) shows that 100 nm ammonium sulfate (AS) particles do not grow in subsaturated ethanol vapour but toluene oxidation products do grow. These results supported the application of the organic TDMA methods to the study of urban aerosol (e.g., Vaattovaara et al. 2001; Vaattovaara and Laaksonen 2005a; Tiitta et al. 2009). Furthermore, it was demonstrated that inorganics (i.e. AS) and secondary organics (toluene oxidation products) behave quite independently in the O-TDMA in the internally mixed particles (Table 1, Vaattovaara et al. 2004a). The interaction of ammonium sulfate and toluene oxidation products were studied in the

internally mixed particles by calculating the independency factor, ξ ,from the ZSR (Zdanovskii-Stokes-Robinson; Zdanovskii 1948; Stokes and Robinson 1966) method:

$$\xi = (GF^3_{mix} - GF^3_{inorg}) / [\varepsilon_o (GF^3_{org} - GF^3_{inorg})]. \tag{1}$$

The independency factor describes the change in solvent (i.e. ethanol) consumption for internally mixed particles. In the above equation, GF_{mix} is the growth factor of ammonium sulfate and toluene oxidation products, GF_{inorg} is growth factor of ammonium sulfate, ε_o is organic volume fraction calculated from DMPS (differential mobility particle sizes), and GF_{org} is growth factor of toluene oxidation products (see Vaattovaara et al. 2004a for more details). It is noteworthy that ξ should be close to 1 for mixtures where the solutes do not interact with each other, otherwise, the solutes do not behave independently (see e.g., Cruz and Pandis 2000; Hämeri et al. 2001). This independent behaviour should occur, for example, if one solute is insoluble (e.g., ammonium sulfate) and the other solute is soluble (e.g., toluene oxidation products) to a solvent a (e.g., ethanol). Thus, the ZSR method should be valid in the O-TDMA method and consequently the independency factor ξ should be close to 1. Importantly, the boreal forest analysis of Raatikainen et al. (2009) supports the observation that inorganics and organics behave quite independently in an ethanol TDMA.

The α-pinene ozonolysis experiments were also carried out in the smog chamber in order to study the relevancy of the organic TDMA methods in conditions representative of boreal forests (**Paper V**). Additionally, the smog chamber measurements were carried out in parallel with an H-TDMA (Vaattovaara et al. 2004a). Overall, the smog chamber results suggested that the organic TDMA could be useful to study organic content of atmospheric particles both in urban and rural environments, especially when used in parallel with an H-TDMA.

Additional test measurements were carried out with the O-TDMA (Figure 1) in the Kuopio aerosol laboratory. The ammonium bisulfate measurements for 100 nm particles were suprising. Even though ammonium bisulfate is insoluble in ethanol, the particles grew slightly (GF about 1.05) in subsaturated ethanol vapour (**Paper II**). The reason behind this behaviour was due to the high hygroscopicity of ammonium bisulfate (water from the particles production process) and from the reactivity of the acid with the alcohol (i.e. esterification).

The esterification phenomenon was further studied using a longer ethanol treatment time for the particles. A schematic diagram of this reactivity organic TDMA (RO-TDMA), is shown in figure 2 (**Paper II**). The RO-TDMA is otherwise similar to the O-TDMA expect that in the RO-TDMA the ethanol treatment time of the particles is regulated by the aerosol treatment unit situated between DMA-1 and DMA-2. The measurements indicated that the GFs changed when the ethanol treatment time of the acidic particles was increased. As a conclusion, time dependent auto-protonation acid-catalyzed esterification reactions took place during ethanol vapour treatment of ammonium bisulfate, citric acid, and tartaric acid (**Paper II**). From the view point of an H-TDMA, the treatment time effect on the measured particles also requires further study.

Additionally, the ethanol reactions observed in **Paper II** are important from the perspectives of atmospheric chemistry of alcohols (Grosjean 1997) and ethanol reactions with sulfuric acid in upper tropospheric conditions (Timonen and Leu 2005). From a human health perspective, an interesting aspect is also the effect of the ethanol vapour on the size of inhaled particles (depending on the particle composition).

In **Paper II**, the reaction observations also have a larger meaning related to an acid-catalyzed particle phase esterification reactions on the atmosphere. This also includes the formation sulfate esters which has recently been a relevant topic in the secondary organic aerosol (SOA) research

(e.g., Liggio and Li 2006; Ng et al. 2007; Surratt et al. 2007; **Paper V**). Other particle phase reactions observed include peroxyhemiacetal formation (Tobias and Ziemann 2000), polymerization (Jang and Kamens 2001; Kalberer et al. 2004), hemiacetal and acetal formation, hydration, and aldol condensation (Jang et al. 2002). A common feature of those reactions is an acid catalyst, which is regularly present in atmospheric conditions. A common name for these types of particle phase reactions is aging (e.g., Rudich et al. 2007). The aging was observed and discussed as a function of ultrafine particle size (with connected inorganic and organic chemistry) in the **Paper V**. As suggested already by Haagen-Smit (1952), the condensed phase chemical reactions may form products of low volatility. This might partially explain the very initial growth of new atmospheric nuclei (Zhang and Wexler 2002; Kulmala and Kerminen 2008; **Paper V**). On the other hand, aging can also produce semivolatile emissions from the particle phase (e.g., Robinson et al. 2007). In any case, because aging changes the composition and thus the properties of the particles, those reactions are relevant for climate and health.
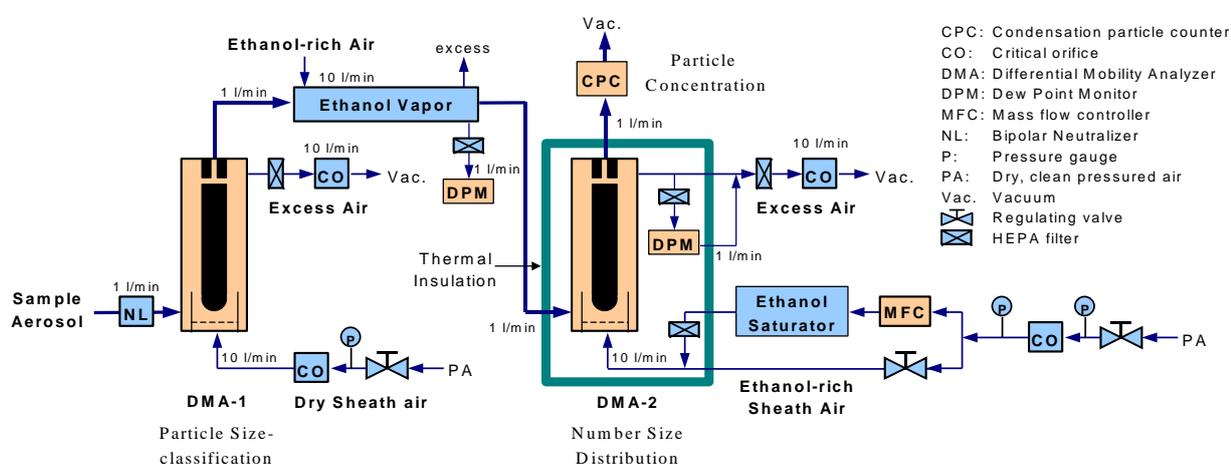
Figure 2. A schematic presentation of the RO-TDMA system.

As a summary, the development of the O-TDMA branched off into two directions: the system with the shortest possible ethanol treatment time of the particles (O-TDMA) and the system with ethanol treatment time regulation (RO-TDMA; **Paper II**).

Furthermore, I carried out different organic TDMA measurements for 20-150 nm particles at an urban background station in Melpitz, Germany during spring 2001; (RO-TDMA, Figure 2) and a rural forest station in Hyytiälä, Finland during autumn 2001 (O-TDMA, Figure 1, Boy et al. 2004). Figure 3 presents a photo of the RO-TDMA during a field campaign condition (Germany, spring 2001).

The published Hyytiälä 2001 results (Boy et al. 2004) indicated that the O-TDMA (Figure 1) is applicable in long lasting and intensive field experiments too, even though one of the first versions of the O-TDMA was not automated and continuous supervision was needed for operational and safety reasons during the measurements. The results also indicated that the O-TDMA gives additional information about the composition of 50 nm and 100 nm particles as a function of particle size and time compared to H-TDMA, demonstrating the power of the parallel usage of TDMAs in atmospheric measurements. The average growth factors of 100 nm particles in the O-

TDMA and H-TDMA showed (Boy et al. 2004) a diurnal variation with maxima during the daytime in the Hyytiälä forest (Finland, autumn 2001). After a review of different sampling and analytical methods and the TDMA measurements, we recognized a clear contribution of organic matter originating from the oxidation of terpenes from the local biosphere to the sampled aerosols.
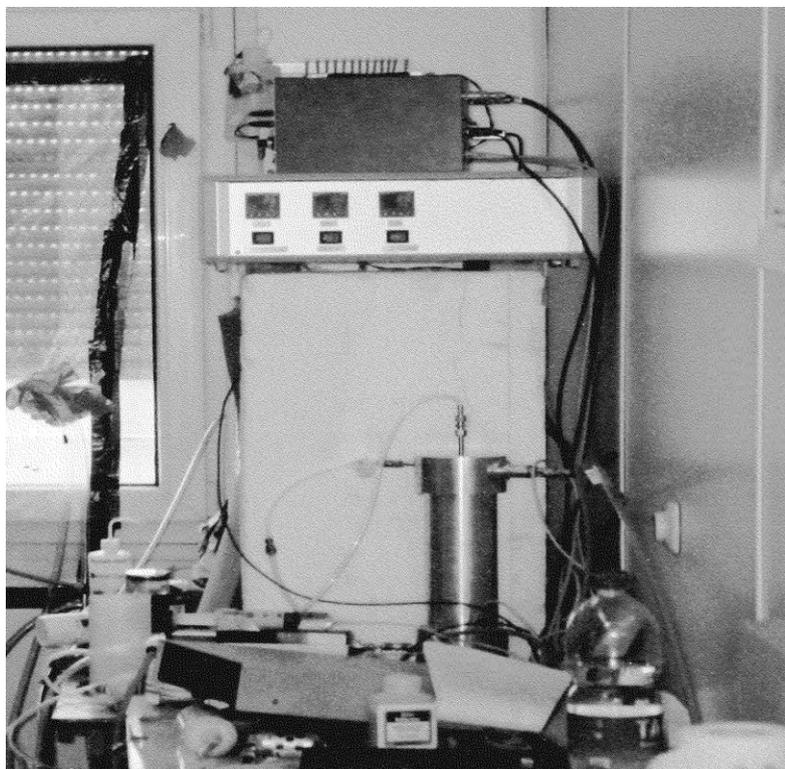
Figure 3. One of the first versions of the RO-TDMA under construction at the Melpitz field station.

Overall, the hard work and the success with the O-TDMA in laboratory, chamber and the first field measurements led to the development of the O-TDMA forward to the next generation product, the UFO-TDMA (ultrafine organic differential mobility analyzer; **Paper III**). Unfortunately, further development of the O-TDMA itself stopped for several years. During years 2002-2003, we had a while both O-TDMA and UFO-TDMA but they were never used in parallel because the H-DMPS (Laakso et al. 2004; Räsänen 2006), the H-TDMA (e.g., Anttila et al. 2009; Kivekäs et al. 2009) or the UFH-TDMA (Tiitta et al. 2009) were typically used instead of the O-TDMA. However, our aerosol research group has very recently built a new O-TDMA with a parallel H-TDMA unit following the guidelines of **Paper I** and **Paper III**. This system has recently been used in Pallas arctic cloud 2009 campaign. The next campaign will be Boston reaction chamber 2009 experiments. My plan is that this system will also be used in parallel with the UFO-TDMA in coming measurement campaigns. They would cover together a larger particle size range which could also enhance the possibility of combining results with a wider range of measurement instruments (e.g., an aerosol mass spectrometer; see Raatikainen et al. 2009). Suprisingly, both the O-TDMA and the UFO-TDMA instruments are probably still unique.

3 The UFO-TDMA: Instrument development and laboratory studies

The first version of the UFO-TDMA (i.e. ultrafine organic tandem differential mobility analyzer; similar to Figure 1, **Paper III**; Unofficially, UFO also means unidentified flying object, as in a particle in air with an unknown composition) was constructed in order to study the composition of atmospheric particles in the nucleation mode (d < 20 nm) and at the lower end of Aitken mode (d < 50 nm) sizes. The first version of the UFO-TDMA was built as a result of the success and the experiences in the construction of, operation of and transportation of the O-TDMA and RO-TDMA in different environments during years 2000 and 2001.

The UFO-TDMA (**Paper III**) was built following guidelines of the O-TDMA (Figure 1; **Paper I**) system but with some differences: Shorter DMAs (Hauke type, center rod length 11 cm; Winklmayr et al., 1991) with 1:10 aerosol (1 lpm) to sheath (10 lpm) flow ratios and high voltage power supplies with lower maximum voltages (1.25 kV for the first DMA and 2 kV for the second DMA) is used in the UFO-TDMA. In addition to a high sheath air flow rate, all line lengths were minimized in the whole system in order to decrease diffusion losses of the ultrafine particles. A high sheath flow reduces the diffusional broadening of the transfer function when the particles go through the DMA (Stolzenburg 1988). This is a useful feature if the size distribution of the sampled particles is narrow or if chemical reactions are needed to avoid using a lower solvent (e.g. ethanol) treatment time (i.e. the higher total flow, the shorter solvent treatment time). In the UFO-TDMA, the ethanol saturator is only used in the sheath line and thus ethanol treatment time is minimized to about 1 s in order to avoid chemical reactions. The system is called RUFO-TDMA (reactivity ultrafine organic tandem differential mobility analyzer) if a longer ethanol treatment time is used (e.g., Hyytiälä 2003 and 2009 campaigns). In the UFO-TDMA, ethanol-rich sheath air is produced by bubbling clean and dry air through liquid ethanol, which is heated slightly over room temperature in a temperature controlled water bath. Furthermore, in order to avoid temperature differences in the flows of the second DMA and to keep the temperature constant even in quite extreme temperature conditions, the system temperature (typically ~25 $^{\circ}$C) is controlled by an effective water bath capable of heating/cooling a water circulation covering the second DMA in the thermal insulated box. Ethanol friendly SolVent (Gelman Sciences) filters are used instead of HEPA filters in the ethanol vapour lines, because HEPA filters may be occasionally clogged when ethanol vapour flow continuously into the filter. The saturation ratio of the ethanol vapour is determined using a similar dew point meter as in the O-TDMA but with a corrosive durable mirror. The saturation ratio can be changed stepwise by automatically selecting values between 0.0-0.9 and thus studying the growth behaviour of atmospheric particles as function of saturation ratio (see **Paper V**). The temperature difference between the saturator and the condenser in the CPC (condensation particle counter) was maximized to 25 K (condensation particle counter, TSI 3010; Quant et al. 1992) to detect particles down to 6 nm (Mertes et al. 1995). Additionally, the detection efficiency of TSI 3010 is quite untroubled by ethanol because ethanol is soluble to butanol. This is not the case with water and butanol in an H-TDMA because water solubility to butanol is quite limited. In contrast, a water based CPC should not pose a problem in an O-TDMA, because ethanol and water are mutually soluble. Thus, the continuous detection of nucleation mode size particles should be possible using a water or butanol based CPC in the UFO-TDMA.

The largest measurable particle diameter is about 85 nm with this configuration. In practice, the selection of six different sizes for consequent measurements makes it possible to compare the

content of several sized particles between 6-60 nm. The measurement time per one data point is usually 3-4 minutes, giving an adequate time resolution for the changes in the particle composition. Due to relatively low particle losses in the whole instrument and high sensitivity for the nucleation mode size particles, the UFO-TDMA is an effective near online tool for the composition of particles in the clean environments too.

Due to the comparably low voltages used in the short DMAs, sparks do not easily ignite the ethanol vapour. Thus, the diurnal field measurements are quite safe. Consequently, the usage of the UFO-TDMA is possible without continuous supervision, when an automatic ethanol refill system is used with a large enough ethanol storage taking care of the stable ethanol level in the water bath warmed bottle of very pure bubbling ethanol. Typically, diurnal ethanol consumption has been about 2.2 liters. Figure 4 shows a quite recent photo of the UFO-TDMA with the automatic ethanol refill system including insulated filling and evaporation lines. The UFO-TDMA was fixed to the Swedish icebreaker Oden in order to study the ultrafine particle composition during the summer 2008 Arctic Ocean expedition (Arctic Summer Cloud Ocean Study, ASCOS).

Figure 4. A ship version of the UFO-TDMA ready for an expedition.

In the laboratory, the UFO-TDMA measurements were carried out with several atmospherically relevant inorganic and organic compounds in 6-50 nm sizes. As a result, a new method for detecting the presence of organic fraction in nucleation mode sized particles was discovered (**Paper III**). In regards to the detection of organic fraction, our laboratory measurements indicated that the usefulness of the UFO-TDMA in field experiments would arise especially from the fact that atmospherically the most relevant inorganic compounds do not grow in subsaturated ethanol vapour, when particle size is 10 nm in diameter and saturation ratio is about 86% or below. Furthermore, when internally mixed particles composed of ammonium bisulfate and sulfuric acid with sulfuric acid mass fraction up to 33%, they show no growth at 85% saturation ratio. In contrast, 10 nm particles composed of various oxidized organic compounds fof atmospheric

relevance are able to grow in those conditions. Thus, those results led to make the final decision that the type of construction shown in Figure 1 will also be used in the UFO-TDMA, because it is not necessary to lift the saturation ratio over 90% using an aerosol treatment unit (see Figure 2). With this arrangement the ethanol treatment time of aerosols is low and chemical reactions are minimized (**Paper II**). It is also possible to detect the organic fraction in higher sizes when lower saturation ratios are used. Thus, this information is useful also for an O-TDMA with the longer DMAs.

Furthermore, the laboratory measured various organic model compounds (citric acid, tartaric acid and benzoic acid) exhibited clear growth behaviour as a function of size, when the particle size is 10-50 nm or even below that. The growth behaviour was smooth and the GF increases with increasing particle size (**Paper III**). Earlier, Hämeri et al. (2000) were first to observe size dependent growth behaviour of ultrafine particles with UFH-TDMA (ultrafine hygroscopicity TDMA). The theoretical EGF (ethanol growth factor) calculations (**Paper III**) were qualitatively in a good agreement with the measured growth behaviour but the theoretical Kelvin effect (i.e. the effect of curvature on equilibrium vapor pressure; Thompson 1871) was not enough to alone explain the observed differences in the GFs in the smallest sizes. Biskos et al. (2006a) made similar observations and calculations using an UFH-TDMA for ammonium sulfate. The difference in the calculations of Biskos et al. (2006a) and **Paper III** is that we had to use the density of solvent instead of the density of the solution. In **Paper III** we discussed that a higher Laplace pressure (i.e. the difference in pressure between the inside and outside of a droplet due to surface tension) in the smallest particles could be an additional reason to the change of GF, in addition to Kelvin effect. Interestingly, Biskos et al. (2006b) physically explained the nanosize effect on the deliquesence and the efflorescence of sodium chloride particles by the free energy balance of NaCl increasingly favouring smaller particles (i.e. those without solvent). Importantly, Centrone et al. (2008) recently presented that the "wetting" behaviour on surfaces with nanostructuring on a molecular scale are dominated by steric constraints and cannot be explained with mesoscopic theories. Clearly, these effects are also important in discussing the growth behaviour of the smallest ultrafine particles.

Importantly, the analysis principles of the UFO-TDMA method have been applied in several campaigns. So far, I have successfully carried out UFO-TDMA measurements in total of 19 field or chamber campaigns: Mace Head summer marine coast 2002 (Ireland, **Paper IV**); Hyytiälä spring boreal forest 2003 (Finland, Vaattovaara et al. 2004b and 2005b; Petäjä et al. 2005; Laaksonen et al. 2008a; **Paper V**); Po Valley spring urban pollution 2004 (Italy, Vaattovaara and Laaksonen 2005a); Hyytiälä spring boreal forest 2005 (Finland, Raatikainen et al. 2009); Kuopio summer traffic 2005 (Finland, Tiitta et al. 2009), Mace Head summer marine coast 2006 (Ireland, Vaattovaara et al. 2007), Hyytiälä spring boreal forest 2007 (**Paper V**), Kuopio summer plant chamber 2007 (Finland, **Paper V**), Puijo tower autumn cloud 2007 (Finland, unpublished), Kuopio autumn plant chamber 2008 (unpublished; see Hao et al. 2009), Kuopio Baltic Sea winter bubble bursting chamber 2008 (Finland, unpublished), Po Valley spring urban pollution 2008 (unpublished), Kuopio spring plant chamber 2008 (unpublished), Atlantic Ocean summer 2008 (icebreaker Oden, unpublished), Arctic Ocean summer 2008 (icebreaker Oden, Vaattovaara et al. 2009 and Paatero et al. 2009), Arctic Ocean summer bubble bursting 2008 (icebreaker Oden, unpublished), Kuopio winter SO_2 plant chamber 2009 (unpublished), Po Valley summer urban pollution 2009 (unpublished), and Arctic Ocean summer bubble bursting 2009 (unpublished). The next planned measurement campaign for the UFO-TDMA is Kuopio winter plant chamber 2009-2010.

The data analysis development of the UFO-TDMA is also one very important issue. So far, the basic principle for the detection of the presence of an organic fraction has been introduced (**Paper III**) and applied with a minimum organic volume fraction (OVF) estimate in marine (e.g., **Paper IV** OVF minimum about 10-50% for clean nucleation mode particles), forest (e.g., **Paper V** OVF

minimum over 95% for the cleanest nucleation mode particles), urban (e.g., Tiitta et al. 2009 OVF 70-90% for road side nucleation mode particles) and arctic (e.g., Vaattovaara et al. 2009 OVF minimum 40-70% for clean nucleation mode size particles) environments. Even though the UFO-TDMA data library is quite extensive from different field measurement environments and from chamber measurements, especially additional experimental knowledge about the effects of different functional groups on the growth factors would be useful. This would aid to interpret in more detail the atmospheric UFO-TDMA measurement, especially, when aging reactions occurring as a function of time are discussed in nucleation mode and Aitken mode particles. It is also partly possible to gather this kind of information for Aitken mode particles when the UFO-TDMA 50 nm is compared with aerosol spectrometer data (see Raatikainen et al. 2009). The development of analysis of the reactivity UFO-TDMA (i.e. RUFO-TDMA) could also be useful for nucleation mode particle studies. Useful experimental data would also be additional new particle formation measurements with atmospherically relevant mixtures of inorganics and versatile organics (i.e. with various functional groups), with and without an acid catalyst.

The other techniques that can be used for obtaining information on the chemical composition of particles smaller than 20 nm include UFH-TDMA (Hämeri et al. 2000), UFV-TDMA (ultrafine volatility TDMA; e.g., Ehn et al. 2007) TEM (transition electron microscopy; Mäkelä et al. 2002), PHA-UCPC (pulse height analyzer ultrafine condensation particle counter; O'Dowd et al. 2002), CPCB (condensation particle counter battery; Kulmala et al. 2007) and TDCIMS (thermal desorption chemical ionization mass spectrometer; Smith et al. 2004). These methods are naturally most effective when they are used in parallel or in combination. This results in information from a new perspective. At the moment, such combinations published in the literature are from different VH-TDMAs (volatility/hygroscopicity tandem differential mobility analyzers; Johnson et al. 2005; Sakurai et al. 2005). Importantly, the UFO-TDMA can produce additional information about an organic fraction of nucleation mode particles compared to those previously mentioned methods. In the publications include to this thesis, the UFO-TDMA data is used with PHA-UCPC data (**Paper IV**) and successfully combined with UFH-TDMA data and organic and inorganic gas phase measurements data (**Paper V**). As regards to three UF-TDMAs (i.e. UF-TDMA battery), a combination of them (i.e. the UFO-TDMA, the UFH-TDMA and the UFV-TDMA) is a useful tool package for atmospheric particle composition analysis too, and to estimate an organic fraction and properties in nucleation and Aitken mode size particles (Tiitta et al. 2009). The UF-TDMA battery can also diversify the analysis of an aerosol mass spectrometer (Raatikainen et al. 2009). An interesting combination for the analysis of nucleation mode particle compositions could also be the CPC battery (CPCB) and the UF-TDMA battery (UF-TDMAB). Especially, the data combination of CPC battery with the UFO-TDMA could be useful because they use different organic vapours (i.e. butanol and ethanol, respectively).

A next step in the UFO-TDMA field version development could be a closed loop arrangement (e.g., Jokinen and Mäkelä 1997) for the DMAs. However, careful tests with ethanol vapour are necessary to make sure that a critical orifice, a pump, a drier, a buffer, a heat exchanger and a filter are appropriate for the UFO-TDMA closed loop arrangement. Because a compressor is not always available or possible to setup in different measurement locations (e.g. certain remote locations, airplanes or helicopters), one useful advantage of a successful closed loop system would be in field conditions that a separate compressor is not needed for dry and clean sheath air production then. A compressor is not always available or possible to setup in measurement locations (e.g., certain remote locations, airplanes or helicopters).

Furthermore, several other practical development steps would be useful with the UFO-TDMA: a CPC with the capability to measure particles down to 1-3 nm, nano-DMAs (e.g., Chen et al. 1998),

automated flow checks, an external power source for electrical brakes, a heating/cooling system with low electricity consumption, a newly TDMA data inversion algorithm (e.g., Gysel et al. 2009) with automatic measurement data figures saving to aid data handling, and a small space demanding ethanol/butanol exhaust trap, for example. One useful step would also be the selection of another organic solvent applying the early mentioned advantage list of ethanol. However, the solvent solubility properties should be clearly different than ethanol or water has.

4 Composition of freshly nucleated particles in a marine environment

The first instrumental marine nanometer-sized particle observations were made on the Scottish coast of Atlantic at the end of 19th century (Aitken 1897). After the end of 19th century, newly-formed nanometer-sized particles have been observed at coastal and remote marine environments worldwide (see references within Kulmala et al. 2004). Importantly, such nanoparticles can grow into larger sizes (O'Dowd et al. 2001), generally being able to scatter incoming radiation and contribute to direct and indirect (via clouds) cooling effects to the Earth's radiation budget (Slingo et al. 1990). Especially, marine coastal nucleation events are frequently observed (e.g., O'Dowd and Hoffmann 2005) and the size and composition of newly-formed particles have been intensively studied on the west coast of Ireland (see O' Connor et al. 2008; Pollak and Murphy 1952; **Paper IV**) but also to a lesser extent in other coastal locations: around eastern Atlantic Scottish (O'Dowd et al. 1996), English, French (Paugam 1975) and Portuguese (Weise et al., 1998) coasts and on Tenerife's (Raes et al. 1997) coastline. Other locations include on easily continental or a ship pollution-affected Baltic Sea coasts of Lithuania (Zeromskiene et al. 2000; Ulevicius et al. 2002) and Finland (Hyvärinen et al. 2008), on an Arctic Ocean coast (e.g., Ström et al. 2003), in North-America at Alaska (Ferek et al. 1995) and California (Wen et al. 2006) coasts, in East-Asia at Korea coast (Lee et al. 2008), and in southern hemisphere at Australian (e.g., Bigg and Turvey 1978; Johnson et al. 2005; Mejía and Morawska 2008; Modini et al. 2009) and Antarctica coasts (e.g., Jaenicke et al. 1992; Gras 1993; O'Dowd et al. 1997; Yoon et al. 2008). On the other hand, the observations of nucleation events have been much rare on open oceans (e.g., Covert et al. 1992; Wiedensohler et al. 1996; see Katoshevski et al. 1999). A common feature of the coastal and open water nucleation events is that they have occurred on highly biologically active waters (**Paper IV**; Figure 5). A potential source for open ocean particle production is highly biologically active warm water coral reefs (Bigg and Turvey 1978; Modini et al. 2009), located especially on tropical and subtropical marine areas. It is also important to note that the surface area of biologically active surface waters has expanded on the polar region during the last decades due to climate warming and consequent ice melting (see e.g., Arrigo et al. 2008). Interestingly, the marine ice regions are also known to be able to produce newly-formed particles (e.g., Covert et al. 1996).
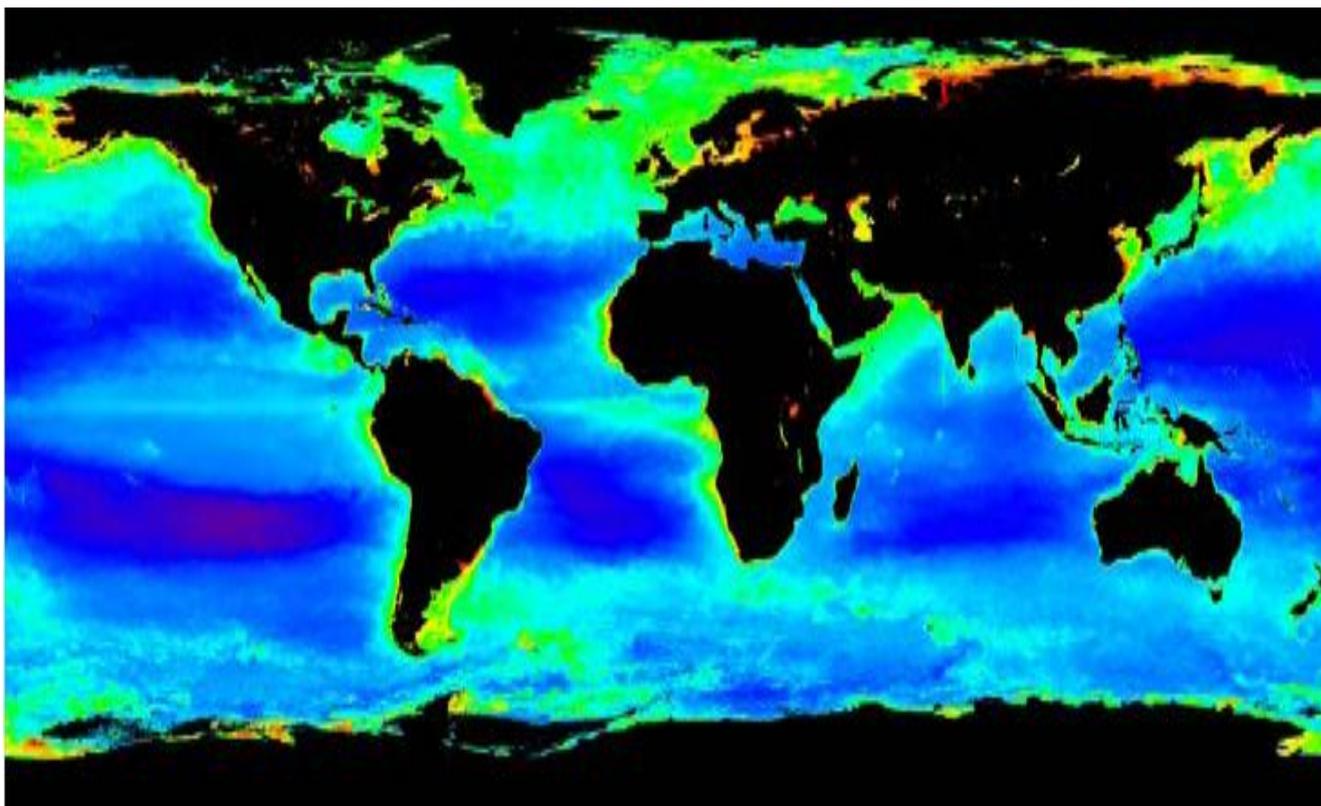
Figure 5. An annual average chrolofyll-α concentration of the surface waters (order from high to low value: red, yellow, green, blue, and purple; **Paper IV**).

Paper IV brought new insights to the coastal and marine particle formation, growth, transformation, and properties in the form of marine and coastal secondary organic aerosols (see and compare the **Paper IV** (2006), the papers of Blanchard 1964 (sea to air transport of surface active organic material), Charlson et al. 1987 (CLAW hypothesis with DMS oxidized to sulfate), Novakov and Penner 1993 (organic anthropogenic contribution on marine cloud condensation nuclei), O'Dowd et al. 2004 (primary origin of marine organic aerosol), O'Dowd and Hoffmann 2005 (review of coastal particle formation) and O'Dowd and de Leeuw 2007 (review of the knowledge of the secondary and primary marine particle formation). In **Paper IV**, the overall results of the ultrafine organic tandem differential mobility analyzer and the pulse height analyzer measurements indicated that coastal and marine nucleation mode particles include a remarkable fraction of secondary organic products, beside iodine oxides, which are though likely to be responsible for the nucleation at Mace Head, the North-East Atlantic coast. An overview of the marine particle formation and growth are shown in Figure 6 (**Paper IV**), including both primary and secondary marine particle production in biologically active waters. Isoprene was suggested (**Paper IV**) as a probable secondary organic precursor compound in those processes, as an example of reactive alkenes. Earlier, Bonsang et al. (1992) already showed a proof of marine production of isoprene but suggested that isoprene would be a minor compound in the gas phase and could be a useful tracer for marine emission of gaseous compounds. Recently, the role of marine isoprene is a hot topic in the area of global marine particle research (**Paper IV**; Meskhidze and Nenes 2006; Wingenter 2007; Meskhidze and Nenes 2007; O'Dowd and de Leeuw 2007; Arnold et al. 2009; Gantt et al. 2009). The finding of particle phase importance of marine secondary organics (**Paper IV**) is currently supported by the indirect composition measurements of marine newly-formed

particles (Vaattovaara et al. 2007; Modini et al. 2009) and chemical aerosol flux measurements (Ceburnis et al. 2008), for example. Potential compounds for the precursors of the secondary organic contribution to particle phase could be atmospherically very reactive marine biota biosynthesized alkenes (**Paper IV**) such as isoprene (e.g., **Paper IV**, Gantt et al. 2009), chlorobenzenes (Colomb et al. 2008) and monoterpenes (Yassaa et al. 2009), and their derivates. Furthermore, the organic derivates of DMS (dimethyl sulfide; e.g., Kettle and Andreae 2000) such as MSA (methyl sulfonic acid; e.g., Fitzgerald 1991; Berresheim et al. 2002) and methanesulfonate (e.g., Bardouki et al. 2003), dimethyl- and diethyl amines (Facchini et al. 2008) and their derivates are potential secondary organic compounds in marine particle phase.

Paper IV also concluded that the marine biota driven secondary organic contributions to marine and coastal particle formation and composition can be anticipated in all biologically active oceans and fresh-water areas around the world. Thus, secondary organics may also be significant to global radiative budget, atmosphere-biosphere feedbacks, and climate change. Naturally, a primary marine production is clearly dominating the properties of the particles on the waters which have a low biological activity due the location, the season or the moment, and where an anthropogenic effect is low or wind speed is adequate for an efficient bubble bursting. However, marine secondary organics can change the physical and chemical properties of the primary particles in biologically active marine areas.
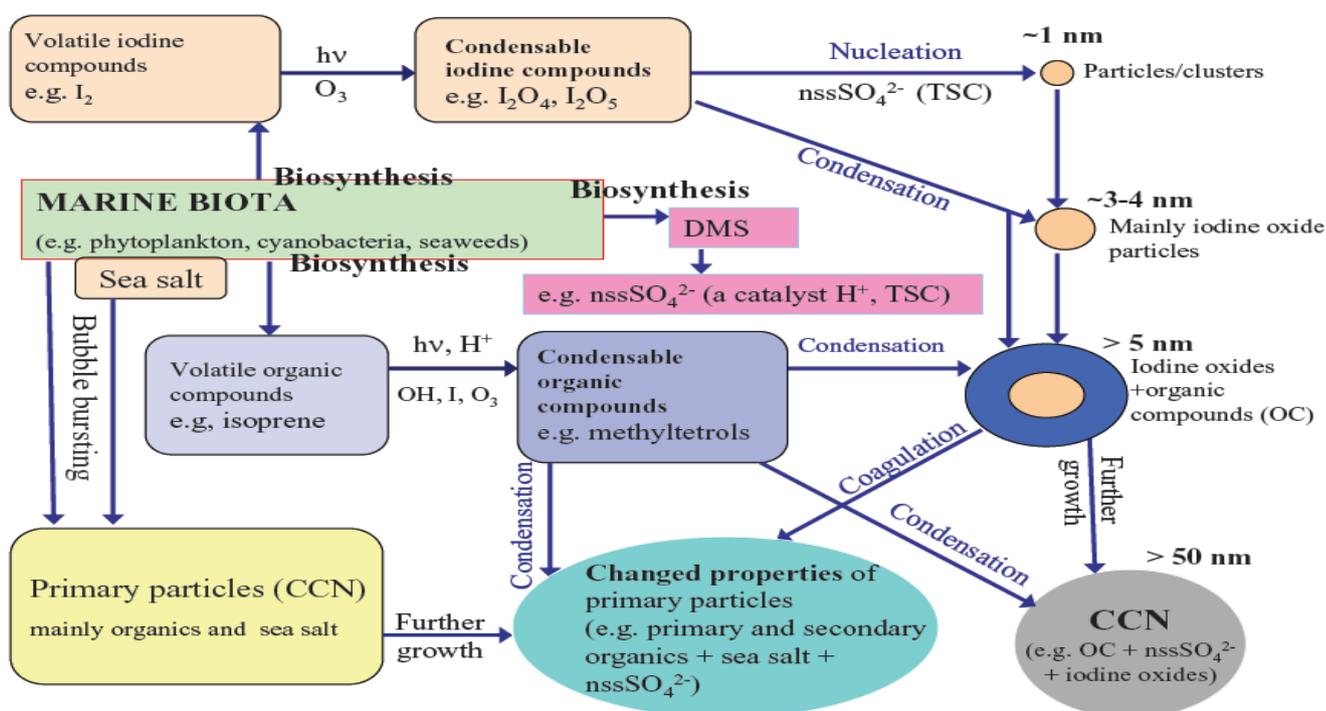

Figure 6. An overview of the marine particle formation and growth.

As regards to secondary particles formation in Figure 6, it is important to note that kelp forests, which produce precursors for atmospheric iodine compounds, are found throughout the world in shallow open coastal waters (Sentelices 2007) extending to both the Arctic (e.g. Lund 1959) and Antarctic Circles (e.g., Smith and Bayliss-Smith 1998), grow in various climate conditions and on the various levels from the sea surface (Lüning 1990; Steneck et al. 2002). Thus, the importance of iodine containing molecules, radicals (see O'Dowd and Hoffmann 2005) and ions (Küpper at al. 2008) in particle formation and atmospheric chemistry would be different in different coastal environments. Additionally, the iodine emissions seem to be dependent on the season and the time of the day (Seitz 2009) and have a complex time signature with short and strong bursts (Dixneuf et al. 2009). At Mace Head, iodine is able to regularly participate in nucleation (O'Dowd and Hoffmann 2005) in addition to participating in atmospheric radical initiated oxidation reactions (e.g., **Paper IV**) whereas in conditions where kelps grow clearly below sea surface, their contribution to atmospheric reactions could be someway limited. However, a contribution would still be possible in local atmospheric chemistry. Over the open ocean, the amount of iodine species is expected to be lower than on the coasts (Seitz 2009) and thus the role of iodine would also be limited in the atmospheric chemistry of the open ocean. For those reasons, the role of iodine compounds should be limited or removed from Figure 6 in those limited cases. Consequently, the role of different organics and sulfur compounds should be more dominant then, and the ratio of different organic and inorganic biogenic compounds mainly depends on the amount of different micro- and macroalgae and corals in each marine location. Furthermore, the role of halogens other than iodine and the reactions between organics and sulfur compounds (see e.g., **Paper V**) are also needed to take into account when considering the local marine atmospheric chemistry.

Overall, the marine ultrafine particle composition research around the world has not been so intensive and there has been an absence of state-of-art measurement techniques. Therefore, the knowledge about the composition and dominating precursor gases of coastal and marine ultrafine particles, and thus about marine atmospheric chemistry, a role of anthropogenic compounds, and atmospheric-marine connections, are mainly poor. This is especially true from the viewpoint of secondary organic compounds in ultrafine particles. Finding new growing locations and species of subsurface and surface micro- and macroalgae and corals, and understanding of life and the emissions of different algae and corals are also an important part to solve these issues.

5 Composition of freshly nucleated particles in a forest environment

The geographical extent of the tropical, temperate and boreal forests is about 30% of the Earth's land surface (Bonan 2008). Those forests are located around the world in different climate zones (see Köppen 1936; Peel et al. 2007) effecting widely on atmospheric composition. Boreal forests solely cover one third of the forests extent and are one of the largest vegetation environments. The boreal forests form a circumpolar band throughout the continents of the northern hemisphere (Figure 7), with a high potential to affect climate processes (e.g., Tunved et al. 2006; Spracklen et al. 2008; Bonan 2008).

An effect of forests was already noticed about 500 years ago by Leonardo da Vinci. He discussed the role of trees in the formation of atmospheric bluish haze (F.W. Went 1960). Da Vinci thought that the released water vapour from trees would be the reason for the observations. Later in the

1960s, F.W. Went (1960) discussed a similar blue haze phenomenon over forests and demonstrated blue haze formation (i.e. ultrafine particles) by adding crushed pine or fir needles to a jar with dilute ozone. He suggested biogenic emissions being terpenes and removed by ozone reactions with double bonds, applying to forest environment the demonstration of Haagen-Smit (1952) where oxidation of olefin with ozone produced a blue haze. On the other hand, F.W. Went also had the possibility to use the information from the light and gas demonstrations of John Tyndall (e.g., 1869, see Gentry 1997). Tyndall correctly deduced that the formed blue haze and its colour change in the presence of light as a function of time was related to particle formation and growth. The forest related work of Went (1960) was later supported by terpene chamber experiments of Westberg and Rassmussen (1972) and Schuetzle and Rassmussen (1978), for example, about three decades ago. The terpene chemistry chamber experiments during following 15 years (e.g. Hatakeyama et al. 1989; Hatakeyama et al. 1991; Grosjean et al. 1992) lead then to a biogenic SOA (secondary organic aerosol) yield prediction model from the equilibrium of the oxidation products of the precursors between the gas and the particle phases (Pankow 1994).

In chamber conditions, the terpenes research intensively concentrated on the gas phase chemistry and particle formation, growth, and composition with selected injected biogenic hydrocarbons (e.g. Odum et al. 1996; Hoffmann et al. 1997; Hoffmann et al. 1998; Christoffersen et al. 1998; Jang and Kamens 1999; Noziére et al. 1999; Bonn and Moortgat 2002; Bonn and Moortgat 2003; **Paper V**) during following ten years. However, a problem in the chamber experiments is to reach atmospherically relevant conditions and thus the atmospheric SOA predictions cannot be simply extrapolated from smog chamber experiments. Recently, direct tree emission oxidation experiments have also been carried out (e.g., VanReken et al. 2006; Mentel et al. 2009; **Paper V**; Hao et al. 2009) in order to better demonstrate real forest emissions, in addition to selected injected hydrocarbons (e.g., Burkholder et al. 2007). Additionally, the particle phase transformation observations during the last ten years (see e.g., Kroll and Seinfeld 2008 for a review; **Paper II**; **Paper V**) have complicated the SOA yield predictions as well as the interpretation of the particle composition and properties (see e.g., Czoschke et al. 2003; Barsanti and Pankow 2004).

Very importantly, the new particle formation has also been studied in atmospheric forest conditions during the last fifteen years: in European coniferous forests (e.g., Mäkelä et al. 1997; Kavouras et al 1999; Held et al. 2004; Vehkamäki et al. 2004; **Paper V**), in European mixed coniferous and deciduous forest (Tunved et al. 2003), in European deciduous forest (Tunved et al. 2003), in European eucalypt forest (Kavouras et al. 1998), in European arctic hill region forest (Lihavainen et al. 2003), in European wetland forest (Svenningsson et al. 2008), in North-American coniferous forests (Marti et al. 1997; Leaitch et al. 1999; Lunden 2006), in South-American rain forest (Rissler et al. 2006), in Australian eucalypt forest (Suni et al. 2008; Ristovski et al. 2009), and in Asian mixed coniferous and deciduous forests (Dal Maso et al. 2008). Additionally, European aquatic kelp forests are known to produce a high amount of new nanometer-sized particles (e.g., O'Connor et al. 2008). Finally, Asian aquatic mangrove forests (Chatterjee et al. 2006) and African savanna forests (Laakso et al. 2008) have a high potential to contribute to new particle formation.

However, the mechanisms of the nanoscale particle formation have been a big question (e.g., Kulmala and Kerminen 2008) due to the difficulties of experimentally studying the nanometer-sized particles. As a result of the pioneering works of Tyndall (1869) and Went (1960), solar radiation and terpenes were known to be important factors for particles formation, when the first new particle formations in a clean forest environment were observed in nanometer sizes about 15 years ago (see Mäkelä et al. 1997). The presence of photo-oxidation products from terpenes in newly-formed Aitken mode particles of forest environments were also experimentally confirmed (Kavouras et al. 1998; Kavouras et al. 1999). However, a close connection between sulfuric acid and particle

formation at clean atmospheric conditions observed by Weber et al. (1997) and unknown mass in the analyzed atmospheric particles have given a reason to discuss the relative roles of terpenes and sulfur compounds (e.g., Leaitch et al. 1999; Hämeri et al. 2001; Jansson et al. 2001; Held et al. 2004; Lunden et al. 2006; **Paper V**) in the formation and growth of ultrafine particles in the forest environments.

New particles are known to be frequently formed in boreal forests (e.g., Mäkelä et al. 1997; Kulmala et al. 2004; Dal Maso et al. 2008) and this have provided an opportunity to study the presence of biogenic secondary organic aerosols and sulfur compounds in situ during nucleation event days. The first experimental hint of organics in the nucleation mode size particles of the boreal forest was found in Hyytiälä, Finland (O'Dowd et al. 2002) while the forest was known to emit numerous volatile and semivolatile organic gases such as various monoterpenes (Jansson et al. 2001; Spanke et al. 2001) and the presence of their oxidation product in gas and particle phase was detected (Spanke et al. 2001). Diurnal hygroscopic behaviour of those particles was also detected then (Hämeri et al. 2001).

Substantial progress in the understanding of the boreal forest particle formation occurred as a result of the spring 2003 intensive field campaign in Hyytiälä with the state-of-art gas and particle phase instrumentation. The concentration of monoterpene emissions (Tarvainen et al. 2006), concentrations (Sellegri et al. 2006) and their oxidation products (Sellegri et al. 2006) proved the importance of terpenes photo-oxidation products in the forest atmosphere. Additionally, the "blue haze" region particle phase measurements in over 50 nm size confirmed (Allen et al. 2006; Cavalli et al. 2006) the remarkable presence of biogenic secondary organics during nucleation event days. However, a more detailed study of the newly-formed particles was not possible with those methods due to time and size resolution limitations. Finally, the UFO-TDMA related experimental work by Laaksonen et al. (2008a) connected the Aitken mode and nucleation mode composition changes. Consequently, they found that a key role of monoterpenes oxidation products (MTOP) in the composition of nucleation mode particles during the nucleation events. During the same campaign, the parallel data of the UFO-TDMA and UFH-TDMA measurements were in agreement with the MTOP finding (**Paper V**). Additionally, the UFO-TDMA measurements **(Paper V)** indicated the remarkable organic fraction with an estimated fraction of over 95% during the clean nucleation events.

On the other hand, the high time resolution gas phase sulfuric acid measurements (Boy et al. 2005) during the same campaign had shown that sulfuric acid molecules have a minor contribution to the particle composition especially when they have grown more than a few nanometers. However, the nucleation analysis of Sihto et al. (2006) showed that sulfuric acid molecules with ammonia could play an important role in the nucleation process. Both of those observations are supported in **Paper V**: Firstly, the role of the sulfur compounds was found to be minor in the nucleation mode particle composition, especially in clean cases. Secondly, the sulfuric acid was found to be necessary for the nucleation event (i.e. if the sulfuric acid number concentration dropped to 10^5 cm^{-3}, the nucleation did not occur or it stopped). This refers to the importance of sulfuric acid especially in the first steps of the nucleation. Overall, **Paper V** proves the dominating role of secondary organic compounds.
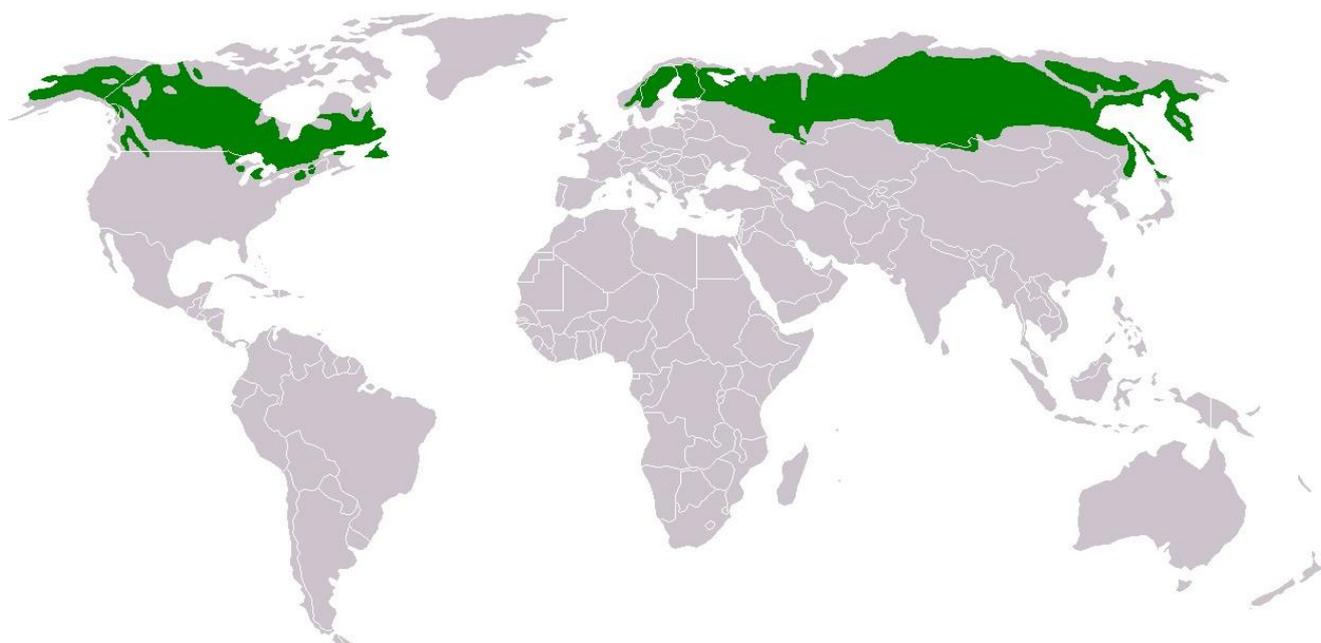
Figure 7. The world's boreal forest region is shown in dark green (Free Software Foundation, Inc).

In **Paper V,** the UFO-TDMA and UFH-TDMA data analysis results also showed a clear anthropogenic SO_2 and NO_x levels influence on the nucleation and Aitken mode particle composition during the new particle formation events in the Hyytiälä boreal forest. Petäjä et al. (2005) also reported an SO_2 effect on the Aitken mode particle composition. An anthropogenic effect on particle formation has also been studied in a North-American coniferous forest environment by Marti et al. (1997). They concluded that terpenoid compounds may have contributed to new particle formation during the day when sulfate particle production was suppressed. However, the exact nucleation mode results have been lacking during the nucleation events. **Paper V** agrees with the Marti et al. (1997) conclusion about the anthropogenic effect and shows that the SO_2/MTOP and NO_x/MTOP (monoterpene oxidation products) ratios very strongly explain the variation in the nucleation mode particle composition during clean and pollution-affected events.

The forest environment results of **Paper V** also support the recent findings about the presence of organic sulfur compounds and suggestions about a novel SO_2 oxidation pathway (Berndt et al. 2007 and 2008; Laaksonen et al. 2008b), combining the findings also to the particles formation, composition, transformation and properties in various boreal forest conditions. The results of **Paper V** also bring new insights into organic and sulfur chemistry, suggesting the importance of nitrogen chemistry in the reactions chains. During the cleanest events, MTOP strongly explain the time behaviour of the 10-nm particle composition with an estimated organic fraction of over 95%. Lunden et al. (2006) suggested in a North-American coniferous forest environment that a significant portion of the material responsible for the observed particle growth is due to oxidation products of naturally emitted very reactive organic compounds.

Additionally, the comparison of 6-50 nm measurements in **Paper V** reveals that the composition is different in nucleation and Aitken mode sizes, supporting the recent observations about particle

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phase aging as a function of time (e.g., Rudich et al. 2007), when the particles increase in size. Thus, the aging has an important effect on the composition of the particles and potential cloud condensation nuclei and thus on climatically important issues.

6 Review of papers

The papers included in this thesis deal with the development and application of a novel method to study and understand the formation, growth, transformation, and content of ultrafine particles to laboratory and natural environments.

Paper I introduces a novel tandem differential mobility analyzer with organic vapour treatment of aerosol particles. The instrument is called an organic tandem differential mobility analyzer (O-TDMA). The chosen organic vapour was ethanol. The growth curves of the particles were measured and compared as a function of saturation ratio in both ethanol vapour and in water vapour. The results showed that the working principles of the O-TDMA are operational. The results also showed that O-TDMA may be useful in atmospheric particle organic composition studies, especially, when operated parallel with a hygroscopicity TDMA.

Paper II presents time dependent growth behaviour of acid aerosol in ethanol vapour with an O-TDMA, called RO-TDMA. Time dependence of the change in the particle size due to interaction with ethanol vapour was determined. The results showed that certain types of organic and inorganic acidic compounds can react with ethanol undergoing auto-protonation catalyzed esterification. Further studies will solve if this method can be used for the detection of an acidic fraction in atmospheric conditions. The observations also have a larger meaning in atmospheric acid-catalyzed particle phase aging reactions which occur as a function of time and thus affect the particle composition and properties.

Paper III introduces the ultrafine organic tandem differential mobility analyzer (UFO-TDMA) method which is capable to detect the presence of organics in nucleation and Aitken mode particles. This finding is based on measurements which show that the growth behaviour of inorganic and organic particles have a clear logical change as a function of size and saturation ratio. The GFs of inorganics are close to unity in the smallest sizes where as the GFs of oxidized organics are clearly larger than one. The purpose of this application is to shed light on the presence of an organic fraction and thus on the composition and properties of the nucleation and Aitken mode size particles in different atmospheric environments and conditions.

Paper IV shows the evidence for marine secondary organic contribution in the composition of nucleation and Aitken mode particles during marine coastal nucleation events. The overall results of the UFO-TDMA and the pulse height analyzer ultrafine condensation particle counter measurements indicated that nucleation mode particles formed at the marine coastline include a remarkable fraction of secondary organic products, besides iodine oxides. The origin of organics was related to marine biota sources and their oxidation by iodine radicals and hydroxyl radicals, acid catalysis and ozone, when solar radiation intensity was sufficient. During modified marine conditions, an anthropogenic organic contribution is also probable. The results also suggest that biogenic secondary organic compounds accelerate the growth of freshly nucleated particles and

increase their survival probability to cloud condensation nuclei and even larger radiatively active sizes. The paper reveals that aquatic biota driven secondary organic contributions from biologically active marine and fresh-water areas (see Figure 5) have an affect on the particle formation, growth, transformation, composition and properties. This may be significant from the viewpoint of the global radiative budget, atmosphere-biosphere feedbacks and climate change.

Paper V applies two tandem differential analyzer methods (i.e. UFO-TDMA and UFH-TDMA) to shed light on the evolution of the nucleation and Aitken mode particle composition at a virgin boreal forest site during nucleation events in varying conditions. The inorganic and organic gas ratios, SO_2/MTOP and NO_x/MTOP (monoterpene oxidation products), best explain the variation in the nucleation mode composition during clean and pollution affected events, indicating a clear anthropogenic inorganic influence in addition to a biogenic secondary organic influence. MTOP significantly explain the nucleation mode composition with over 95% estimated organic fraction during the cleanest events. However, a certain amount of sulfuric acid vapour seems to be needed for the nucleation. The results also suggest the presence and formation of organosulfur compounds and reveal the importance of aging in the composition and properties of nucleation and Aitken mode particles when particles grow as a function of time. The anthropogenic influence makes the particles more hygroscopic, thus increasing the capacity of Aitken-mode particles to act as cloud condensation nuclei and affect on the radiative balance of the boreal forest. The dominating organic fraction, anthropogenic influence and aging are also expected to be applicable to other vegetation zones (see Figure 8), being an important factor from the viewpoint of climate. The role inorganic of anthropogenic compounds may be remarkable also from the historical perspective of new particle formation as well as health effects.
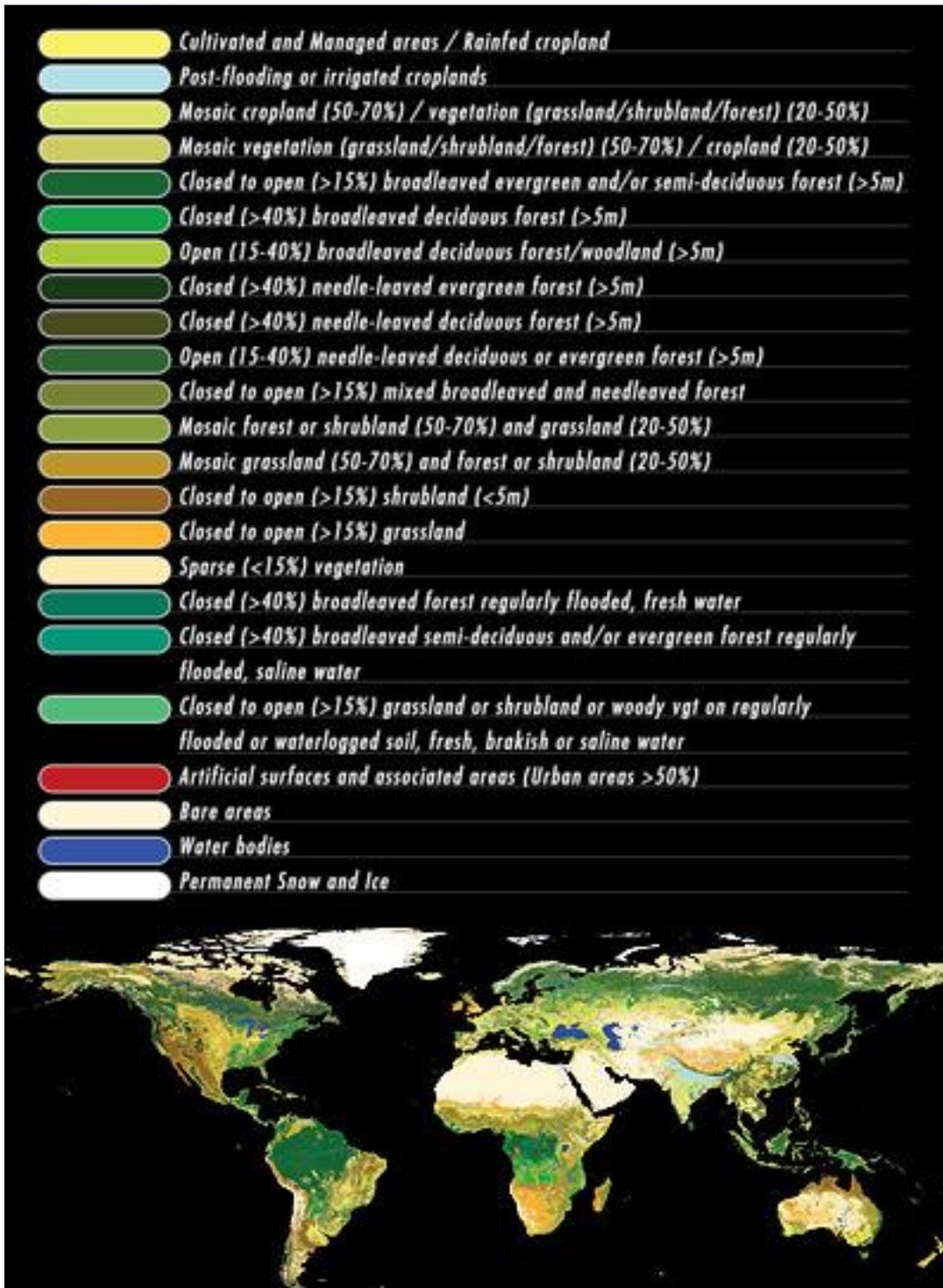
Figure 8. ESA's (ESA=European space Agency) global land cover map, published December 19, 2008, http://www.esa.int/esaEO/SEMXB7TTGOF_planet_1.html. This map maybe used freely with mandatory credits going to ESA/ESA Globcover Project, Led by Medias France/Postel.

7 Author's contribution

I wrote the summary of this thesis. In **Paper I**, I contributed to the planning, setup and development of the H-TDMA and O-TDMA. I also contributed to planning and mainly made the laboratory experiments. I participated in the writing process, especially on the experimental section of the paper. In **Paper II**, I made the first chemical reaction observations and supervised the measurements especially at the beginning of the study. I contributed to the writing process of the paper, particularly, the chemistry related parts were my responsibility. In **Paper III**, I co-planned and collaboratively setup the first versions of the UFO-TDMA. I planned and supervised the laboratory measurements. Additionally, I carried out measurements that contained sulfuric acid. I interpreted the experimental data and made the theoretical calculations. I also planned and mainly wrote the paper from the beginning to the end. In **Paper IV**, I planned and carried out the UFO-TDMA field experiments. I also mainly analyzed the data, planned and wrote the paper from the introduction to the conclusions, except for the PHA-UCPC data analysis and text. In **Paper V**, I planned and mainly conducted the UFO-TDMA measurements. I made the experimental and statistical UFO-TDMA and UFH-TDMA data analysis and interpretation and mainly planned and wrote the paper from the introduction to the conclusions.

8 Conclusions

Secondary organic aerosols accounts for a large fraction of the organic aerosols burden and a significant fraction of ambient tropospheric aerosols (Heald et al. 2005; Zhang et al. 2007; Hallquist et al. 2009). A detailed knowledge of the formation, growth, transformation, composition and properties of SOA and secondary organic gases is therefore required to evaluate their impact on climate and human health. The chemical and physical processes associated with SOA formation are complex and varied, and therefore represent a major research challenge in atmospheric science (e.g., Hallquist et al. 2009).

This thesis introduces a novel method (i.e. O-TDMA, organic tandem differential mobility analyzer; **Paper I**) to study the organic content of atmospheric particles. The method was successfully planned, built and further developed (i.e. RO-TDMA, reactivity organic tandem differential mobility analyzer, **Paper II**; and UFO-TDMA, ultrafine organic tandem differential mobility analyzer, **Paper III**) to investigate the organic fraction, the composition and the composition change of atmospheric nucleation and Aitken mode sized particles in different conditions and locations. In this thesis, the UFO-TDMA (**Paper III**) was applied to shed light on 6-50 nm particle formation, growth, transformation, composition and properties in situ during new particle formation events at the most well-studied atmospheric marine (Mace Head, Ireland, **Paper IV**) and boreal forest environments (Hyytiälä, Finland, **Paper V**), representing two major natural environments in the world. Furthermore, the UFO-TDMA method has been successfully applied to urban and arctic environments. The results of the UFO-TDMA measurements indicated (e.g., **Paper IV** and **Paper V**) the importance and the remarkable and role of secondary organic compounds in the nucleation mode and Aitken mode size particle growth, transformation and compositions both in biologically active marine and forest areas. In addition, these results demonstrated that a secondary inorganic

contribution seem to be necessary for nucleation, and chemically interact with the organic contribution. The results also reveal that anthropogenic inorganics are important even in remote environments, affecting natural ultrafine particle formation, transformation, composition, properties, and thus climate. In addition to impacts to climate, those ultrafine particle contributions are also relevant from the viewpoint of health effects (see e.g., Nel 2005; Pöschl 2005; Löndahl 2009).

In regards to forest nucleation events, a remarkable point is that nucleation events seem to require sulfur compounds. Because anthropogenic SO_2 is the main precursor for those sulfur compounds, the quantity of nucleation events can be dependent on the concentration of SO_2 derivatives, in addition to secondary organic contribution, in different forest locations. In marine areas, anthropogenic precursor production is not necessary for nucleation events in biologically active areas where the marine biota itself can produce precursor gases which form low-volatility inorganic iodine and sulfur containing compounds, and secondary organic compounds.

When considering natural environments from past to the present, it is possible that sulfur compounds related to human activity have affected the amount and the distribution of nucleation events. This can be crucial from the viewpoint of the chemical and physical properties of organics in different sized ultrafine particles, because the properties of newly-condensed organics and aged organics are clearly different. On the other hand, because those secondary organic gases can affect the particle properties outside of nucleation events, the role of secondary organic compounds is important everywhere (e.g., biologically active marine and continental areas, and also urban areas) where particles are present and organic compound sources and oxidants are available.

Due to the expected amount of biogenic emissions around the world and their interaction with anthropogenic emissions, the origin, life, fate and properties of secondary and primary gases and particles need further study in order to more fully understand the climate and health effects. The composition studies should be carried out in combination with near real time state–of-the-art instrumentation in various geographical locations and atmospheric conditions. Especially interesting locations to study would be different marine areas in different weather conditions and different continental vegetation areas. Therefore, it would also be beneficial to develope the quantity and quality of research stations. Consequently, this requires informed interaction between the scientists, the public, and the policymakers.

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