

Finnish–Estonian air ion and aerosol workshops

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Atmospheric air ions and aerosol particles participate in atmospheric processes and have several important effects on e.g. global climate and human health. When measured, air ions and aerosol particles have been observed to be present always and in every place. In this overview we present a brief summary of the motivation, history and main achievements in air ion research. The papers in this special issue are the result of a set of bi-annual workshops taken place since 2003. The contents of the papers reflect the collaborative research efforts lead by the University of Helsinki and University of Tartu, with an increasing contribution of other partners. The main objective of these workshops has been to provide a discussion forum for the development of air-ion theory and measurement techniques. This special issue presents main achievements in a set of 14 original papers.

Background and motivation

Air ions exist everywhere in the Earth's atmosphere (e.g. Israël 1970, Arnold *et al.* 1977, Hörrak 2001, Eichkorn *et al.* 2002, Lee *et al.* 2003). They participate in different atmospheric processes like in cloud processes and precipitation (Pruppacher and Klett 1997, Laakso *et al.* 2003, Andronache *et al.* 2006), and new aerosol particle formation (e.g. Laakso *et al.* 2006). In addition to direct ion studies, observations of ions offer indirect information on atmospheric aerosols and air chemistry.

Observations made during the last decade or so demonstrate clearly that production of new aerosol particles by nucleation and subsequent nuclei growth is a frequent phenomenon that takes place in most atmospheric environments (e.g. Kulmala *et al.* 2004a). Later analyses have shown that this phenomenon is capable of affect-

ing particle number concentrations all the way up to global scales (Spracklen *et al.* 2006). More regionally, atmospheric aerosol formation is likely to affect the population of particles affecting cloud properties and thereby climate (Kerminen *et al.* 2005, Laaksonen *et al.* 2005).

Atmospheric aerosol formation is likely to involve multiple different pathways due to, for example, variations in the amount and type of important aerosol precursors such as low-volatile trace gases. One pathway for aerosol formation is ion-induced, or ion-mediated, nucleation. The role of ions in atmospheric aerosol formation has remained a controversial topic (Hörrak *et al.* 1998, Tammet *et al.* 1988, Turco *et al.* 1998, Yu and Turco 2001, Laakso *et al.* 2002, Lee *et al.* 2003, Kazil and Lovejoy 2004, Lovejoy *et al.* 2004, Eisele *et al.* 2006, Kanawade and Tripathi 2006, Yu 2006). Some of the studies made so far, suggest that the contribution of ion-

induced nucleation to the total nucleation rate is important or even dominant, whereas some other studies indicate that the role of ions in aerosol formation is negligible.

The main motivation for the research presented here has been, and is, to understand atmospheric nucleation and the role of air ions play in this process. Several open questions were identified at an initial workshop in 2002:

1. How often and in how large areas new-particle formation occurs?
2. What takes place below 3 nm diameter?
3. Are there neutral clusters in the atmosphere?
4. What is the composition of nucleation mode aerosol particles?
5. What is the related thermodynamics?

The close co-operation between University of Helsinki and University of Tartu started in January 2000. After that the general meetings were held nine times until March 2007. Seven of these meetings were labelled as “Air ion and aerosol workshops” (Table 1). The workshops were supported and organised by the Research Unit on Physics, Chemistry and Biology of Atmospheric Composition and Climate Change (Centre of Excellence, Academy of Finland) and by the Nordic centre of Excellence (BACCI: Biosphere–Aerosol–Cloud–Climate Interactions). The workshops have acted as a forum for exchanging ideas and research results in order to address the questions mentioned above. The relevance that air-ion research has in atmospheric research is reflected in the fact that the number of participants in the workshops has doubled during

the last three years. The scientific collaboration between the participants has led to about 40 published research articles both in this special issue and elsewhere, and to three master theses and one Ph.D. thesis.

Instrument development

The continuing collaboration between the universities (Helsinki and Tartu) and long experience gained in Tartu have resulted in the development of novel instruments for detecting ion clusters and, more recently, neutral clusters. The developed instruments have been used in a number of field experiments and laboratory studies. These instruments provide information on positive and negative ion concentrations from molecular cluster sizes up to several tens of nanometers. Apparently, the instruments give us excellent opportunity to investigate and understand atmospheric nucleation and cluster dynamics.

Briefly, air ion mobility spectrometers are a class of instruments based on electric mobility analysis (e.g. Misaki 1961, Hörrak *et al.* 1998, and references therein). Ion mobilities are segregated in a similarly way as is done in a DMPS (*see e.g.* Aalto *et al.* 2001), but an array of electrometers is typically used to simultaneously measure the various mobility fractions. Unlike the DMPS and SMPS systems which utilize bipolar chargers to bring the aerosol particles into Boltzmann equilibrium before being classified by the DMA, ion mobility spectrometers measure naturally occurring mobility distributions. Ion mobility spectrometers can detect

Table 1. History of Finnish–Estonian air ion and aerosol workshops.

Name of the workshop	Location	Date
Workshop in Tartu	Tartu, Estonia	31 Oct. 2000
Workshop in Helsinki	Helsinki, Finland	25 Mar. 2002
First Air ion and aerosol workshop	Helsinki, Finland	25–26 June 2003
Second Air ion and aerosol workshop	Helsinki, Finland	25–26 Feb. 2004
Third Air ion and aerosol workshop	Pühajärve, Estonia	30 May–1 June 2004
Fourth Air ion and aerosol workshop	Helsinki, Finland	12–13 Jan. 2005
Fifth Air ion and aerosol workshop	Pikakärve, Estonia	27–29 Jan. 2005
Sixth Air ion and aerosol workshop	Hyttiälä, Finland	15–16 Mar. 2006
Seventh Air ion and aerosol workshop	Pühajärve, Estonia	21–23 Aug. 2006
Eighth Air ion and aerosol workshop	Hyttiälä, Finland	20–22 Mar. 2007

charged particles of any size, extending down to the size of molecular ions (ca. 0.4 nm). A limitation is that the sensitivity of electrometers limits the lowest detectable particle concentration to 20–50 cm⁻³.

The two recently-developed and already relatively widely-used instruments are the Balanced Scanning Mobility Analyzer (BSMA) (Tammet 2006) and Air Ion Spectrometer (AIS) (Mirme *et al.* 2007), both manufactured by AIREL Ltd., Estonia. The BSMA consists of two plain, aspiration-type differential mobility analyzers, one for positive and the other one for negative ions. The electric mobility range is 0.032–3.2 cm² V⁻¹ cm⁻¹ and the ions are measured without distorting the air temperature and relative humidity inside the instrument. The mobility distribution is converted into the size distribution using a specific algorithm (Tammet 1995). The corresponding size distribution range is 0.4–7.5 nm in diameter.

The Air Ion Spectrometer (AIS) is measuring the mobility distribution of air ions (naturally-charged clusters and aerosol particles). The spectrometer consists of two identical cylindrical, aspiration-type differential mobility analyzers, one for measuring positive ions and the other one for measuring negative ions. The mobility range is 0.00075–2.4 cm² V⁻¹ s⁻¹ and the corresponding diameter range of singly-charged particles calculated according to the algorithm by Tammet (1995) is 0.46–55 nm.

Recently, the so-called Neutral cluster and Air ion Spectrometer (NAIS) was developed. Unlike the AIS, the NAIS can be used to measure neutral clusters below 2 nm diameter. The measurement principle of the NAIS is based on a unipolar charging of sampled particles and their subsequent detection with an electrical mobility analyzer.

Main results

A brief synopsis of main results obtained during the last few years could start from instrumental development presented in the previous section, or from mode development.

The motivation behind model development was to find out the importance of ion-induced nucleation in the atmosphere (Laakso *et al.* 2002)

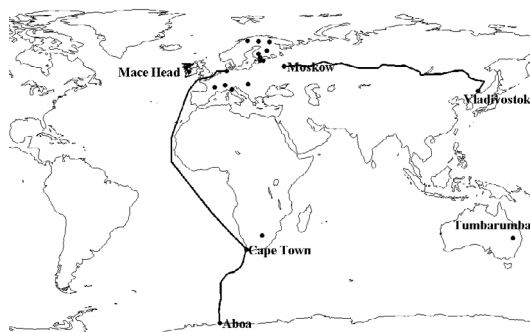


Fig. 1. Sites of AIS and BSMA measurements. Points are local sites and lines are ship cruises (two) and train trips (one).

and to investigate of the effect of charges on particle condensation growth (Laakso *et al.* 2003). Next, we calculated ion production rates — a crucial parameter in ion studies — based on two independent methods (Laakso *et al.* 2004a) and investigated different nucleation mechanisms in a boreal forest environment (Laakso *et al.* 2004b). At the same time, we noticed that it is possible to utilize ion spectrometers for studying size-dependent particle growth rates and concentrations of different vapours participating in particle growth processes (Kulmala *et al.* 2004b). We also combined data from ion spectrometers and other devices (condensation particle counters) with mode data in order to detect the potential existence of neutral molecular clusters (Kulmala *et al.* 2005a).

We characterized cluster ion populations in forest environments (Hirsikko *et al.* 2005, Hörrak *et al.* 2005) and utilized our measurements to calculate the charging state (a trace of new-particle formation mechanism) of nanometer-size particles (Vana *et al.* 2006). Recently, we studied air ion deposition processes in the atmosphere (Tammet *et al.* 2006), as well as the characteristics of new-particle formation based on ion measurements (Hirsikko *et al.* 2007b). The latest improvement from observational point of view was a measurement setup that allows us to estimate the contribution of ions to atmospheric nucleation based on direct measurement of the particle charging state (Laakso *et al.* 2007a).

Air ion measurements were performed increasingly at different sites (Fig. 1), including in Finland, Estonia, Australia, Sweden, Hungary,

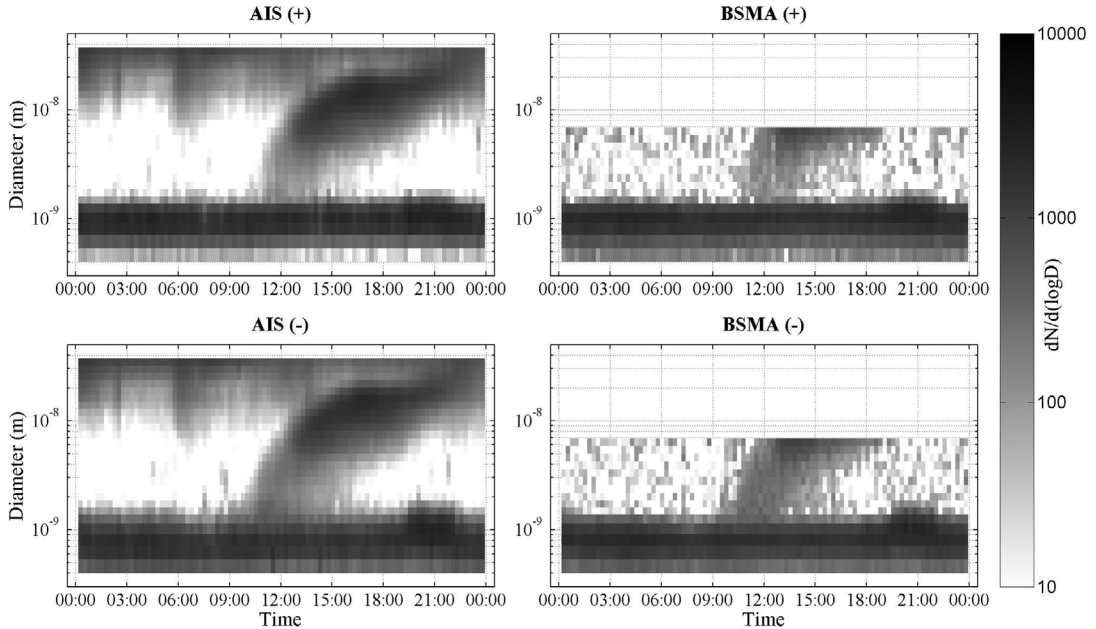


Fig. 2. A typical aerosol formation and subsequent growth event (3 Apr. 2004) measured using an ion spectrometers (AIS and BSMA) in SMEAR II station, Hyytiälä, Finland. The time of day is given in the x -axis and the size (diameter) of ions is given in the y -axis. The concentration of ions (in cm^{-3}) is indicated by the gray colour scale on the right. The formation of new particles starts after 09:00. The subsequent growth continues during the day and particles reach sizes of 30 nm. The growth rate can be estimated to be around 3 nm h^{-1} . Note that the ion measurements extend down to 0.5 nm diameter, whereas typical aerosol size distribution measurements start from 3 nm.

Italy, Ireland, Antarctica (Virkkula *et al.* 2007), high Alpine site, trip from Europe to Antarctica (using a vessel), and a train trip from Moscow to Vladivostok and back (Vartiainen *et al.* 2007). During those measurements, we investigated air ion dynamics in a continental boundary layer (Hirsikko *et al.* 2005, 2007a), marine boundary layer (Komppula *et al.* 2007), free troposphere (Venzac *et al.* 2007), coastal areas, inside clouds (Lihavainen *et al.* 2007), near traffic (Tiitta *et al.* 2007) and indoors (Hirsikko *et al.* 2007c). Recently, we also studied vertical profiles of air ion concentrations and aerosol formation using hot air balloon (Laakso *et al.* 2007b). As a summary of all our results we can state that ion clusters are always present, and that ion spectrometers make it possible to detect nucleation events very often.

We also started studying processes related to water droplets during raining and snowing, in addition to which we measured air ion size distributions near a water fall (Hörrak *et al.* 2005, Parts and Luts 2005, Laakso *et al.* 2006,

Hirsikko *et al.* 2007b). Due to the complexity of water in its different phases, this kind of investigations will continue (e.g. Parts *et al.* 2007).

The above investigations are promising (*see also e.g.* Kulmala *et al.* 2005a, Kulmala *et al.* 2007) and demonstrate the rapid progress that has been made recently in detecting thermodynamically stable clusters formed during atmospheric nucleation events and, even more interestingly, also during non-event times (e.g. Kulmala *et al.* 2005a). This becomes apparent when considering that already more than ten years ago Weber *et al.* (1995) showed that clusters were present when 2.7–4 nm particles were detected.

In Fig. 2 examples of air ion size spectra (naturally-charged cluster ions and charged aerosol particles) measured with the AIS and BSMA are presented. One of the most important features revealed by the ion instruments is that cluster ions (ions smaller than 1.5 nm) appear to be present always. This seems to be the case both during days with clear aerosol formation (event days) and during non-event days. Therefore,

we can confidently say that there are always ion clusters in a boreal forest environment. Several measurements carried out recently in different locations (marine atmosphere, urban air, free troposphere, coastal areas) confirm this observation. The other important feature seen from Fig. 2 is that atmospheric nucleation seems to start from sizes (mass or Tammet's diameter) of around 1.5 nm.

Another important observation is that after new-particle formation, ion measurements show particle growth patterns ("banana-shaped") similar to those shown by DMPS measurements. According to a recent overview (Kulmala *et al.* 2004a), the measured growth rate of nucleation mode particles is typically remarkably constant above the sizes of 5–8 nm. In our own stations, atmospheric nucleation is seen to be frequent and important (e.g. Dal Maso *et al.* 2005, Pugatsova *et al.* 2007).

From the point of view of cluster dynamics and especially new-particle formation, the chemical composition of clusters is important (e.g. Mäkelä 1992). In the continuously-ionized atmosphere, the mobility spectrum of natural small ions is a mixture of ions of different age and chemical composition, evolving via ion-molecule reactions (e.g. Mohnen 1977, Luts 1995, Beig and Brasseur 2000). The composition of cluster ions depends strongly on their age and concentrations of trace species in the air, as well as on the thermodynamic properties of the clusters and surrounding air (e.g. Bricard *et al.* 1972, Castleman *et al.* 1978, Eisele and Tanner 1990, Nagato and Ogawa 1998, Parts and Luts 2004).

To summarise and conclude, the studies presented above and in the following articles give the following answers to our initial set of questions (*see above*):

1. New-particle formation seems to occur over large areas, being an important phenomenon (e.g. Kulmala *et al.* 2004a). However, more air ion and particularly neutral cluster measurements are still needed.
2. Ion spectrometers can show some part of the evolution and dynamics of small ion clusters. Therefore we have developed several ion spectrometers.
3. Ion clusters are anyhow present, in practice everywhere. Model calculations suggest that there should also be neutral clusters (Kulmala *et al.* 2000). There is increasing evidence on the existence of neutral clusters (e.g. Kulmala *et al.* 2005a), and we have developed new instruments for detecting them.
4. Recently we have developed new *in situ* methods like the CPC battery for studying the water solubility of very small particles (Kulmala *et al.* 2007)
5. Although we know that the saturation concentration of condensing vapours seems to be around $3 \times 10^6 \text{ cm}^{-3}$, a deep insight on the thermodynamical properties of atmospheric clusters is still missing.

Future perspectives

Although our extensive investigations have given a lot of new insight on air ion dynamics and fresh aerosol particle formation, there are still, even increasing, number of open questions. In future we will work with these research questions using both theoretical and experimental approaches. We will focus on the following issues:

1. Continuous air ion cluster and nucleation mode aerosol particle measurements at the SMEAR II station in Hyytiälä and simultaneous air ion measurements in Estonia will continue. The routine measurements of air ion mobility distributions in Tahkuse, Estonia, have been running since 1988. We started ion measurements in Hyytiälä in spring 2003. Currently we are measuring atmospheric ions with several devices: Air Ion Spectrometer (AIS, 0.4–40 nm), Balanced Scanning Mobility Analyzer (BSMA, 0.4–7.5 nm), Neutral cluster Air Ion Spectrometer (NAIS, ions: 0.4–40 nm, neutral particles: 1.8–40 nm) and ion-Differential Mobility Particles Spectrometer (ion-DMPS, the charging state of 3–15 nm particles). In addition, we are measuring size distributions of 3–900 nm particles with a normal DMPS. In future we will decrease the cut size of both normal and ion-DMPS systems toward 2 nm.
2. Since the NAIS is a prototype version of a new measurement device, we will con-

- tinue its development together with University of Tartu and AIREL Ltd. The NAIS and ion spectrometer will be calibrated and tested under laboratory conditions and used in different laboratory experiments in order to obtain data under well-defined conditions. The ion spectrometers are relative new devices, so we continue their development (Mirme *et al.* 2007). However, this will take several years. We will also continue our laboratory experiments with the AIS and NAIS.
3. World-wide measurements will be conducted as campaign-wise measurements. With the ion spectrometers and NAIS's, we can detect atmospheric nucleation (both neutral and ion induced nucleation or activation) and its importance in different regions. Currently, we have measured ion size distributions in Finland, Estonia, Atlantic Ocean, Siberia, Arctic regions, boreal forest, urban environment, South-African savannah, coastal environment at Mace Head, Ireland, Pusta in Hungary, the Alps, Antarctica and Australia. Preliminary results from these environments emphasize the importance of ion-induced nucleation, especially under cold and clean conditions.
 4. The data set we have collected is unique and subsequent data analysis will take several years. With this data, we will calculate (a) the contribution of ion-induced nucleation to total atmospheric nucleation, (b) concentrations and source rates of condensable vapours (*see* Kulmala *et al.* 2001, Kulmala *et al.* 2005b, Dal Maso *et al.* 2005), and (c) ion characteristics and their differences in various environments. As a part of these studies, we will develop theoretical methods for the data analysis of ion spectrometers and ion-DMPS.
 5. Our recent observations have shown that there are several unknown ion phenomena related to water droplets and ice crystals (Hirsikko *et al.* 2007b). Based on our extensive data set and laboratory experiments, we will study these phenomena in more detail. These processes include the formation of small intermediate ions in the presence of ice crystals and the formation of nanometer-size water droplets from rain droplets and waterfalls.
 6. Our measurements have shown some inconsistency between the predicted and measured air ion generation rates in a boreal forest (Laakso *et al.* 2004a, Tammet *et al.* 2006, Hirsikko *et al.* 2007a). We will develop the methods of air ion generation measurement and the air ion balance models with aim to achieve an adequate description of air ion dynamics in a boreal forest. This includes consideration of the height profiles inside the forest canopy.
 7. One of unknown phenomena related to climate change is the possible interaction between solar activity and ion-induced nucleation in the atmosphere (e.g. Svensmark and Friis-Christensen 1997). We will study processes related to cosmic ray-climate interactions in an aerosol and cloud chamber in CERN, Switzerland, in a project called CLOUD.
 8. We will continue to develop basic theories related to ion processes (e.g. Noppel *et al.* 2003, Lushnikov and Kulmala 2004a, 2004b, Lushnikov and Kulmala 2005), and to apply quantum chemistry models (Kurten *et al.* 2007). The basic theories related to different hypothesis made for cluster dynamics and nucleation processes will be tested and further developed (e.g. Kulmala *et al.* 2006). Since ion spectrometers measure clusters consisting of few molecules, we will investigate air chemistry by combining ion measurements and molecular modeling (Bonn *et al.* 2006). We will also look in more detail the possibilities to utilize time-of-flight-mass spectrometers for the chemical analysis of clusters and air chemistry.
 9. During last years, we have developed a complete ion process model AEROION (Laakso *et al.* 2002). We will continue developing this model as a part of the UHMA model family (Korhonen *et al.* 2004) to find out the importance of air ions in different aerosol dynamic processes. Ultimately, we aim to parameterize the results for global climate models.

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