

## The legacy of Finnish–Estonian air ion and aerosol workshops

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Atmospheric air ions, clusters and aerosol particles participate in a variety of atmospheric processes and considerably affect e.g. global climate and human health. When measured, air ions as well as atmospheric clusters and particles have been observed to be present practically always and everywhere. In this overview, we present a brief summary of the main achievements and legacy of the series of workshops organized mainly by the University of Helsinki and the University of Tartu. The legacy covers the development and standardization of new instruments, such as ion spectrometers, mass spectrometers and aerosol particle counters, as well as work toward theoretical understanding of new-particle formation and evolution of atmospheric clusters. One important legacy is the establishment of the SMEAR-Estonia station at Järvelja.

### Background and motivation

Air ions exist everywhere in the Earth's atmosphere (e.g. Israël 1970, 1973, Arnold *et al.* 1977, Hörrak 2001, Eichkorn *et al.* 2002, Lee *et al.* 2003, Hirsikko *et al.* 2011). Besides air ions, Kulmala *et al.* (2000) postulated the presence of small neutral clusters in the atmosphere, and recently the existence of such clusters was also confirmed through observations (e.g. Kulmala *et al.* 2013). Both cluster ions and neutral clusters are central to atmospheric new-particle formation because they act as aerosol precursors below the size range of 3 nm in particle diameter (e.g. Kulmala *et al.* 2014).

A forum devoted to research on air ions and atmospheric clusters has been the series of Finnish–Estonian air ion and atmospheric aerosol workshops dating back to the year 2000 (Table 1). The main motivation of these workshops was to bring together researchers working with air ions and clusters in order to exchange data and knowledge acquired from measurements and modelling, and to provide a discussion forum for the development of theory and measurements techniques. In addition, the workshops served as user meetings that provide recommendations regarding the operation of measurement instruments in the field and laboratory, the maintenance and calibration of

instruments, and solving specific issues with the current instruments.

Before 2007, the workshops were organised by the University of Helsinki and the University of Tartu (summarized in Kulmala and Tammet 2007), and the workshop participants came mainly from those two universities. More recently, however, participants from other countries, universities and research institutions have also been involved. Therefore, the workshops, originally called “Finnish–Estonian air ion and atmospheric aerosol workshops”, became actually international. Also, the University of Helsinki research group led by Markku Kulmala is an international research community by itself, having representatives from many countries (e.g. Germany, France, Russia, China, etc.). As a result, young scientists and students from many European and developing countries have benefited from those workshops.

During 2007–2010, the co-operation between the University of Helsinki and the University of Tartu was also supported by the European Integrated project on Aerosol, Cloud, Climate, and Air Quality Interactions (EUCAARI), led by the University of Helsinki, in which the University of Tartu together with the spin-off company of the Tartu University, Airel Ltd., participated as part-

ners (Kulmala *et al.* 2011, *see also* Kerminen *et al.* 2010, Manninen *et al.* 2010). As an acknowledgment of this mutual co-operation between the two universities, in 2008 Markku Kulmala was awarded the degree of Doctor Honoris Causa by the University of Tartu. During the Finnish–Estonian collaboration, the two universities have exchanged postdoctoral researchers, and organized jointly instrument calibration and inter-comparison workshops and training courses for students and researchers in Hyytiälä and Järvelja. Within the last two workshops, we had three official partners as the Estonian University of Life Sciences and the INSMEARIN cooperation initiated.

The aim of this article is to summarize the activities and achievements related to the Finnish–Estonian air ion and aerosol workshops. First, we describe the development of different ion spectrometers and condensation particle counter applications in the framework of the workshop series, the efforts to combine data from ion spectrometers and mass spectrometers, and the development of new research infrastructures, especially SMEAR Estonia. Then we provide an overview of the measurements conducted with ion spectrometers around the world,

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

Workshop title	Time	Workshop location
Kick-off workshop, Estonia	31 Jan. 2000	Tartu, Estonia
Kick-off workshop, Finland	25 Mar. 2002	Helsinki, Finland
1th Air ion and aerosol workshop	25–26 June 2003	Helsinki, Finland
2th Air ion and aerosol workshop	25–26 Feb. 2004	Helsinki, Finland
3th Air ion and aerosol workshop	30 May–01 June 2004	Pühajärve, Estonia
4th Air ion and aerosol workshop	12–13 Jan. 2005	Helsinki, Finland
5th Air ion and aerosol workshop	27–29 June 2005	Pikajärve, Estonia
6th Air ion and aerosol workshop	15–16 Mar. 2006	Hyytiälä, Finland
7th Air ion and aerosol workshop	21–23 Aug. 2006	Pühajärve, Estonia
8th Air ion and aerosol workshop	19–21 Mar. 2007	Hyytiälä, Finland
9th Air ion and aerosol workshop	24–26 Sep. 2007	Pühajärve, Estonia
10th Air ion and aerosol workshop	17–19 Mar. 2008	Hyytiälä, Finland
11th Air ion and aerosol workshop	8–10 Sep. 2008	Pühajärve, Estonia
12th Air ion and aerosol workshop	31 Mar.–1 Apr. 2009	Helsinki, Finland
13th Air ion and aerosol workshop	10–11 Nov. 2009	Lund, Sweden
14th Air ion and aerosol workshop	14–16 June 2010	Pühajärve, Estonia
15th Air ion and aerosol workshop	23–25 May 2011	Hyytiälä, Finland
16th Air ion and aerosol workshop	12–14 June 2012	Pühajärve, Estonia
17th Air ion and aerosol workshop	11–12 June 2013	Hyytiälä, Finland
18th Air ion and aerosol workshop	2–4 June 2014	Pühajärve, Estonia
19th Air ion and aerosol workshop	24–26 Aug. 2015	Pühajärve, Estonia

and discuss the improvements in the theoretical and modelling work on air ions and particles. We conclude by reviewing the nine future research topics identified by Kulmala and Tammet (2007) and give our view on the current, most important open questions in this field.

## **Ion spectrometer development in Estonia and Finland**

### **Special considerations when measuring with ion spectrometers**

Concentration and size distribution of electrically charged nanoparticles with Tammet's diameters of about 1.5–7 nm is an essential source of information about new-particle formation in the atmosphere. These particles have electric mobilities ranging from 0.04 to 0.6 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and are called intermediate air ions (Hörrak *et al.* 2000). Size distributions of air ions are measured using ion spectrometers. Such measurements are difficult due to the very low number concentrations of ions: in Tartu, median concentrations in logarithmic 1/8-decade mobility bins of intermediate ions are often below 2 cm<sup>-3</sup> (Tammet *et al.* 2014).

One way to measure extremely low concentrations is to use simultaneous data from a multichannel (i.e. from several electrometers) instrument. Air Ion Spectrometer (AIS) and Neutral cluster and Air Ion Spectrometer (NAIS) built by Airel Ltd., Estonia, are examples of wide-range multi-channel ion spectrometers. They are able to measure the complete distribution of both polarities of ions rapidly with parallel columns. Thus, the advantage of the (N)AIS is a high time resolution (minimum 1 s).

Another method to deal with low ion concentrations is to increase the air flow rate in order to collect more ions. This method was adopted in the single-channel scanning mobility spectrometers BSMA and SIGMA, which were developed in the University of Tartu especially for studying charged clusters and particles in the Tammet's diameter range of 0.4–7 nm. The use of a single electrometer in the full mobility range reduces the risk of instrumental distortions in the distribution curves. The method of continuous scanning excludes random errors caused by

switching of the electrometer inlet. Continuous scanning is common in traditional differential mobility analyzers of the Whitby type, in which the particles are detected by means of CPC (Flagan 1998). The drawbacks of the BSMA compared to the (N)AIS are the narrower measurement range, decreased time resolution (several minutes) and practical sampling difficulties due to the high inlet flow rate. However, the high flow rate minimizes ion losses efficiently.

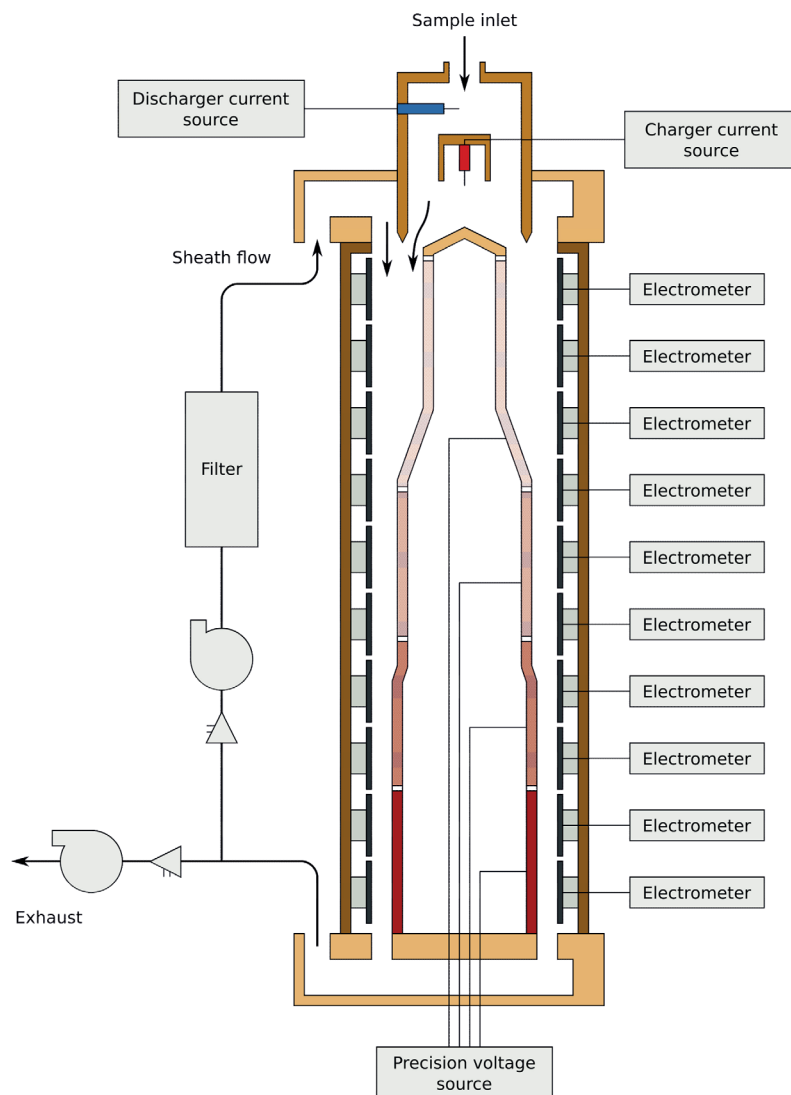
In a typical air ion mobility analyser, the collecting electrode is exposed to a driving electric field, and variations in this field induce a displacement current through the electrode. The displacement current may exceed the electric current carried by ions by several orders of magnitude. A solution for this problem is to neutralize the disturbing current with a displacement current of opposite polarity by using a bridge circuit. Another possibility is to carry the ions with the air flow away from the separation zone and collect them in an electrostatically shielded ion filter. Both methods have been applied in the instruments developed in the University of Tartu (Tammet 2011).

### **Characterization of ion spectrometers**

Over the years, we have improved the accuracy and comparability of ion spectrometer measurements by characterising these instruments in laboratory experiments (e.g. Mirme *et al.* 2007, Asmi *et al.* 2009, Manninen *et al.* 2011, Wagner *et al.* 2016). We have organized international ion-spectrometer user meetings as well as calibration and inter-comparison workshops (Asmi *et al.* 2009, Gagné *et al.* 2011). This has increased our understanding on the performance of the instruments, and has directly affected the ion spectrometer development. All this has been a result of the direct interaction between the instruments users and the manufacturer.

### **Development of multichannel ion and aerosol spectrometers**

Several different aerosol instruments employing the method of multichannel electrical aero-



**Fig. 1.** The design of a measurement column of a multi-channel electrical aerosol spectrometer.

sol spectrometry have been developed at the University of Tartu. The first such instrument was the Electrical Aerosol Spectrometer (EAS, Tammet *et al.* 2002) that measures the particle size distribution in the size range from 3 nm to 10  $\mu\text{m}$ . In 2003, the Air Ion Spectrometer (AIS, Mirme *et al.* 2007) based on the EAS technology was developed and built in cooperation with Airel Ltd., a spin-off company of the University of Tartu. The unique design of the instrument allows for measurements of air ion distributions of both polarities in the mobility range from 3.2 to 0.0013  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ , corresponding to the mobility equivalent diameters of 0.8–42 nm. In

2005, AIS was superseded by the Neutral cluster and Air Ion Spectrometer (NAIS, Mirme and Mirme 2013, Manninen *et al.* 2009). This improved instrument is able to measure, in addition to ions, the size distribution of neutral particles in the size range from 2 nm to 42 nm. There are currently about twenty NAIS, five AIS and five EAS instruments operating around the world.

The primary components of the ion spectrometers are cylindrical multi-channel, second-order differential mobility analysers (DMAs; Fig. 1). The analysers have many charge collecting electrodes on their outer wall and a central



electrode that is divided into several sections with different applied constant voltages. For the sheath air flow, the instruments use recirculated air from the exhaust that is passed through an electric filter (e.g. Mirme *et al.* 2007).

The mobility analyzers are equipped with software-controlled preconditioning units which, depending on the operating mode of the instrument, may perform charge neutralization, electric filtering and controlled charging of the aerosol sample before it enters the DMA.

The EAS and (N)AIS use unipolar corona chargers for both charge neutralization and charging. The neutralizer, also called a discharger, charges the aerosol sample with ions of the opposite polarity relative to what is detected by the mobility analyser. This allows EAS and NAIS to measure aerosol particles with a naturally-occurring non-steady-state electric charge distributions without the need for an external (radioactive) neutralizer.

The signals from all collecting electrodes of the DMA are measured in parallel using integrating electrometric amplifiers, in which the fluxes of electric charge carried by aerosol particles are collected on high-quality electrical capacitors. The output voltages of the amplifiers are proportional to the collected electric charge. The method provides the best possible signal-to-noise ratio and also ensures that no signal is lost regardless of the measurement frequency.

The size or mobility distribution is calculated using the generalized least squares method that takes into account the noise level of individual electrometers to find the best estimate for the particle size or mobility distribution. The apparatus matrix of the spectrometer is based on a mathematical model of the instrument that considers particle losses, charging probability, electric field and air flow inside the mobility analyser (Mirme and Mirme 2013).

### Electrical Aerosol Spectrometer

EAS has two DMAs for measuring particles in different size ranges. The first column uses a diffusion corona charger and a DMA with 20 electrode sections to measure the particle size distribution from 3 nm to 1  $\mu\text{m}$ . The second column

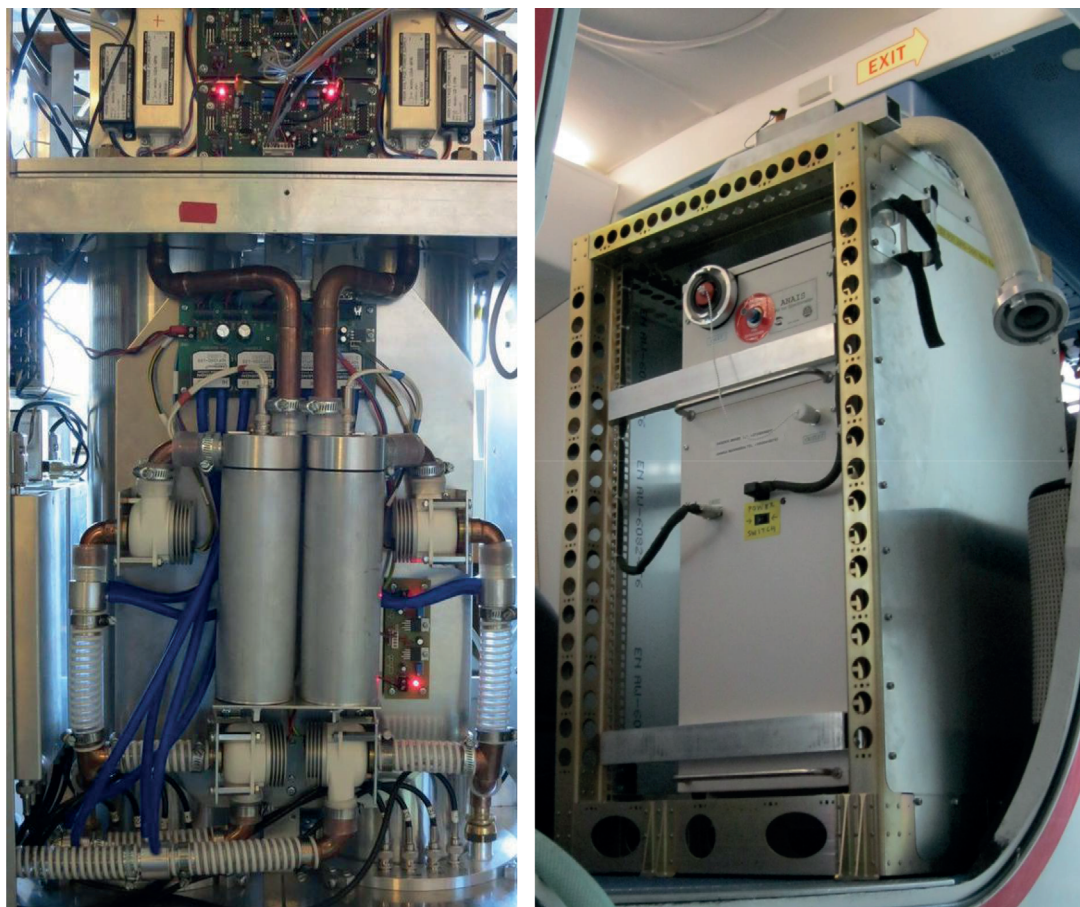
uses a strong electric field corona charger and a DMA with 12 electrode sections to measure the particle size distribution from 300 nm to 10  $\mu\text{m}$ . The signals from the 32 electrometers of both analysers are processed together to produce a complete particle size distribution from 3 nm to 10  $\mu\text{m}$ . The EAS can run in particle and offset operating modes. The sample flow rate of the EAS is 30 litres per minute (lpm).

### Neutral cluster and Air Ion Spectrometer

Both AIS and NAIS use two mechanically identical mobility analyser columns with 21 charge-collecting electrodes — one column for measuring positive ions and the other column for measuring negative ions (Mirme and Mirme 2013). The preconditioning units of AIS comprise a discharger and an electric filter. NAIS also includes a charger and additional electric filter called the post-filter. The instruments use a total sample flow rate of 54 lpm which corresponds to 27 lpm per analyser.

AIS and NAIS can operate in different measurement modes depending on the state of the preconditioning unit. During the “ions measurement mode”, the aerosol sample flow is passed unmodified through the preconditioning unit and naturally-charged particles, called also air ions, are measured. During the “offset measurement mode”, the discharger and directly-following electric filter are switched on. As a result, no detectable particles can enter the mobility analyser and the zero level signal of the electrometers can be measured. During the “particle measurement mode”, which is only available for NAIS, the main charger and post-filter are switched on. The charger will provide a known charge distribution to the aerosol sample. The post-filter prevents the excess of charger ions from entering the mobility analyser. For typical environmental monitoring, NAIS runs in a five-minute measurement cycle, measuring particles, air ions and offset for two, two and one minute, respectively.

In 2008, a new version of NAIS was developed that could operate on board an aircraft and measure correctly at decreased atmospheric pressure at altitudes up to 8 km (Fig. 2). NAIS



**Fig. 2.** Left-hand-side photograph: The new generation of Neutral cluster and Air Ion Spectrometer (NAIS) used in a CLOUD experiment at CERN. Right-hand-side photograph: NAIS in a flight rack installed on board a Zeppelin.

became the first instrument to measure sub-3 nm particles above the planetary boundary layer (Mirme *et al.* 2010). The instrument has a completely updated airflow system with separately controlled sheath and sample flows that can be adjusted by software to accommodate the air density changes. Also the data acquisition system has been replaced in order to increase the measurement frequency and to achieve a one-second time resolution. All the enhancements were later also employed in a new version of EAS. New NAIS has been actively used in CLOUD (Cosmics Leaving OUtdoor Droplets, Kirkby *et al.* 2011) chamber experiment in CERN, Switzerland, where the instrument has to endure air pressure of up to 1300 mbar and also extremely low temperatures down to  $-30\text{ }^{\circ}\text{C}$  (Franchin *et al.* 2015).

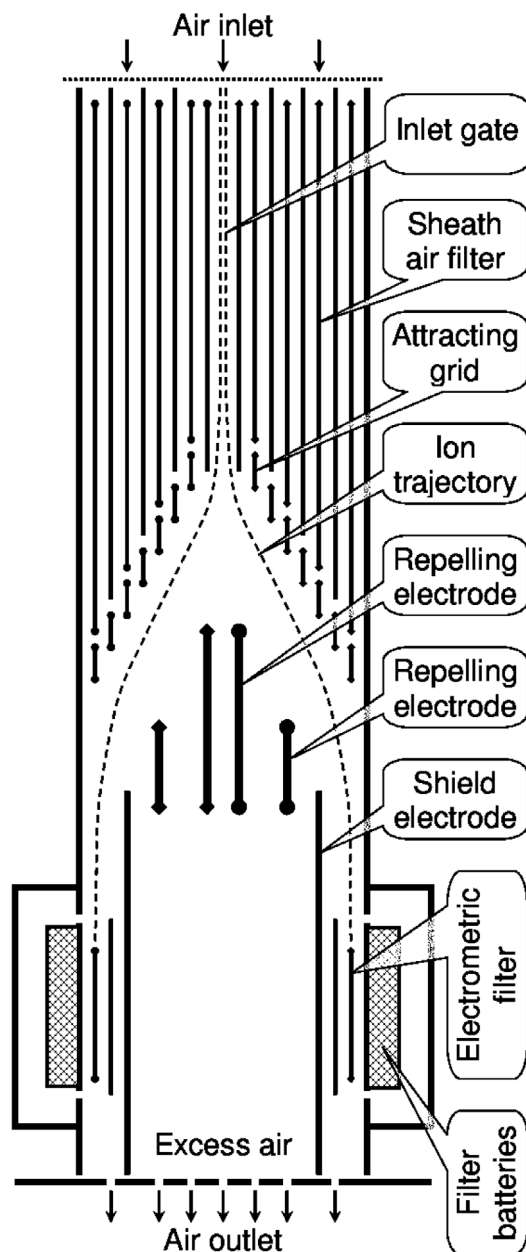
### Development of single-channel ion spectrometers

The Balanced Scanning Mobility Analyzer (BSMA, Tammet 2006) makes use of a balanced bridge where the arms are two similar second-order differential aspiration condensers simultaneously collecting the positive and negative air ions. The large air flow rate of about 3000 lpm through the instrument makes the loss of particles in the air inlet tract very low. A short passage time of about 0.06 s makes sure that the composition of ions is not changed during the measurement procedure. The planar aspiration condensers are equipped with electrostatic filters acting as inlet gates for ions. The control computer alternates between three measuring phases while the inlet can be opened only for positive

ions, opened only for negative ions, or closed for all ions.

The characteristic mobility is controlled by voltage, which is exponentially decayed from 3000 to 26 V during a scan. A standard 10-minute cycle consists of up to 30 scans and delivers mobility and size distributions for both positive and negative ions. The random errors of the fraction concentrations of about  $5 \text{ cm}^{-3}$  in the 10-minute records are low enough to allow investigation of new-particle formation events. However, the smoothing of measurements in a time window of several hours is necessary when the subject is the mobility distribution of intermediate air ions during non-event periods.

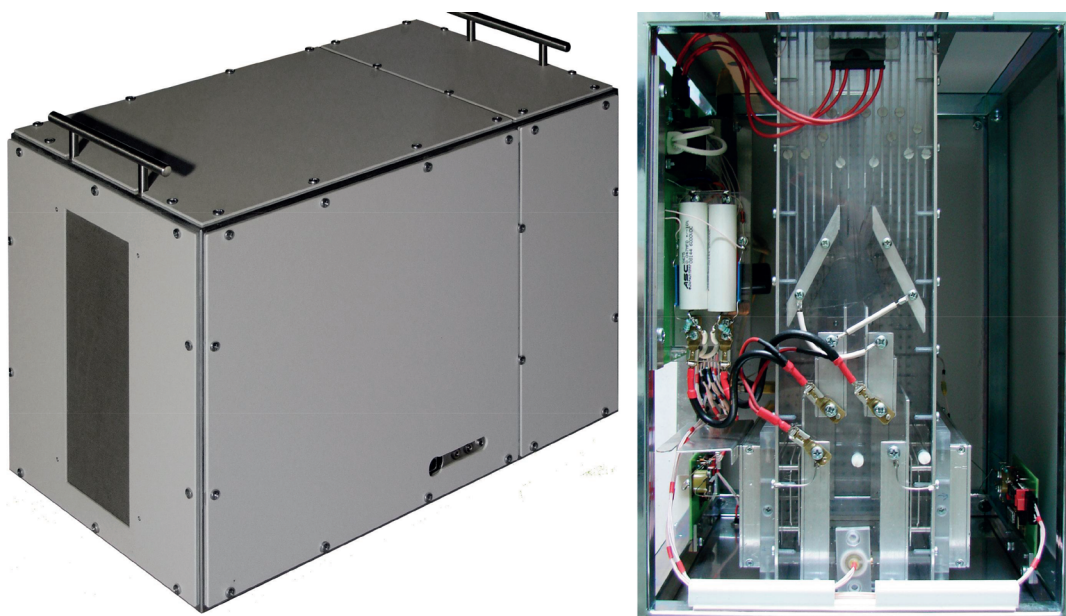
The instrumental noise is essentially decreased in the Scanning Inclined Grid Mobility Analyzer (SIGMA, Tammet 2011), which is designed as a replacement for BSMA and covers the same size range of 0.4–7 nm (Tammet's diameter). Here, the alternative method of shielded ion electrometric filter is applied to measure an electric current carried by ions. SIGMA is the first ion spectrometer, in which the positive and negative ions enter within the same inlet air stream (Fig. 3). The air enters the instrument through an inlet grid with a flow rate of 1800 lpm. The grid protects the instrument from spiders, insects, fuzz and hairs. Next, the air passes the inlet gate and the sheath air filter. The voltage of the sheath air filter is 520 V. The inlet gate is composed of the two central plates of the filter. The distance between the plates is 10 mm and the mean air speed is about  $2 \text{ m s}^{-1}$ . The loss of ions in the inlet tract due to the adsorption is 5% at the mobility of  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The inlet gate is open for the passage of air ions when the gate plates are on the zero potential. The potentials are computer-controlled. The critical mobility of the closed gate of  $0.031 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  is about the same as the mobility of the largest particles to be measured. A closed gate scan yields a zero record, which includes the effect of few large ions that may penetrate the sheath air filter, as well as the effect of the residual displacement current. The positive and negative ions are homogeneously mixed in the inlet gate just as in the outside air (Fig. 4). The ions that passed the inlet gate are deflected in the inclined electric field between the attracting and repelling electrodes depending on their polarity and mobility. The ions of critical mobility follow the trajectories (see Fig. 3) and reach the electrometric



**Fig. 3.** Simplified section of the SIGMA aspiration condenser. The condenser is symmetric, the left part measures the positive ions and right part the negative ions. The plates are marked with their ends indicating the polarity: ends with diamonds mark positive, with dots negative, and without markers zero potentials. The real geometric edges of all plates are straight.

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**Fig. 4.** The Scanning Inclined Grid Mobility Analyzer (SIGMA) is the first ion spectrometer, where the positive and negative ions enter within the same inlet air stream. The internal structure of the instrument is shown in the right-hand-side panel.

filters. The electrometric filters are shielded from the variable electric field with long zero-potential shield electrodes. A battery-powered and well-insulated electrometric filter consists of one attracting plate between the two zero-potential plates. The filters of positive ions and negative ions are connected to electrometric amplifiers and their output signals are recorded by the control computer. High sensitivity allows measuring of 16 fractions of positive and 16 fractions of negative air ions through two mobility decades in atmospheric air at standard 5-minute time resolution with random errors of about  $1 \text{ cm}^{-3}$ .

### Standardizing the ion spectrometer measurements and data processing

Recently we have harmonised both measurement performed by ion spectrometers and their data analysis (Manninen *et al.* 2016). We introduced a standard operation procedure on how to perform NAIS measurements and subsequent data processing. This standardization work was based on discussions between the NAIS users within the ACTRIS project (Aerosols, Clouds, and

Trace gases Research InfraStructure network) and the NAIS manufacturer (Airel Ltd., Estonia). The atmospheric particle formation data analysis routines for the NAIS, BSMA and SIGMA data, including estimating the contribution of ions to particle formation, calculating the cluster ion and aerosol particle formation and growth rates as well as ion-ion recombination rates, are described in detail in Kulmala *et al.* (2012).

### Our contribution to CPCs and PSMs development

#### Special considerations when measuring with condensation particle counters

Besides ion spectrometers, an important method to detect small aerosol particles is the condensation particle counting technology. The history of condensation particle counters (CPCs) dates back to the end of the 19th century, but only with the development of modern electronics in the 1970s, which made fast and continuous measurements possible, they became a widely used tool in aerosol science (McMurry 2000). The

working principle of CPC is to lead the aerosol sample into a region where a supersaturated vapor condenses onto the particles, growing them until they are large enough to be detected optically. Based on how the supersaturated vapor is created from the working liquid, CPCs can be classified into expansion type, mixing type and laminar flow type. The cut-off size (i.e. the smallest size when the instrument still detects 50% of particles) of CPC depends on the particle losses inside the instrument, and the activation efficiency of the particles. The activation efficiency describes the fraction of particles which start growing in CPC and can thus be measured. Due to the Kelvin effect, small particles require higher supersaturations to become activated, and therefore their activation efficiency decreases drastically. For a long time, the lowest cut-off size of commercial CPCs, so called Ultrafine CPCs (UCPC), was about 3 nm (Stolzenburg and McMurry 1991), as using higher supersaturation required to activate smaller particles, would lead to homogeneous nucleation inside the instrument.

In order to detect neutral atmospheric clusters, the cut off size of condensation particle counters should be below 3 nm. After theoretical estimation of the existence of big pool of very small particles and atmospheric clusters in size range 1–3 nm (Kulmala *et al.* 2000), the need to measure also sub-3 nm particles was obvious. The laboratory experiments conducted in Vienna (e.g. Winkler *et al.* 2008) showed that heterogeneous nucleation occurs much earlier than homogeneous one, as theoretically predicted. Kulmala *et al.* (2007c) developed a CPC battery to investigate the activation spectra of small particles as a function of their size and composition. They also performed theoretical studies comparing activation due to the Köhler effect or heterogeneous nucleation. The development of true low-cut-off CPCs started with the work of Iida *et al.* (2009) who evaluated the suitability of different condensing vapors for CPC measurements. They claimed that choosing a vapor with a high surface tension, but low saturation vapor pressure, would make it possible to measure at higher supersaturations without homogeneous nucleation.

## Development of condensation based techniques

Condensation Particle Counter applications with low cut-off sizes have been developed simultaneously and independently by several research groups around the world (e.g. Gamero-Castaño and Fernández de la Mora 2000, Sgro and Fernández de la Mora 2004, Hering *et al.* 2005, Jiang *et al.* 2011, Kuang *et al.* 2012). Here, we describe the work carried out at the University of Helsinki and its spin-off company Airmodus Oy, to allow detection of atmospheric neutral clusters, which cannot be measured with ion spectrometers. Thus, this work has been tightly connected to the goals of the air ion and aerosol workshops (*see* the last section of this manuscript), and the results were widely discussed during the workshops.

Our first effort to decrease the cut-off size was the modification of so-called Lithuanian CPCs (Mordas *et al.* 2005). A step towards measuring smaller particles was achieved, when it was recognized that if the counts originating from homogeneous nucleation could be separated from the sample particles, one could use higher supersaturations and thus activate smaller particles. Two CPC methods were applied by the University of Helsinki with this idea: expansion CPC and pulse-height (PH) CPC. They were first deployed at SMEAR II in Hyytiälä in 2007 and proved to be suitable for detection of sub-3 nm particles in field conditions (Sipilä *et al.* 2008).

Expansion CPC was used so that the expansion ratio (and therefore supersaturation) was changed periodically and a diffusion tube was applied to every second supersaturation scan to separate the activation of small particles from homogeneous nucleation. This clearly showed the existence of small clusters, but the method was not very quantitative (Lehtipalo 2011). The pulse-height analysis method can be used to give information about the size of small particles based on the fact that smaller particles activate later in the saturator and yield lower pulse-height (Saros *et al.* 1996). Sipilä *et al.* (2009) showed that PH-CPC can also be used to separate homogeneous nucleation from the activation of particles. It was used to measure the first long time series of nano-CN (clusters and sub-3 nm particles activated in CPC) at Hyytiälä and Mace Head (Lehtipalo *et al.* 2009,

2010) and the results were found to be comparable to measurements with ion spectrometers.

After the work of Iida *et al.* (2009), CPCs using diethylene glycol (DEG) were developed independently by several research groups (Vanhanen *et al.* 2011, Jiang *et al.* 2011, Wimmer *et al.* 2013). Unfortunately, diethylene glycol cannot grow the particles large enough for optical detection, so all of these applications use normal water/butanol CPC as a second growth stage after the initial growth with DEG.

The prototype version of the Particle Size Magnifier (PSM, Vanhanen *et al.* 2011) was developed in Helsinki in 2010. It differs from the other DEG-CPCs in the working principle, as it is a mixing-type instrument following the design of Sgro and Fernandez de la Mora (2004). This helps minimizing particle losses before activation, and allows changing the supersaturation easily. Before this, nobody to our knowledge had managed to make long-term measurements in field conditions with their mixing-type instruments, although low cut-off sizes have been reported in laboratory conditions. PSM was commercialized by Airmodus Oy. The current version of PSM together with its CPC is called nano Condensation Nucleus Counter (nCNC).

PSM was the first instrument to have a cut-off size close to 1.5 nm, and even lower for certain particle types (Vanhanen *et al.* 2011, Wimmer *et al.* 2013), while the previous CPC applications detected clusters with much lower detection efficiencies. PSM can also be used in a scanning mode, providing the activation spectrum of small particles which can be converted into a size distribution in the size range of about 1–3 nm (Lehtipalo *et al.* 2014) given a calibration between particle size and the response in PSM. Recently, there has been progress in the calibration methods in sub-3 nm sizes (Kangasluoma *et al.* 2013), and in the understanding of the performance of PSM for different particle types (Kangasluoma *et al.* 2014) and different environmental conditions (Kangasluoma *et al.* 2015).

## Combining mass and ion spectrometer measurements

In the framework of the Finnish–Estonian Air

Ion and Atmospheric Aerosol Workshops, several types of mass spectrometers have been used in combination with ion spectrometers.

The composition of negative air ions as a function of ion age and selected trace gases (iodine, diethylamine, water vapor) was studied in a laboratory by Luts *et al.* (2011a). They applied an advanced method, which combines the study of aging of air ions by both mobility and mass-spectrometry, using in parallel a triple quadrupole mass spectrometer (Sciex API-300, Applied Biosystems-SCIEX, Canada) and AIS. To gain more information on ion molecular structure and their building blocks, the mass spectrometer was operated also in MS-MS mode, where the selected ions were further separated in the dissociation chamber. It was found that the composition of negative air ions at an age of about 1 s is clearly different from that at about 20 s. Both diethylamine and iodine generate changes in the size distribution of air ions at sizes of 0.5–40 nm associated with atmospheric new-particle formation. The most prominent changes were induced by addition of iodine, which converts the mass spectrum of cluster ions into few dominant peaks at mass-to-charge ratios of 381 and 635, and generates numerous new large air ions with sizes of 4–40 nm. Examination of mass spectra of cluster ions enables identifications of the chemical species, which can be responsible for the observed mass peaks.

Ion spectrometers have been the main tools for studying atmospheric ions for a long time (Hörrak *et al.* 1994, 2000, Tammet 1995, 1998, Vana *et al.* 2004, Hirsikko *et al.* 2005, 2007b, 2011). While being excellent instruments with a robust design, good signal-to-noise ratio and high time resolution, they lack in a molecular-level resolving power. The ion spectrometers can separate between different mobility groups of ions, including small or cluster ions, intermediate ions and large ions (Hörrak *et al.* 2003). Commonly, the decade-to-eight mobility resolution was used for atmospheric measurements: eight fractions of ions on a mobility decade for small and intermediate ion mobility rangers. For a detailed understanding of ion kinetics and chemistry and their role in atmospheric gas-to-particle transformation, more accurate information about the chemical structure of the atmos-



pheric ions is needed. For this purpose, mass spectrometers combined with ion spectrometers provide an excellent means.

In addition to laboratory studies, ion spectrometers were compared with mass spectrometers also during field campaigns. The atmospheric ion number concentrations are relatively low (about  $1000\text{ cm}^{-3}$ ), and in order to be able to measure ambient ions, the instruments must have a good enough transmission and sensitivity. Typical mass spectrometers are not capable of sampling ions directly from the ambient air, but instruments specially developed for this purpose, such as APi-TOF (Atmospheric Pressure interface Time-Of-Flight mass spectrometer, Junninen *et al.* 2010), make this possible. At the Hyytiälä forest station SMEAR II, three instruments were operated in parallel: AIS, BSMA and APi-TOF (Ehn *et al.* 2011). This inter-comparison experiment revealed interesting information about the chemical composition of ions in the mobility channels measured by the ion spectrometers. The ions in the highest mobility channels were associated with inorganic ions (nitric and sulfuric acid), while gradually organic composition started to dominate when moving lower on the mobility scale. All three instruments compared well with each other after the conversion from mobility to mass-to-charge was mastered.

The first ambient measurements with APi-TOF (Ehn *et al.* 2010) revealed a set of organic peaks with composition  $\text{C}_{10}\text{H}_{14-16}\text{O}_{1-10}$  that were unknown at the time. Later studies (Ehn *et al.* 2012, 2014, Jokinen *et al.* 2014, Rissanen *et al.* 2014, Sipilä *et al.* 2014) showed that these compounds are products of  $\alpha$ -pinene reacting with  $\text{O}_3$  and OH. These reactions are initiated by  $\text{O}_3$  attacking the double bond in the  $\alpha$ -pinene molecule, which starts an auto-oxidation process that proceeds very fast after collisions with  $\text{O}_2$ , resulting in extremely-low-volatile oxidized organic compounds (ELVOC) that play an important role in aerosol growth (Ehn *et al.* 2014). APi-TOF, while measuring accurately the chemical composition and having an extreme sensitivity, is not quantitative. To obtain quantitative measurements, the ionization has to be controlled. This motivated the adaptation of the chemical ionization (CI) inlet introduced by Eisele and Tanner (1993) to APi-TOF,

and the development of  $\text{NO}_3\text{-CI-APi-TOF}$  (Jokinen *et al.* 2012). This instrument had a resolution and accuracy of APi-TOF and the sensitivity and selectivity of nitrate-based chemical ionization. The instrument is particularly suitable for ambient sulfuric acid, methanesulfonic acid and ELVOC measurements, and in fact for all the compounds that are stronger acids than nitric acid and form clusters with the  $\text{NO}_3^-$  ion.

This work also initiated a software development for analysing raw mass spectrometer data. At the University of Helsinki a *tofTools* toolbox for Matlab was developed (Junninen *et al.* 2010, Junninen 2013). The toolbox has all key functions for converting the raw acquired mass spectrometer signal to concentrations of ions or neutral molecules. It includes functions for mass calibration, sticking, high-resolution peak fitting, elemental composition and isotopic pattern calculations. It was used in multiple high impact scientific works (e.g. Kirkby *et al.* 2011, Kulmala *et al.* 2012, Almeida *et al.* 2013, Kulmala *et al.* 2013, Schobesberger *et al.* 2013, Ehn *et al.* 2014, Kürten *et al.* 2014, Riccobono *et al.* 2014, Jokinen *et al.* 2015).

## Development of research infrastructures

### SMEAR concept

The concept of a Station for Measuring Ecosystem–Atmosphere Relations (SMEAR) was introduced by Hari and Kulmala (2005). It has provided a valuable platform for conducting multi-disciplinary research on atmosphere–ecosystem exchange processes since 1995 when the SMEAR II station was established. Over that period, a network of SMEAR stations (Hari *et al.* 2009, Järvi *et al.* 2009) was created and the latest member of the family became operable in Estonia in 2013. Together with SMEAR I–IV (<https://www.atm.helsinki.fi/SMEAR/>) in Finland, the station transect spans more than 1000 km over northern Europe. The stations are located in different parts of the boreal biome ranging from the subarctic to the hemi-boreal transition zone at the southern edge of the boreal ecosystems. This enables studying and comparing processes

throughout different climatic zones and boreal ecosystems.

## SMEAR Estonia

Integrated and inter-disciplinary measurements of atmosphere–biosphere relations began in southeast Estonia in August 2008 at Järvelja. The first measurement campaign, which took place in close co-operation among the University of Helsinki, University of Tartu, University of Innsbruck and Estonian University of Life Sciences, produced a short but comprehensive data set (Noe *et al.* 2011) that initiated further common research (Noe *et al.* 2012, Bourtsoukidis *et al.* 2014, Niinemets *et al.* 2013, Laan *et al.* 2014, Smolander *et al.* 2014) utilizing the location in Järvelja, also in the following years. The planning and building of the SMEAR Estonia station (<http://smear.emu.ee/>) began in 2010 within the framework of a large-scale scientific infrastructure project: the Estonian Research Infrastructures Roadmap project “Estonian Environmental Observatory”. Since then, the station grew to a delocalized research infrastructure (with measurement sites in Apna and Liispõllu) employing a 130-m-high atmospheric mast, two 30-m and one 24-m high scaffolding towers, a main cottage to control atmospheric composition, fluxes and ecosystem related measurements and an aerosol cottage to control measurements of air ions and aerosol particle number concentrations, fluxes and size distributions located at the Järvelja Experimental Forestry Station.

In contrast to Finnish SMEAR I–IV, the forests at the SMEAR Estonia station are mixed, and the share of deciduous trees can reach 50%. The main coniferous species are the Scots pine and Norway spruce, whereas the main deciduous tree species are the silver and downy birch. The alder, aspen and rowan are also present but to a smaller degree. The forest around the SMEAR Estonia station grows on a drained peatland, which is a very fertile substrate, so typically the trees are up to 30–35 m in height. The canopy is dense and has one or more suppressed tree layers within it, which leads to a different turbulent flow inside the forest canopy than the flow in typical boreal forest canopies at SMEAR I–II and IV.

Additional measurement locations of SMEAR Estonia are the Valgjärve telecom tower, where meteorological parameters are measured at the height of up to 200 m above ground, and the Tartu Observatory (located in Tõravere) where spectral analyses and remote sensing research are being conducted.

Measurements of aerosols and air ions close to the current location of the SMEAR II Estonia station have been conducted since 2008. During the first years, these had been limited to measurement campaigns of short to mid-range time frames, mostly during summer and autumn months. Since June 2012, the measurements have been carried out during the whole season and started to be continuous with only short breaks for the instrument maintenance. In addition to measuring the mobility and size distributions of air ions and aerosol particles, the station measures continuously the atmospheric chemical composition (CO<sub>2</sub>, water vapor, methane, ozone, NO<sub>x</sub> and SO<sub>2</sub>), basic meteorological variables and episodically also CO and volatile organic compounds. Soil gas exchange and properties are being measured partly automatically, and tree-related parameters are being assessed either continuously or episodically depending on the measurement methodology.

Air ions and aerosol particles are measured with a multitude of analyzers (NAIS, EAS), spanning a size range from 0.4 nm to 10 μm. Measurements cover aerosol particle number concentrations and size distributions, air ion mobility distributions and also aerosol particle concentrations are measured above and inside the tree canopy. The particle flux measurements by Eddy-covariation technique (applying the NAIS and Metek 3D sonic anemometer) were started on the top of the 30-m-high scaffolding tower. The SMEAR Estonia station is still developing, and new equipment (aerosol spectrometers SMPS, APS, OPS, FMPS, radon and gamma-radiation monitor, etc.) will be installed in 2016 or 2017 to complete the set of measurements.

An overview of the development of the SMEAR Estonia station since 2008 and the first results have been published by Noe *et al.* (2015). These include meteorological variables and eddy covariance fluxes of carbon dioxide (CO<sub>2</sub>) and water vapor (H<sub>2</sub>O) to characterize the general

forest ecosystem parameters: net ecosystem exchange, gross primary production and ecosystem respiration, as well as dynamic footprint the fetch area of the 130-m tower. Some results of aerosol measurements were discussed during Finnish–Estonian workshops and published in the paper by Laan *et al.* (2014), but the paper by Vana *et al.* (2016) is the first one in which the measurements carried out at SMEAR-Estonia are thoroughly discussed.

## Atmospheric observations with ion spectrometers all around the world

### Direct observations of atmospheric new-particle formation

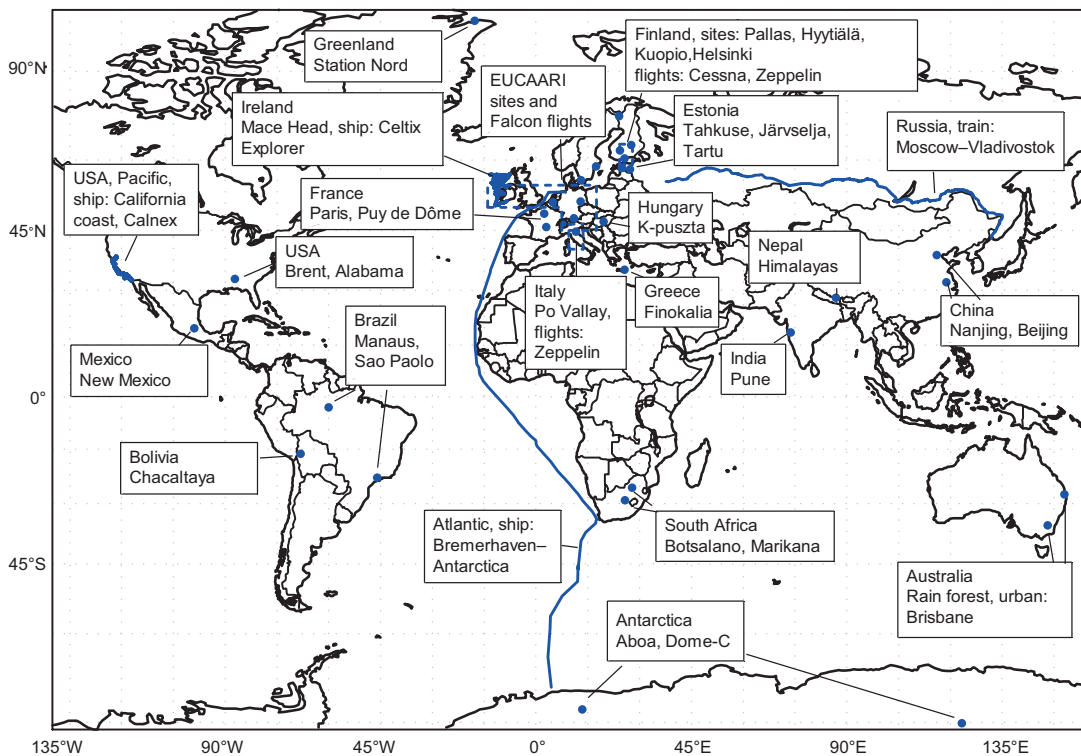
A clear indication of neutral clusters were found by Kulmala *et al.* (2007b) and their size dependent growth in 2013 (Kulmala *et al.* 2013). Besides air ion spectrometers also PSMs as well as CI-API-TOFs have been utilised in recent observations. For example, in 2015 our most recent field campaigns were performed at an Arctic site Station Nord in Greenland, at an Antarctic site Aboa in Antarctica, and at a high-altitude site in the Himalayas, Nepal. All these campaigns included AIS/NAIS, PSM and CI-API-TOF measurements.

The list of locations and altitudes where frequent aerosol particle formation has been observed is still growing as new measurement campaigns are organized and field sites are being established (reviewed by Kulmala *et al.* 2004, Hirsikko *et al.* 2011). Here, however, we focus on measurements performed using air ion spectrometers. Locations where ion spectrometer measurements were carried out using instruments which have originated from the Finnish–Estonian air ion workshops are shown in Fig. 5. Among those are the Trans-Siberian railroad (Vartiainen *et al.* 2007) and the hot air balloon flights at Hyytiälä, Finland (Laakso *et al.* 2007b). The ion spectrometer measurements performed within the EUCAARI project (Kerminen *et al.* 2010) were, so far, the most comprehensive effort to experimentally characterize nucleation and growth of atmospheric molecular clusters

and nanoparticles at ground-based observation sites on a continental scale (Manninen *et al.* 2010). Atmospheric new-particle formation (NPF) is often a regional phenomenon. Our most recent (2013–2015) in-flight measurements with NAIS on-board Zeppelin PEGASOS and a Cessna airplane showed that even within regional NPF bursts, there exist small-scale variations in both number concentration and size of newly-formed particles.

Extensive experiments to investigate the vertical extend of NPF with NAIS were made at high-altitude stations in Jungfraujoch, Swiss Alps (3580 m a.s.l.; Manninen *et al.* 2010), on the Puy de Dôme, France (1465 m a.s.l.; Boulon *et al.* 2011), and in Chacaltaya, Bolivia (5240 m a.s.l.; Rose *et al.* 2015), as well as using aircraft (Laakso *et al.* 2007b, Mirme *et al.* 2010). Depending on the measurement location, the NPF studies conducted within a boundary layer can roughly be divided into two types: (1) clean or remote environments, including Aboa in Antarctica (Virkkula *et al.* 2007), Pallas in Finland (Lihavainen *et al.* 2007), Eucalypt forest in Australia (Suni *et al.* 2008), Amazon in Brazil (Martin *et al.* 2010), Pune in India (Siingh *et al.* 2013), Tahkuse and Tõravere in Estonia (Tamm et al. 2014), Järvelja (SMEAR-Estonia) and Estonia in general (Vana *et al.* 2016); and (2) polluted urban environment, including Sao Paulo in Brazil (Backman *et al.* 2012), Marikana in South Africa (Hirsikko *et al.* 2013), Nanjing in China (Herrmann *et al.* 2014), Melpitz station in Germany (Größ *et al.* 2015) and Po Valley in Italy (Kontkanen *et al.* 2016). Anthropogenic particles have been studied with (N) AIS at road sides and indoors (Tiitta *et al.* 2007, Hirsikko *et al.* 2007a, Jayaratne *et al.* 2014). Several atmospheric relevant laboratory studies were conducted to investigate the connection between small cluster ions and NPF (Duplissy *et al.* 2010, Kirkby *et al.* 2011, Ortega *et al.* 2012b, Franchin *et al.* 2015).

Investigation of the NPF events by means of ion spectrometers (BSMA, SIGMA, UT-7509 (KAIS), (N)AIS) revealed that intermediate ions are always present in the atmosphere, also during the quiet periods between NPF events, and should be considered an indicator and mediator of NPF (Tamm et al. 2013, 2014). The KAIS



**Fig. 5.** Locations where ion spectrometer measurement were carried out. Measurement sites are indicated with blue dots, the trip by train through Siberia (Russia); the boat trips from Europe to Antarctica, along the California coast, and in North Sea with solid blue lines; and the flights in Europe within EUCAARI and PEGASOS projects with blue dashed lines. All these measurements were made using instruments originating from either the University of Tartu or Airel Ltd., Estonia.

mobility spectra of ions with an age of about 1 s demonstrated almost no ions below the mobility of  $0.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (ca 1.3 nm in Tammet's diameter), which is also valid in the case while the BSMA spectra demonstrate NPF events (Luts *et al.* 2011b). We conclude that the ions, which appear in the BSMA spectra during NPF events, are definitely older than about 1 s.

NPF can occur over distances of 100 km, and moderate air pollution in small cities like Tartu cannot suppress regional-scale NPF events (Tammet *et al.* 2014).

The concentration of intermediate ions at stations separated by around 100 km appeared to be correlated. The lifespan of intermediate ions in the atmosphere is a few minutes, so they cannot be carried by wind over long distances. Thus, the observed long-range correlation is explained by simultaneous changes in air composition over large distances. Studies by Vana *et al.* (2004,

2016) showed that NPF is a regional or synoptic-scale phenomenon that can occur simultaneously at several stations (Värriö, Hyttiälä, Tahkuse, Järvelja) over distances 1000 km when Arctic anticyclonic air masses move from the north to the south.

### Open access data sets of atmospheric observations with ion spectrometers

Some air ion mobility and size distribution measurements are stored in the open access DataCite repository (Tammet 2015). The data set whose doi:10.15155/repo-4 includes measurements made during 2003–2006 using a multichannel spectrometer in Tahkuse (Estonia) and using BSMA-s in Hyttiälä (Finland) and Tartu (Estonia). The measurements made during 2010–2011 using SIGMA in Tartu are available

in the dataset doi:10.15155/repo-2. The dataset doi:10.15155/repo-7 contains mobility distributions of one-second-aged corona-generated small air ions recorded in Tartu by means of air ion spectrometer UT-7509 (also called KAIS) in 2011 during three months in year 2011. The data set consisting the EUCAARI ion spectrometer measurements at 12 European sites was submitted to EBAS database (<http://ebas.nilu.no/>).

### **Evaluation of intermediate ion bursts: Balloelectric effect**

Measurements in Hyytiälä, Tahkuse and Tartu showed formation of large amounts of negative intermediate ions (1.6–7.4 nm) during rain events due to the balloelectric effect when the raindrops are splashing on the ground, trees or roofs of buildings. The effect was first discovered during the BSMA and AIS measurements carried out in Hyytiälä in August 2003 and reproduced in the laboratory experiments in Tartu in May 2004 (Hörrak *et al.* 2006). The mechanism of this phenomenon was studied by Tammet *et al.* (2009, 2014). The balloelectric ions produced in the laboratory from tap water with a high concentration of dissolved solids had the same mobility distribution as ions produced from rainwater. The balloelectric ions cannot therefore be solid residues of evaporated spray droplets, but they are rather expected to be singly charged water nano-droplets or superclusters with diameters of about 2.5 nm. The observations can be explained by the hypothesis that the pressure of saturated vapor over the surface of a balloelectric ion is suppressed by several orders of magnitudes due to the specific internal structure of the water droplets near the size of 2.5 nm. The records of rain-event balloelectric ion mobility distributions in the atmosphere are similar to the records during new-particle formation events. However, the balloelectric ion events cannot be qualified as new-particle formation because the water nanoparticles are not growing but shrinking.

The balloelectric mechanism was found to be responsible for the intermediate ion formation in the vicinity of waterfalls (Laakso *et al.* 2007c, Parts *et al.* 2007, Luts *et al.* 2009). Some hypotheses of waterfall-induced intermediate ion

formation were outlined by Laakso *et al.* (2006), but unfortunately not discussed in the following paper (Laakso *et al.* 2007c). Correlative study of air ion classes of small (diameter < 1.5 nm), intermediate (1.5 nm < diameter < 10 nm) and large air ions (10 nm < diameter < 40 nm), modification of air ion mobility distributions nearby the waterfall and some pathways of waterfall generated ions, with preference to negative intermediate ions, were discussed by Luts *et al.* (2009).

### **Theoretical improvements, models, relations to quantum chemistry**

#### **Improvements in classical theory**

In the frame of the classical nucleation theory, our model for ion-induced nucleation was developed further (Noppel *et al.* 2013a, 2013b). The earlier model assumed a complete spherical symmetry of the nucleating system, implying that the seed ion is immediately surrounded by the condensing liquid from all sides. In the developed model, more realistic geometries were considered, where a cap-shaped dielectric liquid cluster forms on the surface of the charged seed particle. A thermodynamically consistent expression for reversible or minimal work needed to form a nucleus within a uniform macroscopic one- or multicomponent mother phase was derived. The expression takes into account the spontaneous polarization of surface layer molecules of nucleus. The derived equilibrium conditions describe the shape, size, and composition of critical nucleus.

Luts *et al.* (2015) developed a new method for automated estimation of parameters controlling atmospheric new-particle formation (NPF), applying previously published simulation tool for atmospheric aerosol nucleation bursts (Tammet and Kulmala 2005, 2007) as a core component of the method. The new method solves automatically the inverse problem estimating the physical input parameters of NPF by recurrent simulations according to the criterion of best fit of the simulated output parameters with the measured and known data. The



method enables the estimation of several physical parameters, e.g. the nucleation rate, particle growth rate, contribution from ion-induced and neutral nucleation, and particle charging state.

### Cluster dynamics

Molecular clustering is a crucial step in new-particle formation (e.g. Kulmala *et al.* 2014), and we have first developed simple cluster dynamic code based on the concept of virtual monomers (Kulmala 2010), and later a more advanced Atmospheric Cluster Dynamics Code (ACDC, McGrath *et al.* 2012), which solves the multi-component birth and death equations for a set of small clusters. The collision and evaporation rates in ACDC can be taken from any level of theory, for example kinetic gas theory and classical liquid drop model or molecular dynamic simulations and quantum chemical cluster binding energy calculations (Ortega *et al.* 2012a).

We used ACDC particularly for the sulphuric acid-ammonia system (Kurtén and Vehkamäki 2008) as well as for the sulphuric acid-dimethylamine system (Loukonen *et al.* 2010), by taking the collisions rates from the kinetic gas theory and using quantum chemistry to predict the evaporations rates. For these systems, ACDC has been successfully used to explain experimental cluster compositions observed e.g. in the CLOUD chamber (Almeida *et al.* 2013, Olenius *et al.* 2013). ACDC is a detailed and physically sound model particularly for small clusters (< 10-mers), where evaporation coefficients can be calculated by using quantum chemistry.

### Ions and atmospheric aerosol dynamics

Over the years, we have developed various theoretical and modelling tools for investigating the effect of ions on basic aerosol dynamical processes in the atmosphere. An example of the conducted model development is Ion-UHMA (Leppä *et al.* 2009), a zero-dimensional sectional box model that simulates the dynamics of neutral and electrically-charged aerosol particles under atmospheric conditions. Ion-UHMA does not

simulate the actual nucleation process but takes the formation rates of neutral and charged particles as model inputs. It is thereby not restricted to any particular nucleation mechanism or specific chemical compounds.

A widely-used theoretical concept in atmospheric-ion studies is the aerosol charging state which tells us whether the particles have more or less charges than what one would expect based on their equilibrium charge fraction (Laakso *et al.* 2007a). Kerminen *et al.* (2007) developed a general theoretical framework that describes the evolution of the charging state of a growing nanoparticle population, and Gagne *et al.* (2012) refined this framework further. We have applied these tools to several measurement data sets in order to estimate the contribution of ion-induced nucleation to atmospheric new-particle formation (e.g. Gagne *et al.* 2008, 2010) and, together with ion-UHMA simulations, to investigate whether the charging state could also be used to determine nanoparticle growth rates (Leppä *et al.* 2013).

Leppä *et al.* (2011) investigated the effect of ions on aerosol growth processes and derived simple analytical formulae by which one can estimate the real growth rate of nucleation mode particles due to their self-coagulation as well as their apparent growth rate due to their coagulation scavenging with larger pre-existing particles. They also found that compared with a neutral particle population, the presence of ions increases the rate of self-coagulation and coagulation scavenging by a factor of 1.5–2 under typical atmospheric conditions.

### Parameterizations

We developed parameterizations on ion-induced nucleation and size-dependent atmospheric nanoparticle growth based on our observations (e.g. Paasonen *et al.* 2010, Nieminen *et al.* 2011, Yli-Juuti *et al.* 2011, Kontkanen *et al.* 2013, Häkkinen *et al.* 2013). Implementation of these parameterizations to large-scale atmospheric models is an interesting next step in order to reach the full scientific understanding.



## Current status and future outlook

Kulmala and Tammet (2007) have defined nine research topics to be studied in the future. Here we summarize these topics and also give a brief update on the current status of our joint research.

1. Continuous air ion cluster and nucleation mode aerosol particle measurements particularly at the SMEAR II station in Hyytiälä and simultaneous air ion measurements in Estonia, particularly at Tahkuse, Estonia, and elsewhere will continue.

Current status: The continuous measurements are being performed at several sites around the world, and recently PSM, NAIS and CI-API-TOF are used when available.

2. Development of NAIS and other instrument (BSMA, SIGMA, ion-DMPS, etc.) is continued.

Current status: The new instruments developed and also NAIS was notably updated, including air sample preconditioning unit, airflow system, data acquisition system, and measurement software that is now much more user orientated than before. The most important modifications were a new flow scheme improving the reliability of the instrument and allowing it to perform measurements at varying air pressure (e.g. aircraft-based measurements) and updated data acquisition electronics improving the time resolution and signal-to-noise ratio of the measurements.

3. The world-wide measurements will continue as campaign-wise measurements.

Currents status: Several campaigns were performed (Fig. 5), and also increasing numbers of continuous measurements are currently in operation.

4. The data set we have collected is unique and data analysis will take several years. Using these data, we will calculate: (i) the contribution of ion-induced nucleation to total atmospheric nucleation, (ii) concentrations and source rates of condensable vapours (see Kulmala *et al.* 2001, Kulmala *et al.* 2005, Dal Maso *et al.* 2005), (iii) ion characteristics and their differences in different environments. As a part of this study, we will develop theo-

retical methods for ion spectrometer and ion-DMPS data analysis.

Currents status: The results of the analyses that have been made to date are presented in e.g. Gagne *et al.* (2008, 2010), Hirsikko *et al.* (2011), Manninen *et al.* (2010), and Kerminen *et al.* (2010).

5. Our recent observations have shown that there are several unknown ion phenomena related to water droplets and ice crystals (Hirsikko *et al.* 2007b).

Currents status: This work is still in progress. This phenomenon has been observed in several studies (e.g. Virkkula *et al.* 2007, Manninen *et al.* 2010), including studies on the formation of balloelectric intermediate ions (Tammet *et al.* 2009, 2014).

6. Our measurements have shown some inconsistency of the air ion generation and balance models in the boreal forest (Laakso *et al.* 2004, Tammet *et al.* 2006, Hirsikko *et al.* 2007a).

Currents status: This work is still in progress. It was found that the small ion sink caused by ion deposition inside the coniferous forest canopy should be taken into account in the balance equation (Tammet *et al.* 2006, Hörrak *et al.* 2008). A new method for the estimation of ionization rate of air and ion sink has been developed by Hörrak *et al.* (2015).

7. One unknown phenomenon 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 the processes related to cosmic ray-climate interactions in an aerosol and cloud chamber in CERN, Switzerland in a project called CLOUD.

Currents status: Based on analysing an extensive set of field measurements, we found no evidence on the potential association between the flux of cosmic rays into the atmosphere and atmospheric new-particle formation (Kulmala *et al.* 2010). The CLOUD experiments, while not directly connected to our air ion workshops, have provided a lot of new data and insight into this phenomenon (e.g. Kirkby *et al.* 2011, Franchin *et al.* 2015), and

the work is still in progress.

8. We will continue to develop basic theories related to ion processes (e.g. Lushnikov and Kulmala 2004a, 2004b, 2005, Noppel *et al.* 2003), and also apply quantum chemistry models (Kurtén *et al.* 2007).

Currents status: This work is in progress. Heterogeneous nucleation theories in multi-component vapours on charged particles have been advanced (Noppel *et al.* 2013a, 2013b), and the role of clusters properties in the atmospheric sulfuric acid nucleation was investigated (Kurtén *et al.* 2010).

9. During the last years, we 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 for several aerosol dynamic processes. Ultimately, we aim to parameterize the results for global climate models.

Currents status: The ION-UHMA model was developed (Leppä *et al.* 2009) and several new parametrisations on aerosol formation and growth were derived (Nieminen *et al.* 2011, Kontkanen *et al.* 2013, Häkkinen *et al.* 2013).

In summary, we have made a lot of progress particularly in developing new instruments and right now we are able to measure the 1–3 nm size range from the concentration and composition point of view pretty well. Currently, our main open research questions related directly to the work that builds on the Finnish–Estonian air ion and aerosol workshops are the following:

1. What is the ion-induced contribution to NPF at different environments and how has it been changing comparing past, present and future climate?
2. How accurately are we able to measure gaseous precursors and their oxidation to extremely-low-volatile compounds, and what are these compounds?
3. Why is the ion-induced nucleation rate always smaller than the ion production rate in atmospheric conditions?
4. Are we able to estimate or even quantify the composition of neutral clusters using only ion spectrometers and API-ToF?

In a wider perspective, we strive to contribute to addressing the following research issues:

6. How to improve models from basic processes to global climate and urban air quality based on the knowledge we already have and will obtain?
7. Where does the nucleation process starts in the atmosphere? Does it start from the ground level or residual layer of atmospheric boundary layer?
8. How does the forest ecosystem affect the NPF and particle fluxes?
9. What is the contribution of new particles produced during quiet periods of nucleation to the concentration of nucleation mode particles in the atmosphere, and how it is affected by the concentration of pre-existing aerosol particles.

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