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# Atmospheric ions and nucleation: a review of observations

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## Abstract

This review is based on ca. 250 publications, from which 92 published data on the temporal and spatial variation of the concentration of small ions (<1.6 nm in diameter) in the atmosphere, chemical composition, or formation and growth rates of sub-3 nm ions. The small ions exist all the time in the atmosphere, and the average concentrations of positive and negative small ions are typically 200–2500 cm$^{-3}$. However, concentrations up to 5000 cm$^{-3}$ have been observed. The results are in agreement with observations of ion production rates in the atmosphere. Concentrations of small ions increased in the early morning hours due to night time inversion, which leads to accumulation of radon. We also summarised observations on the conversion of small ions to intermediate ions, which can act as embryos for new atmospheric aerosol particles. Those observations include the formation rates ($J_2$[ion]) of 2-nm intermediate ions, growth rates (GR[ion]) of sub-3 nm ions, and information on the chemical composition of the ions. Unfortunately, there were only a few studies which presented $J_2$[ion] and GR[ion]. Based on the publications, the formation rates of 2-nm ions were 0–1.1 cm$^{-3}$ s$^{-1}$, while the total 2-nm particle formation rates varied between 0.001 and 60 cm$^{-3}$ s$^{-1}$. The ion-mediated processes were observed to dominate when the total particle formation rates were small, and, accordingly the importance of ion-induced mechanisms decreased with increasing total 2-nm particle formation rates. Furthermore, small ions were observed to activate for growth earlier than neutral nanometer-sized particles and at lower saturation ratio of condensing vapours.

## 1 Introduction

Atmospheric aerosol particles influence the Earth's climate system (e.g., Myhre, 2009; Quaas et al., 2009), impair visibility (Hand and Malm, 2007), and have adverse effects on human health (e.g., Russell and Brunekreef, 2009). These effects of atmospheric aerosol particles are dependent on their number concentration, size, chemical composition, and to some extent, their charge.

Atmospheric ions or air ions are carriers of electrical current in the atmospheric air. Electrical conductivity of air was discovered by G.W. Richmann at 1744 (Richmann, 1744, 1956) and rediscovered by C.A. Coulomb (1785). The ionisation of neutral molecules was proposed as the source of conductivity by M. Faraday (1834) who wrote: "*…Finally, I require a term to express those bodies which can pass to the electrodes… I shall call them ions*". The quantitative research of laboratory-generated air ions begun under supervision of J.J. Thomson in the Cavendish Laboratory (Thomson, 1903), where the time-of-flight method was proposed by E. Rutherford (1897) and the aspiration method was proposed simultaneously by J. Zeleny (1898) and J.A. McClelland (1898). Natural atmospheric ions were not considered in these early studies. The pioneers in the atmospheric ion studies were Elster and Geitel (1899), Ebert (1901), and Langevin (1905). The early research of air ions is well summarised by Israël (1970) and Flagan (1998). Formerly, research on air ions mainly focused on atmospheric electricity, however, the data has also been used to monitor air quality and radioactivity (e.g., Misaki et al., 1972a,b, 1975; Tuomi, 1989; Israelsson and Knudsen, 1986; Retalis and Pitta, 1989). During the last decades atmospheric aerosol scientists have also recognised the importance of air ions.

Air ions larger than 1.6 nm in mass diameter are considered charged aerosol particles according to their physical nature (Tammet, 1995), whereas smaller air ions are charged molecules or molecular clusters (e.g., Ehn et al., 2010a; Junninen et al., 2010). The atmospheric electricity measurement community usually divides the air ion population into small, intermediate and large ions considering to size, and these ion modes were already observed in the early decades of electrical aerosol measurements (Elster and Geitel, 1899; Langevin, 1905; Pollock, 1915; Israël, 1970; Flagan, 1998). The same classification scheme will be used in this paper. However, in some studies the term "cluster ion" has been used to describe the whole small ion population (e.g. Hõrrak et al., 2000; Hirsikko et al., 2005). The air ion classification was further developed based on long term measurements at Tahkuse Observatory, Estonia, and the boundary between the intermediate and large ions was found to be at 7.4 nn in mass diameter (Hõrrak et al., 2000, 2003).

The primary sources of air ions are radon decay, gamma radiation, and cosmic radiation (Israël, 1970; Bazilevskaya et al., 2008). Other ionisation mechanisms are insignificant sources of air ions in the lower atmosphere (Harrison and Tammet, 2008). Other known sources for small ions are traffic, power lines and splashing water (e.g., Eisele 1989a,b; Haverkamp et al., 2004; Tammet et al., 2009). Primary ions (single charged positive ions and free electrons) form via ionisation of air molecules, and they change into small ions in less than a second. During their life time of ca. 100 s, small ions undergo a series of ion-molecule reactions and continuously change their chemical identity. Thus, the chemical composition of small ions depends on the age of the ions and on the trace gas concentration in the air (Mohnen, 1977; Keesee and Castleman, 1985; Viggiano, 1993; Luts and Parts, 2002; Parts and Luts, 2004). Air ions are redistributed into particles of different sizes by coagulation with pre-existing aerosol particles and by their growth to larger sizes, whereas they are lost by ion-ion recombination and dry deposition (Hidy, 1984; Hoppel and Frick, 1990; Seinfeld and Pandis, 1998; Tammet et al., 2006).

Small ions exist practically all the time and throughout the troposphere, as evidenced by a large number of observations made both close to the Earth's surface and at various altitudes up to several kilometres (e.g., Arnold et al., 1978; Eichkorn et al. 2002; Dhanorkar and Kamra, 1993a; Vartiainen et al., 2007; Hirsikko et al., 2005, 2007c; Virkkula et al., 2007; Vana et al., 2008, Suni et al., 2008; Laakso et al., 2008; Venzac et al. 2007, 2008; Mirme et al., 2010). In contrast, intermediate ions are usually detected only during periods of new-particle formation, snowfall or falling water droplets, or at high-wind speed conditions (snowstorm) in winter (e.g. Hõrrak et al., 1998b; Hirsikko et al., 2005, 2007a; Virkkula et al., 2007; Laakso et al., 2007b; Tammet et al., 2009; Manninen et al., 2010). When new aerosol particles are formed by nucleation, intermediate ions are produced by ion-mediated pathways or via the attachment of small ions to newly-formed neutral particles (e.g., Iida et al., 2006).

Several review articles that discuss various aspects of air ions have recently been published. These reviews show that while atmospheric new-particle formation is a frequent phenomenon taking place almost all over the world (Kulmala et al., 2004a; Smirnov, 2006; Kulmala and Kerminen, 2008), the role of ions in this process is not well quantified (e.g., Kulmala and Tammet, 2007; Enghoff and Svensmark, 2008; Arnold, 2008; Yu and Turco, 2008; Manninen et al., 2010). In a global perspective, ion-aerosol-cloud interactions have potential climatic implications (Harrison and Carslaw, 2003; Kazil et al., 2008).

Despite the increasingly active research on air ions during last decade, no comparative studies on the evolution of small ion concentrations in different environments have been published to date. The main focus of this review is to provide a comprehensive overview of the spatial and diurnal variations of the naturally created small ion concentrations in atmosphere, along with the dependence of these concentrations on the ion sources and sinks. Another focus is to look at the connection between the air ions and atmospheric new-particle formation. We begin our analysis by introducing theory of the mobility-diameter conversion and balance equation for small ion population (Sect. 2), continue with the relevant measurement devices (Sect. 3), small ion observations (Sect. 4) and connections between ion and atmospheric new-particle formation (Sect. 5), and complete by presenting some concluding remarks (Sect. 6).

## 2 Air ions

In this section we discuss the understanding related to conversion of mobility to diameter, since typically mobility distributions are measured but size distributions presented (Sect. 2.1). In Sect. 2.2 we discuss the balance equation for small ions and in the Sect. 2.3 connection between air ions and conductivity is discussed.

## 2.1 Physical parameters of air ions

The physical parameters of an air ion are its mass $m$, diameter $d$, density of ionic matter $\rho$, electric charge $q$, and electrical mobility $Z$. The electric charge of small ions in the atmosphere is always one elementary charge $q=e$ (e.g., Hinds, 1999) and the diffusion coefficient $D$ is related to the mobility according to the Einstein relation

$$D = \frac{kTZ}{q}, \tag{1}$$

where $k$ is the Boltzmann constant and $T$ is temperature in Kelvin. The mass of an ion can be unambiguously measured by means of a mass spectrometer and the electrical mobility can be measured by means of a mobility analyser. Thus only two parameters, diameter ($d$) and density ($\rho$) of particles, are not unambiguously defined.

A term "mobility size" is often used in aerosol research. Unfortunately, this term is ambiguous, because different authors use different models of size-mobility relation (see Mäkelä et al., 1996; Li and Wang, 2003; Ehn et al., 2010b). The traditional macroscopic model that assumes a particle as a sphere with an exactly determined geometric surface is not adequate in the nanometer size range. In atomic physics, the microscopic particles are characterised by the interaction potential and collision cross-sections. The concept of the surface is sometimes not applicable and particles are characterised by continuous coordinate functions. Mason (1984) proposed mass diameter

$$d_\mathrm{m} = \sqrt[3]{\frac{6m}{\pi\rho}} \tag{2}$$

as a parameter of an ion. The concept of size of an aerosol particle was analysed by Tammet (1995) and the mass diameter was recommended as a preferable universal model parameter of an ion or aerosol particle.

Tammet (1995) derived a semi-empirical size-mobility model, which approaches the Chapman-Enskog equation when the particle size decreases and the Millikan equation when the particle size increases (Chapman and Cowling, 1970; Millikan, 1923).

The concept of size was preserved using the (∞-4) potential from kinetic theory and the transfer between the microscopic and macroscopic limits was accomplished by accounting for the dependence of the law of the reflection of gas molecules on the particle size and considering of the collision distance as a function of the interaction energy. The result was formulated as a computing algorithm given by Tammet (1995) and later corrected by Tammet (1998). Another sophisticated model (Li and Wang, 2003) is based mostly on theoretical calculations.

Unfortunately, the sophisticated models are in some respects inconvenient in the practice of air ion and aerosol measurements. If the size range below 1.5 nm is not important, the models can be essentially simplified. In this case the main difference between the Tammet model and the classic Stokes-Millikan model is the consideration of the gas molecule size that is approximately 0.3 nm. In Fig. 1 we present a simple relationship between mass diameter, mobility and mobility diameter. The solid lines show the conversion between mass diameter and mobility according to a modified Stokes-Millikan formulation (Ku and de la Mora, 2009), and the dashed lines a similar conversion based on the formulation by Tammet (1995).

Ku and de la Mora (2009) studied the size to mobility conversion in laboratory with different liquid and solid particle samples. They found that the original Stokes-Millikan law, as presented by Friedlander (1977) agrees with the observation down to $d = 1.3$ nm for spherical particles if $d_{\text{Millikan}} = d_m + d_g$, where the gas molecule diameter $d_g = 0.3$ nm. These results were confirmed by observation in natural air in Hyytiälä, Finland (Ehn et al., 2010b). Larriba et al. (2011) found that the 0.3 nm correction was accurate to within 3.84% and 14.3%, respectively for particles with volume diameters of 1.21 nm and 0.68 nm.

The small negative ions typically have a larger mobility than the positive ones (Hõrrak et al., 1994, 2000; Harrison and Aplin, 2007). Air chemistry, temperature (Salm et al., 1992) and pressure as well as sink due to aerosol particles affect the mean mobilities of small ions. Thus different values of the mean mobility of small ions in both polarities have been reported in literature (e.g., Eichmeier and Braun, 1972; Suzuki et al., 1982;

Hõrrak et al., 1994).

## 2.2 The formation and loss of small ions

The concentration of air ions changes in time due to different formation and loss processes according to the simplified balance equations:

$$\frac{dn}{dt} = q - \beta_{\mathrm{eff}} Z_{\mathrm{tot}} n - \alpha n^2 \tag{3}$$

or

$$\frac{dn}{dt} = q - \mathrm{CoagS} \cdot n - \alpha n^2 . \tag{4}$$

Equation (3) is from Israël (1970) and Eq. (4) is a modified form of that equation from Kulmala et al. (2001). New air ions are formed via air molecule ionisation (the first terms on right hand side). At the same time they are lost by the coagulation with the pre-existing aerosol with a total concentration of $Z_{\mathrm{tot}}$ (the second term in Eq. 3). In Eq. (4), coagulation is described by coagulation sink coefficient CoagS (Kulmala et al., 2001), which is obtained by integrating over the particle size distribution. In addition ions are lost via ion-ion recombination (the third terms on right). The coefficient $\alpha$ is the ion-ion recombination coefficient, and $\beta_{\mathrm{eff}}$ is the efficient ion-aerosol attachment coefficient. Growth and dry deposition are additional sinks for small ions, which are missing from Eqs. (3) and (4) (Tammet et al., 2006; Hõrrak et al., 2008). When using Eqs. (3) and (4) we assume equal concentrations of small positive and negative ions and symmetrical charging of aerosol particles.

Based on the balance Eqs. (3) and (4) we can calculate the maximum limit for small ion concentration if we assume a steady state situation and exclude the effect of background aerosol, thus ending up to the equation $q=\alpha n^2$. The coefficient $\alpha$ is about $1.6\times10^{-6}\mathrm{cm}^3\mathrm{s}^{-1}$ under typical atmospheric conditions (Israel, 1970; Hoppel, 1985; Hoppel and Frick, 1986). With these assumptions, ion production rates $q$=2, 10 and

$100\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$ lead to concentrations of positive and negative small ions of 1100, 2500 and $7900\,\mathrm{cm}^{-3}$, respectively.

### 2.3 Relation between small ions and air conductivity

As discussed in the introduction air conductivity was discovered already 1700s (Richmann, 1744, 1956; Coulomb, 1785). Small ions make most of the air conductivity, however, larger ions have observed to have contribution as well (e.g., Dhanorkar and Kamra, 1992, 1993b). Hõrrak (2001) carried out and analysed long term air ion measurements (containing 8615 hourly average air ion mobility distributions) at Tahkuse, Estonia, to obtain relative contribution of small ions into air conductivity. According to Hõrrak (2001), the relative standard deviation of the small air ion mobility variation was about 6% while the relative standard deviation of the small ion concentration variation was about 36%, and the correlation between the conductivity and the small air ion concentration was 98–99%. The small ions appeared to be responsible for 96.3% of the full air ion conductivity. Thus, the small air ion concentrations $n_+$ and $n_-$ can be estimated according to measured air polar conductivities $\lambda_+$ and $\lambda_-$ according to equations

$$n_+ \approx 0.96\lambda_+/(Z_+e) \tag{5}$$

and

$$n_- \approx 0.96\lambda_-/(Z_-e) \tag{6}$$

where $Z$ is the mean electric mobility and $e$ is the elementary charge. The mean electric mobilities of small ions at Tahkuse were $Z_+=1.36\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ and $Z_-=1.53\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ according to Hõrrak (2001). This fact is essential because the available datasets of atmospheric air conductivity supersede the datasets of air ion concentration measurements. For example, the largest composite open-access dataset ATMEL2007A (Tammet, 2009) consists of 1 615 159 hourly mean values of measured polar conductivities, while the number of direct measurements of small ion concentrations in the dataset is 305 605.

## 3 Instrumentation used in air ion measurements

In this section we briefly discuss the recent developments in air ion measurement techniques. We begin with the integral aspiration counter (Sect. 3.1). Then we continue by introducing the single-channel differential aspiration spectrometers (Sect. 3.2), multichannel aspiration spectrometers (Sect. 3.3), special configurations of aspiration condensers (Sect. 3.4) and drift tube mobility analysers (Sect. 3.5). Finally, we finish the section with the applications of mass-spectrometry to studies of the chemical properties of air ions (Sect. 3.6) and a short summary of the instrumentation (Sect. 3.7).

### 3.1 Integral aspiration counter

Ventilated coaxial condensers were introduced in the first studies of air ions and a correct theory for the functioning of such instruments was established by Riecke (1903). However, the simplest aspiration condenser is often called a Gerdien condenser because it became a popular tool for atmospheric air conductivity and air ion concentration measurements after publications by Gerdien (1903, 1905).

A steady voltage $V$ is applied between the two coaxial electrodes of an integral aspiration condenser, and the space between the electrodes is ventilated with an air flow $Q$. The electric current of deposited air ions $I$ is measured by means of an electrometer. As shown by Riecke (1903), the air ion current at a low voltage is

$$I = \frac{CV\lambda}{\varepsilon} \tag{7}$$

where $C$ is the active capacitance between the electrodes, $\lambda$ electric conductivity and $\varepsilon$ is the absolute permittivity of the air, which is close to the electric constant. The electric current caused by air ions saturates for voltages that exceed a critical value. This saturated current is

$$I = neQ\,, \tag{8}$$

where $n$ is the concentration of ions and $e$ is the elementary charge. The theory above allow using the integral aspiration condenser at a low driving voltage for measuring the air conductivity, and at a high driving voltage for measuring of the ion concentration. A detailed discussion of aspiration condensers can be found in the books by Israël (1970) and Tammet (1970).

The current of mono-mobile ions in an axi-symmetric integral aspiration condenser saturates abruptly according to Eq. (7), and reaches saturated current calculated according to Eq. (8). The transition criterion is

$$Z = Z_o = \frac{Q\varepsilon}{CV} \tag{9}$$

where $Z_o$ is called limiting mobility. The characteristic function of an integral aspiration condenser (volt-ampere characteristic) is piecewise linear in the case of the mono-mobile ions and increases smoothly and systematically with increasing voltage in the case of a continuous mobility distribution. The distribution of air ions according to the mobility is related to the second derivative of this volt-ampere characteristic curve. The air ion concentration is fluctuating in the atmospheric ground layer due to turbulence in the conditions of a vertical gradient in ion concentration, which is forced by the atmospheric electric field. The fluctuations in the measured air ion concentration complicate experimental determination of the volt-ampere characteristic curve and, therefore, amplify the uncertainties when estimating the derivatives from that volt-ampere characteristic. Thus an instrument based on an integral aspiration condenser has a very low mobility resolution allowing the distinguishing of only a few groups of air ions in a wide mobility range. The integral aspiration condensers are mostly used in integral air ion counters that are not capable for mobility spectrometry.

Israël's portable ion counter (Israël, 1929) contributed significantly to our understanding of air ions (Israël 1931, 1970). This integral aspiration counter allowed measurements over a wide range of mobility, including large ions. The instrument consists of two identical aspiration condensers that can be used for simultaneous measurements of positive and negative air ions, or connected in series for measurements of ions of one polarity. The design of many further instruments was based on the Israël's counter.

Several integral air ion counters were developed and used for extensive measurements in Tartu, Estonia (Matisen et al., 1992). The counter by Reinet (1956) had separate aspiration condensers for small and large ions. It was used for long term measurements of several air ion mobility classes (Reinet, 1958). During these measurements, bursts of intermediate ions were recorded, but the nature of the bursts was not understood. The counter was upgraded by Prüller and Saks (1970), who added automatic data recorders replacing manual data collection. Thereafter portable integral counters with an external collector electrode were developed (Tammet, 1970; Matisen et al., 1992) and manufactured for more than 100 instruments for various scientific institutions, mostly in former Soviet Union. These ion counters have been used also in the measurements at Vilsandi island in Estonia during different expeditions. The measurements in July–September 1984 showed the average concentrations of positive and negative small ions (limiting mobility $0.32\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) 261 and $173\,\mathrm{cm^{-3}}$, respectively Hõrrak (1987).

Dhanorkar and Kamra (1992, 1993b) operated three Gerdien counters in parallel with a common fan for air flow, each set to measure a different mobility range, i.e. small ions ($\geq 0.75\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$), intermediate ions ($\geq 2\times10^{-2}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) and large ions ($\geq 2.3\times10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$). This Gerdien counter setup was further modified by Dhanorkar and Kamra (1993a) to allow for measurements at a set of voltages for each condenser. This modified instrument enables measurements of mobility distributions in the ranges of $0.24–3.37\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$, $0.0243–0.147\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ and $6.91\times10^{-4}–0.0132\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. Ion concentration measurements by Gerdien counters have also been conducted in the Antarctica (Siingh et al., 2007; Kamra et al., 2009) and on-board a ship in the Arabian Sea (Siingh et al., 2005; Pawar et al., 2005). In the Gerdien counter setup by Pawar et al. (2005) and Kamra et al. (2009) the mobility ranges for small, intermediate and large ions were $<1.45$ nm ($>0.77\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$), 1.45–12.68 nm ($1.21\times10^{-2}–0.77\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) and 12.68–130 nm ($0.97\times10^{-4}–1.21\times10^{-2}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$), respectively. Dupplissy et al. (2010) used a Gerdien counter during a CLOUD experiment in CERN.

Aplin and Harrison (2000) used a Gerdien counter, which was modified to be able to vary the electric field between the cylinders as the air flowed through the annular gap between them. An electrometer measured the current delivered by the ions as they deposited on the central electrode. Further development by Harrison and Aplin (2007) is the Programmable Ion Mobility Spectrometer PIMS. A bias voltage is applied to the outer cylinder and the electric current of ions deposited on the inner cylinder electrode is recorded. The PIMS measures small mobility ranges at a time by alternating the voltage step by step from positive to negative. The whole measurement cycle takes 30 min.

Ling et al. (2010) used two modern portable Alphalab air ion counters, one for positive and the other for small negative ions when measuring at 32 different urban sites in an Australian city. Unfortunately, name of this city was not mentioned. The limiting mobility of the ion counters is 0.5 $cm^2\,V^{-1}\,s^{-1}$.

## 3.2 Single-channel differential aspiration spectrometers

In single-channel differential aspiration spectrometers, ions are collected onto a collector ring or plate. If this ring is narrow, the distribution of air ions according to the mobility is related to the first derivative of the volt-ampere curve, and corresponding ion spectrometers are called also first order differential spectrometers. Thus the effect of fluctuations in the ion concentration is partially suppressed compared to the integral condenser. Also, this instrument includes separate inlets for ions and sheath air. The sheath air is deionised by means of a filter. If both the collector electrode and the inlet air flow are divided, we get a differential aspiration condenser of the second order, where the operation of calculating the derivatives is replaced by a physical differentiation (Sect. 3.3).

In the first aspiration condensers the air ions were collected onto an electrode inside of the condenser and the electric current caused by ions was measured by single electrometer connected to the electrode. This electrode was exposed to a driving electric field, and the smallest changes in the electric field caused large error in the electrometer output signal. Thus, Hewitt (1957) replaced the divided electrode in the differential aspiration condenser with a divided output air flow, where larger amount of excess air was sucked away and only a small amount of classified air was passed to a detector. This kind of first order differential aspiration condenser is commonly called a DMA (Differential Mobility Analyzer). The amount of classified air ions is measured by means of a Faraday cup electrometer or a condensation particle counter (CPC), which can be used in case of large ions.

The DMA was initially developed as a tool to produce particles of known size, composition and concentration for calibrating aerosol instruments (Liu and Pui, 1974). Knutson and Whitby (1975) derived a theory that accurately describes the mobility distribution of non-diffusing particles classified by the DMA. Stolzenburg (1988) theory was later extended to account for the effects of diffusion (Stolzenburg and McMurry, 2008).

Laakso et al. (2007a) and Gagné et al. (2010) used an Ion Differential Mobility Particle Sizer (Ion-DMPS) for detecting the charging state of aerosol particle populations, which is one way to study the role of ions in particle formation (Vana et al., 2006a; Iida et al., 2006; Laakso et al., 2007a; Kerminen et al., 2007; Gagné et al., 2008). The charging state describes whether the particles are in charge equilibrium or if they are over- or under-charged. The Ion-DMPS is a DMPS completed with a bipolar charger which can be switched on and off, and a DMA that can measure both polarities in turns to get four different kinds of particle size distributions: (1) naturally charged positive particles, (2) naturally charged negative particles, (3) charge equilibrium negative particles, and (4) charge equilibrium positive particles. This setup avoids systematic errors when estimating the charging state of aerosol particles compared to commonly used two separate instruments to measure air ion and aerosol particle concentrations in the same size range due to differences in the instruments or inlets.

In principal, CPCs are more sensitive detectors of air ions when compared with the aerosol electrometers. Unfortunately, the traditional CPCs are not able to detect particles of diameter below 3 nm. Only recent advances in the developments of CPCs allow the use of CPC-equipped DMA-s for measuring the air ions of diameter down to 1 nm (Sgro and de la Mora, 2004; Kulmala et al., 2007; Sipilä et al., 2008, 2009; Iida et al., 2009; Vanhanen et al., 2010).

Based on the Nolan's subdivided condenser (Nolan and Sachy, 1927), Misaki (1950) introduced a method using the first order differential ion probes to measure small and intermediate ion mobility distributions. Both of two instruments consist of two coaxial cylindrical electrodes separated by annular gaps. The inner electrode is divided into four sections: the first and the fourth are grounded, while the second and the third sections are the measuring electrodes. The outer cylinder is connected to a voltage supply. The voltage is divided into 20 or 30 steps. Later, Misaki (1961a,b) used this setup with mobility ranges of 0.2–3.0 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ and 0.005–0.2 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ at Tokio and Karuiwaza.

The Balanced Scanning Mobility Analyser BSMA (Tammet, 2006) is a single-channel differential aspiration condenser that includes two parallel aspiration condensers, connected as a balanced capacitance bridge. This eliminates the electro statically induced current and makes possible to continuously scan through the mobility range of 0.032–3.2 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, which approximately corresponds to ion mass diameters of 0.4–7.5 nm. An extra high flow rate of 2400 LPM may cause difficulties in installing the instrument but leads to lower inlet losses of ions than occurs with instruments that operate at lower flow rates. The BSMA has been used for measurements in Hyytiälä, Finland (Kulmala et al., 2005), since spring 2003 (Hirsikko et al., 2005), and in San Pietro Capofiume, Italy, for over six months in 2008 (Manninen et al., 2010) as well as for studies of rainfall-induced ions in Tartu (Tammet et al., 2009). The BSMA enables calibration according to the geometric dimensions, voltage and flow rate, and it was used as reference in calibration of different mobility spectrometers (Asmi et al., 2009) and the mass-spectrometric instrument APi-TOF (Junninen et al., 2010).

### 3.3 Multichannel aspiration spectrometers

An aspiration condenser with a divided collector electrode was proposed already in the early stage of air ion research (Zeleny, 1900). In a multichannel aspiration condenser the collector electrode is divided into many rings and the collected ions are measured simultaneously. As a results, the time required to obtain whole spectrum is shorter compared to that when mobility range is scanned, which is necessary in single-channel instruments to obtain the air ion mobility distribution. The multichannel instruments have many advantages: (1) the data are collected simultaneously with several electrometers and the full distribution is measured as fast as the signal from a single channel becomes available, (2) additionally, simultaneous measurements avoid errors associated with fluctuations of air ion concentrations. The main factor limiting the usage of multichannel instruments is complicated construction and calibration, causing a high price and complex maintenance.

A second order differential aspiration condenser was first designed by Erikson (1921) for use in laboratory experiments. Yunker (1940) developed the first successful multichannel air ion spectrometer. The air ion mobility distribution measured by Yunker is in a good agreement with contemporary knowledge about the air ions. Yunker (1940) measured the mobility-spectrum of atmospheric ions in the range of mobilities between $10^{-3}$–2.0 $\mathrm{cm^2\,s^{-1}\,V^{-1}}$ using a divided-electrode air-blast method. A continuous recording method was employed and the entire spectrum covered about one hour. The spectrum shows the ordinary small ions, and then a practically continuous distribution out to the lowest mobility measured. However, it was not practical to use multichannel methods for long term measurements before automated data acquisition techniques were developed.

In Tartu, Estonia, work was begun in the 1970s to develop multichannel aspiration spectrometers (Tammet et al., 1973). A long series of routine measurements by means of the multichannel analysers have been carried out at the Tahkuse station from 1988 to this day, although not continuously (e.g. Hõrrak et al., 1994, 2000). The

Tahkuse instrument complex covers the mobility range of 0.00041–3.14 cm$^2$ V$^{-1}$ s$^{-1}$ and includes three multichannel aspiration condensers: one for small ions, one for intermediate ions, and one for large ions. The details and analysis of the results are available publications by Hõrrak et al. (1994, 1998b, 2000, 2003).

The most advanced multichannel air ion spectrometers developed in the University of Tartu in cooperation with SME AIREL, Estonia, are the Air Ion Spectrometer (AIS, Mirme et al., 2007) and its modifications (NAIS and airborne NAIS). The AIS consists of two parallel DMAs, one for positive ions and the other for negative ions. Each DMA consists of two concentric cylinders. Four different electric fields are introduced between the cylinders. Ions are classified according to their electrical mobility and the signals they produce are recorded by 21 insulated electrometers inside the outer cylinder. Thus, the whole mobility spectrum is simultaneously measured for both polarities. The AIS operates at 30 litres per minute (LPM) sample flow and 60 LPM sheath air flow per analyser. Mobility spectra for both polarities are typically obtained every five minutes in routine atmospheric measurements, but the integration time is user-adjustable. The AIS measures small ions and charged particles in the 0.0013–3.2 cm$^2$ V$^{-1}$ s$^{-1}$ mobility range (mass diameter 0.5–40 nm). Different size ranges are given in the literature due to the different conversion from mobility to size (Fig. 1).

The newest instruments based on the AIS are: (1) the Nanoparticle and Air Ion Spectrometer NAIS, which can also measure neutral particles beginning from ca. 2 nm (see e.g., Kulmala et al., 2007; Asmi et al., 2009; Manninen et al., 2009a), and (2) the airborne NAIS (Mirme et al., 2010), which is suitable for aircraft or different altitude measurements.

The BSMA, 5 AISes, and 5 NAISes were calibrated and inter-compared in a laboratory campaign (Asmi et al., 2009). Asmi et al. (2009) found that the ion spectrometers measure quite accurately when the aerosol was mono-disperse and the concentrations were high. However, when the ion/particle concentrations were decreased down to few hundred cm$^{-3}$ measured concentrations were overestimated due to the background noise of signal. When measuring non-mono-disperse aerosol (as ambient air is), the data inversion of the AIS moves the ion spectrum towards smaller sizes in both polarities. However, different ion spectrometers showed consistent ion size distributions, although differences in particle concentrations were observed when applying the spectrometers in parallel. These problems were explained as issued from the data processing algorithms.

During the CLOUD experiment in CERN, measurements of small ions with an AIS and Gerdien counter in parallel were in good agreement for positive ions, whereas differences were observed for concentrations of small negative ions (Duplissy et al., 2010). Recently, Ehn et al. (2010b) compared the AIS and BSMA mobility spectra against an Atmospheric Pressure Interface Time-of-Flight Mass Spectrometer mass spectra (APi-TOF, introduced in Sect. 3.6). The BSMA and the APi-TOF showed a good agreement, whereas the AIS and the APi-TOF showed some differences probably due to incorrect sizing and the asymmetry in transfer functions of the AIS.

The AIS, NAIS and airborne NAIS have been used in many kinds of environments: on the sea shore in Mace Head, Ireland (Vana et al., 2008), on ships (Vana et al., 2007), on a train trip from Moscow to Vladivostok (Vartiainen et al., 2007), at high altitudes mountains (Venzac et al., 2007, 2008), in a hot air balloon and onboard an air craft (Laakso et al., 2007b; Mirme et al., 2010) and in urban and rural regions that include e.g., Helsinki, Kuopio and in Hyytiälä, in Finland (Hirsikko et al., 2005, 2007b; Tiitta et al., 2007), at 12 locations in Europe during EUCAARI campaign (Manninen et al., 2010), South Africa (Laakso et al., 2008; Vakkari et al., 2010), and Tumbarumba, in Australia (Suni et al., 2008).

### 3.4 Special configurations of aspiration condensers

Most of the aspiration condensers have an axi-symmetric geometry. Alternative parallel plate geometries are not favourable in integral instruments but can be used in differential instruments, in which limiting of the width of the collector electrode allows to avoid edge distortions. Among the above mentioned instruments the plane geometry was used by Erikson (1921), Tammet (2002, 2003, 2006) and in the DMA P5, which was recently commercialised by SEADM (Boecillo, Spain).

Hurd and Mullins (1962) proposed a radial geometry of the planar aspiration condenser, which turned out popular for laboratory research but only had few applications for atmospheric research. The radial DMA by Zhang et al. (1995) was used to study atmospheric particle formation by Iida et al. (2008).

Loscertales (1998) showed that the diffusion broadening of the DMA transfer function can be suppressed when a component of the field is directed opposite to the flow. Tammet (1999) proposed the method of inclined grids, which puts in practice Loscertales' idea, and pointed out that longitudinal electric fields had before been used by Zeleny (1898). The inclined grids method was used in the Inclined Grid Mobility Analyzer (IGMA, Tammet, 2002, 2003), which was used by Eisele et al. (2006) and Iida et al. (2006, 2008) for measuring ion and charged particle mobility/size distributions in atmospheric aerosol nucleation studies. The IGMA is single-channel differential aspiration condenser, and classifies naturally charged air ions according to their mobility and measures the concentrations of mobility-classified ions with a highly sensitive electrometer (Faraday's method). The flow rate is high (3000 LPM) to improve the signal-to-noise ratios and reduce sampling losses. The mobility range of the IGMA ($0.05$–$3.2\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) corresponds to a mass diameter range of 0.4–6.3 nm. Although the inclined grid method was proposed to enhance the mobility resolution, in operation high mobility resolution was sacrificed so as to achieve high sensitivity, which is necessary for measuring small concentrations of intermediate ions.

Flagan (2004) proposed another instrument with inclined electric field, called the Opposed Migration Aerosol Classifier (OMAC). The principle and configuration of the fields is the same as in the case of inclined grids, but the grids are replaced by porous electrodes. In contrast to the IGMA, where the primary goal was high sensitivity, the OMAC is designed to obtain a high mobility resolution at relatively low classifying voltages.

### 3.5 Drift tube mobility analysers

In the chemical applications of ion mobility spectrometry (IMS), ions are generated inside the instrument and measured a few milliseconds after they are generated. In this case the ion sampling problem is precluded and the ion concentrations may exceed the atmospheric concentrations by several orders of magnitude. An overview of the methods used in chemical applications can be found in the book by Eiceman and Karpas (2005). The dominating methods are the time-of-flight or drift tube method, where ions are generated by radioactive or corona source and drifted in a homogeneous electric field until the collector electrode. The time of the drift depends on the mobility of the ions and the mobility distribution can be derived when analysing the shape of the electric pulse generated by ions that reach the collector electrode.

IMS technique is useful especially in laboratory studies to obtain information on ion process. For example, Pedersen et al. (2008) used the IMS technique to characterise proton-bound acetate dimmers. Using a drift tube, Nagato and Ogawa (1998) studied aging (up to 5 s) and temperature dependence of artificially generated ion spectra in ambient laboratory air, and Nagato et al. (1999) studied the same effects in atmospheric conditions at Green Mountain Mesa. However, atmospheric spectra by the IMS is typically complex, and, thus, there are less attempts to use drift tubes to analyse atmospheric ions. Zvang and Komarov (1959) used a special drift tube to measure natural small ions in the atmosphere the heights up to 5 km, but encountered difficulties due to the method. Myles et al. (2006) used IMS technique to study ammonia concentrations in atmosphere.

### 3.6 Mass-spectrometry in air ion research

Mass spectrometers are able to measure the mass-to-charge ratio of ions in a vacuum. Thus, the main problem in mass spectrometry of air ions is transferring the ions into the vacuum without high losses or perturbation of ion composition. As stated earlier, small air ions are typically singly charged, which mean that we can convert the mass-to-charge ratio directly into ion mass. Identification of the masses of several atmospheric ions has been made by Eisele and his collaborators in a long series of papers beginning with Eisele (1983) and finishing with Eisele et al. (2006). The identification process has recently been continued by Junninen et al. (2010) at Helsinki, Finland, and Ehn et al. (2010a) at Hyytiälä, Finland, by means of a high resolution time-of-flight mass spectrometer (Atmospheric Pressure Interface Time-of-Flight Mass Spectrometer, APi-TOF, manufactured by Tofwerk AG, Switzerland).

Another new tool is the Cluster Chemical Ionization Mass Spectrometer (Cluster CIMS) (Zhao et al., 2010), which detects sulphuric acid vapour and neutral molecular clusters formed by nucleation. As shown by Jiang et al. (2011), the clusters measured by the Cluster CIMS overlap in size with the smallest nano condensation nuclei measured by the Diethylene Glycol Scanning Mobility Particle Sizer (DEG SMPS, Iida et al., 2009), and the measured concentrations were in reasonable agreement. The measurements with the Cluster CIMS provide valuable new information about the mechanism of neutral nucleation and growth.

### 3.7 Summary of the instruments used in air ion studies

The instrumentation used in air ion studies has evolved from single channel integral instruments to multichannel instruments which simultaneously measure the entire size range of ions. The most widely used instruments today are air ion spectrometers by Airel Ltd., Gerdien counters and DMAs connected to CPCs. The latest inventions have come in particle mass spectrometry, allowing high resolution mass measurements of the ions, and the possibility to measure selected neutral clusters. With these instruments ions in size range of 1-nm or even below that can be measured.

## 4 Measured air ion properties

In this section we discuss observations on ion production rate via ionisation (Sect. 4.1), concentration of small ions as a function of height from the ground and altitude from the sea level (Sect. 4.2.1), effect of environment to small ion concentrations (Sect. 4.2.2), other sources for small ions (Sect. 4.2.3) and temporal variation (Sect. 4.2.4), as well as observations of the chemical composition of small ions both in the boundary layer and the upper troposphere (Sect. 4.3).

The measurements presented in this study were conducted all over the world (Table S1, Figs. 2 and 3): in both rural and urban environments in Europe, Asia, America, South-Africa, Australia and Antarctica. Some results from marine environments and high altitudes at mountains are also presented. Table S1 cites references to studies relevant to this review.

### 4.1 Observations of ion production rate via ionisation

The formation of small ions is limited mainly by the ionisation rate of air molecules. The ionisation mechanism and strength are spatially and temporally dependent. Close to the Earth's surface, the dominant ionisation mechanisms are radon decay and external radiation, which consists of gamma radiation from the ground and cosmic radiation (Harrison and Aplin, 2001; Hirsikko et al., 2007b; Harrison and Tammet, 2008).

Factors affecting radon concentrations include release rates from the surface affected by soil and rock types, radon activity concentration in soil as well as moisture of the soil (e.g., Shashikumar et al., 2008; Mehra et al., 2009; Gupta et al., 2010). The ionisation rate via radon decay is highly sensitive to elevation from ground. In contrast, ionisation due to gamma and cosmic radiation is relatively constant for several of tens of meters. Measurements in continental stations show that radon and gamma radiation are reduced by the snow cover in winter (Siingh et al., 2007; Hirsikko et al., 2007b).

Galactic cosmic rays (charged particles, i.e. protons) produce ca. 2 ion pairs $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$ at the ocean surface and contributes ~20% of ionisation over the land surface (Harrison and Carslaw, 2003; Bazilevskaya et al., 2008). Furthermore, galactic cosmic rays are mainly responsible for ion pair production at 3–50 km altitude, with a maximum rate of 35–50 ion pairs $cm^{-3}$ at around 15 km (Rosen et al., 1985; Hoppel and Frick, 1986; Bazilevskaya et al., 2008; Kirkby, 2008). Ion production by galactic cosmic radiation is determined by air density, ionising particle flux and latitude (i.e. the energy of the radiation). The ion pair production is smaller in the polar region than at the equator. At high altitudes, solar energetic particles, X-rays and gamma rays have also a contribution to the ion production rates (Bazilevskaya et al., 2008).

Table S2 shows observations of radon activity concentrations and respective ion pair production rates as well as total ion production rates calculated according to Eq. (3). Laakso et al. (2004a) compared two methods to evaluate the ion production rates at the SMEAR II station, Finland: (1) direct measurement of radon decay and external radiation, and (2) using the balance equation (Eq. 3) and ion/particle size distribution measurements. The former method led to larger values (Table S2). This was thought to be due to the underestimation of the sink of small ions or the hygroscopic growth factors of the aerosol. In addition, Tammet et al. (2006) showed that the small ions are scavenged by dry deposition onto the forest canopy.

According to review by Ilic et al. (2005), the radon activity concentrations are well smaller than 1 $Bqm^{-3}$ in Antarctica (compare with values in Table S2), but some higher concentrations have been observed. Dhanorkar and Kamra (1994) estimated the maximum small ion concentrations to be around 04:00 LT in Pune, India, when air mixing is at a minimum and down slope wind blows from the surrounding mountains indicating radon to be mainly responsible for the high values. According to a study by Nagaraja et al. (2003) in Pune, the diurnal variation of directly measured radon concentration and derived ion production rate were in agreement with Dhanorkar and Kamra (1994) results, only the ion pair production rates were smaller (Table S2). In Tumbarumba, Australia ion production rates via radon decay were high, with also maxima early in the morning (Suni et al., 2008, Table S2). In contrast to radon, the gamma radiation and cosmic radiation do not have a daily cycle.

## 4.2 Small ion concentration

Table S3 together with figures 4–10 summarises observations of small air ions, excluding the results from exhaust and water induced ion experiments in laboratory. Table S3 and Figs. 4–10 are constructed either based on tables, text or estimations from figures in the references. One must also note that in some studies mobility limit was set so that all small ions were not counted.

Concentrations up to 5000 $\text{cm}^{-3}$ per polarity were observed at some of the sites (Dahnorkar and Kamra, 1993b; Vartiainen et al., 2007). As discussed earlier, such high concentrations require high ionisation rates (>100 ion pares $\text{cm}^{-3}\,\text{s}^{-1}$) and reduced sink due to pre-existing aerosol. Such high concentrations were only observed during short time period. Thus, the observations are in the limits of the possible ion production rates.

Before the 1950's, there were only a few measurements of air ion mobility distributions in the atmosphere (e.g., Nolan and de Sachy, 1927; Israël and Schulz, 1933; Hogg, 1939; Yunker, 1940; Misaki, 1950; Siksna, 1950). Thus the earliest data shown in Table S3 are from Misaki (1950), and Norinder and Siksna (1950). These are the first measurements made with instruments of adequate sensitivity and accuracy to allow for quantitative comparisons with the modern observations.

### 4.2.1 Observations at different heights from the ground and altitudes from the sea level

Typically all the ion measurements have been done at or below 2 m height (Table S1, Fig. 4), except in Tahkuse, Estonia, where measurements were done at 3 and 5 m (e.g. Hõrrak et al., 1994). Note that all observations are not included in Fig. 4 due to missing information of measurement height from the ground. In Tahkuse the small ion concentrations are one of the smallest observed worldwide. This could be due the measurement height and thus the reduced effect of radon decay compared to the other sites.

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The only study of small ion concentration at two heights (2 and 14 m) from the ground was carried out in Hyytiälä by Tammet et al. (2006). They found that small ion concentrations were higher at 2 m than at 14 m (Table S3, Fig. 4) for two main reasons: (1) the forest is a sink for small ions and (2) the ion production by radon decay is larger closer to the ground.

According to ground based measurements the median concentration of small ions seemed to decrease with increasing altitude (distance from sea level), while the mean concentrations were independent of the altitude (Fig. 5). This is despite the fact that the galactic cosmic radiation produces ca. 2 ion pairs $\mathrm{cm^{-3}\,s^{-1}}$ at sea level, and 5–10 ion pairs $\mathrm{cm^{-3}\,s^{-1}}$ at 5 km (Bazilevskaya et al., 2008). The contribution of radon may hide the slightly enhancing effect of galactic cosmic radiation on small ion concentration.

Ions of one polarity (usually positive) are drifting in atmospheric electric field downward to the ground and ions of opposite polarity upward. The ground is not emitting the ions and thus only positive ions are present immediately near the surface. Negative ions will appear in some distance of the ground due to the ionising radiations. In the calm air, which nearly never happens in nature, the height of the layer of prevailing positive ions should be a few meters. Turbulence will mix the air and suppress the effect of electric field that is called the atmospheric electrode effect.

Garmisch-Partenkirchen is the only place where parallel ground based measurements at two altitudes have been conducted (Reiter, 1985, Table S3). Reiter (1985) reported very low small ion concentrations during fog episodes and periods of high relative humidity in Garmisch-Partenkirchen (1780 m a.s.l.), when the concentrations of small negative ion decreased nearly to zero, while the small positive ion concentrations remained at a clearly higher level of about 100 $\mathrm{cm^{-3}}$. Reiter (1985) also found that small ion concentrations were the highest during high visibility conditions due to the small scavenging rate of small ions when the air is clean.

The sink effect of clouds is clearly seen at four other sites: (1) Pallas, Finland (Lihavainen et al., 2007), (2) Aboa, Antarctica (Virkkula et al., 2007), (3) Puy de Dôme, France (Venzac et al., 2007), and (4) the High Altitude Research Station at Jungfraujoch, Switzerland (Vana et al., 2006b, Table S3). The observations at the Puy de Dôme mountain (1465 m a.s.l.), which is in the free troposphere, shows that negative ions were more abundant than positive ions during cloudy periods, in contradiction with Reiter (1985). The median concentrations of small negative and positive ions were about 350 cm$^{-3}$ and 100 cm$^{-3}$, respectively, during high ambient RH and about 700 cm$^{-3}$ and 400 cm$^{-3}$ in clear sky conditions. However, due to atmospheric electric electrode effect, the concentration of positive ions should be higher. Venzac et al. (2007) concluded that clouds were the main sink for the small ions. However, in Aboa the negative ions were more efficiently scavenged (Virkkula et al., 2007), in agreement with Reiter (1985). The effect of fogs and high moisture, i.e. hygroscopic growth of pre-existing aerosol, was also observed by Hõrrak et al. (2008) at SMEAR II, Finland, where the small ion concentrations reached values less than about 150 cm$^{-3}$.

In addition to scavenging effect of clouds, the data from Jungfraujoch (at 3500 m altitude) show much smaller concentrations for negative than positive small ions (Vana et al., 2006b). This was thought to be due to increased mobility of small ions as the pressure decreases, and thus more negative than positive ions were out of the measurement range.

Laakso et al. (2007c) measured ion concentration vertical profiles from a hot-air balloon in Hyytiälä, Finland. According to their observations, 1.5–3-nm intermediate ion concentrations were in range 0–75 for negative and 0–65 for positive ions depending on the height from the ground. During their flight over Europe, Kulmala et al. (2010) and Mirme et al. (2010) measured vertical profiles of air ion concentrations. The concentrations of 2.5–3 nm intermediate ions were highest near the ground, but were nevertheless very low (1–10 cm$^{-3}$). In addition, concentrations of 0.75–2 nm ions were low (100–300 cm$^{-3}$) but were increasing with increasing altitude up to 4 km. After 4 km altitude the results became unreliable due to instrumental issues.

### 4.2.2 Observations in different environments

In different environments, small ion concentrations are affected by the different combinations of production and sink rates. Therefore, in Fig. 6 the mean and median concentrations of small ions are presented separately for each measurement site, divided into three types of environments: marine/coastal, urban and rural.

At the shore in San Sebastian, Eichmeier and von Berckheim (1979) measured small ions (mobility $>0.9\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) with two ion-counters, one for positive and the other for negative ions. According to their measurements, the average concentrations were 250 and $650\,\mathrm{cm^{-3}}$ for small positive and negative ions, respectively. Observations by Vana et al. (2008) from the coastal site of Mace Head show that small ion concentrations were smaller when the wind was blowing from the sea than from the land, when radon was contributing.

In the beginning of 1960's, Blanchard (1966) measured the space charge with a Faraday cage and the potential gradient by means of a radioactive probe along the shore of Hawaii. He, however, observed a positive space charge and higher values of potential gradient when the air came across the surf zone, while concentrations were close to zero when the wind came over the land. He concluded that the surf is a source of positive charges carried by small water droplets formed via bubble burst at the surface of sea water.

During a cruise from Europe to Antarctica, Vana et al. (2007) observed small ion concentrations to be typically between 100 and $600\,\mathrm{cm^{-3}}$ per polarity. According to observations by Smirnov et al. (1998), three-hour-average concentrations of small ions from the whole measurement period were $1000–2000\,\mathrm{cm^{-3}}$ per polarity measured with an ion counter UT-840 (from University of Tartu, Estonia) at Zigler Island (Western Arctic, Franz-Joseph Archipelago). Average concentrations $<1000\,\mathrm{cm^{-3}}$ and up to $3000–4000\,\mathrm{cm^{-3}}$ were observed in various wind speeds and directions.

Komppula et al. (2007) compared ion concentrations and their sources and sinks at the marine environment in Utö and two rural continental sites (Hyytiälä, Finland

and Tahkuse, Estonia, Table S3). The small ion concentrations were lowest in Utö, where the ion production rate was also the smallest and the sink due to the background aerosol was of the same order as the one measured in Hyytiälä. In Tahkuse, the concentrations were also lower than in Hyytiälä due to a lower ion production rate, since the measurements were done at 5-m height, and a slightly higher aerosol sink. Hirsikko et al. (2005) observed high small ion ($d$<1.6 nm) concentrations (200–1500 cm$^{-3}$) at the rural site of Hyytiälä. The monthly-average concentrations were approximately 600–900 cm$^{-3}$. Similar concentrations were observed by Dhanorkar and Kamra (1992) at Pune, India (Table S3).

At University of Reading, England, Aplin and Harrison (2000) measured small negative ion concentrations with the Gerdien counter. According to their observations, small ion concentrations were high, on average 1820 and 1760 cm$^{-3}$ for negative ions of mobility larger than 0.77 and 1.08 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. They obtained similar results from Mace Head. However, using a different instrument (the PIMS) Harrison and Aplin (2007) measured very low small ion concentrations (<200 cm$^{-3}$/polarity) at Reading University, England in the summer of 2005.

Wilding and Harrison (2005) used the PIMS at the Norfolk coast. Their results confirm the influence of background aerosol on the mean mobility, concentration and lifetime of small ions, i.e. the larger the background concentration of particles, the smaller the concentration and the lifetime of small ions but the larger the mean mobility. Thus, the small ions attach rapidly onto pre-existing aerosol particle and have therefore little time to grow. The importance of the background aerosol on the small ion concentrations were also confirmed by observations at the polluted urban environment of Athens, Greece (Retalis, 1977; Retalis et al., 2009).

In laboratory, Haverkamp et al. (2004) measured small ion concentrations in the immediate vicinity of a jet aircraft engine exhaust with an ion mobility analyser (IMA). They observed extremely high concentrations of small ions (up to 10$^8$ cm$^{-3}$). Generally, negative ions were smaller than 1500 amu (1.5 nm) and positive ions smaller than 3000 amu (1.9 nm). Lähde et al. (2009) were able to measure ion mobility distributions with an AIS in the vicinity of a diesel engine exhaust tailpipe. They observed that without any exhaust after-treatment, the particles had a non-volatile core and the ion size distribution followed the particle size distribution. This implies that the volatile compounds condense on a non-volatile core (of several nanometers) formed in the high temperature and an ionising environment. The results were similar if the exhaust was treated with an oxidation catalyst. However, particles downstream of a diesel particle filter were volatile and neutral, which indicates no contribution of ions to the particle formation process.

Ling et al. (2010) measured air ions at five different kinds of urban locations in an Australian city: park, woodland, city center residential area and freeways. The part of their measurements that were affected by power lines, which are known to be a source of unipolar ions, are excluded because they are out of the scope of this review due their quick scavenging rate in the strong electric field, in which they are formed. Furthermore, the concentrations they observed were in agreement with other urban sites (Fig. 6). Vehicles, especially heavy duty trucks, were observed to be sources of ions in both polarities, while the woodlands were thought to be the sources of volatile organics and biogenic precursors for nucleation. There was a difference in concentrations between the polarities in the park and the city centre.

On the sea South West of India, Gopalakrishnan et al. (2005) measured charged particle size distributions in Southwest of India, and found that both small (up to $2500\,\mathrm{cm}^{-3}$) and intermediate ion concentrations increased when sampling from ship exhausts (Table S3). However, according to Tiitta et al. (2007) small ion concentrations decreased when the wind was from the nearby road in Kuopio, Finland, contrary to the observations reported by Ling et al. (2010).

Hirsikko et al. (2007c) measured air ion size distributions both indoors and outdoors in urban Helsinki. The observed outdoor small ion concentrations (on median 590 and 630 for positive and negative polarity, respectively, Table S3) and sinks were somewhat higher than at the rural Hyytiälä site. The small ion concentrations were dependent on wind direction and the sink due to pre-existing particles, whereas intermediate and large ion concentrations were affected by traffic density of the nearby road and wind direction. The diurnal cycle of indoor small ion concentrations (on median 966 and 1065 for positive and negative polarity, respectively, Table S3) was affected by ventilation, being the highest during night with very little or no ventilation. Hirsikko et al. (2007c) expected that the source rate for small ions by radon activity (ca. 12 ion pairs $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$) was elevated indoors. Earlier measurements made by Fews et al. (2005) showed similar small ion concentrations for indoor air, on small periods of time.

Comparatively high small ion concentrations were observed in Abisko, Sweden, where mean concentrations for positive and negative ions were 1650 and 2380 $\mathrm{cm}^{-3}$, respectively (Svennigsson et al., 2008), as well as in Tumbarumba, Australia, where mean concentrations for positive and negative ions were 1700 and 2400 $\mathrm{cm}^{-3}$, respectively (Suni et al., 2008). Abisko is surrounded and next to mountains and thus the atmospheric conditions are different compared more flat and open areas. The observations in Tumbarumba were thought to be due to enhanced radon efflux compared to many other sites, while the aerosol sink was quite low compared to other rural sites like Hyytiälä (Suni et al., 2008). Vartiainen et al. (2007) also observed high concentrations during a train trip through Russia.

### 4.2.3 Other sources for small ions

After the accident in the nuclear power plant at Chernobyl on 26 April 1986, Hõrrak et al. (1994) observed that the small ion concentrations increased to 800 $\mathrm{cm}^{-3}$ per polarity from its background level (ca. 300 $\mathrm{cm}^{-3}$ per polarity) in Tahkuse, Estonia. The concentrations decreased slowly during the following month back to close to the normal concentrations. The observations from Uppsala, Sweden (Israelsson and Knudsen, 1986), and Athens, Greece (Retalis and Pitta, 1989), support the observations from Tahkuse. Thus, couple of days after the accident, air conductivity, which is directly proportional to small ion concentration, increased an order of magnitude in both Sweden and Greece due to the increased radioactive radiation. According to Retalis and Pitta (1989) the concentration of positive small ions increased from the normal level of 200 $\mathrm{cm}^{-3}$ to 700 $\mathrm{cm}^{-3}$. Similarly to observations by Hõrrak et al. (1994), the small ion concentrations began to constantly decrease after couple of days.

Waterfalls (Laakso et al., 2007b) and rainfall (Norinder and Siksna, 1950; Hõrrak et al., 2006, Hirsikko et al., 2007a; Vana et al., 2008) produce high concentration of ions, especially negatively-charged ions smaller than 10 nm. The rainfall phenomenon is more frequent with negative intermediate ions, which typically appears immediately after the beginning of the rainfall. Positive intermediate ions are observed after the rain has continued for a longer period (Hirsikko et al., 2007a; Junninen et al., 2008). The phenomenon of rainfall induced ions is known as the Lenard effect and Tammet et al. (2009) studied the phenomenon via so called balloelectric ions (i.e. the generation of charge by splashing water), with mobilities of 0.1–0.42 $\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$. The main outcome of their laboratory study was that these balloelectric ions are singly charged water nanoparticles. Although they could repeat the phenomenon in the laboratory, the exact mechanism of the formation of balloelectric ions remains unknown.

Virkkula et al. (2007) found that concentrations of small and intermediate ions in Antarctica increased with high wind speeds and when snow was drifting or falling. A similar increase in ion concentrations during high winds was also observed by Vana et al. (2006b) at the High Altitude Research Station at Jungfraujoch in Switzerland. Virkkula et al. (2007) and Vana et al. (2006b) argued that the additional ions were formed by friction when snow and ice crystals are transported at high speeds by the wind. High wind speeds have been observed to correlate with high concentrations of small ions in the polluted urban Athens, Greece (Retalis, 1977; Retalis et al., 2009). However, some opposite observations have been done (Siingh et al., 2007; Kamra et al., 2009).

### 4.2.4 On the temporal variation of small ion concentrations

Many studies have reported enhanced concentrations of small ions during early morning hours due to the accumulation of radon (e.g., Dhanorkar and Kamra, 1994).

Norinder and Siksna (1950) observed the highest small ion concentrations (ca. 3000 cm$^{-3}$) in early morning hours (ca. 04:00 LT) in Sweden, while the average was 1200–1500 cm$^{-3}$. Dhanorkar and Kamra (1993a) observed that the concentrations of ions in every mobility/size interval were highest early in the morning in Pune, India. Similar kind of results was obtained in their other study at the same site (Dhanorkar and Kamra, 1993b). In Tokyo, Misaki (1961b) observed high small ion concentrations early in the morning just before sunrise. Based on three days of data, small ion concentrations were 100–600 cm$^{-3}$ both in the rural Karuizawa and the urban Tokyo sites (Table S3).

Junninen et al. (2008) reported an increase in both the concentrations and mean sizes of small ions observed in a boreal forest environment in Hyytiälä during night-time. These increases were most frequently seen on nights following a new particle formation event day, suggesting a possible contribution from the same vapours in both day and night-time growth. Furthermore, Siingh et al. (2005) observed higher night-time than day time concentrations in fair weather conditions during their cruise on the Arabian Sea.

Retalis et al. (2009) observed with their ion counters (by Laboratory in Physics in Aarau, Switzerland) very low small ion concentrations in Athens, Greece. Concentrations typically reached a maximum early in the morning, indicating the enhanced contribution of radon decay. Concentrations reached a minimum in the daytime due to the increased sink onto the background aerosol. Later the background aerosol was diluted and the small ion concentrations increased again. Furthermore, the mean annual concentrations of negative and positive ion concentrations decreased from 170 and 210, respectively, to 130 and 170, respectively in 17 years.

At Himalaya, Nepal (5079 m a.s.l. in free troposphere) concentrations up to 3000 cm$^{-3}$ were observed (Venzac et al., 2008). The small ion concentrations increased before a new particle formation event and decreased after it was over. Moreover, clearly lower (<500 cm$^{-3}$) concentrations were observed between the events. More typically, the opposite has been observed, i.e. decrease in small ion concentrations during particle formation (e.g. Hõrrak et al., 2000, 2003; Nieminen et al., 2009; Gagné et al., 2010). The explanation for this kind of adverse temporal variation can be similar as observed by Vana et al. (2006b). Thus, the mobility of small ions increases as the pressure decreases, and more ions were out of the measurement range during non-event periods than during particle formation events, when the small ions have grown in size.

During the monsoon period, small ion concentrations above the Arabian Sea decreased by almost an order of magnitude compared to those in the pre monsoon period, whereas the concentration of large ions increased (Pawar et al., 2005; Siingh et al., 2005, Table S3). This was thought to be due to high wind speeds accompanied by the bubbling of the white caps. Furthermore, the small ion concentrations first increased and then began to decrease when the distance from the coast increased prior to the monsoon period (Siingh et al., 2005). Radon transported from the coastal sand was thought to be responsible for the pre monsoon observations. Such a clear trend was missing during the monsoon. Siingh et al. (2005) showed that the small ion concentrations increased, while intermediate ion concentrations decreased, during drizzle-type rain. In contrast to other observations (Norinder and Siksna, 1950; Hõrrak et al., 2006; Hirsikko et al., 2007a; Vana et al., 2008), the concentrations of ions in all size classes decreased during heavy rain.

### 4.3 Observations on the chemical composition of air ions

The composition of air ions reacts to changes in the trace atmospheric gases rapidly, with negative charges acquired by the compounds that have the lowest proton affinities, and positive charges acquired by the compounds having the highest proton affinities. Arnold et al. (1978) measured the composition of positive ions smaller than 330 amu with the balloon-borne mass spectrometers at 33–37 km above South-West France. According to their results, two families of ion species exist in the stratosphere, called proton hydrates and non-proton hydrates (with fractions of 0.43/0.57), although both families contain proton (H). Typical proton hydrates were $H^+(H_2O)_3$, $H^+(H_2O)_4$,

$H^+(H_2O)_5$, and non-proton hydrates were $H^+x(H_2O)_2$, $H^+x(H_2O)_3$, $H^+x(H_2O)_4$. Based on their results, Arnold et al. (1978) proposed acetonitrile as possible candidate for compound marked with x.

Ferguson (1978) disagreed with Arnold et al. (1978) about the existence of acetonitrile in the stratosphere. According to Ferguson (1978), the observed non-proton hydrates (Arnold et al., 1978) would rather be sodium hydroxide cluster ions ($NaOH_2+(H_2O)_w(NaOH)_m$, where m=0…4 and w=0…2). Regarding negative ions, Arnold (2008) found that negative ions in the stratosphere were more likely to contain sulphuric and nitric acids ($NO_3^-(HNO_3)_n(H_2O)_w$ and $HSO_4^-(H_2SO_4)_a(H_2O)_w$).

Eichkorn et al. (2002) measured the composition of large positive ions, i.e. smaller than 2500 amu or ca. 1.7 nm in diameter, with an aircraft-based large ion mass spectrometer (LIOMAS) on an aeroplane at 9–10 km over Europe. They found three types of positive ions in the upper troposphere: (1) $H^+B_b(H_2O)_w$, where B is most likely acetone ($(CH_3)_2CO$) and b≤2, (2) $H^+B_b(H_2SO_4)_a(H_2O)_w$, and 3) $H^+B_b(H_2O)_w$-ions attached to $(H_2SO_4)_x(H_2O)_y$ neutral clusters. Eichkorn et al. (2002) proposed that $(H_2SO_4)_x(H_2O)_y$ clusters were formed by an ion-induced process.

Eisele et al. (1989a) measured the gas phase ion composition by mass spectrometry at the Forestry Commission site close to Dawsonville, Georgia, USA. They found that the four most abundant species in negative atmospheric ions were $NO_3^-$ (*m/z*=62), $NO_3^-\cdot HNO_3$ (*m/z*=125), $C_3H_3O_4^-\cdot HNO_3$ (*m/z*=166) and $HSO_4^-\cdot H_2SO_4$ (*m/z*=195). In addition, $HSO_4^-\cdot(H_2SO_4)_2$ (*m/z* 293) clusters, $C_3H_3O_4^-$ (*m/z*=103), $NO_3SO_3^-$ (*m/z* 142) and $NO_3SO_4^-$ (*m/z*=158) were also observed (Eisele et al., 2006). The most abundant identified positive ion species were *m/z*=60, 70 and130, identified as trimethylamine, isoxazole and isoquinoline, respectively (Eisele, 1989b).

In the urban Helsinki environment at SMEAR III, using a with a time-of-flight mass spectrometer (APi-TOF) Junninen et al. (2010) observed the negative ion daytime spectrum to be dominated by inorganic acids (nitric, sulphuric and iodic acids). Two main ion groups (alkyl amines and alkyl pyridines) for positive ions were observed. Ehn et al. (2010a) measured the ion chemical composition with the APi-TOF in Hyytiälä.

During daytime particle formation, the negative ion spectrum was dominated by sulphuric acid and di-, tri- and tetramer sulphuric acid clusters. They also observed sulphuric acid tetramer-ammonia ions. The night-time negative ion spectrum was thought to contain highly-oxygenated organic acids, possibly from the oxidation of monoterpenes. Through ion measurements, Ehn et al. (2010a) were the first to observe gas phase organosulphates. Although the positive ion spectrum was spread out over a large amount of peaks, Ehn et al. (2010a) could determine that the spectra consisted of species like alkyl pyridines, quinolines, alkyl amines, pyrroles and pyrrolines during both day and night.

## 5 Ions and atmospheric new particle formation

Atmospheric new-particle formation by nucleation may take place thermodynamically, kinetically or by the activation of pre-existing nanometer-size clusters. Nucleation is driven by sulphuric acid and possibly other low-volatile vapours, in addition to which it may be assisted by ammonia and other bases as well as by ions (e.g., Weber et al., 1996, 1997, 1998, 1999; Eisele and McMurry, 1997; Clarke et al., 1999; Nadykto and Yu, 2004; Kulmala et al., 2004b, 2006; Sihto et al., 2006; Riipinen et al., 2007, 2009; Ehn et al., 2007; Kulmala and Kerminen, 2008; Kuang et al., 2008; Enghoff et al., 2008; Sipilä et al., 2010).

Ion-induced nucleation usually means nucleation in the presence of electric charges, while ion-mediated particle formation also takes into account the ion-ion recombination in the small ion size range. As concluded by Curtius et al. (2006) and Yu (2010), ion-mediated particle formation mechanisms are expected to be important in locations with low temperature and pre-existing aerosol surface area, together with high ion and sulphuric acid concentrations. These kinds of conditions are typically encountered in the middle and upper troposphere, and even in the lower stratosphere (Arnold, 1982; Lee et al., 2003; Froyd and Lovejoy, 2003; Kanawade and Tripathi, 2006). Higher up in the stratosphere, there is insufficient super saturation of any vapour for the classical ion-induced particle formation mechanism to produce growing condensation nuclei (Arnold, 1980), so most condensation nuclei are thought to originate from the troposphere or may be of meteoritic origin from extraterrestrial regions (Cadle and Kiang, 1977).

This section discusses the role of ions in new particle formation. Even visual inspection of ion size distribution contour plots can offer useful insights into the role of ions in new particle formation due the low size limit (ca. 1 nm) of ion spectrometers (Sect. 5.1). Nucleation and growth rates of ions and neutral particles are then discussed (Sect. 5.2), which allow assessments of the importance of ions in particle formation (Sect. 5.3).

### 5.1 Monitoring the aerosol formation events by ion measurements

The lessons that can be learned about the first steps of particle formation based on size distribution data for larger particles (~10 nm, for example) are limited because the particles have typically been growing already for several hours before they were detected. Because data of ion mobility distributions provide information on the processes as they occur, they provide valuable insights into mechanisms of particle formation and growth. For example, Venzac et al. (2008) were able to confirm that new particle formation took place in situ at the Himalayas (at 5079 m a.s.l.) and at other free troposphere sites, such as at Puy de Dôme in France (1465 m a.s.l., Venzac et al., 2007) as well as through the whole boundary layer (Laakso et al., 2007c). Furthermore, differences in the concentrations of positive and negative ions during nucleation bursts can provide clues about the roles of ions in particle formation as well as chemistry related to particle formation.

Hirsikko et al. (2007a) describe the modified method of that typically used for DMPS data (Dal Maso et al., 2005) to classify charged particle formation events. Refinements to this classification scheme for specified sites have also been published (e.g., Virkkula et al., 2007; Vana et al., 2008; Suni et al., 2008; Yli-Juuti et al., 2009; Manninen et al., 2009a). These schemes involve classifying the particle formation events into groups according to: (1) the strength of the particle formation event, (2) the extent to which particles grow (i.e. does growth stop at 3–5 nm or do the new intermediate ions grow within the nucleation mode), and (3) whether or not a gap is observed in the size distribution between small ions and intermediate ions. Furthermore, also (4) non-event days, and (5) rain-induced intermediate ions were separated. This method was used to study new particle formation events based on DMPS and BSMA measurements in the boreal pine forest in Finland. Hirsikko et al. (2007a) found that the ion spectrometer could detect particle formation events that were suppressed, due to low concentrations of condensing vapours or high sink by pre-existing aerosol particles, before the DMPS (detection limit $>3$ nm) detected any particles.

Junninen et al. (2008) continued the work by Hirsikko et al. (2007a) by studying particle formation events taking place during the night-time, i.e. nocturnal events. Nocturnal events were typically suppressed at the lower limit of the DMPS (around 2–5 nm) due to the lower concentration of condensing vapours and the coagulation loss of slowly growing ions. Junninen et al. (2008) observed that the nocturnal events occurred more frequently for negative ions in winter, indicating that negative ions require less condensing vapours than positive ones, or that negative ions have greater affinity for the condensing vapours. In other times of the year, such a clear difference was not observed. Furthermore, Junninen et al. (2008) found that on 90 days when particle formation occurred, it was also observed in the following night, while after about 28 non-event days a particle formation event took place in the night. The nocturnal particle formation events were independent of ambient weather conditions and air mass origin but dependent on small ion and sulphuric acid concentrations. Junninen et al. (2008) concluded that particle formation mechanisms or vapours participating in particle formation and growth are different on day- and night-time. Lehtipalo et al. (2010a) showed that the night-time events in Hyytiälä are seen as often also in neutral particles, and that the night-time concentrations of sub-3 nm particles and ions have a clear connection to oxidised organic molecules.

At the Stordalen mire in Abisko, particle formation could take place several times during a day, and night-time events were also observed (Svenningsson et al., 2008).

Photochemical reactions or boundary layer reactions were assumed not to be the main driving factors of these nocturnal events (Svenningsson et al., 2008). In Tumbarumba, Southern Australia, nocturnal new particle formation was observed on 32% of the analysed nights and the phenomenon was estimated to be an important particle source (Suni et al., 2008; Lee et al., 2008). One must note that new particles were typically able to grow during the nocturnal events in both Sweden and Australia, unlike at the SMEAR II station in Finland. According to Lee et al. (2008), nocturnal particle formation takes place throughout the tropospheric column. Suni et al. (2009) continued their earlier work and observed the inflow of clean and dry air from polar ocean together with terpene emissions from vegetation to contribute the most on new particle formation events. These results are in accordance with earlier observations for day-time events in the boreal forest (Sogacheva et al., 2005).

Laakso et al. (2008) presented one of the first results of ion and particle size distribution measurements in Africa at a rural background station in the Savannah. They observed particle formation on over 90% of the days. Vakkari et al. (2010) continued thus preliminary work (Laakso et al., 2008) and ended up with a bit smaller percentage (83%) of particle formation events. Also at Aboa, Antarctica, the particle formation has been observed to take place (Virkkula et al., 2007; Asmi et al., 2010). Vana et al. (2007) observed only one particle formation event during their cruise from Europe to Antarctica when the ship was in a pack-ice region.

New particle formation has also observed indoors in laboratory air in Helsinki (Hirsikko et al., 2007c). Based on their ion size distribution and total particle concentration data, Hirsikko et al. (2007c) concluded that indoor new particle formation was only slightly dependent of outdoor air, i.e. there were enough condensing vapours available indoors in this special case. Also measurements of air ions in urban environments like in a park in Australia (Ling et al., 2010) and in Helsinki, Finland (Hirsikko et al., 2007c) showed that new particle formation took place locally.

## 5.2 Aerosol formation and growth rates

### 5.2.1 The estimation of formation and growth rates

The total (neutral+charged) formation rates of 2-nm particles can be calculated as (Kulmala et al., 2007)

$$J_2[\mathrm{tot}] = \frac{dN_{2-3}[\mathrm{tot}]}{dt} + \mathrm{CoagS}_2 \cdot N_{2-3}[\mathrm{tot}] + \frac{f}{1\,\mathrm{nm}}\mathrm{GR}_3 \cdot N_{2-3}[\mathrm{tot}] \tag{10}$$

and the simplified balance Eq. (4) for ions can be improved to be able to calculate the formation rates of 2-nm ions (Kulmala et al., 2007)

$$\begin{aligned} J_2^{\pm}[\mathrm{ion}] = {} & \frac{dN_{2-3}^{\pm}[\mathrm{ion}]}{dt} + \mathrm{CoagS}_2 \cdot N_{2-3}^{\pm}[\mathrm{ion}] + \frac{f}{1\,\mathrm{nm}}\mathrm{GR}_3 \cdot N_2^{\pm}[\mathrm{ion}] + \alpha N_{2-3}^{\pm}[\mathrm{ion}] N_{<3}^{\mp}[\mathrm{ion}] \\ & - \beta \cdot N_{2-3} N_{<2}^{\pm}[\mathrm{ion}]. \end{aligned} \tag{11}$$

Thus, the formation rates of new 2-nm particles/ions are proportional to the time changes in the number concentration of 2–3 nm particles/ions (the first terms on right hand side), the coagulation loss of 2–3 nm particles/ions with the pre-existing aerosol (the second terms), the growth of 2–3 nm particles/ions into larger sizes with growth rate (GR) and activation fraction to growth *f* (the third terms). In addition, ions are lost via ion-ion recombination (the fourth term on the right) and formed via ion-neutral attachment (the fifth term). Typically, the coefficients $\alpha$ and $\beta$ are $1.6\times10^{-6}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ and $0.01\times10^{-6}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$, respectively (Israel, 1970; Hoppel, 1985; Hoppel and Frick, 1986).

There are several ways to estimate ion/particle growth rates (GR[ion] and GR[tot]) based on ion mobility/particle size distribution data. Lehtinen and Kulmala (2003), Kulmala et al. (2004b) and Hirsikko et al. (2005) described a method to also obtain the GR[ion] of the smallest ions. The method, which is commonly used by the group at the University of Helsinki for both ion and particle size distribution data, is based on determining the maximum concentration of each selected size bin as a function of time by fitting a Gaussian curve. From these time-diameter pairs, the growth rate can be calculated for any size range.

The main problem is to estimate the growth of the smallest particles correctly. Indeed, the coagulation of small particles with pre-existing aerosol may cause the apparent (i.e. calculated) GRs to exceed the true GRs (Hirsikko et al., 2005). In addition Hirsikko et al. (2005) noted that self-coagulation is also excluded from the analysis, which causes some error in the results if concentrations are high (Anttila et al., 2010). Ions have similar enhancing effects on the calculated GR[tot]. When introducing this method to obtain the GR, Lehtinen and Kulmala (2003) pointed out that the growth seems to be linear, which mean that a constant amount of vapour contributes to the growth process. Kulmala et al. (2004b) noted that this method leads to an uncertainty of factor of two.

The other method to obtain GR[ion] or GR[tot], used by University of Helsinki researchers, is to fit log-normal modes into the size distribution data (see more in Hussein et al., 2005; Dal Maso et al., 2005). Again, the growth rate is obtained as a slope of the line fitted to the diameter vs. time data. This method assumes that the air mass is homogeneous and that all the particles are formed at the same time. Svenningsson et al. (2008) used this method with their ion data measured with the AIS in Abisko, Sweden.

Iida et al. (2008) introduced a new method using air ion data to determine the GR of particles that involved comparing size-dependent charged fractions with their stationary state values. They assumed that particle charge is determined by competing rates of particle growth, coagulation, and charging by small ions. If particles grew very slowly, they would acquire the stationary state distribution, and no additional information about growth rates could be determined from the charged fractions. Useful information, however, can be obtained if particles grow fast enough, and thus their original (under or over) charging state was visible (Kerminen et al., 2007). In Mexico City, where neutral processes dominate nucleation, charged fractions for sub 10 nm particles were below stationary state values, but approached stationary state as the particles grew (Iida et al., 2008). Because they only measured the charged fractions for particles larger than about 3.7 nm, they were only able to obtain information on growth rates for particles above that threshold. However, this approach could also be used for smaller particles if charged fraction data were available. An advantage of this approach is that the GR can be determined from a single measurement of size-dependent charged fractions.

### 5.2.2 Observations of particle growth rates

The growth rates of sub-3 nm ions are presented in Table S3 and Figs. 7 and 8. Particle growth rates seem to be size dependent, i.e. small particles tend to grow slower than large particles in Hyytiälä (Dal Maso et al., 2005; Hirsikko et al., 2005). Similar results were obtained at K-Puszta (Yli-Juuti et al., 2009) and during the EUCAARI measurement period at 12 European sites (Manninen et al., 2010). Different factors could contribute to this size dependence. Particles grow with time, so this apparent dependence on size could be due to changes in the chemical processes that occur during the day. It is also possible that the growth rates vary with size at a given time due to the effect of size on vapour uptake. An understanding of particle growth kinetics will require an understanding of the relationships between the gas phase compounds that contribute to the growth and the size-dependent rate at which they accumulate in particles. This demands for advances in the measurements of both the particle composition and the gas phase aerosol precursors.

Vakkari et al. (2010) studied new particle formation events measured with an AIS in the South-African Savannah. They observed a different kind of size dependence in the particle growth. Generally, 3–7 nm ions grew faster than 7–20 nm ions, while the growth of the smallest ions was the slowest as in other sites. This kind of size dependence of growth can be due to the time dependence of condensing vapours. In winter, the growth of 1.5–3 nm ions could be the faster than the growth of larger particles, as reported by Hirsikko et al. (2005), Suni et al. (2008) and Manninen et al. (2010). This could be due to the enhancing effects due to ions in particle formation (Yu and Turco, 2000; Kulmala et al., 2004b), when air temperature and sometimes the particle sink are lower, thereby favouring ion-mediated processes (Curtius et al., 2006; Yu 2010). However, the growth rates of sub-3 nm ions are almost constant throughout the year, while the growth of particles is reduced in winter and enhanced in summer (Hirsikko et al., 2005; Vakkari et al., 2010).

Hirsikko et al. (2007c) estimated similar growth rates for sub-3 nm ions in the outdoor and indoor air of urban Helsinki as in the rural Hyytiälä air (Hirsikko et al., 2005). However, somewhat higher growth rates were observed in Helsinki, which were thought to be due to low condensation sinks, high concentrations of condensing vapours and the important role of ions.

Furthermore, according to Table S3, the GRs[ion] of few nanometer ions were similar at every site, except in Stordalen mire, Sweden, where Svenningsson et al. (2008) observed one of the quickest growth rates of 1–10-nm ions during their measurements, up to 40 nm $h^{-1}$. Furthermore, the high GR coexisted with the high condensation sink values, which was unexpected and indicates very high source rates of condensable vapours.

Sulphuric acid together with some organics are believed to be involved in the particle formation process and in particle growth with as fast growth rates as observed (e.g., Hirsikko et al., 2005; Yli-Juuti et al., 2009; Dal Maso et al., 2005, 2009; Paasonen et al., 2009, 2010; Ristovsky et al., 2010). Arnold (2008) concluded that in the upper troposphere organics are irrelevant, while sulphuric acid may contribute due to the long life-time of $SO_2$. Kuang et al. (2010) showed that in locations throughout the troposphere, sulphuric acid accounted for between 1% and 100% of the growth of freshly nucleated particles, with average values in the 5–10% range. According to the air mass and sulphuric acid proxy studies in South Africa, Vakkari et al. (2010) concluded that sulphuric acid contributes 20–30% on the growth of the smallest ions and 10–20% to the growth of larger than 3 nm ions and particles. Smith and co-workers developed the thermal desorption chemical ionisation mass spectrometer (TDCIMS) to measure the composition of freshly nucleated particles as small as 8 nm (Voisin et al., 2003; Smith et al. 2005, 2008, 2010). They found that organic salts, formed by the reactions of amines with organic acids, account for 20–50% of the growth, and the contributions from other organic compounds were also important.

Gagné et al. (2010) studied particle formation with Ion-DMPS in Hyytiälä, Finland. They observed the GRs[ion] were independent of the contribution of ions in particle formation, whereas GR[tot] and the sulphuric acid saturation ratio seemed to be higher on days when ions were less important in particle formation.

### 5.3 Formation rates of 2-nm particles and ion-induced nucleation

The observed total formation rate ($J_2$[tot]) of neutral and charged 2-nn particles varies in the range of 0.001–60 $\mathrm{cm^{-3}\,s^{-1}}$ depending on the particle formation event (Table S3). However, the formation rate of 2-nm ions ($J_2$[ion]) has been observed to exceed 1 $\mathrm{cm^{-3}\,s^{-1}}$ only at South-African Savannah (Table S3 and Figs. 9 and 10). Note that, the small $J_2$[ion] (order of $10^{-6}\,\mathrm{cm^{-3}\,s^{-1}}$) values from Hyytiälä, Finland, presented by Laakso et al. (2007c) are out of the range in Fig. 10. According to Kulmala et al. (2010), Manninen et al. (2010) and Gagné et al. (2010), the contribution of ions increases as a function of decreasing formation rate of the whole 2-nm population. Despite this the formation of two-nanometer particles is mainly driven by neutral mechanisms.

Lehtipalo et al. (2009) used ion measurements to study small neutral particles by subtracting small ion concentrations from the total small particle concentrations measured with a Pulse Height Condensation Particle Counter (Saros et al., 1996) operated at a high saturation ratio to allow the activation of sub-2 nm particles (e.g., Sipilä et al., 2008, 2009). Lehtipalo et al. (2009, 2010b) showed that ion-ion recombination can explain only a minor fraction of the high concentrations of small neutral particles that were detected in Hyytiälä, Finland, which is supported by the results of Manninen et al. (2009a). However, in Mace Head when the air masses came from the ocean, a significant fraction, at night-time even all, of the particles in the size range 1.3–3 nm could be ions and their recombination products (Lehtipalo et al., 2010b).

Using the Ion-DMPS and AIS/NAIS at SMEAR II, Manninen et al. (2009a) showed that negative and positive ion overcharging accompanied with a decrease in the ratio of total population and ions in 1.8–3 nm size range on 51% and 34%, respectively, of particle formation days. That indicates the importance of ions in particle formation on such days. Gagné et al. (2010) also studied the charging state of newly formed aerosol with the Ion-DMPS. They found that overcharged particle formation events are frequent throughout the year, while undercharged events were observed from November to January in Hyytiälä. They concluded that the overcharged days were observed typically on dryer and warmer days, with higher solar radiation than the undercharged days, and overcharged days were more frequent for the negative polarity than for the positive one. Additionally, the nucleation mode particle (3–25 nm) concentrations were higher during undercharged days, which is in accordance with Vana et al. (2006a). Gagné et al. (2010) and Nieminen et al. (2009) have reported a decrease in the small ion concentrations during particle formation events. This decrease can be due to ion-induced nucleation or increased sink after new particle formation.

According to the observations by Hirsikko et al. (2007a) at the SMEAR II station, negative ions were sometimes favoured over the positive ones, since more particle formation events were observed in the negative polarity than in the positive one. Based on the measurements from April 2003 to March 2006, during 19 and 6 particle formation events observed for positive and negative ions, respectively, there was a gap in the size distribution between the small and intermediate ions indicating the dominance of neutral mechanisms over ion-induced pathways during particle formation. The gap in the size distribution could also indicate that particle formation occurs further away, and the grown particles are transported to the measurement site.

While ion-mediated pathway has been observed to contribute on some days at the SMEAR II station, neutral mechanisms were nearly always dominating (e.g., Vana et al., 2006a; Laakso et al., 2007a; Gagné et al., 2008). Yu and Turco (2008), however, reanalysed the data of Laakso et al. (2007a) with their model and argued that the events were dominated by ion-mediated processes. In some cases, ion-mediated processes have been observed to be important at the beginning of the events and the negative ions to be favoured over the positive ones (Laakso et al., 2007a,c). During particle formation small ions seem to activate earlier than neutral 2-nm particles in Hyytiälä (Laakso et al., 2007c; Manninen et al., 2009b, 2010). This is in accordance with the earlier laboratory observations that small ions activate at lower super saturation than neutral ones (Winkler et al., 2008).

Despite its frequent occurrence (Manninen et al., 2009a), the ion-mediated particle formation has been observed to contribute on average 10% of the total particle formation in Hyytiälä (Manninen et al., 2009b). In addition, Kulmala et al. (2010) reported that ion-mediated mechanisms could explain about 10% of the particle formation in Hyytiälä, Hohenpeissenberg and Melpitz rural continental sites. These are in consistent with earlier observations (e.g., Kulmala et al., 2007). Gagné et al. (2008) obtained similar contributions of ions in particle formation in Hyytiälä based on their charging state measurements: median value of 6.4% with range 1.7–16.5%, which, however, did not include sub-3 nm ion-ion recombination. Similarly, nocturnal particle formation seems to be driven by neutral mechanism in Hyytiälä, Finland (Lehtipalo et al., 2010a).

Iida et al. (2006) estimated that the contribution of positive ion-induced particle formation was 0–3.8% and negative ion formation 0–2.6% during their measurements in Boulder, Colorado, USA. On the other hand, Asmi et al. (2010) were able to study particle formation measured with both an AIS and a DMPS on only one day during their campaign in Antarctica. The results from that day clearly indicate that ion-mediated particle formation contributed to about 30% of the total particle formation rate.

Based on aircraft measurements, Kulmala et al. (2010) and Mirme et al. (2010) concluded that the contribution of ions to particle formation is minor for the whole tropospheric column. However, Arnold (2008) estimated that ion-induced nucleation could be the dominant process at altitudes of ca. 8 km over Central Europe with a maximum particle formation rates of 25 $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$, which is the same as the maximum ion production rate via ionisation at 8 km (Bazilevskaya et al., 2008). Arnold (2008) concluded that neutral and ion-induced nucleation is frequent phenomena in the upper troposphere, but further growth is limited.

## 6 Concluding remarks

This review is based on ca. 250 publications, from which 92 articles presented observations on small air ions and size distribution measurements, chemical composition as well as formation and growth rates of sub-3 nm ions. Our main focus was on the spatial and temporal variation of small ion concentrations, and the secondary focus was in the observations of the role of ions on nucleation and growth.

The main natural sources of small ions are: air molecule ionisation by radon decay, gamma and cosmic radiation, all of them exhibiting strong spatial and temporal variations. This variability of ion source rates is evident from the comparison of results from different sites. In marine environments the only important source of small ions is cosmic radiation, and the low source rates lead to lower concentrations of small ions than are found in terrestrial environments.

Most of the concentration measurements were made in the boundary layer, excluding the high altitude sites like Puy de Dôme, France, and Pyramid in Himalaya, Nepal, which were affected by free troposphere conditions. The median concentrations of small ions seemed to decrease with increasing altitude, even though the mean concentrations did not have an altitude dependence. Thus, the potential enhancing effect of cosmic radiation induced ion production resulting in the increased concentration of small ions as a function of altitude in the lower atmosphere (Chalmer, 1967) remained without confirmation due to the vicinity of ground at most of the concentration measurements. However, enhanced radon activity concentration was observed to be behind the temporal increase in small ion concentrations observed at certain sites (e.g. Hõrrak et al., 2003; Dhanorkar et al., 1994; Suni et al., 2008).

The enhancing effect of car exhaust on small ion concentrations has been confirmed in the laboratory (Haverkamp et al., 2004; Lähde et al., 2009). Some studies revealed increased small ion concentrations due to traffic (Ling et al., 2010), while some others observed no influence (Hirsikko et al., 2007c) or even a decrease in concentration due to traffic (Tiitta et al., 2007). Additionally, falling water droplets have been observed to increase ion concentrations (e.g., Hirsikko et al., 2007a; Laakso et al., 2007b; Tammet et al., 2009).

Sinks of small ions include recombination, loss by growth to larger sizes and coagulation with the pre-existing particles. The growth and coagulation processes vary significantly with time. Small ion measurements inside the forest confirm an additional sink due to ion deposition in the forest canopy (Tammet et al., 2006). High aerosol concentrations, such as those found in polluted urban environments, act as increased sinks for small ions (e.g., Retalis et al., 2009; Ling et al., 2010). However, the aerosol sink in some of the urban environments was not substantially increased (e.g., Hirsikko et al., 2007c). Clouds were observed to be effective sinks for small ions (Reiter et al., 1985; Lihavainen et al., 2007; Venzac et al., 2007; Virkkula et al., 2007). Thus, each observation site has different combinations of sink and production terms for small ions.

The effect of electric charge can lead to enhanced growth rates of the smallest particles (e.g., Yu and Turco, 2000; Kulmala et al., 2004b). Enhanced growth of sub-3 nm ions has been observed at least at the coastal site Mace Head, Ireland (Manninen et al., 2010) as well as in winter at SMEAR II, Finland (Hirsikko et al., 2005) and in Tumbarumba, Australia (Suni et al., 2008). However, usually the opposite has been observed (Kulmala et al., 2004b, Hirsikko et al., 2005, Virkkula et al., 2007; Suni et al., 2008, Yli-Juuti et al., 2009; Manninen et al., 2010) indicating that ions would be less important than neutral processes in particle growth. The growth rate results are often presented as median or average values over a month, and the information about each individual event is lost. Furthermore, it has been observed that on days when ion-mediated processes are almost inexistent, 3–7 nm particles grow faster than on days with some contribution of ions, while the growth rates of ions were independent of the role of ions in the particle formation (Gagné et al., 2010). The enhanced growth of 3–7 nm particles on days, when formation rates were high and ions had unsubstantial contribution, may be explained by enhanced saturation ratios of condensing vapours.

Ion-mediated nucleation has been observed in chamber experiments (Enghoff et al., 2008; Duplissy et al., 2010). Atmospheric observations suggest, however, that the role of ion-mediated particle formation is usually small compared to neutral pathways, approximately 10% or even less of the total at various European rural, urban and coastal sites (e.g., Gagné et al., 2008; Kulmala et al., 2010; Manninen et al., 2009b, 2010) and less than 5% during summertime events in Boulder (Iida et al., 2006).

The observations from Antarctica (Asmi et al., 2010) support the theory of an enhancing effect of low temperature and aerosol surface area to ion-mediated particle formation processes (Curtius et al., 2006; Yu, 2010). The observations by Gagné et al. (2010), however, show that overcharged events took place during warm days in Hyytiälä, Finland, while undercharged days occurred on cold days.

At low total formation rates of 2-nm particles, the ion-mediated mechanism could explain the observed nucleation rates and the observations that ion concentrations (charged fraction) decrease with increasing total particle formation rates (Vana et al., 2006a; Nieminen et al., 2009; Kulmala et al., 2010; Gagné et al., 2010; Manninen et al., 2010). The largest variation was found in the $J_2$[tot], whereas $J_2$[ions] was typically below 1 $\mathrm{cm^{-3}\,s^{-1}}$ in the boundary layer (e.g., Manninen et al., 2010). On the other hand, ions may contribute only for a short time at the beginning of the particle formation event and become less important as time progresses and neutral mechanisms take over (Laakso et al., 2007a). Ion-mediated nucleation is limited by ion production and is sometimes even negligible. However, it is an important particle formation mechanism under certain conditions, as discussed in this review.

At high altitudes, the ion pair production rate by galactic cosmic radiation shows an 11-year cycle opposite to the solar cycle (Bazilevskaya et al., 2008). The overview by Harrison and Carslaw (2003) discuss the effect of ions on cloud formation and processes therein. References cited in that overview show that the albedo of the planet varies in phase with the solar cycle. There have also been studies about the possible connection between the galactic cosmic ray intensity reaching the Earth's atmosphere and the global cloud cover (Kirkby, 2008). Galactic cosmic rays ionise air molecules, and thus could potentially affect the production of cloud condensation nuclei in the atmosphere. The changes in the activity of our Sun modulate the amount of galactic cosmic rays coming to Earth, and this could serve as a mechanism for altering the global cloud cover and, consequently, climate. This connection is currently, however, unclear and under active research (Kirkby, 2008; Duplissy et al., 2010). In contrast, the solar cycle seems to have no influence on secondary particle formation or ion production rates close to the Earth's surface, as observed in the boreal forest (Kulmala et al., 2010).

In future, the CLOUD experiment in CERN should give new information about the particle formation processes and has advantages over field measurements (e.g. controlled gas composition) that may help to understand new particle formation in nature (Duplissy et al., 2010). More measurements, and longer continuous measurement periods, are needed at different altitudes and longitudes.

**Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/10/24245/2010/acpd-10-24245-2010-supplement.pdf.**

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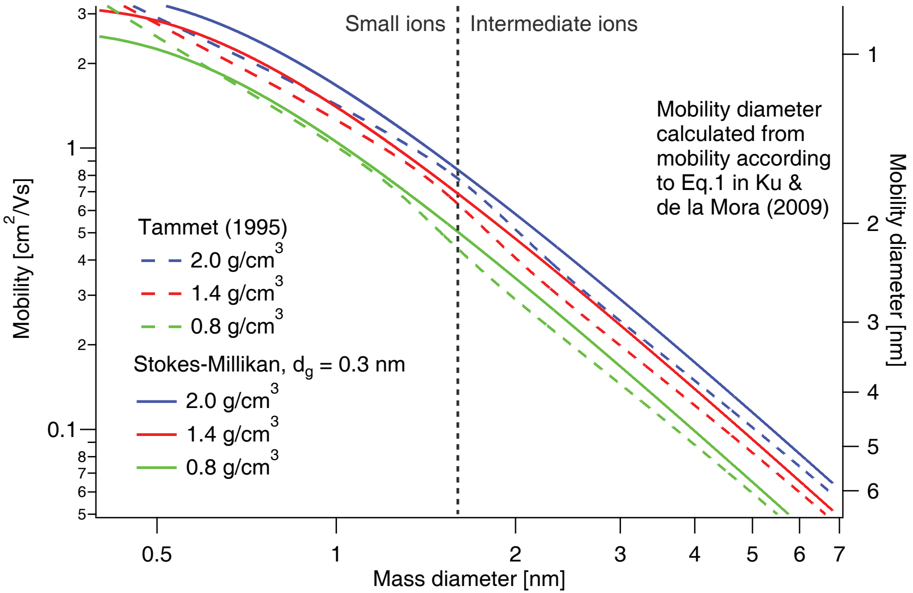

**Fig. 1.** Mobility versus mass- and mobility diameter calculated according to Tammet (1995) and modified Stokes-Millikan (Ku and de la Mora, 2009) using three different densities.

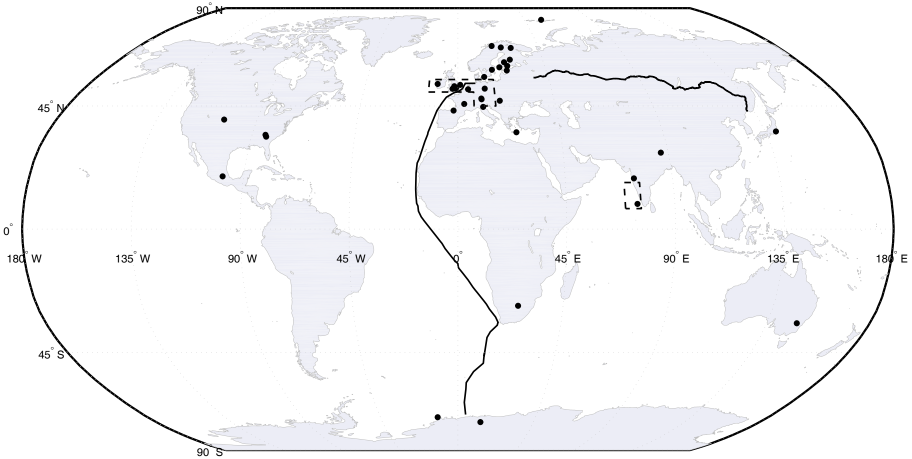

**Fig. 2.** The map of world: measurement sites are indicated with black dots, the trip by train through Siberia, Russian, and boat trip from Europe to Antarctica with black curves.

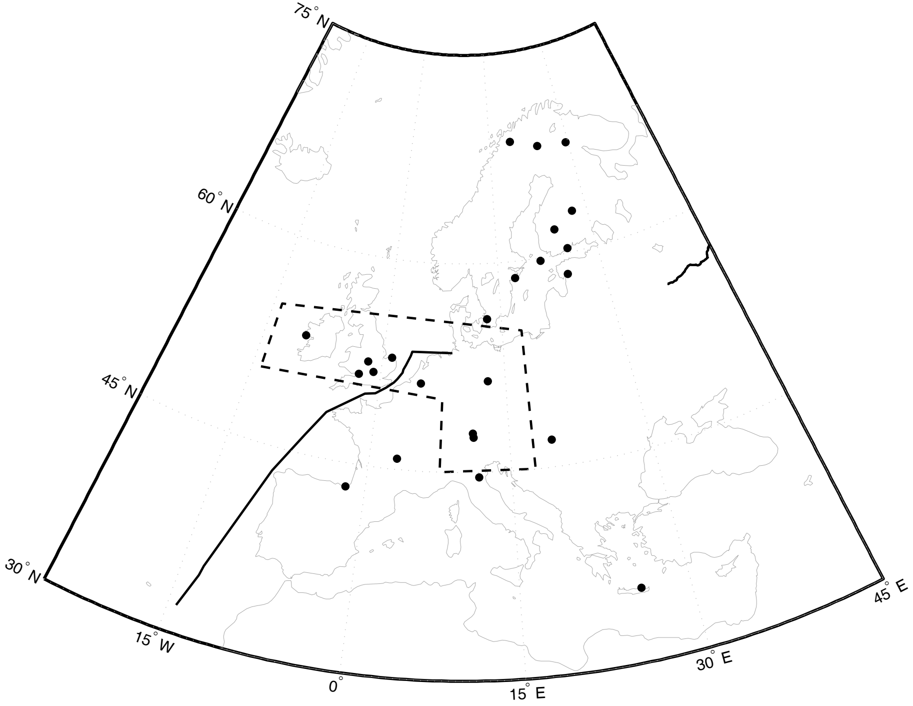

**Fig. 3.** The map of Europe: measurement sites are indicated with black dots and the aircraft flew inside the area indicated by dashed line. Also the parts of boat and train trips are shown.

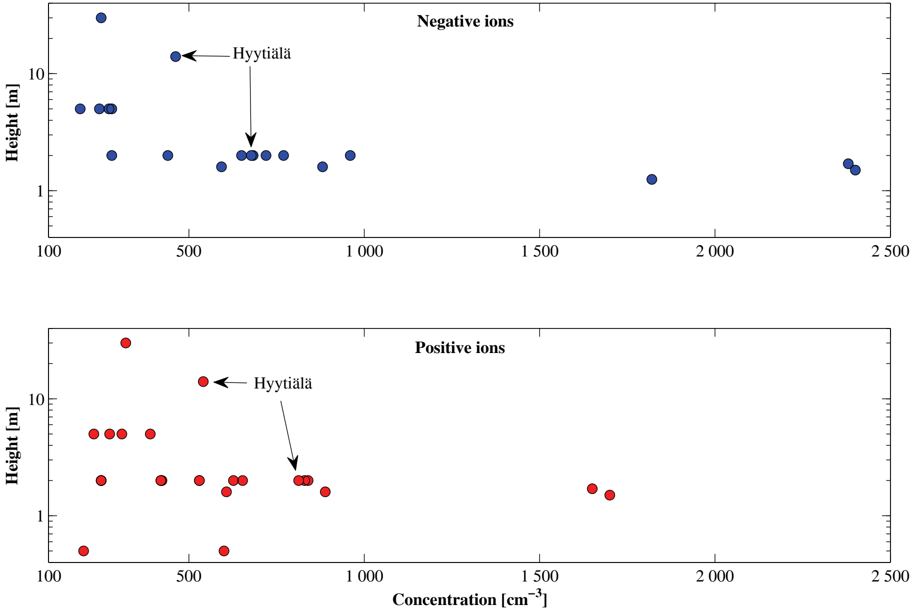

**Fig. 4.** Mean concentrations as a function of height from the ground. Red colour indicates positive and blue colour negative sign. Data at 30 m is from ocean.

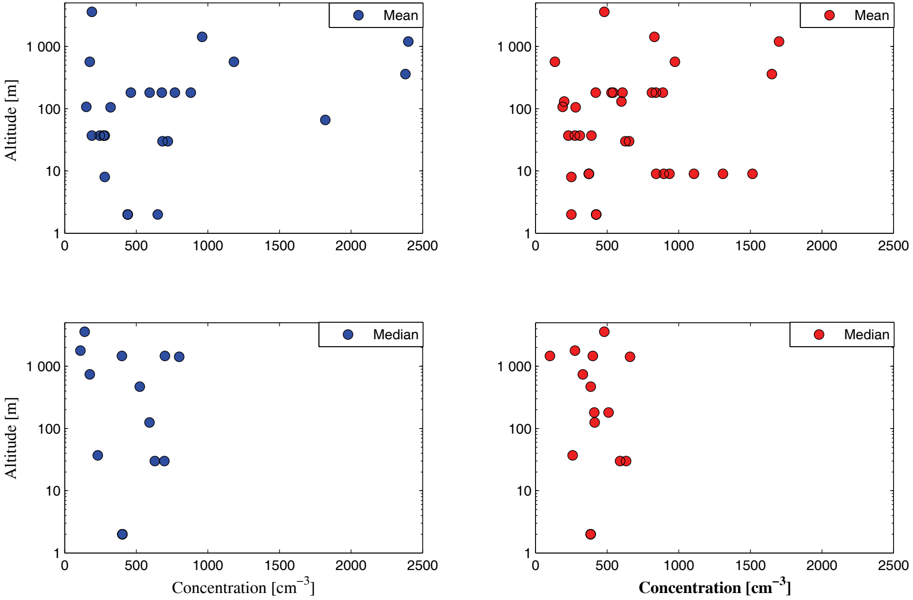

**Fig. 5.** The mean (top panel) and median (bottom panel) concentrations of small ions as a function of altitude from sea level, airborne measurements are not included. Red colour indicates positive and blue colour negative sign.

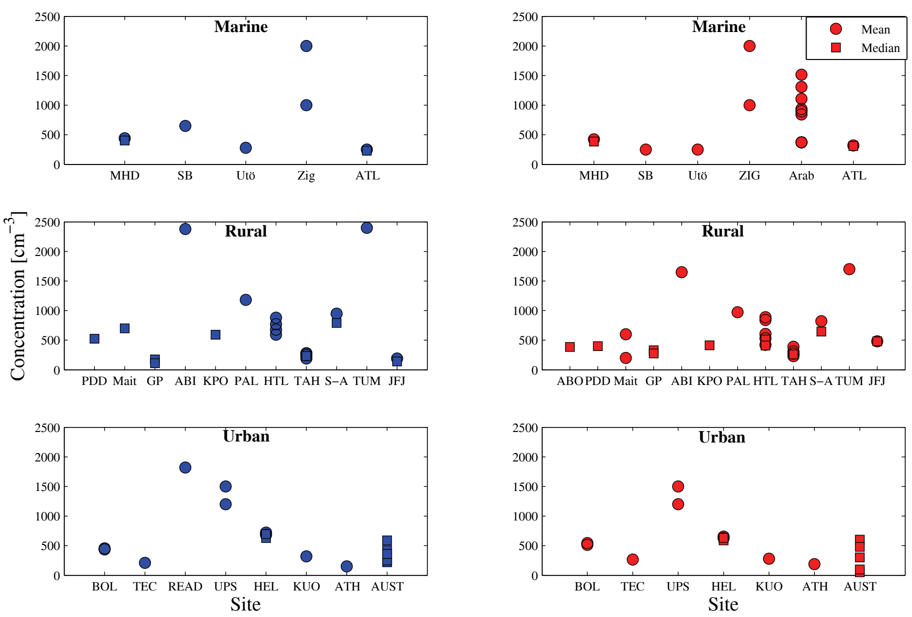

**Fig. 6.** The mean and median concentrations of small ions as a function of site in marine (top panel), rural (middle panel) and urban (bottom panel) environments based on measurements on the ground. Red markers are for positive and blue markers for negative ions. MHD=Mace Head, SB=San Sebastian, Zig=Ziegler, Arab=Arabian sea, ATL=Cruise on Atlantics, PDD=Puy de Dôme, Mait=Maitri, GP=Garmisch-Partenkirchen, ABI=Abisko, KPO=K-Puzsta, PAL=Pallas, HTL=Hyytiälä, TAH=Tahkuse, S-A=South-Africa, TUM=Tumbarumba, ABO=Aboa, JFJ=Jungfraujoch, BOL=Boulder, TEC=Tecamac, Read.=Reading University, Ups=Upsala, HEL=Helsinki, KUO=Kuopio, ATH=Athens and AUST=Australia (Ling et al., 2010).

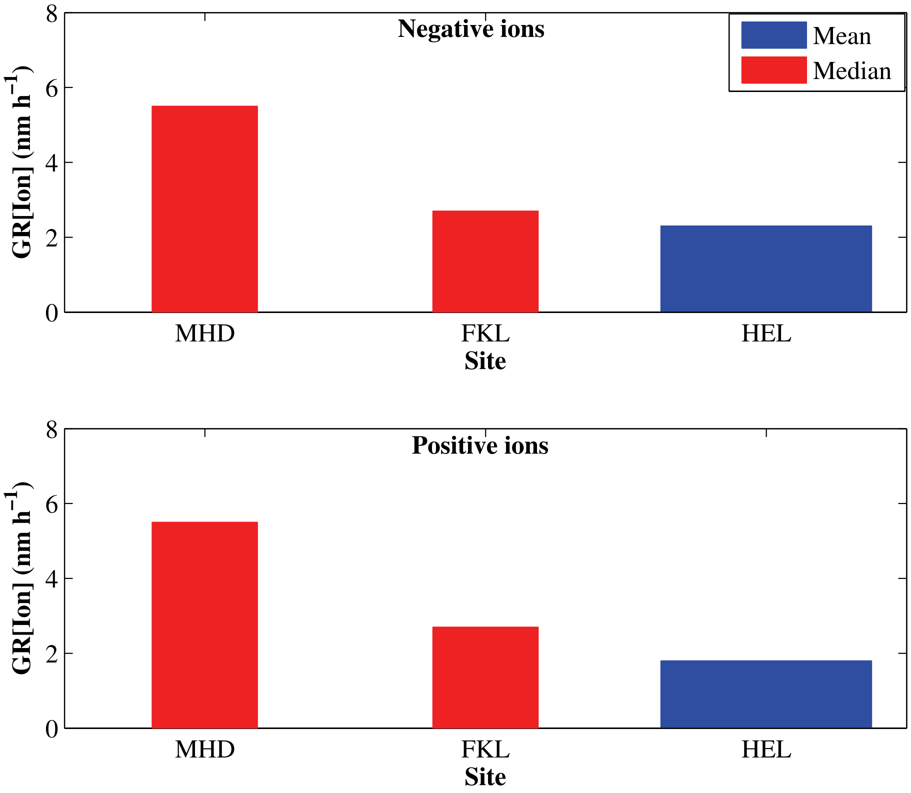

**Fig. 7.** The mean (blue bar) and median (red bar) GR[ion] as a function of site in marine and urban environments for negative ions (top panel) and for positive ions (bottom panel). MHD=Mace Head, FKL=Finokalia, HEL=Helsinki.

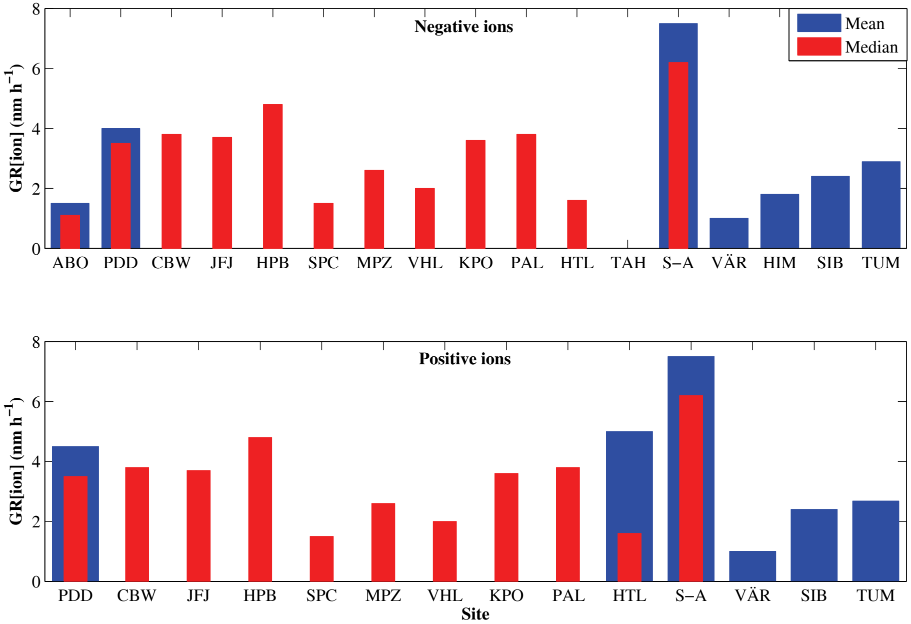

**Fig. 8.** The mean (blue bar) and median (red bar) GR[ion] as a function of site in rural environments for negative ions (top panel) and for positive ions (bottom panel). ABO=Aboa, PDD=Puy de Dôme, CBW=Cabauw, JFJ=Jungfraujoch, HPB=Hohenpeissenberg, SPC=San Pietro Capofiume, MPZ=Melpitz, VHL=Vavihill, PAL=Pallas, HTL=Hyytiälä, TAH=Tahkuse, S-A=South-Africa, VÄR=Värriö, HIM=Himalaya, SIB=Siberia, TUM=Tumbarumba.

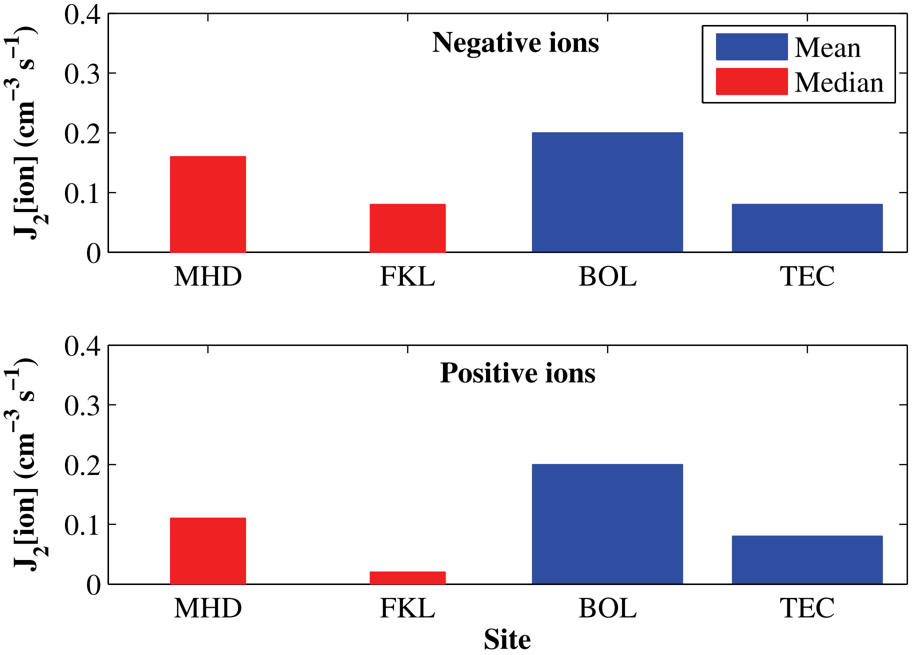

**Fig. 9.** The mean (blue bar) and median (red bar) $J_2$[ion] as a function of site in marine and urban environments for negative ions (top panel) and for positive ions (bottom panel). MHD=Mace Head, FKL=Finokalia, BOL=Boulder, TEC=Tecamac.

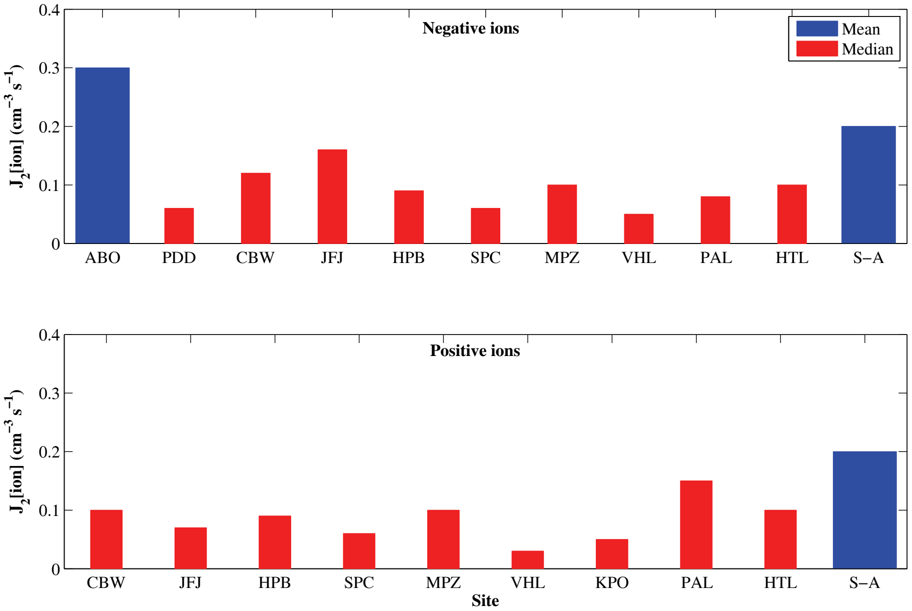

**Fig. 10.** The mean (blue bar) and median (red bar) $J_2$[ion] as a function of site in rural environments for negative ions (top panel) and for positive ions (bottom panel). ABO=Aboa, PDD=Puy de Dôme, CBW=Cabauw, JFJ=Jungfraujoch, HPB=Hohenpeissenberg, SPC=San Pietro Capofiume, MPZ=Melpitz, VHL=Vavihill, PAL=Pallas, HTL=Hyytiälä, S-A=South-Africa.