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ON FORMATION, GROWTH AND CONCENTRATIONS OF AIR IONS

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Academic dissertation

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## **On formation, growth and concentrations of air ions**

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University of Helsinki, 2011

### **Abstract**

The aims of this work were to gather comprehensive view of air ion sources and sinks, to observe evolution of small ion concentrations in spatial and temporal scale, to develop and test data-analysis methods, and to gain new knowledge of particle formation and initial growth. We determined natural ion sources directly by measuring ionising components (radon activity concentrations and external radiation dose rates) at the SMEAR II station (Station for Measuring Forest-Ecosystem Atmosphere Relations). Based on six years of data, the mean ionisation rate was  $10 \text{ ion-pairs cm}^{-3} \text{ s}^{-1}$  owning large temporal variation. Other ion sources (e.g. car exhaust, power lines) have only spatially and temporally limited contribution, as was discussed in a literature review.

Small ion (< ca. 1.6 nm in mass diameter) concentrations depend on balance between the ion sources and sinks. Atmospheric mixing, ventilation of room air, deposition, ion-ion recombination, growth to larger sizes and coagulation with background aerosol particles modify efficiently the small ion concentrations. Intermediate ions (ca. 1.6-7.4 nm in mass diameter) have been observed only during particle formation events, rainfall and in high wind conditions.

Due to detection range of ion spectrometers (below 3 nm) and nature of ions, new guidelines for particle formation event analysis based on ion size distribution data were developed and utilised. The results showed that particle formation may be suppressed at 3-5 nm diameters, which have not been observed with former instruments owning cut-off size of 3 nm. We also utilised a recently developed growth rate analysis method. Results showed that with the applied method the initial growth of particles can be followed with some limitations. A comprehensive literature review of observations of small ions and particle formation showed that the results presented in Papers I-IV were in good agreement with other findings.

Keywords: Air ions; small, intermediate and large ion concentrations; ion-pair production; particle formation and growth

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## List of publications

This thesis consists of an introductory part, four research articles and one review article. The papers are reproduced with the permission of the journals.

Paper I **Hirsikko Anne**, Paatero Jussi, Hatakka Juha and Kulmala Markku: The  $^{222}\text{Rn}$  activity concentration, external radiation dose and air ion production rates in a boreal forest in Finland between March 2000 and June 2006. *Boreal Environment Research*, 12, 265–278, 2007a.

Paper II **Hirsikko Anne**, Laakso Lauri, Hörrak Urmas, Aalto Pasi, Kerminen Veli-Matti and Kulmala Markku: Annual and size dependent variation of growth rates and ion concentrations in boreal forest. *Boreal Environment Research*, 10, 357–369, 2005.

Paper III **Hirsikko Anne**, Yli-Juuti Taina, Nieminen Tuomo, Vartiainen Eija, Laakso Lauri, HusseinTarek and Kulmala Markku: Indoor and outdoor air ions and aerosol particles in the urban atmosphere of Helsinki: characteristics, sources and formation. *Boreal Environment Research*, 12, 295-310, 2007b.

Paper IV **Hirsikko Anne**, Bergmann Tommi, Laakso Lauri, Dal Maso Miikka, Riipinen Ilona, Hörrak Urmas and Kulmala Markku: Identification and classification of the formation of intermediate ions measured in boreal forest. *Atmospheric Chemistry and Physics*, 7, 201-210, 2007c.

Paper V **Hirsikko Anne**, Nieminen Tuomo, Gagné Stephanie, Lehtipalo Katrianne, Manninen Hanna, Ehn Mikael, Hörrak Urmas, Kerminen Veli-Matti, Laakso Lauri, McMurry Peter, Mirme Aadu, Mirme Sander, Petäjä Tuukka, Tammet Hannes, Vakkari Ville, Vana Marko and Kulmala Markku: Atmospheric ions and nucleation: A review of observations. *Atmospheric Chemistry and Physics*, 11, 767-798, doi:10.5194/acp-11-767-2011, 2011.

## 1. Introduction

Aerosol particles have a large impact on the Earth-climate system, air quality, visibility and even on human health (Myhre, 2009; Quaas et al., 2009; Hand and Malm, 2007; Russell and Brunekreef, 2009; Arneth et al., 2009). Aerosol particles absorb and scatter solar radiation and have an influence on the penetration of outgoing infrared radiation. Thus, the aerosol particles have direct cooling and warming effects on climate (IPCC, 2007). Aerosol particles may become cloud condensation nuclei. More aerosol particles mean more small cloud droplets, brighter clouds and less precipitation. Therefore, aerosol particles affect climate indirectly by modifying cloud properties (Lohmann and Feichter, 2005). Overall, aerosol particles are estimated to cool the atmosphere, and thus to lessen global warming (IPCC, 2007).

In polluted urban areas visibility is solely due to the large number concentration (up to  $10^6 \text{ cm}^{-3}$ ) of aerosol particles (e.g. Mönkkönen et al., 2005). In clean environments (e.g. in Antarctica) the particle concentrations are orders of magnitude lower and the visibility higher (Koponen et al., 2003; Asmi et al., 2010). Air pollution, including aerosol particles, has often harmful, sometimes even toxic, effect on human health (e.g. Curtis et al., 2006; Becker et al., 2010).

Aerosol particles can be liquid or solid, and their size ranges from 1 nm to 10  $\mu\text{m}$ . Particle shape varies from a sphere to different geometries and agglomerates depending on chemical composition and formation processes. Primary particles are formed via mechanical processes or result from gas-to-particle conversion mechanisms. For example, stormy winds raise sand from deserts, studded tyres scrape fragments from asphalt roads, splashing of the sea produces salt particles, car exhaust contains soot particles. Forest fires and volcanic eruptions produce ash-particles, soot and organics. Pollen and bacteria are also large aerosol particles.

Secondary aerosol particle formation is a globally frequent phenomenon (Kulmala et al., 2004a; Kulmala and Kerminen, 2008). The particles are formed via nucleation, which may happen via neutral or ion-induced pathways (Kulmala et al., 2006, 2007; Iida et al., 2006; Yu, 2010). The precursors of aerosol particle formation are of anthropogenic and biogenic origins. Sulphuric acid together with water vapour and possibly with some low volatile vapours (e.g. ammonia and organics) are expected to be responsible for nucleation (Weber et al., 1996, 1997, 1998, 1999; Eisele and McMurry, 1997; Clarke et al., 1999; Sihto et al., 2006; Vartiainen et al., 2006; Riipinen et al., 2007, 2009; Kulmala and Kerminen, 2008; Kuang et al., 2008; Kazil et al., 2008 and references therein; Zhang et al., 2009; Paasonen et al., 2009, 2010; Sipilä et al., 2010, Kerminen et al., 2010). After

formation, the evolution and residence time of the aerosol particle population in the atmosphere is determined by the competition between different removal and redistributing processes. These processes include growth by vapour condensation (e.g. sulphuric acid and organics), coagulation, agglomeration, as well as dry and wet depositions.

Most of the large particles carry an electric charge or several charges, while less than 1 % of the smallest particles are electrically charged (Hoppel et al., 1985; Hinds et al., 1999). Charged particles are called air ions, which are divided into small, intermediate and large ions, as was observed already at the beginning of the 20<sup>th</sup> century (Flagan, 1998) and was further analysed by e.g. Hörrak (2000, 2003). The limiting diameters cannot exactly be determined to cover all situations due to differing atmospheric conditions. Typically a diameter  $d \sim 1.6$  nm (in mass diameters, Tammets, 1995) is used as a limit between the small and intermediate ion populations. The limit between intermediate and large ions is in the range of 7-8 nm (ca. 7.4 nm according to Hörrak et al., 2000). Small ions are singly charged molecules and clusters (Eisele 1989a,b; Ehn et al., 2010; Junninen et al., 2010). The small ions were called "cluster ions" in the Papers I-IV of this work.

Small ions are formed via air molecule ionisation produced by radon decay and external radiation (gamma radiation and cosmic radiation), in corona discharges formed by power lines and point-like sources in the presence of a strong electric field (e.g. towers during thunderstorms, Eisele, 1989a, b; Paper I; Jayaratne et al., 2008; D'Alessandro, 2009; Matthews et al., 2010). They are emitted from car exhaust, induced by waterfalls, and in high wind/storm conditions (Virkkula et al., 2007; Laakso et al., 2007a; Vana et al., 2006b; Jayaratne et al., 2010). Intermediate ions are formed via ion-induced nucleation, by growth of small ions, by small ion attaching on particles formed via neutral mechanisms, via splashing of water, and in high wind/storm conditions (Paper IV, Virkkula et al., 2007; Laakso et al., 2007a, b; Vana et al., 2008; Tammets et al., 2009).

Air ions are part of the atmospheric electrical circuit (e.g. Harrison, 2004). The atmospheric layer above the 80 km height is called the ionosphere. In the ionosphere the atmosphere is influenced by high ionisation rates, which are modulated by the Sun. The ionosphere reflects, and in some conditions disturbs by absorbing, radio wave propagation. As summarised by Harrison and Carslaw (2003), the ionosphere is in a positive potential, while the Earth's surface is in a negative potential. This causes a vertical electric field in the atmosphere. Due to the atmospheric electric field positive ions drift downwards and negative ions drift to the opposite direction. This phenomenon is called the atmospheric electrode effect. However, due to turbulence, ions are quite equally distributed in the atmosphere.



Inside clouds the electric field is enhanced due to vertical upward transport of positive ions (light ice crystals), while negative ions (larger hailstones) tend to be less mobile. The separation of electric charge inside clouds results in the formation of thunderstorms.

Air conductivity ( $\lambda$ ) is sum of polar conductivities ( $\lambda^\pm$ )

$$\lambda = \lambda^- + \lambda^+, \quad (1)$$

where polar conductivities are sums of the number concentration ( $n^\pm$ ) of small ( $s$ ), intermediate ( $i$ ) and large ( $l$ ) ions multiplied by the respective average mobility ( $Z^\pm$ ) and electric charge ( $e$ ) of ions, as presented by Dhanorkar and Kamra (1992)

$$\lambda^\pm = en_s^\pm Z_s^\pm + en_i^\pm Z_i^\pm + en_l^\pm Z_l^\pm. \quad (2)$$

Typically small ions make up most of the conductivity due to their high mobility. For example, in Tahkuse, Estonia, on average 96 % of the air conductivity was due to small ions (Hõrrak, 2001). Increases in aerosol concentration due to pollution episodes increase the contribution of large ions to the air conductivity (Dhanorkar and Kamra, 1992). However, the air conductivity decreases if more small ions coagulate with large particles, decreasing their contribution to the conductivity. Nevertheless, when the concentrations of intermediate and large ions are large enough, the value of conductivity may increase (Dhanorkar and Kamra, 1997).

As discussed here, aerosol particles are produced and modified by various processes. The particles and processes they are involved have several direct or indirect effects on our everyday life (IPCC, 2007). The aim of atmospheric aerosol science is to understand and evaluate the importance of aerosol particles (from both primary and secondary sources) in local and global scale phenomena (e.g. Lihavainen et al., 2003; Spracklen et al., 2008; Merikanto et al., 2010; Kurtén et al., 2011). Therefore, investigation of aerosol particle properties and dynamics starting from the initial steps of particle formation and ending up to cloud dynamics is essential.

The aims of this thesis are

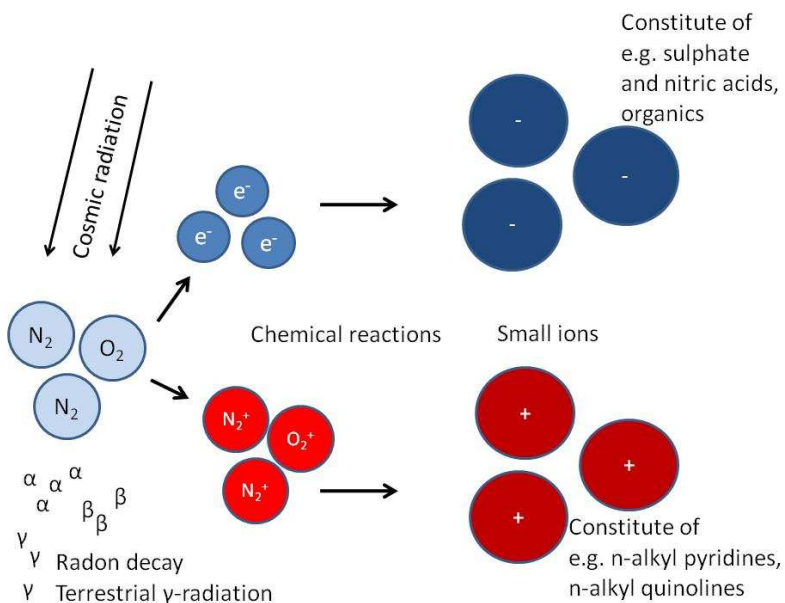
1. to develop and test data analysis and classification methods (Papers II and IV)
2. to evaluate air ion sources based on directly measured radon activity concentrations and external radiation dose rates at the SMEAR II station (Station for Measuring Forest-Ecosystem Atmosphere Relations, Paper I), and based on literature (Paper V),

3. to observe the evolution of small ion concentrations in different spatial and temporal scales, and to further obtain a comprehensive view of the sources and sinks in different environments (Papers II, III and V),
4. to obtain new information of particle formation and initial growth based on ion size distribution measurements, which offer information below the traditional size limit ( $\sim 3$  nm), and the connection between air ions and particle formation (Papers II-V).

## 2. Air ions — sources and sinks

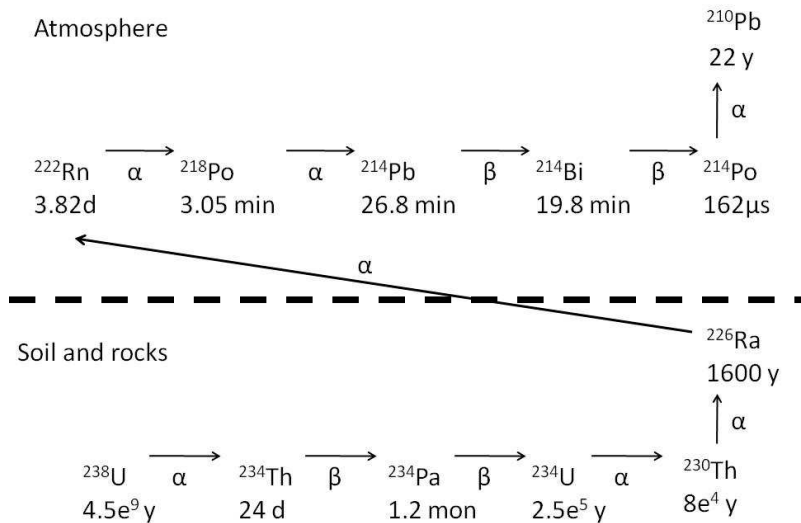
Ionisation of air molecules ( $N_2$  and  $O_2$  constitute 78 % and 21 %, respectively, of air composition) produces primary air ions, i.e. positive ions and free electrons (Fig. 1). Primary ions undergo rapid chemical reactions, getting neutralised and charged again, and become small ions in less than a second from their formation. The life-time of a small ion is determined by its removal processes. The life-time is of the order of 100 seconds in rural sites and less in polluted environments (Hörrak, 2001). The chemical composition and size distribution of small ions depend on the proton and electron affinities of available trace gases (Arnold et al., 1978; Ferguson et al., 1978; Eichkorn et al., 2002; Eisele, 1989a,b; Junninen et al., 2010; Ehn et al., 2010).

The concentration balance of air ions in the atmosphere is determined by competition between production and loss mechanisms (e.g. Israël, 1970). In the boundary layer, the dominant natural source of air ions is ionisation via radon decay and external radiation (Sect. 2.1, Harrison and Tammet, 2008). In the lower boundary layer, there are also other sources of air ions (Sect. 2.2), which have spatially and temporally limited contributions. Observations of the removal processes (Sect. 2.3) have been discussed in Paper V.



**Fig.1.** A schematic picture of the small ion formation via air molecule ionisation.

## 2.1. Radon and external radiation



**Fig.2.** Decay series of  $^{238}\text{U}$ : the decay pathway of  $^{222}\text{Rn}$  has atmospheric relevance. The half-life for each component is presented in the figure.

Radon ( $^{222}\text{Rn}$ ) is a noble gas suspended as a single atom in the air and it is emitted from the ground (soil and rocks). The  $^{222}\text{Rn}$  decay series starting from Uranium ( $^{238}\text{U}$ ) is shown in Fig. 2. Many of the decay products have a long half-life (up to  $1e^9$  years), while the radon daughters  $^{218}\text{Po}$  (Polonium),  $^{214}\text{Pb}$  (Lead),  $^{214}\text{Bi}$  (Bismuth) and  $^{214}\text{Po}$  have a half-life from less than a second to 27 minutes, forming a continuous ionising source. The  $^{222}\text{Rn}$  has a half-life of 3.82 days, which is long compared to other radon isotopes  $^{220}\text{Rn}$  (half-life = 55s) and  $^{219}\text{Rn}$  (half-life = 4s). Therefore, the  $^{222}\text{Rn}$  is the dominant radon isotope in the atmosphere, while the  $^{220}\text{Rn}$  may contribute, as well. In addition to air molecule ionisation process, radon activity concentrations are also suitable tracers of continental air masses and in estimations of emission rates of e.g. green house gases (e.g.  $\text{CO}_2$  and  $\text{N}_2\text{O}$ ) due to its half-life and loss via radioactive decay (Zaharowski et al., 2004).

The spatial variations of radon emissions and concentrations are large (Hörrak et al., 2003; Nagaraja et al., 2003; Robertson et al., 2005; Galmarini, 2006; Paper I; Suni et al., 2008; Szegvary et al., 2009). This variation is due to differences in the radon (or  $^{238}\text{U}$ ) content in soil and rocks, as well as differences in the release rates from soil (Shashikumar et al., 2008; Mehra et al., 2009; Gupta et al., 2010). The latter depends for example on soil moisture: from wet soil less radon is exhaled into the atmosphere (Paper I). On continental sites, where the ground is covered by snow in

winter, the release rate of radon is reduced compared to conditions with no snow cover (e.g. Hatakka et al., 2003; Siingh et al., 2007; Paper I). Therefore, radon activity concentration (decays in cubic meter) has an annual cycle, while the diurnal cycle of activity concentration is mainly due to atmospheric mixing (Table 1; e.g. Hatakka et al., 2003; Paper I). At night-time there is less mixing in the atmosphere and the height of mixed layer is smaller; thus the radon activity concentration begins to accumulate and more ion pairs are produced compared to a more mixed atmosphere in day-time.

External radiation includes three main components: 1) natural  $\gamma$ -radiation, 2) artificial  $\gamma$ -radiation, and 3) cosmic radiation (e.g. Szegvary et al., 2007). The natural terrestrial  $\gamma$ -radiation originates from decay series of  $^{238}\text{U}$  (Uranium),  $^{232}\text{Th}$  (Thorium) and  $^{40}\text{K}$  (Potassium). Thus,  $\gamma$ -radiation from radon decay is included in the components of external radiation. The artificial  $\gamma$ -radiation is from the decay of  $^{137}\text{Cs}$  (Caesium), which at the site of this study originates from Chernobyl fallout and nuclear weapon tests. The contribution of the artificial component to the total  $\gamma$ -radiation has been evaluated to be of the order of a couple of percents (Szegvary et al., 2007).

The diurnal cycle of the ground based  $\gamma$ -radiation dose rate is practically nonexistent (e.g. Hatakka et al., 1998; Paper I). However, the seasonal cycle due to changes in soil moisture and snow cover, both preventing the  $\gamma$ -photon emission, is more pronounced (e.g. Hatakka et al., 1998; Paper I; Szegvary et al., 2007). The spatial variation is large even in Europe (Szegvary et al., 2007).

Cosmic radiation originates from solar flares and from outside the solar system. Cosmic radiation constitutes mainly of fast moving protons ( $\text{H}^+$ ) and  $\alpha$ -particles ( $\text{He}^+$ ) (e.g. Reitz, 1993; Bazilevskaya et al., 2008). In the atmosphere, these primary particles (called cosmic radiation) collide with air molecules generating a decay cascade of collisions. The processes included in the cascade are various and complex: 1) secondary radiation, 2) nuclear reactions, and 3) chemical reactions (Reitz, 1993). Secondary radiation consists of electromagnetic radiation (e.g.  $\gamma$ -radiation) and elementary particles (e.g. muons and neutrons). In surface air, the muons are the most efficient molecule ionisers of the cosmogenic components. As an example of the nuclear reactions, the cosmic ray interaction with certain air atoms (N, O, Ar) forms radioactive isotopes (e.g.  $\text{C}^{14}$  (Carbon) and  $\text{Be}^7$  (Beryllium)) to the atmosphere. The cosmogenic isotopes have a long half-life, from half a month to millions of years. These isotopes attach to large aerosol particles and are scavenged from the atmosphere by rainfall (Doering and Akber, 2008).

**Table 1.** A summary of spatial and temporal variation of radon activity concentration and external radiation ( $\gamma$ - and cosmic radiation) dose rate.

	<b>Radon activity concentration</b>	<b>Terrestrial <math>\gamma</math>-radiation dose rate</b>	<b>Cosmic radiation dose rate</b>
<b>Height from the ground (in meters)</b>	Decreases rapidly	The largest changes in the first 5 m, after that small decrease as a function of height	Relatively constant for several tens of meters
<b>Altitude from the sea level (in km)</b>	Concentrations are small above ca. 2 km above the ground	Contributes up to ca. 0.5 km (Li et al., 2007)	Dominant mechanism at 3-50 km, maximum around 15 km
<b>Spatial variation</b>	Strong	Strong	Small, due to Earth's magnetic field the smallest at equator, the largest at circum-polar
<b>Annual cycle</b>	Large variation	Large variation	11-year cycle
<b>Diurnal cycle</b>	Max in (early) morning hours (site dependent), min during the strongest atmospheric mixing	Almost non-existent	Nonexistent

The ionisation by cosmic radiation does not have a clear annual cycle at ground level. However, the cosmic radiation intensity in the atmosphere has an opposite 11-year cycle compared to Sun (Usoskin and Kovaltsov, 2006; Bazilevskaya et al., 2008). This is because of the increase in the interplanetary and Earth's magnetic field strengths, when the solar wind strengthens. Both the cosmic radiation from outside the solar system and towards the atmosphere become somewhat prevented.

The contribution of cosmic radiation on ion production is smallest at sea level (e.g. Usoskin and Kovaltsov, 2006); however, it is the main ionising pathway over oceans (Hensen and van der Hage, 1994). The contribution of cosmic radiation on

ion-pair production rate increases as the altitude increases, and it becomes the dominant mechanism above 3 km (Rosen et al., 1985; Bazilevskaya et al., 2008; Kirkby, 2008). In surface air, the external radiation (including all components) dose rate is relatively constant for several tens of meters, while the radon activity concentration decreases rapidly with increasing elevation in the atmosphere (Robertson et al., 2005).

## **2.2 Other sources for ions — local contribution**

There are also other ion sources, which produce primary ions or release small and intermediate ions (Paper V and references therein). The primary ions are produced due to additional releases of radioactive material into the atmosphere and by corona chargers. Small and intermediate ions are emitted via car exhaust, produced by falling and splashing water, as well as generated during snow storms or otherwise very high wind conditions. The sources discussed in this section have only a temporally and spatially limited effect.

The release of extra radioactive material was experienced e.g. in 1986. A large amount of radioactive material was released into the atmosphere due to an accident in the nuclear power plant at Chernobyl, in the former Soviet Union. This incident caused an additional source for small ions as reported for example from Sweden, Estonia and Greece (Israelsson and Knudsen, 1986; Retalis and Pitta, 1989; Hörrak et al., 1994). After air masses from the accident area passed through measurement stations, the small ion concentrations were doubled. Shortly after that, the concentrations began to decrease back to the normal level within a month.

High-voltage power lines constitute a corona charger for air molecules. Increased small ion concentrations have been observed in the vicinity of power lines (Eisele, 1989a, b; Jayaratne et al., 2008). Ions are quickly scavenged onto the ground in the electric field in which they are formed. However, some fraction of these ions gets attached to larger particles, which may be transported by wind (Chalmers, 1952; Henshaw, 2002; Matthews et al., 2010). Tall objects (tower, trees, etc.) constitute point-like corona chargers during thunderstorms, when the electric field in the vicinity of such objects becomes large enough for corona discharge to occur (Flagan, 1998 and references therein; D'Alessandro, 2009).

Aerosol particles are known to be produced during fuel burning processes in engines or via nucleation from exhaust gas (e.g. Maricq et al., 2002). Small ion (up to  $10^8 \text{ cm}^{-3}$ ) emissions in fuel burning processes have been studied theoretically and experimentally (e.g. Yu and Turco, 1997; Haverkamp et al., 2004; Lähde et al., 2009; Jayatane et al., 2010). In laboratory, Lähde et al. (2009) observed that the

existence of small ions in exhaust was dependent on the exhaust after-treatment system. The study by Jayaratne et al. (2010) showed that by increasing the engine speed the small ion concentration increased. Measurements in the vicinity of a road, showed an increase in small ion concentrations compared to other locations (Jayaratne et al., 2010; Ling et al., 2010). However, the results by Tiitta et al. (2007) from Kuopio road-side experiment showed lower small ion concentrations when the wind was from nearby road compared to other wind directions, which were in contradiction to observations by Jayaratne et al. (2010) and Ling (2010).

Waterfall has been observed to produce lots of small and especially intermediate ions (Laakso et al., 2007b). The mechanism behind this observation, however, is uncertain despite to some attempts to solve the question (Parts et al., 2007; Luts et al., 2009). In many studies rainfall has been observed to enhance intermediate ion concentrations (e.g. Paper V and references therein). The change in ion concentrations has been observed to depend on intensity of precipitation (Hörrak et al., 2006). The ions are formed when water droplets splash on the surface. This phenomenon is known as the Lenard effect, and the ions are called ballo-electric ions (see Tammet et al., 2009 and references therein). Tammet et al. (2009) produced ballo-electric ions in laboratory conditions. They concluded that the studied ions had mobilities in the range of  $0.1\text{-}0.42\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ , and they were singly charged water nano-particles.

There are observations that high wind speeds ( $> 10\text{ m s}^{-1}$ ), snow storms and increased small/intermediate ion concentrations are related to each other at least in Jungfrauoch, Switzerland and in Aboa, Antarctica (Vana et al., 2006b; Virkkula et al., 2007; Paper V). The reason for this phenomenon is uncertain; however, these ions are thought to be generated in friction processes between ice crystals in high wind speeds. In lower wind speeds the ion concentrations may be diluted and ions may get lost via enhanced coagulation and scavenging by aerosol particles and during the snow storms by snowflakes (Siingh et al.; 2007; Kamra et al., 2009). Type of snowfall may affect on observations of the snowfall associated intermediate ion concentrations in locations, where wind speeds were moderate (i.e. Paper IV). Precipitation may be wet snow in near-zero temperatures and high relative humidities ( $> 80\%$ , Saltikoff, 2011). In above-zero temperatures ( $< 5\text{ }^\circ\text{C}$ ) and low relative humidities (30-60 %) precipitation can settle as snowfall due to evaporation cooling (Saltikoff, 2011). High wind speeds and ion concentrations have also been observed to correlate in Athens, Greece, without snowstorm (Retalis, 1977; Retalis et al., 2009).



## 2.3 Removal processes

Temporal variation of small ion concentrations ( $n$ ) is determined by the competition between sources and sinks

$$\frac{dn^{\pm}}{dt} = q_{ion} + q_{ot} - \beta \cdot N \cdot n^{\pm} - \alpha \cdot n^{-} \cdot n^{+} - CS \cdot n^{\pm} - f_a \cdot n^{\pm} - Dep \cdot n^{\pm} - Mix \cdot (n^{\pm} - n_{out}). \quad (3)$$

Small ions are produced via air molecule ionisation ( $q_{ion}$ ) and via other local sources ( $q_{ot}$ ), as was discussed in previous sections. Small ions are lost or redistributed in the atmosphere via interaction between neutral ( $N$  in  $\text{cm}^{-3}$ ) and charged small particles ( $n^{\pm}$  in  $\text{cm}^{-3}$ , the 3<sup>rd</sup> and 4<sup>th</sup> terms on the right-hand side), by attaching to (larger) aerosol particles (the 5<sup>th</sup> term), by growth to larger sizes (the 6<sup>th</sup> term), by depositing due to electric field or thermal motion (the 7<sup>th</sup> term) and via air mixing/dilution (the 8<sup>th</sup> term). Term  $n_{out}$  describes concentration of incoming small ions from outside the studied volume (i.e. room air). The interaction rates of ion-ion recombination and neutral-ion attachment are described by the coefficients  $\alpha$  ( $\text{cm}^3\text{s}^{-1}$ ) and  $\beta$  ( $\text{cm}^3\text{s}^{-1}$ , Israël, 1970; Hoppel, 1985; Hoppel and Frick, 1986). The term CS describes condensation sink ( $\text{s}^{-1}$ ),  $f_a$  growth activation factor ( $\text{s}^{-1}$ ), Dep deposition rate ( $\text{s}^{-1}$ ) and Mix mixing/ventilation rate ( $\text{s}^{-1}$ ) of small ions.

Aerosol particles collide and stick together due to thermal (Brownian motion), electrical or gravitational forces. Such a process is called agglomeration and it leads to aerosol particles sticking together as chains (agglomerates) or different geometries. Interaction between small neutral particles and ions may result an ion, which is larger than small ions, while interaction between two ions results a neutral nano-particle. In this work (Papers I and III) the effect of pre-existing aerosol particles on small ion concentrations was described by the term condensation sink (CS), which was calculated according to Pirjola et al. (1999), Kulmala et al. (2001) and Dal Maso et al. (2005). CS describes the diffusion rate of condensing vapours (typically sulphuric acid is assumed) on aerosol particles. Small ions are molecules and clusters (Eisele, 1989a, b; Junninen et al., 2010; Ehn et al., 2010). We believe that it was reasonable enough to use CS to describe this process, when qualitatively estimating the effect of background aerosol.

Aerosol particles grow by vapour condensation. Electrical interactions may enhance vapour uptake and reduce evaporation both in formation and growth (e.g. Yu and Turco, 2000; Laakso et al., 2003; Lovejoy et al., 2004). However, verification of the enhancing effect of electric charge on growth requires further experimental

investigation. Small particles change their charge identity fast from charged to neutral and back, while growing in size. We are only able to follow apparent temporal changes of whole ion/particle population in certain size ranges. The growth rate analysis is further discussed in Sect. 6.4.

Deposition means the settling of particles on a surface. Due to gravitation, the deposition is the most efficient for large and heavy particles. As an example, the forest canopy serves as deposition surface for aerosol particles and small ions (e.g. Tammet et al., 2006). An electric field (e.g. under power lines) controls the movement of ions (e.g. Eisele, 1989a, b). Nevertheless, the natural atmospheric electric field moves positive and negative ions to opposite directions.

Wet deposition includes removal of particles after dissolution or collision with water droplets. According to Seinfeld and Pandis (2006), the particles that serve as nuclei for cloud and fog droplets are considered to be removed by wet deposition. The observations by e.g. Lihavainen et al. (2007), Virkkula et al. (2007) and Venzac et al. (2007) have shown that clouds are effective sinks for small ions. Precipitation scavenges aerosol particles effectively from the atmosphere. However, during precipitation, the number of intermediate ions rather increases than decreases (Norinder and Siksnas, 1950; Hörrak et al., 2006; Paper IV; Vana et al., 2008; Tammet et al., 2009). Hörrak et al. (2006) have observed that the increased intermediate ion concentrations may serve as a larger sink for small ions of opposite polarity during precipitation.

Ventilation mix and exchange the room air with fresh air. Due to evolution of boundary layer the radon activity and small ion concentrations accumulate during night-time and become diluted during daytime. The observations of mixing and dilution on small ion concentrations will be discussed more in the Results (Sect. 7).

### 3. Measurement sites

This thesis contains ion and particle size distribution data measured at the SMEAR II station, at the vicinity of SMEAR III in Helsinki, and indoors. The radon activity concentrations and external radiation dose rates were measured at SMEAR II. The review Paper V summarises observations of air ions based on literature and presents a brief introduction to 1) history of ion counters, 2) mobility and mass spectrometers used in aerosol science, as well as 3) development of these instruments during last century.

Most of the data was measured at the SMEAR II ( $61^{\circ}50'N$ ,  $24^{\circ}17'E$ , 181 m ASL), which is in Hyytiälä, Southern Finland. The station is surrounded by an almost 50 years old coniferous forest and is considered a rural background site (see details in Hari and Kulmala, 2005). Radon activity concentrations (Sect. 4.1) and external radiation dose rates (Sect. 4.2) were measured at 6 and 1.5 m heights, respectively. The ion and particle size distribution measurements were carried out at a height of ca. 2 m with a Balanced Scanning Mobility Analyser (BSMA, Sect. 5.1), an Air Ion Spectrometer (AIS, Sect. 5.2) and a Differential Mobility Particle Sizer (DMPS, Sect. 5.4). The Neutral cluster and Air Ion Spectrometer (NAIS, e.g. Manninen et al., 2009a) and Airborne NAIS are recent modifications of the AIS. Observations made with the NAIS were utilised in the review Paper V.

Ion size distribution measurements with the AIS (at 2 m height) were conducted in urban Helsinki at a car parking area behind the building of the Physics Department, which is close to SMEAR III station ( $60^{\circ}12'N$ ,  $24^{\circ}57'E$ , 30 m ASL). We also utilised DMPS outdoor measurements from the fourth floor of the Physics Department. The measurement site was 100 m away from a major road. The site was surrounded by buildings, and there was a park between the site and major road. Additionally, there was some building activity in neighbouring area. The SMEAR III station and its surroundings are described in more detail by Järvi et al. (2009).

Indoor measurements with the AIS together with two Condensation Particle Counters (CPC, TSI 3010 and 3025) were carried out in a laboratory room in the Physics Department. The room was a normal laboratory room without other activities or human presence except on a couple of days, which were excluded from further analysis. The indoor measurements were carried out without any inlet tube. The outdoor measurements with the AIS required the use of an additional inlet tube.

## 4. Radon activity concentration and external radiation dose rate

Radon activity concentration is expressed in units of disintegrations per cubic meter =  $\text{Bq m}^{-3}$ , and external radiation dose rate in  $1 \text{ Gy h}^{-1} = 1 \text{ J kg}^{-1} \text{ h}^{-1}$ .

### 4.1 Radon activity concentration measurements and data processing

The  $^{222}\text{Rn}$  activity concentrations cannot directly be measured. However, the decay products (Fig. 2) are quickly scavenged by aerosol particles. Thus, by collecting the aerosol particles onto a glass-fibre filter (Whatman GF/A) we were able to measure beta-particle emission with a Geiger-Müller tube. The measurement setup consists of two identical filter-Geiger-Müller tube systems covered by lead shielding to avoid artificial counts. The measurements were conducted in four-hour turns using  $20 \text{ m}^3 \text{ h}^{-1}$  flow rate. During the first four hours air passed through the filter 1, while during the next four-hour period air passed through the filter 2. During the decay period, when no air was drawn through the filter, beta emission decreased to the background level. The counts were recorded every 10 minutes. The filters were changed after being used for two weeks. The measurement uncertainty was approximately 10 %.

The data processing, which was based on publication by Paatero et al. (1994), was complicated and some sources of error may be pointed out. Since we were only able to count the beta emission rate, we had to make some assumptions before obtaining the  $^{222}\text{Rn}$  activity concentration from the beta activity count rates of decay products. We assumed that 1) the activity concentrations of  $^{222}\text{Rn}$  and  $^{218}\text{Po}$  were almost equal, 2) the activity concentration ratios of  $^{218}\text{Po}$ ,  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  were constant and equal, and 3) the short lived beta emitters were from decay series of  $^{222}\text{Rn}$ , not from  $^{220}\text{Rn}$  or some other radionuclides.

The equilibrium of  $^{222}\text{Rn}$ ,  $^{218}\text{Po}$ ,  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  may be disturbed during a strong inversion. However, we believed that the 6-m measurement height overcomes this problem. The contribution of  $^{220}\text{Rn}$  can be easily checked. The count rate of beta activity reaches a certain base (minimum) value at the end of decay period, if only the  $^{222}\text{Rn}$  is responsible for the counts. The base line is on a higher level if  $^{220}\text{Rn}$  is also contributing. Therefore, the temporal effect of  $^{220}\text{Rn}$  can be removed from the analysis. We believed that the contribution of other radionuclides (i.e.  $^{137}\text{Cs}$ ,  $^{210}\text{Pb}$ ,  $^7\text{Be}$ ,  $^{14}\text{C}$  and other cosmogenic nuclides) was negligible, due to their small activity concentrations (order of  $\mu\text{Bq m}^{-3}$ -  $\text{mBq m}^{-3}$ ). Beta-emitter  $^{85}\text{Kr}$ , which originates from reprocessing of nuclear fuel, exists in similar activity concentrations as the  $^{222}\text{Rn}$  in the atmosphere. However, we considered that the contribution of  $^{85}\text{Kr}$  to ion production rate was small compared to  $^{222}\text{Rn}$ .

We used the following equation by Paatero et al. (1994) to calculate the activity concentration of  $^{218}\text{Po}$  (~ activity concentration of  $^{222}\text{Rn}$ ):

$$\text{Conc} = \frac{R}{V\varepsilon_{214\text{Pb}}\left(\frac{S_1}{\lambda_{218\text{Po}}} + \frac{S_2}{\lambda_{214\text{Pb}}}\right) + V\varepsilon_{214\text{Bi}}\left(\frac{S_3}{\lambda_{218\text{Po}}} + \frac{S_4}{\lambda_{214\text{Pb}}} + \frac{S_5}{\lambda_{214\text{Bi}}}\right)} \quad (4)$$

Here, Conc is the activity concentration,  $R$  is the count rate difference of adjacent records,  $V$  is flow rate,  $\varepsilon$  is counting efficiency (0.96% for  $^{214}\text{Pb}$  and 4.3% for  $^{214}\text{Bi}$ ),  $\lambda$  is decay constant and values of  $S_{i-5} = f(\lambda, t)$  are constant since  $\lambda$  and  $t$  (=10 min) are constant (see Paatero et al., 1994 and Paper I for details).

Finally, the activity concentration was converted into ion-pair production rate by taking into account only the energies of three alpha and two (average values) beta particles emitted during the decay process of short lived daughters. Furthermore, we assumed that 34 eV (eV  $\sim 1.6 \cdot 10^{-19}$  J) is needed to produce one ion pair.

## 4.2 External radiation measurements and data processing

The external radiation was measured with NaI(Tl)-detector surrounded by glass-fibre box and thermal insulator made from polyurethane foam. The temperature was kept constant inside the box to avoid fluctuation. The measurement uncertainty was approximately 1 %. The NaI(Tl)-detector measured  $\gamma$ -radiation and muons. The latter are of cosmogenic origin.

The data analysis was straightforward: the dose rates were calculated by multiplying the count rates with a constant factor, which was obtained in calibration before the measurements. When calculating the ion production rate from the dose rate, we again assumed that on average 34 eV is needed to produce one ion pair and that air density is constant, in this case  $\rho_{\text{air}} = 1.29 \text{ kg m}^{-3}$ . The assumption of the constant air density can be considered as the largest source of error when calculating the ion production rate.

## 5. Ion and particle size distribution instrumentation

The BSMA, the AIS and the DMPS are based on classifying ions according to their electrical mobility  $Z$  ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )

$$Z = \frac{v_d}{E} = \frac{q_e D}{kT}, \quad (5)$$

which describes the mobility of ion in given electric field ( $E$ ) and drifting velocity ( $v_d$ ). In the atmosphere, where the electric field is weak,  $Z$  can be expressed in terms of electric charge of the particle ( $q_e$ ), diffusion coefficient ( $D$ ), temperature ( $T$ ) and the Boltzmann constant ( $k$ ). Therefore, change in ambient parameters has effect on ion mobility.

Although the mobility is the primary measured quantity, researchers prefer to present their data as a function of diameter. In this work the mobilities of singly charged ( $e$ ) ions (measured with the AIS and BSMA) were converted to diameters according to Tammet's derivation (Tammet 1995, 1998) of the Cunningham-Knudsen-Weber-Millikan equation

$$Z = f \sqrt{1 + \frac{m_g}{m_p}} \cdot \frac{e \left\{ 1 + \frac{l}{\delta} [a + b \exp(-c \frac{\delta}{l})] \right\}}{6\pi\eta\delta}. \quad (6)$$

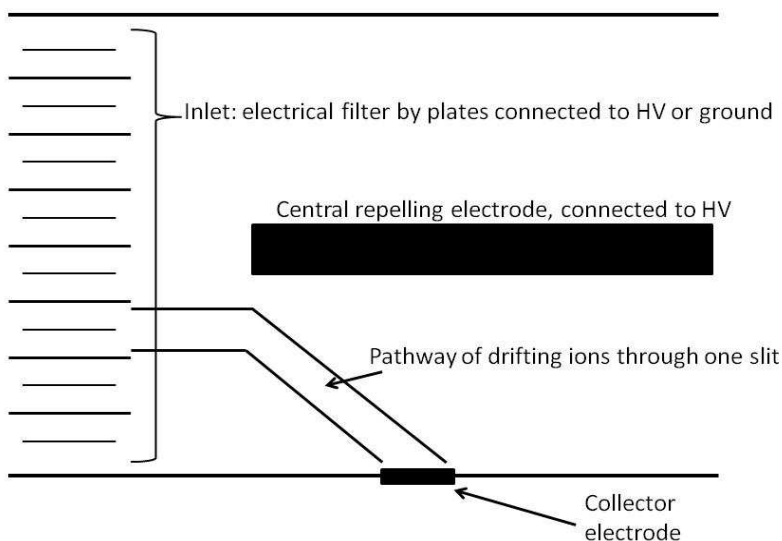
In the Eq. (6)  $m_g$  and  $m_p$  are masses of a gas molecule and a particle, respectively. A correction factor  $f$  takes into account inelastic collisions and polarization interactions. The slip factor coefficients  $a = 1.2$ ,  $b = 0.5$  and  $c = 1$  are empirical parameters,  $\eta$  is the gas viscosity and  $l$  is the mean free path of gas molecules. The collision distance ( $\delta = r_m + h + r_g$ ) includes the particle mass radius ( $r_m$ ), the difference between particle collision and mass radii ( $h$ ), and half of the gas molecule collision distance ( $r_g$ ). The parameter  $h$  was obtained based on empirical data (Tammet, 1998). The mass radius depends on the mass ( $m$ ) and density ( $\rho$ )

$$r_m = \sqrt[3]{\frac{3m}{4\pi\rho}}. \quad (7)$$

The mobility-diameter conversion according to Tammet agrees quite well with the original Stokes-Millikan equation (Friedlander, 1977). Laboratory experiments by Ku and de la Mora (2009) showed that the difference is only of the order of a gas molecule diameter ( $d_g = 0.3$  nm), when using bulk densities (see also Fig. 1 in Paper V). Therefore, we may roughly say that Millikan diameter = mass + gas molecule radii ( $d_{\text{Millikan}} = d_m + d_g$ ). The DMPS data was converted by using the

Millikan diameter, as has traditionally been done in the research group of the University of Helsinki.

## 5.1 BSMA



**Fig.3.** A schematic picture of a mobility analyser in the BSMA.

The BSMA (Tammet, 2006) is considered as a single-channel differential aspiration spectrometer, as discussed in Paper V. The instrument consists of two sets of plain condensers (Fig. 3), which are connected as a balanced capacitance bridge. One condenser scans the negative and the other the positive ion spectrum in the whole mobility range of the instrument. Sheath air is produced with plain electro-filters at the inlet. The BSMA has a large inlet and a high flow rate (2400 LPM), which may cause problems when installing the measurement setup. However, a high flow rate reduces ion losses during sampling.

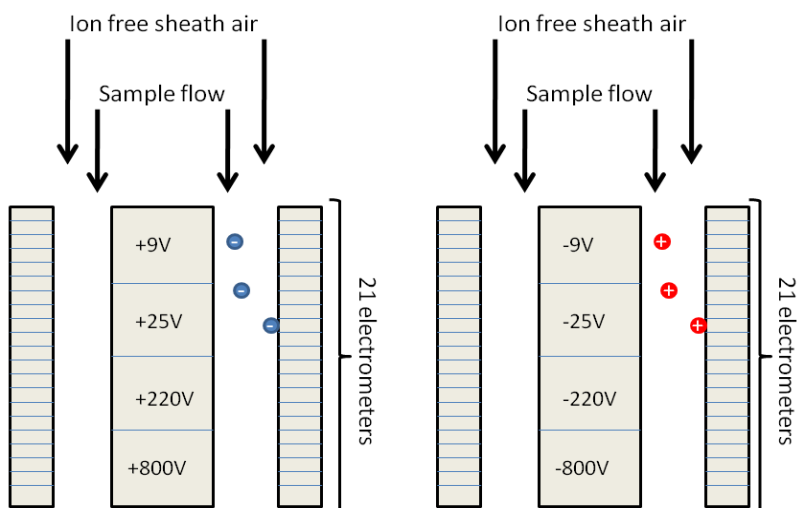
At the beginning of the measurement period described in Papers II and IV, the BSMA measured one mobility spectrum in 3 minutes and a spectrum of the other polarity in next 3 minutes. Starting in August 2005, the BSMA was set to measure one mobility spectrum for both polarities in 10 minutes. During 3-minute cycles, the BSMA performed five sample and four offset scans in one polarity. During the 10 minutes period, the BSMA scanned first through one polarity, and then through the other polarity followed by an offset scan. This cycle was repeated 4-5 times.

The mobility range of the BSMA is  $3.2\text{-}0.032\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , which corresponds to mass diameter range ca. 0.4-7.5 nm. This range is divided into 16 fractions. The measurement algorithm also calculates 10-fraction size distributions to the mass diameter range of 0.4-6.3 nm, which was utilised in this work.

## 5.2 AIS

The AIS (Mirme et al., 2007) is considered as a multichannel aspiration spectrometer (Paper V). The collector electrodes inside each of the two differential mobility analysers (DMA) are divided into 21 rings (Fig. 4). This enables the measurements of the whole spectrum at the same time for both polarities. The sample flow rate per analyser is 30 LPM and the corresponding sheath flow rate is 60 LPM.

During this work, mobility distributions were typically measured in 5-minute cycles. During the measurement cycle, the offset and sample currents were recorded for the whole range in turns to obtain final distributions. However, the measurement frequency may be adjusted to be suitable for the demands of each experiment. The outdoor data included in this thesis was measured using 16-mm inlet tubes. The inlet tube diameter was later increased to reduce the losses of very mobile small ions.



**Fig.4.** A schematic picture of the mobility analysers in the AIS.



The measuring range changed somewhat during the first years. At the beginning the range was 2.4-0.0013  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  (Paper II); later the range was extended to 3.16-0.0013  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  (Paper III). The corresponding mass diameter ranges were 0.46-40.3 nm and 0.34-40.3 nm, respectively.

### 5.3 About calibration and comparison of ion spectrometers

The AIS measurements for this thesis were made with "first generation" instruments. This means that the inlet tube diameter was smaller (16 mm versus 35 mm), and the transfer function and data inversion were almost purely theoretical. The AISes were calibrated in laboratory at the Universities of Helsinki and Tartu (Hirsikko et al., 2005). However, the main conclusions of the first calibration results for the AISes with a larger inlet (Mirme et al., 2007) were in quite good agreement with the calibration of the AISes used in this work. The main conclusions were: 1) mobilities were accurately resolved with some clear exceptions (i.e. at 6-8 nm), 2) the AIS underestimated the concentration, and 3) the signal at small ion sizes was noisy. The uncertainties were mainly issued to problems in data inversion. Later the inversion was also improved, which enhanced the accuracy of the AISes (Asmi et al., 2009; Gagné et al., 2011).

In addition to the calibration, the proper functioning of the AIS is also determined by the constant ratio of flow rate to ion mobility ( $Q/Z$ ) and by the maintenance of the electrometers (Mirme et al., 2010). It has been observed that when measuring at high altitudes the ratio  $Q/Z$  changes without adjusting the flow rate (e.g. Vana et al., 2006b). On highly polluted sites the flow pathways get blocked and the flow rate decreases. These result in unrealistic ion size distributions, i.e. a fraction of the smallest ions end up out of the measurement range. The data also become too noisy to be further analysed when measuring with a dirty DMA.

The BSMA has a very high flow rate and a large inlet hole, which complicates the calibration. For these reasons, the AIS and BSMA instruments have been inter-compared to find out the consistency of the measured size distributions. The BSMA measured higher small ion concentrations compared to the first versions of the AIS, which were underestimating the concentrations (Mirme et al., 2007). In recent comparisons, the BSMA measured lower small ion concentrations compared to current modifications of the AIS-instruments, which were in better agreement with calibration instruments (Asmi et al., 2009; Gagné et al., 2011). Ehn et al. (2011) also compared the BSMA against a mass spectrometer (Atmospheric Pressure Interface Time-of-Flight Mass Spectrometer, APi-TOF). The BSMA and APi-TOF showed a good agreement after the BSMA's theoretical transfer function widths were multiplied by a factor of 1.5.

## 5.4 DMPS

Size distributions of aerosol particles were measured with DMPS (Aalto et al., 2001) at 2 m height until the end of September 2004, after which at ca. 8 m height in Hyytiälä and at fourth-floor level from Physics Department in Helsinki (Papers II-IV). The diameter ranges of particle distributions were 3-520 nm in Hyytiälä and 3-950 nm in Helsinki.

The DMPS used contained two DMAs and two CPCs. The first DMA was 10.9-cm Hauke-type one connected to a TSI-3025 CPC. The second system contained a 28-cm long Hauke-type DMA together with a TSI-3010 CPC. Each DMPS had its own closed loop sheath air arrangement. The aerosol was neutralised with a  $^{85}\text{Kr}$  source.

## **6. Particle formation and growth — definitions and data analysis**

The ion spectrometers offered a unique set of information by measuring size distributions of charged particles below 3 nm. The determination of formation and growth rates of sub-3 nm (charged) particles became possible. In this section, basic concepts concerning the ions in particle formation (Sect. 6.1), and data-analysis methods relevant for this thesis (Sect. 6.2-6.4) are discussed.

### **6.1 Ions in particle formation**

Many theoretical and laboratory experiments have studied kinetics and formation of primary and small ions, their clustering, recombination and further growth (Raes and Janssens, 1986; Turco et al., 1998; Yu and Turco, 2000, 2008; Laakso et al., 2002, 2003; Lovejoy et al., 2004; Nadykto and Yu, 2004; Fisenko et al., 2005; Nagato et al., 2005; Winkler et al., 2008; Kazil et al., 2008 and references therein; Duplissy et al., 2010; Leppä et al., 2011). The presence of ions is expected to enhance the nucleation process (ion-induced nucleation) by lowering the energy required for the formation of stable clusters. Ion-ion recombination resulting in a neutral particle is also considered as an ion-mediated particle formation pathway.

Ion-induced particle formation mechanisms is expected to be favoured when temperature and background aerosol sink are low but ionisation rate and nucleating vapour concentrations are high enough (e.g. Laakso et al., 2002; Fisenko et al., 2005; Curtius et al., 2006; Boy et al., 2008; Yu, 2010). These conditions are met from the boundary layer up to the lower stratosphere (e.g. Lovejoy et al., 2004; Boy et al., 2008; Manninen et al., 2010; Yu, 2010; Boulon et al., 2011). However, the amount of nucleating/condensing vapours is higher in the boundary layer due to anthropogenic and vegetation sources (e.g. Arnold, 1980). The observations from Hyytiälä by Gagné et al. (2010), however, showed that ions may be more important in particle formation in warm days compared to colder days, which is in contradiction to theories (e.g. Laakso et al., 2002; Yu, 2010).

To understand the ion and particle concentrations during the formation of particles via neutral and ion-induced nucleation we need the concept of charging state. The charging state of aerosol particles describes whether the particles are in charge equilibrium, under- or overcharged (Vana et al., 2006a; Kerminen et al., 2007; Laakso et al., 2007a; Gagné et al., 2008, 2010). If 3-7 nm aerosol particle population is overcharged, ions are important in particle formation. If the aerosol population is in charge equilibrium or undercharged, the contribution of ions is less important.

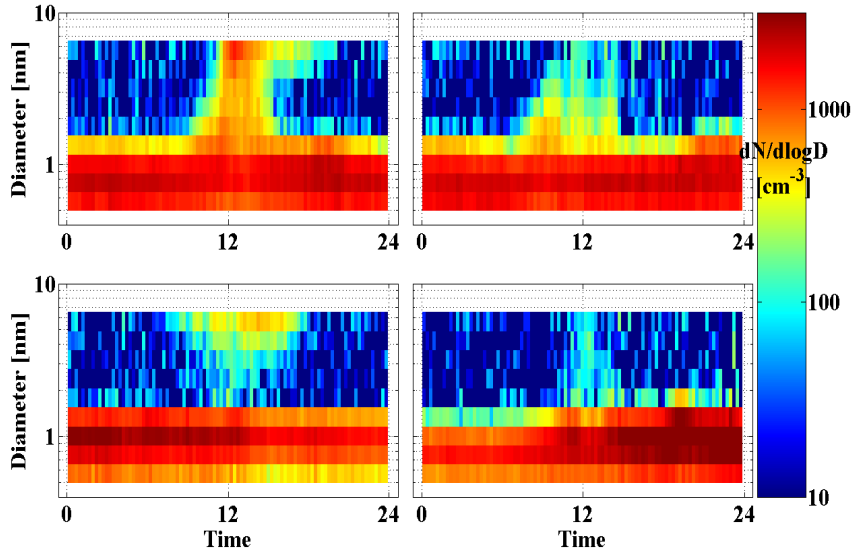
## **6.2 Classification of particle formation events based on ion size distribution data**

The visual evaluation and classification of size distribution data is the first step of particle formation analysis. Earlier guidelines were based on the DMPS data for particles larger than 3 nm in diameter (Dal Maso et al., 2005). However, the existing guidelines did not take into account the nature of air ions or the size range of ion spectrometers. Therefore, a detailed guideline for classifying the air ion formation events based on the BSMA data was developed (Table 2) in the Paper IV, and the analysis was compared with the corresponding results obtained from the DMPS data (Sect. 7.3). Each day was classified as 1) a particle formation event (Fig. 5), 2) undefined (Fig. 6), or 3) non-event day.

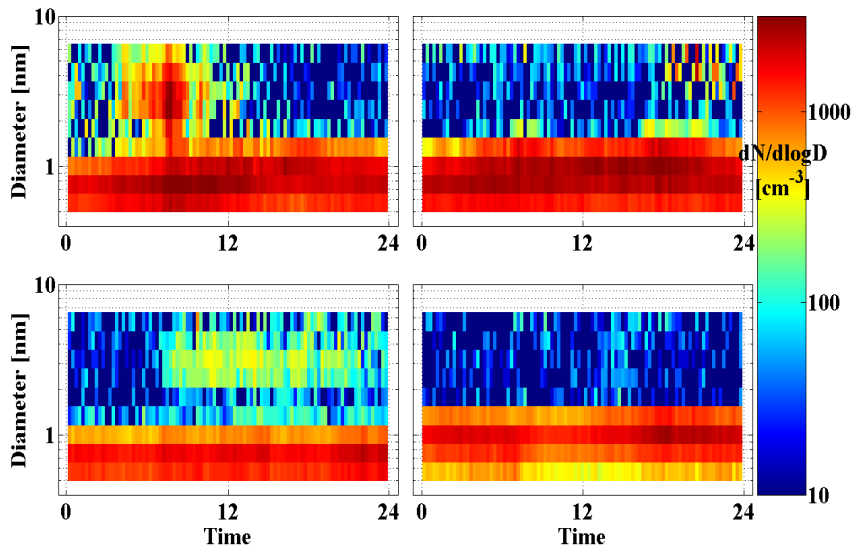
Further developments and renaming of this classification scheme have recently been introduced due to new observations in various environments (Virkkula et al., 2007; Vana et al., 2008; Suni et al., 2008; Yli-Juuti et al., 2009; Manninen et al., 2009a). In principle, the new identified features include the following: "apple", "hump", "mixed-type", nocturnal events and "wind-snow induced" intermediate ions. The term "apple" refers to new intermediate ion mode, which is separate from small ion and above 25-nm particle modes. The "hump" refers to events where the growth is stopped before 10 nm, i.e. should have also been observed with the DMPS. The "mixed-type" events include features of other types but could not be identified as any of them. Nocturnal particle formation takes place in the evening or during night-time (Junninen et al., 2008; Suni et al., 2008; Svenningsson et al., 2008). In the current work nocturnal particle formation events were included in class undefined (i.e. rain- or snowfall induced particle formation). The Paper IV analysed phenomena related to air ions, but the main focus was on daytime particle formation. The observations of the actual nocturnal particle formation (i.e. suppressed growth events of small ions during night-time) were noticed by mentioning the time evolution of maximum size of small ion mode. The "wind-snow induced" intermediate ions were discussed in context of other sources for ions (Sect. 2.2).

**Table 2.** Air ion formation event classification scheme developed based on the BSMA data (modified from Table 1 in Paper IV).

<b>Class</b>	<b>Classification scheme</b>
<b>Ia</b>	The formation of particles and subsequent growth was observed for several hours. Due to a clear continuous shape of the events, we are able to characterise these events by means of e.g. formation and growth rates.
<b>Ib</b>	The formation of particles and subsequent growth was observed for several hours also during these events. These events had also a clear continuous shape, and we are typically able to characterise these events by means of e.g. formation and growth rates.
<b>Ib.1</b>	During these events the intermediate ion concentrations were typically lower compared to class-Ia events. The events with suppressed growth were included this class.
<b>Ib.2</b>	Only the particle formation events with a gap between the small and the intermediate ion modes were included this class.
<b>II</b>	We are not typically able to further analyse these events by means of formation and growth rates due to low concentrations of intermediate ions, or a difficult and unclear shape of growing mode. During some events the BSMA had a break in measurements due to power failure. We included such events in this class.
<b>Undefined</b>	Due to low concentration of intermediate ions or the noise of measuring electrometers we had difficulties to define whether an event occurred or not. Rain-induced intermediate ion burst and intermediate ions associated to snowfall were included this class. Additionally the total number of days when these phenomena occurred was counted.
<b>Non-Event</b>	Intermediate ions were not observed.



**Fig.5.** Particle formation event days (figure adapted from Paper IV): class Ia (upper left corner), class Ib (upper right corner and lower left corner) and class II (lower right corner).



**Fig.6.** Undefined days (figure adapted from Paper IV): intermediate ions associated with rainfall (left top corner), bad data due to instrumental issues (right top corner), intermediate ions associated with snowfall (left bottom corner) and possible particle formation event (right bottom corner).

### 6.3 Formation rate of 2-nm particles

The concept of the formation rate of 2-nm ions and particles was used in review Paper V, when collecting the information of the contribution of ions in particle formation based on observations. The formation rate of 2-nm particles is derived from measured size distribution data according to Kulmala et al. (2007):

$$J_2(tot) = \frac{dN_{2-3}(tot)}{dt} + CoagS_{2-3} \cdot N_{2-3}(tot) + GR_{<3} \cdot N_{2-3}(tot) \quad (8)$$

and the formation rate of 2-nm ions is described as

$$J_2^\pm(ion) = \frac{dN_{2-3}^\pm(ion)}{dt} + CoagS_{2-3} \cdot N_{2-3}^\pm(ion) + GR_{<3} N_{2-3}^\pm(ion) \\ + \alpha N_{2-3}^\pm(ion) N_{<3}^\mp(ion) - \beta N_{2-3} N_{<2}^\pm(ion). \quad (9)$$

The formation rates of new 2-nm particles/ions are proportional to the time changes in number concentration ( $N$ ) of 2-3 nm particles/ions, the coagulation loss (CoagS) of 2-3 nm particles/ions with the pre-existing aerosol, the growth of 2-3 nm particles/ions to larger sizes (growth rate = GR). Ions are also lost via ion-ion recombination and formed via ion-neutral attachment. The values  $1.6 \cdot 10^{-6} \text{ cm}^3 \text{ s}^{-1}$  and  $0.01 \cdot 10^{-6} \text{ cm}^3 \text{ s}^{-1}$  are often used for the recombination ( $\alpha$ ) and attachment ( $\beta$ ) coefficients, respectively (Israel, 1970; Hoppel, 1985; Hoppel and Frick, 1986).

The reader should notice that the equations (8 and 9) ignore the formation pathway (i.e. neutral or ion-induced) of sub-2 nm particles. The ion-induced fraction can be calculated by e.g. Manninen et al. (2010)

$$\text{Ion – induced fraction} = \frac{J_2^+(ion) + J_2^-(ion)}{J_2(tot)}. \quad (10)$$

The maximum contribution of ions is obtained by including ion-ion recombination rate ( $J_2(\text{rec})$ ), which results 2-3 nm ions

$$\text{Ion – mediated fraction} = \frac{J_2^+(ion) + J_2^-(ion) + J_2(\text{rec})}{J_2(tot)}. \quad (11)$$

## 6.4 Growth rates from size distributions

There are different ways to estimate diameter growth rate (GR) of particle population based on size distribution data (e.g. Hussein et al., 2005; Lehtinen et al., 2003; Iida et al., 2008). The "maximum concentration"-method, which was for the first time described by Lehtinen et al. (2003) and Kulmala et al. (2004b), was tested with a long ion size distribution data in Papers II and III.

The idea of the method was to follow maximum concentration of every size bin as a function of time. At every size bin a Gaussian curve was fitted to concentration data (see Fig. 1 in Paper II). The place of maximum of Gaussian curve in time axis should have been coincided and we obtained the time of maximum concentration in each size bin. If the fitting of the Gaussian curve was impossible, the timing of the maximum has been selected manually. When fitting a linear curve to these size and time pairs we obtained growth rate in desired size range (see Fig. 2 in Paper II).

However, when studying ion size distributions, the method may have led to false results if data was fluctuating due to changing atmospheric conditions or a weak/changing contribution of ions. Then, the maxima of the Gaussian curve and the concentration data did not coincide, or the timing of the maximum concentration fluctuated in time. The growth rate of the smallest particles was most often influenced by this kind of problems, and, therefore, some of the events had to be left out from analysis.

Due to self-coagulation and coagulation to background aerosol particles the obtained (i.e. apparent) growth rates may be somewhat larger compared to pure condensational growth (Stolzenburg et al., 2005; Anttila et al., 2010; Leppä et al., 2011). According to theory, the effect of self-coagulation and coagulation to background aerosol particles is size depended and enhanced by electric charges (e.g. Leppä et al., 2011). The effect of coagulation may be considered small with the concentrations relevant in our study (Leppä et al., 2011). Continuous charging and neutralising of sub-3 nm ions and activation of negative ions before positive ions have been observed to result larger apparent growth rates for positive than negative sub-3 nm ions (Yli-Juuti et al., 2011).

As a conclusion, the "maximum concentration"-method was observed to be able to follow the initial (sub-3 nm) growth of particles, or ions in this case. The GR-method used in this study may be considered a reasonably good method at nucleation mode sizes (< 20 nm), and when the growing mode is relatively narrow (personal communication with J. Leppä, Yli-Juuti et al., 2011). At larger sizes, for



example, the mode fitting method would be better (Hussein et al., 2005; Dal Maso et al., 2005).

## 7. Results and discussion

This section discusses the main results of this thesis starting from ion production rates at SMEAR II (Sect. 7.1), continuing with the observations of small ion concentrations in Hyytiälä and Helsinki (Sect. 7.2). The last two sections (Sect 7.3 and 7.4) discuss the observations of particle formation and growth especially in Hyytiälä and Helsinki.

### 7.1 Ion production rate at SMEAR II

The radon activity concentration and external radiation dose rate measurements were carried out for six years (2000-2006) at the SMEAR II station. The measured radon activity concentrations (Table 3; Paper I) were in agreement with the observations at Matorova and Sammaltunturi (mean values in range 1-2 Bq m<sup>-3</sup>) stations in Northern Finland (Hatakka et al., 2003). The observed external dose rates agreed with the results presented by Szegvary et al. (2007) based on a European measurement network.

According to the observation in Hyytiälä, the average ion production rate was 10 ion-pairs cm<sup>-3</sup> s<sup>-1</sup> (Table 3; Paper I). Based on the mean values presented in the Table 3 we may estimate that 10 % (1 ion-pair cm<sup>-3</sup> s<sup>-1</sup>) of ion production rate was due to radon decay, 20 % (ca. 2 ion-pairs cm<sup>-3</sup> s<sup>-1</sup>, Hensen and van der Hage, 1994; Bazilevskaya et al., 2008) due to cosmic radiation, and 70 % due to terrestrial  $\gamma$ -radiation. One has to remember that due to temporal variation of radon activity concentration and  $\gamma$ -radiation dose rate (Table 1; Paper I), the relative contributions of different components is not constant. However, we may conclude that external radiation is mainly responsible for the ion pair production at the SMEAR II station.

**Table 3.** The mean and median values of radon activity concentration, external radiation dose rate, and ion production rate via radon decay and external radiation at the SMEAR II station (Paper I).

	<b>Radon activity concentration (Bq m<sup>-3</sup>)</b>	<b>External radiation dose rate (<math>\mu</math>Gy h<sup>-1</sup>)</b>	<b>Ion production via radon (ion-pairs cm<sup>-3</sup> s<sup>-1</sup>)</b>	<b>Ion production via external radiation (ion-pairs cm<sup>-3</sup> s<sup>-1</sup>)</b>	<b>Total ion production (ion-pairs cm<sup>-3</sup> s<sup>-1</sup>)</b>
<b>Mean</b>	1.84	0.13	1.1	8.7	10.1
<b>Median</b>	1.49	0.14	0.9	9.5	10.4

## 7.2 Small ion concentrations

The temporal and spatial evolution of concentrations of especially small ions was topic of all the papers included to this thesis. This topic is important, since the ion-mediated particle formation pathway is limited by small ion concentrations, which in turn is defined according to balance between sources and sinks. Intermediate ion concentrations were also reported. However, intermediate ion concentrations were close to zero, if no particle formation or rainfall events occurred. The information of intermediate ions is important in particle formation and growth studies (Sect. 7.3 and 7.4).

### 7.2.1 Indoor small ion concentrations

The small ion concentrations showed a clear diurnal cycle when measuring ion size distributions indoors at the University of Helsinki (Paper III). The concentrations followed the cycle of ventilation. During daytime on working days, when ventilation was on, room air was mixed and exchanged with fresh outdoor air. At the same time the small ion concentrations decreased to 1/3 of the night-time concentrations. During night-time and weekends, when the small ion concentrations increased, the ventilation was off and no mixing or connections to outdoor air occurred (Table 4; Paper III).

The observations by Chandrashekhara et al. (2005) confirmed that the indoor radon activity concentrations follow the ventilation cycle. Therefore, we expected that radon activity concentrations, which were not measured, behaved similarly as small ion concentrations. During the time of measurements, the radon activity concentrations at the Physics Department were higher than regulations allow due to problems of radon ventilation in the building. This problem was fixed after our measurements were finished.

**Table 4.** The medians and means of small ion concentrations in Helsinki and Hyytiälä (Papers II and III).

	<b>HEL Mon-Fri indoors +/-</b>	<b>HEL Sat-Sun indoors +/-</b>	<b>HEL Mon-Fri outdoors +/-</b>	<b>HEL Sat-Sun outdoors +/-</b>	<b>HYY outdoors +/-</b>
<b>Median</b>	966 / 1065	1357 / 1376	590 / 630	632 / 696	–
<b>Mean</b>	1019 / 1127	1396 / 1389	627 / 683	653 / 720	607-889 / 593-881

Ion concentrations measured indoors are seldom reported in literature (Paper V). However, Fewes et al. (2005) reported that they measured high small ion concentrations indoors (median concentrations: 1180-1250 cm<sup>-3</sup> and 938-1090 cm<sup>-3</sup> for positive and negative ions, respectively). Our observations (Table 3) are in accordance with the results by Fewes et al. (2005).

### **7.2.2 Outdoor small ion concentrations**

Outdoor small ion concentrations in Helsinki were considerably lower compared to indoor concentrations (Table 4; Paper III). This was due to the larger sink to background aerosol particles and air mixing, which was practically non-existent indoors during night-time. The total ionisation source was expected to be of the same order both indoors and outdoors. However, radon activity concentration may be order of magnitude higher indoors compared to outdoors (Zaharowski et al., 2004).

In our measurements, any increase in small ion concentrations due to car exhaust emissions was not observed, in contrast to the observations by Ling et al. (2010) and Jayaratne et al. (2010) in Australia. We expected that coagulation and ion-ion recombination sinks were elevated due to car exhaust. Therefore, we observed a decrease instead in small ion concentrations when the wind was from the road. The decrease in small ion concentrations as a function of distance from the road was later confirmed by Jayaratne et al. (2010).

Due to the lower background aerosol concentration, the average small ion concentrations in rural Hyytiälä were somewhat higher compared to the urban Helsinki environment (Table 4). Our observations were in accordance with other observations at rural and urban sites (Paper V and references therein). As shown by the literature review, small ion concentrations have been observed to be the lowest in marine and coastal environments (Paper V). Ion-pair production (mainly due to cosmic radiation) or small ion emissions are lowest over the oceans, where the ion sink is also lower compared to urban and rural environments.

In Helsinki, the diurnal cycle of small ion concentrations was affected by traffic intensity, which increased coagulation sink and consequently decreased small ion concentrations, during working days (Paper III). No cycle was observed in concentrations when measured during weekends. In Hyytiälä, the daily cycle of small ion concentrations followed the boundary layer evolution. Therefore, the concentrations were highest during night-time and lowest during daytime. An increase in the background aerosol sink may have sometimes disturbed the

described diurnal cycle. Participation in particle formation by growing or attachment to other particles further decreases the daytime small ion concentrations.

We were able to follow the annual cycle of small ion concentrations in Hyytiälä. The observed cycle was similar compared to ionisation rate cycle (Papers I and II). The minimum monthly average concentrations were observed in February and July. However, both ionisation rate and sink due to aerosol particles were on their highest in July. The air pathway of ion spectrometers may get blocked due to pollen and insects, which may have somewhat disturbed the concentration measurements in summer.

### **7.3 Air ion and particle formation**

Particle formation was the most frequent at SMEAR II station in spring and autumn, which is in accordance with earlier observations (Dal Maso et al., 2005). The visual inspection and classification of ion/particle formation events resulted in several interesting observations: 1) the particle formation events were more frequently observed with the DMPS (21-32% of the analysed days) than with the BSMA (for negative ions 24-28 % and for positive ions 20-24 % of the analysed days), 2) the particle formation events were more frequently observed in negative polarity than in positive polarity, 3) a gap in size distribution at ca. 2 nm, between the small and intermediate ions, was observed on 25 days during three years, 4) sometimes (21 and 6 times in negative and positive polarities, respectively) the growth of new mode was suppressed at 3-5 nm, 5) rain-induced intermediate ion formation was observed more frequently with negative ions, and 6) we probably observed intermediate ions associated with snowfall.

Point (1) is most likely due to fact that many events detected with the DMPS start at 10-20 nm sizes, while the upper limit of the BSMA is 7.5 nm. Based on point (2) the negative polarity is sometimes favoured over positive one during particle formation in Hyytiälä. According to literature, neutral and ion-mediated mechanisms are competing during the event and from event to event (Paper V and references therein). Therefore, sometimes neutral mechanisms are more important, while sometimes ion-induced (negative or positive) mechanisms are more important (e.g. Iida et al., 2006; Laakso et al., 2007a,c; Winkler et al., 2008; Manninen et al., 2009a, 2010; Gagné et al., 2008, 2010).

The gap in size distributions at 2 nm (point 3) may result if particle formation occurs via neutral pathways, or the formation event has taken place away from the measurement location and already grown particles have drifted to the station. The interesting new observation of the suppressed growth (the 4<sup>th</sup> point) was mainly

observed in February and March, and was issued to low concentrations of condensing vapours or increase in background aerosol sink. The observations of suppressed particle growth are still under further study, and special interest is in nocturnal events (Junninen et al., 2008). The observations by Lehtipalo et al. (2011) have shown that the nocturnal events are as frequent among charged and neutral particles. Observations of frequent nocturnal particle formation events in Tumberumba, Australia (Suni et al., 2008) and in Abisko Sweden (Svenningsson et al., 2008) have showed that during night-time, newly formed particles may grow with growth rates comparable to daytime values.

The ions during rainfall are due to splashing of water droplets (point 5), as was already discussed in Sect. 2.2. Droplet probably breaks up several small negatively charged droplets and one large positively charged droplet. The snowfall associated intermediate ion modes (point 6) require further investigation to understand the mechanisms behind these observations. Similar observations have been reported from Antarctica and Jungfraujoch (Vana et al., 2006b; Virkkula et al., 2007).

Ion size distribution measurements in Helsinki showed that particle formation was a frequent phenomenon indoors. Concentrations in the indoor air were only slightly dependent of the outdoor air. Therefore, we expected that the indoor air in our laboratory contained sufficient amount of nucleating and condensing vapours, the identity of which remained unknown. In urban air particle formation was observed frequently (15 times during the measurement period in August), and it was found to take place in-situ.

The observations with ion spectrometers have given the possibility to study the initial steps of particle formation due to their sub-3 nm measurement range. Unfortunately, based on observations presented in Papers I-IV we were not able to evaluate the relation between neutral and charged sub-3 nm particles in particle formation. However, recent developments of CPCs and NAISes have enabled observations of sub-3 nm neutral particles (Saros et al., 1996; Sipilä et al., 2008, 2009; Lehtipalo et al., 2009, 2010, Manninen et al., 2009a).

The literature review (Paper V and references therein) showed that formation rates of 2-nm ions were relatively constant (on average  $< 0.2 \text{ cm}^{-3} \text{ s}^{-1}$ ) despite the varying environments studied. However, the total 2-nm particle formation rates showed large variation ( $0.001\text{-}60 \text{ cm}^{-3} \text{ s}^{-1}$ ) from day to day. The observations showed that 2-nm particle formation is often controlled by neutral mechanisms. Ion-mediated mechanisms were also important in some environments, characterised by low total 2-nm particle formation rate, low temperature and low background particle

concentration. For example, in Jungfraujoch, Antarctica and Pallas the average ion-induced fraction (minimum contribution) was estimated to be 20-30 % (Manninen et al., 2010; Asmi et al., 2010). The observations by Lehtipalo et al. (2010) showed that ion-ion recombination can be responsible for a significant fraction of sub-3 nm neutral particles in Mace Head, and responsible for the most of the night-time sub-3 nm neutral particles there. In Hyytiälä, where sub-3 nm neutral particle concentrations were high, ion-ion recombination was only able to explain some percents of neutral particles (Lehtipalo et al., 2010).

## 7.4 Growth rate analysis

The size distributions measured with ion spectrometers offered scientists the possibility to evaluate the growth of sub-3 nm particles for the first time. Based on 13 months of observations in Hyytiälä and a month both indoors and outdoors in Helsinki, the growth of the smallest particles seemed to be slower compared to larger particles especially in summer (Table 5; Papers II and III). In winter the growth of large particles became slower and comparable to sub-3 nm particle growth rates. Nevertheless, the growth rates showed large variation from day to day in each size class.

The observed size dependence could be due to availability of condensing vapours (e.g. sulphuric acid and organics) during a day and season (e.g. Hakola et al., 2003; Smith et al., 2010) and/or the effect of size in vapour uptake. Electrical charge may enhance the initial growth (e.g. Yu and Turco, 2000; Laakso et al., 2003; Kulmala et al., 2004b; Leppä et al., 2011). As discussed in Paper V, further investigations with regard to particle growth kinetics are required.

**Table 5.** The 1<sup>st</sup> row: median growth rates over 13 months based on the BSMA, AIS and DMPS in Hyytiälä, the 2<sup>nd</sup> row: outdoor growth rate range based on the AIS and DMPS in Helsinki, the 3<sup>rd</sup> row: indoor growth rate range based on the AIS (Papers II and III). Only two particle formation events were studied both indoors and outdoors in Helsinki.

	GR (nm h <sup>-1</sup> ) < 3 nm	GR (nm h <sup>-1</sup> ) 3-7 nm	GR (nm h <sup>-1</sup> ) 7-20 nm
<b>Outdoors, Hyytiälä</b>	< 2	2-3.5	3.5-5
<b>Outdoors, Helsinki</b>	1.8-2.3	3.1-13.0	5.9-17.7
<b>Indoors, Helsinki</b>	2.3-4.9	6.5-8.7	5.1-8.7

Since publishing the Paper II the ion spectrometers have been utilised in various environments, and numerous amount of particle formation events have been studied (Paper V and references therein). Later observations of particle growth from e.g. Australia and Antarctica, 12 EUCAARI sites in Europe are similar to our results (e.g. Dal Maso et al., 2005; Virkkula et al., 2007; Suni et al., 2008; Yli-Juuti et al., 2009, 2011; Manninen et al., 2009b, 2010). However, there are some exceptions. For example, Svenningsson et al. (2008) observed extremely high growth rates (up to 40 nm h<sup>-1</sup>) in Abisko, Sweden. Vakkari et al. (2011) observed that 3-7 nm particle growth exceeded the growth of larger particles indicating a time dependence of the condensing vapours in South-African Savannah.



## 8. Review of the papers and author's contribution

This thesis includes five peer-reviewed scientific papers, the aims of which were to develop and test data analysis methods, to evaluate air ion sources, sinks and small ion concentrations in spatial and temporal scale, and to gain new information about particle formation and initial growth. In the following short summaries of the main results and author's contribution are discussed.

**Paper I** investigated the air molecule ionisation rate due to radon decay and external radiation at the SMEAR II station. The results showed that the average ion production rate was  $10 \text{ ion-pairs cm}^{-3} \text{ s}^{-1}$  with large temporal variation. The external radiation was mainly responsible for the air molecule ionisation at the SMEAR II. Ionisation rate is the limiting factor when studying small ion concentrations, and finally the contribution of ions in particle formation. I was the responsible author and performed most of the data analysis.

**Paper II** analysed for the first time the observations of the ion (small and intermediate) concentrations at the SMEAR II station over one year. The results were in agreement with other observations from rural continental locations. In addition a recently developed method to evaluate particle growth rates based on size distribution data was tested. We observed that the method was usable, with some limitations, for determination of the initial particle growth. The particle growth seemed to be size dependent. We observed that the growth of sub-3 nm ions/particles was typically slower, and larger ions/particles grew faster. In winter the growth rates of large particles were slower compared to summer, while sub-3 nm growth rates were more or less constant throughout the year. The observations may be due to availability of condensing vapours and/or the effect of size in vapour uptake. Based on our results, we were not able to conclude whether electric charge enhances the initial growth or not. I performed the data analysis and was responsible author of the article.

**Paper III** introduced ion size distribution data from a short experiment period both indoors and outdoors in urban Helsinki. The outdoor ion concentrations were dependent on traffic intensity, and indoor concentrations on ventilation. We observed that indoor air concentrations were only slightly dependent on the outdoor air, and that there were enough condensing vapours for particle formation to frequently take place indoors. Particle formation was also observed to take place in-situ in urban environment. The particle growth rates were comparable to observations at the SMEAR II station. I was responsible for the measurements, most of the data analysis and writing the paper.

**Paper IV** introduced new guidelines and criteria to classify particle formation events based on ion size distribution data. Although we were not able to determine the importance of the electric charge in particle formation, we made interesting observations: 1) particle formation event was typically stronger in negative polarity, 2) particle growth was sometimes suppressed at ca. 3-5 nm, and 3) there was sometimes a gap in intermediate ion size distributions around 2 nm. The latter may indicate the dominance of neutral particle formation mechanisms. As a responsible author, I was developing the classification scheme and made the data analysis.

**Paper V** reviewed 260 publications of the air ions. The literature review gave a comprehensive overview of the current knowledge of the spatial and temporal variation of small ion sources, sinks and concentrations in various environments, and of the global importance of ions in particle formation in lower troposphere. Based on the observations, the relative importance of ions in particle formation seems to be determined by neutral particle formation pathways. As a responsible author, I read and analysed most of the publications included to the paper.

## 9. Concluding remarks

Air ions have specific importance in the climate system due to atmospheric chemistry and electric circuit, as well as their participation in particle formation and growth. Characterisation of air ion evolution is one of the basic information needed to understand nucleation mechanisms. We measured ion mobility distributions in rural Hyytiälä for 13 months and indoors and outdoors in urban Helsinki for a month, as well as ionising components in Hyytiälä for six years. Observations of air ions and their connection to particle formation were also analysed by reviewing 260 publications.

**Development and testing of data analysis and classification methods:** In this work, new guidelines for particle formation event classification based on ion size distribution data were developed due to the measurement range of ion spectrometers and the nature of air ions. The classification scheme has been utilised and further revised suitable for all environments, where the air ion measurements have been conducted (e.g. Virkkula et al., 2007; Vana et al., 2008; Yli-Juuti et al., 2009). Growth rate method introduced by Lehtinen et al. (2003) and Kulmala et al. (2004b) was tested with 13 months data set, and it was observed to be suitable for studies of initial (sub-3 nm) particle growth. The method is currently being further analysed and compared against other growth rate methods (Leppä et al., 2011; Yli-Juuti et al., 2011).

**Evaluation of the ion sources based on directly measured radon activity concentrations and external radiation dose rates at the SMEAR II station, and based on literature:** The ion production rate due to  $^{222}\text{Rn}$  and external radiation was determined according to direct measurements at the SMEAR II station. Based on observations the average ion production rate was  $10 \text{ ion-pairs cm}^{-3} \text{ s}^{-1}$ . Temporal variation was large because the release of radon and  $\gamma$ -radiation from the ground was prevented due to snow cover and soil moisture in winter and spring. The  $^{222}\text{Rn}$  content was also affected by the boundary layer evolution. External radiation had a larger contribution to ionisation than radon decay. Our observations were in agreement with other studies (e.g. Hatakka et al., 2003; Szegvary et al., 2007). There are also ion sources, which have spatially and temporally limited contributions (Paper V and references therein). Such sources include car exhaust, falling or splashing water, release of artificial radioactive material into the atmosphere, and corona chargers (e.g. power lines).

**Observations of the evolution of small ion concentrations:** The small ion concentrations followed the cycle of boundary layer evolution, the sink due to background aerosol particles, and the changes in ionisation rate in rural Hyytiälä. In

urban Helsinki the small ion concentrations depended on traffic (i.e. sink due to aerosol particles) in outdoor air, and on ventilation in indoor air. The literature review discussed on the changes in small ion concentrations in various local conditions (i.e. different combinations of sources and sinks). Analysis presented in this work gave valuable information and comprehensive picture of the evolution of small air ion concentrations.

**Information obtained of particle formation and initial growth based on ion size distribution measurements:** The classification of particle formation events based on ion size distribution data resulted in interesting observations: 1) typically particle formation was stronger in negative polarity compared to positive polarity, 2) the particle growth was sometimes stopped at 3-5 nm size, and 3) a gap in the ion size distribution between small and intermediate ions was sometimes observed. The latter may indicate the dominance of neutral mechanisms in particle formation. The literature review showed that formation rates of 2-nm ions were relatively constant in most of the environments, however, formation rates of the whole 2-nm particle population showed more variation. Therefore, the relative importance of ions in particle formation may be determined by neutral particle formation pathways. The debate concerning the nucleation mechanism and contribution of ions in particle formation still continues.

The growth rate analysis showed that the obtained growth rates were size dependent, i.e. typically sub-3 nm particles grew slower than larger particles. However, the growth rates of the sub-3 nm particles were almost constant throughout the year, while the growth of larger particles was faster in summer compared to winter. The observations were thought to be due to the temporal changes in condensing vapours participating in growth (e.g. Hakola et al., 2003; Smith et al., 2010) and/or the size dependence of vapour uptake. However, the importance of ions in the initial growth could not be confirmed based on our results. Later studies have shown comparable observations and conclusions (Paper V and references therein, Yli-Juuti et al., 2011).

**Future directions:** Despite the intensive research hitherto, there are still issues concerning the ions in particle formation, which require further investigation. Among the interesting questions are for example: 1) the contribution of ion-mediated pathways in particle formation, 2) the vertical extent of (charged) particle formation and consequent growth to climatically relevant sizes, and 3) the effect of solar cycle on particle formation and subsequently on cloud properties.

The role of ions in particle formation is not yet well characterised and understood, which is seen as a conflict between the conclusions based on field experiments and

theoretical calculations. Field studies have resulted in rather constant formation rates for 2-nm ions despite the varying atmospheric conditions of the measurement locations. At the same time the formation rates of the whole 2-nm particle population have varied in the large scale. Therefore, the conclusion based on the field studies has been that the neutral particle formation mechanisms control the particle formation process (e.g. Paper V and references therein). However, some existing theoretical studies have suggested ions to be more important in the initial particle formation, i.e. in nucleation process (e.g. Yu and Turco, 2008; Yu et al., 2010; Yu and Turco, 2011). Simultaneous measurements of neutral nano-particles and ions, ion production rate, as well as chemical species involved in the particle formation and growth are better available today. In future, improvements in experimental applications (i.e. instrumental development as well as innovative laboratory and field experiments) and in theoretical approaches are still required.

The atmospheric conditions vary as a function of altitude. However, particle formation has been observed at locations, which were inside the boundary layer as well as in the free troposphere (Venzac et al., 2008; Manninen et al., 2010; Boulon et al., 2011, Paper V and references therein). Ground based measurements at high altitudes may be used to investigate, although not entirely representatively, the particle formation in free troposphere. Due to challenging operation airborne measurements have only lately become more popular (Stratmann et al., 2003; Laakso et al., 2007c; Wehner et al., 2010; Mirme et al., 2010). The airborne measurements would offer insight not only into vertical extent of particle formation and possibilities for the growth of freshly nucleated clusters and particles, but also into the scale of ion-mediated particle formation. The latter may be favoured in the conditions prevailing in the free troposphere (e.g. Laakso et al., 2002; Fisenko et al., 2005; Curtius et al., 2006; Boy et al., 2008; Yu, 2010).

The solar cycle may affect atmospheric particle formation via changing intensity of cosmic radiation, which would be followed by changes in the ionisation rate, in the ion-mediated particle formation rate and finally in the number concentration of particles acting as cloud condensation nuclei. The reports of a link between the changing ionisation intensity of cosmic radiation and cloud properties are inconsistent (e.g. Kazil et al., 2008 and references therein). According to ground based measurements at the SMEAR II station, no connection between parameters related to the particle formation and the ionisation intensity of cosmic radiation has been found (Kulmala et al., 2010). Model study by Kulmala et al. (2010) showed only 10 % difference in cosmic radiation ionisation rate between solar minimum and maximum at the SMEAR II station. Unfortunately, the external radiation dose rate data presented in this thesis were too short and slightly discontinuous to be able

draw conclusions of the effect of changing cosmic radiation intensity on ionisation rate based on direct measurements at the SMEAR II station.

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