

# Road-side measurements of aerosol and ion number size distributions: a comparison with remote site measurements

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We measured the number concentrations and size distributions of aerosol particles and air ions with a differential mobility particle sizer and air ion spectrometer, respectively, during a roadside campaign conducted in Kuopio (Savilahti), Finland, between 16 June and 2 July 2004. The average cluster ion (0.3–1.8 nm) concentrations were quite low (around 320 cm<sup>-3</sup> and 280 cm<sup>-3</sup> for negative and positive ions) during the whole period. For comparison, cluster ion concentrations in a rural SMEAR II station in Hyytiälä, southern Finland, were at the same time almost three times higher. Negative intermediate ions (1.8–7.5 nm) reached maximum concentrations of 620 cm<sup>-3</sup> in Kuopio, while the average concentrations were in the range 60–80 cm<sup>-3</sup> depending slightly on the wind direction. Positive intermediate ion concentrations were lower. We observed higher amounts of the intermediate ions usually during rain but also during non-rain periods indicative of short-term secondary particle formation. Large ion (7.5–40 nm) concentrations (average values of 500–800 cm<sup>-3</sup>) were 2–3 times higher in Kuopio than at the SMEAR II station. Straightforward impact of traffic was observed when the wind blew from the road: an increase in the traffic density increased concentrations of large ions.

## Introduction

Motor vehicle emissions are considered to be the main source of fine particles in cities. Primary particles emitted from internal combustion engines are mostly sub-micrometer agglomerates of carbonaceous particles, including adsorbed material, and their size ranges from 50 to 500 nm with highest concentrations at 80–100 nm (Kittelson *et al.* 2000, Harris and Maricq 2001).

Traffic-related secondary particles are formed immediately after the tailpipe. These particles are highly volatile and smaller in size than primary particles, and their concentrations peak at around 15–20 nm (Kittelson *et al.* 2006). Particles containing elemental carbon dominate the emissions of ultrafine particles of newer petrol-operated vehicles and diesel vehicles, whereas older petrol-operated vehicles produce particles with a larger

organic content (e.g. Kleeman *et al.* 2000).

In addition to electrically neutral aerosol particles, charged particles ranging from small cluster ions to larger ions are observed in the ambient air (e.g. Hörrak *et al.* 2000, Laakso *et al.* 2004, Hirsikko *et al.* 2005). The high-energy radiation, such as alpha and beta particles or gamma radiation, ionises air molecules into pairs of a positive ion and free electron. New ions react with other air molecules and form cluster ions within microseconds (Israël 1970). Larger charged particles can be formed by ion-induced nucleation, by collisions between neutral and charged particles or cluster ions, or by water droplet splitting (e.g. Israël 1970, Laakso *et al.* 2006, 2007). An investigation of air ion characteristics is essential for understanding the factors that affect the air conductivity and aerosol formation. As charge carriers, air ions determine the conductivity of air and thereby they also influence parameters of the global atmospheric circuit, such as the conduction current from the ionosphere to the ground and the potential gradient of the atmospheric electric field or space charge density (Rycroft *et al.* 2000).

Because reliable instruments for measuring ion size distributions are quite novel, not many experimental studies have been conducted so far in urban environments, even though routine measurements of atmospheric ions were started in Estonia in 1988 (Tammet 2006). Hörrak (2001) gave a detailed description of these measurements in his thesis. The thesis included a detailed analysis of the mobility spectra of air ions, the annual and diurnal variation of these spectra, photochemical nucleation and charging probability. Size distributions of air ions and ion-induced nucleation in a boreal forest have been investigated at the SMEAR II station (Kulmala *et al.* 2001, Hari and Kulmala 2005) since 2003 (Hirsikko *et al.* 2005, 2007c, Laakso *et al.* 2007). These studies have confirmed the idea that ions can participate in new particle formation, in addition to which information about particle formation processes has been obtained. Air ions have also been reported to affect new-particle formation in urban areas (Tammet 2006, Hirsikko *et al.* 2007b).

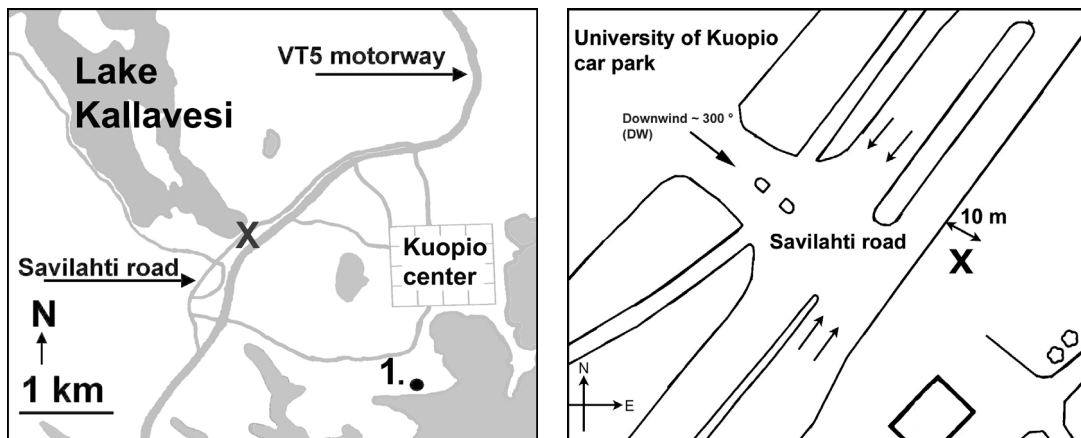
The open questions that we try to answer in this paper are: how do traffic-related particles

affect air ions and their size distributions, and is the vehicle exhaust a source or sink of air ions? We measured the concentrations and size distributions of air ions and aerosol particles during a three-week roadside campaign that took place in Kuopio, Finland, during in summer. In this paper we focus on Air Ion Spectrometer (AIS) measurements, which information on particle number size distributions below 3 nm in diameter. We will compare our measurement results with those made at a rural boreal forest site.

## Methods

We carried out the measurements in the Savilahti suburban area of Kuopio. The city is located in central/eastern Finland with 90 000 inhabitants (62°53'N, 27°38'E). The main local vehicular emission source during the measurements campaign (16 June–2 July 2004) was the nearest road (the Savilahti road), which was about 10 m north-west of the site (Fig. 1). The traffic density was 14 000–16 000 vehicles per day from Monday to Friday, and 6000–8000 vehicles per day during weekends and holidays. There is also a motorway (VT5) some 100 meters south-east of the measurement cabin. The average traffic density on the VT5 motorway was about 19 000–21 000 vehicles per day. Parallel measurements were conducted at the SMEAR II station in a rural site in Hyytiälä, southern Finland (61°51'N, 24°17'E, 180 m above the sea level). Kulmala *et al.* (2001) and Hari and Kulmala (2005) have described the SMEAR II station in detail. The distance between these two measurement sites is about 210 km.

Meteorological data from two local weather stations were recorded continuously at 5-minute intervals and hourly averages were used in this study. Meteorological parameters were measured on-site at a height of 3 m. Another local meteorological unit was located at the distance of 350 m north of the measurement site at the height of 20 m. The traffic density on the nearest road (the Savilahti road) was electrically measured using an induction coil technique and reported every 15 minutes. The traffic density information obtained from the Technical Office of Kuopio



**Fig. 1.** Layout of the Savilahti measurement site and its location with respect to the Kuopio city centre, located approximately 2 km from the measurement site. X indicated the location of the measurement site between the Savilahti road and VT5 motorway. Also shown is the power plant (1) that uses peat as a fuel, being the most important stationary emission source of particulate matter in the city area.

was used for the traffic data on the VT5 motorway. Sampling lines were placed at the height of 1.5 m (AIS) and 2 m (DMPS, *see* below) above the ground. However, the ground level of the measurement site was below both Savilahti road and VT5 motorway, the Savilahti road level being about 1 m and motorway about 9 m above the measurement site.

### Aerosol and air ion size distribution measurements

A Twin Differential Mobility Particles Sizer (Twin-DMPS) system measured aerosol number size distributions. The Twin-DMPS included two DMPS setups: one with an ultrafine condensation particle counter (CPC, TSI 3025) and Vienna-type 10.9-cm-long differential mobility analyser (DMA) for measuring particles in diameter range 3–45 nm, and the other one with a TSI 3010 CPC and Vienna-type 28-cm-long DMA to measure 15–900 nm particles. Thus, we obtained the overall size distribution in the range 3–900 nm with a five-minute time resolution. The sheath/aerosol flow rates were 19.2/4 l min<sup>-1</sup> for the first DMPS and 5/1 l min<sup>-1</sup> for the second DMPS.

The air ion spectrometer (AIS, <http://www.airel.ee>) measured naturally-charged positive and negative air ions (or charged particles) in the mobility range of 3.16–0.00133

cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> which, according to the algorithm of Tammet (1995, 1998), corresponds to the electrical mobility diameters of 0.34–40.3 nm under at the temperature of 293 K and pressure of 1013 hPa. We obtained ion size distributions in 28 size fractions with a time resolution of five minutes.

Here we provide a short summary on the operation principle of the AIS. For further information on AIS, we refer to the paper by Mirme *et al.* (2007). The AIS consists of two identical cylindrical aspiration-type differential mobility analysers, one for positive and the other one for negative ions. The sample air flow is 0.5 l s<sup>-1</sup> and sheath air flow 1 l s<sup>-1</sup> through each analyser. The electric field is applied between the cylinders of the analysers and the ions are attracted to different measuring elements of the mobility analysers according to their electrical mobility. The electrometers connected to the collecting elements measure the current carried by the ions. Thus, the AIS measures simultaneously the whole ion size distribution for both polarities. The noise of the measuring electronics is checked by charging and removing ions from the sample flow with a corona charger and electric filter at the inlet, which are not used when the sample air is measured. The AIS performs the offset-level measurements 1/3 of the time. The sheath air is circulated via a closed-loop and is ensured to be charge-free with additional corona chargers and electric filters, one for each analyser.

## Balance equation for cluster ions

The time evolution of the cluster ion concentration,  $dn/dt$ , was determined using the following equation (Israël 1970):

$$\frac{dn}{dt} = Q - \alpha n^2 - Sn. \quad (1)$$

Here  $Q$  denotes the ion production rate due to ionisation process of air molecules and their further reactions with other air molecules,  $\alpha$  is the ion–ion recombination coefficient (often assumed to be  $1.6 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ , Israël 1970),  $n$  is the concentration of positive or negative ions, and  $S$  describes the sink due to pre-existing aerosol particles. Equation 1 is simplified and does not take into account other possible cluster ion sinks such as ion-induced nucleation or deposition onto tree leaves and other surfaces (see Tammet et al. 2006). Additionally,  $n^2$  actually denotes the product of positive and negative cluster ion concentrations  $n_+$  and  $n_-$ , respectively. Furthermore, Eq. 1 is identical for positive and negative cluster ions.

## Results

We measured ion number concentrations and size distributions next to a road in Kuopio. At the same time, we measured ion size distributions at the SMEAR II station at a rural site in southern Finland. The nature and sources of particles and their precursors were very different between these two environments, so we hope that a comparison of the two datasets will add to the general understanding of the influence of different factors on air ions.

### General results over the campaign

During the measurements, ambient conditions varied considerably from high to low traffic densities and from upwind to downwind conditions. By the downwind sector ( $270^\circ < \text{wind direction} < 360^\circ$ ) we mean winds blowing from the Savilahti road toward the measurements site, and by the upwind sector ( $90^\circ < \text{wind direction} < 180^\circ$ ) we refer to winds blowing from the VT5 motor-

way toward the measurements site (Fig. 1). Five weekdays were classified both in the downwind sector and upwind sector.

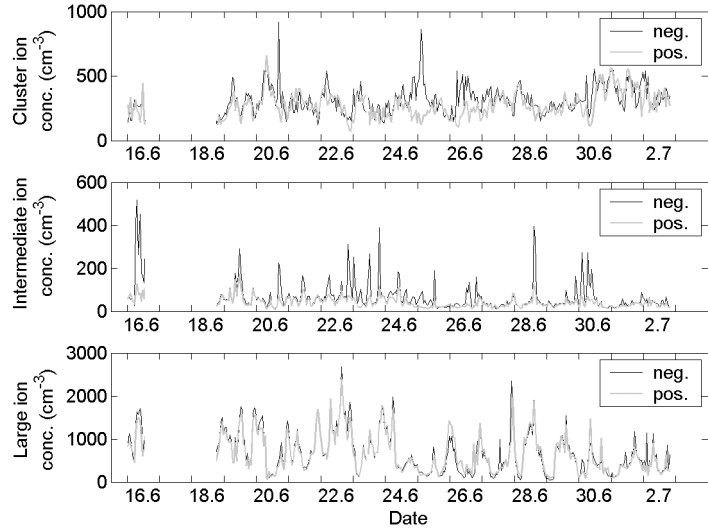
The average temperature was  $14^\circ\text{C}$  during the measurement campaign, with hourly temperatures ranging from  $6$  to  $24^\circ\text{C}$ . The average relative humidity was  $77\%$  with high nighttime values ( $> 90\%$ ). The average wind speed at the 20-m height was  $2.8 \text{ m s}^{-1}$  and its hourly values varied from calm to  $8.3 \text{ m s}^{-1}$ .

Changes in the traffic volume influenced ultrafine particle number concentrations (UFP, 3–100 nm) in quite a straightforward manner under downwind conditions. During the rush hours (06:00–08:00), UFP concentrations rose up to  $20\,000$ – $30\,000 \text{ cm}^{-3}$  and began to decline after 17:00 toward background concentrations of around  $3000 \text{ cm}^{-3}$ . Quite a similar concentration pattern was observed for accumulation mode particles (100–900 nm), with peak concentrations of around  $2000 \text{ cm}^{-3}$  during the morning and afternoon rush hours. However, higher accumulation mode particle number concentrations were observed during weekends (and holidays) when the traffic density was only half of the weekday traffic. This indicates that the traffic was not the main source of accumulation mode particles.

When the wind blew from the VT5 motorway, we did not observe a similar well-defined traffic-induced aerosol concentration pattern as under the downwind conditions. The distance from the VT5 motorway to the measurement site was about 100 meters, so the residence time of exhaust particles transported to the measurements site was longer (around 30–60 s), allowing for more dilution compared with particles coming from the Savilahti road. At the same time, the influences of regional sources were stronger because both city center and peat-fired power plant are located in the upwind sector about 2 km from the VT5 motorway.

The 24-hour-average particle number concentrations (UFP/accumulation mode) were  $20\,000/1500 \text{ cm}^{-3}$ ,  $18\,000/1700 \text{ cm}^{-3}$  and  $7000/1900 \text{ cm}^{-3}$  for downwind, upwind and weekend data, respectively. By considering the whole three-week period and all wind directions, the average number concentrations of ultrafine and accumulation mode particles were  $14\,000$  and  $1600 \text{ cm}^{-3}$ , respectively.

**Fig. 2.** Hourly-average cluster ion (0.3–1.8 nm), intermediate ion (1.8–7.5 nm) and large ion (7.5–40 nm) concentrations during measurement campaign. The data between 13:00 on 16 June 2004 and 20:00 on 18 June 2004 is not valid because of a failure in the measurement system so the data have been removed from further analysis.



## Air ion concentrations

For a more detailed analysis, we grouped air ions into three different size ranges: cluster ions (0.3–1.8 nm), intermediate ions (1.8–7.5 nm) and large ions (7.5–40 nm). During the measurement period the average cluster ion number concentrations were quite low,  $320 \text{ cm}^{-3}$  and  $280 \text{ cm}^{-3}$  for negative and positive ions, respectively (Table 1). The number concentrations varied between 50 and  $1000 \text{ cm}^{-3}$  for negative cluster ions and between 60 and  $720 \text{ cm}^{-3}$  for positive ones (Fig. 2). At the same time, the average cluster ion number concentrations ( $790$  and  $900 \text{ cm}^{-3}$  for negative and positive ions, respectively) at the SMEAR II station in Hyttiälä were almost three times higher than in Savilahti (Table 1).

In Savilahti, negative intermediate ions (1.8–7.5 nm) had concentrations of up to  $600$

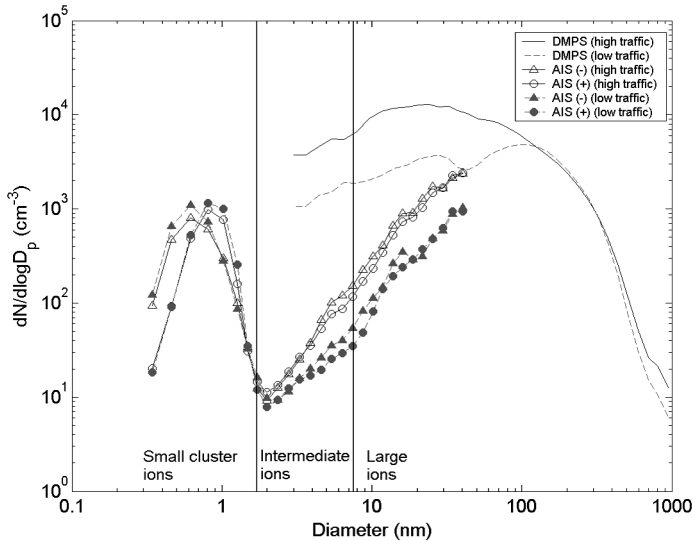
$\text{cm}^{-3}$  with the average value of  $70 \text{ cm}^{-3}$  (Table 1 and Fig. 2). Positive intermediate ions had a maximum concentration of  $190 \text{ cm}^{-3}$  and average of  $40 \text{ cm}^{-3}$ . Rain was mainly responsible for the highest intermediate ion concentrations, even though we observed intermediate ion bursts during fine weather also, which is indicative of secondary particle formation. However, we did not observe similar nucleation events as has been reported to take place in Hyttiälä and Helsinki (e.g. Hirsikko *et al.* 2007b, 2007c).

Large ions (7.5–40 nm) followed the daily variation of the ultrafine particle number concentration with average concentrations of  $680$  and  $650 \text{ cm}^{-3}$  for negative and positive ions, respectively (Table 1). The average large ion concentrations were 2–3 times higher in Savilahti than at the SMEAR II station in Hyttiälä (Table 1).

For comparison, Hirsikko *et al.* (2007b)

**Table 1.** Cluster ion (0.3–1.8 nm), intermediate ion (1.8–7.5 nm) and large ion (7.5–40 nm) concentrations ( $\text{cm}^{-3}$ ) and negative-to-positive ion ratios for averages of total dataset of Savilahti measurements 16 June–2 July 2004 for downwind conditions (DW) for upwind conditions (UW), and for averages of total dataset of Hyttiälä SMEAR II station. Given values are mean  $\pm$  SD. The statistics were calculated based on the data with 30-minute time resolution.

	Cluster ions			Intermediate ions			Large ion		
	negative	positive	ratio	negative	positive	ratio	negative	positive	ratio
Savilahti, tot	$320 \pm 120$	$280 \pm 100$	$1.2 \pm 1.2$	$70 \pm 80$	$40 \pm 30$	$1.6 \pm 2.7$	$680 \pm 500$	$650 \pm 470$	$1.1 \pm 1.1$
Savilahti, DW	$280 \pm 90$	$260 \pm 90$	$1.1 \pm 1.0$	$90 \pm 100$	$50 \pm 30$	$1.8 \pm 3.9$	$910 \pm 530$	$870 \pm 480$	$1.1 \pm 1.1$
Savilahti, UW	$350 \pm 110$	$320 \pm 110$	$1.1 \pm 1.0$	$60 \pm 50$	$40 \pm 20$	$1.5 \pm 2.3$	$550 \pm 380$	$500 \pm 370$	$1.1 \pm 1.0$
Hyttiälä, tot	$790 \pm 190$	$900 \pm 200$	$0.9 \pm 1.0$	$24 \pm 74$	$14 \pm 30$	$1.7 \pm 2.5$	$210 \pm 170$	$260 \pm 190$	$0.8 \pm 0.9$



**Fig. 3.** Daytime number size distributions measured by the AIS and DMPS during low traffic density (27 Sep. 2004, 6500 vehicles per 24 h) and high traffic density conditions (29 June 2004, 14 000 vehicles per 24 h). Three ion size fractions have been separated in the figure: cluster ions (< 1.8 nm), intermediate ions (1.8–7.5 nm) and large ions (> 7.5 nm).

measured air ion size distributions approximately 100 m away from a major road in Helsinki in August 2004. In the study by Hirsikko *et al.* (2007b), the average cluster ion concentrations were two times higher than those observed here. During the working days, Hirsikko *et al.* (2007b) measured average number concentrations of 630 and 680  $\text{cm}^{-3}$  for negative and positive cluster ions, respectively. The average intermediate and large ion concentrations were almost equal in Kuopio and Helsinki. The maximum concentrations of negative intermediate and large ion concentrations were significantly higher in Helsinki (6700 and 9500  $\text{cm}^{-3}$ , respectively) than in Kuopio (620 and 3300  $\text{cm}^{-3}$ , respectively). This indicates that the concentrations of nucleation and Aitken mode particles, and therefore of large air ions, are usually similar in Kuopio and Helsinki. However, maximum concentrations are larger in Helsinki due to stronger sources.

### Ion size distributions

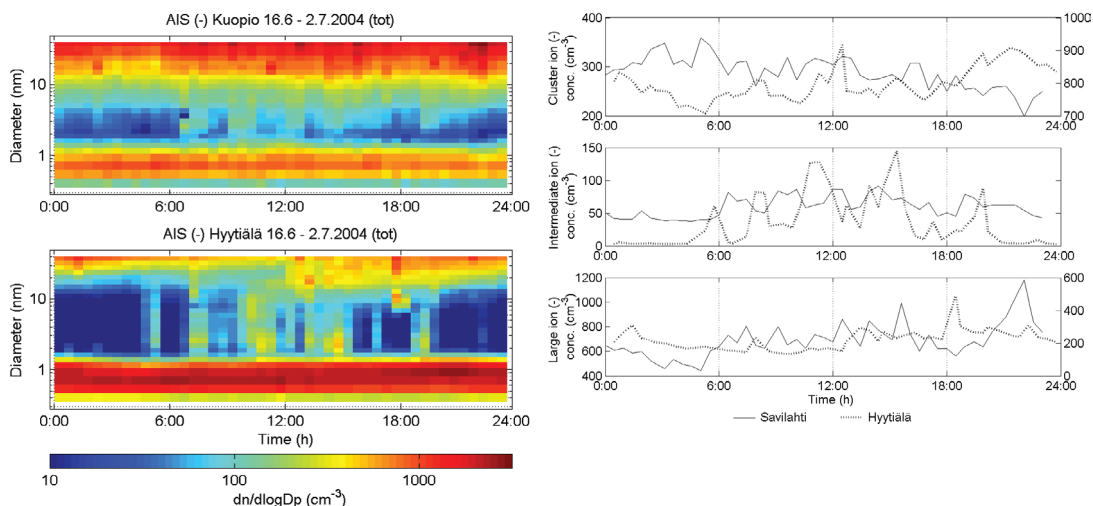
Due to the different proton affinities of different chemical compounds, the composition and size of negative and positive ions are different from each other (e.g. Amad *et al.* 2000; Fig. 3). Based on average ion size distributions measured during a low and high traffic density day (06:00–20:00) on the Savilahti road, the traffic

was found to influence more cluster ion concentrations than their size (Fig. 3). Traffic densities were 6500 and 14 000 vehicles per 24 h for the low and high traffic density days, respectively. These two days (27 June and 29 June 2004) were selected because of almost identical daytime weather conditions, making it possible to compare the influence of different traffic densities. As one might expect, intermediate and large ion concentrations were lower during the low-traffic-density day than during the high-traffic-density day. However, here we did not consider the effect of wind direction, which we discuss in more detail below.

The main differences in air ion size distributions between the rural Hyytiälä and urban Savilahti site were the lower cluster ion concentrations and higher large ion concentration in Savilahti (Fig. 4). In Kuopio, variations in the traffic density had the largest effect on the ion size distributions. The formation of intermediate ions related to the secondary particle formation processes was more frequent at the rural site, causing large concentrations of intermediate ions around the noon. Other bursts of intermediate ions were mostly due to the rain.

### Downwind and upwind conditions

The downwind and upwind sector data were



**Fig. 4.** Left-hand side: diurnal variation of negative ions size distributions at the Savilahti measurement site (top) and SMEAR II station (bottom). Right-hand side: concentrations at the Savilahti measurement site (solid line) and at SMEAR II station (dotted line). Note: the right-hand-side y-axis for cluster ions and large ions for the SMEAR II station (Hyytiälä) data.

selected for investigation of the impact of the nearest road on ion concentrations and size distributions. The road had a clear effect on ion concentrations (Fig. 5 and Table 1): large ions had their highest concentrations when the wind blew from the downwind sector, i.e. from the Savilahti road 10 meters away, ensuring that the vehicular source of particles seen by our instruments was maximized. The opposite was true for cluster ions which showed maximum concentrations during the upwind periods when aerosol particle concentrations were slightly reduced. For intermediate ions, the effect of the wind direction was not evident.

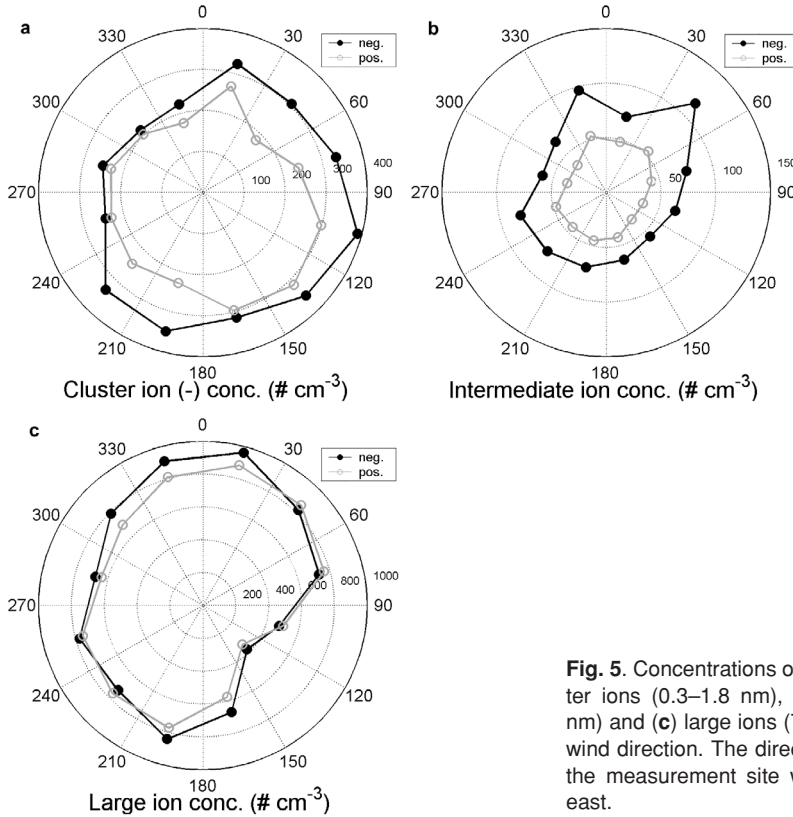
Both morning (06:00–08:00) and afternoon (15:00–17:00) rush hours had a major influence on ion concentrations and size distributions during the downwind periods (Fig. 6). Increases in the traffic density increased concentrations of large ions, while at the same time concentrations of cluster ions declined. Rapid increases in the traffic volume (rush hours) increased also concentrations of intermediate ions. We observed a slight increase in negative intermediate ion concentrations during the evenings (around 21:00), which might be due to changes in meteorology, especially the declining wind speed. The decreasing wind speed and solar radiation intensity during the evening reduces vertical atmospheric

mixing, as a result of which the contribution of local ion sources (radon and gamma radiation) will increase during the night-time and the concentrations of ion-cluster ions and sometimes also of intermediate ions will increase. For intermediate ions also the increased concentrations of condensable vapors will have an effect.

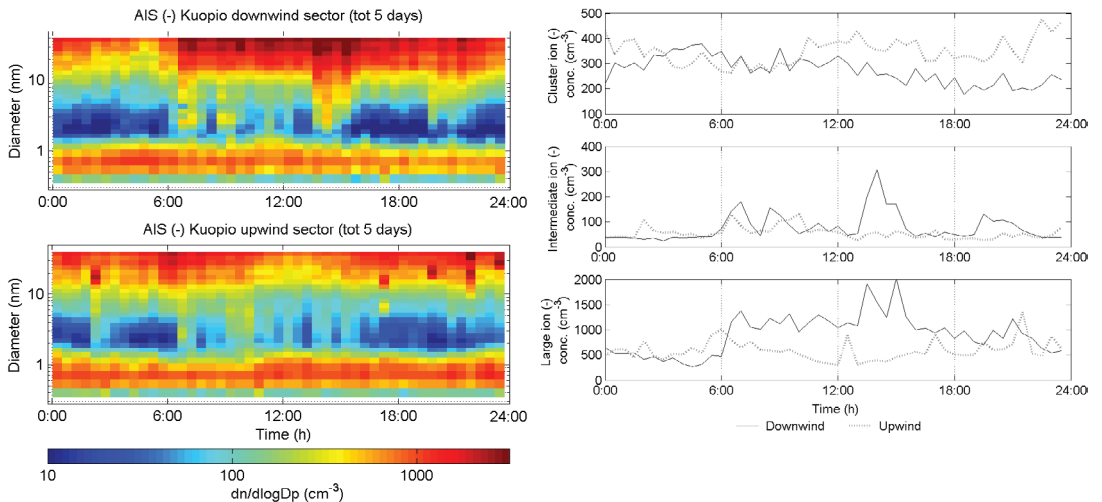
Intermediate ion bursts were mainly due to rain and secondary particle formation (the ratio between rain and secondary particle formation events was 2:1). In the absence of rain, the bursts of intermediate ions occurred more frequently when the traffic volume was low or wind blew from the upwind sector (no fresh traffic emissions).

## Discussion

The SMEAR II station is a rural site, in which cluster ion concentrations are affected more by the sink due to pre-existing aerosol particles than by ion production due to ionisation (Hirsikko *et al.* 2007a). In addition to the aerosol sink and ion production, the composition of aerosol particles and gaseous compounds differ significantly between the two sites: the Savilahti area is dominated by local anthropogenic sources, especially traffic exhaust, whereas Hyytiälä is a rural site



**Fig. 5.** Concentrations of negative and positive (a) cluster ions (0.3–1.8 nm), (b) intermediate ions (1.8–7.5 nm) and (c) large ions (7.5–40 nm) as a function of the wind direction. The direction of the traffic lanes next to the measurement site was from south-west to north-east.



**Fig. 6.** Diurnal variation of negative ion (left-hand side) size distributions during downwind (top) and upwind condition (bottom), (right-hand side) concentration during downwind (solid line) and upwind condition (dotted line).

where the forest emits organic precursors for secondary particles.

In Savilahti we did not measure the radon concentration or external radiation, the latter of

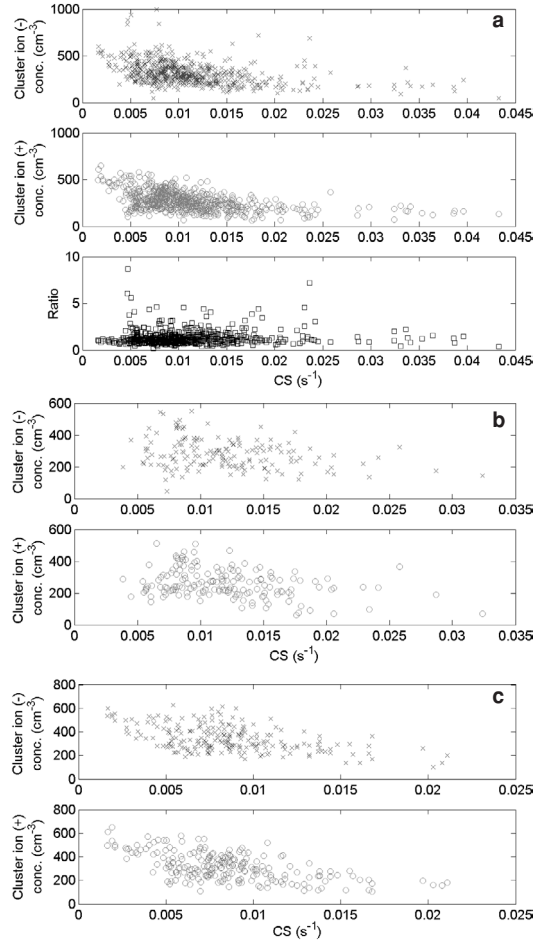
which consists mainly of gamma radiation from the ground and cosmic radiation. As a result, we cannot estimate the natural ion production in Savilahti. Furthermore, we do not have infor-



mation about ion production at the SMEAR II station in Hyytiälä in June 2004 (Hirsikko *et al.* 2007a). However, the average total ion production rate was around  $10.7 \text{ cm}^{-3} \text{ s}^{-1}$  ( $9.5\text{--}13.3 \text{ cm}^{-3} \text{ s}^{-1}$ ) in Hyytiälä in June 2006. According to Hirsikko *et al.* (2007a) the total ion production had a similar annual cycle every year, so we can expect that the average total ion production rate was approximately  $10 \text{ cm}^{-3} \text{ s}^{-1}$  in Hyytiälä also in June 2004.

Cluster ion concentrations are linked with the sink due to pre-existing aerosol particles via the balance equation (Eq. 1). The condensation sink (CS) describes the removal rate of vapour molecules by aerosol particles (*see e.g.* Dal Maso *et al.* 2005). We utilised CS as an indicator of the aerosol sink for cluster ions, although it is not exactly the sink terms  $S$  in Eq. 1. When the condensation sink increased (*e.g.* because of local emissions), cluster ion concentrations decreased (Fig. 7a), whereas the ratio between the negative and positive cluster ions was almost independent of CS. The average ratios between negative and positive cluster ion concentration was 1.2 in Kuopio (maximum ratio of 8.7) and 0.9 in Hyytiälä (maximum ratio of 2.0) (Table 1). The average ratios were the same during the upwind (1.1) and downwind conditions (1.1), but the ratios varied significantly from 0.5 to 4.3 during the upwind conditions and from 0.2 to 3.9 during the downwind conditions (Table 1).

Interestingly, the concentration of cluster ions and CS did not clearly correlate with each other during the downwind conditions (Fig. 7b.). This is partly in contradiction to our other observations (Figs. 3 and 5) which showed that cluster ion concentrations were lower when the wind was blowing from the downwind sector and traffic density was high. Firstly, the distance from the nearest road was only 10 m and due to the short residence time, so the traffic exhaust particles did not have enough time to affect cluster ion concentrations as predicted by Eq. 1. However, the temporal variation in the wind speed changed the residence time. We also have to take into consideration that CS had its maximum value when the wind was blowing parallel to the road. Secondly, there is Lake Kallavesi beyond the Savilahti road. Water reduces radon emissions and especially the penetration of gamma



**Fig. 7.** Cluster ion concentrations as a function of condensation sink (CS) (a) in overall data and the ratio between negative and positive cluster ions, (b) in downwind sector, (c) in upwind sector.

radiation from the lake bottom. Thus, ion production over water surfaces is mainly due to the cosmic radiation and radon transported from the shore, whereas above the ground ion production is faster due to increased dose rates of gamma radiation.

When the wind was blowing from the VT5 motorway (upwind sector), the residence time was not very crucial because of the longer distance from the road, so the connection between cluster ion concentrations and CS was obvious (Fig. 7c). Our results indicate that the ratio between the cluster ion sources and sinks was higher when the wind came from the upwind sector.

## Summary and conclusions

We measured number concentrations and size distributions of air ions and aerosol particles in an urban environment using an AIS and DMPS during a road-side study that was conducted between 16 June and 2 July 2004 in Kuopio, Finland. The measurement site was in the vicinity of the road Savilahdentie about 10 m from the traffic lanes with a traffic density of 14 000–16 000 vehicles per workday. During downwind conditions, the concentration pattern of 7.5–40 nm ions followed the traffic density, whereas at the same time the concentration of cluster ions declined. During the whole measurement period, negative and positive intermediate ions had maximum concentration values of 620 and 190  $\text{cm}^{-3}$ , respectively, while the corresponding average concentrations were 70 and 40  $\text{cm}^{-3}$ . Intermediate ion concentrations were affected by traffic, rain and secondary particle processes depending on meteorological (i.e. wind direction and precipitation) and traffic conditions. During the three-week measurement period, we did not observe similar secondary particle formation events as has been observed, for example, by Hirsikko *et al.* (2007b) in an urban background site in Helsinki.

The average cluster ion (0.3–1.8 nm) concentrations were quite low during the whole measurement period, being on average around 320  $\text{cm}^{-3}$  and 280  $\text{cm}^{-3}$  for negative and positive ions, respectively. Cluster ion concentrations in a rural SMEAR II station were almost three times higher than in Savilahti. We observed the highest cluster ion concentrations when the wind blew toward the nearest road and lowest concentrations when the wind blew from the road. These results indicate the ratio of source to sink for cluster ions was smaller in a site close to a road than in a rural site and during upwind than downwind conditions.

## References

- Amad M., Cech N., Jackson G. & Enke C. 2000. Importance of gas-phase proton affinities in determining the electro-spray ionization response for analytes and solvents. *J. Mass Spectrometry*. 35: 784–789.
- Dal Maso M., Kulmala M., Riipinen I., Wagner R., Hussein T., Aalto P.P. & Lehtinen K.E.J. 2005. Formation and growth of fresh atmospheric aerosols: eight years of aerosol size distribution data from SMEAR II, Hyytiälä, Finland. *Boreal Env. Res.* 10: 323–336.
- Hari P. & Kulmala M. 2005. Station for Measuring Ecosystem–Atmosphere Relations (SMEAR II). *Boreal Env. Res.* 10: 315–322.
- Harris S.J. & Maricq M.M. 2001. Signature size distributions for diesel and gasoline engine exhaust particulate matter. *J. Aerosol Sci.* 32: 749–764.
- Hirsikko A., Laakso L., Hörrak U., Aalto P., Kerminen V.-M. & Kulmala M. 2005. Annual and size dependent variation of growth rates and ion concentrations in boreal forest. *Boreal Environ. Res.* 10: 357–369.
- Hirsikko A., Paatero J., Hatakka J. & Kulmala M. 2007. 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 Env. Res.* 12: 265–278.
- Hirsikko A., Yli-Juuti T., Nieminen T., Vartiainen E., Laakso L., Hussein T. & Kulmala M. 2007. Indoor and outdoor air ions and aerosol particles in the urban atmosphere of Helsinki: characteristics, sources and formation. *Boreal Env. Res.* 12: 295–310.
- Hirsikko A., Bergman T., Laakso L., Dal Maso M., Riipinen I., Hörrak U. & Kulmala M. 2007c Identification and classification of the formation of intermediate ions measured in boreal forest. *Atmos. Chem. Phys.* 7: 201–210.
- Hörrak U., Salm J. & Tamm H. 2000. Statistical characterization of air ion mobility spectra at Tahkuse Observatory. *J. Geophys. Res.* 105: 9291–9302.
- Hörrak U. 2001. *Air ion mobility spectrum at a rural area*. Ph.D. thesis, University of Tartu.
- Israël H. 1970. *Atmospheric electricity, vol. 1: Fundamentals, conductivity, ions*. Israel Program for Scientific Translations, Jerusalem.
- Kittelson D.B., Johnson J., Watts W., Wei Q., Drayton M., Paulsen D. & Bucowicki C. 2000. *Diesel aerosol sampling in the atmosphere*. SAE Paper No. 2000-01-2212.
- Kittelson D.B., Watts W.F. & Johnson J.P. 2006. On-road and laboratory evaluation of combustion aerosols, part 1: Summary of diesel engine results. *J. Aerosol Sci.* 37: 913–930.
- Kleeman M.J., Schauer J.J. & Cass G.R. 2000. Size and composition distribution of fine particulate matter emitted from motor vehicles. *Environ. Sci. Technol.* 34: 1132–1142.
- Kulmala M., Hämeri K., Aalto P.P., Mäkelä J.M., Pirjola L., Nilsson E.D., Buzorius G., Rannik Ü., Dal Maso M., Seidl W., Hoffman T., Janson R., Hansson H.-C., Viisanen Y., Laaksonen A. & O'Dowd C.D. 2001. Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR). *Tellus* 53B: 324–343.
- Laakso L., Anttila T., Lehtinen K.E.J., Aalto P.P., Kulmala M., Hörrak U., Paatero J., Hanke M. & Arnold F. 2004. Kinetic nucleation and ions in boreal forest particle formation events. *Atmos. Chem. Phys.* 4: 2353–2366.
- Laakso L., Hirsikko A., Grönholm T., Kulmala M., Luts A. & Parts T.-E. 2006. Waterfalls as sources of small

- charged aerosol particles. *Atmos. Chem. Phys. Discuss.* 6: 9297–9314.
- Laakso L., Gagne S., Petäjä T., Hirsikko A., Aalto P.P., Kulmala M. & Kerminen V.-M. 2007. Detecting charging state of ultra-fine particles: instrumental development and ambient measurements. *Atmos. Chem. Phys.* 7: 1333–1345.
- Mirme A., Tamm E., Mordas G., Vana M., Uin J., Mirme S., Bernotas T., Laakso L., Hirsikko A. & Kulmala M. 2007. A wide-range multi-channel Air Ion Spectrometer. *Boreal Env. Res.* 12: 247–264.
- Rycroft M., Israelsson S. & Price C. 2000. The global atmospheric electric circuit, solar activity and climate change. *J. Atmos. Solar. Terrestrial Phys.* 62: 1563–1576.
- Tammet H. 1995. Size and mobility of nanometer particles, clusters and ions. *J. Aerosol Sci.* 26: 459–475.
- Tammet H. 1998. Reduction of air ion mobility to standard conditions. *J. Geophys. Res.* 103: 13933–13937.
- Tammet H. 2006. Continuous scanning of the mobility and size distribution of charged clusters and nanometer particles in atmospheric air and the Balanced Scanning Mobility Analyzer BSMA. *Atmos. Res.* 82: 523–535.
- Tammet H., Hörrak U., Laakso L. & Kulmala M. 2006. Factors of ion balance in coniferous forest according to measurements in Hyttälä, Finland. *Atmos. Chem. Phys.* 6: 3377–3390.