

Indoor and outdoor air ions and aerosol particles in the urban atmosphere of Helsinki: characteristics, sources and formation

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We measured air ion size distributions with an air ion spectrometer in the size range of 0.34–40.3 nm both indoors (in July) and outdoors (in August) in Helsinki, Finland in 2004. At the same time we measured particle number concentrations and size distributions with two condensation particle counters (indoors) and differential mobility particle sizer (outdoors). Our main focus was to study new-particle formation in an urban site. We observed new-particle formation indoors almost every day, even many times a day, and four times outdoors. Indoors, the observed growth rates were 2.3–4.9 nm h⁻¹ for 1.3–3-nm ions, 6.5–8.7 nm h⁻¹ for 3–7-nm ions and 5.1–8.7 nm h⁻¹ for 7–20-nm ions. Outdoor ions (3–7 nm) grew at rates as large as 15.4 nm h⁻¹. Outdoor ion and particle number concentrations were dependent on the wind direction, whereas indoor concentrations were dependent on ventilation conditions. Secondary particle formation and growth affected concentrations both indoors and outdoors. We concluded, based on our measurement results and simulated penetration of outdoor particles through the ventilation system, that we had indoor sources for secondary particles.

Introduction

In urban environments there are many sources for primary and secondary aerosol particles, such as the traffic and industry (e.g. Burtscher *et al.* 2001, Wehner *et al.* 2002, Hussein *et al.* 2005a, Arnold *et al.* 2006). An urban environment has also sources for natural aerosol precursors, including forests and parks. Most pollution-related aerosol particles are thought to be harm-

ful to human health because of their number or mass concentration, size or chemical composition (Pope *et al.* 2002). Some of the chemical compounds in particles can even be toxic for human. In addition to human health, aerosol particles influence visibility, global radiation balance, cloud cover and other cloud properties, and precipitation (Kaufman *et al.* 2002).

Recently Hussein *et al.* (2004b) observed that during the six years of study the number

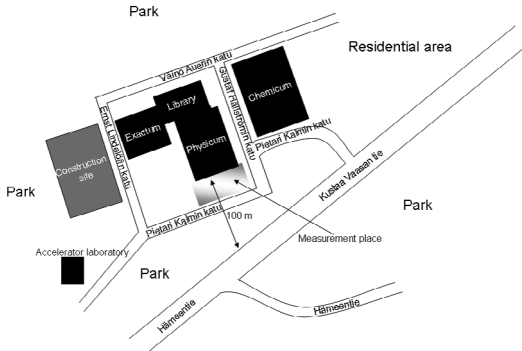


Fig. 1. Schematic map of the measurement site in Helsinki in autumn 2004. The outdoor air measurements were performed at the parking area next to the building of the Department of Physics (Physicum).

concentration of fine aerosol particles decreased in the urban background atmosphere of the Helsinki metropolitan area while the traffic density slightly increased. This was related to the new engine technology used in modern vehicles. In the absence of indoor sources of aerosol particles, indoor air quality is directly related to that outdoors. The indoor-to-outdoor relationship of aerosol particles can be characterized by filtration, ventilation and deposition processes. The indoor sources of aerosols or their precursors may induce aerosol particle formation in the indoor air (e.g. Hussein *et al.* 2006, Vartiainen *et al.* 2006). However, the processes leading to new-particle formation in the indoor air remain unknown. In contrast, new-particle formation in the outdoor air (*see* Kulmala *et al.* 2004a) has attracted more interest and there are several theories capable of explaining the processes leading to new-particle formation. The proposed mechanisms in this regard include kinetic nucleation, ion-induced nucleation and activation of neutral clusters (e.g. Kulmala 2003, Kulmala *et al.* 2006, Sihto *et al.* 2006). Each of these mechanisms can involve two (binary nucleation) or three (ternary nucleation) nucleating vapours.

Ion spectrometers developed by AIREL Ltd., Estonia, to measure the size distributions of charged aerosol particles (or air ions) down to molecular sizes (Tammet 2006, Mirme *et al.* 2007) enable us to study the air ion size distributions and formation in the atmosphere more efficiently (Kulmala *et al.* 2004b). Typically, air ion

measurements have concentrated on secondary particle formation studies conducted at rural sites (*see* for example Laakso *et al.* 2004b, Hirsikko *et al.* 2007b). On the other hand, studies in urban environments with air ion spectrometers are rare. Tammet (2006) demonstrated that the secondary charged aerosol particles formed in the urban environment of Tartu, Estonia. These measurements were based on a new air ion spectrometer called the balanced scanning mobility analyzer. Long-term data sets on small air ions (down to molecular sizes) have been lacking from both urban environments and indoor air so far.

In this paper we present, for the first time, observations of indoor air ion number concentrations and size distributions over the particle diameter range of 0.34–40 nm. The main objective of our study was to investigate new-particle formation and growth rate of indoor aerosol particles induced by pre-existing air ions. We also investigated the indoor-to-outdoor relationship of air ions in the urban background atmosphere of Helsinki.

Measurements and methods

We measured indoor and outdoor air ion size distributions in a laboratory room of the Department of Physical Sciences, University of Helsinki, Finland (60°10'N, 24°57'E), and in the backyard of the Department of Physics 'Physicum' (Fig. 1). Our measurements included also indoor total particle number concentrations in the laboratory and outdoor particle number size distributions. The indoor measurements were carried out during 7–28 July 2004 and the outdoor measurements were carried out during 30 July–7 September 2004.

Indoor and outdoor environments and conditions

The laboratory room, in which we carried out the measurements, was located in the fourth floor. The room was used for other measurement purposes during short periods. For example, aerosol particles were generated in a fume chamber on 12–13 and 19–21 July 2004. The compounds

used in aerosol particle generation were hexane, a mixture of caryophyllene and hexane, heptane, and a mixture of caryophyllene and heptane. Although the particles were generated inside the chamber, this process may have influenced slightly the ion size distributions measured in the same room during those days. At other times and especially during nights and weekends, there were no indoor activities in the laboratory.

The whole building was mechanically ventilated on workdays between 04:00 and 19:00. During this time, the ventilation rate for the laboratory room was about 2.6 h^{-1} . When the mechanical ventilation was turned off, we assumed an effective ventilation rate of about 0.13 h^{-1} . The standard filter installed in the mechanical ventilation system was F7-class. We assumed a friction velocity of 10 cm s^{-1} during the high ventilation period (workdays 04:00–19:00) and 1 cm s^{-1} during all other times. The floor area and volume of the laboratory were 41 m^2 and 140 m^3 , respectively. The overall surface area (floor, walls, ceiling and the surfaces of tables and cabinets) of the laboratory was approximately 271 m^2 .

We carried out the outdoor ion measurements from a cabin in the backyard of the Department of Physics (Fig. 1). The backyard is a car park and the Department of Physical Sciences is located on a hill close to a busy major road (Kustaa Vaasan tie) with three crossroads near the measurement site, two in the north-east direction (about 100 and 180 m away) and the third one in the south-east direction (about 250 m away). There is a coal power plant to the south-east of the site. The major road is located about 100 m east of the site and there is a deciduous tree park between the site and the road. The centre of Helsinki is located approximately 4 km south-east of the measurement site. There was a building construction near the Department of Physics that may have increased concentrations of large particles due to increased traffic activities.

In Finland, July is the summer holiday month when most of the people travel outside Helsinki. The same people normally return to their work in August. This causes differences in the number of vehicles moving within the Helsinki area, but the overall daily traffic pattern remains similar to other months. The daily traffic counts on the

nearby street (Kustaa Vaasan tie) were of the order of 30 000 in August, with rush hour peaks in the morning (between 6:00 and 9:00 in Finnish winter time) and in the afternoon (between 13:00 and 17:00).

Air ions size distribution (AIS) measurements

We measured air ion size distributions (0.34–40.3 nm) using an Air Ion Spectrometer (AIS, by AIREL Ltd., Estonia). This instrument measures air ion mobility distributions within the mobility range of $3.16\text{--}0.00133 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (<http://www.arel.ee>). Mirme *et al.* (2007) described the AIS instrument, its functioning, calibration and data inversion in detail. Here we give only a short description on the setup of the device. The AIS consists of two identical cylindrical aspiration-type differential mobility analysers, one for positive and the other one for negative ions. Both mobility analysers have 21 insulated collector electrodes that are connected with electrometrical amplifiers. The amplifiers measure the electric current carried by the ions. The analysers classify and measure simultaneously all air ions in the mobility range of the device. The sample and sheath air flow rates of each analyser are 500 and $1000 \text{ cm}^3 \text{ s}^{-1}$, respectively. The corona charger and subsequent electric filter at the inlet of the AIS instrument are used only for charging and removing particles from the sample air when the offset level and noise of electrometrical amplifiers are measured. However, corona charging and electrical filtration are not used when ion concentrations are measured. The inlet corona charger and filter are electronically controlled. The sheath air is continuously filtered with the additional corona chargers and electric filters. The two analysers have their own closed-loop sheath flow arrangements. As a default the time resolution of the AIS is five minutes, which was utilised also in our study.

We converted the mobility size distributions (0.34–40.3 nm) measured with AIS instrument to the particle number size distributions of air ions with the algorithm developed by Tammet (1995) and the corrections according to Tammet (1998). The algorithm assumes that particles are singly

charged. We usually operated the AIS under special conditions (temperature 0 °C, pressure 1013 mb) only for the consistency and comparability of our data. Changing the operation temperature from 0 to 20 °C changes the measured diameter of e.g. 1.5 nm ions by approximately 2%. This, however, does not change the concentration of cluster ions presented in this study, since the limits of cluster mode are chosen so that they contain the whole mode.

We did not use any additional inlet tubing when measuring the indoor air. When we measured outdoors, the AIS had approximately a 0.5-m-long inlet tube, with inner diameter of 16 mm, and sampled at 2 m height. The losses due to the inlet were tested and seen to have minor effect.

Total particle number concentrations and particle number size distributions

We measured the indoor total particle number concentrations with two Condensation Particle Counters (CPC): an ultrafine particle CPC (model TSI 3025 with cut-off size 3 nm and flow rate of 1.5 l min⁻¹) and a CPC (model TSI 3010, with flow rate of 1 l min⁻¹ and cut-off size 10 nm). In order to minimise particle losses, we did not use additional inlets or tubes. We evaluated the number concentration of particles between 3 and 10 nm by calculating the difference between these measurements.

We also used the outdoor particle number size distribution (10–950 nm, dry diameters) data, obtained from continuous measurements conducted at the fourth-floor level in the building of the Department of Physical Sciences. These measurements have been made using a twin Differential Mobility Particle Sizer system (DMPS) (Aalto *et al.* 2001). The outdoor air was sampled from the same direction where the major road (Kustaa Vaasan tie) is located (Fig. 1).

The twin DMPS consisted of two Differential Mobility Analysers (DMA): an ultrafine DMA (10.9 cm long Hauke-type) connected to a TSI 3025 CPC to measure particle number size distributions between 3 and 50 nm, and a 28-cm-long Hauke-type DMA connected to a TSI 3010 CPC to measure particle number size distributions between 10 and 950 nm. The sheath/sample flow

rates were 17/3 l min⁻¹ and 5/1 l min⁻¹ for the first and second DMA, respectively. The sheath air was circulated via a closed loop (Jokinen and Mäkelä 1997). A radioactive ⁸⁵Kr-source was used as a particle neutralizer before the DMA units.

The outdoor particle number size distribution measurements provided information about the indoor/outdoor (I/O) ratios of aerosol particles between 3 and 10 nm with the help of the simultaneous measurements of the total particle number concentrations in the indoor air with the two CPC's. We also utilized outdoor particle number size measurements along with indoor model simulations, as will be described in the next section, for providing more information about how big fraction of indoor aerosol particles originated from outdoors.

Model simulations of the indoor aerosol particles

We utilized a simplified form of our indoor air model (MC-SIAM, Hussein *et al.* 2005b, 2006) to estimate the indoor particle number concentrations originating from outdoors. In the simplified form of the MC-SIAM we assumed the change rate of the indoor particle number concentration of a certain particle size-section to follow the balance equation:

$$\frac{d}{dt} N_{in,i} = lP_i N_{out,i} - lN_{in,i} - \frac{1}{V} \sum_j A_j v_{d,j,i} N_{in,i} + J_{sources,i} \quad (1)$$

Here i denotes a certain particle size section (sectional approach), N_{in} and N_{out} are the indoor and outdoor particle number concentrations, respectively, l is the ventilation rate, V is the laboratory volume, A_j is the total area of indoor surfaces denoted by the index j (upward facing, downward facing, and vertical), v_d is the corresponding deposition velocity of aerosol particles onto the surface j , and J_{source} is the source rate of aerosol particles.

In the model simulations, we assumed that the laboratory was a well-mixed domain separated from other rooms. This was a reasonable assumption because the laboratory door was kept closed almost all the time during the measurement campaign. As input parameters to the

model, we used the actual values related to the indoor environment and conditions.

Ion growth rates and the concentrations of condensing vapours

We calculated the particle growth rates (GR) based on the AIS and DMPS data using the method described by Lehtinen and Kulmala (2003) and Hirsikko *et al.* (2005). The basic principle was to follow the maximum particle concentration of each small size fraction. We obtained the growth rate as a slope of the fitted linear line to the timings of the maximum concentrations as a function of particle size.

We calculated the vapour concentration that is needed for particle growth using eq. 4 given by Kulmala *et al.* (2001).

Results and discussion

Indoor and outdoor air ion concentrations

The observed cluster ions were smaller than 1.8 nm in diameter. In general, the maximum size of cluster ions depends on the site, season, time of day, and charge polarity (Hirsikko *et al.* 2007b). Here, we refer to the air ions in the size range of 3–10 nm in diameter as intermediate ions and those in the size range of 10–40 nm as large ions.

The cluster ion concentrations were higher indoors than outdoors (Tables 1 and 2). Polarity differences in cluster ion concentrations were generally small both indoors and outdoors and especially during the weekends (Tables 1 and 2). We observed the largest polarity differences during maximum cluster concentrations when negative ions showed much larger concentra-

Table 1. Indoor and outdoor ion concentrations (cm^{-3}) during workdays. The concentrations are presented for cluster (smaller than 1.8 nm in diameter), 3–10 nm, and 10–40 nm ions. The +|– sign refers to positive|negative ions.

	Cluster ions + – Indoor (Outdoor)	Ions 3–10 nm + – Indoor (Outdoor)	Ions 10–40 nm + – Indoor (Outdoor)
Mean	1019 (627) 1127 (683)	59 (51) 70 (74)	232 (652) 209 (710)
SD	477 (233) 437 (346)	89 (101) 103(177)	416 (528) 248 (646)
Median	966 (590) 1065 (630)	22 (36) 28 (46)	164 (512) 142 (539)
10%	441 (370) 599 (308)	3 (12) 3 (14)	67 (239) 63 (246)
25%	669 (470) 803 (447)	6 (20) 7 (25)	100 (357) 87 (360)
75%	1348 (754) 1444 (858)	73 (61) 87 (79)	270 (783) 255 (847)
90%	1669 (946) 1718 (1137)	164 (94) 190 (134)	411 (1198) 425 (1304)
Min	0 (0.2) 12 (1.4)	0 (0) 0 (0)	2 (2) 10 (27)
Max	3651 (2452) 5987 (4 781)	684 (6653) 771 (8003)	11521 (9501) 10357 (13882)

Table 2. Indoor and outdoor ion concentrations (cm^{-3}) during weekends. The concentrations are presented for cluster (smaller than 1.8 nm in diameter), 3–10 nm, and 10–40 nm ions. The +|– sign refers to positive|negative ions.

	Cluster ions + – Indoor (Outdoor)	Ions 3–10 nm + – Indoor (Outdoor)	Ions 10–40 nm + – Indoor (Outdoor)
Mean	1396 (653) 1389 (720)	21 (26) 25 (39)	211 (373) 221 (393)
SD	312 (233) 310 (322)	47 (34) 54 (76)	117 (324) 242 (331)
Median	1357 (632) 1376 (696)	9 (18) 9 (24)	196 (288) 189 (308)
10%	973 (389) 1017 (309)	2 (6) 2 (7)	82 (143) 70 (136)
25%	1165 (495) 1180 (513)	4 (10) 5 (12)	125 (199) 114 (198)
75%	1584 (798) 1576 (913)	15 (31) 18 (44)	275 (461) 293 (479)
90%	1783 (938) 1775 (1 131)	37 (51) 46 (75)	352 (692) 379 (748)
Min	123 (0.3) 266 (3)	0 (0.2) 0 (0)	6 (0.7) 6 (19)
Max	2601 (2417) 4 075(2645)	475 (965) 527 (2157)	1785 (9276) 8551 (7344)

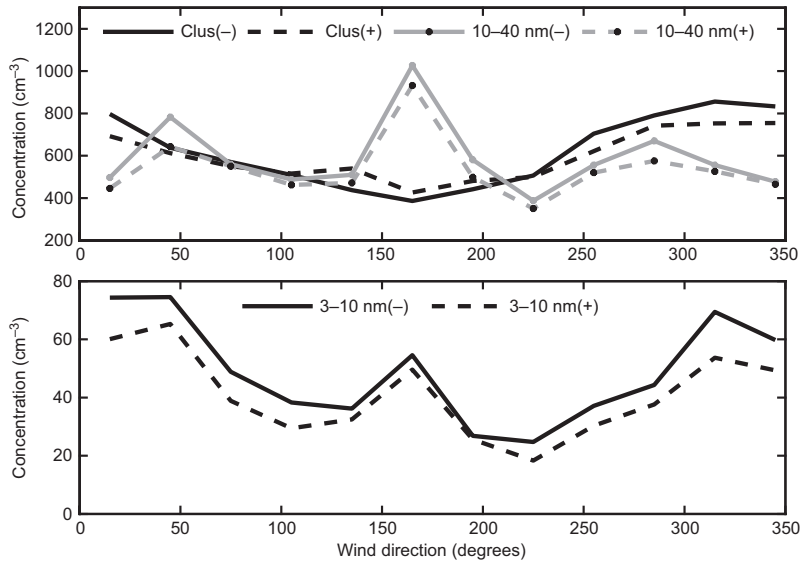


Fig. 2. Median outdoor cluster ion (smaller than 1.8 nm), intermediate ion (3–10 nm) and large ion (10–40 nm) concentrations as a function of wind direction on workdays.

tions than positive ions. While cluster ions have been observed in all outdoor environments (e.g. Hirsikko *et al.* 2007b), here we observed zero concentrations indoors, especially for positive cluster ions. We believe that was due the operational problems with the AIS instrument.

We observed 3–10-nm particles, which are related to intermediate ions, during periods of particle formation in primary or secondary processes only. This resulted in low average concentrations of intermediate ions and minimum values close to zero (Table 1 and 2). In the outdoor air, maximum concentrations of intermediate ions reached occasionally very high values of 6653 and 8003 cm^{-3} for positive and negative ions, respectively. These concentrations were observed on workdays. The corresponding weekend maxima were lower, being 965 and 2157 cm^{-3} for positive and negative ions, respectively. The concentrations of large air ions were typically higher outdoors than indoors. While on average we observed similar number concentrations of large ions for both polarities, the maximum values differed remarkably between the two polarities.

Wind sector analysis of outdoor air ions

Based on the wind sector analysis, outdoor ions larger than 3 nm were probably produced by traffic-related sources (Figs. 2 and 3). The highest

concentrations were observed during easterly winds (especially during south-east wind) from the direction of the major road, crossroads and power plant. High intermediate ion concentrations came also from between the north-west and north-east, which is the direction where many major highways at distances between 1 and 30 km can be found.

The cluster ion concentrations were at their minimum when the wind was blowing from the nearest road (Kustaa Vaasan tie). The distance to this road was more than 100 m and there was a park with deciduous trees between the road and our measurement site. This indicates that there was plenty of time for different sink mechanisms to affect cluster ion concentrations. The air coming from the south-east direction crossed the sea before arriving at the town. Above sea surfaces cluster ion concentration are small because the ionisation is caused by cosmic radiation only. Due to the short life time of cluster ions, low wind speeds and archipelago sheltering the nearby bays, we may assume that no wave-generated ions were observed (*see* Reiter 1994).

When wind blew from other directions we observed the urban background of cluster ion concentrations. Thus, based on our results it is difficult to conclude how the traffic or other pollution sources influence cluster ions or their precursors. According to Yu (2002), traffic produces a significant number of ions having a very short

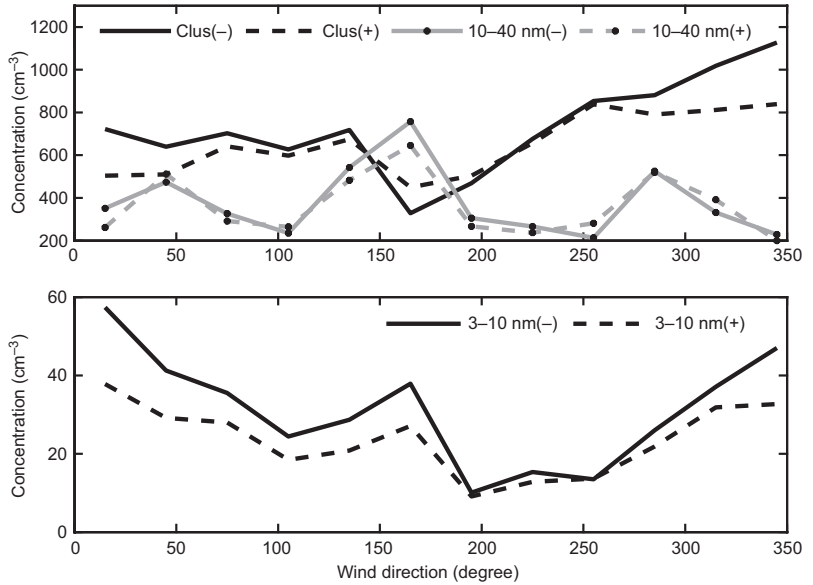


Fig. 3. Median outdoor cluster ion (smaller than 1.8 nm), intermediate ion (3–10 nm) and large ion (10–40 nm) concentrations as a function of wind direction on weekend days.

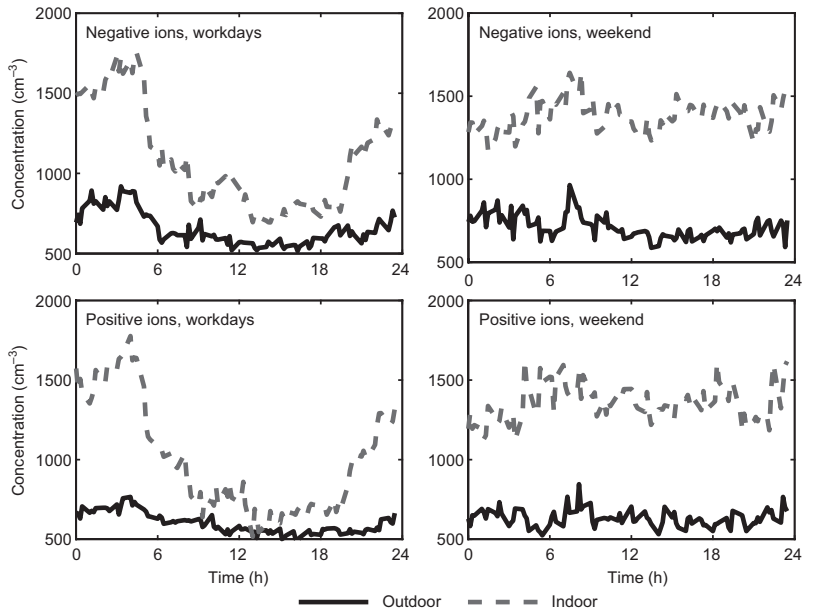


Fig. 4. Daily median concentrations of cluster ions in Helsinki indoors and outdoors. The medians were calculated over the periods 7–28 July 2004 and 30 July–7 Sep. 2004 based on indoor and outdoor measurements, respectively.

lifespan. Since the distance to the closest road was more than 100 m, most of the traffic-related ions were probably lost by coagulation into pre-existing aerosol particles and by recombination before entering our measurement site.

Tiitta *et al.* (2007) measured air ion size distributions about 10 m away from a road in Kuopio, eastern Finland, and their observations of ion concentrations as function of wind direction were similar to ours. However, due to the short distance from the road in Kuopio, the sink

processes did not have enough time to affect cluster ion concentrations when the wind blew from the nearest road.

Temporal variations of air ion concentrations

The concentrations of cluster, intermediate and large ions had different daily cycles between the workdays and weekends, both indoors and outdoors (Figs. 4–6). On weekends the cluster

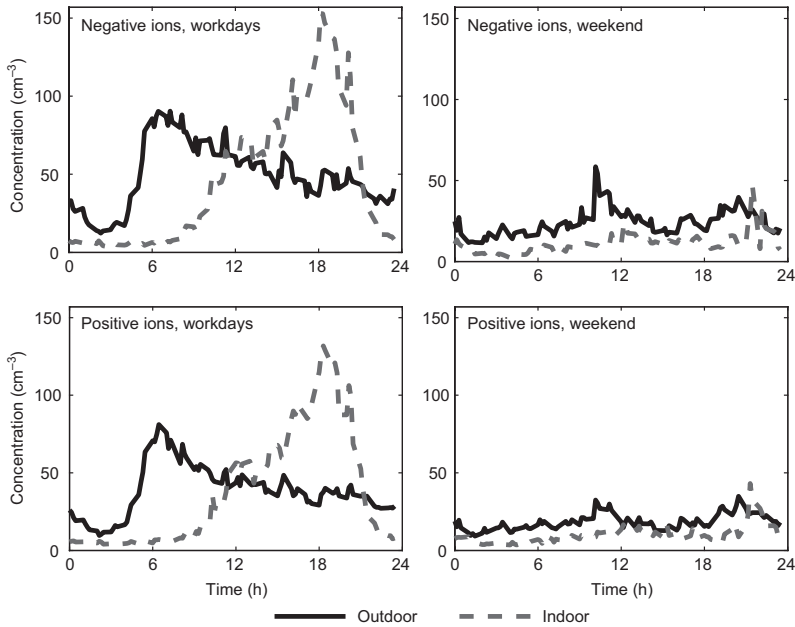


Fig. 5. Daily median concentrations of 3–10-nm ions in Helsinki indoors and outdoors. The medians are calculated over the periods 7–28 July 2004 and 30 July–7 Sep. 2004 based on indoor and outdoor measurements, respectively.

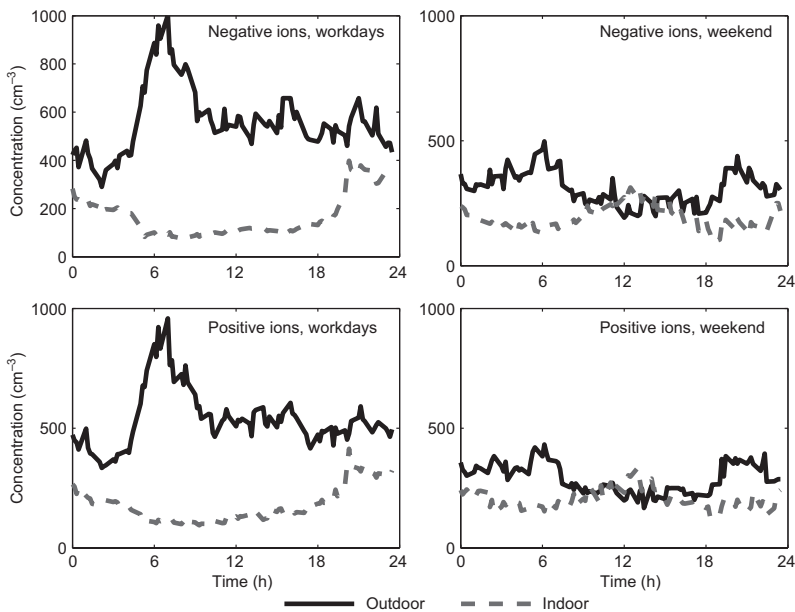


Fig. 6. Daily median concentrations of 10–40-nm ions in Helsinki indoors and outdoors. The medians are calculated over the periods 7–28 July 2004 and 30 July–7 Sep. 2004 based on indoor and outdoor measurements, respectively.

ion concentrations were quite stable throughout the day and the indoor concentrations were 2–3 times higher. On workdays the indoor cluster ion concentrations had their maximum values when the ventilation was off. When the ventilator was turned on, cluster ion concentration began to decrease toward their steady-state level as a result of removal processes and indoor and outdoor sources. In the outdoor air, cluster ion

concentrations decreased somewhat during the mornings from their night-time levels. The probable reason for this was the increase in larger ion and particle concentrations at the same time.

On workdays, outdoor intermediate ions reached their maximum concentration during the morning rush hour, while indoor intermediate ions had their maximum concentration in the evening (Fig. 5). This was probably due to sec-

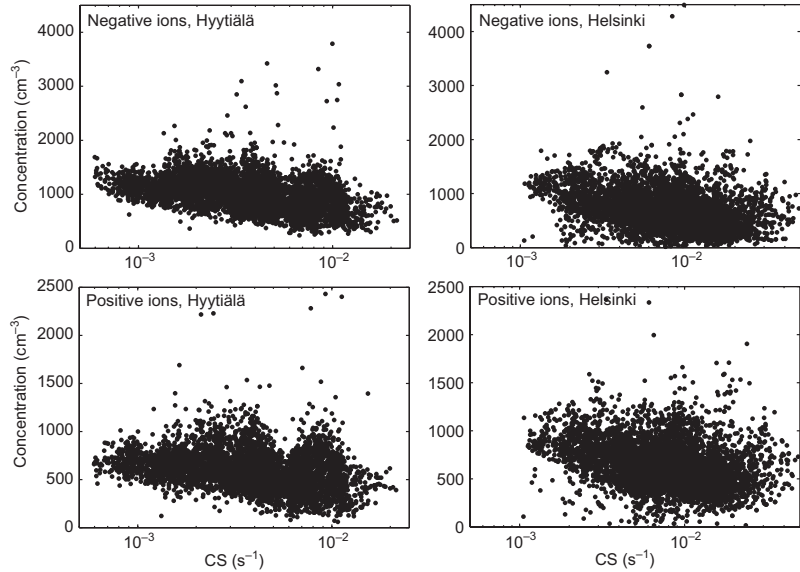


Fig. 7. Cluster ion (smaller than 1.8 nm in diameter) concentrations as a function of condensation sink in Helsinki and Hyytiälä. The time resolution was ten minutes according to the DMPS.

ondary particle formation indoors, which will be discussed later in more detail. On weekends the intermediate ion concentrations were low and quite stable indoors. In outdoor air, these concentrations were only slightly higher and followed a similar pattern as the daily traffic activity.

Outdoor large ion concentrations had a similar daily cycle as intermediate ions on workdays (Fig. 6). On weekends, however, these ions had their first maximum concentration couple of hours earlier than intermediate ions, and the second maximum occurred late in the evening due probably to the growth of smaller particles and traffic. On workdays, large ions in the indoor air had their maximum concentration after the intermediate ions had grown to larger sizes and ventilation was turned off. On weekends the indoor concentrations were more stable with maximum values around noon.

As a reference, we utilised air ion size distribution measurements by the AIS at the SMEAR II station (Hari and Kulmala 2005) in Hyytiälä, Southern Finland (61°51'N, 24°17'E, 181 m above the sea level), where the continuous air ion measurements have been carried out since March 2003. Since the urban background site in Helsinki and boreal forest site in Hyytiälä are different from each other, we calculated the condensation sink (CS) (see Kulmala *et al.* 2001, Dal Maso *et al.* 2005), a variable characterizing the loss rate of vapour molecules to pre-existing

aerosol particles, based on DMPS measurements and investigated cluster ion concentrations as a function of CS (Fig. 7). The DMPS in Hyytiälä was identical to that in Helsinki, but it measured particles in the diameter range of about 3–500 nm. Since the concentration of particles larger than 500 nm is typically very low in Hyytiälä, lack of their size distribution had not a significant effect on the results.

As one might expect, the cluster ion concentration was a strong function of CS in Hyytiälä (Fig. 7). The highest concentrations were measured when CS was lowest, and the concentration decreased with increasing CS. In Helsinki the highest cluster ion concentrations were measured with the lowest sinks, but also very low concentrations were measured at the low values of CS. Furthermore, cluster ion concentrations were of the same order of magnitude in both Hyytiälä and Helsinki. This indicates that in Helsinki we had stronger ion sources because the aerosol sink was higher there as compared with Hyytiälä.

In both Hyytiälä and Helsinki, negative and positive cluster ion concentrations were typically $< 2000 \text{ cm}^{-3}$ and $< 1500 \text{ cm}^{-3}$, respectively. These are much higher concentrations than those measured 10 m away from a road in Kuopio, even at similar values of CS (Tiitta *et al.* 2007). Apparently, different source and sink terms are affecting cluster ion concentrations between Kuopio, Helsinki and Hyytiälä. According to Tiitta *et*

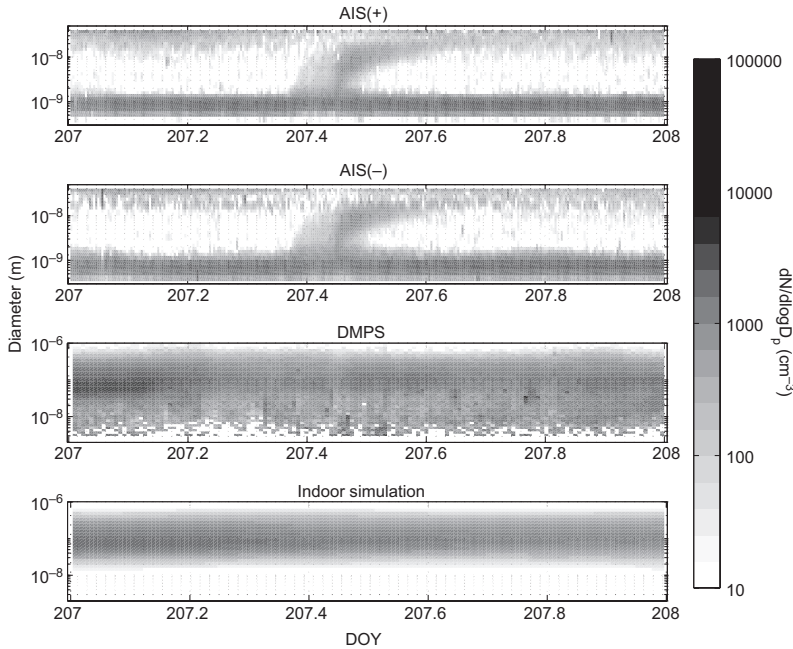


Fig. 8. An example of the charged particle formation indoors (first and second panels) measured in the laboratory room on Sunday 25 July 2004. The DMPS size distributions (third panel) from the outdoor air simulated indoor distributions caused by outdoor air (bottom panel) are also presented.

al. (2007), traffic was clearly not an additional source of cluster ions. Furthermore, differences in the chemical composition of new or pre-existing aerosol particles can have different effects on ion sinks between urban and rural sites.

Possible sources of air ions

Our results indicate clearly that cluster ions were produced indoors. We assumed that radon emitted from the ground level could have only minor effects on the ionisation rate in the laboratory because the measurements were carried out at the fourth-floor level. Furthermore, we assumed that the radon released from the walls, which contain some soil material, affected the indoor ionisation rate in our conditions. We did not measure the radon activity concentration. However, it is commonly assumed that indoor radon activity concentration is about 20 Bq m^{-3} at the fourth-floor level in Finland. Such an activity concentration induces the production of approximately $12 \text{ ion pairs cm}^{-3} \text{ s}^{-1}$, providing that 34 eV is needed for producing an ion pair from one air molecule and that the ion pairs are caused by the short-lived progeny of ^{222}Rn with the total energy of three alpha particles and two beta particles.

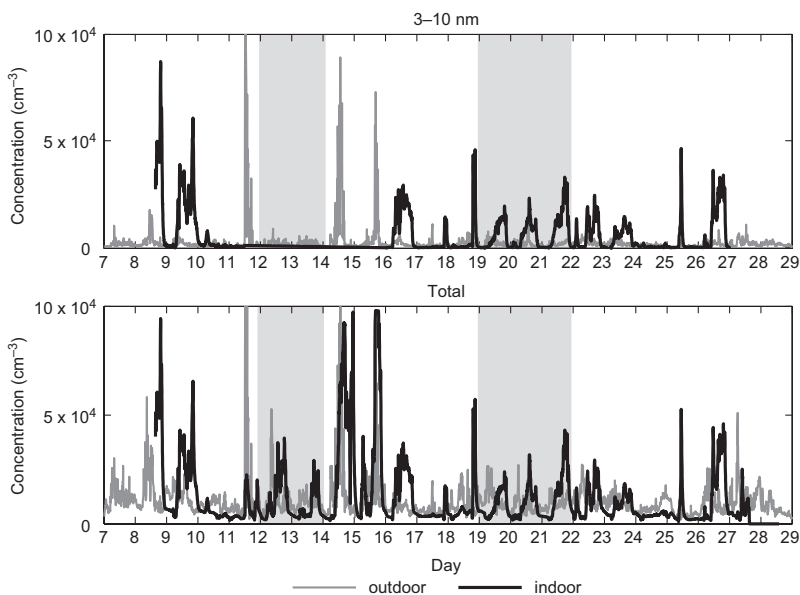
Such an ion production rate due to radon is two times higher than the maximum rate observed by Hirsikko *et al.* (2007a) in a rural background site in mid-Finland. The gamma radiation released in ^{222}Rn decay process is only a small fraction of the total natural gamma radiation.

It is very likely that a fraction of cosmic radiation and ground-based gamma radiation, the main components of external radiation, penetrated indoors through the walls and windows and ionised air molecules. The ionisation rate by external radiation is quite constant because it does not have a diurnal variation (Hirsikko *et al.* 2007a). During our measurements the outdoor dose rate due to the external radiation was approximately $0.1 \mu\text{Sv h}^{-1}$ (<http://www.stuk.fi>). We believe, however, that aerosol chargers used in our DMPS-systems did not participate in the ionisation of air molecules in the laboratory because these chargers were well shielded.

New particle formation

We observed the formation of new particles starting from cluster ion sizes followed by a clear growth to bigger sizes on a daily bases (Fig. 8). There was only one day (Saturday, 24 July)

Fig. 9. Concentrations of 3–10-nm particles (top panel) and particles larger than 3 nm (bottom panel) indoors and outdoors in July 2004. Indoor 3–10-nm particle concentration is the difference of two CPC readings: the total indoor particle concentration reading of the CPC 3025 and corresponding outdoor concentration calculated from the DMPS data. The two periods during which there was additional particle production due to other measurement activities are indicated with grey rectangles.



when no new-particle formation was observed. We found that the new-particle formation started from cluster ion sizes, and that intermediate ion concentrations were close to each other for both charge polarities during the new-particle formation events. Based on measured particle concentrations indoors and outdoors, we were able to pinpoint the periods when new-particle formation was taking place indoors only (Fig. 9). With the help of the indoor aerosol model simulations, we found that the fraction of indoor aerosol particles coming from outdoors was negligible during these periods. Furthermore, according to model runs, the ventilation reduced efficiently the penetration of particles smaller than 10 nm from outdoors to indoors.

The indoor to outdoor (I/O) ratio of 3–10 nm particles varied in the range of 0–115, with average and median values of 7.8 and 2.7, respectively. The high I/O-ratios, together with the results in Figs. 8 and 9 and the size distributions given by the indoor model, indicate clearly that we had vapours capable of producing and growing cluster ions and particles indoors. What were the sources of these vapours? They could not be cooking or candle burning which are typical sources at homes. If the vapour was butanol, used typically with the CPCs, we should have observed cluster ion growth and intermediate ion formation all the time. Recently, Singer *et al.*

(2006) and Wand and Morrison (2006) investigated and discussed possible vapour sources, and brought up the effect of organic compounds and ozone. Vartiainen *et al.* (2006) studied new-particle formation indoors and found indirectly high concentrations of neutral clusters.

We detected two new-particle formation events having a clear growth outdoors during our indoor measurement period. These two events were also observed indoors. On both cases, however, the particle formation indoors did not begin from the cluster ion sizes but from 3–6 nm sizes. One of those days was Sunday (11 July). The overall air exchange between the indoor and outdoor air was not zero during that day although the ventilation was turned off. By using a ventilation rate of 5%, the model predicted a small increase in the concentration of particles smaller than 10 nm during that day, but not a growing particle mode. Probably the real exchange between the outdoor and indoor air was larger than the 5% of the total ventilation. During the second new-particle formation day, also the model predicted a growing particle mode.

We measured two new-particle formation events that could be utilised in calculating particle growth rates (Fig. 10 and Table 3). These events were observed both with the AIS and DMPS. In addition to these two events, we observed either particle formation or growth of

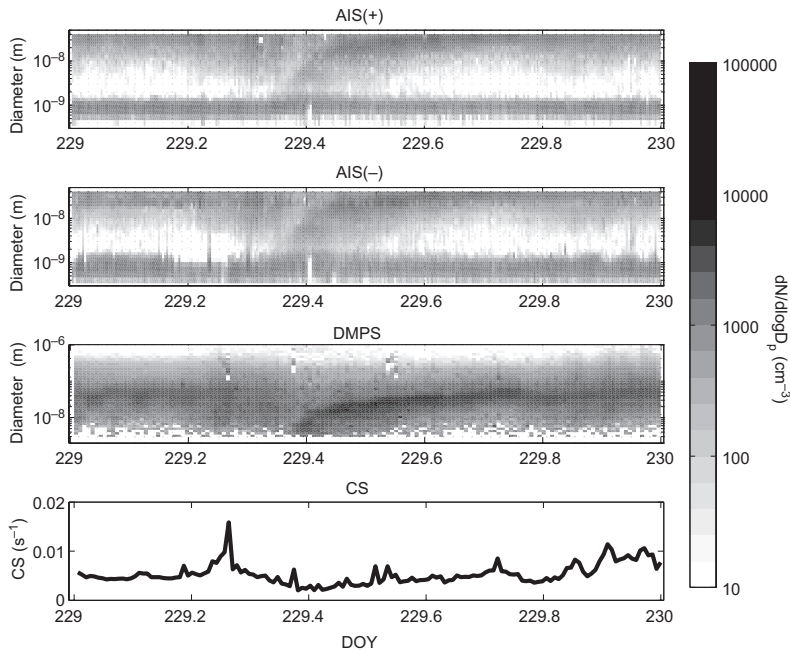


Fig. 10. A particle formation event in the urban atmosphere on 16 Aug. 2004, measured with the AIS (first and second panels) and DMPS (third panel). Also the condensation sink is presented (bottom panel).

cluster ions on at least 13 days with the AIS. These events were typically such in character that particle growth rates could not be calculated: the growth of particles either stopped at small sizes (well below 10 nm), the intermediate ion concentrations were low, or the shape of the growing mode was unsuitable for fitting the growth rate. We believe that the stop of the

growth was due to a high condensation sink and lack of suitable condensing vapours.

Particle growth

We observed similar particle growth rates (Table 3) as observed in Hyytiälä at the same time (*see* Hirsikko *et al.* 2005). However, there were two exceptions: the growth of 1.3–3-nm indoor particles was very fast on Sunday, 25 July, and the same was true for the outdoor particles larger than 3 nm in diameter on Tuesday, 10 August. On 25 July the growth of the small indoor ions was two times faster than typically observed in a boreal forest. The low condensation sink, high enough condensing vapour concentration and the important role of ions in particle formation/growth could explain the fast growth of small ions. On Sunday (25 July), the ventilation was turned off the whole day. The concentrations of cluster ions were high (1200–1500 cm⁻³) during that day (Fig. 8), and the contribution of large outdoor particles to the condensation sink was smaller than on workdays. On Tuesday (10 August) when outdoor particles grew very fast, the sources and concentrations of condensing vapours were larger than on the second outdoor example day (16 August).

Table 3. Growth rates (nm h⁻¹) of particles in different size ranges based on the AIS and DMPS measurements on four example days in 2004: indoors on July and outdoors on August. AIS+ refers to positive ions and AIS- to negative ions.

Size range	GR (nm h ⁻¹)			
	9 Jul.	25 Jul.	10 Aug.	16 Aug.
AIS+ (1.3–3 nm)	2.3	4.9	–	1.8
AIS- (1.3–3 nm)	2.8	4.8	2.3	–
AIS+ (3–7 nm)	6.7	8.7	–	8.2
AIS- (3–7 nm)	6.5	7.4	13.0	9.4
AIS+ (7–20 nm)	8.7	5.1	15.4	8.9
AIS- (7–20 nm)	8.7	6.6	13.2	7.9
AIS+ (3–20 nm)	8.8	5.9	12.9	6.0
AIS- (3–20 nm)	8.5	7.1	11.5	5.7
DMPS (3–7 nm)	–	–	4.8	3.1
DMPS (7–20 nm)	–	–	17.7	5.9
DMSP (3–20 nm)	–	–	8.9	4.9

It is not known what vapours were responsible for the particle growth. However, we assume that at least sulphuric acid (H_2SO_4) and some organic vapours were involved in the particle growth outdoors and indoors, respectively. Using eq. 4 given by Kulmala *et al.* (2001), we calculated the extreme concentrations of H_2SO_4 and butanol (an example of an organic vapour) needed for the observed particle growth by assuming that they were the only vapours condensing onto particles. Our calculation procedure predicts, in general, too large vapour concentrations when molecules and particles are of the same size, especially below 3 nm. However, here we did not consider the question of size, as discussed by Lehtinen and Kulmala (2003), since other uncertainties like origin of vapour sources were big.

The growth rates of 1.3–3-nm ions varied in the range 1.8–4.9 nm h⁻¹, which means that H_2SO_4 and butanol concentrations had to be in the ranges $1.3\text{--}3.6 \times 10^7 \text{ cm}^{-3}$ and $1.5\text{--}4.1 \times 10^7 \text{ cm}^{-3}$, respectively. Particles in the size range 3–7 nm grew at a rate of 6.5–13 nm h⁻¹, which corresponds to vapour concentrations of $4.8\text{--}9.7 \times 10^7 \text{ cm}^{-3}$ (H_2SO_4) and $5.6 \times 10^7\text{--}1.1 \times 10^8 \text{ cm}^{-3}$ (butanol). The large ions (7–20 nm) grew at a rate of 5.1–15.4 nm h⁻¹, which requires H_2SO_4 concentrations of $4.0 \times 10^7\text{--}1.2 \times 10^8 \text{ cm}^{-3}$ and butanol concentrations of $4.7 \times 10^7\text{--}1.4 \times 10^8 \text{ cm}^{-3}$.

We obtained quite different growth rates for 3–7-nm particles based on the AIS and DMPS data on outdoor days (Table 3). This was probably due the inability of the DMPS to measure size distributions close to its lower measuring limit at which the data can fluctuate, especially when concentrations are not stable. An enhanced growth of particles due to charging should, however, be negligible at sizes above 3 nm (*see* Kulmala *et al.* 2004b, and references therein).

Other pathways for intermediate ion formation

Rain has been observed to induce bursts of intermediate ions as a result of the break up of water droplets into smaller positive and negative droplets (Hörrak *et al.* 2005, 2006, Hirsikko *et al.* 2007b, and their references). During our outdoor measurements we observed rain-induced

ion bursts on 13 days, which is every time when it was raining and the instrument measuring the rain was working. Based on ion size distributions, we could identify 7 additional days when rain was probably producing intermediate ions, but we did not have information about rain conditions for those days. Typically the concentrations of negative ions were higher during the rain (Fig. 11), which indicates that positively charged droplets were larger. The negative ion concentrations were higher in Helsinki during the rain as well. Contrary to observations in Hyytiälä (Hirsikko *et al.* 2007b), we observed rain-related bursts for both negative and positive ions.

Summary and conclusions

We measured air ion and particle number concentrations and size distributions in a laboratory room and outdoors at an urban background site in Helsinki. Ion size distributions were measured with the AIS both indoors and outdoors, even though on consecutive periods. For comparison, the total indoor particle number concentrations were monitored with two CPCs having different cut-off sizes, 3 and 10 nm. The count difference between these CPCs gave the concentration of 3–10-nm particles. We also measured the outdoor particle size distributions continuously with the DMPS.

The daily cycle in the concentration of outdoor air ions larger than 3 nm followed the daily traffic pattern and depended on the wind direction. We observed the highest concentrations during the rush hours and especially for ions larger than 10 nm in diameter when the wind was blowing from the nearest road and from over large crossroads. The cluster ion concentrations were also dependent on the wind direction, with highest concentrations observed at winds blowing from the nearest road. Furthermore, the cluster ion concentrations depended on the sink (CS) caused by pre-existing aerosol particles, as one might expect. However, sometimes we observed low cluster ion concentrations also with small values of CS, similar to observations next to a road in Kuopio, Finland (Tiitta *et al.* 2007), but unlike in a rural site at the SMEAR II station in Hyytiälä. Based on our results, it is difficult to

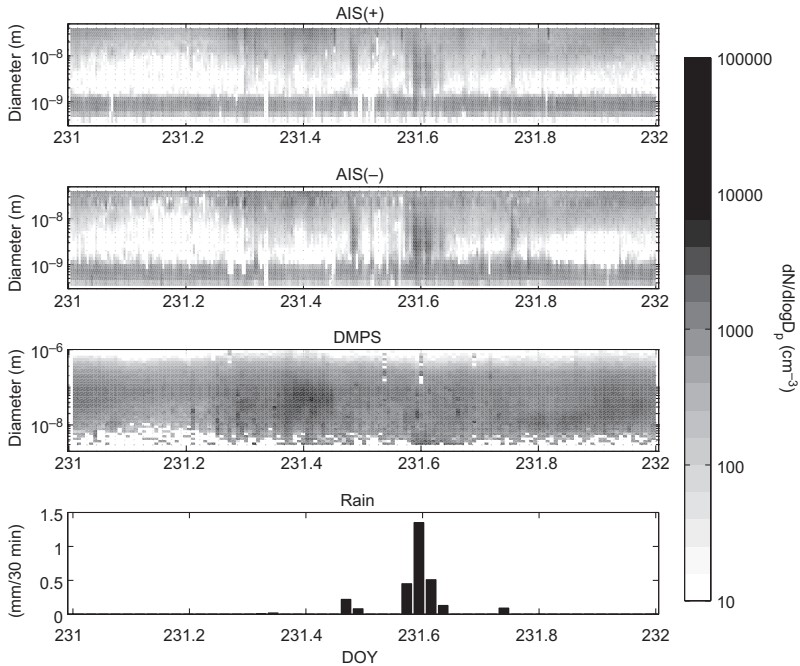


Fig. 11. An example of the effect of rain on ion size distributions on 18 Aug. 2004, measured with the AIS (first and second panels) and DMPS (third panel). Also the rain intensity is presented (bottom panel).

conclude which fraction of cluster ions or their precursors were produced by vehicles, since the distance from the road was at least 100 m. Many sink processes affected cluster ion concentrations when they travelled from the road to our measurement place. However, Tiitta *et al.* (2007) found extremely low cluster ion concentrations next to a road (10 m away) when the wind was blowing directly from the road.

Indoor cluster ion concentrations depended mainly on ventilation conditions, with highest values (around 1500 cm^{-3}) observed when the ventilator was turned off. The dependence of ions larger than 3 nm in diameter on ventilation was not as evident, since secondary particle formation and growth were observed indoors also when the ventilation was turned off. We observed secondary particle formation both indoors and outdoors, and the particle growth rates were $1.8\text{--}4.9 \text{ nm h}^{-1}$ for $1.3\text{--}3\text{-nm}$ ions, $6.5\text{--}13 \text{ nm h}^{-1}$ for $3\text{--}7\text{-nm}$ ions and $5.1\text{--}15.4 \text{ nm h}^{-1}$ for $7\text{--}20\text{-nm}$ ions. The fast growth of these ions indicates that we had a strong source of condensing vapours indoors.

Importantly, we observed new-particle formation indoors even without outdoor particle formation, which is a clear evidence of indoor sources. Recently, Vartiainen *et al.* (2006) reported on new-particle formation related to

the activation of neutral clusters (*see* Kulmala *et al.* 2006) indicative of pretty high indoor cluster concentrations. This finding is in agreement with our results on indoor new-particle formation.

To obtain more information about the indoor new-particle formation, continuous AIS or DMPS measurements at the same time both indoors and outdoors should be made. Also measurements related to the chemical composition of the gas phase as well aerosol composition would be needed. For measuring the composition of nuclei mode aerosol particles, only indirect methods are currently available, such hygroscopicity measurements (Hämeri *et al.* 2001) and set of condensation particle counters (Kulmala *et al.* 2007). Hygroscopicity measurements would make it possible to assess the real penetration of different-size particles and air ions through the ventilation system. The set of CPC's would offer valuable information about particle precursors and their sources. These issues remain, however, the subject of future research.

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