

# FORMATION OF CHARGED NANOMETER AEROSOL PARTICLES ASSOCIATED WITH RAINFALL: ATMOSPHERIC MEASUREMENTS AND LAB EXPERIMENT

U. Hörrak<sup>1,2</sup>, H. Tammet<sup>1</sup>, P.P. Aalto<sup>2</sup>, M. Vana<sup>1,2</sup>, A. Hirsikko<sup>2</sup>, L. Laakso<sup>2</sup> and M. Kulmala<sup>2</sup>

<sup>1</sup>Institute of Environmental Physics, University of Tartu, Ülikooli 18, 50090 Tartu, Estonia

<sup>2</sup>Department of Physical Sciences, University of Helsinki, P.O. Box 64, FIN-00014, Helsinki, Finland

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## INTRODUCTION

The air ion spectrometers AIS and BSMA (manufactured by Airel Ltd., Estonia) have been successfully used to investigate the charged fraction of nanometer aerosol particles during nucleation bursts in the atmosphere at the Hyytiälä SMEAR station, Finland (Laakso et al., 2004). Recently, the generation of charged nanometer particles (intermediate air ions) during rainfall was discovered (Hörrak et al., 2005). It is generally known that the breaking or splashing of water drops, as well as the bursting of bubbles in a freshwater-air interface can generate negatively charged particles and, therefore, the negative space charge in the atmosphere during rainfall and close to lakes and waterfalls (Gathman and Hoppel, 1970; Levin, 1971; Reiter, 1994). This is commonly attributed to the Lenard effect (Lenard, 1892), which occurs when drops of pure fresh water break up into numerous fine negative droplets and some residual larger positively charged drops.

The purpose of this work is to study the formation of nanometer aerosol particles and the evolution of the mobility/size distribution of air ions and aerosol particles during rainfall.

## MEASUREMENTS AND METHODS

Atmospheric aerosols and air ions (naturally charged small or cluster ions and aerosol particles) have been measured simultaneously in a boreal forest at the Hyytiälä SMEAR station (61° 51'N, 24° 17'E, 181 m asl), Finland, since the spring of 2003. Aerosol particle size distribution was measured by means of a dual Differential Mobility Particle Sizer (DMPS) system covering the sizes of 3–500 nm. The Air Ion Spectrometer (AIS) and the Balanced Scanning Mobility Analyzer (BSMA) were applied for the measuring of air ions in the diameter range of 0.46–40 nm and 0.34–7.4 nm, respectively. The sampling height of the instruments was about 2 m above the ground and the distance between the air ion and aerosol particle measurement locations was about 30 m. The intensity and amount of precipitation (rain) was measured by the rain gauge ARG-100 (tipping bucket counter, Vector Instruments) and by the rain detector DRD11A (Vaisala) installed on the mast (tower) at the height of about 18 m from the ground.

Besides the atmospheric measurements, a lab experiment was carried out to simulate the charged nanometer particle generation by rainfall. The experiment was performed on May 12, 2005 in a small room at the Institute of the Environmental Physics of the University of Tartu. The splashing of rain droplets was imitated using a thin water-jet streaming out from a nozzle of the diameter of 2.5 mm. The water stream broke into droplets, which hit a vertical ceramic wall at the distance of 65 cm from the nozzle. The water was drawn from the city waterworks. The flow rate of the water was 55 cm<sup>3</sup> s<sup>-1</sup> and the ejection speed about 11 m s<sup>-1</sup>. The flow rate divided to the room floor area (2.9×1.9 m<sup>2</sup>) corresponds to a heavy shower of 36 mm/h. The mobility distribution of air ions was measured by the BSMA2 (Tammet, 2004) and converted into a size distribution in the diameter range of 0.34–7.4 nm. The BSMA2 was installed near the wall at the distance of about 2.4 m from the spot where the water stream broke into droplets. It was elevated by about 1 m from the water-jet, thus preventing the penetration of macroscopic droplets into the BSMA2. The air in the room was slowly circulated, forced by the large flow rate (44 liters per second) of the BSMA2.

## RESULTS AND DISCUSSION

Rainfall typically affects the mobility (size) distribution of air ions, generating negatively charged particles below the diameter of about 10 nm with the concentration peak at 2–3 nm. The mean size of this mode is nearly constant. The concentration maximum of negative intermediate ions in the size range of 1.5–5.4 nm can rise up to about 3000 cm<sup>-3</sup> or even more, depending on the intensity of rainfall. Typically, the concentration of positively charged particles is about an order of magnitude smaller. The lifetime of these particles is relatively small, decreasing quickly after the rain, probably due to the coagulation with larger particles. A clear correlation between the concentration bursts of negatively charged nanometer particles (intermediate ions) and rainfall can be found in Figure 1. The examples of the evolution of air ion mobility distributions measured by the BSMA and converted into the size scale assuming single charges on particles are depicted in Figure 2.

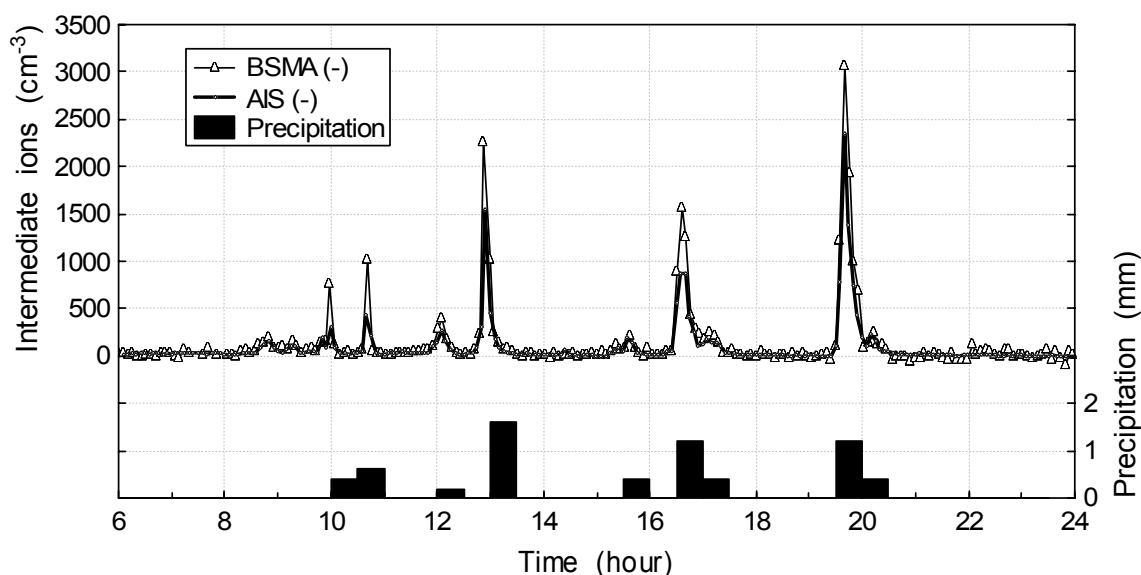


Figure 1. Time series of the concentration of negative intermediate air ions (charged particles of 1.5–5.4 nm) measured by the BSMA and AIS and the amount of precipitation on May 21, 2004 at Hyytiälä.

The measurements of both of the ion spectrometers (the BSMA and AIS), installed side by side, showed a good correlation during the charged nanometer particle concentration bursts (Figure 1), but the DMPS (located about 30 m off) did not. During the most prominent rain episodes on May 21, 2004 (when the amount of precipitation was more than 1 mm per 30 min), the concentration of 3–6 nm particles measured by the DMPS was close to the low background (less than 200 cm<sup>-3</sup>). Detailed examination of the DMPS data (measured in August, 2003 and August, 2005) revealed that the DMPS only occasionally showed enhancement in the concentration of nanometer particles during rainfall. For example, on August 28, 2003, the concentration of particles in the size range of 3–6 nm measured by the DMPS rose up to 640 cm<sup>-3</sup> during the short rainfall (intensity about 3.6 mm per 30 min) at about 16:30, while the naturally charged particle concentration in the same size range measured by the BSMA was about 1660 cm<sup>-3</sup> and 220 cm<sup>-3</sup> for positive and negative polarity, respectively. A better correlation was found during heavy showers (intensity of about 30–60 mm/h), when the concentrations of neutralized particles with the diameters of 3–6 nm up to 1400 cm<sup>-3</sup> were recorded. The latter is in accordance with the fact that the falling speed of raindrops at the impact with the ground is proportional to their size. Thus, the heavy showers can produce more particles by the splashing of larger water drops, which is also accompanied by the generation of numerous nanometer particles.

Accordingly, we can conclude that the bipolar charging/neutralization of particles used in the DMPS could drastically reduce the concentration of naturally negatively charged particles. Also, the particles containing liquid (water) could evaporate inside the DMPS. On the other hand, the overall weak correlation between the ion spectrometers (BSMA and AIS) and the DMPS measurements of nanometer particle concentration during rainfall is due to the effective scavenging of ultrafine particles by raindrops (Andronache, 2004; Laakso et al., 2003).

During the rain, the DMPS measurements showed a significant increase in the concentration of ultrafine particles only in the size range below about 10 nm. Therefore, the naturally charged nanometer particles measured by the ion spectrometers are supposed to be mainly single charged and the conversion of the measured mobility distribution ( $0.032\text{--}3.2\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) into the size distribution does not bring along problems due to multiple charges on particles. In the case of atmospheric measurements during the rain, as well as in the experiments with water-jet, this assumption is not self-evident and the mobility-size conversion creates problems in the interpretation of results. For example, the raindrops and droplets formed after the breaking of raindrops can be highly charged (Takahashi, 1973; Beard and Ochs, 1986). Unfortunately, no tools other than the comparison of the DMPS and ion spectrometer (BSMA, AIS) measurements were available for the determination of actual charges on ultrafine particles in the present study.

The evolution of the mobility-size distributions of negative and positive air ions during a short-term shower on August 23, 2003 at the Hyytiälä SMEAR station is depicted in Figure 2. After a sudden increase in the rainfall intensity from 1 mm/h up to 7.2 mm/h at about 16:30, the concentration of negative intermediate air ions (1.6–5.4 nm) rapidly increased from the low background up to about  $3000\text{ cm}^{-3}$  and a clear mode appeared in the size range of 2–3 nm. Simultaneously, the concentration of positive small (or cluster) ions dropped from about  $800\text{ cm}^{-3}$  to  $300\text{ cm}^{-3}$  and the coefficient of unipolarity (the ratio of positive to negative cluster ion concentration) was decreasing by a factor of 2 (see Figure 4). Such a drastic imbalance of electric charges on nanometer aerosol particles generated during the rainfall affects the balance of small (cluster) ions (0.4–1.6 nm), decreasing significantly the concentration of cluster ions of opposite (positive) polarity. However, only a small amount of nanometer particles can acquire a positive electric charge after the recharging of negatively charged particles by cluster ions of opposite polarity because of a very low charging probability. The steady state bipolar charging probability is about 0.7% and 3% for 2 nm and 6 nm particles, respectively. After the rain had ceased, the balance of air ions in the atmosphere was quickly restored. There was still a gap in the mobility-size distribution between the cluster ions and charged nanometer particles during an intensive generation of negative intermediate ions (Figure 2), which is located at about 1.2 nm and 1.6 nm for negative and positive air ions, respectively. Note that due to the location of the gap, the generated new charged particles can sometimes contribute to the mobility-size class of small negative ions (0.4–1.6 nm) by increasing their concentration, but not to the class of small positive ions.

The results of the lab experiment with the water-jet, depicted in Figures 3 and 4 (right-hand figure), are very similar to the atmospheric measurements. However, due to the lack of information about the electric charges on particles, the diameters of particles (intermediate air ions) generated by the water-jet should be considered as apparent diameters. An apparent diameter is the diameter of a single charged particle, which has the same mobility as the real particle, but which can have multiple charges as well.

During the experiment, the BSMA2 recorded the data of nine 10-minute measuring cycles (the results of the first and last cycles are not presented in Figure 3). The first three cycles were carried out in the undisturbed air. The water-jet was activated just in the beginning of the cycle No 4 at 13:10 o'clock. The water was running continuously during 30 minutes and the tap was closed just at the end of the cycle No 6 (13:40 o'clock). The last three 10-minute cycles were carried out in the conditions without the water-jet. The atmospheric pressure was 1016 mb and the air temperature remained between 17.8 and 18.4 °C during the experiment. The relative humidity was 37–38% in the undisturbed air. After the activation of the water-jet, it rose continuously from 50% to 60% and decreased to 53% in the end of the experiment (closed tap). The distribution of particles according to the apparent size in first three cycles (background

distributions) was nearly the same. After the activation of the water-jet, a new distribution developed quickly and the measurements during the three following cycles showed nearly the same distribution. The reversion of the initial distribution was pretty rapid as well, but the distribution measured during the cycle No 7 preserves some imprints of the previous cycle. The time variations of the concentrations of small ions and charged particles (intermediate air ions) of the apparent diameter of 1.5–5.4 nm are presented in Figure 4.

The water-jet experiment with extended instrumentation was carried out in the same place on June 17, 2005 and the new results will be presented soon.

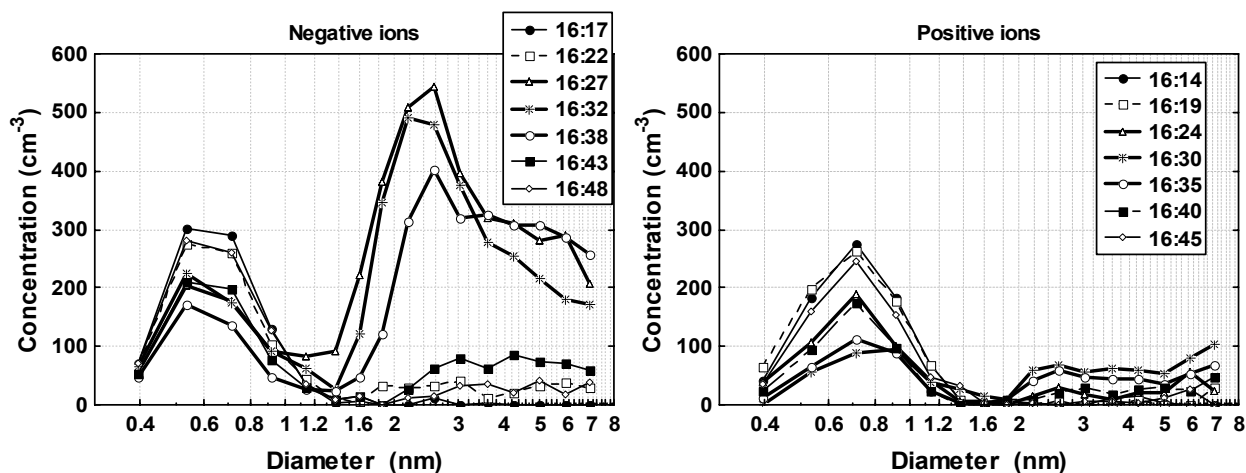


Figure 2. Evolution of negative and positive air ion size distributions measured by the BSMA on August 23, 2003 at the Hyytiälä SMEAR station. The air temperature was 15.4°C, relative humidity 93%.

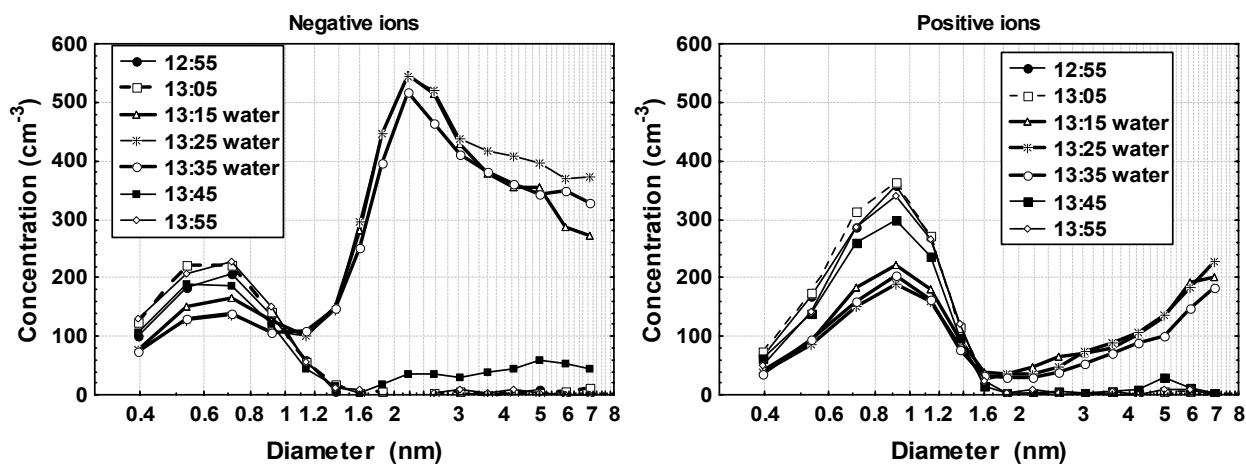


Figure 3. Evolution of negative and positive air ion size distributions measured by the BSMA2 during lab experiments with the water-jet on May 12, 2004 at the Institute of Environmental Physics, University of Tartu. The first two spectra were measured in the dry lab air with relative humidity (RH) 37–38%, the next three correspond to the experiments with the water-jet (RH from 50% to 60%) and the last two were measured in the moderately humid lab air (RH from 57% to 53%) without the water-jet. The air temperature was 18.1±0.3 °C.

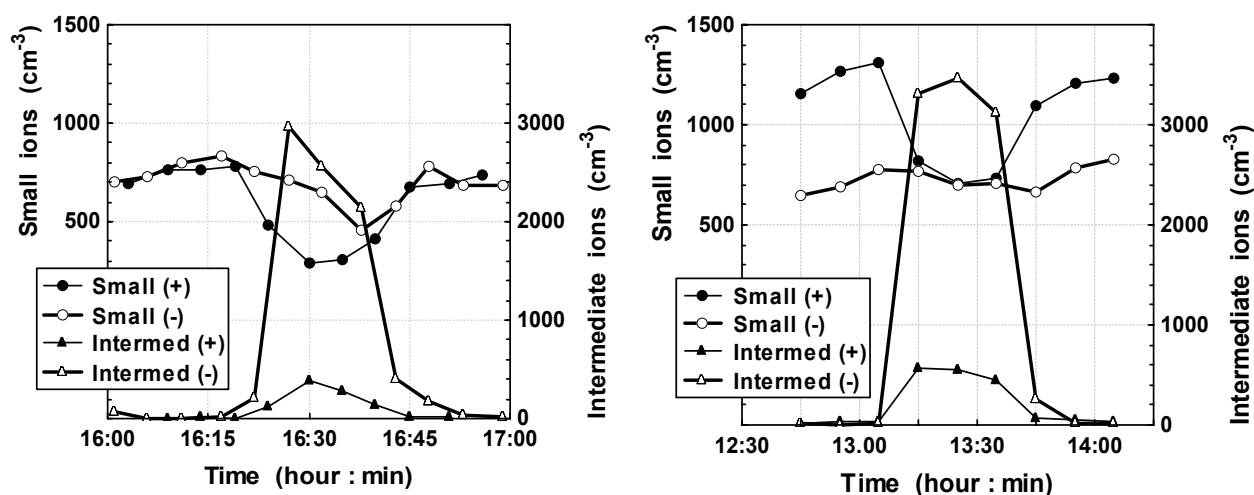


Figure 4. Time series of the concentration of positive and negative small (cluster) ions and intermediate air ions (1.5–5.4 nm) measured by the BSMA at the Hyttiälä SMEAR station on August 23, 2003 (left) and the results of the lab experiments with the water-jet measured by the BSMA2 on May 12, 2004 (right).

The effect of rain on the formation of charged nanometer particles was observed in a boreal forest at Hyttiälä, as well as in an urban environment (in Helsinki, Finland and in Tartu, Estonia). The effect was observed not only during summertime, but also during wintertime, when the air temperature was above 0°C and the precipitation was in the form of the rain. The phenomenon was also found to take place in the marine environment during the measurements on board of the research vessel Akademik Fedorov on its trip from Bremerhaven to Cape Town in autumn 2004 (the Finnish Antarctic Expedition). Besides the formation of nanometer particles, the generation of negative cluster ions (or multiply charged nanometer particles of the same mobility as cluster ions) was often recorded during rain.

The formation mechanism of charged nanometer particles during rainfall is not well known. The mechanical destruction of rain droplets cannot create nanometer size particles. According to the results and a comprehensive overview of the earlier studies on the electrification of water droplets given by Muchnik and Fishman (1982), the contact electrification of water droplets during splashing on solid and wetted surfaces, as well as the drop break-up due to collision and coalescence can result in the formation of numerous highly charged particles. In principle, these particles can, after passing subsequent consecutive Rayleigh explosions and evaporation, reach the size range of nanometer particles (Gamero-Castaño and Fernández de la Mora, 2000a, b). A possible alternative mechanism of the formation of charged nanometer particles is the ion evaporation from charged raindrops or droplets formed by the breaking or splashing of raindrops (Iribarne and Thomson, 1976).

## CONCLUSIONS

The laboratory experiments, where the splashing of raindrops was simulated using a thin water-jet, confirmed the generation of negatively charged nanometer particles. The evolution of the mobility (size) distribution of air ions was very similar to that found in the real atmosphere.

The atmospheric measurements during rainfall and lab experiments with the water-jet showed that both of them affect the mobility (size) distribution of air ions, generating negatively charged particles below the apparent diameter of about 10 nm and with the concentration peak at about 2–3 nm. The mean size of this mode was nearly constant during the rainfall and lab experiments.

The DMPS measurements only occasionally showed enhancement in the concentration of nanometer particles during rainfall. A better consistency was found in the case of heavy showers (intensity of about

30–60 mm/h). Even when the DMPS measurements showed a rise in the concentrations of nanometer particles, the neutralized particle concentration was many times smaller compared to that of naturally negatively charged particles (intermediate air ions) measured by the ion spectrometers.

#### ACKNOWLEDGEMENTS

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