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ON THE CHARGE DISTRIBUTION ON NANOMETER AEROSOL PARTICLES IN THE ATMOSPHERE DURING NUCLEATION BURST EVENTS AT BOREAL FOREST

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Abstract

Charging state of nanometer aerosol particles is investigated based on simultaneous measurements of aerosol particle size distribution and air ion mobility distribution during nucleation burst events. Measurements have been carried out in SMEAR II station at Hyytiälä, Finland, during QUEST project in spring 2003. Measurements indicated that the charge distribution on nanometer aerosol particles is often significantly asymmetric below the particle diameter of about 5 nm, probably due to ion-induced nucleation on negative air ions. However, no considerable depletion of small (cluster) ions during new particle formation was observed. In general, the changes in the concentration of small ions followed the changes in the ion sink caused by aerosol particles.

INTRODUCTION

During recent years the formation and growth of nanometer-size atmospheric aerosol particles have been studied at many different locations around the world because of the crucial impact of aerosols on the radiation balance and thereby on the climate of Earth (Kulmala *et al*., 2004). Despite the frequently observed new nanometer particle formation events, the microphysical mechanisms of nucleation have remained unclear. Besides the different mechanisms of homogeneous nucleation (Korhonen *et al*., 2003) also the ion-induced nucleation is considered as a possible candidate (Yu and Turco, 2000, Laakso *et al*., 2002). The information about new particle generation in the atmosphere is limited due to the very small size of newly born particles (about 1–2 nm). Almost the only method to obtain information about particles in the diameter range below 3 nm is the measurement of the mobility distribution of air ions (naturally charged cluster ions and aerosol particles). So far, the charge distribution on freshly nucleated atmospheric nanoparticles has been briefly discussed by Mäkelä *et al*. (2001), Tamm *et al*. (2001) and by Hõrrak *et al*. (1998, 2003). The purpose of this work is the comparative study of nanometer aerosol particles and their charged fraction (air ions), as well as the balance between the concentration of small cluster ions and aerosol particles during the nucleation burst events in the atmosphere. Simultaneous measurements of the concentration of nanometer aerosol particles, their charged fraction (intermediate ions) and cluster ions is a promising method to detect the new particle formation via ion-induced nucleation in the atmosphere.

MEASUREMENTS AND METHODS

Atmospheric aerosols and air ions (naturally charged cluster ions and aerosol particles) have been measured in a boreal forest at the Hyytiälä SMEAR station (61°51'N, 24°17'E, 181 m asl), Finland, during the QUEST campaign (March, 21–April 10, 2003). Aerosol particle size distributions were measured by means of a dual DMPS (Differential Mobility Particle Sizer) system covering sizes from 3 up to 500 nm. Both devices had Hauke-type differential mobility analyzer (DMA), closed loop sheath flow arrangement

and Krypton-85 aerosol neutralizer. BSMA (Balanced Scanning Mobility Analyzer, AIREL Ltd., Estonia) was applied for the measurements of positive and negative air ion mobility distributions in the range of 0.032–3.2 $cm^2V^{-1}s^{-1}$ (diameter range 0.4–7.4 nm) logarithmically uniformly divided into 16 fractions. The Stokes-Cunningham-Millikan equation was applied to convert the boundaries of the mobility fractions of BSMA into the corresponding size fractions (Tammet, 1995). The sampling height of both instruments was about 2 m above the ground and the distance between measurement locations was about 30 m. To compare air ions and aerosol particles in the coinciding size fractions, the size distribution of particles was fitted with a piecewise linear regression function and the particle concentration was calculated by integrating over the size distribution in the size fractions coinciding with that of BSMA. The charged fraction of aerosol particles (or experimental charging probability) was found from the scatterplot between the concentrations of particles and air ions, which can be fitted with a line of the linear regression function, the intercept of which should be zero, and the slope gives the mean charging probability for the size fraction. Considering the accuracy of nanometer particle measurements, it is possible to study the process only during the nucleation event days, when the enhanced concentrations of nanometer particles (3−10 nm) up to about 12000 cm^{-3} (bursts) were observable in fine weather conditions during daytime.
The effect of atmospheric aerosols on the small ion concentration was estimated applying a simplified model of bipolar diffusion charging of aerosols (by small ions) assuming the steady state conditions and symmetric charging (Tammet, 1991). The sink of small ions caused by aerosol particles was calculated by integrating over the size distribution from 3 to 500 nm.

RESULTS

During the nucleation event days the ratio of the peak concentrations of negative to positive air ions in the size range of 2.2–3.9 nm was almost always bigger than 1 (see Figure 1). It varied in the range of 0.9–3.6, the average was about 2.4. The ratio of the peak concentrations of negative to positive ions in the size range of 3.9–8 nm was commonly close to 1, displaying a variation from 0.9 to 1.8. Sometimes a clear delay in the onset of the generation of positive air ions (2.2–3.9 nm) of about 20–40 min was observed. The ratio of negative to positive aerosol ion concentration (or coefficient of unipolarity) is a robust indicator of ion-induced nucleation in the atmosphere. Therefore, we can state that the ion-induced nucleation occurred preferably on negative small (cluster) ions. The positively charged particles are probably formed by the charging of neutral particles by positive small cluster ions. The dependence of the charged fraction of aerosol particles on particle sizes for a typical day (April 8) is depicted in Figure 2a. The charge distribution on the nanometer aerosol particles is significantly asymmetric below the particle diameter of about 5 nm, while the bigger particles have acquired nearly equal positive and negative charges due to recharging (neutralization). Considering different nucleation event days, the negatively charged fraction displayed a significant variation, but the positively charged fraction stayed nearly at the

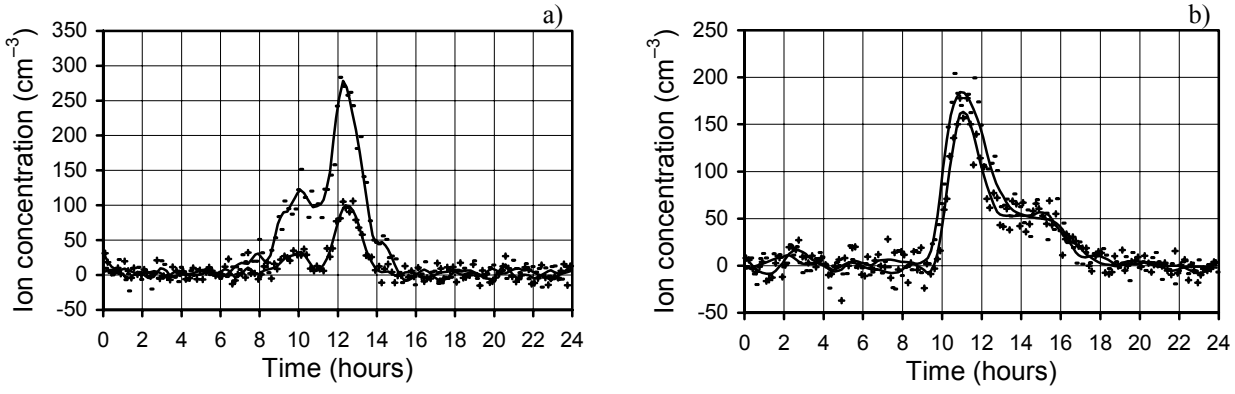

Figure 1. Diurnal variations of positive (+) and negative (-) air ions (2.2–3.9 nm) on April 8 (a) and on April 1, 2003 (b) at the Hyytiälä station.

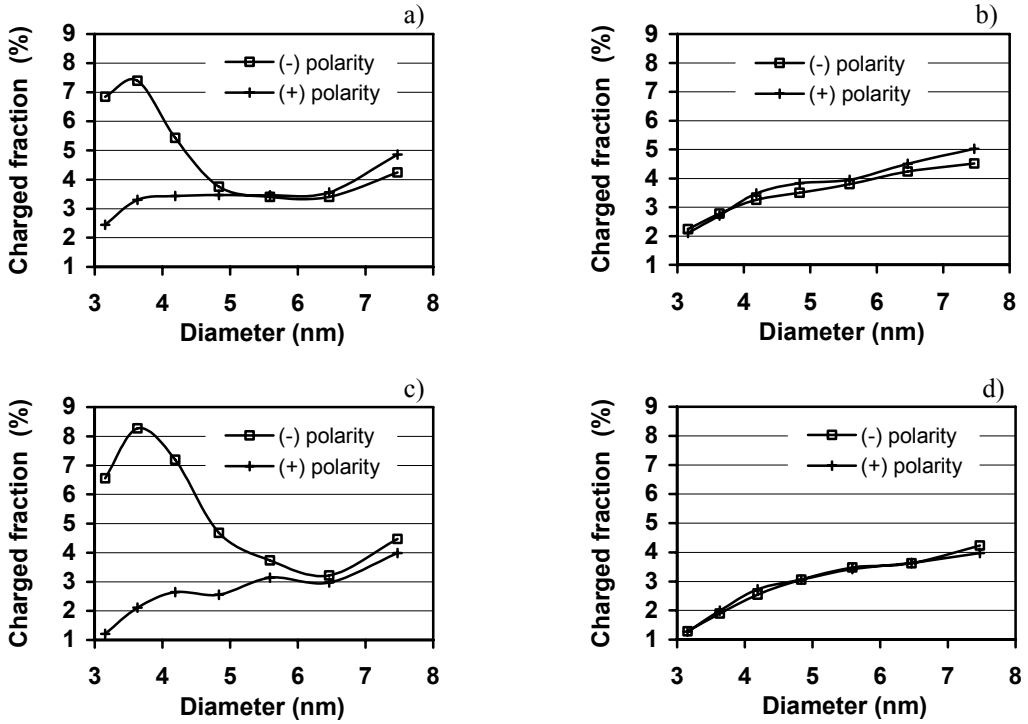

Figure 2. Examples of the charged fractions of aerosol particles in the size rage of 3–8 nm on April 8 (a), April 1 (b), April 3 (c), April 4 (d). Hyytiälä station.

same level. The maximum percentage of the negatively charged fraction of 3–4 nm size particles recoded on March 23 was 15% and 6% for the positively charged fraction. A clear indication of the occurrence of similar asymmetric charge distributions as in Figure 2a with enhanced negative charges on particles below the diameter of 5 nm were also found on March 23, 24, 25, 28 and on April 3, 8. The peculiarity of these days was the moderate concentration of nanometer aerosol particles (3–4 nm) during nucleation events; the peak concentrations were commonly below 1000–1500 cm^{-3}. The lower the peak concentration of nanometer aerosol particles, the higher was the negatively charged fraction. The same tendency was also found in the case of the positively charged fraction. In all these cases the fraction concentrations of air ions were many times higher than the random measuring noise (about 10 cm^{-3}).

In the case of the fast generation of nanometer particles in sufficiently high concentrations a nearly symmetric charge distribution on aerosol particles was found (Figure 2b). Symmetric charge distributions were recorded on March 21, and on April 1 and 4. In these events the concentration of nanometer particles in the size range of 3–4 nm raises above about 2000 cm^{-3} up to 4000–7000 cm^{-3} during a nucleation burst (Figure 3b). Sometimes the rise in the concentration was very fast, reaching from the low background up to maximum within 1 hour. This somewhat contradictory result could be explained by the hypothesis that the particles get charged (recharged) before the measuring by means of ion and aerosol spectrometers. In the second case (Figure 2b), the positively and negatively charged fractions of nanometer particles (3–8 nm) in the atmosphere are about 2–3 times higher compared to the steady state charging probabilities found by Reischl *et al*. (1996) in laboratory experiments. Probably in this case the particles were generated shortly during the nucleation burst in sufficiently high concentrations (e.g. by homogeneous nucleation) so that they could survive during the growth from the initial size (about 1 nm) up to the size range of 3 nm detectable by aerosol instruments. During the growth the particles have acquired charges, which are closer to the steady state charge distribution. The characteristic time for the charging of initially neutral aerosol particles found by Hoppel (1985) is of an order of magnitude of 0.5–1 hour. Symmetric charge distributions on nanometer particles have been recorded also on March 26 and 29. As an exception, on these days, the peak concentrations of nanometer particles (3–4 nm) during nucleation bursts were

comparatively low: 800 and 1100 cm^{-3}, respectively. Also, these new particle formation events have been classified as class 3 with somewhat unclear growth characteristics (Kulmala *et al*., 2001). Taking into account all the relevant nucleation events (when the concentrations of ions and nanometer aerosols were well above the background), we can conclude that a nearly symmetric charge distribution on nanometer particles can occur in the cases, when the peak concentration of nanometer particles is low or high during the intensive generation of particles, but in significantly asymmetric cases, it only occurs when the peak concentration of nanometer particles is below about 1500 cm^{-3}.

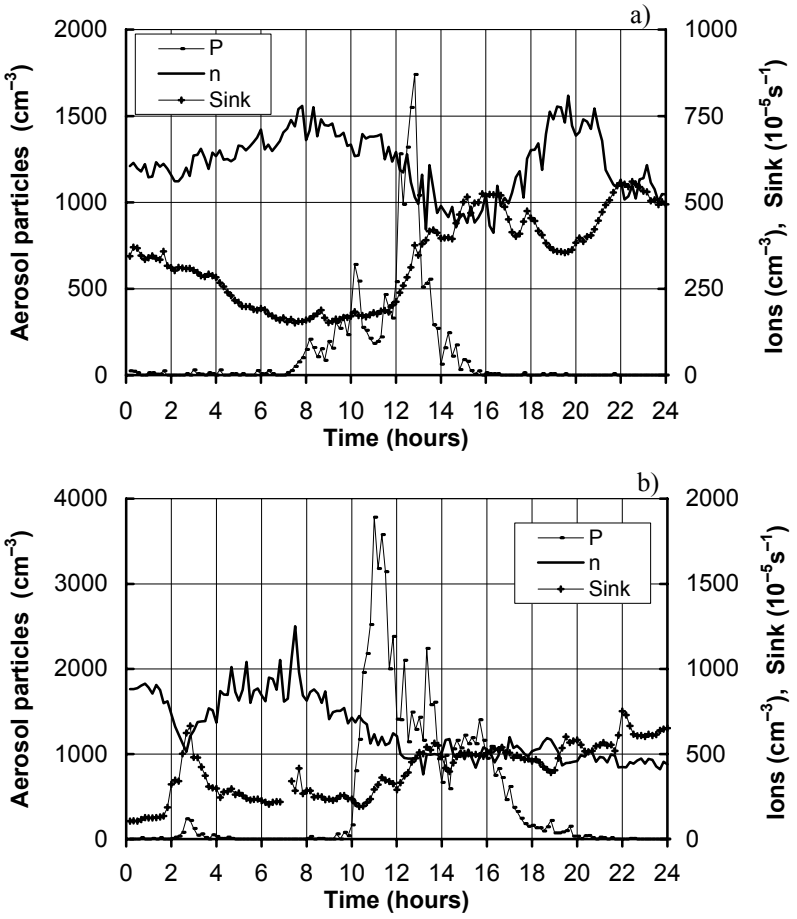

Figure 3. Diurnal variation in the concentration of small negative cluster ions (n), nanometer aerosol particles with diameters of 3–4 nm (P) and the sink of small ions caused by aerosol particles of the sizes of 3–500 nm (Sink) on April 8 (a) and on April 1, 2003 (b) at the Hyytiälä station.

The measurements at Hyytiälä indicate that the atmosphere always contains small air ions that can act as condensation centers (of about 1 nm size) in the nucleation process. Therefore, when the homogeneous nucleation of new aerosol particles take place in the atmosphere it should be accompanied by ion-induced nucleation (Raes and Van Dingenen, 1992; Hoppel *et al*., 1994; Yu and Turco, 2001). Examination of the time series of small cluster ions (Figure 3) cannot reveal any significant decrease in the concentration of small ions during the nucleation bursts of nanometer aerosol particles, which could be interpreted as an evidence of ion-induced nucleation. These variations can well be explained by the changes caused by aerosols (ion sink) and by the changes in the ionization rate of air due to the effect of radon concentration driven by the mixing of boundary layer (Hõrrak *et al*., 2003; Penttinen *et al*., 2003). As an example, the diurnal variations in the concentration of small negative air ions, nanometer aerosol particles (3–4 nm) and the sink of small ions due to aerosol particles (3–500 nm) are given in Figure 3 for two days, when the

peak concentrations of nanometer aerosol particles displayed a considerable difference (about two times). In both cases the small ion concentrations displayed a similar behavior during nucleation bursts, slightly decreasing towards midday, while the charged fractions of nanometer aerosol particles were considerably different probably due to the contribution of ion-induced nucleation (see Figure 2). The diurnal variations of positive and negative small ions were closely correlated; the ratio of positive to negative small ions was about 1.1. To explain the observed peculiarities, it is reasonable to assume that the various nucleation mechanisms (homogeneous and ion-induced nucleation) take place simultaneously in the atmosphere. To maintain the small ion population, the production rate of aerosols by ion-induced nucleation should be limited by the ionization rate (about 4–10 ion pair cm^{-3} s^{-1}).

In general, the behavior of small ion concentration during nucleation events is independent of that of nanometer aerosol particles because of their small contribution to the total ion sink compared to large particles (Hõrrak *et al*., 2003). The effect of scavenging of small ions by aerosol particles increases during the growth of particles toward large sizes. Commonly the minimum of the ion sink is before the onset of the generation of nanometer particles or at about the burst peak. Sometimes, in the case of clean air, when the ion sink was about 10^{-3} s^{-1}, the small ion concentration became nearly independent of that of aerosol particles and the losses of small ions are mainly determined by the dry deposition on the coniferous forest canopy and also by the recombination of small ions.

CONCLUSIONS

The air ion mobility distribution measurements combined with the aerosol size distribution measurements provide valuable experimental information for the study of the aerosol formation processes and physical pathways leading to the nucleation. The measurements indicated that the charge distribution on nanometer aerosol particles is often significantly asymmetric below the particle diameter of about 5 nm during the nucleation bursts. The excess of the negatively charged fraction is probably a robust indicator of ion-induced nucleation on negative air ions. In the case of the fast rise of nanometer particles in considerably high concentrations, a nearly symmetric charge distribution on aerosol particles was found, which is closer to the steady state charge distribution. In general, the changes in the concentration of small (cluster) ions followed the changes in the ion sink caused by aerosol particles; no considerable depletion of small ions during new particle formation was observed. A contribution of different nucleation mechanisms to the aerosol production is still open to question.

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