MEASUREMENTS OF THE MOBILITY DISTRIBUTION OF AIR IONS AS A SOURCE OF INFORMATION FOR THE STUDY OF AEROSOL GENERATION

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ABSTRACT: Complex measurements of atmospheric ions and submicron aerosol particles were performed in Southern Finland during March-April 2000, at the annual maximum of the new particle burst occurrence. Experiments with a systematic charger/no charger arrangement for the ultrafine aerosols and with the supporting extensive atmospheric ion measurements were performed for the first time. Very distinct events of ultrafine particle formation were recorded on 6 days and moderate events on several other days. These nucleation bursts were more intensive at low concentration of pre-existing larger submicron aerosols. The mobility distributions measured by two identical spectrometers with bipolar pre-charging and without charging coincide well. Significant deviations from steady state charge distribution towards an excess or deficit occurred only in the fractions of smallest particles during few nucleation events. The results suggest that different nucleation mechanisms can take place in the atmosphere.

INTRODUCTION

The intermediate ions represent the finest charged aerosol particles that arise in the atmosphere. Beside the known effect on atmospheric conductivity, the intermediate ions can play the key role in the chain of hypotheses connecting cosmic rays, atmospheric ionization, aerosol generation, CCN formation, and global albedo. The mechanism of atmospheric aerosol generation is still an enigma and it has become a focus of research efforts in recent years. Four hypotheses have been proposed as the mechanism:

1. Homogeneous nucleation of a binary vapor system; more often water and sulphuric acid are assumed to be involved [Kulmala et al., 1998; Noppel et al., 2002].
2. Ion-induced nucleation of one or more vapor species [Hõrrak et al., 1998; Yu and Turco, 2000; Tamm et al., 2001]. This phenomenon is well known in the Wilson chamber.
3. Ternary nucleation of sulphuric acid-water-ammonia produces very small, thermodynamically stable 1–2 nanometer sized clusters [Kulmala et al., 2000; Napari et al., 2002].
4. Recombination of cluster ions produces neutral clusters of a size above the critical size of the condensable vapor available in the prevailing atmospheric conditions [Smirnov, 1992; Turco et al., 1998].

The authors concentrate upon ion-induced nucleation. It can play an essential role in some cases, since the ionization rate in the upper troposphere is more than 10 times higher than at the ground level. When an ensemble of particles resides in the atmosphere of bipolar small (cluster) ions for a sufficient period of time, a Boltzmann-Fuchs-type steady state charge distribution arises on the particles. In ordinary atmospheric conditions near the ground (about 300 ion pairs per cm³), the relaxation time of this process can be several hours for charging of neutral particles and considerably shorter for initially charged particles [Hoppel, 1985]. Thus the measurement of the charge distribution of the freshly nucleated nanometer sized particles can give essential information about the role of ion-induced nucleation. Since the conventional aerosol particle sizers measure particles with diameters above 3 nm, but the air ion mobility spectrometers measure them above 0.3 nm, the usefulness of mobility measurements is obvious. The mobility distributions were simultaneously measured by two identical spectrometers: with bipolar pre-charging and without charging. The spectrometer with bipolar pre-charging yields the mobility distribution of air ions in steady state. The spectrometer without charging gives the mobility distribution in the natural atmosphere. The comparison of the spectra of these two types shows eventual deviations from the steady state charge distribution of natural aerosol particles. The possibility of obtaining information on the formation mechanism of the fresh aerosols by measuring their charging state has been discussed by Laakso et al. [2002] and stated to be challenging even for the modern aerosol instrumentation.

MEASUREMENTS

Complex measurements were performed at SMEAR II Station (Station for Measuring Forest Ecosystem-Atmosphere Relations), Hyytiälä, Southern Finland (61 51’N, 24 17’E, 170 m above sea level), from March 20 to April 20, 2000, at the annual maximum of the new particle burst occurrence. The stationary instrumentation of the SMEAR II Station is described in [Vesala et al., 1998]. According to its purpose, the Station has a large
variety of instruments for atmospheric, aerosol, soil and plant measurements. Of stationary facilities, mainly atmospheric and aerosol instrumentation was used for this research. The stationary instrumentation was essentially completed with special instrumentation for aerosol and air ion measurements.

The main novel instrument was a set of two identical differential mobility particle sizers (DMPS) with different pre-charging conditions. One of these DMPS operated in the very customary mode [Vesala et al., 1998]. The aerosol particles in the air sample were charged in a bipolar charger that used a radioactive Kr-85 isotope. The charged particles were analyzed in two differential mobility analyzers (DMA) [Winklmayr et al., 1991] according to their mobility. Of these two, DMA1 operated with the analyzer length of 11 cm for the mobility range of $9.7 \times 10^{-3} - 2.3 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and DMA2 operated with the analyzer length of 28 cm for the mobility range of $2.5 \times 10^{-5} - 9.7 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. After each DMA, a condensation particle counter (CPC; TSI Model 3025 for DMA1 and TSI Model 3010 for DMA2) was used to measure the particle concentration in each mobility class. The mobility distribution of negatively charged particles is interpreted in this study as the size distribution of the charged particles. In a conventional analysis, it is furthermore converted into the size distribution of all aerosol particles in the size range (negative, positive and neutral), using appropriate values for the charging probability. The size distribution is usually presented in the shape of fraction number concentrations in 29 logarithmically distributed diameter intervals with mean diameters from 3.03 nm to 495 nm. Another DMPS was identical, but without the charger. Thus the second DMPS analyzed only naturally charged aerosol particles. Charging conditions in the natural atmospheric environment are usually almost bipolar and steady state. If the charging conditions are deviating from the steady state, then the distribution issued by the second DMA will differ from the distribution recorded by the first DMA. The air inlet into the DMPS was at a height of 2 m above the ground. The output signals were saved as average values for 10 min intervals.

In order to estimate the fraction concentrations of charged nanometer particles or air ions, additionally four integral air ion counters UT-8401 were operating at Hyytiälä from March 24 to April 16, 2000. The common air inlet was at a height of 2 m above the ground. The limiting mobilities of the counters were 0.02; 0.063; 0.2, and 0.64 cm$^2$ V$^{-1}$ s$^{-1}$. The output signals of the counters were also saved for 10 min intervals. The data processing of the output signals enabled to obtain the fraction concentrations of negative air ions in three diameter ranges: $n$ for cluster ions of 0–1.9 nm, $m$ for intermediate ions of 1.9–7.4 nm, $N$ for light large ions of 7.4–20 nm. An independent aspiration instrument measured the negative and positive conductivity of the air. The air inlet was also at a height of 2 m above the ground, at a distance of about 10 m from the air ion counters.

The total number concentration of aerosol particles in a wide range was also measured by means of the counter CPC 3025, which has the smallest detectable particle size of 2.7 nm. The radon content of the air was monitored continuously by counting the beta particle emissions of the particle-bound daughter nuclides that were collected by means of aerosol filters. The air inlet was about 6 m above the ground. There were also other complementary instruments.

RESULTS AND DISCUSSION

A detailed data analysis was performed for the period from March 29 to April 14, 2000, when the maximum number of instruments was operating. The time series of 91 measured parameters with 10 min or 30 min resolution were examined. The set of parameters contains 29 size fractions of naturally charged aerosol particles, 29 size fractions of artificially charged aerosol particles, 3 classes of air ions, negative and positive conductivity, 6 species of trace gases, 10 parameters of solar radiation, radon concentration, and basic meteorological parameters. The correlation analysis of these time series yielded many anticipated results. However, the behavior of $m$ and of the finest DMPS fractions is essential in this study. The concentration $m$ has a significant positive correlation with the $1^\text{st}$ and $2^\text{nd}$ DMPS fractions (2.8–4.8 nm), and a weak positive correlation with the intensity in the nighttime and considerable values around noon on certain days, which indicates the generation of new aerosol particles. The mobility distributions measured by the mentioned spectrometers with bipolar pre-charging and without charging coincide well. Significant deviations from steady state charge distribution towards the excess or deficit occurred only in the fractions of smallest particles during the nucleation events.

Intense or medium nucleation bursts of aerosol particles occurred on March 29 and 30, April 2, 6, 7, 8, and 9. Weak bursts took place also on several other days. As usual, the bursts started at 8–11 LST and lasted for 3–7 hours. The character and intensity of the bursts on different days was different. A remarkable behavior of the finest negatively charged aerosol particles is illustrated in Figure 1. A medium nucleation burst around noon with a significant excess charge of naturally charged particles is clearly presented, despite the fact that the neutralization of charged particles is much faster process than the charging of neutral particles. Obviously this phenomenon indicates ion-induced nucleation.
An intense burst occurred on March 29. The mentioned fraction of artificially charged particles grew rapidly to the peak value of 450 cm$^{-3}$, but that of naturally charged particles reached only 200 cm$^{-3}$. Obviously a neutral mechanism of nucleation, probably the ternary nucleation took place.

On March 30 the pattern was quite different; the burst of intermediate ions was intense, but the burst of aerosol particles in the mentioned range was weak with a small excess charge of natural particles. A similar event was observed on April 2. On April 6 there was a small charge deficit; on April 7 a small excess, and on April 9 almost equal charges. On all the above-mentioned burst days, an Arctic air mass was prevalent; only on March 30 the air was of the North Atlantic origin.

According the overall concept of the nucleation burst [Kulmala et al., 2001], the bursts fall into different types depending on the history of the air mass. Here, the concepts of clean and polluted nucleation events can be introduced along with the arrival of the air mass either from the Arctic regions or via the polluted areas. A clean event usually occurs in clean air masses with a low concentration of pre-existing aerosols. Typically, the polluted events occur during the presence of a high amount of pre-existing submicron particles which create a large condensation sink for condensing vapors due to highly effective surface of the pre-existing particles, but do not seem to fully prevent the nucleation in all cases [Dal Maso et al., 2002].

The attachment of small air ions by the submicron aerosol particles is sometimes characterized by the effective particle surface. Very often the effective particle surface is decreased during the nucleation burst [Dal Maso et al., 2002]. This is most often due to the vertical mixing of the boundary layer air masses during sunshine, which dilutes the ground air from the pre-existing particles. This vertical mixing has been discussed to be the most significant primus motor behind the whole appearance of the nucleation events [Kulmala et al., 2001]. It is not known whether the apparent dilution of the ground air aerosol and temporary decrease in its effective surface is a key issue in the nucleation burst or just a consequence of other processes involved. Nevertheless, when the authors evaluated the effective surfaces for the five most distinct nucleation bursts on March 29 and 30, and April 2, 7, and 8, it was clear that only on March 29 there was no significant reduction of the effective surface of submicron particles just prior to and during the burst. From this we could suggest that on March 29, the particle surface area was able to remove the small ions available for ion-induced nucleation, but on March 30, April 2 and 7, there were abundant small ions in the air due to the reduced surface of the particles.

![Figure 1. Time series of the fraction concentrations (cm$^{-3}$) of charged aerosol particles at Hyytiälä, Finland, on April 8, 2000. 'Natural' denotes naturally charged particles in a diameter range of 2.8–8.6 nm, 'Bipolar' particles in the same size range charged in the bipolar charger, and 'm' intermediate air ions (1.9–7.4 nm) measured by means of air ion counters.](image-url)
As a conclusion, the authors state that they have experimentally observed deviations in the charging state of the newly generated aerosol particles towards the excess or deficit of charges, depending on the particular conditions. The data was obtained by means of two DMPS operating in the mode of mobility spectrometers. If the ultrafine particles are observed to deviate from the steady state, this should be a consequence of their inborn charging state. The result that the deviations from the steady state appear in both directions in the charging state of the freshly generated particles, suggests that different nucleation mechanisms can occur in the atmosphere. Most probably these processes, both neutral and ion-induced, take place even simultaneously. The present data, however, suggests that the effect and the extent of, e.g., ion-induced nucleation should be fairly weak. Otherwise, a more significant and systematic behavior could be expected.

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