

## 12. CONCLUSIONS

The average mobility spectrum in the range of  $0.00041\text{--}3.2\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  shows distinct peaks of small and large ions; intermediate ions with mobilities of  $0.034\text{--}0.5\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  are of low concentration of about  $50\text{ cm}^{-3}$ . The relative standard deviation of the hourly averaged values of fraction concentration is about 50% for small (cluster) ions, 70% for large ions, and up to 130% for intermediate ions. The considerable variability of the concentration of intermediate ions is due to their bursts (up to  $900\text{ cm}^{-3}$ ) in favorable conditions during daytime. During nighttime, intermediate and large ions show nearly equal relative standard deviations of 50–60%.

Small (cluster) ions represent quite isolated and stable groups of ions ( $0.5\text{--}3.2\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) with mean natural mobility and standard deviation of  $1.53 \pm 0.10$  and  $1.36 \pm 0.06\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for negative and positive ions, respectively. The ratio of the concentration of positive ions to that of negative ions (coefficient of unipolarity) is about 1.12, which is also the ratio of the average mobility of negative ions to that of positive ions.

The principal component analysis was applied to detect the structure of an air ion mobility spectrum. As a result, the mobility spectrum in the range of  $0.00041\text{--}3.2\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  (diameters of 0.36–79 nm) was divided into five classes: small cluster, big cluster, intermediate, light large, and heavy large ions. The boundaries between the classes are  $1.3\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  (diameter of 0.85 nm),  $0.5\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  (1.6 nm),  $0.034\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  (7.4 nm), and  $0.0042\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  (22 nm). The five principal components that are closely correlated with the respective ion classes explain 92% of total variance of air ion mobility spectra.

The bursts of concentration of intermediate ions (1.6–7.4 nm) from a low background of about  $40\text{ cm}^{-3}$  up to  $900\text{ cm}^{-3}$  are observable in the mobility spectra in fine weather conditions during daytime as a result of photochemical nucleation. The burst is a factor that considerably changes the general shape of the size spectra of aerosol ions below 80 nm. It can initiate a process of evolution of spectra generating new aerosol particles of 2–3 nm that grow toward large sizes up to about 10–15 nm during 2–3 hours. The disturbed region of air ion size spectra affected by the bursts is from 1.1 to 34 nm ( $0.002\text{--}1.0\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) including the groups of big cluster ions, nanometer particles and a fraction of Aitken particles. A subsequent shift of the peak beyond 23 nm was observed only occasionally in the case of intensive burst events.

Almost all the bursts were recorded in cool Arctic or Polar high-pressure air masses. Spatial scales of the bursts were about 100–150 km, or even more. The number of burst events recorded during 14 months was 101 (about 80 per year), with maximum frequency in spring and minimum frequency in winter.

The annual variation of small ion concentration follows known regularities for continental areas of high latitudes: a slight minimum occurs in the cold season, when the soil is frozen and covered by snow, and a maximum in the

warm season. The concentration of small ions exhibits some considerable diurnal variation (with the maximum during nighttime calms and the minimum in the afternoon) in the warm season only. These variations can be explained by the known effect of radon on the ionization rate of air. It was found that small clusters ( $1.3\text{--}3.14\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) behaved differently from big clusters ( $0.5\text{--}1.3\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ).

The annual and diurnal variations in the concentration of intermediate ions (diameter 1.6–7.4 nm), as well as in light large ions (7.4–22 nm) are strongly affected by the photochemical nucleation bursts. The bursts occurred usually around noon in specific meteorological conditions, e.g. after the inflow of clean Arctic high-pressure air masses in spring and in autumn. The annual variations have minima in winter. The average diurnal variation of the concentration of intermediate ions had one peak around noon, the light large ions reached the peak concentration about 2 hours later. During the days with nucleation bursts the concentration of heavy large ions (charged Aitken particles of 22–79 nm) was enhanced in the afternoon compared with non-burst days. This is explained as a consequence of the particle evolution (growth) towards large sizes.

The monthly median concentrations of heavy large ions (22–79 nm) were quite steady in the warm season and unsteady in the cold season. In the cold season, a clear negative correlation was found between the heavy large ion monthly concentration (changes by a factor 2) and the amount of precipitation. The wet removal process is considered as a factor that likely controlled the concentration of heavy large ions (Aitken particles) in wintertime.

In the warm season the concentrations of heavy large ions (charged Aitken particles of 22–79 nm) increases during nighttime probably due to radiolytic processes (initiated by  $^{222}\text{Rn}$  and  $^{220}\text{Rn}$  decay) favored in conditions of nocturnal calms. In the cold season the average diurnal variation is in the opposite sense to that in the warm season, in general. This contrast can be explained by the different processes of aerosol particle generation (combustion versus radiolytic processes). In winter the concentrations of charged Aitken particles and  $\text{NO}_2$  were positively correlated (the correlation coefficients were 41–77%).

In the cold season, when the rare nucleation events were excluded, all the classes of aerosol ions (2.1–79 nm) showed similar average diurnal variations with minima at 6 LST. The concentration of intermediate ions exhibits the maximum in the afternoon before the heavy large ions reach their maximum in the evening around 20 LST; the decrease during nighttime is probably due to deposition, coagulation and growth of particles by condensation.

The natural mean mobility of small ions is determined by the balance of concentrations of small cluster ions ( $1.3\text{--}3.14\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) and big cluster ions ( $0.5\text{--}1.3\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ). The mean mobilities of positive and negative ions (averages 1.36 and  $1.53\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , respectively) were closely correlated, the correlation coefficient being 80%. The mean mobility of negative small ions shows higher variability compared to that of positive ions.

A diurnal variation of the natural mean mobility of small air ions can take place during anticyclonic weather. The average diurnal variation was significant in the warm season (May-September) and weakly expressed in the cold season. It correlated negatively with air temperature and positively with relative humidity. The solar radiation is considered as essential (real) factor.

In wintertime the variation of the mean mobility was correlated with the type of air mass. The decrease of mean mobility followed the inflow of marine Arctic high pressure air masses, whereas the higher mean mobility was characteristic of the marine Polar air masses. In this connection, cyclonic weather conditions (and probably precipitation) were found to be responsible for the high average mobility of small ions. The effect of Arctic air masses could explain also the dependence of mean mobility on average wind direction. The mean mobility of negative small ions increases about 13% and of positive ions 6% when the wind turns from north to south.

Two characteristic types of the evolution of small ion mobility spectra, which reflected the diurnal variation of natural mean mobility in the warm season and occasional changes in the cold season, were found. This evolution probably reflects the growth of cluster ions via chemical reactions during aging. The factors that affect the lifetime of small ions (aerosol particle concentration, ionization rate) could be responsible for the observed changes of mean mobility.

The mean natural mobility of small ions in winter is higher than in summer. In first approximation, the annual variation of the mean mobility reduced to standard conditions correlated negatively with air temperature. This is not in accordance with the expected independence of reduced mobilities and air temperature. The contradiction probably refers to the different natures of cluster ions in the warm and cold seasons.

In general, the correlations between mean mobility and meteorological parameters (air temperature, relative and absolute humidity) are stronger in the case of the mean mobility of positive small ions than with negative ions. If the mean mobility exhibited diurnal cycles, it would be correlated negatively with air temperature and positively with relative humidity. During long-term variations (trends) there could be different behavior. The correlation with absolute humidity (in the cold season) can be explained by the effect of different air masses. In general, we cannot distinguish between the effects of meteorological parameters on the mean natural mobility and those associated with the origin and composition of air masses.

The mean mobility of small ions was correlated negatively with the fraction concentrations of intermediate ions (1.6–7.4 nm) and positively with heavy large ions (52–79 nm). The correlation changes from slightly negative to positive in the range of 11–79 nm. The accumulation mode particles (100–500 nm) showed the highest correlation, the correlation coefficients being 62–65% (50–53%) for the mean mobility of negative (positive) small ions.

Multiple regression analysis was applied to evaluate the influence of various statistically interdependent factors (concentration of heavy large ions (52–79 nm), intermediate ions (1.6–7.4 nm), air temperature and relative humidity) on the natural mean mobility of small ions. Considering the whole measurement period (14 months) the linear regression model describes 49% of the total variance of the mean mobility of negative and positive small ions; in different months this explained variance was in the range of 37–70% (the higher values were found in the warm season). The first two factors (relative humidity and heavy large ion concentration) account for 44% (38%) of variance of the mean mobility of positive (negative) small ions, on average. The intermediate ions (1.6–2.3 nm) are a factor in the case of mean mobility of negative small ions. The explained variance then increases about 7%. The effect of air temperature on the mean mobility was mostly insignificant. The solar radiation is considered as a real factor and the relative humidity as an indirect factor which are correlated with the mean mobility of small ions. Thus the tree factors, which are probably related to the changes of mean mobility, are solar radiation, concentration of aerosol particles, and nucleation bursts.

We accept that the conductivity of air is mainly caused by small ions. The relatively higher concentration of large ions does not compensate the decrease in their mobility. However, in specific situations the concentrations of intermediate and light large ions (1.6–22 nm) make a considerable contribution to conductivity (up to 26%) and should not to be neglected. The mean mobility of small ions is a factor to be considered. The deviation of mean mobility of small ions from the average could cause changes in conductivity from about –12% to +15% and from –14% to +26% for positive and negative polarity, respectively.

The time variations of the air ion mobility spectrum and the aerosol particle size spectrum are well correlated in a size range of 10–80 nm, considering coinciding fractions. The correlation coefficient varies from 93% to 98%, decreasing with mean size of the fraction (probably because of multiple charges on the particles). The estimated mean values of the percentages of charged fractions of aerosol particles (air ions) are 6.6, 10 and 19% for size fractions 10–18, 18–32, 32–56 nm, respectively. This is in general accordance with the bipolar charging probability of single charge on a particle. These aerosol particles in weakly polluted rural air are mostly in a quasi-steady charging state. Therefore air ion measurements could give essential information about atmospheric aerosols. The aerosol particle size distribution measured directly by the electrical aerosol spectrometer and calculated from intermediate and large air ion measurements according to the appropriate procedures of conversion between mobility distribution and size distribution showed satisfactory agreement in atmospheric conditions. Disagreement between the results is not large and can be explained by uncertainties in the calibration of the spectrometers.