4. STATISTICAL CHARACTERIZATION OF AIR ION MOBILITY SPECTRUM

4.1. Average mobility spectrum of air ions

The average mobility spectra of air ions are presented in Figure 11. There are two wide spectral groups with the mobility ranges of 0.5–3.2 and 0.00032–0.034 $cm^2V^{-1}s^{-1}$, which are traditionally called small ions and large ions, respectively. More detailed average spectra of small ions are presented in Figure 12. The corresponding particle diameters, derived from the electrical mobilities, are presented in the figures assuming single-charged particles [*Tammet*, 1995]. The third group lies between large and small ions, with the mobility range of 0.034–0.5 $cm^2V^{-1}s^{-1}$, and is called intermediate ions. This group appears from time to time as burst events, occasionally occurring around local noon, and its average concentration is about 50 cm^{-3}. Physically, large and intermediate ions may be called aerosol ions and small ions may be called cluster ions [*Hõrrak et al.*, 1994].

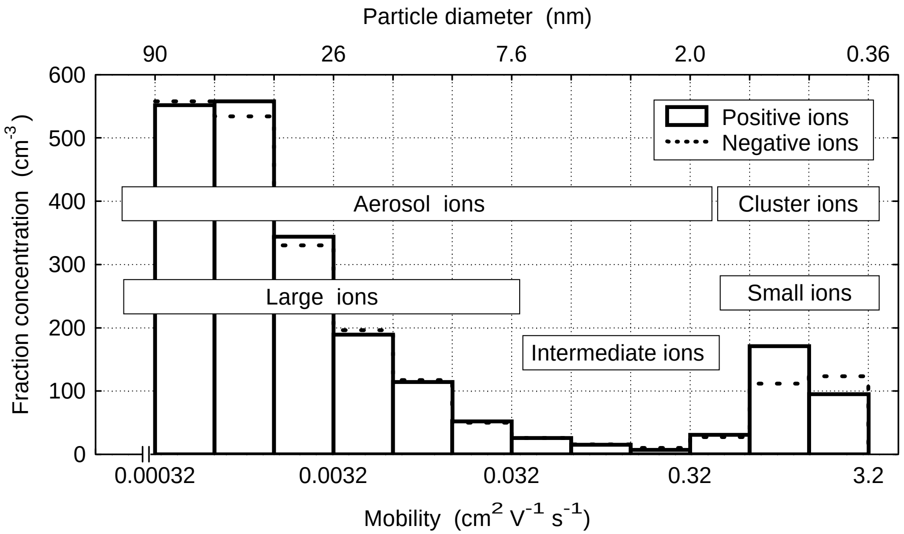

Figure 11. Average mobility spectra of air ions at Tahkuse. Sept. 1993 – Oct. 1994.

Small (cluster) ions represent quite an isolated and stable group of ions with the mean natural mobility and standard deviation of 1.53 ± 0.10 and 1.36 ± 0.06 $cm^2V^{-1}s^{-1}$ for negative and positive ions, respectively. The general shape of the mobility spectra of negative and positive small ions is astonishingly similar to that observed by *Misaki* [1976], whose modes of small ion mobility spectra, 1.56 $cm^2V^{-1}s^{-1}$ and 1.26 $cm^2V^{-1}s^{-1}$, are close to those presented in Figure 12. Small (cluster) ions are formed in charged state and evolved via ion-molecule reactions in the atmosphere before they obtain their final size [*Mohnen*, 1977; *Luts and Salm*, 1994; *Luts*, 1995; *Nagato and Ogawa*, 1998]. The growth of small ions is thermodynamically hindered at a mobility of 0.5 $cm^2V^{-1}s^{-1}$ (1.6 nm) in ordinary conditions.

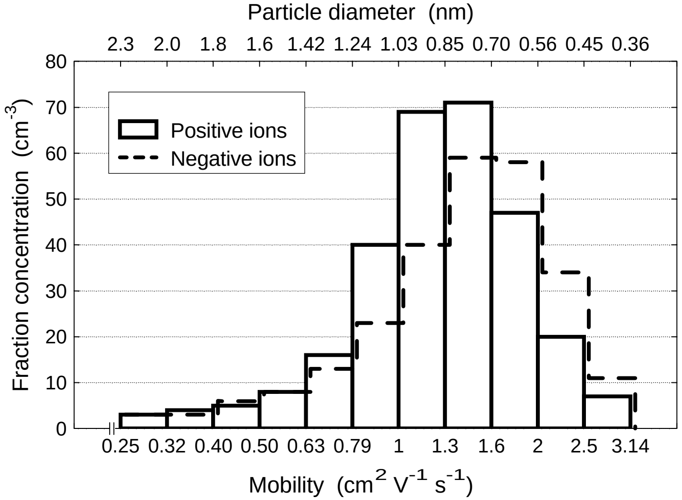

Figure 12. Average spectra of small (cluster) ions at Tahkuse, Sept. 1993 – Oct. 1994.

The overall shape of the average spectra in the range of large ions (aerosol ions) is in accord with calculations based on the theory of bipolar charging of aerosol particles by small air ions [*Salm*, 1988, *Hõrrak et al.*, 1998a]. The concentration of large ions diminishes toward higher mobilities owing to the reduction of charging probability and the concentration of aerosol particles. The lower boundary of the spectrum at a mobility of 0.00032 $cm^2V^{-1}s^{-1}$ is determined by technical limitations of the spectrometer of large ions.

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. The correlation coefficient varies from 0.91 to 0.97, depending on the size fraction. These aerosol particles in weakly polluted rural air are believed to be in a quasi-steady charging state [*Hõrrak et al.*, 1998c].

The electrical state of aerosol particles in the intermediate ion range (nanometer particles) is not well known in natural atmosphere. The estimates of charging probability obtained by theoretical considerations and laboratory experiments vary from about 0.5% to 5% for particles from 2 to 10 nm, respectively [*Hoppel and Frick*, 1986; *Reischl et al.*, 1996]. Experimental investigation of competitive ion-induced and binary homogeneous nucleation in gas mixtures shows that the above values may be greatly modified when ions are involved in the nucleation process [*Kim et al.*, 1997; 1998].

4.2. Variability of air ion spectra

The relative standard deviation (coefficient of variation) of the hourly averaged values of fraction concentrations is about 50% for small (cluster) air ions and 70% for large air ions. The average fraction concentrations of intermediate ions are relatively low, but their standard deviations are high, up to 130%, owing to the burst events with concentrations up to 900 cm^{-3} [*Hõrrak et al.*, 1998b]. The enhanced concentrations of intermediate ions are recorded from 10 to 19 LST, with the duration of 6–10 hours, in fine weather conditions. The relative standard deviations of the fractions of air ion mobility spectra in the daytime (7–20 LST) and nighttime (20–24–7 LST) are presented separately in Figure 13. A change of scale is set at a mobility of 0.32 cm^{2}V^{-1}s^{-1}, according to technical limitations of the spectrometers, and for better resolution of the spectral regions of aerosol ions and cluster ions.

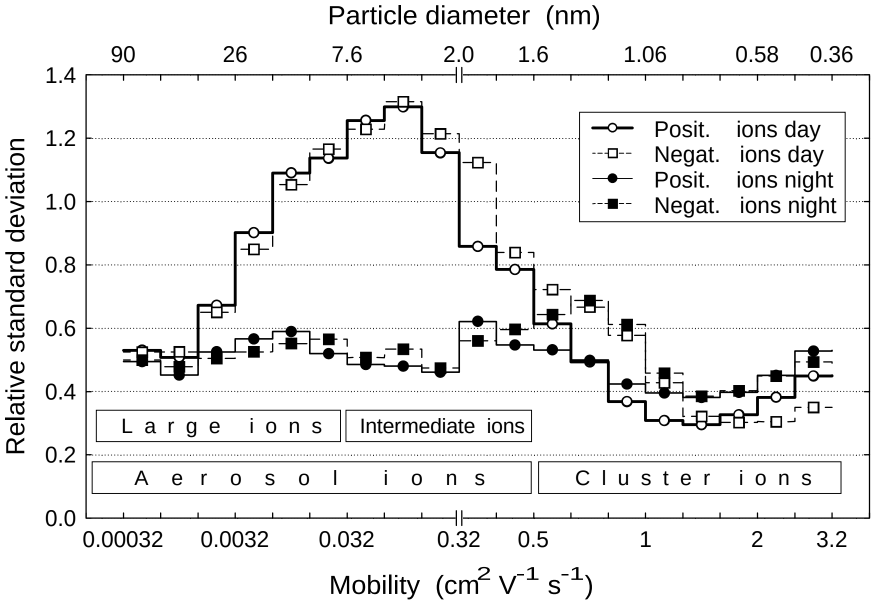

Figure 13. Relative standard deviations of the concentration of air ion spectral fractions at daytime (7–20 LST) and at nighttime (20–24–7 LST) at Tahkuse Observatory, September 1, 1993 – October 27, 1994.

Considering the whole data set, the relative standard deviation is close to the maximum values depicted in Figure 13 (in the case of large and intermediate ions close to that of daytime and in the case of small ions close to that of nighttime values). The crossing point of the curves for daytime and nighttime, at a mobility of about 0.5 cm^{2}V^{-1}s^{-1} (1.6 nm) in Figure 13, is in accordance with the boundary between cluster ions and aerosol ions [*Tammet*, 1995]. The above estimates of the relative standard deviations are equally valid for the large and intermediate air ion concentrations of both polarities, taking into account the random measuring errors.

The estimates of relative standard deviations of fraction concentrations of air ions in the region of large ions show quite a good agreement with those of aerosol measurements in a diameter interval of 10–100 nm [*Kikas et al.*, 1996]. According to the latter measurements, the relative standard deviation of aerosol particle concentrations has a minimum value in the size range of the accumulation mode, 100–300 nm, and rises in the flanks. This is also in accord with model calculations of deposition velocities of aerosol particles [*Jaenicke*, 1982, 1984; *Hoppel et al.*, 1990].

Normally, the positive air ion spectrum has a mode in a mobility range of 1.0–1.3 cm^{2}V^{-1}s^{-1} or 1.3–1.6 cm^{2}V^{-1}s^{-1}, and the negative ion spectrum, in a mobility range of 1.3–1.6 cm^{2}V^{-1}s^{-1} or 1.6–2.0 cm^{2}V^{-1}s^{-1}. Sometimes the “low mobility mode” of 1.0–1.3 cm^{2}V^{-1}s^{-1} becomes dominant in the negative ion spectrum, and the mobility spectrum of negative small ions expands over a wider region as compared to positive ions. The mode of positive ion spectrum only shifts from the mobilities of 1.3–1.6 to 1.0–1.3 cm^{2}V^{-1}s^{-1}. These variations could explain the higher relative standard deviation of the big cluster ion concentration of negative polarity compared with the ions of positive polarity.

The low-mobility modes of small air ions of both polarities were recorded when the large ion concentration was decreasing, but not vice versa. The low concentration of heavy large ions allows small air ions to evolve (grow) toward clusters of large sizes, and consequently to lower mobilities, within their lifetime. The evolution of the mobility spectra of small air ions described above was more regular in the warm season under conditions of anticyclones, particularly in June and August. In June and August, under conditions of hot and sunny anticyclonic weather, the low-mobility mode of negative ions in a mobility range of 1.0–1.3 cm^{2}V^{-1}s^{-1} preferentially became dominant in the afternoon (or in the evening) and disappeared before sunset.

Considering the whole data set, the fractions of small ions of the mobilities of 1.0–1.3 cm^{2}V^{-1}s^{-1} and 1.3–1.6 cm^{2}V^{-1}s^{-1} are the most conservative, the fractions of higher or lower mobility show higher relative standard deviations. Accordingly, the mobility of 1.3 cm^{2}V^{-1}s^{-1} (diameter 0.85 nm) may be used as a conventional boundary between small and big cluster ions. The fractions of negative small cluster ions at daytime display almost equal variabilities.

In general, small air ion concentrations have higher relative standard deviations in the nighttime than in the daytime, because of higher concentrations raised during nocturnal calms, in fine weather conditions in warm season. The highest relative standard deviations of small cluster ion concentration were recorded in July in conditions of very hot and stable anticyclones, probably due to increasing ionization rate caused by accumulation of radon and their daughters near the ground during nocturnal calms that produced numerous new young ions. The higher the mobility of small cluster ions, the higher the relative standard deviation was: for example, 40% for the ions of 1.3–1.6 $cm^2V^{-1}s^{-1}$ and 60% for the ions of 2.5–3.14 $cm^2V^{-1}s^{-1}$.

4.3. Average characteristics and variability of small ions

The statistical characteristics of small air ion concentrations are presented in Table 3. The average concentrations of small air ions and their standard deviations are $n_{-} = 245 \pm 88$ cm^{-3} and $n_{+} = 274 \pm 6$ cm^{-3}. The correlation coefficient between the polar concentrations is 98%. The mean natural mobility of small air ions of both polarities is calculated by averaging over the mobility interval from 0.5 to 3.2 $cm^2V^{-1}s^{-1}$. The hourly mean mobilities and standard deviations, averaged over the whole measurement period of 14 months, are $k_{-} = 1.53 \pm 0.10$ and $k_{+} = 1.36 \pm 0.06$ $cm^2V^{-1}s^{-1}$. Approximately the same values of mean mobility have been found for different annual periods from 1985 to 1994. The correlation coefficient between polar mean mobilities is 80%. The mean mobility of small ions reduced to standard conditions is not discussed here because of the complicated nonlinear character of the reduction procedure [*Tammet*, 1998b].

Table 3. Statistics of negative/positive small ion concentrations (cm^{-3}). Number of measurements: 8615 hourly average spectra.

Mobility, $cm^2\,V^{-1}\,s^{-1}$	Mean	Median	Maximum	Lower Quartile	Upper Quartile	Relative s.d.
2.51–3.14	12/7	10/7	67/42	8/5	13/8	0.45/0.51
2.01–2.51	33/19	29/17	180/99	24/14	37/23	0.41/0.44
1.60–2.01	56/45	51/41	265/207	44/34	62/51	0.37/0.38
1.28–1.60	59/69	55/64	252/303	44/54	68/79	0.36/0.35
1.02–1.28	42/69	40/66	157/284	28/54	54/83	0.44/0.36
0.79–1.02	24/41	21/39	107/154	12/29	33/51	0.59/0.40
0.63–0.79	13/16	11/14	83/74	6/10	18/21	0.68/0.50
0.50–0.63	8/8	6/7	58/45	4/5	9/10	0.72/0.59
0.50–3.14	245/274	231/259	990/1167	183/210	290/319	0.36/0.35
1.28/1.00–3.14	159/209	148/196	737/928	124/162	178/238	0.37/0.35
0.50–1.28/1.00	86/65	78/61	361/239	50/44	115/82	0.51/0.43

The frequency distributions of the concentration of positive small ion categories (original fractions P_1–P_8, classes of small and big clusters and their total concentration) are approximately lognormal, and can be derived from the moments of distribution presented in Table 3. In the case of positive small cluster ions, the distribution of the largest extreme gives a closer approximation, and in the case of big cluster ions, the gamma distribution is closer. The concentration of negative small cluster ions behaves similarly, but the concentration of negative big cluster ions shows different character. Its frequency distribution is extremely asymmetric, with a maximum at about 45 cm^{-3}, below the lower quartile (see Table 3).

The concentration and the mean mobility of small ions mainly determine the conductivity of air. The average negative and positive polar conductivities are nearly equal; that can be explained by the relatively high position (5 m) of air inlet and the screening of the electric field by trees surrounding the building where the instrumentation is located. The average polar conductivities calculated according to the entire measured mobility interval of 0.00032–3.2 $cm^2V^{-1}s^{-1}$ are $\lambda_{-} = 6.18 \pm 2.14$ fS m^{-1} and $\lambda_{+} = 6.18 \pm 2.14$ fS m^{-1}. These polar conductivities are nearly equal with those of small ions $\lambda_{-s} = 5.96 \pm 2.11$ fS m^{-1} and $\lambda_{+s} = 5.97 \pm 2.11$ fS m^{-1}; the increased average mobility of negative small ions as compared to that of positive ions entirely compensates differences in the concentration, on average. The ratio of positive ion concentration to that of negative ions (coefficient of unipolarity) is 1.127 ±0.074, and the ratio of the average mobility of negative ions to that of positive ions is 1.124 ±0.049.

The conductivity (also small ion concentration) underwent decrease since 1985–1986 from about 9 fS m^{-1} to 6 fS m^{-1} in 1993–1994. The average natural mobilities of small air ions are nearly the same for all three measuring periods. *Klimin and Shvarts* [1996] have found that conductivity has regularly decreased since 1920 to nowadays, probably due to the increase in the concentration of fine aerosol particles (10–200 nm) as a result of man-made pollution.

The concentration of small ions was found to be dependent on the concentration of heavy large ions (aerosol particles), the stability of air close to the ground and the state of the soil (probably due to the variation of the ionization rate caused by changes in radon concentration). The diurnal and annual variations of ion classes, as well as the correlation between small and large ions are discussed in the respective sections.

4.4. Average characteristics and variability of intermediate ions

The statistical characteristics of intermediate ion concentrations are presented in Table 4. The average concentration of intermediate ions is relatively low, about 50 cm^{-3}, but occasionally very high concentrations up to 900 cm^{-3} were recorded around local noon. The bursts occurred during the time of intensive sunlight, with a duration of 6–10 hours, probably due to photochemical nucleation process. The correlation coefficient between the total concentrations of positive and negative intermediate ions is 97%.

In contrast to the light intermediate ions (0.32–0.50 $cm^2V^{-1}s^{-1}$), the fraction concentrations of which are nearly equal, the heavy intermediate ions (0.034–0.293 $cm^2V^{-1}s^{-1}$) show a rise in concentration toward lower mobilities. During the days with intermediate ion bursts, the ratio of concentrations of heavy to light fraction varies from about 3 to 7. The frequency distributions of the concentration of light intermediate ion fractions are asymmetric, approximately lognormal, because of the burst events. The concentrations of heavy intermediate ion fractions are roughly lognormally distributed because of extremely high values recorded during the burst events.

The maximum concentrations of intermediate ions of negative polarity are higher than those of positive polarity. Sometimes during the burst events the total concentration of negative intermediate ions exceed that of positive polarity by about 100–150 cm^{-3}.

Table 4. Statistics of the negative/positive intermediate ion concentrations (cm^{-3}). Number of measurements: 8615 hourly average spectra.

Mobility, $cm^2 V^{-1} s^{-1}$	Mean	Median	Maximum	Lower Quartile	Upper Quartile	Relative s.d.
0.40–0.50	5/5	4/5	49/48	3/3	6/6	0.82/0.73
0.32–0.40	3/4	2/3	52/37	1/2	4/5	1.15/0.80
0.25–0.32	3/2	2/2	56/42	1/1	3/3	1.21/1.10
0.150–0.293	8/7	5/5	155/116	4/4	8/7	1.19/1.08
0.074–0.150	12/12	8/8	279/250	6/6	12/12	1.28/1.23
0.034–0.074	25/25	18/18	447/437	14/14	25/25	1.14/1.16
0.034–0.50	57/55	40/41	1008/874	31/32	58/57	1.08/1.03
0.25–0.50	11/12	9/10	157/116	6/7	13/13	0.95/0.78
0.034–0.293	45/44	31/31	851/761	24/24	45/44	1.14/1.13

4.5. Average characteristics and variability of large ions

The statistical characteristics of large ion concentrations are presented in Table 5. As compared with intermediate ions, the frequency distributions of the concentration of light large ion categories (original fractions 15–17 and their total concentration) are closer to lognormal. As an exception, the frequency distribution of the fifteenth fraction shows similarity to that of intermediate ions. In all cases the frequency distributions are asymmetric because of high outliers. The frequency distributions of the concentration of heavy large ion categories (original fractions 18–20 and total concentration) are close to gamma distribution. There is no substantial difference between large ions of negative and positive polarity.

The whole range of large ions 0.00041–0.034 $cm^2V^{-1}s^{-1}$ (diameters 7.4–79 nm) can be divided into two classes with the mobilities of 0.0042–0.034 $cm^2V^{-1}s^{-1}$ (7.4–22 nm) and 0.00041–0.0042 $cm^2V^{-1}s^{-1}$ (22–79 nm) called by convention as light large ions and heavy large ions, respectively. In general, the ratio of concentrations of light large and heavy large ions is low, about 0.2, but in some cases (nucleation events) the ratio may be extremely high up to about 2.5. These two categories show different behavior in the case of the bursts of intermediate ions, when enhanced concentrations of light large ions have also been recorded. As a rule the concentration of heavy large ions decreases before the burst of intermediate ions [*Hõrrak et al.*, 1998b].

Examining the time-series of heavy large ion concentration, it was found that besides short time variations (bursts with duration less than 1 day), this fraction also has a variation of 4–6 days (typical synoptical period) and even long time trends (1–2 weeks, or more). The short time variations have higher amplitudes of 2000–4000 cm^{-3}, that is, about 10 times higher than the amplitude of average diurnal variation. The short time variations are probably caused by pollutant transport processes.

Koutsenogii [1997] concluded that submicron particles with the modal diameter of 170 nm represent regional and global aerosols. Such particles have the longest residence time of about 10 days and can be transported over distances up to 8000 km. The heavy large ions as particles with diameters of 23–80 nm have the residence times of 1.5–6 days [*Jaenicke*, 1984]; they are transported by air masses, are accumulated in the atmosphere, and are removed from the atmosphere preferentially by precipitation and thermal diffusion. The estimates of decay constants (similar to the residence times) given by *Hoppel et al.* [1990] for marine boundary layer are considerably smaller, about 10–30 hours, considering diameters of 20–80 nm. The latter estimates also take into account the loss of particles in cloud processes.

Table 5. Statistics of the positive large ion concentration (cm^{-3})

Mobility, $cm^2 V^{-1} s^{-1}$	Mean	Median	Maximum	Lower Quartile	Upper Quartile	Relative s.d.
0.0016–0.034	45	34	810	25	46	1.03
0.0091–0.0205	96	74	1684	53	107	0.97
0.0042–0.0091	157	128	1852	91	182	0.79
0.00192–0.0042	282	251	2172	171	344	0.60
0.00087–0.00192	493	460	2626	321	627	0.47
0.00041–0.00087	610	562	3311	380	792	0.50
0.00041–0.034	1783	1578	8099	1116	2103	0.47
0.0042–0.034	297	238	4279	168	336	0.84
0.00041–0.0042	1385	1295	6908	910	1751	0.47