7. THE MEAN MOBILITY OF SMALL AIR IONS

7.1. Average characteristics

In the continuously ionized atmosphere the mobility spectrum of natural small ions presents a mixture of ions of different ages and different chemical composition, evolving via ion-molecule reactions [*Mohnen*, 1977]. Such a mobility spectrum is almost continuous (without separated spectral lines). One way to study the evolution of continuous mobility spectra is to use an integral parameter, the mean mobility of small ions, instead of spectral presentation.

The mean natural mobility of small air ions is calculated by averaging over the mobility interval from 0.5 to 3.2 cm^{2}V^{-1}s^{-1}. The statistical characteristics of the mean mobility of positive and negative small ions are presented in Table 10. The average values of mean mobility are comparable with those found by *Dhanorkar and Kamra* [1992], 1.37 and 1.25 cm^{2}V^{-1}s^{-1}, and *Tammet et al.* [1992], 1.56 and 1.36 cm^{2}V^{-1}s^{-1} for negative and positive polarity, respectively. The average values of reduced mobility at STP, as reported by *Mohnen* [1977], are 1.24 and 1.14 cm^{2}V^{-1}s^{-1} for negative and positive ions, respectively. In all cases the ratio of negative to positive mobility is about 1.1. The polar mean mobilities at Tahkuse were closely correlated, the correlation coefficient was 80%. In general, the correlation coefficients varied in a range from 72% to 92%, considering various months. Lower correlation coefficients of about 56–59% were recorded in November, December and February, when the variability of the mean mobility was about 1.5–2 times less compared with other months.

The mean mobility of negative small ions shows higher variability than that of positive ions. The frequency distribution of the mean mobility of positive small ions is close to normal one, but that of negative small ions is considerably asymmetric, with maximum at about upper quartile 1.6 cm^{2}V^{-1}s^{-1} (Figure 21).

The dependence of the mean mobility on wind direction shows that the mean mobility of positive small ions increases from about 1.32 to 1.41 cm^{2}V^{-1}s^{-1} and that of negative ions from 1.43 to 1.62 cm^{2}V^{-1}s^{-1} on an average when wind turns from north to south.

Table 10. Statistics of the natural mean mobility of small ions (cm^2 V^{-1} s^{-1}). Number of measurements: 8615 hourly average spectra.

	Mean	Median	Min	Max	Lower Quart.	Upper Quart.	Std. Dev.	Rel.Std. Dev
Positive ions	1.36	1.36	1.16	1.59	1.32	1.40	0.064	0.05
Negative ions	1.53	1.55	1.15	1.78	1.46	1.61	0.106	0.07
Ratio of mobilities	1.12	1.13	0.95	1.29	1.09	1.16	0.049	0.04

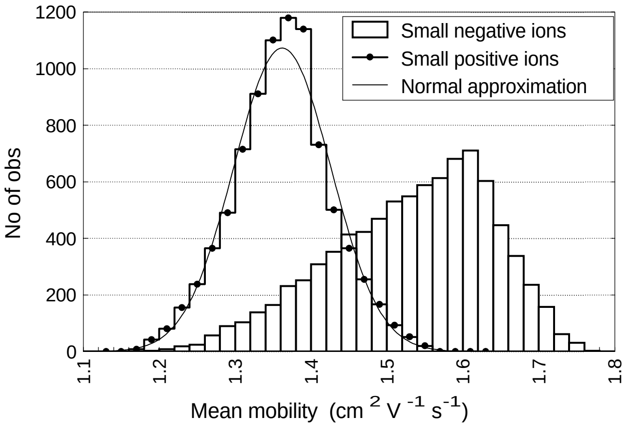


Figure 21. The frequency distributions (histograms) of the mean mobility of positive and negative small ions.

It was found that in the first approximation the mean mobility of small ions is proportional to the ratio of the concentration of small cluster ions (1.3–3.14 cm^{2}V^{-1}s^{-1}) to big cluster ions (0.5–1.3 cm^{2}V^{-1}s^{-1}). The ratio of the concentrations correlated closely with the mean mobility. The correlation coefficients are 97% and 94% for positive and negative polarity, respectively. The nonlinear regression (logarithm from the ratio of the concentrations) shows higher correlation coefficients with the mean mobility, about 99%. Despite the observed nonlinearity, the general regularities of the mean mobility (diurnal and annual variation, correlation with meteorological parameters) discussed hereinafter could be interpreted also in terms of the ratio of small to big cluster ion concentrations.

7.2. Time series of the mean mobility

The time series analysis revealed the correlation between the mean mobility of small air ions and meteorological parameters. Drastic changes in meteorological parameters are related to the exchange of air masses, and diurnal variations, in its turn, related to the dynamics of atmospheric boundary layer.

During anticyclonic weather conditions the mean mobility of small ions could have a diurnal variation. For example, the regular diurnal variation of the mean mobility was recorded in the beginning of September 1993 (Figure 22), during which the mean mobility correlated closely with air temperature (the correlation coefficient was about –48% for both polarities). Conformably with the bursts of intermediate ions, there was no diurnal variation of the mean mobility in cloudy and rainy days (September 15–17 and 21–23). The amplitude of the diurnal variation of the mean mobility decreased when a series of bursts of intermediate ions took place (September 10–14). Regular diurnal variations in September (1–14, 18–20 and 25–30) were connected with the inflow of cool air (marine Arctic air masses) from the north [*Berliner Wetterkarte*, 1993-1994].

Regular diurnal variations of the mean mobility and air temperature correlated oppositely (negatively) also in July, while the long-term variations in air temperature and absolute humidity showed positive correlation with the mean mobility (especially considering negative small ions). The covariation was recorded during successive alternation (and subsequent transformation) of Polar air masses and Subtropical air masses.

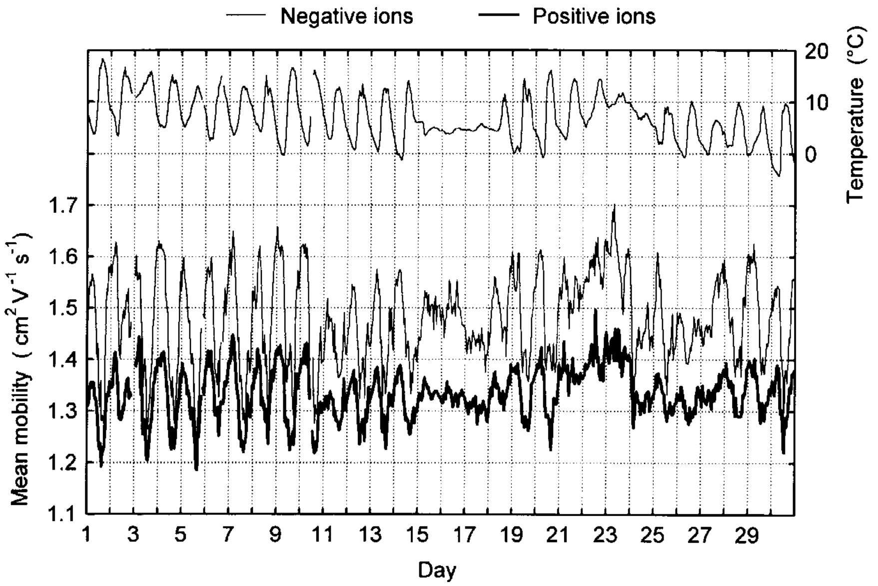


Figure 22. Variation of the mean mobility of negative and positive small ions and air temperature at Tahkuse, September 1–30, 1993.

In wintertime, when the diurnal variation of the mean mobility was weak or entirely absent, the variation of the mean mobility correlated with the type of air mass. Especially in January, a clear alternation of air masses (followed by air temperature and absolute humidity) and a variation of the mean mobility was observed (Figure 23). The decrease in the mean mobility on January 4, 9, 16, 24 and 29 was connected with the inflow of marine Arctic (or transformed into Polar) air masses, whereas the high mean mobility was characteristic to marine Polar air masses. The inflow of warmer marine Polar air masses from the westerly directions was related to the activity of cyclones, while anticyclones commonly formed in cool Arctic air masses coming from the north.

Similar oscillation of the mean mobility with a period of about 3–4 days recorded in October 1993 was also correlated with the alternation of marine Polar and marine Arctic air masses. A low concentration of heavy large ions and a respectively higher concentration of small ions also characterized the periods of low mean mobility typical to Arctic air masses.

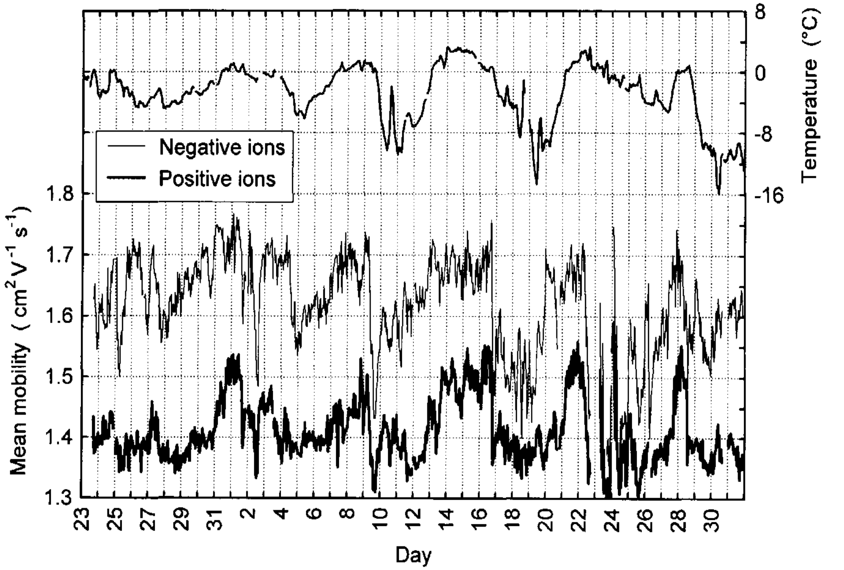


Figure 23. Variation of the mean mobility of negative and positive small ions and air temperature at Tahkuse from December 23, 1993 to January 31, 1994.

The measurements of aerosol particle size spectra from April 14 to May 16, 1994 indicated that the mean mobility correlated with the accumulation mode aerosol particle (100–500 nm) content in air (Figure 24). The correlation coefficients were 63% and 52% for the mean mobility of negative and positive ions, respectively. The high mean mobility and a high concentration of aerosol particles of 100–500 nm (also heavy large ions) were recorded during April 21–29, when Polar and Subpolar air masses were present. The Arctic air masses present during April 18–21 and May 1–4 were characterized by a very low concentration of accumulation mode aerosol particles and a lower diurnal average mean mobility.

Anticyclonic weather conditions prevailed during both periods (April 21–29 and May 2–12), and air temperature showed a considerable amplitude of diurnal variation of about 10–20 °C, but only a weak diurnal variation of the mean mobility of positive small ions can be found during the April period in Figure 24. On May 1, the inflow of a cool and clean Arctic air mass occurred after the passage of a cyclone. The drop in diurnal average air temperature was from about 10 °C to 5 °C. A period of a regular diurnal variations of the mean mobilities (especially of positive small ions), as well as the bursts of intermediate ions followed after that.

In general, we cannot distinguish between the effects of meteorological parameters on the mean natural mobility of small ions and those associated with the origin and composition of air masses without having detailed information about the air masses. Below only general regularities of the mean mobility of small air ions are discussed.

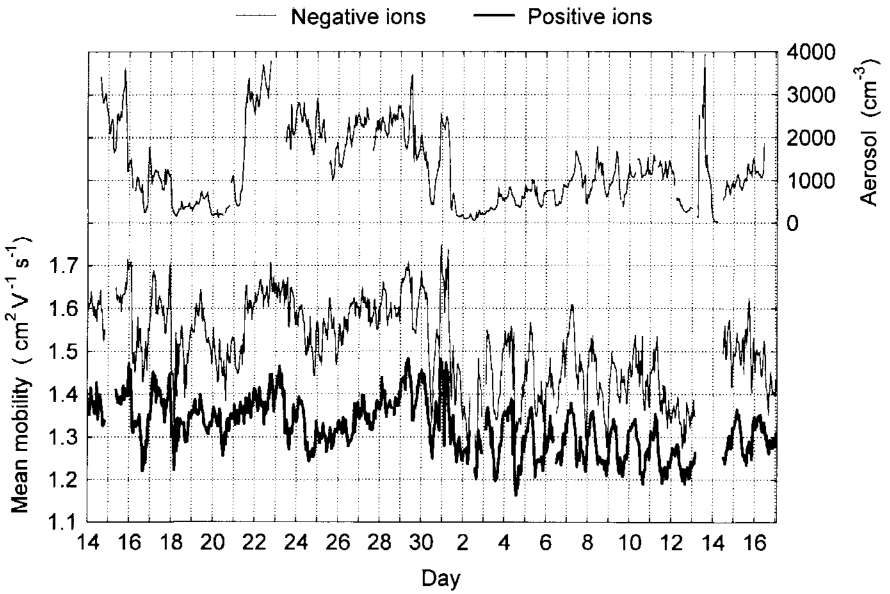


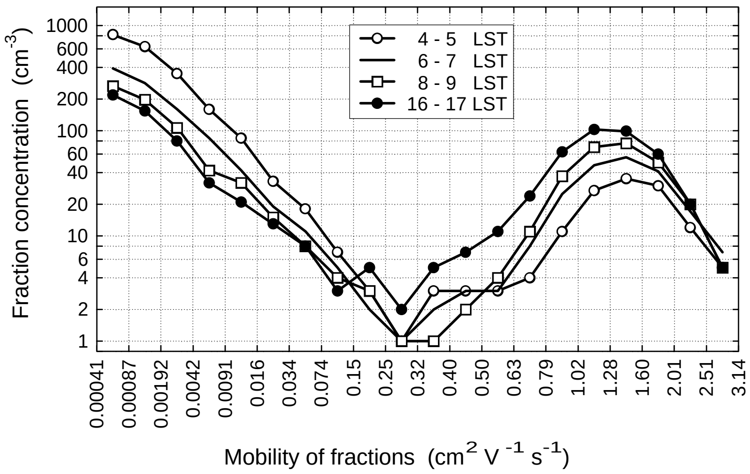
Figure 24. Variation of the mean mobility of negative and positive small ions and accumulation mode aerosol particle (100–500 nm) concentration at Tahkuse from April 14 to May 16, 1994.

7.3. The mean mobility and the evolution of small ion mobility spectra

The examples of the evolution of small ion mobility spectra that show changes in the natural mean mobility are presented in Figures 25 and 26.

The first type of the evolution of small ion mobility spectra caused the variation in the mean mobility preferentially during the cold season when the ionization rate is expected to be nearly constant. The first type mostly shows changes in the low mobility flank of spectra (see Figure 25). The concentration of small ions increases gradually and that of heavy large ions decreases.

a) Positive ion mobility spectra.



b) Negative ion mobility spectra.

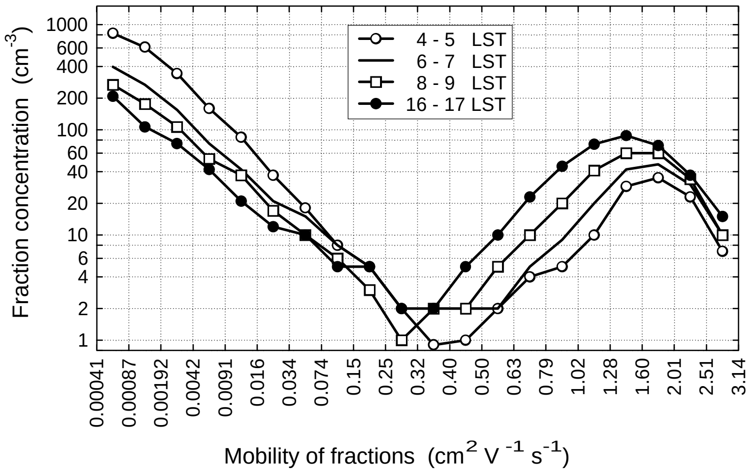


Figure 25. Evolution of air ion mobility spectra at Tahkuse, January 9, 1994.

The mode of small ion spectra shifts by about one mobility fraction and the spectrum expands towards lower mobilities at daytime (especially considering negative small ions). Accordingly, the mean mobility of negative small ions in Figure 25 decreases from about 1.70 cm^{2}V^{-1}s^{-1} at 4–5 LST to 1.44 cm^{2}V^{-1}s^{-1} at 16–17 LST, and the mean mobility of positive small ions from 1.50 to 1.31 cm^{2}V^{-1}s^{-1}. The mean mobility increases again towards nighttime, showing changes in the mobility spectra in the reverse order. During the process the mean mobility is correlated negatively with the concentration of small ions and positively with the concentration of heavy large ions.

The evolution of small ion mobility spectra probably reflects the growth of cluster ions via chemical reactions during aging. The aging of ions is expected, since the increment in the concentration of big cluster ions followed the decrease in the heavy large ion concentration (the lifetime of cluster ions is inversely proportional to the aerosol particle diameter concentration in air). The low diameter concentration of aerosol particles also favors the presence of trace gaseous species in the air (because of lower sticking probability) that could lead to the formation of cluster ions of large sizes.

Such an evolution was recorded in the course of a diurnal cycle, as well as during drastic changes (drop down, rapid increase) in the mean mobility, which probably were related to the exchange of air masses. Sometimes, the burst of intermediate ion concentration followed the decrease in the mean mobility.

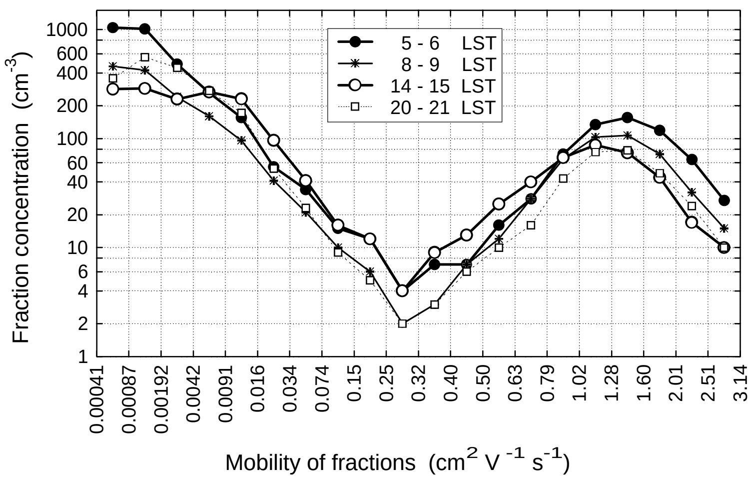
The second type of the evolution of small ion mobility spectra (Figure 26) was characteristic to the warm season, for the periods of anticyclonic weather (typically inversions at nighttime and intensive mixing in the afternoon). The variation in the mean mobility clearly reflects the balance of the concentrations of small clusters (1.3–3.14 $cm^2V^{-1}s^{-1}$) and big clusters (0.5–1.3 $cm^2V^{-1}s^{-1}$) during a diurnal cycle. In contrast to the first type of evolution, the second type showed a high mean mobility when the concentration of small ions was high – during the nighttime calms (expected effect of radon accumulation on the ionization rate). In Figure 26 the mean mobility of negative small ions decreases from about 1.68 $cm^2V^{-1}s^{-1}$ at 5–6 LST to 1.28 $cm^2V^{-1}s^{-1}$ at 14–15 LST, the mean mobility of positive small ions from 1.46 to 1.24 $cm^2V^{-1}s^{-1}$, respectively. The mode of positive small ion spectra shifts by about one mobility fraction and that of negative small ions by two mobility fractions (more than the first type of evolution commonly shows). A shift in the spectral mode towards lower mobilities followed a decrease in the heavy large ion concentration, just as in the case of the first type of evolution.

The second type of evolution shows a distinct diurnal variation of the mean mobility that correlated with meteorological parameters. The ratio of the concentration of big to small cluster ions shows maximum in the afternoon, when the fluxes of trace gases from the soil, and those emitted by plants, and the activity of photochemical processes are expected to be intensive. The photochemical processes are known to produce ions of high molecular weight [*Eisele and Tanner*, 1990; *Tanner and Eisele*, 1991; *Nagato et al.*, 1999].

In the warm season, besides the evolution of the first or the second type also the combinations of these two can be found, probably because of the variation in the ratio of ionization rate to aerosol particle content in air.

As discussed earlier, the burst of intermediate ions can also modify the small ion spectrum below of about 1 $cm^2V^{-1}s^{-1}$; the generated big cluster ions reduce the mean mobility of small ions.

a) Positive ion mobility spectra.



b) Negative ion mobility spectra.

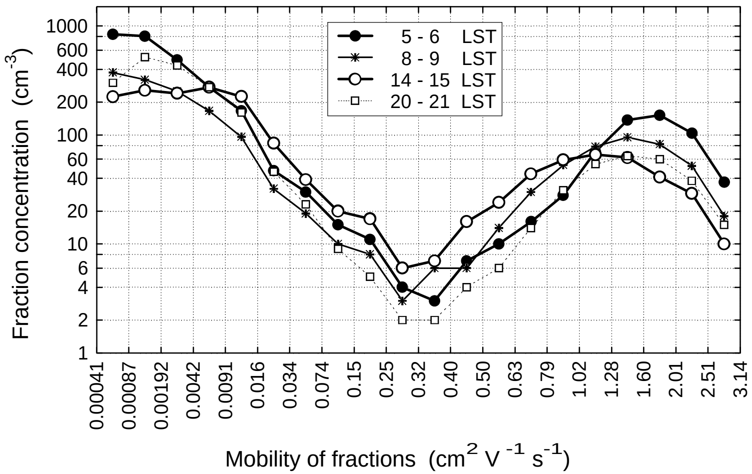


Figure 26. Evolution of air ion mobility spectra at Tahkuse, August 17, 1994.

7.4. Diurnal variation

The diurnal variation of the natural mean mobility of small air ions was significant during anticyclonic weather. It was more frequently recorded in the warm season compared with the cold season.

The average diurnal variations of the mean mobility of small ions in the warm season from May to September are depicted in Figure 27. The median mean mobilities had maxima of 1.39 and 1.59 $cm^2V^{-1}s^{-1}$ in the nighttime and minima in the afternoon of 1.29 and 1.42 $cm^2V^{-1}s^{-1}$ for positive and negative small ions, respectively. The amplitude of the average diurnal variation of the median mean mobility is about 10% of the average; it is about 1.7 times higher in the case of negative ions compared to positive ions. The ratio of negative to positive mean mobility medians is about 1.1 all through the day.

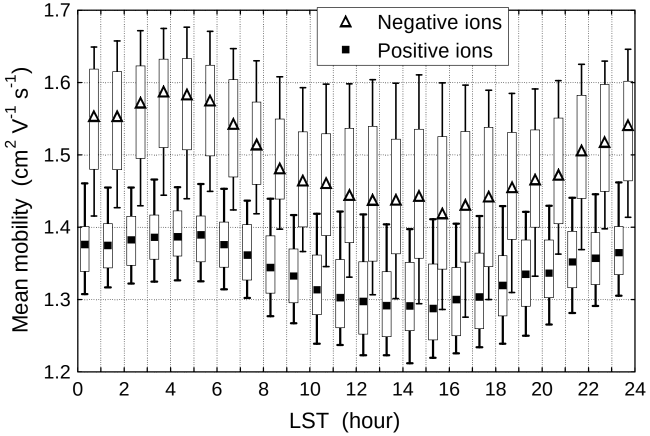


Figure 27. Average diurnal variation of the natural mean mobility of small positive and negative ions in the warm season (Sept. 1993 and May – Sept. 1994). Descriptive statistics: median, box (25% and 75%) and whiskers (10% and 90% quantiles).

The higher amplitudes of the diurnal variation of the mean mobility of negative and positive small ions were 0.34 and 0.20 $cm^2V^{-1}s^{-1}$ (recorded on the same day) in September 1993, and 0.40 and 0.21 $cm^2V^{-1}s^{-1}$ in May 1994. The both were recorded during the days without any bursts of intermediate ions. The higher amplitudes of diurnal variations found in the presence of the bursts of intermediate ions were about 1.5–2 times smaller. Perhaps, this is related to the peculiarity of the nucleation process – the big clusters (being above the critical size for nucleation of about 1.2 nm) rapidly grow toward large sizes of stable particles [*Raes and Janssens*, 1985].

In the warm season the average diurnal variation of the mean mobility is correlated positively with the average diurnal variations of the concentrations of small ions and heavy large ions and negatively with intermediate ions. If the mean mobility has a diurnal cycle, then it is correlated negatively with relative humidity and positively with air temperature and wind speed, but not vice versa.

In the cold season during the period from November to February, the average diurnal variation of the mean mobility was very weak (amplitude below 0.05 $cm^2V^{-1}s^{-1}$), as well as the average diurnal variation of meteorological parameters. The median of the mean mobility stayed at a high level all through the day, at about 1.38 and 1.60 $cm^2V^{-1}s^{-1}$ for positive and negative small ions, respectively. These medians are comparable with the nighttime high values of the mean mobilities recorded in the warm season. A weak average diurnal variation of the mean mobility was also in accordance with a few bursts of intermediate ions from November to February. The increase in the average diurnal variation in March (amplitude of about 0.1 and 0.05 $cm^2V^{-1}s^{-1}$ for negative and positive small ions, respectively) was related to the beginning of the period of regular bursts of intermediate ions. The higher amplitudes of the diurnal variation in the polar mean mobilities in March were about 0.2 and 0.15 $cm^2V^{-1}s^{-1}$, respectively.

In general, the diurnal variation of the mean mobility of small positive ions was more regular (more frequently recorded) compared to the mean mobility of negative small ions. That can be followed also in Figure 27 considering higher quantiles (75% and 90%).

The general shape of the average diurnal variation of the mean mobility is the same as previously measured at Tahkuse [*Tammet et al.*, 1987b; 1992; *Hõrrak et al.*, 1988b]. The measurements of small ion mobility spectra by Misaki [*Misaki*, 1961b; *Misaki et al.*, 1972] showed no remarkable change in the mobility distribution of small ions through a day.

The ion composition measurements [*Eisele*, 1989a; *Eisele and Tanner*, 1990] showed a clear diurnal variation of negative cluster ions: bisulphate ions $HSO_4^-(H_2SO_4)$ dominated in the daytime due to the photochemical formation of gas phase H_2SO_4, while $NO_3^-(HNO_3)$ ions prevailed during the nighttime. Characteristically, the low-mass part of the mass spectra (below about 200 u) dominated in the nighttime but the high-mass part (up to 700 u) often had large peaks in the daytime. Some indications of the diurnal variation of positive ion mass spectra are described in [*Tanner and Eisele*, 1991]. These variations are thought to result from the formation of reactive photolysis products, which attach to ion clusters giving them rise to lager masses.

Thus the potential factors that could be responsible for the diurnal variation of the mean natural mobility of small ions are solar radiation, trace species in the air (including aerosol particles and radon), and also the mixing state of boundary layer air (indirect factor).

7.5. Annual variation

The annual variations of the mean natural mobilities of small positive and negative ions depicted in Figure 28 are similar to each other. The mean natural mobility of small ions in winter is higher than in summer. The averaged maximum and minimum values and their standard deviations recorded in December and May are $k_{-\mathrm{Dec}} = 1.63 \pm 0.07$ cm^{2}V^{-1}s^{-1}, $k_{+\mathrm{Dec}} = 1.40 \pm 0.04$ cm^{2}V^{-1}s^{-1} and $k_{-\mathrm{May}} = 1.44 \pm 0.09$ cm^{2}V^{-1}s^{-1}, $k_{+\mathrm{May}} = 1.30 \pm 0.05$ cm^{2}V^{-1}s^{-1}. The ratio of annual maximum and minimum is about 1.1.

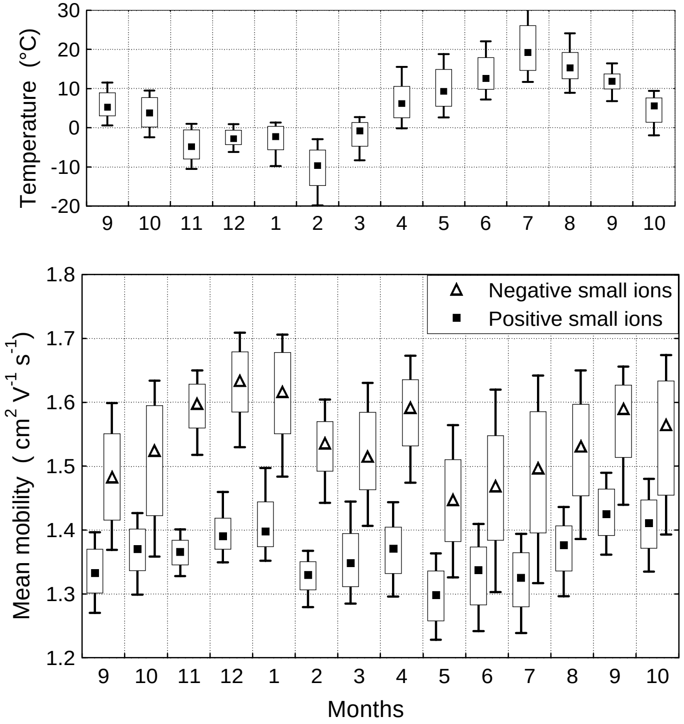


Figure 28. Annual variation of the natural mean mobility of small positive and negative ions (0.5–3.14 cm^2 V^{-1} s^{-1}) and air temperature from September 1993 to October 1994. Descriptive statistics: median, box (25% and 75%) and whiskers (10% and 90% quantiles).

The overall shape of the annual variation of median mean mobility is not in accordance with the annual variation of meteorological parameters or any other variable measured. The reduction of the natural mean mobility to standard pressure did not affect considerably the shape of annual variation. The first considerable decrease in the mean mobility in February followed the drop in the monthly mean temperature from about –2 °C in January to –10 °C in February (see Figure 28). The drop in temperature from about +4 °C in October to –5 °C in November did not significantly affect the mean mobility (expecting positive correlation between the variables). The next decrease in the mean mobility in May was in accordance with the beginning of the early vegetation and the period of intensive bursts of intermediate ions. When the supposed influence of the bursts was eliminated, the annual variation still retained its shape.

The reduction of the mean mobility to the standard temperature, assuming the simple proportional Langevin rule or temperature dependence of $T^{0.6}$ (as average for small ions proposed by *Tammet* [1998b]), leads to more clear character of annual variation. The annual variations of reduced mobilities showed maxima in the cold season (November–February) and minima in the warm season (May–July). The reduced mobilities of annual maxima and minima are 1.63 and 1.42 cm^{2}V^{-1}s^{-1} for negative small ions and 1.4 and 1.27 cm^{2}V^{-1}s^{-1} for positive small ions. In the first approximation, the annual variation of the mean mobility reduced to standard conditions correlated negatively with air temperature. That is not in accordance with the expected independence of reduced mobilities and air temperature. The contradiction probably refers to the different nature of cluster ions in the warm and cold season. Some of the peculiarities of the annual variation are still open, because the weather was rather variable, far from the long-term average climatic standard. In general, the reduced mobilities showed similar annual variation as recorded earlier, in 1985–1986, at Tahkuse [*Hõrrak et al.*, 1988b].

7.6. Correlation of the mean mobility with meteorological parameters

The correlation coefficients between the natural mean mobility of small ions and meteorological parameters (air temperature, relative and absolute humidity) are presented in Table 11. In general, the correlations are stronger in the case of the mean mobility of positive small ions than with negative ions. The correlation of the mean mobility of negative small ions with air temperature and absolute humidity is weak (relative humidity is an exception), and only some of the correlation coefficients calculated for monthly periods are many times higher than the critical correlation coefficient (absolute value of about 8%). Hence, the conclusions drawn in this section can apply to the mean mobility of negative small ions with certain reservations.

The correlation of the natural mean mobility of small ions and air temperature is complicated. If the mean mobility had a diurnal cycle, it was correlated negatively with air temperature (e.g. May–August). During long-term variations (trends) there could be different behavior. According to the proportion of diurnal and long-term variations (their frequency of occurrence and amplitude) the correlation coefficients in different monthly periods varied in the ranges of –44%…+30% and –66%…+59%, considering the mean mobility of negative and positive small ions, respectively (Table 11). The correlation coefficients calculated for the whole period are –19% and –26%, respectively.

The positive correlation found in December, January and March (also in October 1993) was probably not the real temperature dependence of the mobility of cluster ions, but an artifact caused by the influence of different air masses on the composition of cluster ions (see below).

Table 11. The correlation coefficients (%) of the natural mean mobility of positive/negative small ions with relative and absolute humidity, air temperature, the concentrations of heavy large ions, light intermediate ions and heavy intermediate ions. The absolute value of critical correlation coefficient at a confidence level of 95% is 8%, considering monthly periods, and about 3% considering annual period. Warm season (Sept. 1993, May – Sept. 1994), cold season (Nov. 1993 – March 1994).

Period	Rel. Hum.	Abs. Hum.	Temp.	Large ions	Light int. ions	Heavy int. ions
September 1993*	67/66	41/35	-28/-31	50/47	-37/-39	-38/-35
October	44/32	47/48	21/ 28	46/65	-48/-49	-37/-34
November	56/51	48/20	22/ -4	-2/ 9	-34/-42	-36/-40
December	47/11	64/13	59/ 10	26/42	-6/-33	6/ -8
January 1994	68/67	65/46	50/ 29	33/43	-20/-38	0/-12
February	37/34	-16/ -7	-25/-16	38/40	-37/-52	-30/-45
March	63/56	56/36	20/ 3	11/26	-39/-49	-30/-39
April	65/33	24/36	-41/ -1	44/57	-28/-39	-17/-28
May	60/22	26/14	-54/-16	29/47	-50/-38	-37/-21
June	68/49	11/17	-55/-35	49/60	-57/-56	-33/-24
July	68/48	31/43	-40/-15	50/56	-8/-50	-4/-13
August	66/56	-24/ -6	-66/-44	20/40	-2/-30	8/ -2
September	40/40	27/32	-6/ 1	43/51	-31/-36	-18/-22
October	41/17	32/ 8	1/ -8	55/64	-46/-41	-35/-26
Warm season	69/51	27/29	-29/-14	26/43	-35/-42	-21/-20
Cold season	61/53	60/34	38/16	-2/16	-33/-47	-25/-36
Entire period	63/47	8/ -5	-19/-26	18/35	-36/-47	-24/-29

* Period September 11 – September 30, 1993.

The real temperature dependence of the mobility of a single cluster ion of the same chemical composition (structure) observed in the laboratory experiments could scarcely be followed in real atmosphere. The temperature variation of the cluster ion chemical composition obscures the physical effect. The temperature effect on the composition and structure of cluster ions was found to be significant also by *Nagato et al*. [1999]. Despite all this, the effect of temperature could be significant, considering the annual variation of the mean mobility. The opposite correlation between the natural mean mobility (or reduced to STP) and air temperature above 0 °C was found also formerly at Tahkuse in 1985–1986 [*Tammet et al*., 1992; *Salm et al*., 1992].

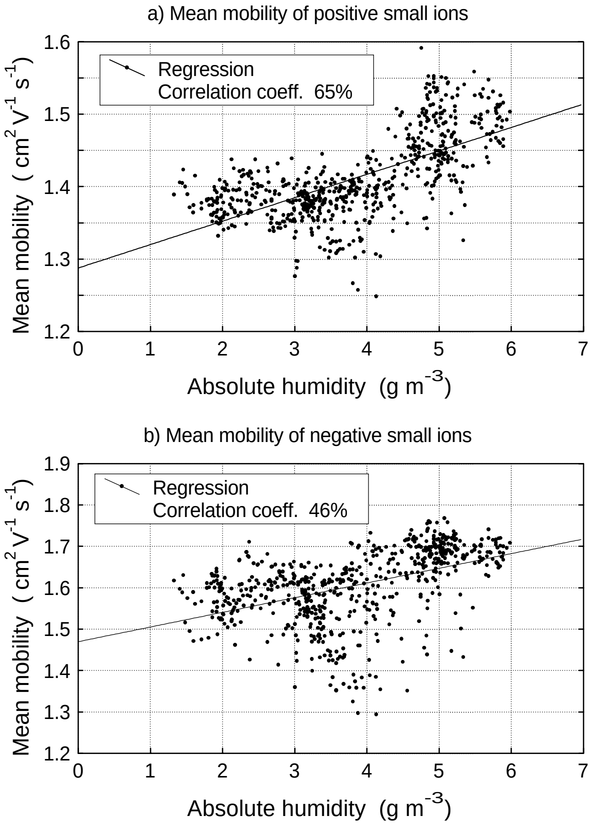


Figure 29. Scatterplots of the mean mobility of small ions of positive polarity (a) and negative polarity (b) with absolute humidity at Tahkuse, January, 1994.

The absolute humidity showed a substantial positive correlation with the mean mobility of small (positive) ions from October to March (February was an exception), when diurnal variations of both quantities were weak and the variations were found to be correlated with changes in air masses. The scatterplots between the mean mobility and absolute humidity revealed various diffusive groups (classified by the absolute humidity) that caused the correlation (see Figure 29). The relatively separated group with the high average mobility of positive small ions and the absolute humidity more than 4–4.5 g m^{-3} (placed on the correlation field) was found in December, January and March. Speaking of the mean mobility of negative small ions in Figure 29, the data points are more scattered. This separate group with high mean mobility is characterized also by high relative humidity (more than 90%) and high (for the cold season) temperature –1…3 ºC. This group probably corresponds to the periods of intensive precipitation (snowfall and sleet), often recorded during these months. In this connection, the cyclonic weather conditions (possibly precipitation) were responsible for the high average mobility of small ions.

During the warm season the correlation with the absolute humidity was weak in general, in part due to the average diurnal variation of the absolute humidity that showed a modest opposite variation to the mean mobility. The higher positive correlation coefficients found in July were caused by long-term variations. The groups with different average mean mobilities (classified by the absolute humidity) were found also in the warm season (e.g. in September) and probably corresponding to different air masses.

The mean mobility of negative and positive small ions was correlated with relative humidity to a larger extent through the whole year compared to air temperature and the absolute humidity (Figure 30).

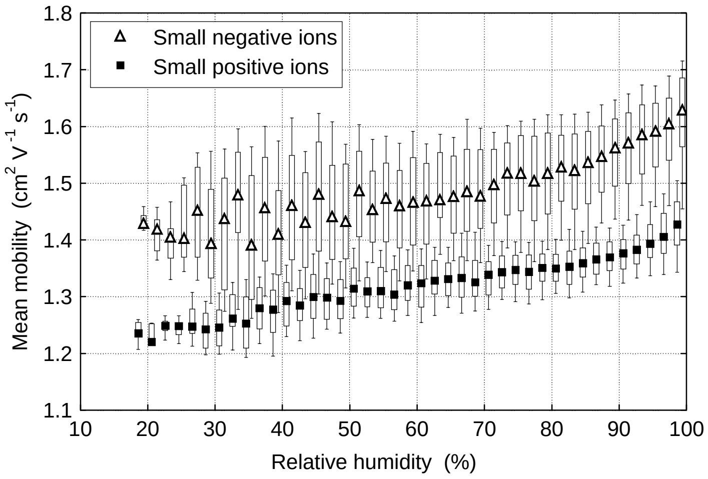


Figure 30. The box plot of the mean mobility of positive and negative small ions versus relative humidity. September 1993 – October 1994. Statistics: median, box (25% and 75%) and whiskers (10% and 90% quantiles). Statistics of positive and negative ions are shifted within classes for better presentation.

The correlation coefficients calculated for the whole period are 47% for the mean mobility of negative small ions and 63% for positive small ions. Considering different monthly periods the correlation coefficients vary in the ranges of 11–67% and 37–68%, respectively. The lowest correlation coefficient between the mean mobility of negative small ions and relative humidity (11%) was recorded in December, when relative humidity showed the least variability (80% of measurements higher than 90%).

During the warm season, the correlation between the mean mobility and relative humidity was stronger than that with air temperature, probably because the expected real factor, solar radiation, correlated closely with relative humidity during a diurnal cycle while the air temperature could have considerable trends.

7.7. Correlation of the mean mobility with the fraction concentrations of mobility spectra

The correlation coefficients of the mean mobility of small ions with the fraction concentrations of mobility spectra are depicted in Figure 31. In the warm season (May–September) the mean mobility correlated positively with the fraction concentrations of small cluster ions (1.3–3.14 cm^{2}V^{-1}s^{-1}) and oppositely with big cluster ions (0.5–1.3 cm^{2}V^{-1}s^{-1}). The absolute value of the correlation coefficient diminishes reaching the fraction close to the average mobility. This is in general accordance with our understanding of the behavior of the mean mobility that reflects the balance of small and big cluster ions in the spectrum.

In July and August, when the mean mobility and the concentration of small ions showed a regular diurnal variation of high amplitude with the maxima recorded during nighttime calms, the mean mobility of positive small ions correlated mainly with the concentration of small cluster ions. Speaking of negative ions, the decrease in the correlation coefficient between the mean mobility and the concentration of big cluster ions was not recorded.

In the cold season (from October to April), when the meteorological conditions (few calm days, wet or/and frozen soil) did not favor the accumulation of radon close to the ground, the variation of the mean mobility was preferably determined by the concentration of big cluster ions (Figure 31).

The peculiarities of the correlation between the mean mobility and the fraction concentrations of small ions in the warm and cold season are in accordance with the evolution of small ion mobility spectra (Figures 25 and 26).

The mean mobility of small ions is correlated negatively with the fraction concentrations of intermediate ions. In Figure 31 the light intermediate ions (0.25–0.5 cm^{2}V^{-1}s^{-1}) show a little higher correlation coefficients with the mean mobility compared with heavy intermediate ions (0.034–0.29 cm^{2}V^{-1}s^{-1}). In general, the correlation coefficients in Table 11 vary from +8% to –57%

considering various monthly periods. The scatterplot of the mean mobility of small ions plotted with respect to the intermediate ion concentration did not show a distinct relationship between the variables. The contour defining the maximum of recorded mean mobility decreases with the increasing of the intermediate ion concentration. Thus, the higher intermediate ion concentrations were recorded when the mean mobility of small ions was low.

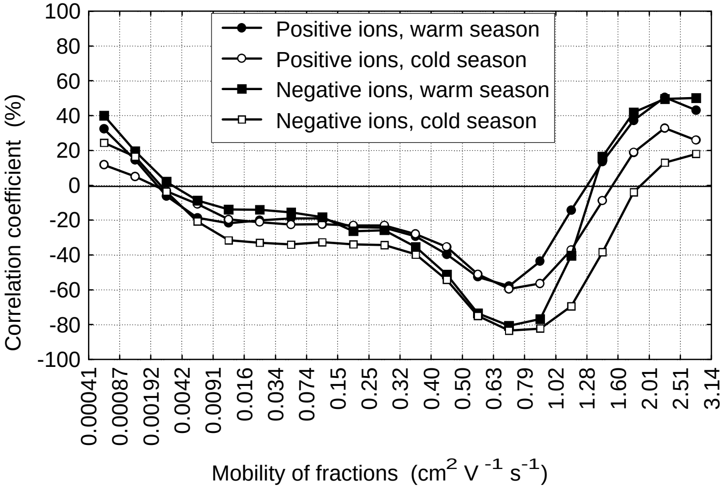


Figure 31. The correlation coefficients of the mean mobility of positive and negative small ions with the fraction concentrations of the same polarity in the warm season (May – September) and in the cold season (October – April).

As to large ion concentration, the correlation with the mean mobility of small ions changes from slight opposite to positive in the mobility range of 0.00041–0.034 cm^{2}V^{-1}s^{-1} (see Figure 31). In general, only heavy large ions (0.00041–0.00087 cm^{2}V^{-1}s^{-1}; 52–79 nm) showed a substantial positive correlation with the mean mobility. Examining different monthly periods, the correlation coefficients ordinarily varied in the ranges of 40–65% and 20–55%, considering negative and positive polarity, respectively (Table 11). Commonly, the correlation between the heavy large ion concentration and the mean mobility of small ions was stronger in the case of negative polarity, compared to that of positive polarity. This was not caused by the different behavior of polar heavy large ions (the correlation coefficient was 98%).

As concluded from Figure 32, the median mean mobility of negative small ions shows a non-linear correlation with the heavy large ion concentration. The mean mobility increases mostly due to the rise in the 5% quantile, while the 95% quantile shows less variation. The estimates of non-linear correlation coefficients (assuming a power function from the heavy large ion concentration) could give about 10% higher values compared to linear correlation coefficients.

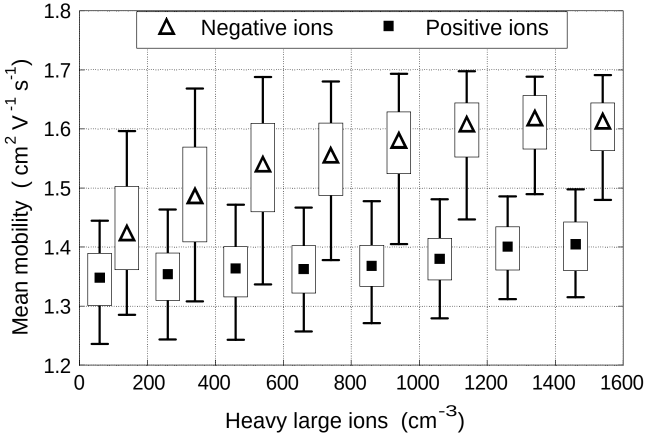


Figure 32. The mean mobility of small ions versus the concentration of heavy large ions (0.00041–0.00087 cm^{2}V^{-1}s^{-1}; 52–79 nm). Descriptive statistics: median, box 25% and 75%) and whiskers (5% and 95% quantiles). Sept. 1993 – Oct. 1994. The last class (1400; 1600) is opened; statistics of positive and negative ions are shifted within classes for better presentation.

The correlation coefficients increasing with the size of heavy large ions in Figure 31, let us assume that the correlation between the mean mobility and particle concentration could be stronger reaching the size range of the accumulation mode particles (100–500 nm). This assumption was confirmed by simultaneous measurements of air ion mobility spectra and aerosol particle size spectra at Tahkuse during about one month period from April 14 to May 16, 1994. The mean mobility of small ions correlated positively with the fraction concentrations of the accumulation mode particles (100–500 nm), the correlation coefficients were in the rages of 62–65% and 50–53% for the mean mobility of negative and positive small ions, respectively. The correlation coefficients between the mean mobility and the heavy large ion concentration were considerably lower, about 38% and 29%, respectively.

In April–May 1994, the correlation coefficient between the concentrations of heavy large ions and the accumulation mode particles was about 72% (88% in April and 80% in May). The relatively independent behavior of heavy large ions (charged Aitken particles of 52–79 nm) and the accumulation mode particles could explain the absence of correlation with the mean mobility during the joint period of the cold season (Table 11), when the monthly median concentrations of heavy large ions exhibited a significant variation by a factor two.

The correlation of the mean mobility with the surface area concentration of aerosol particles was the strongest in the case of the accumulation mode particles (100–500 nm). The correlation coefficients were 65% and 53% for the mean mobility of negative and positive polarity, respectively. The observed increase in the mean mobility of small ions with the increasing surface area of aerosol particles is consistent with expectations. The aerosol particles, due to their absorbing and sticking properties, could change the concentration of trace gases (vapors) in the air and thus, via gas phase chemistry, also the mobility spectra of small (cluster) ions, resulting in an increase in the mean mobility. Another mechanism – the attachment of small ions to aerosol particles, also leads to the increase in the mean mobility, diminishing the lifetime of small ions, and therefore, the aged ion (big cluster ions) content in the air.

7.8. The multiple regression analysis

The meteorological parameters, as well as the concentrations of the mobility spectra fractions (intermediate and heavy large ions) are not statistically independent parameters. The method of multiple regression analysis was applied to evaluate the influence of various factors on the mean mobility of small air ions. The linear regression analysis was carried out with the program package of "Statistica for Windows" StatSoft Inc. (1998). The regression model included the relative humidity, the concentration of heavy large ions (0.00041–0.00087 $cm^2V^{-1}s^{-1}$; 52–79 nm), light intermediate ions (0.32–0.50 $cm^2V^{-1}s^{-1}$; 1.6–2.3 nm), heavy intermediate ions (0.034–0.293 $cm^2V^{-1}s^{-1}$; 2.3–7.4 nm) and air temperature as the independent factors of the model. The concentration of heavy large ions was taken as the mean concentration of polar heavy large ions. The multiple correlation coefficients (square root from the determination coefficients) between the independent factors and the mean mobility of positive and negative small air ions are presented in Table 12.

For a detailed analysis, a stepwise approach to the calculation of the multiple correlation coefficients was used, including independent factors step by step into the model in addition to those already existing in it. The results are given in Table 12. The order of including of factors (relative humidity, the concentration of heavy large ions, light intermediate, heavy intermediate ions and air temperature) was selected according to the highest commonly observed growth rate of the multiple correlation coefficients. In general, the potential increment of the correlation coefficient associated with the including of a new factor into the model is not specified as the contribution of a new factor, but a new set of the factors. If the increment of the multiple correlation coefficient in Table 12 is 1%, then the new included factor could not be significant.

Table 12. The multiple correlation coefficients (%) between the mean mobility of positive/negative small ions and the independent factors of the linear regression model (for details see text). The absolute value of the critical correlation coefficient at a confidence level of 95% is about 8%, considering monthly periods, and about 3% considering the entire period. Tahkuse, September 1993 – October 1994. Warm season: Sept. 1993, May – Sept. 1994; cold season: Nov. 1993 – March 1994.

Period	Factors				
	Rel. Hum.	+ Heavy large ions	+ Light int. ions	+ Large int. ions	+ Temp
September 1993	67/66	80/78	80/78	81/79	81/79
October	44/32	64/73	70/79	73/80	75/82
November	56/51	59/58	61/66	61/66	65/66
December	47/11	58/46	59/61	60/62	73/64
January 1994	68/67	68/69	68/73	69/74	73/74
February	37/34	53/52	56/64	57/65	62/66
March	63/56	64/63	65/68	68/70	72/71
April	65/33	74/62	75/69	77/70	77/72
May	60/22	71/55	74/60	77/64	78/64
June	68/49	78/73	81/77	84/81	84/81
July	68/48	79/69	82/78	82/79	84/84
August	66/56	68/67	68/71	70/73	76/75
September	40/40	54/60	59/67	61/68	61/71
October	41/17	75/69	76/73	77/74	77/75
Warm season	69/51	74/66	74/70	76/73	78/75
Cold season	61/53	61/57	62/63	63/65	69/67
Entire period	63/47	66/61	67/67	69/70	70/70

As expected, the multiple correlation coefficients are almost always substantially higher than the correlation coefficients between the independent factors and the mean mobility, considering different monthly periods. The amount of variance, explained by the independent factors, from the total variance of the mean mobility is given by the multiple determination coefficients (square of the correlation coefficient). The model describes from 41% to 71% of the total variance of the mean mobility of negative small ions, and from 37% to 71% of the variance of the mean mobility of positive small ions, considering different monthly periods. The lower description ability of the model in November, December and February was in part probably due to a lower variation of the mean mobility itself (1.5–2 times compared to other months). Considering the whole measurement period (14 months), the model describes 49% of the total variance of the mean mobility of negative and positive small ions.

The summarized results of the regression analysis are presented in Table 13. The contribution of independent factors to the predicted variable (the mean mobility) are described by the regression coefficients (B-coefficients, weights), and in proportion to other factors by standardized regression coefficients (Beta-coefficients). The value of t-statistic and the resulting p-level are used to test the hypothesis that the intercept is equal to 0, and the statistical significance of the factors. The F-statistic and the resulting p-level are used as the characteristics of the F-test of the relationship between the dependent variable and the set of independent variables (significance of the model). The regression coefficients (Beta-coefficients) represent the independent contributions of each independent variable to the prediction of the dependent variable, similarly to the partial correlation coefficients.

Table 13. The results of multiple regression analysis of the mean mobility of small ions (dependent variable, $\mathrm{cm^2V^{-1}s^{-1}}$) and independent factors: relative humidity (%) and air temperature (°C), concentration of light intermediate and heavy large ions ($\mathrm{cm^{-3}}$). September 1993 – October 1994.

a) Positive ions.

Statistics of Multiple Regression	$R = 0.683$ $R^2 = 0.466$ Adjusted $R^2 = 0.466$ $F(4, 8192)=1792$ $p < 0.000$ Std. Error of estimate: 0.0466					
N = 8197	Beta	St. Err. of Beta	B	St. Err. of B	t(8191)	p-level
Intercept			1.1624	0.003395	342.3	0.00
Rel. hum.	0.658	0.0097	0.002239	0.000033	67.8	0.00
Temperature	0.144	0.0091	0.000913	0.000058	15.8	0.00
Int. ions	-0.130	0.0088	-0.000910	0.000062	-14.8	0.00
Large ions	0.203	0.0081	0.000042	0.000002	25.1	0.00

b) Negative ions.

Statistics of Multiple Regression	$R = 0.671$ $R^2 = 0.4497$ Adjusted $R^2 = 0.450$ $F(4, 8192)=1674$ $p < 0.000$ Std. Error of estimate: 0.0779					
N = 8197	Beta	St. Err. of Beta	B	St. Err. of B	t(8191)	p-level
Intercept			1.3295	0.005620	236.6	0.00
Rel. hum.	0.360	0.0099	0.002052	0.000055	36.4	0.00
Temperature	-0.020	0.0093	-0.000210	0.000096	-2.2	0.03
Int. ions	-0.308	0.0090	-0.002984	0.000087	-34.3	0.00
Large ions	0.364	0.0082	0.000124	0.000003	44.2	0.00

The factors in the model can have a different effect on the mean mobility (followed by the sign of the regression coefficients) than those given by the Pearson correlation coefficients in Table 11. The analysis of the regression coefficients, calculated for the monthly and annual periods, shows that the relative humidity and the concentration of heavy large ions that correlated positively with the mean mobility of small ions have the same effect also in the regression model. Also, the regression coefficients and the Pearson correlation coefficients between the mean mobility and the concentration of light intermediate ions have the same sign (negative). The concentration of heavy intermediate ions that is closely correlated with light intermediate ions (the correlation coefficient is about 86%) has the opposite effect – positive regression coefficient. In general, the effect of including large intermediate ions into the model is weak, the increase in the determination coefficient is lower than about 5%. That is why the large intermediate ions were excluded from the common list of factors in Table 13. The air temperature can have negative or positive regression coefficients (mostly positive) with the mean mobility, or be insignificant in the model, considering monthly periods.

Summarizing the results of the multiple regression analysis, we can conclude that relative humidity and heavy large ion concentration are the main factors of the model that affect the natural mean mobility of small ions. The first two factors explain 44% of the variance of the mean mobility of positive small ions and 38% of the variance of the mean mobility of negative small ions, considering the entire period. The light intermediate ions are considered as a factor in the case of the mean mobility of negative small ions. The explained variance increases about 7%. As discussed above, the solar radiation is considered as a real factor and relative humidity as an indirect factor that are correlated with the mean mobility of small ions.