8. ANNUAL VARIATIONS OF AIR ION MOBILITY CLASSES

8.1. Concentration of small air ions

The annual variation in the monthly median concentration of small ions was weakly expressed: a slight minimum in the cold season (from November to April) and a maximum in the warm season; the variation of the 90% quantile was more expressive (Figure 33). The course of negative small ions was close to that of positive ions, but their median concentrations were reduced by about 10% and 16% in the warm and cold season, respectively. In general the variation follows the known regularities for the continental areas of high latitudes: a minimum is in the cold season, when the soil is frozen and covered by snow, and a maximum is in the warm season [*Israël*, 1970]. This is probably due to different exhalation rate of radon from the soil that controls the ionization rate of the air close to the ground.

Porstendörfer [1994] writes that the seasonal variation in the activity concentration of radon in continental areas shows a maximum of about 12 Bq m^{-3} during summer months (June–August) and a minimum of 4 Bq m^{-3} in winter (January–February). Seasonal variations that considerably depend on the soil conditions generally exhibit a ratio between 2 and 4. *Mattsson* [1970] has recorded the burst of ^{212}Pb (thoron progeny) concentration in May, which followed the melting of snow cover and the thawing of the soil and.

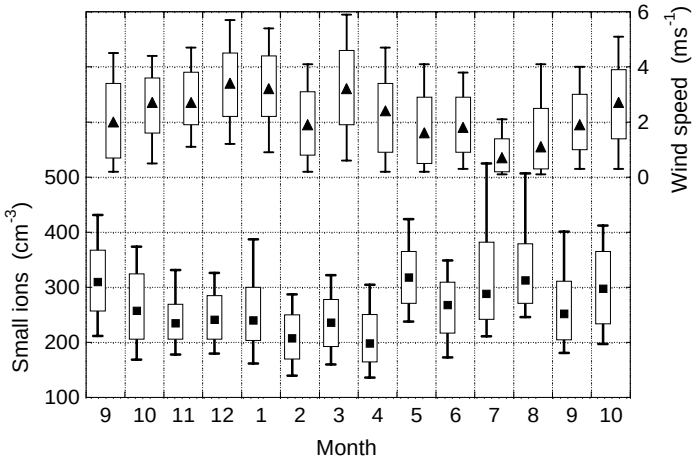

Figure 33. Monthly concentrations of small ions (0.5–3.14 $cm^2V^{-1}s^{-1}$) and wind speeds. September 1993 – October 1994. Statistics: median, box (25% and 75%) and whiskers (10% and 90% quantiles).

The measurements of soil temperature and freezing-depth performed by weather stations, surrounding Tahkuse at the distances of 27–50 km, showed that the upper 2–8 cm of the soil were wet and often frozen starting from the second part of October [*Agrometeorological survey*, 1993–1994]. The rapid freezing of soil started at the beginning of November. At the end of November the freezing-depth was about 50 cm, maximum 60 cm in February. Intensive thawing of soil was recorded starting from the third decade of March. The soil thawed in full during April 17–26 and dried by the end of the month (see Figure 34). A stable snow cover was formed on the third decade of November, and it melted mostly at the end of March. This was in accordance with the low concentration of small ions from October to April and bursts in May.

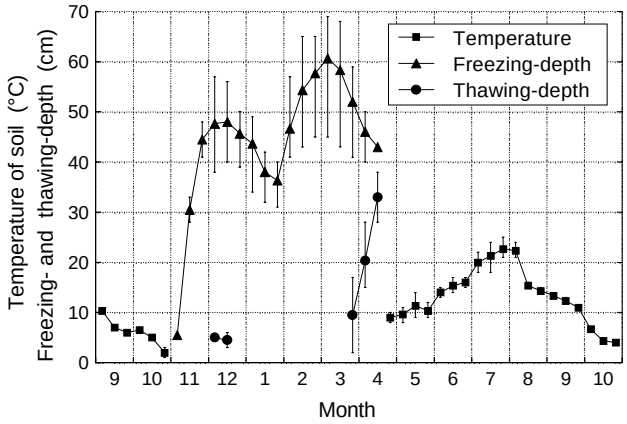

Figure 34. Decade means of freezing- and thawing-depths of the soil and the temperatures of the soil at the depth of 10 cm. September 1993 – October 1994. Statistics: the average of four weather stations and whiskers (min and max of decade means of stations).

In the last decade of April, the concentration of small ions was relatively steady, about 200 cm^{-3}. On May 1, the concentration increased up to about 320 cm^{-3} and stayed approximately on the same level through May, considering diurnal average values. After May 1, a regular diurnal variation of small ion concentration started. The increase in the background concentration was probably caused by the increased ionization rate due to the exhalation of radon from the arid soil and accumulation during nocturnal calms. The median of relative humidity in May was 60% (in April and June about 80%) and frequently a calm prevailed at nights and in the early morning hours. Owing to the high amplitude of diurnal variation of wind speed, the influence of wind on the small air ion concentration cannot be followed by the average value of wind speed in Figure 33. The abrupt increase in small ion concentration on May 1 was also supported by the decrease in the aerosol particle concentration after the

inflow of clean Arctic high-pressure air mass. On the May 1, the concentration of aerosol particles in the accumulation mode size range (100–560 nm) dropped from about 2400 cm^{-3} to 100 cm^{-3}, and after that started to increase again.

July and August were characterized by high extremes (see Figure 33); the maxima of positive small ions were correspondingly 875 cm^{-3} and 1176 cm^{-3}. The origin of the high extremes was the calm weather recorded almost all the nights (25 in July and 18 in August) that favored the accumulation of radon near the ground. In July (also in the first decade of August) the weather was exceptionally stable, hot and sunny (solar radiation duration 370–440 hours in July) with the average temperature of 20 ºC (on 15 days over 30 ºC at noon). The long lasting drought in July and in the first week of August dramatically decreased the water content in the soil [*Agrometeorological survey*, 1993–1994]. The lack of soil moisture content is known to be a factor that favors the flux of radon from soil [*Mattsson*, 1970; *Porstendörfer*, 1994].

Another factor that caused the variation in the concentration small ions, the heavy large ions of mobility 0.00041–0.0042 $cm^2V^{-1}s^{-1}$ (diameter 22–79 nm), showed no clear correlation concerning the monthly median concentrations. A closer correlation between both quantities was found in the cold season from November to April, when the soil was frozen or wet; the correlation coefficient between the hourly mean values was –70%. Contrary to the cold season, when the opposite correlation was evident, in the warm season and transition period (May – October) the correlation between the monthly median concentrations was absent. Only roughly opposite correlation appeared, when the periods of low winds less than 0.5 m s^{-1} (preferentially nocturnal calms) were eliminated.

It is rational to compare the results with the measurements carried out at Tahkuse Observatory in 1985–1986 [*Hõrrak et al.*, 1988b]. Then the average concentration of small ions was roughly 1.5 times higher than in 1993–1994, but the time variation was roughly the same: the minimum in winter in February–March of about 220–240 cm^{-3}. The average concentration in May 1986 was the highest, 560 cm^{-3}; this was obviously due to the radioactive fallout after the accident at the Chernobyl nuclear power plant. Although, the thawing of soil that favored radon release also occurred at the same time.

Since air conductivity is mainly determined by the concentration of small ions, the variations of both quantities should be closely correlated. The correlation coefficient was 98–99%; the variation of the monthly average mean mobility of small ions was less than 10%. *Tuomi* [1989] has published the average annual variation of conductivity for years 1977–1986 measured at Helsinki-Vantaa Airport, *Retalis et al.* [1991] above Athens for 1968–1980, and *Israelsson and Tammet* [2001] at Marsta Observatory, Sweden, for 1993–1998. In all these cases, the annual variation in conductivity is in agreement with the present measurements; the conductivity also displays a minimum in winter and maximum in summer.

8.2. Concentration of intermediate and light large air ions

The annual variation in the concentration of intermediate ions (mobility 0.034–0.5 $cm^2V^{-1}s^{-1}$; diameter 1.6–7.4 nm) has a minimum in the cold season from November to February (Figure 35). In other months the distribution of the concentrations was far from normal one due to the bursts of intermediate ions [*Hõrrak et al.*, 1998b]. In general, the concentrations of light large ions (0.0042–0.034 $cm^2V^{-1}s^{-1}$; 7.4–22 nm) and intermediate ions varied similarly, except in February and during the period from July to October 1994, when the higher quantiles showed a slightly different behavior (Figure 35). The ratio of the median concentrations of light large ions to that of intermediate ions was about 5 through the year. The concentrations of both ion classes are influenced by the photochemical nucleation phenomenon [*Hõrrak et al.*, 2000].

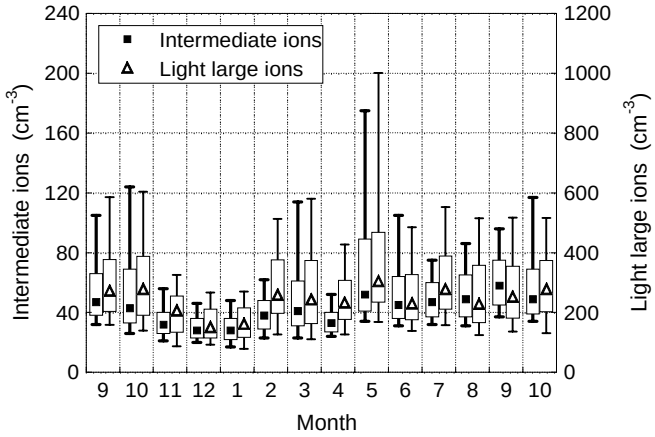

Figure 35. Monthly concentrations of intermediate ions (0.034–0.5 $cm^2\,V^{-1}\,s^{-1}$; 1.6–7.4 nm) and light large ions (0.0042–0.034 $cm^2\,V^{-1}\,s^{-1}$; 7.4–22 nm). Sept. 1993 – Oct. 1994. Statistics: median, box (25% and 75%) and whiskers (10% and 90% quantiles).

Observations of the bursts of intermediate ions showed that the nucleation events at Tahkuse occurred preferably during spring and autumn. A clear correlation with the types of air masses was found. In general, the bursts followed the inflow of clean marine Arctic air masses (anticyclones) from the north [*Berliner Wetterkarte*, 1993–1994]. The low percentage of Arctic air masses (during 4 days) was probably one of the causes of the low concentration of intermediate ions in April 1994.

In order to present some statistical description of the bursts of intermediate ions, the number of days in the month when the concentration of intermediate ions was higher than a certain value is given in Table 14. Only more pronounced burst events are considered, when the intermediate ion polar concentration exceeds 100 cm^{-3} (background of about 50 cm^{-3}) during at least 2

hours. Commonly, the burst duration was 6–10 hours (from the background up to maximum and down to the background). An asterisk in Table 14 marks the bursts of shorter duration. The same is also true for negative intermediate ions, but sometimes the peak values of the concentration of negative intermediate ions exceed those of positive polarity by about 100–150 cm^{-3}.

Table 14. Number of days in the month when the concentration of positive intermediate ions exceeds a certain value.

		>100 cm^{-3}	>200 cm^{-3}	>300 cm^{-3}	>400 cm^{-3}	>500 cm^{-3}	>600 cm^{-3}	Maximum cm^{-3}
Sept.	1993	13	8	3	0	0	0	381
Oct.	1993	8	8	7	5	1	1*	874
Nov.	1993	5	3	3	0	0	0	442
Dec.	1993	2	1	1	1*	0	0	457
Jan.	1994	1	1	1	1*	0	0	471
Feb.	1994	2	2	2	2	2	1	601
March	1994	8	6	3	2	1	1	708
April	1994	5	2	2	2	1	1	860
May	1994	18	12	7	6	4	1	712
June	1994	11	6	2	1	0	0	470
July	1994	5	1*	0	0	0	0	205
Aug.	1994	6	1	0	0	0	0	205
Sept.	1994	6	2	2	1	1	0	506
Oct.	1994	11	6	3	2	1	1	652
	Sum	101	59	36	23	11	6	

* Burst of short duration: October and December within 2 hours, January within 3 hours more than 100 cm^{-3}.

In the period from November 24 to February 24, only three bursts were recorded, and even those bursts were of short duration, being higher than 100 cm^{-3} for only 2–3 hours. This is probably due to the fact that the conditions in winter did not favor photochemical nucleation because of low solar radiation intensity and duration at this latitude. Also the decreasing mixing rate of the boundary layer and the accumulation of aerosol pollutants (providing a high condensational sink for nucleating low-pressure vapours) may be responsible for the absence of burst events in wintertime.

Regular bursts started as early as February 25 and 26, when bursts up to 600 cm^{-3} were recorded. The higher concentrations in May could be related to the beginning of the period of early vegetation and intensive agricultural works. On the basis of the side-by-side measurements of aerosol particle size spectra [*Hõrrak et al*., 1996, 1998a] it can be concluded that the period of intensive bursts of intermediate ions followed the inflow of cool and clean Arctic high-pressure air mass. On the May 1, the concentration of the accumulation mode particles (100–560 nm) decreased rapidly from about 2400 cm^{-3} to 100 cm^{-3} and during the following week increased gradually up to about 1000 cm^{-3}.

In the measurements at Tahkuse in 1985–1986, the narrow fraction of intermediate ions (0.32–0.5 $cm^2V^{-1}s^{-1}$) also showed enhanced concentrations in autumn (September–October) and maximum in spring (May) [*Hõrrak et al*., 1988b]. Enhanced concentrations over 60 cm^{-3} (annual average of about 25 m^{-3}) were observed during 4% of hours [*Tammet et al*., 1988].

Mäkelä et al. [2000b] and *Birmili* [1998] have found the same regularities: the low concentration of ultrafine aerosol particles (below 10 nm) during wintertime and bursts in spring. The number of days with nucleation bursts of nanometer particles observed at *Hyytiälä* station, southern Finland, was 40–50 during one-year periods in 1996–1999. This number has the same order of magnitude as the number of bursts of intermediate ions, about 80, for a one-year period at Tahkuse in 1993–1994. The number of nucleation events recorded in central Europe, near Leipzig, was between 38 and 60 during different seasons in 1996–1997 [*Birmili* , 1998]. The measurements of ultrafine aerosol particles at *Värriö* station, in northern Finland, also showed a maximum in spring [*Kulmala et al*., 1996]. The events of high particle concentration were recorded in clean air masses originating from the Norwegian Sea, but also in polluted air masses coming over the Kola Peninsula (indicator high SO_2 concentration).

8.3. Concentration of heavy large air ions

Variation in the concentration of heavy large ions (mobility 0.00041–0.0042 $cm^2V^{-1}s^{-1}$; diameter 22–79 nm) for different monthly periods is presented in Figure 36. The median concentrations of heavy large ions in the warm season (from April to October) were quite steady, about 1300 cm^{-3}. In the cold season (November – March) the median concentrations were unsteady, their lowest and highest values differ up to 2 times. The median concentrations recorded in November and February were higher, and in December and January (also in March) lower compared with the annual average. Changes in the background concentrations were responsible for changes in the concentration medians. The peak concentrations were comparable, considering all the months. An increase in the background concentration of heavy large ions (as well as NO_2) in November and February followed the decrease in air temperature (see Figure 36), caused by the inflow of cold Arctic high-pressure air masses.

In November the enhanced background concentration was recorded during about a two-week period of cold weather, from November 9 to 22, with the average temperature of –9°C (minimum –18.7°C). The sudden increase in the background concentration from about 1200 cm^{-3} to 1950 cm^{-3} on November 9 was in accordance with the passage of a cold front from the NE and was caused probably by the transport of aerosol pollutants by air mass. During the

following decade the concentration gradually increased up to its maximum about of 3100 cm^{-3}.

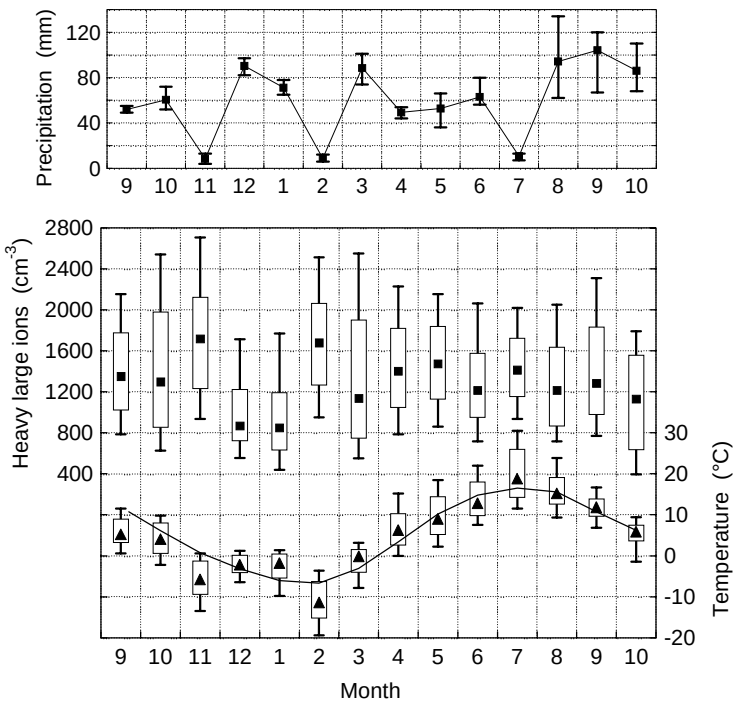

Figure 36. Monthly concentrations of heavy large ions (0.00041–0.0042 $cm^2V^{-1}s^{-1}$) and air temperatures (statistics: median, box (25% and 75%) and whiskers (10% and 90% quantiles; the lineplot is the long-term climatic standard of air temperature), and the monthly precipitation (statistics: average of four weather stations, whiskers (minimum and maximum of the monthly mean values of the stations)). Sept. 1993 – Oct. 1994.

In February, an increase in the background concentration followed (with some delay) the inflow of cold air mass on the last days of January. The concentration of heavy large ions increased gradually during 4–6 days from the background of about 600 cm^{-3} to 1700 cm^{-3} and remained nearly at this level during the first two weeks of cold weather in February (average temperature was –15°C, minimum –25°C). Higher concentrations were recorded during the whole February and in the first week of cold weather in March. After the first week of March, the background concentration dropped to about 860 cm^{-3} and was comparable with those found in December and January.

This particular variation in the concentration of heavy large ions in the cold season is rather complicated to explain. The particles with diameters of 22–79 nm, the charged fraction of which is mainly formed the heavy large ions of the mobility of 0.00041–0.0042 $cm^2V^{-1}s^{-1}$, have residence times in the lower troposphere for about 1.5–6 days, considering different sizes [*Jaenicke*, 1982]. The estimates of decay constants (similar to the residence times) given by *Hoppel et al*. [1990] for a marine boundary layer are considerably smaller, about 10–30 hours. These estimates are the averages, determined by several loss processes, and could be substantially modified according to the prevailing weather conditions. Consequently, many of these factors could be significant: the dependence of aerosol particle content, growth and sink (dry and wet removal) on the origin and history of air masses, as well as on the atmospheric air exchange controlling the accumulation of pollutants near the ground.

In November and February, the dominant wind direction was from continental areas (sector S–NE) and large ion concentration was considerably higher than in December, January and March, when the contribution of winds from areas closer to the Baltic Sea (sector SSW–NW) was higher or prevailed. The detailed analysis could not explain the variation in heavy large ion concentration as the effect of wind direction. Considering different months from November to March, all the wind directions, which were statistically significant, showed similar decrease or increase in the large ion concentration.

Significant differences in the meteorological parameters (air temperature, relative and absolute humidity, air pressure and the amount of precipitation) characterize these two periods in the cold season. The active cyclones with frontal systems prevailed in December, January and March, and stable anticyclones in November and February. A clear opposite correlation was found between the heavy large ion monthly median concentrations and the monthly precipitation (Figure 36). The air pressure showed positive correlation with large ions. In December, January and March the precipitation more than 1 mm per day was recorded during 14–17 days in each month with the total amount of about 70–90 mm per month. Accordingly, the concentration of heavy large ions was lower than the annual average. On the contrary, in November and February the precipitation more than 1 mm per day was recorded only on 1–3 days with the total amount of about 8–9 mm per month; the concentration of heavy large ions was higher than the annual average, respectively.

Probably the synoptical processes together with human activity affected the aerosol particle content in air masses, and therefore, also the variation in the concentration of heavy large ions in wintertime. The wet-removal process is considered as a factor that is likely to control the concentration of heavy large ions in winter. This factor was more efficient in the cold season (Figure 36), when the precipitation was in the form of snow or sleet, than in the warm season, when the precipitation was in the form of rain, and an equivalent amount of precipitation was recorded at shorter duration.

This group of large ions represents a certain part of condensation nuclei (CN) and information about the regularities of large ions should be comparable with that about CN [*Shine and Forster*, 1999; *Raes et al*., 2000].