

6. CLASSIFICATION OF AIR IONS AND CORRELATION BETWEEN THE CONCENTRATIONS OF MOBILITY CLASSES

6.1. Problem of the classification of air ions

The classification has been established gradually during the history [Israël, 1970; Flagan, 1998], but it has not been satisfactorily formulated until now.

The first widespread classification of atmospheric ions, which was rather a convention, was given by Israël [Israël and Schulz, 1933; Israël, 1970]. Summarizing the preceding results obtained by various researchers, Israël [1970] concluded that the atmospheric ion spectrum contains two primary “lines” (ion groups), one corresponding to small ions at about $1.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and the second to the large ions at about $3 \cdot 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The spectral region between these two lines is sparsely and variably populated by intermediate ions. Beyond the large ions (Langevin ions), the spectrum continues with what Israël called ultra-large ions. The concentration of particles, as well as ultra-large ions, above the diameter of about 100–200 nm decreases dramatically [Junge, 1955]. Five ion groups distinguished in the atmospheric ion spectrum in accordance with Israël’s proposal [Israël, 1970] are presented in Table 6.

After Israël, the small ions generated by ionization process form a group of *primary atmospheric ions*, whereas intermediate and large ions formed after the subsequent attachment of small ions to uncharged particles called *secondary atmospheric ions*. Israël restricted the use of the term “ion” to those charged particles the fall velocity of which in the Earth’s gravitational field is negligible compared to their motion in the Earth’s electrical field (critical diameter of about 0.2 μm). The designation of ions according to their spectral regions by Israël’s proposal has become customary (e.g. Tverskoi, 1949; Junge, 1965; Reinet, 1958; Prüller and Reinet, 1966). Tammet [Tammet et al., 1987b, 1988] later applied the concept of *primary and secondary aerosol ions* to distinguish between two possible routes of intermediate ion formation in the atmosphere by ion-induced nucleation and by the diffusion charging of neutral particles.

Table 6. Air ion classification after Israël [1970].

Mobility range $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	Diameter range nm	Name
>1	>1.32	Small air ions
0.01–1	1.32–15.6	Small intermediate ions
0.001–0.01	15.6–50	Large intermediate ions
0.00025–0.001	50–114	Large ions of Langevin
< 0.00025	>114 (up to 200)	Ultralarge ions

The long-term measurements of various categories of small, intermediate and large air ions at Tartu University, Estonia, during the annual period of 1951 and 1960–1963 [Reinet, 1958; Prüller and Reinet, 1966] revealed a boundary between small and large ions at about $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The mobility range of small ions was divided into a subrange of molions and small intermediate ions with a limiting mobility of $1.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The mobility of $0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was proposed as a conventional boundary between small and large ion classes [Prüller, 1970]. The detailed measurements of ion mobility spectra confirmed this assumption later [Tammet et al., 1987b, 1992; Hörrak et al., 1994].

The episodic measurements of air ion mobility spectra (e.g. Yunker, 1940a; Misaki, 1961; Hoppel and Kraakevik, 1965; Hoppel, 1970; Eichmeier, 1972; Cabane and Milani, 1983) also showed a minimum in the range of 0.2–0.5 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. In general, the bulk of small air ions were recorded in the mobility range of 0.4–3 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$.

Two classes of small ions have been found in the laboratory experiments studying the evolution of mobility spectra produced by ionizing radiation under atmospheric pressure in different gases [Bricard et al., 1972, Cabane et al., 1976]. The first class, which consisted of ions of discrete mobilities above $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, probably corresponded to the group of thermodynamically stable clusters. The second class (0.1–1 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) corresponded to the ions above the critical size for nucleation, which grew towards large sizes during aging.

Intermediate ions have the highest variability in the mobility spectrum of atmospheric ions, considering the concentration and mean mobility. During the generation of intermediate ions by photochemical nucleation [Kojima, 1984], the peak particle size shifts toward large sizes in the spectrum [Misaki, 1964]. Therefore, the determination of mobility boundaries, especially the lower mobility limit, is complicated. Weiss and Steinmaurer [1937] proposed the mobility interval of 0.02–1.0 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for intermediate ions. Mobility spectra of air ions (10^{-4} –3.2 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) measured by Misaki et al. [1972, 1975] have a deep depression between small and large ions from about 0.5 to 0.03–0.1 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, depending on the measurement site and time. The range of depression could be considered as the range of intermediate ions. The measurements by Dhanorkar and Kamra [1991] showed the presence of all three categories of ions: small, intermediate and large, at all times of the day at the tropical land station at Puna in India [Dhanorkar and Kamra, 1991, 1993a]. Intermediate ions showed maxima at about 0.076 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ (diameter 4.6 nm), the minima in the mobility spectrum could be found approximately at 0.01–0.03 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and 0.2–0.3 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$.

The classification of air ions represents one essential problem that can be studied by long-term measurements of air ion spectra. The concepts of small and large ions have a clear physical background (molecular clusters and macroscopic particles, respectively) [Tammet, 1995]. Problems arise when trying to specify the concept of intermediate ions and to settle the mobility

boundaries. The boundaries defined in atmospheric electricity textbooks have so far been rather speculative conventions. One way to address the problem is the statistical analysis of the air ion spectra measured in a wide mobility range, in order to search for air ion groups with different statistical properties. A natural classification should explain the coherent behavior of air ions inside class intervals and the relative independence of the ions of different classes. Measurements used in the verification of the classification are required to record air ion mobility fractions that are narrow compared with mobility classes. The analysis of the statistical behavior of fraction concentrations requires thousands of mobility spectra recorded during at least one full year. The first measurements that allow statistical classification of air ions have been carried out at Tahkuse Observatory.

6.2. Principal component and factor analysis of the set of fraction concentrations

The principal component analysis (PCA), known in multivariate mathematical statistics, is applied to detect the structure of an air ion mobility spectrum, e.g., for the search of mobility boundaries between different groups of air ions. Fraction concentrations of a mobility spectrum of air ions may be interpreted as a set of closely correlated variables (see Table 7). The formal correlation is caused by: (1) physical and chemical processes embracing a group of fractions (causing positive correlation) or acting between different groups of fractions (causing negative correlation), and (2) an unavoidable smoothing of a spectrum due to the finite resolution of the measuring apparatus. The information about variance and covariance, which is included in different fractions of a mobility spectrum, can be transferred by a considerably less number of new variables, called as principal components or factors, which are proper linear combinations of original variables. The search for the principal components reduces to the search for the eigenvalues (characteristic roots, portions of common variance explained by factors) and factor loadings (characteristic vectors) of a correlation matrix of original variables.

Before performing PCA, the original variables (fractions of air ion mobility spectra) were treated with a non-linear transformation by logarithmic scaling. This procedure transforms asymmetric frequency distributions of variables closer to the normal ones, assumed by PCA. In our case, the logarithmic scaling does not affect significantly the results of the classification of air ions. Finally, the variables were standardized to provide variables of a comparable variance. To obtain a clear pattern (“*simple structure*”) of loadings, the VARIMAX rotation, often used in factor analysis, has been performed hereinbefore.

The eigenvalue problem was solved separately for the correlation matrices of logarithmically rescaled and standardized variables of positive and negative ions (Table 7). A certain clear structure can be found in these correlation

matrices. Results are presented in Figure 20 for negative ions. Factors of the air ion mobility spectra for positive ions showed the same regularities [Hörrak *et al.*, 2000]. The boundaries of spectral fractions and corresponding diameter intervals for single-charged particles are given in Table 2 in Chapter 3.

The first five successfully extracted factors explain 92% of the total variance. The total variance that can potentially be extracted is equal to the number of variables, which is 20. Each of the first five factors extracts at least as much variance as the equivalent of one original variable, i.e. 5% (it is expected that the variance of a single standardized variable is 1); a deep drop follows thereafter. The subsequent 14 factors explain only 8% of the total variance. Each of the latter factors explains less than 1.5% of the total variance. A part of this variation is caused by instrumental noise. Thus we can conclude that the mobility spectrum, in the first approximation, has five degrees of freedom, or that the spectrum can be described almost completely by these five factors representing 92% of all measured information. The first factor (Factor 1 in Figure 20) is closely correlated with intermediate ions (fractions 9–14), and thus it can be called as the “burst factor” of intermediate ions. It explains 24% of variance, more than the others do. Factor 2 is closely correlated with big cluster ions (fractions 4–8), Factor 3 with small cluster ions (fractions 1–4), and Factor 4 with light large ions (fractions 15–18). They explain approximately equal variances of 20%, 18% and 17%, respectively. The contribution of Factor 5, associated with heavy large ions (fractions 18–20), is the lowest, 13%. This factor is correlated also oppositely with cluster ions (fractions 2–7). In the same sense Factor 2, which is closely correlated with big cluster ions (fractions 5–8), is correlated negatively with heavy large ions (fractions 19–20).

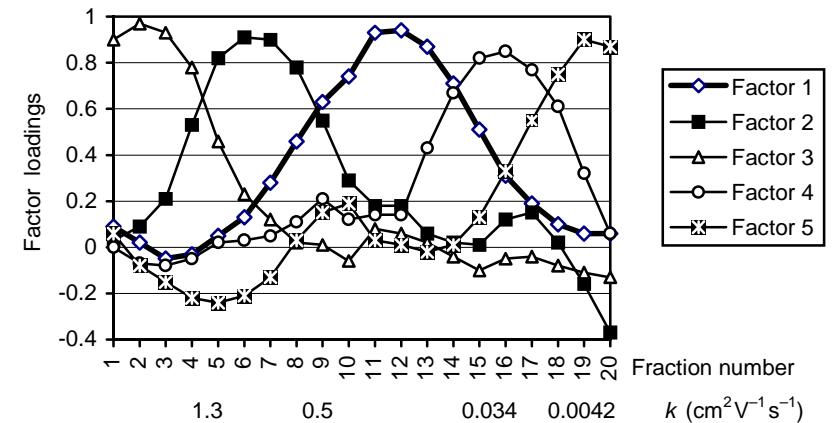


Figure 20. Factors of air ion mobility spectra for negative ions. The mobility and diameter boundaries of fractions are given in Table 2.

Table 7. Correlation coefficients (%) between negative air ion mobility fractions, September 1993 – October 1994. The absolute value of critical correlation coefficient at a confidence level of 95% is 3%.

	N ₁	N ₂	N ₃	N ₄	N ₅	N ₆	N ₇	N ₈	N ₉	N ₁₀	N ₁₁	N ₁₂	N ₁₃	N ₁₄	N ₁₅	N ₁₆	N ₁₇	N ₁₈	N ₁₉	N ₂₀
N ₁	100	85	76	62	38	24	19	13	12	3	13	12	7	2	-4	3	4	-5	-8	-8
N ₂	85	100	93	80	51	31	23	11	6	-4	9	8	1	-8	-16	-11	-11	-18	-22	-24
N ₃	76	93	100	92	65	41	28	15	5	-4	5	4	-4	-12	-19	-17	-17	-21	-29	-35
N ₄	62	80	92	100	88	70	56	36	22	6	12	12	1	-7	-14	-11	-14	-22	-36	-48
N ₅	38	51	65	88	100	94	82	61	41	21	24	24	13	6	-2	1	-2	-17	-35	-55
N ₆	24	31	41	70	94	100	93	73	51	28	32	32	20	13	5	9	5	-13	-32	-52
N ₇	19	23	28	56	82	93	100	82	63	40	44	44	33	26	17	20	15	-4	-23	-42
N ₈	13	11	15	36	61	73	82	100	72	54	56	57	48	42	34	35	30	13	-5	-23
N ₉	12	6	5	22	41	51	63	72	100	66	66	68	63	59	52	50	44	29	12	-5
N ₁₀	3	-4	-4	6	21	28	40	54	66	100	69	71	66	60	52	46	40	31	18	5
N ₁₁	13	9	5	12	24	32	44	56	66	69	100	97	87	73	58	43	34	22	10	1
N ₁₂	12	8	4	12	24	32	44	57	68	71	97	100	89	75	58	43	33	20	9	0
N ₁₃	7	1	-4	1	13	20	33	48	63	66	87	89	100	92	78	61	47	34	19	6
N ₁₄	2	-8	-12	-7	6	13	26	42	59	60	73	75	92	100	93	77	62	47	29	13
N ₁₅	-4	-16	-19	-14	-2	5	17	34	52	52	58	58	78	93	100	88	77	65	44	23
N ₁₆	3	-11	-17	-11	1	9	20	35	50	46	43	43	61	77	88	100	92	78	54	31
N ₁₇	4	-11	-17	-14	-2	5	15	30	44	40	34	33	47	62	77	92	100	90	70	46
N ₁₈	-5	-18	-21	-22	-17	-13	-4	13	29	31	22	20	34	47	65	78	90	100	89	66
N ₁₉	-8	-22	-29	-36	-35	-32	-23	-5	12	18	10	9	19	29	44	54	70	89	100	87
N ₂₀	-8	-24	-35	-48	-55	-52	-42	-23	-5	5	1	0	6	13	23	31	46	66	87	100

6.3. Statistical classification of air ions

The study of the correlation between the factors and air ion fractions shows that all the air ions can be divided into two main classes:

- aerosol ions with mobilities below $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$;
- cluster ions with mobilities above $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

These two classes can in turn be divided into two classes of cluster ions (small and big cluster ions) and three classes of aerosol ions (intermediate, light and heavy large ions). The classification, based on statistical analysis, is given in Table 8. This classification is still to a certain extent conventional, and the boundaries have been not exactly determined, because the factors that were chosen as representative, have crossloadings (any variable is correlated with more than one factor, see Figure 20).

Table 8. Classification of air ions.

Class of air ions	Mobility $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	Diameter nm	Traditional name
Small cluster ions	1.3–3.2	0.36–0.85	Small ions
Big cluster ions	0.5–1.3	0.85–1.6	Small ions
Intermediate ions	0.034–0.5	1.6–7.4	Intermediate ions
Light large ions	0.0042–0.034	7.4–22	Large ions
Heavy large ions	0.00041–0.0042	22–79	Large ions (Langevin)

Considering the warm season (from May to September) separately from the entire period, the factor analysis revealed different boundaries between small cluster ions and big cluster ions of different polarity: negative small and big cluster ions have a boundary of $1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and positive ions $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (diameter 1 nm). The mobility boundary of $1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ halves the peak in the mobility spectrum of positive small ions. If we use the boundary of $1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for cluster ions of both polarities, then we obtain a lower concentration of positive small cluster ions compared to negative ions, and this would be in contradiction with our understanding about the electrode effect near the ground. The use of the boundary of $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for positive ions also facilitates the description of the average diurnal variation of cluster ion characteristics. Therefore we suggest the use of a boundary of $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ between small and big cluster ions of positive polarity instead of $1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, such a specification is rather speculative, measurements of small ion mobility spectra with higher resolution are necessary to establish the boundary more precisely.

In the warm season, the boundary between light and heavy large ions is shifted to a lower mobility of $0.00192 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (diameter 34 nm) compared to that of the cold season of $0.0043 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (diameter 22 nm).

The boundary mobility of $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ or a diameter of 1.6 nm is the same boundary, which has been considered physically as the boundary between molecular clusters and macroscopic particles [Tamm, 1995]. The same value of $0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was also considered as the lower boundary of small air ions formerly [Hörrak et al., 1992, 1994].

The classification of air ions presented in Table 8 may also be obtained by PCA without the Varimax rotation procedure, using the first two factors (with respect to eigenvalues) as classifiers. In this case at first, the boundary between cluster ions and aerosol ions can be determined more accurately when excluding the burst events of intermediate ions. The subsequent classification within the separated classes of cluster ions and aerosol ions makes it possible to gradually detail the boundaries between different classes of air ions. The presented classification is in general also predictable from the average spectrum and from the relative standard deviations of fraction concentrations.

The above classes of air ions could be physically characterized as follows:

- Small cluster ions: mobility $1.3\text{--}3.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, estimated diameter 0.36–0.85 nm, mass 30–400 u, and typical lifetime 5–60 s. Considering ion diameters, the core of a cluster could contain one inorganic molecule and be surrounded by one layer of water molecules. After recombination, small cluster ions would be destroyed and again separated into initial components (cores and water molecules).
- Big cluster ions: mobility $0.5\text{--}1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, estimated diameter 0.85–1.6 nm, and mass 400–2500 u. Considering ion diameters, the core of a cluster could contain one organic molecule, and be surrounded by a layer of water molecules. The enhanced concentrations have been recorded when large ion concentration is low, which makes it possible for them to evolve to large sizes within their longer lifetime. In the case of intensive nucleation events (bursts) the enhanced concentrations were recorded simultaneously with intermediate ion concentrations. On the contrary to aerosol ions, collisions between cluster ions and ambient gas molecules are considered to be elastic [Tamm, 1995].
- Intermediate ions: mobility $0.034\text{--}0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, diameter 1.6–7.4 nm. The corresponding class of aerosol particles: *fine nanometer particles*. Some intermediate ions are a product of ion-induced nucleation: nucleating vapor condenses onto cluster ions, which grow to the size of intermediate ions, called *the primary aerosol ions*. Particles born in the neutral stage of the process of gas-to-particle conversion or nucleation, and charged by the attachment of cluster ions, are called *the secondary aerosol ions*.

- Light large ions: mobility 0.0042–0.034 cm²V⁻¹s⁻¹, diameter 7.4–22 nm. The corresponding class of aerosol particles: *ultrafine particles* or *coarse nanometer particles*. They are single-charged and often in a quasi-steady state of stochastic charging with cluster ions.
- Heavy large ions: mobility < 0.0042 cm²V⁻¹s⁻¹, diameter > 22 nm. The corresponding class of aerosol particles could be called *the Aitken particles*. They are as a rule in a quasi-steady state of stochastic charging with cluster ions, and some of them may carry multiple charges.

We suppose that small cluster ions represent a group of young ions and big clusters a group of aged ions. This assumption is in accordance with the measurements of the mobility spectra of ions generated in laboratory air [Nagato and Ogawa, 1998]. They have found no ions below 0.8 cm²V⁻¹s⁻¹ in the mobility spectrum of young ions, while a considerable number of ions was observed down to 0.3 cm²V⁻¹s⁻¹ in the spectrum of natural ions. It was supposed that the cluster ions between 0.3 and 0.8 cm²V⁻¹s⁻¹ could be formed by mechanisms other than those for the ions above 0.8 cm²V⁻¹s⁻¹. Our measurements show the boundary between two groups at 1.0 cm²V⁻¹s⁻¹ and 1.3 cm²V⁻¹s⁻¹ for the ions of positive and negative polarity, respectively. The boundary at about 1–1.3 cm²V⁻¹s⁻¹ (diameter 0.85–1 nm) did not have a clear physical background. It is possible that the ions below about 1 cm²V⁻¹s⁻¹ are mostly generated by other mechanism than ordinary ion-molecular reactions [Mohnen, 1977], e.g. by the condensation of some low-pressure vapor on ions (see e.g. Bricard et al., 1972; Cabane et al., 1976, 1977).

The presented classification of aerosol ions is in accord with the three-modal structure of the submicron aerosol particle size distribution found in continental sites and also in the Arctic marine boundary layer [Kulmala et al., 1996, Covert et al., 1996; Mäkelä et al., 1997, 2000a; Birmili, 1998]. These modes have mean diameters of about 150–250 nm, 40–70 nm and 5–14 nm and are referred to as the accumulation, Aitken, and nucleation (or ultrafine) modes, respectively. There were clear minima in number concentrations between these modes that appeared at 20–30 nm and 80–100 nm. Thus the intermediate ions (0.034–0.5 cm²V⁻¹s⁻¹; 1.6–7.4 nm) and light large ions (0.0042–0.034 cm²V⁻¹s⁻¹; 7.4–22 nm) may be classified as two classes of nucleation mode particles; and heavy large ions (0.00041–0.0042 cm²V⁻¹s⁻¹; 22–79 nm) as charged Aitken mode particles. It may be concluded that in the atmosphere there exists a natural boundary dividing ultrafine particles at about 7.4 nm, and when studying aerosol processes, the size range of 1.6–7.4 nm can be considered as the range of fine nanometer particles.

6.4. Correlation between the concentrations of air ion mobility classes

The general regularities between air ion classes can be studied applying the correlation analysis. The correlation coefficients between different air ion classes of positive and negative polarity are presented in Table 9.

Table 9. Correlation coefficients (%) between air ion classes of positive and negative polarity at Tahkuse Observatory. The absolute value of critical correlation coefficient at a confidence level of 95% is 3%.

a) Cold season: November 1, 1993 – April 30, 1994.

	P ₁₋₅	P ₆₋₈	P ₉₋₁₄	P ₁₅₋₁₇	P ₁₈₋₂₀	N ₁₋₄	N ₅₋₈	N ₉₋₁₄	N ₁₅₋₁₇	N ₁₈₋₂₀
P ₁₋₅	100	73	1	-26	-68	97	74	1	-27	-70
P ₆₋₈	73	100	31	6	-47	62	92	29	3	-50
P ₉₋₁₄	2	33	100	66	11	-3	31	98	66	10
P ₁₅₋₁₇	-26	6	66	100	52	-30	9	64	99	49
P ₁₈₋₂₀	-68	-47	11	52	100	-67	-44	10	52	99
N ₁₋₄	97	62	-4	-30	-67	100	62	-4	-31	-68
N ₅₋₈	74	92	29	9	-44	62	100	29	6	-48
N ₉₋₁₄	2	31	98	64	10	-4	30	100	64	9
N ₁₅₋₁₇	-27	3	66	99	52	-31	6	64	100	51
N ₁₈₋₂₀	-70	-50	10	49	99	-68	-48	9	51	100

b) Warm season: September 1993 and May 1 – September 30, 1994.

	P ₁₋₅	P ₆₋₈	P ₉₋₁₄	P ₁₅₋₁₇	P ₁₈₋₂₀	N ₁₋₄	N ₅₋₈	N ₉₋₁₄	N ₁₅₋₁₇	N ₁₈₋₂₀
P ₁₋₅	100	71	-3	-10	-1	98	49	-9	-11	-8
P ₆₋₈	71	100	20	9	-17	59	89	17	07	-18
P ₉₋₁₄	1	26	100	68	16	-1	16	97	68	17
P ₁₅₋₁₇	-10	9	69	100	48	-9	2	63	100	49
P ₁₈₋₂₀	-1	-17	16	48	100	5	-31	13	49	98
N ₁₋₄	98	59	-4	-9	5	100	34	-10	-9	-1
N ₅₋₈	49	89	11	2	-31	34	100	10	0	-32
N ₉₋₁₄	-7	22	97	62	12	-9	16	100	63	13
N ₁₅₋₁₇	-11	07	69	100	49	-9	0	64	100	50
N ₁₈₋₂₀	-8	-18	17	49	98	-1	-32	14	50	100

Contrary to the cold season, when the concentrations of small ions (N₁₋₄/P₁₋₅ and N₅₋₈/P₆₋₈) are correlated negatively (oppositely) with the heavy large ions (N₁₈₋₂₀/P₁₈₋₂₀), the correlation was weak or vanished entirely in the warm season. This was probably because of the increased exhalation rate of radioactive gases (radon) from the soil that affected the ionization rate of air

close to the ground during the warm season. The negative correlation between concentrations of small ions and large ions appeared when nocturnal calm events were excluded. In general, the negative correlation between the concentrations of small ions and large ions is the stronger the lower is the mobility (Table 7). Small ions are absorbed mainly by the abundant particles of the size of large ions, because the rate of attachment of small ion to aerosol particle is proportional to the particle diameter [Hoppel and Frick, 1986].

The concentration of big cluster ions of negative polarity showed different behavior compared to positive polarity. The big cluster ions of negative polarity N_{5-8} are correlated oppositely with heavy large ion concentrations (N_{18-20}/P_{18-20}) also in the warm season (the correlation coefficient is about -32%). The correlation between the concentrations of small and big cluster ions of negative polarity had decreased compared with that of positive polarity, especially in the warm season, when the correlation coefficients are 34% and 71% , respectively.

The intermediate ions (N_{9-14}/P_{9-14}) represent a quite isolated group that is correlated mainly with light large ions (N_{15-17}/P_{15-17}); the correlation coefficients are about $62-68\%$. This is probably because of the nucleation bursts of intermediate ions and the subsequent growth of particles that comprise also the group of light large ions. During the period from November 14 to February 24, when the bursts were recorded only on 4 days, the light large and heavy large ion concentrations showed closer correlation. The correlation coefficient was 75% compared to that of 47% found for the whole period (14 months).

Considering the air ions of different polarity, the concentrations of the classes of small cluster ions (N_{1-4}/P_{1-5}), intermediate (N_{9-14}/P_{9-14}) and large ions (N_{15-17}/P_{15-17} and N_{18-20}/P_{18-20}) were closely correlated, the correlation coefficients were more than 96% . The big cluster ions (N_{5-8}/P_{6-8}) showed a slightly worse correlation; the correlation coefficients were in the range of $89-92\%$. Also a group of light intermediate ions (fractions 9–11) was not so strongly related; the correlation coefficients were about $84-87\%$. The latter is partially due to the instrumental noise of measuring the usually low concentrations of about $2-5 \text{ cm}^{-3}$ per fractions. The closely correlated fractions of negative and positive small cluster ions and negative and positive large ions confirm that the electrode effect did not affect significantly the measurements of the mobility spectra at Tahkuse. The average coefficient of unipolarity (the ratio of the concentrations of positive to negative small ions) was about 1.12 for small ions, and nearly 1 for other groups.