CLASSIFICATION OF NATURAL AIR IONS NEAR THE GROUND

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ABSTRACT: The structure of air ion mobility spectrum recorded at Tahkuse Observatory, Estonia, during 14 months, is studied using factor analysis. The air ions in a mobility range of 0.00041–3.2 $cm^2 V^{-1} s^{-1}$ (diameters 0.36–80 nm) are divided into five classes: small and big cluster ions, intermediate ions, light and heavy large ions. The boundaries between the classes are **1.3** $cm^2 V^{-1} s^{-1}$, **0.5** $cm^2 V^{-1} s^{-1}$, **0.034** $cm^2 V^{-1} s^{-1}$, and **0.0042** $cm^2 V^{-1} s^{-1}$. Five factors correlated with respective ion classes explain 92% of total variance. According to their physical nature, the intermediate and large ions are called aerosol ions. The classification of air ions according to their mobility leads to a correlated classification of atmospheric aerosol particles according to size. The 1.6 nm boundary diameter between clusters and aerosol particles is confirmed, and the boundary diameters between the fine nanometer particles, the ultrafine or coarse nanometer particles, and the Aitken particles as classes of tropospheric aerosol are estimated to be 7.4 nm and 22 nm.

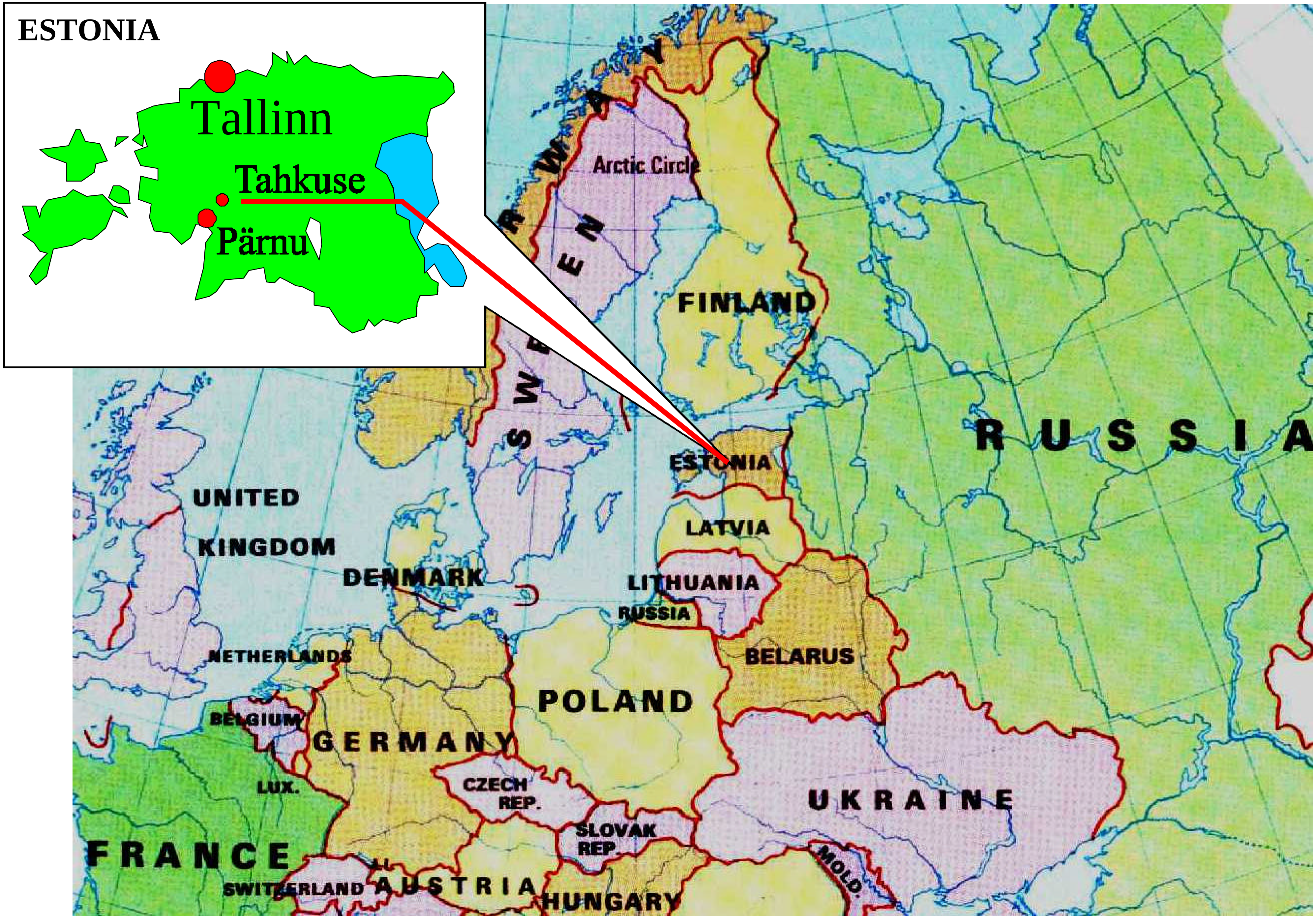
INTRODUCTION

The concepts of small and large air ions have a perceptible physical background. Problems arise when trying to specify the concept of intermediate ions and settle the mobility boundaries. The boundaries defined in atmospheric electricity textbooks are rather conventions. A natural classification is assumed to explain coherent behavior of air ions inside class intervals and relative independence of the ions of different classes. A requirement to measurements used in the verification of the classification is that the recorded air ion mobility fractions should be narrow when 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. First measurements that simultaneously satisfy both of these requirements have been carried out at Tahkuse Observatory where a 20-fraction air ion mobility spectrometer covering a mobility range of 0.00041–3.2 $cm^2 V^{-1} s^{-1}$ is running almost continuously since 1988 [*Hõrrak et al*., 1994].

The large and intermediate ions are charged aerosol particles, and their mobility is correlated with the particle diameter. Thus the problem is related to the atmospheric aerosol particle size classification. As well as in the case of mobility measurements, the measurements of particle size distribution in a wide size range have been episodic and the boundaries between the particle size classes are conventional. Obviously the air ion mobility data contains the largest available statistical information about long term variations of tropospheric aerosol size spectrum. Thus the analysis of mobility spectra at Tahkuse Observatory could provide essential information about natural classification of atmospheric aerosol particles according to their size.

LOCATION

Tahkuse Observatory (coordinates 58°31'N and 24°56'E) is located 27 km northeast of the city of Pärnu and 100 km south of Tallinn, the capital of Estonia, in a sparsely populated rural region. Pärnu, with 52000 inhabitants, lies on the coast of the Gulf of Riga. The terrain surrounding the observatory is flat open country with about 100 trees within a radius of 100 m, small woods, grassland and agricultural land. The Pärnu river is 50 m to northwest; the nearest farmhouse is about 200 m west. A road with little automobile traffic passes about 180 m east from the measurement point. The average traffic frequency was about 10 motor vehicles per day, mainly from 7 to 19 LST, in 1993–1994. The *Soomaa National Park* (Swampland) extends from 6 to 30 km southeast.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CZECH REP.
SLOVAK REP.
UKRAINE
MOLD.
FRANCE
SWITZERLAND
AUSTRIA
HUNGARY

INSTRUMENTATION

A complex of air ion spectrometers covering a mobility range of 0.00041–3.2 $cm^2 V^{-1} s^{-1}$ was installed at Tahkuse in 1988. The upper mobility limit was chosen to collect the smallest existing air ions. The lower mobility limit is determined by the technical parameters of the equipment. The complex consists of three original multichannel aspiration spectrometers designed according to the principle of the second order differential mobility analyzer. The whole range of mobility is logarithmically divided into 20 intervals: 9 intervals in the subrange of 0.00041–0.29 $cm^2 V^{-1} s^{-1}$ and 11 intervals in the subrange of 0.25–3.2 $cm^2 V^{-1} s^{-1}$ (see Table 1). The mobility spectra of positive and negative air ions were measured every 5 minutes. The hourly averages and standard deviations of the air ion fraction concentrations inside the hourly periods were recorded and saved on the hard disk of a PC together with the values of wind direction, wind speed, atmospheric pressure, temperature, relative humidity, and concentration of NO_2.

The air is sucked into the mobility spectrometers through an opening in the south gable of a building at a height of about 5 m from the ground. To prevent the effect of wind on the airflow, the air inlet (above) and outlet (beneath the inlet) are placed in the same gable with a separating space of about 1 m. The aluminum tube that conducts an air sample to the spectrometers is about 2 m in length, with a cross-section of 18×20 cm^2. The total air flow rate is about 16 liters per second, and air speed about 0.45 $m\ s^{-1}$. The devices, excluding meteorological sensors, are enclosed in a thermally insulated stable-climate chamber, which makes it possible to use the equipment through all seasons. The chamber and the tube of the air channel are electrically earthed.

MEASUREMENTS

Table 1

Frac. No.	Mobility $cm^2 V^{-1} s^{-1}$	Class of ions	Diameter nm
1	2.51–3.14	Small cluster ions	0.36–0.45
2	2.01–2.51		0.45–0.56
3	1.60–2.01		0.56–0.70
4	1.28–1.60		0.70–0.85
5	1.02–1.28	Big cluster ions	0.85–1.03
6	0.79–1.02		1.03–1.24
7	0.63–0.79		1.24–1.42
8	0.50–0.63		1.42–1.60
9	0.40–0.50	Inter-mediate ions	1.6–1.8
10	0.32–0.40		1.8–2.0
11	0.25–0.32		2.0–2.3
12	0.150–0.293		2.1–3.2
13	0.074–0.150		3.2–4.8
14	0.034–0.074		4.8–7.4
15	0.016–0.034	Light large ions	7.4–11.0
16	0.0091–0.0205		9.7–14.8
17	0.0042–0.0091		15–22
18	0.00192–0.00420	Heavy large ions	22–34
19	0.00087–0.00192		34–52
20	0.00041–0.00087		52–79

The present analysis is based on the data collected during the period from September 1, 1993, to October 27, 1994. Due to occasional pauses in the measurements, about 16% of the available time was lost, and 8615 hourly mobility spectra of both signs accompanied with meteorological data are on record.

Table 1 describes the scheme of mobility fractions and the classification of air ions. Long term averages and standard deviations of hourly averages for sum of cluster ion fractions are given in Table 2.

Table 2

Sign	Concentration cm^{-3}	Mobility $cm^2V^{-1}s^{-1}$	Conductivity $fS\ m^{-1}$
+	274 ± 96	1.36 ± 0.06	5.96 ± 2.1
–	245 ± 88	1.53 ± 0.10	5.95 ± 2.1

The concentration of large ions diminishes towards higher mobilities due to a reduction of charging probability and concentration of aerosol particles. The shape of their mobility spectrum is in accordance with calculations based on the theory of bipolar charging of aerosol particles by diffusion of cluster ions. Average concentration of intermediate ions is 40–50 cm^{-3}. Occasional bursts of intermediate ions up to about 900 cm^{-3} occur during daytime [*Hõrrak et al.*, 1998]. The intermediate ions are formed probably by diffusion charging of nanometer aerosol particles generated by photochemical nucleation process. Another process responsible for the generation of intermediate ions is the ion-induced nucleation. The variation coefficient of the hourly average values of fraction concentration is about 50% for small ions, 70% for large ions, and up to 130% for intermediate ions. At night-time, intermediate and large air ions show a lower variation coefficient of 50–60%.

AVERAGE SPECTRA

The average mobility spectra of air ions for the whole period are presented in Figures 1 and 2. There are two wide spectral groups with mobility ranges of 0.5–3.2 and 0.00032–0.034 $cm^2 V^{-1} s^{-1}$, which are traditionally called small ions and large ions, respectively. Particle diameters corresponding to electrical mobilities are presented in Figures assuming single charged particles [*Tammet*, 1995]. The third group between large and small ions, with mobility range of 0.034–0.5 $cm^2 V^{-1} s^{-1}$, is called intermediate ions. From physical considerations, large and intermediate ions can be called aerosol ions and the small ions can be called cluster ions [*Hõrrak et al.*, 1994].

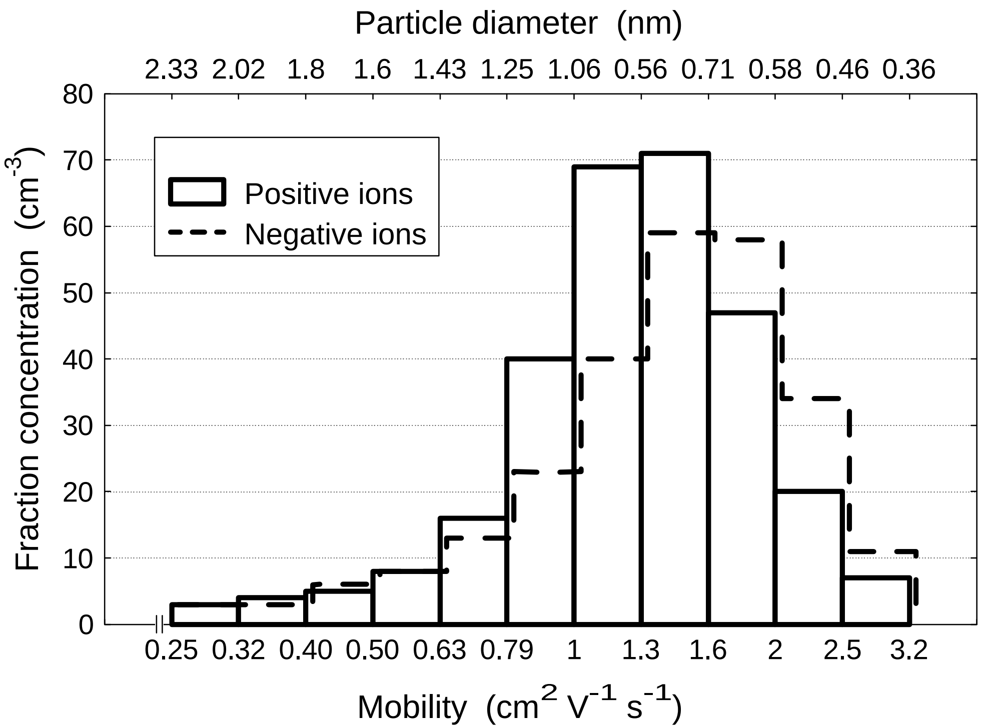

Figure 1. Average spectra of the cluster ions.

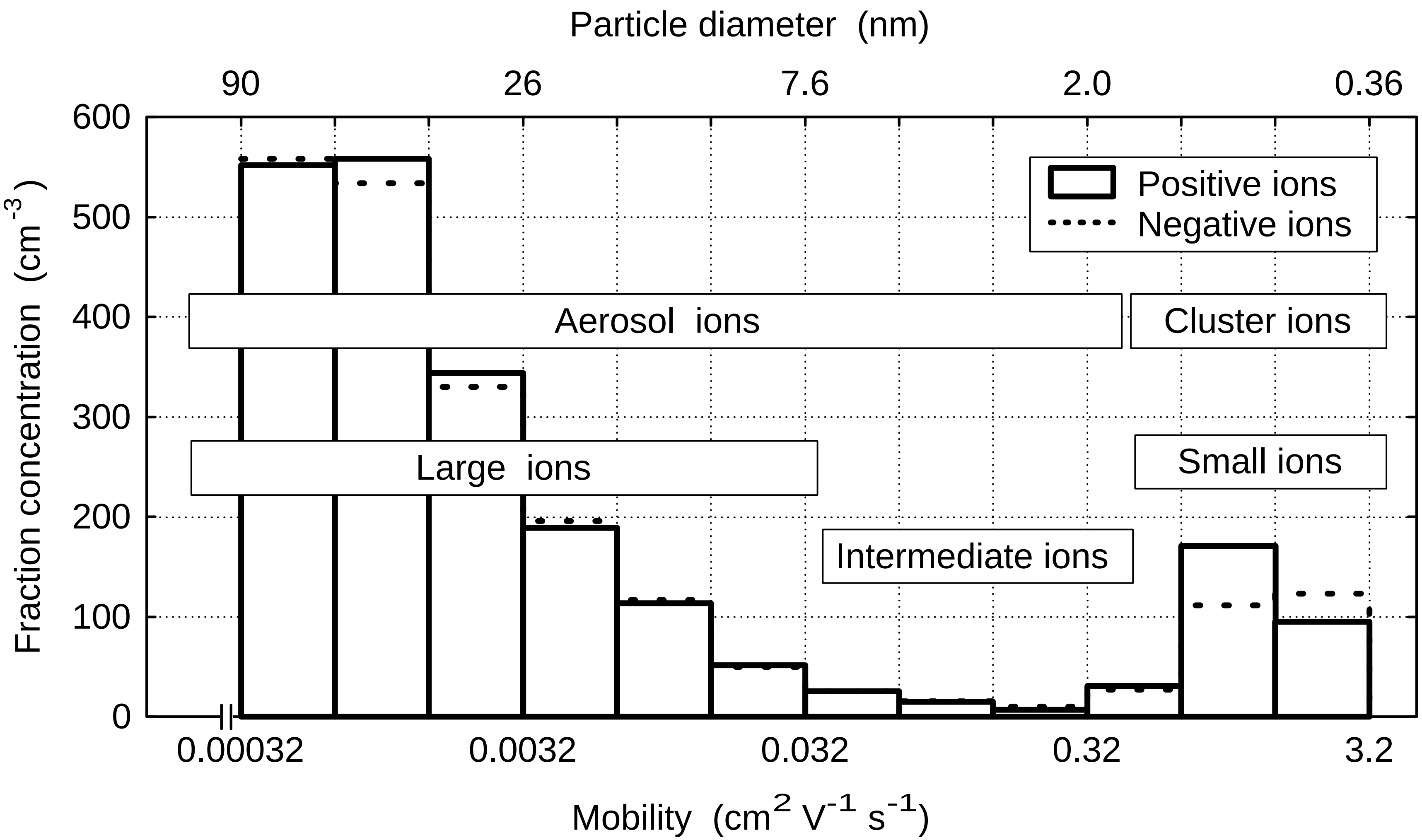

Figure 2. Average spectra of air ions at Tahkuse Observatory, September 1, 1993 – October 27, 1994.

FACTOR ANALYSIS

Fraction concentrations of air ions are interpreted as a set of closely correlated variables. Essential information about correlated variables can be represented by a reduced number of new variables, called the principal components, or factors. The analysis was carried out both in terms of the original values of the 20 fraction concentrations and of their logarithmically rescaled values, and the results are nearly the same. The eigenvalue problem was solved for the correlation matrix, which is equivalent to preliminary standardization of variables, or analysis of relative variations. The principal components were transformed to well interpretable factors with dominating positive factor loadings using the VARIMAX procedure. The factor analysis was carried out separately for positive and negative ions. The results presented in Figures 3 and 4 are very similar for positive and negative ions.

The first five principal components explain 92% of the total variance and each of the five factors presents at least as much variance as the average for one fraction concentration. The subsequent 14 principal components explain only 8% of the total variance. A part of this variation is caused by instrument noise. Thus the mobility spectrum has five essential degrees of freedom, and the set of 20 fraction concentrations can be relatively well described by only five factors representing at least 92% of all the measurement information.

Factor 1 (see Figure 3) is highly correlated with intermediate ions (fractions 9–14) and thus can be called the “burst factor” of intermediate ions. It accounts for 24% of the total variance. Factor 2 is highly correlated with big cluster ions (fractions 4–8, see Table 1), Factor 3 with small cluster ions (fractions 1–4), and Factor 4 with light large ions (fractions 15–18). They account for approximately equal variances, 20%, 18% and 17%. The contribution of Factor 5, associated with heavy large ions (fractions 18–20), is the lowest, 13%. This factor is correlated inversely with cluster ions (fractions 2–7). Factor 2, correlated highly positively with big cluster ions (fractions 5–8), is correlated negatively with heavy large ions (fractions 19–20).

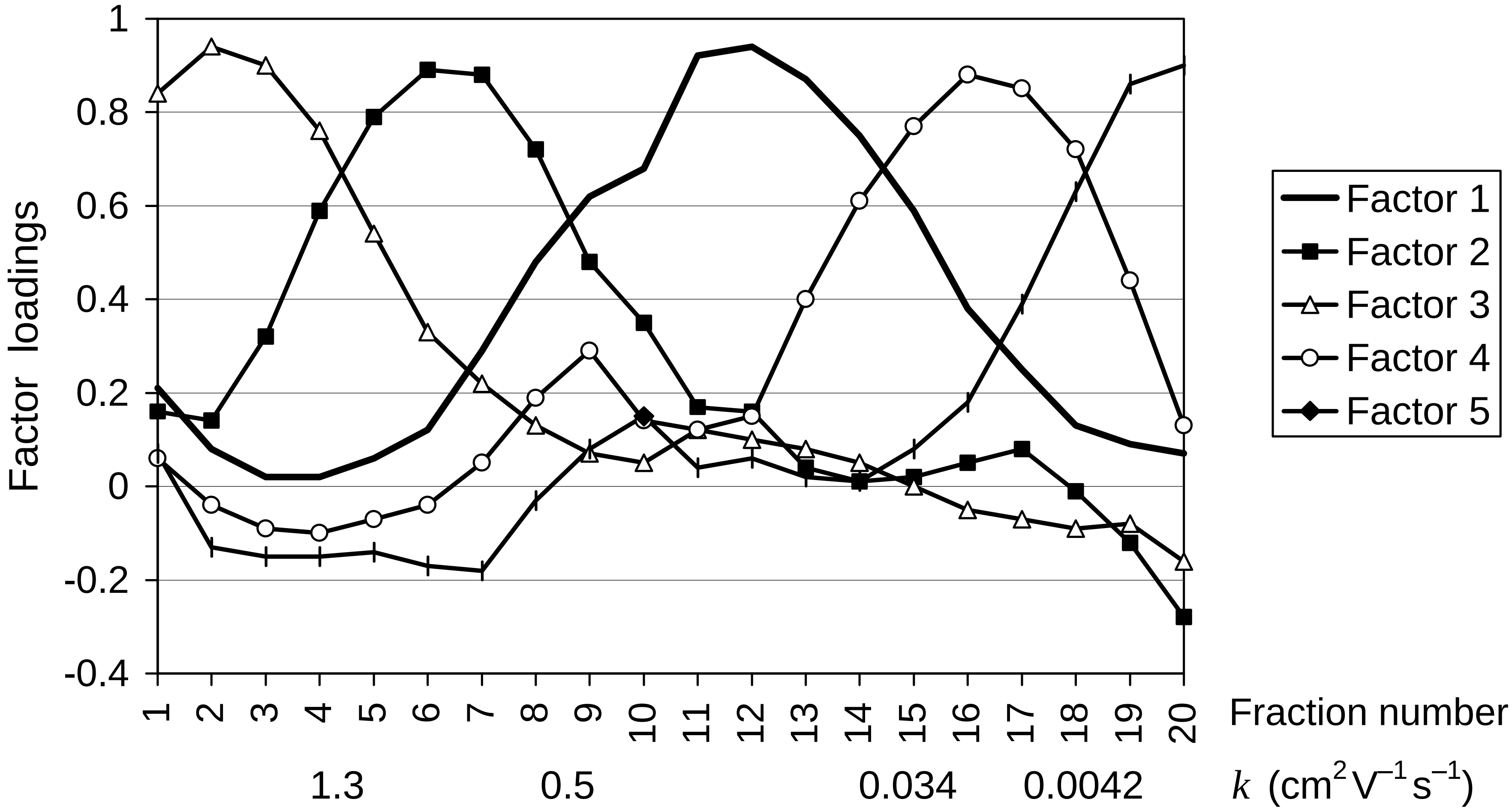

Figure 3. Factors of air ion mobility spectrum for positive ions.
The mobility and diameter boundaries of fractions are given in Table 1.

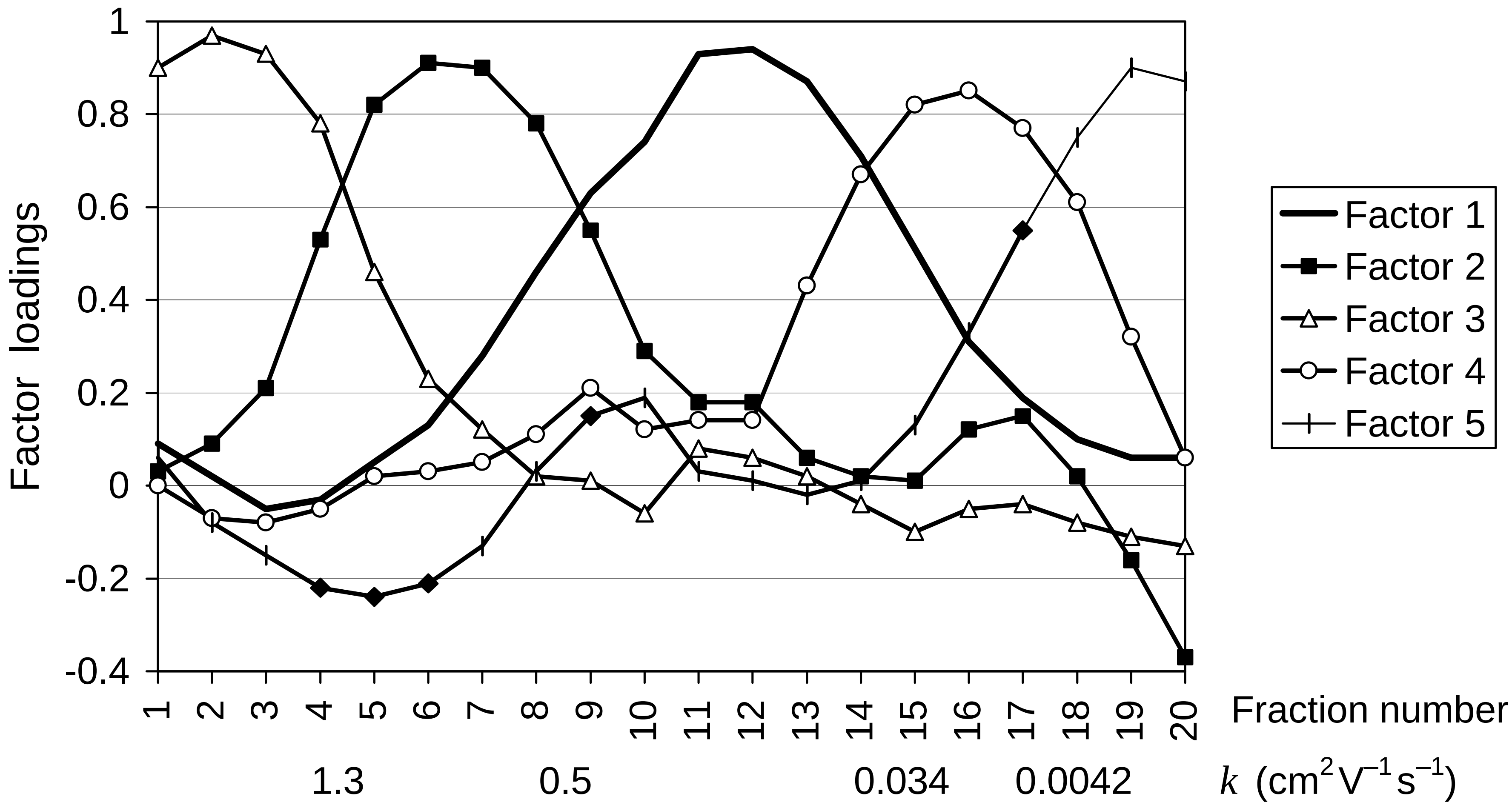

Figure 4. Factors of air ion mobility spectrum for negative ions.
The mobility and diameter boundaries of fractions are given in Table 1.

DISCUSSION AND CONCLUSIONS

The analysis of the correlations between the factors and air ion fraction concentrations shows that all the air ions can be divided into two wide classes: *cluster ions* with mobilities above $0.5\ cm^2\,V^{-1}\,s^{-1}$, and *aerosol ions* with mobilities below this boundary. Aerosol ions are particles with physical properties of macroscopic bodies. The cluster ions can be divided into two subclasses (small and big cluster ions), and the aerosol ions into three subclasses (intermediate ions, light and heavy large ions). This classification, given in Table 1, is still to a certain extent conventional and the boundaries are not exactly determined because the factors have crossloadings (any variable is correlated with more than one factor, see Figures 3 and 4).

A mobility of $0.5\ cm^2\,V^{-1}\,s^{-1}$ 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 [*Tammet*, 1995]. The same value of $0.5\ cm^2\,V^{-1}\,s^{-1}$ was also formerly considered as the lower boundary of small air ions [e.g., *Hõrrak et al.*, 1994].

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

- *Small cluster ions*: mobility $1.3–2.5\ cm^2\,V^{-1}\,s^{-1}$, estimated diameter 0.36–0.85 nm and mass 30–400 u. The core of a cluster could contain an inorganic molecule and be surrounded by one layer of water molecules. After recombination, the cluster would be destroyed and separated back to molecules.
- *Big cluster ions*: mobility $0.5–1.3\ cm^2\,V^{-1}\,s^{-1}$, estimated diameter 0.85–1.6 nm and mass 400–2500 u. The core of a cluster could contain an organic molecule and be surrounded by a layer of water molecules. In the case of intensive nucleation events (bursts) the enhanced concentrations were recorded simultaneously with intermediate and light large ion concentrations. As distinct from aerosol ions, collisions between cluster ions and ambient gas molecules are considered to be elastic [*Tammet*, 1995].

- *Intermediate ions*: mobility 0.034–0.5 $cm^2V^{-1}s^{-1}$, diameter 1.6–7.4 nm. The corresponding class of aerosol particles: the *fine nanometer particles*. Some intermediate ions are a product of ion–induced nucleation: nucleating vapor condenses to cluster ions, which grow to the size of intermediate ions called the *primary aerosol ions*. Particles born in the neutral stage in the process of gas-to-particle conversion, or nucleation, and charged by attachment of cluster ions, are called the *secondary aerosol ions*.
- *Light large ions*: mobility 0.0042–0.034 $cm^2 V^{-1} s^{-1}$, diameter 7.4–22 nm. The corresponding class of aerosol particles: the *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 $cm^2 V^{-1} s^{-1}$, 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.

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