10. CONTRIBUTION OF AIR ION MOBILITY CLASSES TO AIR CONDUCTIVITY

In relatively clean rural conditions, where small air ions are not depleted by aerosol particles, small ions are the key factor that determines the conductivity of atmospheric air. The average mobility distributions of positive air ion concentration and conductivity are presented in Figure 45. The mobility distribution of the concentration of negative ions is close to that of positive ions, but the peak mobility of negative small ions is at about 1.6 $cm^2V^{-1}s^{-1}$. The peaks in the mobility distributions of the conductivity are at the mobilities of 1.6–2.0 and 1.28–1.6 $cm^2V^{-1}s^{-1}$ for negative and positive polarity, respectively. The peak of the conductivity of negative polarity is shifted towards higher mobilities than that of positive polarity. The conductivity of heavy large ions of a mobility of 0.00041–0.0042 $cm^2V^{-1}s^{-1}$ diminishes toward lower mobilities; the increase in concentration does not compensate the decrease in mobility.

In average, small ions are responsible for 96.3%, intermediate ions for 2.2%, and large ions for 1.5% of the total conductivity, considering mobility range of 0.00041–3.2 $cm^2V^{-1}s^{-1}$. Only a small portion of the total conductivity less than 0.15 fS m^{-1}, and on 95% of all cases less than 0.05 fS m^{-1}, was produced by heavy large ions (0.00041–0.0042 $cm^2V^{-1}s^{-1}$). The percentage of the conductivity of heavy large ions was less than about 4% in all cases. The descriptive statistics of the conductivity of different air ion classes of positive and negative polarity are presented in Table 18.

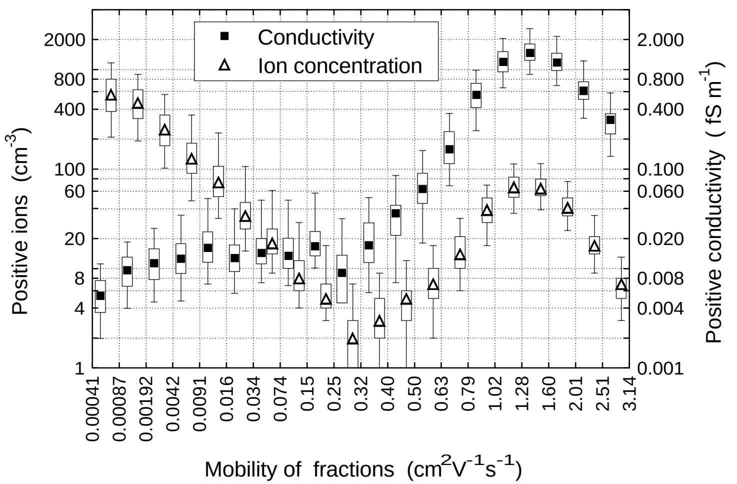

Figure 45. Average mobility distributions of positive air ion concentration and conductivity. Descriptive statistics: median, box (25% and 75%) and whiskers (5% and 95% quantiles). Tahkuse Observatory, 1.09.1993–27.10.1994.

The polar total conductivities (mobility range of 0.00041–3.2 $cm^2V^{-1}s^{-1}$) and the polar conductivities of small ions (0.5–3.2 $cm^2V^{-1}s^{-1}$) were closely correlated; the correlation coefficients were 98–99%. The correlation coefficient between a small ion concentration and the polar total conductivity was 99% and 98% for positive and negative polarity, respectively

The polar total conductivities are nearly equal with polar small ion conductivities $\lambda_- = 5.95 \pm 2.11$ fS m^{-1} and $\lambda_+ = 5.96 \pm 2.11$ fS m^{-1}. The increased mean natural mobility of negative small ions 1.53 $cm^2V^{-1}s^{-1}$, as compared to that of positive ions 1.36 $cm^2V^{-1}s^{-1}$, entirely compensates the differences in the concentration, in general. The mean values and standard deviations of the ratios of concentrations, the mean mobilities and the conductivities of small ions are: $n_+/n_- = 1.13 \pm 0.07$, $k_+/k_- = 0.891 \pm 0.039$ (for reciprocal value 1.12 ± 0.05), $\lambda_{s+}/\lambda_{s-} = 1.00 \pm 0.05$, and the ratio of total conductivity is $\lambda_+/\lambda_- = 1.00 \pm 0.05$.

A regression analysis shows that the average polar total conductivities are nearly equal; considering the entire range of measured values of conductivities from about 1.5 to 26 fS m^{-1}, the correlation coefficient is 99%.

Table 18. Descriptive statistics of conductivity (fS m^{-1}) induced by different air ion classes. The number of measurements: 8615. Tahkuse, 1.09.1993–27.10.1994.

a) positive polarity.

Ion classes	Mean	Median	Min	Max	Lower Quart.	Upper Quart.	Std. Dev.
Small cluster ions	3.86	3.59	0.70	18.03	2.97	4.39	1.44
Big clusters ions	2.10	2.02	0.47	8.28	1.55	2.55	0.78
Cluster ions	5.97	5.61	1.22	26.31	4.62	6.83	2.11
Intermediate ions	0.13	0.11	0.00	1.77	0.08	0.14	0.12
Large ions	0.08	0.07	0.01	0.92	0.05	0.10	0.06
Intermediate and light large ions	0.19	0.15	0.01	2.10	0.11	0.20	0.16
Total polar conductivity	6.18	5.81	1.38	26.74	4.8	7.07	2.14

b) negative polarity.

Ion classes	Mean	Median	Min	Max	Lower Quart.	Upper Quart.	Std. Dev.
Small cluster ions	4.64	4.30	1.16	22.20	3.62	5.16	1.72
Big clusters ions	1.32	1.21	0.26	5.05	0.78	1.76	0.65
Cluster ions	5.96	5.59	1.48	25.86	4.61	6.81	2.12
Intermediate ions	0.14	0.10	0.00	2.23	0.07	0.15	0.14
Large ions	0.08	0.07	0.01	0.92	0.05	0.09	0.05
Intermediate and light large ions	0.19	0.15	0.01	2.47	0.11	0.2	0.17
Total polar conductivity	6.18	5.81	1.71	26.12	4.81	7.05	2.14

The frequency distributions of the conductivity of positive and negative small (cluster) ions and the total polar conductivities are asymmetric because of higher outliers (tails of distributions). The peaks of frequency distributions are at about medians. The frequency distributions are close to lognormal one.

The descriptive statistics of the percentage contribution of the conductivity of different air ion classes to the total polar conductivity are given in Table 19. The distribution of the percentage contribution of the conductivity caused by small ions has a sharp peak at 97–98%; the shape of the distribution is similar to a mirror image of a lognormal distribution and has a long tail down to 75%. The distribution of the percentage contribution of the conductivity caused by small ions is opposite to that of intermediate and large ions. The contribution of intermediate and large ions to the total conductivity is small, in general a few percents. In the case of bursts of intermediate ions (more than 100 cm^{-3}) in the afternoon, the contribution of intermediate and light large ions (0.0042–0.034 $cm^2V^{-1}s^{-1}$) to the total conductivity was considerably higher, up to 26%.

Table 19. Descriptive statistics of the percentage contribution of the conductivity induced by different air ion classes of negative/positive polarity to the total polar conductivity. The number of measurements: 8615. Tahkuse, 1.09.1993–27.10.1994.

Ion classes	Mean	Median	Min	Max	Lower Quart.	Upper Quart.	Std. Dev.
Small cluster ions	75/62	77/63	47/42	91/82	71/59	81/66	7.6/5.8
Big clusters ions	21/34	20/34	7/17	47/50	16/31	25/37	6.8/5.2
Cluster ions	96/96	97/97	73/74	99.7/99.8	96/96	98/98	2.7/2.4
Intermediate ions	2.3/2.2	1.7/1.8	0.1/0.1	24/19	1.2/1.4	2.6/2.5	2.0/1.7
Large ions	1.5/1.5	1.2/1.2	0.1/0.1	12/12	0.8/0.8	1.8/1.8	1.1/1.1
Intermediate and light large ions	3.2/3.2	2.5/2.5	0.1/0.2	27/25	1.8/1.9	3.7/3.6	2.5/2.3

In the conditions of the decreasing conductivity of small air ions at noontime (probably due to the decreasing ionization rate because of intensive mixing of radon and its decay products to upper levels) the burst of intermediate ions may also prevent a decrease in the total conductivity. The decrease in conductivity caused by small ions was compensated with an enhanced concentration of less mobile intermediate ions (see Figure 46).

Misaki [1961] carried out air ion spectra measurements at two locations (in Tokyo and Karuizawa) in Japan in 1960. He has also concluded that "In the polluted air, scores of percent of the conductivity should be attributed to the large or the intermediate ions, while the conductivity in the clean air is practically attributed to the small ions only, as generally believed."

Dhanorkar and Kamra [1993b] measured simultaneously the concentrations of small, intermediate and large ion categories and the total polar conductivities at a height of 1 m above the ground at Pune, India, and calculated the percentage contribution of different air ion categories to the polar conductivity. They found that for most of the days, the contribution of small ions to the polar conductivity is dominant and sometimes it is higher than 95%; intermediate ions contribute less than 20% and large ions less than 5%, in general. On the contrary, in the morning hours, when the concentrations of intermediate and large ions are large compared to that of small ions, the contributions of intermediate and large ions are comparable or even exceed that of small ions. In extreme cases the contributions of small, intermediate, and large ions are estimated to be 5%, 50%, and 45%, respectively. This peculiarity could originate from a relatively low position of spectrometers (1 m above the ground) and from the local orographical and meteorological conditions that could cause the accumulation of pollutants during strong nocturnal inversions.

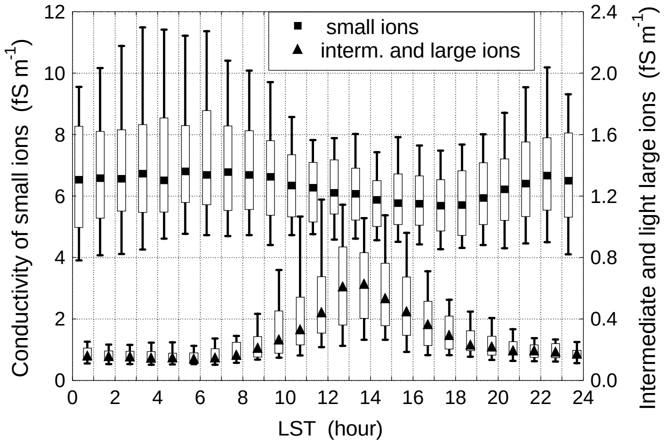

Figure 46. Average diurnal variation of the conductivity of small and intermediate and light large ions considering days of intermediate ion burst events. Descriptive statistics: median, box (25% and 75%) and whiskers (5% and 95% quantiles). Tahkuse Observatory 1.09.1993–27.10.1994.

Since conductivity is mainly caused by the concentration of small ions, the regularities of annual and diurnal variations, and the correlation with large ions are nearly the same as in the case of small ion concentration. In the wintertime conductivity was correlated negatively with heavy large ion concentration (see Table 20). The lower the mobility of heavy large ions, the higher the correlation coefficient was. On the contrary, in the warm period, the correlation was practically absent, in general. The negative correlation was observed also in the warm season when the cases of weak winds (wind speed less than 0.5 m s^{-1}) preferentially during nighttime calms, were eliminated.

Comparing the correlation coefficients of negative small ion fraction concentrations and those of positive ions with conductivity, the reduction of correlation coefficients is evident in the case of negative large clusters of mobility 0.5–1.28 $cm^2V^{-1}s^{-1}$ (see Table 20). This reduction is significant only in the warm season (May–September) and it is probably caused by the appearance of a low mobility mode of negative ions in a range of 1–1.3 $cm^2V^{-1}s^{-1}$. The concentration of these ions usually increased in the afternoon when the conductivity was decreasing, which caused a negative correlation between these quantities during this period; thus the reduction of correlation coefficient, in general. In the warm season the correlation coefficients between conductivity and concentrations of small cluster ions (1.28–2.5 $cm^2V^{-1}s^{-1}$) in Table 20 are reduced when the periods of low winds (commonly nocturnal calms) were eliminated. So the changes in the mean mobility of small ions that affect the conductivity have to be taken into account.

Table 20. Correlation coefficients (%) of negative /positive conductivity ($\lambda_{\pm}$) with the air ion fraction concentrations of the same polarity in the cold season (November–April) and in the warm season (September–May). The absolute value of critical correlation coefficient at a confidence level of 95% is about 3–4%.

Mobility range $cm^2V^{-1}s^{-1}$	Cold season	Cold season without bursts	Warm season	Warm season, wind >1 m s^{-1}	Warm season, wind >1 m s^{-1} without bursts
	λ_-/λ_+	λ_-/λ_+	λ_-/λ_+	λ_-/λ_+	λ_-/λ_+
2.51–3.14	71/66	72/64	86/85	43/54	44/57
2.01–2.51	84/85	87/86	92/88	62/56	66/62
1.60–2.01	92/92	95/94	95/95	77/77	81/84
1.28–1.60	98/98	98/99	97/99	93/94	96/97
1.02–1.28	89/94	88/94	77/95	86/89	88/90
0.79–1.02	76/84	73/84	40/82	74/80	76/81
0.63–0.79	63/71	60/71	28/64	63/72	65/74
0.50–0.63	40/45	32/41	21/51	51/59	51/63
0.40–0.50	22/24	4/10	17/33	37/40	38/46
0.32–0.40	13/19	-10/1	9/35	27/36	20/33
0.25–0.32	17/17	-3/-4	9/17	28/29	20/19
0.150–0.293	17/17	-2/-8	8/16	27/26	20/12
0.074–0.150	16/16	-15/-21	2/7	20/20	1/-3
0.034–0.074	13/13	-22/-27	-3/3	14/16	-14/-10
0.016–0.034	4/5	-28/-31	-6/0	8/12	-21/-13
0.0091–0.0205	-9/-8	-35/-33	-1/-1	7/8	-8/-6
0.0042–0.0091	-30/-28	-44/-43	-1/-3	-5/-4	-17/-16
0.00192–0.00420	-49/-47	-53/-52	-2/-3	-17/-16	-25/-23
0.00087–0.00192	-65/-61	-61/-59	-5/4	-37/-31	-42/-35
0.00041–0.00087	-68/-69	-68/-69	-7/-1	-54/-53	-56/-54

A loose correlation of intermediate and light large ion concentrations with conductivity confirms that their contribution to the total aerosol electrical density (depletion rate of small air ions by aerosol particles) is not significant in the presence of abundant less mobile particles (particles with large size). So it is problematic to use conductivity as an indicator of particulate pollution even in a relatively clean rural location, where conductivity is mainly caused by small ions. Small air ions are depleted by aerosol particles proportionally to their diameter concentration [*Hoppel et al*., 1986, *Tammet*, 1991]; thus the particles of different sizes contribute differently to the reduction of small ion concentration and, accordingly, to the air conductivity [*Kojima*, 1982]. Air conductivity also depends on the ionization rate of air, that may undergo considerable annual and diurnal variations due to the changes in radon concentration [*Porstendörfer*, 1994].

The results obtained from model calculations by *Dhanorkar et al*. [1997] show that the inverse relationship between polar conductivity and aerosol concentration exists only up to a certain critical value of aerosol concentration, which depends upon the ionization rate. Henceforth, when all small ions are depleted by aerosol particles, increase in aerosol concentration causes an increase in polar conductivity due to the contribution made to it by large ions.

The variation of small ion mobility is a factor to be considered when estimating air conductivity according to the ion concentration measurements. Scatterplot of small ion concentration versus conductivity of small ions depicted in Figure 47 shows that the deviation of the mean mobility of small ions from the average could cause an uncertainty in conductivity from about –12% to +15% and from –14% to +26% for positive and negative polarities, respectively (considering a single hourly average measurement). It was found that the natural mean mobility shows a tendency to increase in the case of low or high concentration of small ions (less than about 200 cm^{-3} or more than 500 cm^{-3}), otherwise it shows a considerable variation (see Figure 47). The mean mobility of small ions is higher during nocturnal calms (expected effect of radon decay on the ionization rate, and the ionization rate on the lifetime of ions). The mean mobility of small ions is also positively correlated with the heavy large ion concentration (expected dependence of cluster ion lifetime on aerosol particle concentration). The frequency distributions showed that the natural mean mobility of small positive ions could vary from 1.18 to 1.55 $cm^2V^{-1}s^{-1}$ (maximum at about 1.38 $cm^2V^{-1}s^{-1}$), the same for small negative ions is from 1.2 to 1.76 $cm^2V^{-1}s^{-1}$ (maximum at about 1.6 $cm^2V^{-1}s^{-1}$).

Summarizing the results we confirm the fact that air conductivity is mainly caused by small ions. However, in specific situations the concentrations of intermediate and light large ions have a considerable contribution on air conductivity (up to 26%) and should not to be neglected. The contribution of intermediate and light large ion concentrations could be significant not only in the polluted urban air, but also in the relatively clean rural air during the bursts of intermediate ions. The measurements show definitely that the mean mobility of cluster ions is a factor that should be considered.

The conductivity could be used as an indicator of particulate pollution when the ionization rate is nearly constant compared to the changes in aerosol particle diameter concentration, and small ions are not entirely depleted by aerosol particles. On the contrary, if the expected changes in the diameter concentration of aerosol particles are small compared to those in the ionization rate, then air conductivity could be used as an indicator of the integral ionization rate of environment (α, β, γ radiation and cosmic rays).

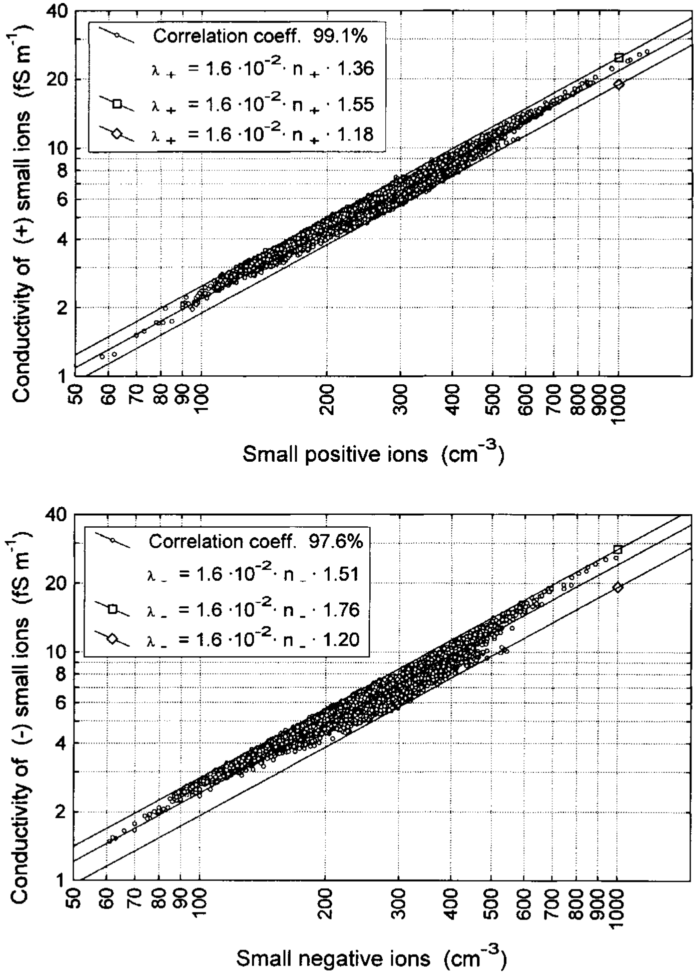

Figure 47. Scatterplot between the polar conductivity of small ions (0.5–3.14 $cm^2V^{-1}s^{-1}$) and small ion concentration. Tahkuse Observatory, 1.09.1993–27.10.1994. Constants 1.18, 1.36, 1.55 and 1.2, 1.51, 1.76 have to be considered as the lower boundary, the mean, and the upper boundary of small ion mobility in units $cm^2V^{-1}s^{-1}$, respectively for positive and negative polarity.