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Comparison of sampling artifacts and ion balances for a Berner low-pressure impactor and a virtual impactor

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Between April 1996 and June 1997, parallel fine particle aerosol samples were collected with a virtual impactor (VI) and a Berner low-pressure impactor (BLPI) at both an urban and a rural site in the Helsinki area. The average size distributions for particulate sulphate, ammonium, oxalate, succinate, MSA, Na^+, K^+ and Mg^{2+} were similar at the two sites, while average concentrations were slightly higher at the urban site. Average BLPI/VI ratios of Na^+, K^+ and succinate were close to one indicating that no major sampling artifacts for these ions were present. The corresponding ratios were larger than one for Ca^{2+} and Mg^{2+}, suggesting that some particle bounce-off occurred in the BLPIs. The ratios smaller than one for pyruvate, malonate, oxalate, ammonium, glutarate, MSA, and sulphate suggest that some fraction of these ions was formed from gaseous precursors on the VI Teflon filters. Particulate nitrate evaporated from the VI Teflon filters and from the BLPI, the average evaporation percentages varying between about 50%–65%. Chloride seemed to evaporate from the VI Teflon filters, the evaporation being more pronounced at the urban site where the concentration of gaseous SO_2 was higher. The fine particle cation/anion ratios were lower for the VI at both sites, and higher at the rural site for both sampler types. The contribution of organic anions to total anions was higher during the summer than during the winter for fine particles, even though these contributions were similar for ultrafine particles.

Introduction

Water-soluble ions in atmospheric aerosol particles play an important role in the formation of clouds and acid precipitation (Cantrell *et al*. 2000, Butler *et al*. 2001), as well as in the aerosol climatic forcing (Adams *et al*. 2001). The inorganic ions sulphate, nitrate and ammonium, formed mainly through various gas-to-particle conversion mechanisms, constitute a major fraction of the fine mass of atmospheric aerosols (Heintzenberg 1989). The coarse maritime particles are usually dominated by the ions Na^+ and Cl^-, which originate from sea-salt, whereas in

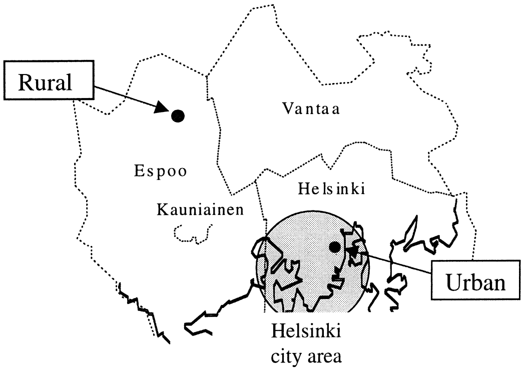

Fig. 1. Location of the urban and rural sampling sites.

coarse continental particles the ion Ca^{2+} is often important. In addition to these, many organic ions are frequently found in atmospheric aerosol particles (Chebbi and Carlier 1996, Limbeck and Puxbaum 1999).

Measuring the concentration and size distribution of inorganic and organic ions in atmospheric aerosols is susceptible to several kinds of artifacts, which may lead to large uncertainties in the experimental results (Wang and John 1988, McMurry 2000). Depending on meteorological conditions and the instruments used, ammonium nitrate and other semi-volatile compounds, present originally in the particle phase, may evaporate inside the instrument during the sampling (Cheng and Tsai 1997, Warner *et al.* 2001, Yao *et al.* 2001). Similarly, compounds originally present in the gas phase may be adsorbed by the collecting filters or react with particles already residing on these filters (Kirchstetter *et al.* 2001, Limbeck *et al.* 2001). An example of the latter phenomenon is the SO_2-to-sulphate conversion that can occur on several filter types and lead to overestimated sulphate concentrations (Tsai and Perng 1998). Occurrence of artifacts is revealed often by intercomparisons where different sampler types are used for measuring various chemical components (Pakkanen *et al.* 1999, Limbeck *et al.* 2001).

In this work, the sampling characteristics of a Berner low-pressure impactor and a virtual impactor were investigated based on simultaneous measurements at an urban and a rural site. Our principal aim was to identify the most important sampling artifacts affecting both the measured ionic concentrations and the ion balances. Mass size distributions of the measured ions were utilised in estimating these artifacts.

Experimental methods

The measurement sites

The measurements were made in Vallila, Helsinki, which is an urban site about 2 km northeast from the city center, and in Luukki, Espoo, which is a rural site about 25 km northwest from the center of Helsinki (Fig. 1). The measurements were performed on the roof of the measurement stations of the Helsinki Metropolitan Area Council, about 3.5 meters above the ground level. At the urban site the distance to the nearest road was 14 meters. Calculations made in 1997 showed that the average daily traffic on this road was about 14 000 cars. The number of different car types can be estimated on the basis of the counting made in 1993: 10 000 gasoline cars, 1500 diesel cars or vans, 2000 buses, and 500 trucks. The rural sampling site is situated in a forest area on the yard of an old farmer house. The house is not used for living except that in the summer it is sometimes used as a camp for children.

Size-segregating aerosol measurements

Between 10 April 1996, and 13 June 1997, a total of 56 and 53 virtual impactor (VI, Loo and Cork 1988) samples were collected at the urban and the rural site, respectively. The sampling time was 24 hours. Fine particles (equivalent aerodynamic particle diameter, EAD < 2.3 μm) were collected on 47 mm Teflon filters (first Millipore, pore size 3 μm and from 12 June onwards Gelman Sciences, pore size 2 μm). Starting from 9 August (sample 16), the volatilisation of nitrate from the Teflon filters during the sampling was measured by collecting the evaporated nitric acid on 47-mm nylon filters (Gelman Sciences, pore size 0.45 μm). At the rural site there were problems in collecting coarse particles, and therefore the VI results for the coarse particles are not discussed in this paper. The VI instruments were equipped with stainless steel inlets including a pre-impactor with a cut-size of about 15.7 μm of EAD (Liu and Pui 1981). The inlet removes efficiently atmospheric nitric acid from the sampled air (Neuman *et al*. 1999, Pakkanen *et al*. 1999).

In order to measure the size distribution of atmospheric particulate ions, 16 and 13 Berner low-pressure impactor (BLPI; Berner and Lürzer 1980) samples were collected at the urban and rural sites, respectively (*see* Table 1 for the sampling schedule). The sampling time for the BLPI was 24 or 48 hours, and the measurements were always conducted in parallel with one or two VI measurements. Collection of the samples 1, 3 and 10 failed at the rural site due to technical problems at the station. The BLPIs collected particles on polycarbonate films (Nuclepore Inc.). The sampling flow rate was 25.2 liters per minute. The 50% cut-off diameters of the ten impactor stages were 7.5, 3.5, 1.8, 0.94, 0.53, 0.32, 0.16, 0.093, 0.067 and 0.035 μm of EAD. Calibration of the BLPI instruments was based on the work of Wang and John (1988) and of Hillamo and Kauppinen (1991). Sample handling and preparation of the collection substrates was made as described by Pakkanen (1996). Similar to the VI, pre-impactors with a cut-size of 15.7 μm of EAD were used. Both VI and BLPI measurements started at about 09.00–10.00.

Mass and chemical analysis

The VI Teflon filters and the BLPI substrates were weighed before and after the sampling using a Mettler M3 microbalance. Before weighing, the samples were stored in a cool (+5 °C) and dark room, and then kept for about 24 hours in the weighing room at a relative humidity (RH) of about 35 ± 5%.

The particle-bound water-soluble ions chloride, sulphate, nitrate, methanesulphonate, oxalate, malonate, succinate, glutarate, pyruvate, ammonium, sodium, potassium, magnesium and calcium were analysed by ion chromatography (IC). Details of the analysis protocol have been presented earlier (Kerminen *et al*. 2000).

Weather conditions and air mass back-trajectories

The weather parameters, including the average temperature, average relative humidity, average wind speed and rain duration, are shown separately for all the BLPI sampling periods in Table 1. Three-dimensional, 96-hour air mass back-trajectories were calculated for all samples according to the method of Valkama and Salonoja (1995).

Results and discussion

Quality control

The lowest concentrations in the individual BLPI stages, as well as the lowest concentrations of certain components in the VI samples, were sometimes close to or even below the average blank values. Therefore, a strict quality control was needed to get reliable results. A comprehensive quality control analysis has been presented in our earlier paper (Pakkanen *et al*. 2001a).

Average size distributions and calculation of fine particle concentrations for the BLPI

The average size distributions of individual ions, presented in Fig. 2, were calculated by summing up the ten individual MICRON-inverted (Wolfenbarger and Seinfeld 1990) BLPI size distributions for each of the two sites (samples 2, 4, 5, 6, 7, 8, 9, 11, 12, and 13). These inverted size distributions were utilised in calculating the fine particle concentrations for the BLPI samples. In order to make the concentrations comparable, the concentrations are expressed as neq m^{-3} (a log-transformation). Note that formation from gaseous precursors and/or evaporation may have occurred for several ions during the sampling. The shape of the size distributions is utilised later when discussing possible sampling artifacts.

Table 1. Sampling schedule: start date, Berner impactor (BLPI) and corresponding virtual impactor (VI) sample numbers, and sampling duration. The measurements always started at about 9.00–10.00. Average weather conditions and air mass origin are shown.

Start date	Sample number		Duration	U	RH	T	Rain	Air mass origin
	BLPI	VI	h	m s^{-1}	%	°C	%	
1996								
12 June	2	10, 11	48	6.6	86	13	8	S Sweden–Denmark–N Germany–Great Britain
15 October	4	24, 25	48	5.3	76	6	0	N Estonia–St. Petersburg–Central Finland–Central Sweden
19 November	5	28, 29	48	5.5	93	6	21	Baltic Countries–Poland–N Germany–Czech–Belarus
9 December	6	32, 33	48	4.3	96	3	1	W Finland–Central Sweden–S Norway
1997								
13 January	7	37, 38	48	5.5	93	1	0	W Finland–Central Sweden–S Norway–Great Britain
4 February	8	39, 40	48	6.6	89	–1	0	SW Finland–S Sweden–S Norway–Great Britain
18 March	9	45, 46	48	4.2	72	–5	0	–
13 May	11	50, 51	48	3.5	71	12	0	SW Finland–S Sweden–Denmark–Benelux–N France
2 June	12	52	24	2.3	50	14	0	SE Finland–Lake Ladoga–Archangel
4 June	13	53	24	3.0	39	12	0	SW Finland–N Sweden–N Norway
6 June*	14	54	24	2.9	49	17	0	Baltic Sea–Central Scandinavia
10 June*	15	55	24	2.6	84	17	0	Estonia–Central Russia
12 June*	16	56	24	1.9	62	22	0	S Finland–W Finland

U = Average wind speed, RH = Average relative humidity, T = Average temperature, Rain = % rain (of time)

* Collection at the urban site only

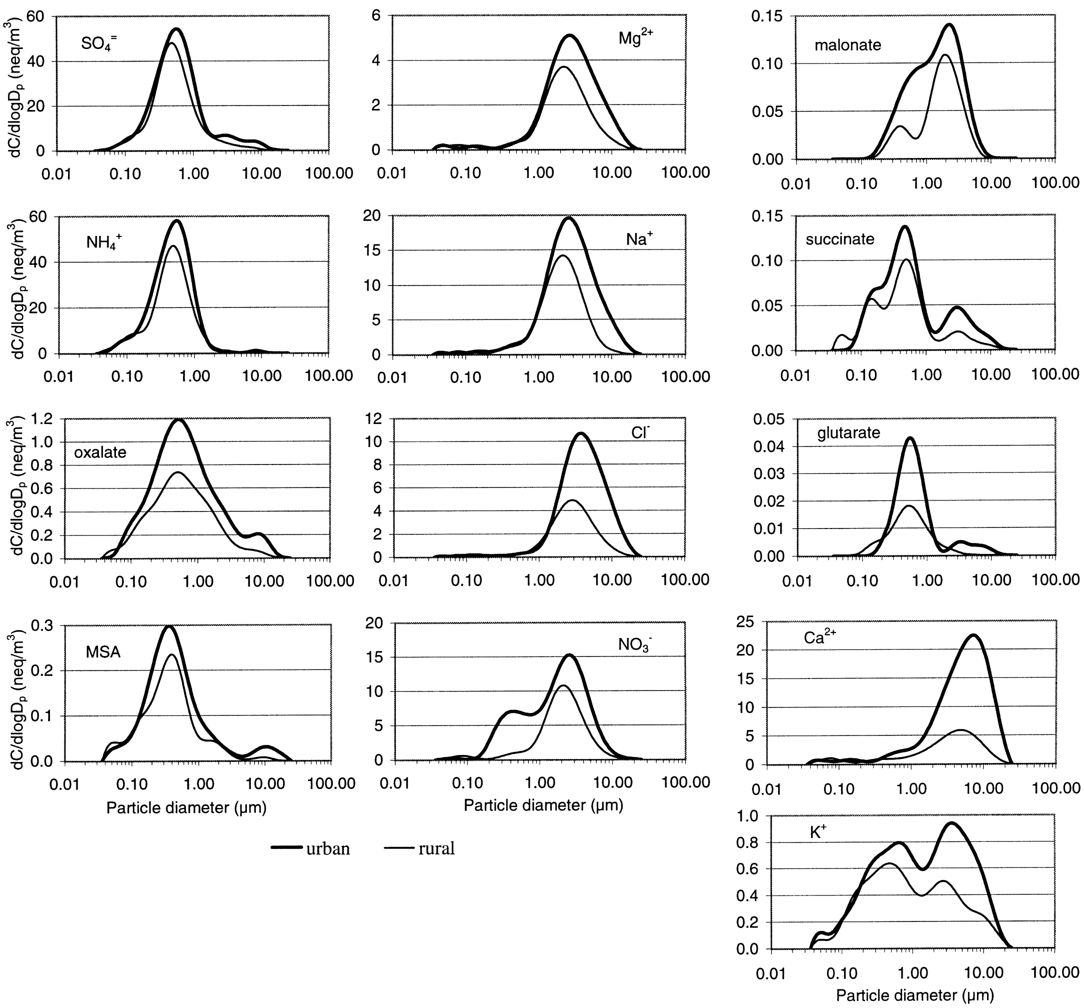

Fig. 2. Average urban and rural size distributions. In the y-axis, *C* refers to the concentration and D_p to the particle diameter.

Fine particle ionic concentrations and possible sampling artifacts in the BLPI and the VI

The average mass and ion concentrations (Pakkanen *et al.* 2001b), as well as the concentration time series for sulphate, sodium, methane sulphonate, oxalate, malonate and succinate (Kerminen *et al.* 2000), have been presented earlier. In this paper, we present a comparison for the average fine particle BLPI/VI ratios of the ions measured simultaneously at each site (Fig. 3). The average ratio was slightly higher at the urban site for all ions, which suggests that there may have been some uncertainties in the sample volume concerning one or more of the sampling instruments. Also a possible coarse particle bounce-off in the BLPI, being likely more pronounced at the urban site, would lead to a trend shown by Fig. 3. Erroneous 50% cut-off sizes are unlikely to be responsible for these differences, since all sampling instruments were calibrated carefully.

When calculating the average BLPI/VI ratios, one to two obvious outlier values were discarded for some components. Often these outliers occurred for some of the lowest concentrations or concentrations below the limit of deter-

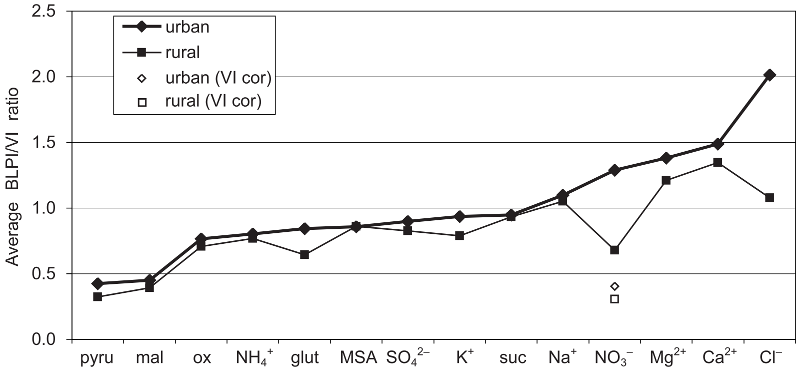

Fig. 3. Average fine particle BLPI/VI ratios at the two sites. For nitrate also ratios with corrected VI concentrations are shown.

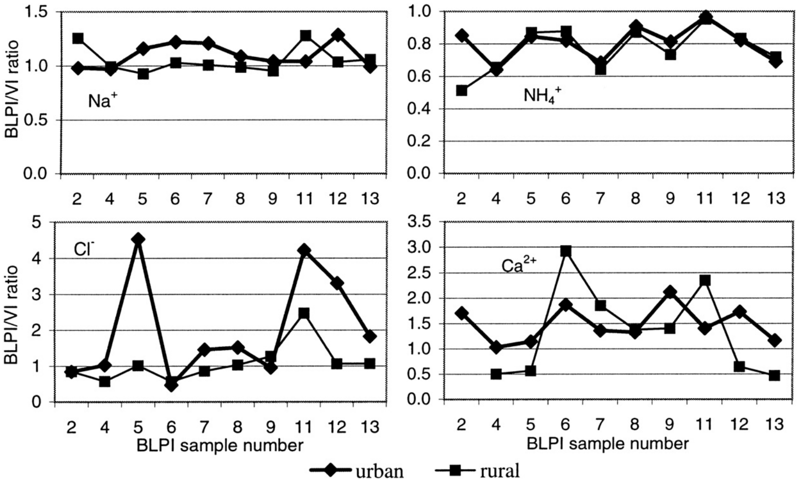

Fig. 4. Fine particle BLPI/VI ratios measured for Na^+, NH_4^+, Cl^- and Ca^{2+}.

mination. At both sites the average BLPI/VI ratios were quite similar for each ion, except for nitrate and chloride. Note that in Fig. 3 we have included the case in which the NO_3^- volatilisation was corrected for the VI but not for the BLPI, which leads to lower BLPI/VI ratios at both sites. The BLPI/VI ratio was relatively stable for MSA, SO_4^{2-}, oxalate, Na^+, NH_4^+, and K^+, whereas for the other ions the ratio showed a considerable variation. This is illustrated in Fig. 4, where Na^+ and NH_4^+ display stable ratios and Cl^- and Ca^{2+} more variable ratios. The similarity of the BLPI/VI time series between the sites, as observed for NH_4^+, Na^+, MSA, NO_3^-, glutarate, SO_4^{2-}, oxalate, K^+ and Mg^{2+}, suggests that these ions experienced similar sampling conditions over large areas and that the sampling instruments operated properly.

In order to explain the differences between the BLPI and the VI, the different potential sources of uncertainty were estimated. The parallel BLPI and VI samples were analysed from same batches of the samples. Therefore, it is estimated that analytical uncertainties had only a minor influence, probably well below 10% (Jordan *et al.* 2000), on the calculated cation/anion and BLPI/VI ratios. Also the uncertainties in the sampled air volumes were estimated to be low, since the most reliably measurable ions, sulphate and sodium, showed ratios close to one. It seems that the differences between the BLPI and the VI were caused mainly by artifacts occurring in the different types of collectors during the sampling. The probable artifacts for each ion are estimated below.

Sodium, potassium, magnesium and calcium

According to our current understanding, transportation of the ions Na^+, K^+, Mg^{2+} and Ca^{2+} between the gas and particle phases should not be possible under atmospheric conditions. The average BLPI/VI ratios (Fig. 3) of Na^+ and K^+ were close to one, while those of Mg^{2+} and Ca^{2+} showed relatively high values between about 1.2 and 1.5. One likely explanation for this can be found by comparing the size distributions of these ions (Fig. 2): a possible coarse particle bounce-off inside the BLPI would increase fine particle concentrations, especially in case of Ca^{2+}.

Chloride

The BLPI/VI ratio for chloride was much higher at the urban site than at the rural site. In the VI all particles having a diameter < 2.3 μm are mixed on the Teflon filter, whereas in the BLPI only particles having approximately the same size are mixed. In the VI this allows for the reaction between potentially acidic accumulation-mode particles and more neutral sea-salt particles. Also gaseous compounds have a higher probability to react with the sampled particles on the VI Teflon filter: in the BLPI there is only a minor contact between the particle deposits and the gaseous components, whereas in the VI all gases pass through the sample and the Teflon filter allowing for gas-particle interactions. Hence chloride can easily react with sulphur dioxide and other acidic gases on the VI Teflon filter, which would lead to chloride evaporation (Tsai and Perng 1998, Yao *et al.* 2001). The different BLPI/VI ratios between the sites can be explained by the fact that, compared with the rural site, the sulphur dioxide concentrations were two to six times higher at the urban site, as indicated by the routine measurements of Helsinki Metropolitan Area Council.

Ammonium, sulphate and nitrate

At both sites the concentrations (as ion charge equivalents) and size distributions of ammonium and sulphate followed each other in fine particles (Fig. 2), which suggests that these ions were present mainly as long-range-transported ammonium sulphate. Submicron nitrate exists usually as an ammonium salt, which easily dissociates and evaporates during the sampling. This evaporation is enhanced if nitric acid (or ammonia) is removed before the particle sampling, as was the case in our VI and BLPI measurements. A significant fraction of sulphate and nitrate may also be associated with sea-salt and soil particles (Song and Carmichael 1999), but obviously both sodium nitrate (Yoshizumi and Hoshi 1985) and sodium sulphate are relatively stable under atmospheric conditions. In ultrafine particles (EAD < 0.1 μm) the concentration of ammonium as ion charge equivalents was higher than that of sulphate plus nitrate, so some fraction of ammonium was probably associated with organic anions (Pakkanen *et al.* 2001a).

Similar to chloride, the average BLPI/VI ratio for nitrate was much higher at the urban site when non-corrected VI concentrations were considered. The average evaporation percentage for fine particle nitrate from the VI Teflon filters was 66% at the urban site and 53% at the rural site (Pakkanen *et al.* 2001b). The corresponding evaporation from the BLPI was different in the sense that it was lower at the urban site (60%) than at the rural site (65%). Evaporation from the BLPIs was calculated by assuming that the parallel VI measurement, expressed as the sum of nitrate on Teflon and nylon filters, gives the correct nitrate concentration (Pakkanen *et al.* 1999). Thus, the different BLPI/VI ratios observed for nitrate at the two sites can largely be explained by the different nitrate evaporation characteristics of the two sampler types between the urban and rural sites. One major difference in the sampling conditions is the much higher concentration of gaseous sulphur dioxide at the urban site, which may enhance nitrate evaporation from Teflon filters at this site. Indeed, the differences between the BLPI and VI seemed to arise mainly from the VI samplers, since the use of the volatility-corrected VI concentrations leads to similar BLPI/VI ratios between the two sites (Fig. 3).

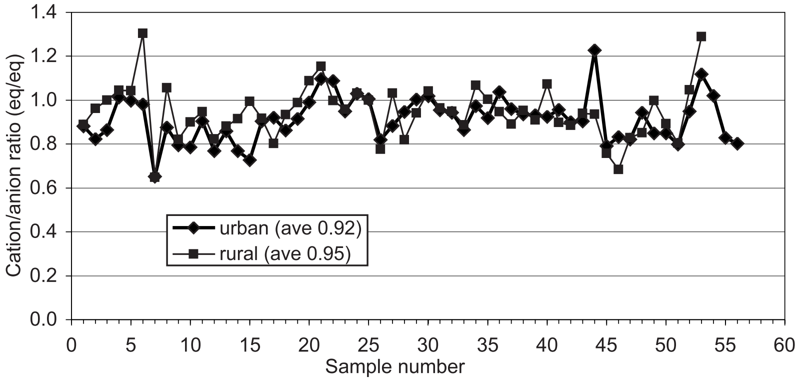

Fig. 5. Cation/anion ratios (eq/eq) for the VI fine particles. The average ratios are shown in the legend text.

An obvious reason for the BLPI/VI ratios below one for sulphate is the SO_2-to-sulphate conversion occurring on the VI Teflon filters, as observed earlier e.g. by Tsai and Perng (1998). During our measurements this artifact sulphate formation was expected to be more pronounced at the urban site than at the rural site, since SO_2, sea-salt and road dust concentrations were higher there. Our data suggests further that the sulphate formation on Teflon filters may have been enhanced slightly during the summer. Tsai and Perng (1998) noticed an average artifact sulphate formation of 15% for Teflon filters in a dichotomous sampler, which is well comparable to the observed BLPI – VI difference in our study.

The BLPI/VI ratios for ammonium were below one for all sampling periods at both sites, and in nine cases out of ten these ratios were nearly identical at the two sites. These features can largely be explained by the fact that ammonium nitrate evaporation was corrected for the VI samples but not for the BLPI samples. Another reason is the possible ammonia-to-ammonium conversion that may occur on the VI Teflon filters, especially if the particles are acidic.

MSA, oxalate, malonate, succinate and glutarate

Kerminen *et al.* (2000) have suggested that concentrations of organic anions in fine particles may be overestimated in the VI because of reactions occurring on the VI Teflon filter or on the particles sampled on the filter. If correct, this could explain the average BLPI/VI ratios below one. In South Africa, Limbeck *et al.* (2001) observed a semi-volatile behaviour for MSA, oxalate, succinate and glutarate, which clearly supports the findings of Kerminen *et al.* (2000). In the present work all, or nearly all, BLPI/VI ratios were below one for malonate, MSA, glutarate and oxalate.

Overall, the detected organic anions are believed to have partitioned mostly into the particulate phase in our measurements, since their partition into the gaseous phase requires a high ambient temperature together with a low aerosol pH and a low relative humidity (Limbeck *et al.* 2001). In our work, even though the pH was not measured, the potential for a low pH was highest during the collection of the BLPI sample 9. The relatively low BLPI/VI ratios for dicarboxylic acids in this sample seem to support the above partitioning theory.

Ion balances in fine particles

If all cations and anions could be measured, there should be an ion balance within the limits of the analytical uncertainties. In this work some important ions, including CO_3^{2-}, HCO_3^- and H^+, were not analysed, which should lead to ion balances different from one. Since sulphate, nitrate, chloride, ammonium, sodium and calcium were the major ionic constituents of atmospheric fine particles measured in this study, the possible differences in ion balances, measured using different sampling devices, are believed to originate

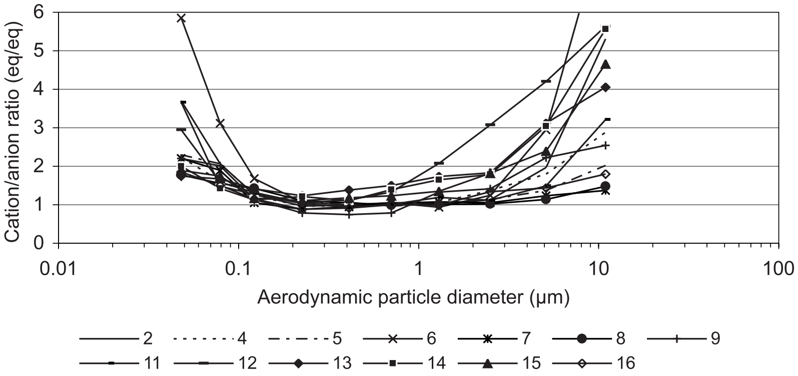

Fig. 6. Cation/anion ratios (eq/eq) for urban BLPI samples. Sample numbers are indicated in the legend.

largely from sampling artifacts concerning these ions.

Ion balances in the VI fine particles

In order to estimate the ion balances measured by the VI and BLPI at the two sampling sites, the ion charge equivalents were summed for the analysed anions and cations. The time series of the cations/anions ratio of the VI fine particle samples were quite similar at the two sites (Fig. 5). Only a few exceptions to this pattern occurred: the samples 6 and 53 had high values at the rural site, the sample 15 showed a large difference between the two sites, and the sample 44 had a high value at the urban site. In case of the samples 6 and 44, the high cation/anion ratios seemed to be due to relatively high Na^+ concentrations. A deficit of ammonium compared to sulphate caused the low ratios for the sample 7 at both sites. This kind of a deficit may indicate that the samples were acidic (Saxena *et al.* 1993, Kerminen *et al.* 2001), even though unanalysed ions may also have played a role.

Ion balances in the BLPI fine particles

The average cation/anion ratios in the individual BLPI stages (size ranges) were nearly identical between the two sites. The ratios were close to one in the size range 0.2–1 μm, as shown for the urban BLPI samples in Fig. 6. The sample 9 was an exception having lower ratios for the accumulation-mode particles. Ratios were also low for the rural BLPI sample 9 and for the parallel VI samples, suggesting that similar atmospheric conditions prevailed over large areas. Higher cation/anion ratios were observed for the size ranges < 0.2 μm and > 1 μm, which suggests that in these size ranges there were some anions not analysed in this study. The ionic composition of ultrafine particles (UFP) has not been studied widely, but it can be speculated that the anion deficit observed in this work may partly be explained by some organic anions not analysed in this study. Coarse particle ion balance has been discussed in an earlier paper (Pakkanen *et al.* 2001a). In the accumulation size range, sulphate, nitrate and ammonium explained more than 90% of the measured ions.

Comparison of ion balances in the VI and BLPI fine particles

Two clear features appeared when looking at ion balances measured in parallel by the VI and BLPI at the two sites (Fig. 7): (i) at both sites the fine particle cation/anion ratios were lower for the VI samples, and (ii) the ratios tended to be slightly lower at the urban site for both collector types. The explanation for the case ‘i’ might be the formation of sulphate and possibly of organic anions on the VI Teflon filter, as suggested earlier by Kerminen *et al.* (2000). The case ‘ii’ is more difficult to explain, but one possible reason might be the higher SO_2 concentration at the urban site, which could lead to a higher sulphate formation on VI Teflon filters at this site.

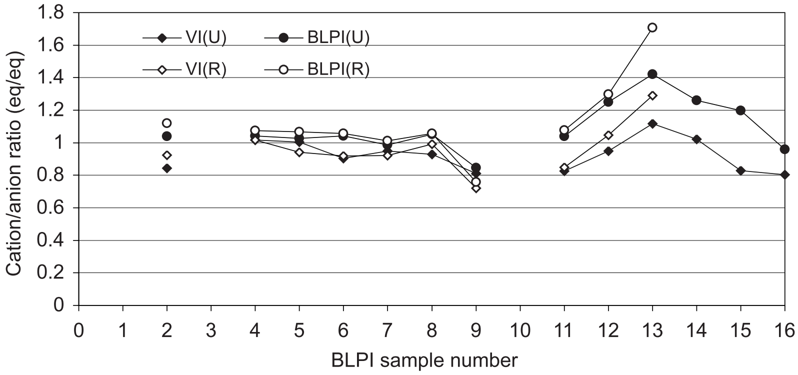

Fig. 7. Comparison of the cation/anion ratios for the parallel fine particle VI and BLPI samples at the urban (U) and rural (R) sites.

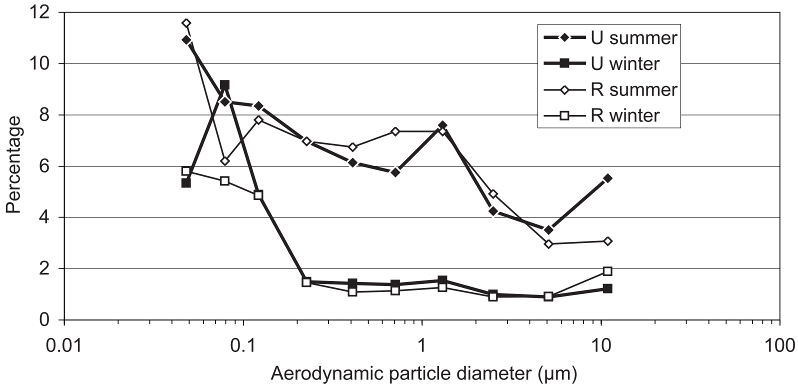

Fig. 8. Average percentage of measured organic anions from total anions (eq/eq) in the urban (U) and rural (R) BLPI samples. Summer stands for May–October (5 samples) and winter for November–March (5 samples).

Contribution of organic anions in different-size particles

The importance of organic anions on the ion balance at the urban and rural site is shown in Fig. 8 for the simultaneous urban and rural BLPI samples. Depending on the particle size, the average percentage of these anions from total anions varied between 3% and 11% during the summer at both sites. During the winter the percentages were only about 1%–2% for both accumulation–mode and coarse particles. Regardless of the season, the organic anions seemed to be especially important for Aitken-mode particles, and even the winter percentages were as large as 5%–8% on average. The higher summer concentrations of organic anions were obvious also for the VI samples (Kerminen *et al*. 2000).

Conclusions

Between April 1996 and June 1997, parallel fine particle aerosol samples were collected at an urban and a rural site in the Helsinki area. At each of the two sites both a VI and a BLPI was utilised. Average size distributions of each ion were similarly shaped at both sites. The contribution of organic anions to total anions was similar for ultrafine particles during the summer and during the winter, but for fine particles the contribution was higher during the summer.

Average BLPI/VI ratios of Ca^{2+} and Mg^{2+} were larger than one at both sites, which suggests that some coarse particle bounce-off may have occurred inside the BLPIs. Ammonium nitrate evaporation is likely to be the most important contributor to the evaporation of fine particle nitrate observed for both the VI Teflon filters (on average 53%–66%) and the BLPI (on average 60%–65%). Since ammonium sulphate is relatively stable, the evaporation of ammonium nitrate does not affect ammonium concentrations as strongly as it does those of nitrate. Acidic fine particles, as well as acidic gases such as SO_2, seem to cause chloride evaporation from the VI Teflon filters. The low BLPI/VI ratios of organic anions and sulphate can largely be explained by gas-to-particle conversion occurring on the VI Teflon filters.

The cation/anion ratios (eq/eq) of the VI and BLPI fine particle samples had similar time series at the two sites with no clear summer to winter differences. The lower ratios observed for the VI samples can largely be explained by the SO_2-to-sulphate conversion occurring on the VI Teflon filters, especially if the involved cations are not analysed.

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