

INTERCOMP2000: ionic constitution and comparison of filter and impactor

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Abstract

The field campaign INTERCOMP2000 was organised within the EUROTRAC-2 subproject AEROSOL for characterisation of aerosol at a rural site. The groups involved used a wide range of measurement methods for aerosol particles. Although the focus was on critical aerosol properties like mass, nitrate and carbon, in this paper particular attention is given to the role of inorganic soluble material being main part of the cloud condensation nuclei. Here, we compare methods used in Europe also for inorganic ion mass concentrations: three high-volume samplers (2 Digitel and 1 Sierra Andersen, equipped with quartz fibre filters), four low-volume samplers (1 Rupprecht Patashnik with Teflon filter; 3 stacked filter units with Teflon, cellulose ester or Whatman 41 filter), and 2 low-pressure impactors (Bernier type with Tedlar foils). Ten parallel 24 h samples were compared. The data for the main ions nitrate, sulphate and ammonium agree well for the PM₁₀ as well for PM_{2.5} aerosol fraction; relative standard deviation of about 20–40% were found. The single values for calcium, sodium and chloride which contribute only minor to the soluble inorganic mass scatter very strongly around the calculated averages: about 50% in PM₁₀ mode, and even 100% in PM_{2.5} mode. While laboratory calibrations typically indicate performance close to design specifications, methods during field operation are subject to a number of sampling and handling artefacts. We know that the different sampling principles used in this study, and the analytical procedures done by each group with their own methodology will cause a main part of the observed uncertainties. In reality, due to different reasons (availability, costs, manpower, different analysis from the same sample, size and time resolution, etc) in many networks and field studies a high variability of methods for aerosol characterisation is used and often those experimental figures will be used for statistical interpretations. Thus, our paper will emphasise that harmonisation among different PM measurements is the “order of the day”.

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1. Introduction

Aerosol particles in the ambient atmosphere originate from a wide range of sources. Recent studies have singled out the particulate matter (PM) as one of the main pollutants responsible for the impact on air quality and human health (e.g., USEPA, 1996; Pope et al., 2002; Austin et al., 2003). Aerosols affect the amount of radiation and provide a surface on which reactions may occur, which do not occur or are very slow in the gas phase (e.g., formation of nitrous acid). The water solubility of the particle is one of the most important properties determining its capacity to act as cloud condensation nuclei. This soluble material dissolves itself in the condensed phase, and partially determines the aqueous phase composition; the in-cloud-chemistry and the amount of pollutants contribute to environmental stress. The assessment of potential effects of aerosols in the atmosphere on environmental and human health requires detailed physical and chemical characterisation of the aerosol particles (size and shape, bulk composition and the distribution of chemical constituents within the particles). Recent developments in atmospheric aerosol measurements were reviewed by Chow (1995) and McMurry (2000).

Generally, impactors or cyclones are used for particle size selection in environmental studies. Cascade impactors are the main devices using inertial and gravitational forces to separate airborne particles according to their aerodynamic diameters. The most common means to obtain the sampled mass and/or chemical characterisation over an integrated period of e.g., 24 h is aerosol sampling on filter in high- or low-volume gravimetric samplers. Nowadays many different filter materials like fibrous, membrane and sintered filters are available and they significantly differ in their physical and chemical properties (Mark, 1998). Membrane filters (e.g. cellulose nitrate, polycarbonate) have the advantage of retaining particles effectively on their surface, whereas fibrous filters are very robust; they have low moisture retention, and high collection efficiencies at relatively low drop in pressure. The use of non-reactive PTFE filters is limited due to the relatively high cost and the amount of sample that can be collected without significant drop in pressure. PTFE filters are very thin; an electrostatic charge build-up can result in the loss of coarse particles during transport. Quartz fibre filters have superior resistance to artefact effects and moisture absorption, but they are very fragile and so require to be handled with extra care. Quartz fibre filters are recommended for routine particle sampling, when mass concentration is determined by weighing (Mark, 1998; New Air Quality Directive 1999/39/EC) and the carbon content of the aerosol will be analysed (Hebisch et al., 2003).

Numerous aerosol intercomparison campaigns, mostly in the US, were designed and carried out (see

references in McMurry, 2000) to test among other things the vulnerability of different low and high volume samplers and cascade impactors (e.g., Mathai et al., 1990; Zhang and McMurry, 1991; Hillamo and Kauppinen, 1991; Howell et al., 1998). A separation of the trace gases from their particulate counterparts is recommended in sampling reactive species, and denuder filter pack combinations, denuder in front of low volume sampler and denuder in combination with an aerosol steam jet collector are described (e.g., Schaap et al., 2002; Drewnick et al., 2003, 2004; Weber et al., 2002; Acker et al., 2004).

In the framework of the EUREKA-EUROTRAC-2 subproject AEROSOL the idea was born to compare the samplers and filter materials most commonly used in Europe for analytical identification of aerosol properties for further joint projects (ten Brink and Baltensperger, 2003). The intercomparison was organised at the IFT research station near Melpitz, a village about 45 km NE of Leipzig. Aerosol was sampled by a total of 24 collectors (16 filter samplers and eight cascade impactors). The intercomparison was focused on the collection and analysis of those aerosol compounds for which artefacts occur in sampling and/or analysis, e.g., nitrate and carbon, see Schaap et al. (2004) and ten Brink et al. (2004). An overview about the groups, the site and the meteorological conditions is given in Müller et al. (2004). The aerosol samplers used are described in detail in Hitzenberger et al. (2004). This paper focuses on the comparison of the water-soluble inorganic compounds of aerosol particles collected by two impactors, three high-volume and four low-volume samplers.

2. Experimental

Data of the following different aerosol samplers were used for this presentation:

2.1. High-volume filter sampler

- HV_1(PM2.5) (Digital_HV, PM2.5 inlet, air flow 500 l min^{-1} , inlet position 1.8 m above ground, operation and analysis by IFT)
- HV_2(PM2.5) (Digital_HV, PM2.5 inlet, air flow 500 l min^{-1} , inlet position 1.8 m above ground, operation by BTU, analysis by BTU (HV_2a(PM2.5) and parallel by TUV (HV_2b(PM2.5))
- HV_3(PM10) (Sierra Andersen HV, PM10 inlet, air flow 1000 l min^{-1} , inlet position 1.8 m above ground, operation and analysis by IFT)

The distance between the two identical HV_1 and HV_2 was 2.5 m. The air flow was under electronic control during the whole operation. Each sampler operation, like start and finish time and filter change

was recorded automatically. The power supply and voltage stability were controlled by an uninterrupted power supply (UPS) to guarantee a stable sampling. Munktell MK 360 quartz fibre filters were used for high volume sampling. The reason for choosing this type of quartz filter was the availability for all type of HV samplers used in this study. A sampling period of 24 h was agreed because of two reasons: daily filter samples are common in aerosol watch networks, and in 24 h also under rural conditions a sufficient amount of aerosol will be obtained on the filter for chemical analysis.

2.2. Low-volume filter sampler

- LV_1(PM2.5) and LV_1(PM10) (Rupprecht-Patashnik Partisol2000, inlet for PM2.5 and PM10, air flow 16.71min^{-1} , Millipore Teflon filter $3\mu\text{m}$ pore size, operation and analysis by IfT).
- LV_2(PM2) and LV_2(PM10) (stacked filter unit (SFU) sampler for PM2 and PM10 fraction, air flow 16.71min^{-1} , Apiezon coated Nuclepore front filter ($8\mu\text{m}$ pore size), fine filter Gelman Teflon $0.4\mu\text{m}$ pore size, operation and analysis by UGent).
- LV_3(PM2) and LV_3(PM10) (stacked filter unit (SFU) sampler for PM2 and PM10 fraction, air flow 16.71min^{-1} , Apiezon coated Nuclepore front filter ($8\mu\text{m}$ pore size), fine filter mixed cellulose ester, $3\mu\text{m}$ pore size, operation and analysis by UGent).
- LV_4(PM2) and LV_4(PM10) (stacked filter unit (SFU) sampler for PM2 and PM10 fraction, air flow 16.71min^{-1} , Apiezon coated Nuclepore front filter ($8\mu\text{m}$ pore size), fine filter Whatman 41, operation and analysis by UGent).

The LV_1 sampler “Partisol 2000” is described in Spindler et al. (1999) and is usually used for weekly sampling within the monitoring research program at the Melpitz site (Spindler et al., 2004). Alternatively, the air flow is passing four different inlet systems (2 PM1, PM2.5, PM10), each for 10 min (electronically controlled). During INTERCOMP2000 the filters were changed daily. Daily values for PM2.5 and PM10 were calculated from the air volume collected during altogether 6 h because of intermittent sampling. The SFU sampler used in this study was developed at Ghent University and is described in detail by Maenhaut et al. (1994) and Hopke et al. (1997). It consists of a PM10 inlet and two 47-mm diameter filters in series to collect the coarse ($10\mu\text{m} > d > 2\mu\text{m}$) and fine ($d < 2\mu\text{m}$) fractions of the aerosol. The time resolution was 24 h in the first half of the campaign and was changed to 12 h by the operator to see possible differences between day and night starting on 9 April. Volume weighted 24 h values were then calculated.

2.3. Low-pressure Berner Impactor

- I_1(PM3.5) and I_1(PM10) (5 size classes ($0.05\text{--}10\mu\text{m}$), flow rate 801min^{-1} , operation and analysis by IfT). The impactor is equipped with a heated inlet consisting of seven tubes of 1.5 m length with laminar flow. The temperature of these tubes is controlled by a humidity sensor keeping the sampled aerosol at a humidity of ($60 \pm 5\%$). The aerosol was sampled for 24 h on Tedlar foils for the chemical analysis.
- I_2(PM2) and I_2(PM8) (LPI 30, 8 size classes ($0.12\text{--}16\mu\text{m}$), flow rate 301min^{-1} , all impaction surfaces were covered with Tedlar foils, operation by UV, analysis by TUV). The time resolution was 12 h, volume weighted 24 h averages were calculated.

Concentrations of individual impactor stages were added to give one data point that can be compared to the relevant PM filter samples: 0.14 , 0.43 , 1.2 and $3.5\mu\text{m}$ for I_1(PM3.5); $10\mu\text{m}$ for I_1(PM10); 0.12 , 0.24 , 0.5 , 1 and $2\mu\text{m}$ for I_2(PM2); 4 and $8\mu\text{m}$ for I_2(PM8).

Blank and loaded filters and foils were weighted after 24 h storage under controlled conditions of humidity and temperature, for more details see Hitzenberger et al. (2004).

For the determination of the inorganic aerosol species, the sampled material was extracted from a defined part of the filter and foils prior to analysis. This was generally done in PTFE vessels with a defined volume of deionised water and by using a shaker or an ultrasonic bath. Standard ion chromatography (IC) was used for analysis of the water soluble inorganic ions. In few cases (HV_1 and HV_3) IC eluents ($1.7\text{mM NaHCO}_3/1.8\text{mM Na}_2\text{CO}_3$; 20mM methanesulphonic acid) were used for extraction. The analysis was mostly carried out in the laboratories of the participating institutes. The uncertainty of the IC analysis conducted by one laboratory using the same equipment, procedure and staff was estimated to be about 10% (Brüggemann and Rolle, 1998). Annually the laboratories involved participated in national and/or international laboratory intercomparison studies (e.g. within the Global Atmospheric Watch Programme of the WMO) to qualify their analytical data.

The analytical results were used to calculate the sampled amount per filter or foil (including blank correction) for each ion. The amount divided by the air volume passing the filter or foils will give the atmospheric concentration.

3. Results

Though sulphate, nitrate and chloride are among the more commonly measured atmospheric aerosol constituents, they are the most problematic to measure. Both

ammonium nitrate and ammonium chloride are potentially volatile, and may be lost if the sampling filter is inside a housing which is warmer than the ambient atmosphere (e.g., Mulawa and Cadle, 1985; Harrison and Kitto, 1990). Apart from filter and volatilisation artefacts, it is possible that chemical reaction artefacts occur. Particles sampled on an air filter are a potential substrate for reaction with atmospheric gases drawn through the filter. Examples for acid-base reactions to alter the composition of airborne particulate matter collected on a filter are described in Claes et al. (1998). In atmospheres with abundant ammonia and hydrogen chloride, secondary ammonium chloride aerosol can form. As a result of atmospheric coagulation processes between particles of different composition, and of the uptake of gases into pre-existing particles but also as an artefact of sampling procedures salts of mixed composition are formed.

During INTERCOMP2000, the aerosol sampling has been carried out under cool and humid meteorological conditions (daily averages below 10 °C, 70–90% relative humidity). The pollution of air masses reaching the field site was only low or medium. More details are given in Müller et al. (2004).

The concentrations observed in Melpitz during the 10 days in April 2000 for inorganic ions were low, but close to seasonal average observed during the last years at this site (Spindler et al., 2004). As can be seen from Fig. 1, the detected soluble inorganic ions amount to 45–65% of the sampled aerosol mass, as well during the cleanest event ever observed in Melpitz (6 April 2000) as during cases when more polluted continental air masses from East Europe reached the site (11 April 2000). Sulphate, nitrate and ammonium are most important for the soluble fraction and they were mainly (80% and higher) found in the fine particle mode, as can be seen in Table 1 and Fig. 2. The amount of nitrate contributing

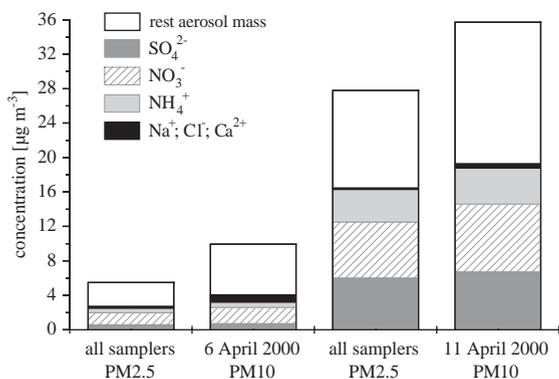


Fig. 1. Contribution of individual ions to the aerosol mass concentrations under unpolluted (6 April) and polluted (11 April) conditions, given as averages of all individual samplers in PM2.5 and PM10 fraction.

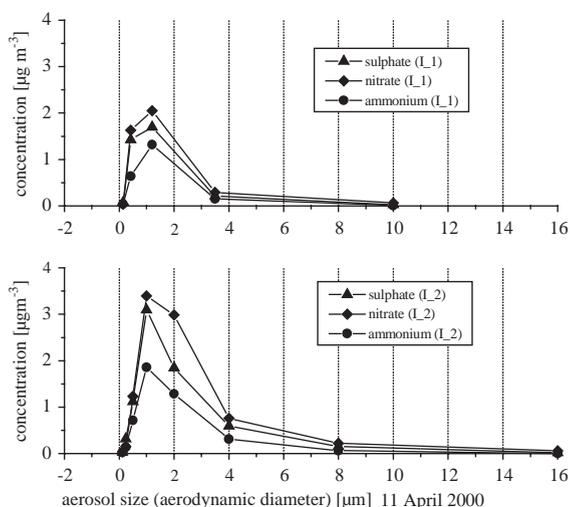


Fig. 2. Typical ion mass size distribution obtained with the Berner low-pressure impactors I_1 (5 stages, upper diagram) and I_2 (8 stages, lower diagram) under polluted conditions (April 11).

to the PM2.5 mass during our experiment is in the same level as sulphate or even higher. Long-term measurements at the Melpitz site (Spindler et al., 2004) showed that the size distribution of sulphate and ammonium concentration peaks in the PM1 mode, indicating that their origin is mainly gas-to-particle conversion of SO₂ and neutralisation of sulphuric acid by gaseous ammonia. Because of the emission situation observed now in Europe nitric acid will increasingly bind part of the ammonia. It appears that nitrate in the coarse particle mode is always present, whereas nitrate in the accumulation mode is an indicator for more polluted atmospheric conditions. The scientific literature concerning the size distribution of individual anions and cations associated with rural continental aerosol confirms our observations (e.g., Sirois and Fricke, 1992; Mehlmann and Warneck, 1995; Lammel et al., 2003).

During INTERCOMP2000 it was found that ammonium compensates about 87% of the acids in the continental influenced aerosol (based on equivalent concentrations). Less ammonia seems to be available in the marine influenced samples to balance the acids (73% on 7 April). These North Atlantic air masses reaching the site from 6 to 9 April are also responsible for higher amounts of sodium and chloride, see also Fig. 5. On average, sodium, chloride and calcium showed three times higher concentrations in the PM10 aerosol compared to PM2.5 (Table 1).

The following methods of comparison correspond with those used in mass and nitrate related papers (Hitzenberger et al., 2004; Schaap et al., 2004).

Table 1

Ion mass concentrations in $\mu\text{g m}^{-3}$, obtained by filter and impactor sampling during INTERCOMP2000 for PM2.5 and PM10

	NO_3^-	SO_4^{2-}	NH_4^+	Ca_2^+	Na^+	Cl^-
<i>PM2.5</i>						
HV_1	2.902 ± 1.677	2.589 ± 1.871	2.871 ± 1.584	0.143 ± 0.027	0.099 ± 0.078	0.215 ± 0.074
HV_2a	2.928 ± 1.756	2.772 ± 1.907	1.665 ± 1.110	0.024 ± 0.013	0.117 ± 0.021	$0.018 \pm \text{nd}$
HV_2b	2.314 ± 1.881	2.340 ± 2.015	0.532 ± 0.381	0.015 ± 0.009	0.050 ± 0.041	0.006 ± 0.004
LV_1	3.370 ± 1.562	2.526 ± 1.559	1.733 ± 1.033	0.162 ± 0.049	0.148 ± 0.090	0.093 ± 0.061
LV_2	3.180 ± 1.407	2.380 ± 1.586	1.310 ± 0.708	0.011 ± 0.013	0.075 ± 0.070	0.158 ± 0.137
LV_3	3.418 ± 1.386	2.277 ± 1.439	1.288 ± 0.707	0.055 ± 0.049	0.048 ± 0.040	0.158 ± 0.098
LV_4	3.197 ± 1.444	2.958 ± 1.247	1.593 ± 0.773	0.042 ± 0.026	0.051 ± 0.045	0.249 ± 0.109
I_1	3.201 ± 1.487	2.042 ± 1.173	1.539 ± 0.739	0.065 ± 0.01	0.213 ± 0.135	0.257 ± 0.229
I_2	3.500 ± 2.013	2.510 ± 1.976	1.455 ± 1.128	—	0.084 ± 0.062	0.023 ± 0.009
<i>PM10</i>						
HV_3	3.605 ± 2.288	2.527 ± 1.838	2.125 ± 1.130	0.156 ± 0.053	0.366 ± 0.252	0.335 ± 0.269
LV_1	4.112 ± 1.798	2.913 ± 1.783	1.896 ± 1.200	0.299 ± 0.069	0.369 ± 0.236	0.279 ± 0.147
LV_2	4.067 ± 1.883	2.813 ± 1.892	1.578 ± 0.891	0.119 ± 0.037	0.298 ± 0.213	0.428 ± 0.381
LV_3	4.291 ± 1.760	2.701 ± 1.703	1.591 ± 0.980	0.177 ± 0.072	0.243 ± 0.259	0.402 ± 0.348
LV_4	2.888 ± 1.838	3.388 ± 1.574	1.903 ± 1.053	0.185 ± 0.074	0.248 ± 0.214	0.499 ± 0.351
I_1	3.295 ± 1.521	2.078 ± 1.166	1.551 ± 0.741	0.088 ± 0.019	0.285 ± 0.188	0.345 ± 0.301
I_2	4.110 ± 2.340	2.676 ± 2.139	1.512 ± 1.229	—	0.271 ± 0.249	0.111 ± 0.161

These averages over the whole campaign (4–13 April 2000) were calculated from the daily means of the individual samplers.

Table 2

Overall average ion concentrations for the whole campaign calculated from PM2.5 ($n=9$) and PM10 ($n=7$) sampler and impactor averages

	NO_3^-		SO_4^{2-}		NH_4^+		Ca_2^+		Na^+		Cl^-	
	$\mu\text{g m}^{-3}$	%										
All PM2.5	3.11	12	2.49	11	1.55	39	0.07	89	0.1	55	0.13	76
All PM10	3.77	14	2.73	15	1.74	14	0.17	36	0.3	17	0.34	42

Table 1 gives an overview of all results in terms of average ion concentrations (and standard deviations) during the whole sampling period of 4–13 April, 2000. From these averages, calculated for each individual sampler, the overall average ion concentrations were calculated for PM2.5 and for PM10. These values are shown in Table 2. Generally lower standard deviations were obtained for PM10 (7 samplers) compared to PM2.5 (9 sampler). Smallest values of the relative standard deviation were found for nitrate and sulphate in both modes with 11–15%, followed by ammonium and sodium with similar values for PM10, but a higher variance (39% and 55%, respectively) for PM2.5. The individual sampler data for chloride and calcium scatter stronger around the calculated campaign averages: about 40% in PM10 mode and even 90% in PM2.5 mode.

For better comparability, average concentrations were calculated for each day (reference values). The concentrations obtained by the individual samplers were

divided by the daily average concentration. The averages of these ratios are given in Table 3 along with their relative standard deviation. All samplers are within 25% of average for nitrate, sulphate and ammonia in PM2.5 as well in PM10. Few data from HV_2b and LV_4 are exceptions. Within 50% of average for sodium, chloride and calcium are all samplers in PM10 mode, excluded I_2. For sodium, chloride and calcium in PM2.5, the correspondence of individual sampler with the average vary between little and 150%. Greatest deviation from the PM2.5 average are found for I_1 and LV_1 in case of sodium, for HV_2a, b and LV_4 in case of chloride and, for HV_1, LV_1 and LV_2 in case of calcium.

Fig. 3 compares the sulphate data for PM2.5 from the individual samplers to the reference value, in Fig. 4 this analysis was done for ammonium. For a single day, the relative standard deviation of the daily mean ranges between 7% and 34% for sulphate and 8 to 53% for ammonium in PM2.5, the values are slightly lower for PM10, see Table 3.

Table 3

Ratio of the average concentration of individual ion in PM2.5 and PM10 over the campaign to the mean of all samplers

	NO_3^-	SO_4^{2-}	NH_4^+	Ca_2^+	Na^+	Cl^-	
	Ratio to average	SD					
<i>PM2.5</i>							
HV_1	0.88	18 1.01	9 1.78	13 2.20	25 1.25	118 1.63	30
HV_2a	0.89	14 1.07	9 0.97	14 0.40	48 0.87	13 0.07	—
HV_2b	0.64	37 0.85	23 0.44	53 0.23	64 0.73	119 0.05	50
LV_1	1.09	10 1.00	17 1.04	14 2.51	22 1.81	54 0.89	98
LV_2	1.04	7 0.93	8 0.82	8 0.17	94 0.64	60 0.99	46
LV_3	1.16	19 0.91	7 0.82	19 0.80	79 0.39	82 1.10	26
LV_4	1.05	11 1.39	34 1.04	22 0.67	60 0.44	73 1.88	29
I_1	1.15	12 0.94	12 1.14	23 1.08	34 2.06	27 1.60	54
I_2	1.09	16 0.90	24 0.82	23 —	— 0.87	40 0.19	49
<i>PM10</i>							
HV_3	0.90	22 0.87	8 1.24	14 0.93	39 1.30	15 1.04	27
LV_1	1.11	12 1.06	13 1.05	19 1.73	15 1.49	39 1.07	75
LV_2	1.08	6 0.98	8 0.89	7 0.68	19 1.04	34 1.11	38
LV_3	1.18	13 0.97	5 0.90	12 1.02	32 0.64	53 1.06	31
LV_4	0.71	27 1.38	28 1.10	12 1.06	38 0.73	31 1.50	22
I_1	0.96	6 0.86	8 1.05	20 0.53	24 1.01	45 0.93	23
I_2	1.05	19 0.87	25 0.78	26 —	— 0.80	37 0.28	72

The calculation was done on a day by day basis and the average ratio is given along with the relative standard deviation in %.

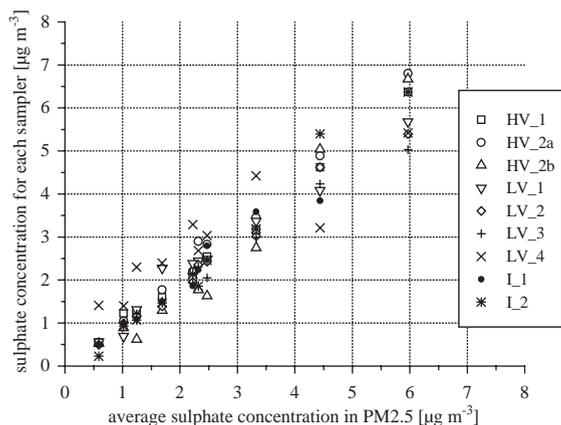


Fig. 3. Comparison between the sulphate concentrations obtained from the individual samplers and the average sulphate concentration in PM2.5.

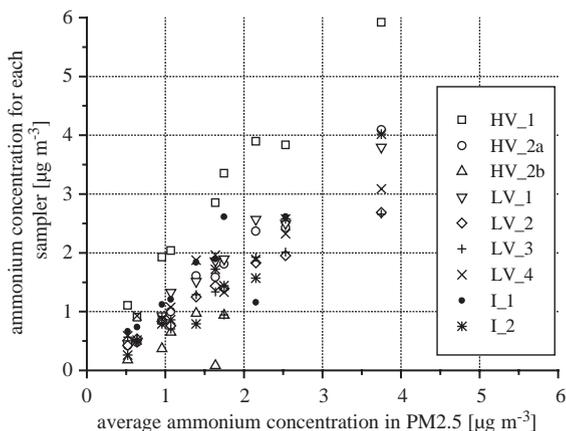


Fig. 4. Comparison between the ammonium concentrations obtained from the individual samplers and the average ammonium concentration in PM2.5.

Ions which contribute only minor to the soluble inorganic mass showed much higher deviations (Table 3). Whereas there is a relatively good correspondence between all samplers for sodium in PM10, see Fig. 5, the individual sampler can deviate between 13% and 119% from the daily average for PM2.5. The results based on the daily averages are similar for chloride (excluding LV_1(PM10) and I_2(PM8)). Also, in PM10 the results for calcium have a high variance, see Fig. 6.

The reasons for the observed scatter are manifold. Each sampler used in this study is well introduced widely (not only in Europe), best characterised and used by well-known researchers in Europe to study atmospheric PM loading on different geographic sites to draw conclusions for science (climate, air chemistry) and politics (air quality, abatement strategy). Surprisingly, using the various samplers the results here for water soluble inorganic species differ for the same site and

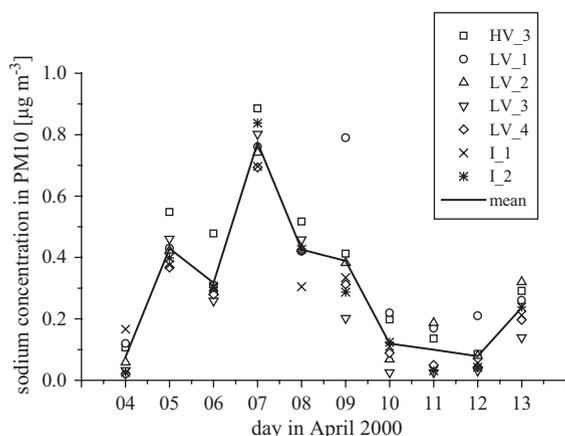


Fig. 5. Sodium mass concentrations collected by the individual samplers. The average of all PM10 data is given as solid line.

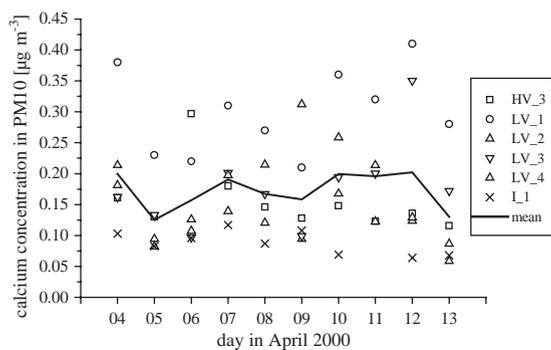


Fig. 6. Calcium mass concentrations collected by the individual samplers. The average of all PM10 data is given as solid line.

identical meteorological conditions. Therefore, the deviation of each sampler from the average over all samplers (reference value) was calculated. As no systematic deviation in one direction for all investigated species was observed, no sampler was excluded from the averaging procedure. Despite intermediate sampling and altogether 6 m^3 sampled air volume per day, the data gave no reason to exclude the LV_1 generally. In long-term studies (Spindler et al., 2004), this sampler is used for weekly sampling at Melpitz and shows only small differences to the parallel operated high volume sampler (HV_1).

Generally filter and impactor data tally, despite the different cut-offs used ranging from 2.0 to $3.5\ \mu\text{m}$ and 8 to $10\ \mu\text{m}$, respectively. Concentrations of individual impactor stages were added to give one data point nearest to the relevant PM filter samples (see Experimental Section). This can give a slight negative or positive bias of single impactor data to the simulated PM sample, but in all INTERCOMP2000-related papers

the data analysis was done in this way. As can be seen from Fig. 2, it is necessary to add the smallest 4 stages of I_1 and the smallest 5 stages of I_2 for any kind of comparison.

In Schaap et al. (2004) the nitrate data for all individual sampling methods used during INTERCOMP2000 are shown and discussed in detail. Known interferences of nitric acid (adsorption on cellulose filters like Whatman 41) were found to be negligible because of much lower concentrations of HNO_3 compared to particulate nitrate during the experiment (Acker et al., 2004). Evaporation artefacts (significantly observed for quartz fibre filter at temperatures above $25\ ^\circ\text{C}$) were not identified because of the low ambient temperature during the campaign. In Hitzemberger et al. (2004), possible artefacts of individual samplers determining the aerosol mass concentration are discussed (e.g., weighing procedures, humidity controlled sampling), which also may influence the data quality for other aerosol properties.

Despite different inlets and sampling principle (including different materials for filters and foils) the data follow the same trend. Based on the database we have, it seems that the analytical procedures followed by each group with their own methodology (handling, storage, analysis) cause the main part of the observed deviations from calculated averages. These deviations can only be minimised by standard operating procedures accepted by all participants. The higher PM2.5 ammonium mass concentrations (HV_1) compared to PM10 (HV_3) is untrustworthy, although both samplers were operated and analysed by the same institute (and both were extracted using IC eluent). The HV_1(PM2.5) ammonium data seem too high, also in comparison to the other ammonium PM2.5 data, see Tables 1 and 3 and Fig. 4. Defined parts of the HV_2(PM2.5) filter were analysed parallel by two different laboratories and the HV_2b results tend to be too low (Table 1 and 3), especially for the ions ammonium (see Fig. 3), calcium and chloride compared to the other PM2.5 sampler. Also the HV_2a data seem too low for the latter two ions.

Attention has to be given to the striking high calcium PM2.5 values from HV_1 and LV_1. The use of an acid ion chromatography eluent (see Experimental Section) for HV_1 cation extraction (which can dissolve more calcium from the aerosol than deionised water) seems not to give an explanation because this eluent was also used for HV_3(PM10) and no increased calcium compared to the PM10 average was observed.

The LV_1(PM2.5) Teflon filter was extracted from deionised water, but the low amount of air passing the PM2.5 inlet of this intermediate sampler and because of its low amount of detectable ions being in the same range or even lower than the filter blanks may cause uncertain LV_1(PM2.5) calcium data. This result holds

also for PM_{2.5} sodium and chloride and for PM₁₀ calcium obtained with LV₁, see Tables 1 and 3.

Often the low pollution level at Melpitz during the INTERCOMP2000 caused an analysis near the quantification limit of the ion chromatography method also for other samplers. Besides the uncertainty of IC analysis (on average 10%), filter blanks can contribute to a further uncertainty. It was found that for the same type of filter (in this case quartz fibre filters Munktell MK360 used in all HV samplers of this paper), the blanks could scatter immensely. The data from 17 single quartz filters from 4 different charges indicate enormous differences in the filter quality and that for at least every production charge the blank has to be determined separately. Converted to “blank” air concentration values (in this case 720 m³ air flow in 24 h) the following blank ranges (in ng m⁻³) were found:

1–20 NO₃⁻, 15–134 SO₄²⁻, 2–19 NH₄⁺,
4–47 Ca₂⁺, 17–68 Na⁺, 2–23 Cl⁻.

The real ion mass concentrations in the ambient aerosol have to be significantly higher than the filter blank thresholds to obtain environmental data on a reliable state. The filter blanks appeared generally to be no problem for nitrate and ammonia measurements, or in most cases also not for the determination of the sulphate content. The filter blanks for calcium, sodium and chloride often reach the same order of magnitude found in the rural aerosol during INTERCOMP2000 (especially in PM_{2.5}) and their high variation may cause a main part of the uncertainty of the measured data.

Much higher uncertainties in the ion concentration data will be expected if this field study would be performed in the same way under much higher ambient temperatures. Evaporation and adsorption artefacts would increase in importance and only reference methods like denuder-filter pack or denuder-steam jet combinations could help in data discussion.

In reality, in many networks and field studies a high variability of methods for aerosol characterisation is used and often those experimental figures will be used for statistical and process interpretations. Harmonisation among different PM measurements requires reliable protocols of the field and laboratory conditions (meta data), standard operating procedures, laboratory inter-comparisons between the partners of the study, and a critical evaluation of the analytical results. Uncertain data should be flagged before given to any kind of database.

4. Conclusions

Aerosol sampling was performed throughout 10 days in April 2000 at a rural site using several PM₁₀ and

PM_{2.5} manual sampling devices most common in aerosol research in Europe. The intercomparison of aerosol chemistry (here water-soluble inorganic ions) data obtained from these different high- and low-volume samplers and impactors running next to each other under the same meteorological conditions allowed to obtain information about the minimum uncertainty, which has to be taken into consideration for any kind of data interpretation. The data show that special attention must be given in cases of: low ambient air concentrations, small differences in ion mass concentrations between different size fractions, and for ions with minor contribution to the soluble inorganic material. Besides differences in sampling principle, analytical procedure and filter characteristics, the obtained single sulphate, nitrate and ammonia data scatter in an expected range around the calculated PM_{2.5} and PM₁₀ averages. The data for sodium, chloride and calcium scatter more in case of PM₁₀, but for PM_{2.5} unexpected high uncertainties were observed for these minor ions. The selection of a filter material depends not only on its chemical blanks, but also on thermal and mechanical stability and its suitability for analysis of a number of different aerosol properties (e.g., mass concentration, carbon content or trace metals) using various different analytical methods, as during INTERCOMP2000.

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