

Intercomparison of methods to measure the mass concentration of the atmospheric aerosol during INTERCOMP2000—influence of instrumentation and size cuts

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Abstract

Within the EUROTRAC-2 subproject AEROSOL, the intensive field campaign INTERCOMP2000 was conducted to compare aerosol samplers and methods to measure various aerosol properties. Here a comparison of mass concentrations measured with different PM_{2.5} and PM₁₀ samplers as well as cascade impactors is described. Different filter types were used. In general, the PM_{2.5} and PM₁₀ mass concentrations obtained on filters agree well. The data agree within 18.1% (PM_{2.5}, all data). If data obtained with the TEOM (18% low) and on Whatman QM-A quartz fibre filters (low face velocity, 38% high) are excluded, PM_{2.5} data agree within 8.1%. For PM₁₀, the agreement is within 6.6% (again excluding the Whatman QM-A quartz fibre filters, 22% high) or 12.1% (all data). For the impactor samples, the data agreed within 6.3% (excluding the ELPI, which was 92% high) and 8.7% for PM_{2.5} and PM₁₀.

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1. Introduction

Particulate matter (PM) standards have been set or are being set in many countries as measures for air quality control. The standards usually apply to PM in the size range below 1 μm (PM₁), 2.5 μm (PM_{2.5}) or

10 μm (PM₁₀). The standards also include definitions of how to measure the PM. Specialized sampling heads were developed to provide a defined upper cut size and efficiency curve for this cut. For filter-based measurements, weighing protocols were developed to ensure comparability of the mass concentrations measured by different laboratories.

Although a lot of attention has been paid previously to sampling artefacts for different aerosol species such as elemental and organic carbon (e.g. Turpin et al., 2000;

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Schmid et al., 2001; Eatough et al., 2003; ten Brink et al., 2004), nitrate (e.g. Pakkanen et al., 1999; Schaap et al., 2004) or chlorine (Witz et al., 1990; Shimohara et al., 2001), sampling artefacts in the determination of gravimetric mass have not received as much attention. Most discussions are concerned with the effect of relative humidity on mass determination. As atmospheric aerosols are known to take up water under conditions of elevated relative humidity (e.g. Hänel, 1976 or McMurry, 2000), the mass obtained from weighing depends to some extent on the relative humidity in the laboratory. As volatile and semi-volatile compounds are present in the aerosol, the temperature also is important. These considerations led to the development of the weighing protocols in the standards. The comparability of methods to determine the aerosol mass concentration has not been investigated in depth (Maenhaut et al., 2001a). Several studies were conducted that compare different PM sampling methods to each other, but most of these studies consider only two types of sampling heads or are concerned with the reproducibility of a prescribed cut curve of one type of samplers.

During the intensive field campaign “INTERCOMP2000”, which was conducted within the framework of the EUROTRAC-2 subproject AEROSOL (an overview is given by Müller et al., 2004), the aerosol was sampled with several types of filter samplers with different sampling heads as well as with several types of cascade impactors. The major aim of the field experiment was to compare sampling and analysis methods for carbon (ten Brink et al., 2004) and nitrate (Schaap et al., 2004) as well as to provide a chemical mass closure of the aerosol (Maenhaut et al., 2001b, 2002). The presence of practically all sampler types used in Europe for aerosol collection provided an unique opportunity for an intercomparison of PM10 and PM2.5 samplers as well as other instruments not specifically designed for a certain PM cut point. An interesting point in this investigation is the performance of Quartz fibre filters, which are the filter material prescribed by EU guidelines for PM sampling. A first comparison of some of the instruments present at INTERCOMP2000 was given by Maenhaut et al. (2001b).

2. Experimental set up

2.1. Description of site and meteorological conditions

The INTERCOMP2000 campaign was conducted from 3 April to 14 April 2000 at the research station of the Institute for Tropospheric Research (IfT) near the village of Melpitz, which is located ca. 45 km northeast of Leipzig, Germany. The station is situated in an agricultural area on a flat meadow that has not been

used for agricultural production (except mowing the grass) for >100 years. A detailed description of the station is given by Spindler et al. (2001). The campaign was conducted in April because during that time of the year, temperatures and humidities were expected to be near-annual averages. During the campaign, however, mass concentrations were very low compared to values observed during the past several years (Müller, 1999). Air masses originating over the North Atlantic, which carried only little pollution, were dominant most of the time. Only on 10 and 11 April, polluted air masses from Eastern Europe reached the site. Because of the low aerosol concentrations, the collection of adequate sample masses was not possible with a high time resolution. Most instruments were run on sampling schedules of 12, 24 or 48 h with nominal start times at 9 a.m. and 9 p.m. for the 12 h samples.

2.2. Filter-based instruments

All instruments were sampling ambient air directly from the atmosphere with inlet heights between 1.8 and 2 m above ground. Table 1 gives an overview of samplers, substrates, inlet cut sizes and relative humidity at weighing (where appropriate). Table 1 also contains a list of the acronyms used for the participating groups. All diameters are aerodynamic equivalent diameters d_{ae} , i.e. the diameters of spheres with the density of water that have the same inertial behaviour as the collected particles. In the case of our measurements, most particles probably contained at least some water so the aerosol consisted mainly of solution droplets (see below), so shape effects are expected only for large particles of mineral origin. As all instrument size cuts are given in terms of d_{ae} , the influence of particle shape and density is not relevant.

2.2.1. Gent PM10 stacked filter unit (SFU) sampler

This sampler was developed at Ghent University (UGent) and is described in detail by Maenhaut et al. (1994) and Hopke et al. (1997). It consists of a PM10 head 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 SFU sampler is operated at a flow rate of 17 Lpm. Although the cut size between fine and coarse is $2\ \mu\text{m}$, the data for the fine fraction are grouped with the PM2.5 filter data. The papers by Maenhaut et al. (2001b, 2002), which are focussed on the chemical mass closure of the Melpitz campaign, give also a first comparison of the mass concentrations sampled with different filter types and inlets. In the Melpitz campaign, four SFU samplers were used. All had Apiezon-coated Nuclepore filters ($8\ \mu\text{m}$ pore size) as front filters. The second filter was either a Nuclepore filter with $0.4\ \mu\text{m}$ pore size, a Gelman Teflo filter ($2\ \mu\text{m}$ pore size) or a Millipore mixed cellulose ester filter with

Table 1
Overview of filter samplers operated by different groups

Sampler type	Upper cut size	Filter material (pore size)	Weighing protocol	Operated by
SFU	PM10	Nuclepore, 8 µm	20 °C, 50% rel. hum.	UGent
SFU	PM2	Nuclepore, 0.4 µm	id.	UGent
SFU	PM2	Teflon, 2 µm	id.	UGent
SFU	PM2	Millipore mixed cellulose ester, 3 µm	id.	UGent
Gent	PM2.5	Quartz fibre Whatman QM-A	id.	UGent
Gent	PM10	id.	id.	UGent
TSP	n.a.	id.	id.	UGent
TEOM 1400A	PM2.5	n.a.	n.a.	UGent
Digitel DHA-80	PM2.5	Quartz fibre, Munktell MK360	20 °C, 50%	Leibnitz Institute for Tropospheric Research Leipzig (IfT)
Sierra–Anderson	PM10	Quartz fibre Whatman QM-A	id.	IfT
Digitel DHA-80	PM2.5	Quartz fibre, Munktell MK 360	id.	BTU Cottbus, Berlin
TSP	Ca. 80 µm	Polycarbonate, 0.2 µm	20–22°, 30–40% rel. hum.	UniV

Upper cut sizes as well as substrate types are given. All stacked filter unit (SFU) samplers had the same kind of front filter (PM10) which is given only once. n.a., Non applicable. id., Same as above.

3 µm pore size. All filters were weighed after at least 24 h acclimatization to laboratory conditions with a Mettler MT5 microbalance at 20 °C and 50% relative humidity. Static electricity had been eliminated with an ionizer prior to weighing. The precision of the balance is 1 µg. Based on repetitive weightings of blank and loaded filters, the precision (1 standard deviation) of the net mass (i.e., of the particulate mass) is estimated at 5 µg for Nuclepore polycarbonate filters and Gelman Teflo filters, and at 30 µg for the Millipore filters. For PM10, the mass concentrations collected on a pair of filters within one sampler were added.

2.2.2. Tapered element oscillating microbalance TEOM

In addition to the filter samplers described in the preceding section, UGent also operated a Rupprecht and Patashnick tapered element microbalance (TEOM, model 1400A, Patashnick and Rupprecht, 1991), which gives PM2.5 mass concentrations of the aerosol quasi on-line, i.e. on a time scale of 5 min. The data were averaged to coincide with the 24-h sampling schedule of the filter samplers. In order to remove water from the particles sampled at ambient humidity, the sampling element is heated to 50 °C. At this temperature, some volatile aerosol material will also be lost (e.g. Eatough et al., 2003).

2.2.3. Other filter samplers

Apart from the SFU samplers, UGent also collected the aerosol with a PM2.5 and two PM10 samplers. The inlet for the PM2.5 sampler was a Rupprecht and

Patashnick PM2.5 inlet. In the PM10 samplers, a Gent PM10 inlet was used (Hopke et al., 1997). The three samplers were operated at 17 Lpm and the filters were 47-mm diameter Whatman QM-A quartz fibre filters. Sampling was conducted with a filter face velocity of 0.216 m s⁻¹. The same weighing protocol was used as for the SFU sampler filters. The precision of the net mass determination for the Whatman QM-A filters is estimated at 30 µg.

2.2.4. Digitel samplers

Two identical Digitel high-volume samplers (DHA-80) equipped with PM2.5 inlets were used by IfT Leipzig and BTU Cottbus. The distance between the devices was 2.5 m. Controlled constant flow rates of 0.5 m³/min resulted in filter face velocities of 0.5 m s⁻¹. Another sampler (Sierra Andersen HV) equipped with a PM10 inlet collected the aerosol on Munktell MK 360 quartz fibre filters with a filter face velocity of 0.5 m s⁻¹. All these samplers operated on a 24-h schedule to collect adequate deposit masses for chemical analysis and also to ensure to follow common procedures of air monitoring networks.

Blank and loaded filters were weighed after 24 h storage under controlled humidity (50%) and temperature (20 °C) on a Mettler AT261 DeltaRange balance (precision ± 10 µg).

2.2.5. TSP samplers

The TSP sampler operated by the University of Vienna (UniV) group collected the aerosol with an

upside down filter holder without specified upper cut point. The particles were collected on a 0.2 μm pore size polycarbonate filter (Poretics). The sampler acted as a vertical elutriator with an estimated upper cut size of 80 μm . Filter face velocities were ca. 0.4 m s^{-1} . The filters were weighed after equilibration times of at least 24 h on a Mettler ME3 microbalance at temperatures between 20 and 22 $^{\circ}\text{C}$ and relative humidities between 30% and 40%, which could give slightly lower sample masses than a measurement at 50% humidity. Electrostatic charges had been removed with an ion source before weighing. Including handling errors, the masses are correct within $\pm 3 \mu\text{g}$.

Another TSP sampler was run by UGent. It was operated at a flow rate of 120 Lpm (corresponding to filter face velocities of 1.55 m s^{-1}) and was loaded with 47-mm diameter double Whatman QM-A quartz fibre filters. The weighing protocol was identical to the protocol used for the SFU filter samples.

2.3. Cascade impactors

The mass size distribution of the Melpitz aerosol was measured with three different kinds of cascade impactors (see Table 2). All diameters are again aerodynamic equivalent diameters. As the main emphasis of the INTERCOMP2000 was on the study of chemical mass closure and artefacts in sampling of chemical species, all impactors were loaded with uncoated substrates, so

particle bounce has to be considered. Dry particles are known to bounce off the impaction surfaces and to pass to the next impaction stages or deposit on the walls of the stage, which gives a distortion of the size distribution. Droplet aerosols, however, are not affected by bounce. As fine atmospheric aerosol particles contain soluble or hygroscopic material, they usually contain enough water to be droplets rather than dry particles. Even in the coarse size range, some droplets still exist, which provide a sort of coating of the substrate after deposition (see e. g. Willeke and Baron, 1993). In the case of INTERCOMP2000, bounce was probably negligible except on 7 April, when daytime humidities dropped below 50% for more than 1 h, so some particles of the aerosol could have been dry (metastable droplets can exist down to humidities of 35% even for substances such as NaCl which has a deliquescence humidity of 75%; Tang et al., 1995). In the 24-h averages, however, the effect of the short period with low humidity will not be visible.

2.3.1. Berner low-pressure impactors

The UniV group used two different Berner impactors (Berner, 1984). One of them (LPI 30) had a flow rate of 30 Lpm and segregated the aerosol in the size range of 0.06–16 μm into eight size classes. The other (LPI 70) had a flow rate of 70 Lpm and a size range of 0.1–10 μm (separated into six size classes). The LPI30 was sampling on a 12-h schedule, while the LPI70 was sampling on a

Table 2
Characteristics of cascade impactors

Impactor type	Berner low-pressure impactor LPI 30	Berner low-pressure impactor LPI 70	Berner low-pressure impactor heated inlet	MOUDI (microorifice uniform deposit impactor)	ELPI (electrical low-pressure impactor)
Flow rate (Lpm)	30	70	75	30	28
Lower cut sizes μm	0.06	0.1	0.05	0.053	0.033
	0.12	0.212	0.14	0.094	0.055
	0.25	0.464	0.42	0.164	0.101
	0.5	1.0	1.2	0.301	0.159
	1.0	2.12	3.5	0.603	0.265
	2.0	4.46	10	1.0	0.390
	4.0	10.0		1.8	0.655
	8.0			3.1	1.04
	16.0			6.2	1.63
				9.9	2.49
				18.0	5.6
Sampling substrates	Aluminum foils	Aluminum foils	Aluminum foils	Aluminum foils	n.a.
Weighing conditions	20–22 $^{\circ}\text{C}$, 30–40% humidity	20–22 $^{\circ}\text{C}$, 30–40% humidity	20 $^{\circ}$, 50% humidity	20 $^{\circ}\text{C}$, 50% humidity	n.a.
Operated by	UniV	UniV	Ift	UGent	Finnish Meteorological Institute (FMI)

All sizes are aerodynamic equivalent diameters, n.a., non applicable.

48-h schedule to collect large sample masses. In Fig. 2, data points corresponding to a LPI70 measurement are also given as supplementary information. As the LPI70 sampled on a 48-h schedule, two points are given for each measurement. If the aerosol situation changed considerably within one such 48-h period, the 48-h average will not be representative of two 24-h averages. The increase of aerosol concentration which occurred during the period 6/7 April cannot be resolved.

All impaction surfaces were covered with uncoated aluminium foils, which were weighed on a Mettler ME3 microbalance at temperatures between 20 and 22 °C and humidities between 30% and 40%. Equilibration times in the laboratory were at least 24 h. The accuracy of the mass determination including the handling errors is $\pm 3 \mu\text{g}$.

Another Berner low-pressure impactor (Table 2, “heated inlet”) was operated by the IfT group. This 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 using a humidity sensor to keep the sampled aerosol at a humidity of $(60 \pm 5)\%$. The aerosol was sampled on pre-fired aluminium foils, which were weighed after 4 h acclimatization at 20 °C and 50% relative humidity on a Mettler At261 DeltaRange (precision $\pm 10 \mu\text{g}$).

2.3.2. Micro-orifice uniform deposit impactor (MOUDI)

The UGent group used a MOUDI (Marple et al., 1991) cascade impactor to measure the aerosol mass size distribution in the size range between 0.053 and 18 μm (ten stages). Nominal flow rate was 30 Lpm, while the actual flow rate was 27 Lpm. Impaction substrates were pre-baked aluminium foils that were weighed on a Mettler MT5 microbalance (precision 1 μg) after equilibration times of at least 24 h at 20 °C and 50% relative humidity. The precision of the net mass determination for the aluminium foils is estimated at 3 μg .

2.3.3. Electrical low-pressure impactor ELPI

An electrical low-pressure impactor (ELPI, Keskinen et al., 1992) was operated by the Finnish Meteorological Institute (FMI) group. In this study, the instrument used was a model designed for atmospheric aerosol studies (Outdoor-ELPI, Dekati Ltd.). This instrument gives mass size distributions of the aerosol in the size range between 0.033 and 5.6 μm on-line. The aerosol particles are charged electrically in a diode-type corona charger before entering the impactor. Each impaction stage is connected to an electrometer, which measures the collected total charge typically with a time resolution of 1 s. An algorithm converts the charge size distributions to mass size distributions. The transport time from ambient air to the impactor is short and without external heating between the aerosol inlet and the ELPI, so the size distribution measurement will be conducted close to

ambient relative humidity. For the comparison with the other samplers, 24-h averages were calculated from the original ELPI data.

2.4. Conversion of mass size distributions to PM concentrations

For each impactor sample, the mass concentrations collected on all stages with upper cut sizes less than the desired PM size were added to give one data point that can be compared to the relevant PM filter samples. As the cut sizes of the stages did not always coincide with a PM size, the stage with the cut size nearest to the PM value was included. This can give a slight negative or positive bias to the simulated PM sample. As particles smaller than the smallest cut size of an impactor are not collected, some underestimation is to be expected. For a first estimate of this effect, two lognormal distribution functions were fitted through the mass size distributions measured with the LPI 30 in the size range of the accumulation and coarse modes using the iterative procedure described by Lürzer (1980). Integrations over these functions from 30 to 100 nm and from 30 nm to 16 μm gave a maximum loss in total mass concentration of less than 1%. Even if the uncertainties of the fitting procedure are taken into account, the fraction of aerosol mass concentration in the size region below 100 nm can be considered negligible.

3. Results and discussion

Table 3 gives an overview of all the results in terms of average concentrations (and standard deviations) during the whole sampling period of 3 April–14 April 2000. For better comparability, average concentrations were calculated for each day excluding the data collected by the TEOM, the SFU samplers equipped with Whatman QM-A filters, and the ELPI, because these instruments gave consistently considerably lower or higher concentrations than all other instruments (see below). The concentrations obtained by the individual samplers were divided by the daily average concentrations. The average of these ratios is also given in Table 3. The discussion of differences between methods is based on the concentration ratios. The paper is focused on the performance of the individual instruments when measuring PM_{2.5} and PM₁₀. Sampling and analysis artefacts caused by carbonaceous aerosol components (ten Brink et al., 2004) and nitrate (Schaap et al., 2004) are discussed in other papers.

3.1. Filter samplers

Fig. 1 shows the comparison for all filter samplers (Fig. 1a gives the data for the PM_{2.5} and Fig. 1b for

Table 3
INTERCOMP2000 average mass concentrations measured with the different sampler types

Sampler type	Average mass concentration ($\mu\text{g}/\text{m}^3$)	Standard deviation ($\mu\text{g}/\text{m}^3$)	Ratio to average	Standard deviation (%)
Filter samplers				
<i>PM_{2.5}</i>				
SFU1, Nuclepore filter, 12 h	12.58	6.00	0.94	4.62
SFU2, Nuclepore filter, 24 h	12.82	6.20	0.95	3.44
Ghent PM _{2.5} , Quartz fibre f*	18.24	8.73	1.38	12.39
SFU, Teflon filter	13.18	6.36	0.98	4.43
SFU, Millipore filter	14.27	6.86	1.08	9.86
TEOM*	10.72	5.22	0.82	13.86
BTU	13.98	7.36	1.02	9.71
IFT	14.14	7.95	1.0	8.51
Average without TEOM	14.19	6.88		
Av. No TEOM, SFU Qu.	13.49	6.60		
<i>PM₁₀</i>				
SFU, Nuclep. + Nuclep.	17.02	7.81	0.96	3.81
SFU, Nuclep. + Nuclep.	17.46	7.57	0.99	3.39
UGent PM ₁₀ , Quartz, 12 h*	21.26	9.35	1.22	10.54
UGent PM ₁₀ , Quartz, 24 h*	21.30	9.09	1.23	8.66
SFU, Nuclep. + Teflon	17.42	7.54	0.99	3.27
SFU, Nuclep. + Millipore	18.72	8.57	1.09	8.10
IFT PM ₁₀	17.41	8.13	0.98	7.07
Average	18.68	8.13		
Average without UGent Qu.	17.63	7.75		
Cascade impactors				
<i>PM_{2.5}</i>				
ELPI (0.033–2.49 μm)*	26.51	15.57	1.92	16.90
UniV LPI70 (0.1–2.12 μm)	12.49	6.40	0.95	22.04
UniV PLI30 (0.06–2.0 μm)	13.22	6.56	0.98	14.54
MOUDI (0.053–3.1 μm)	14.67	7.18	1.08	11.90
Average	16.72	8.59		
Average without ELPI	13.46	6.39		
<i>PM₁₀</i>				
UniV LPI70 (0.1–10 μm)	14.89	6.91	0.96	21.80
UniV LPI30 (0.06–8 μm)	16.74	7.74	1.02	14.55
MOUDI (0.053–9.9 μm)	17.53	8.33	1.11	6.64
IFT (0.05–10 μm)	14.42	6.01	0.91	11.77
Average	15.63	6.98		

The mass concentrations are averaged over the whole campaign (3 April–14 April 2000). For the “ratio to average”, average concentrations were calculated on a day-to-day basis (excluding the data marked by *). The average ratios of individual concentrations to this average are given along with their standard deviations.

PM₁₀). For the short-time samples, concentrations were averaged to coincide with the 24-h samples. Despite the different sampling heads, substrates and weighing protocols, the data all follow the same trend. PM_{2.5} mass concentrations were below $10 \mu\text{g}/\text{m}^3$ on 3 days (5, 6 and 13 April), when the air masses arriving at the site originated over unpolluted regions of the North Atlantic (see Müller et al., 2004). On these days, uncertainties of mass concentrations are highest because of low filter loadings. Only on 11 and 12 April, average PM_{2.5} concentrations exceeded $20 \mu\text{g}/\text{m}^3$, which is still low for

both this season and this site (annual averages are typically in the order of $20 \mu\text{g}/\text{m}^3$; Müller, 1999). In addition, the figures include the average values of the PM_{2.5} and PM₁₀ filter samples. Fig. 1b also shows the concentrations obtained with the two TSP samplers, which were not used in the calculations of the averages. As there was so little aerosol mass present in the size range above $10 \mu\text{m}$ (Fig. 2 shows examples of the size distributions during the clean and polluted days), the TSP concentrations are not significantly higher than the PM₁₀ ones, and in some instances they were even lower,

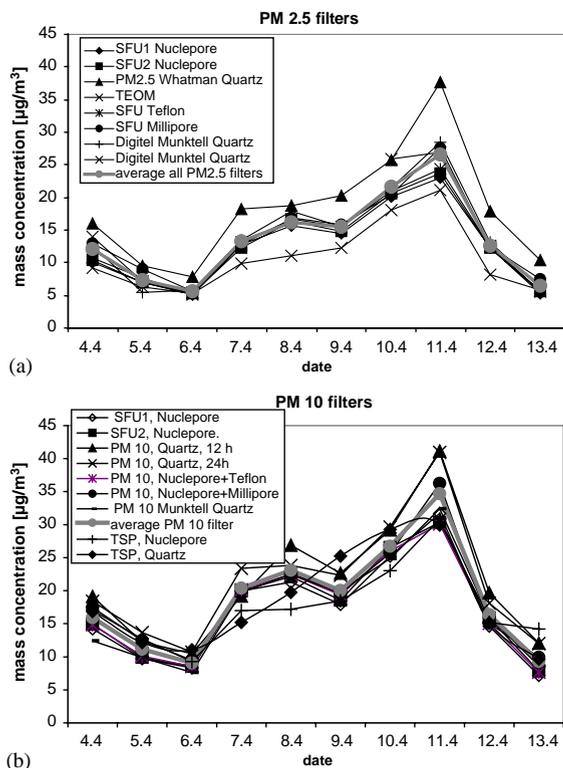


Fig. 1. (a) Mass concentrations measured with all filter-based PM_{2.5} samplers. The abbreviations are defined in Table 1. The grey line gives the average over all concentrations. (b) Mass concentrations measured with all filter-based PM₁₀ samplers. The abbreviations are defined in Table 1. The grey line gives the average over all concentrations. TSP concentrations are also included for comparison purposes; they were not, however, used in the calculation of the average concentrations.

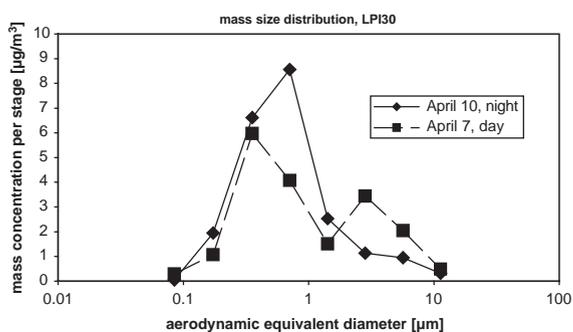


Fig. 2. Typical mass size distributions obtained with the LPI30 impactor under polluted (10 April, night) and unpolluted (7 April, day) conditions. All stages had the same width on a logarithmic scale (i.e. cut sizes are multiplied by a factor of 2).

which might have been caused by the unspecified collection efficiency of the upside down filter holder and/or by the lower relative laboratory humidities at

filter weighing (30–40% UniV, compared to 50% UGent).

The PM_{2.5} mass concentrations agree on average within $\pm 18.1\%$. Most of this variation is caused by the TEOM and the SFU samplers loaded with quartz fibre filters (Whatman QM-A). If those two data sets are excluded, the data agree within $\pm 8.1\%$.

The TEOM sampler gives significantly lower mass concentrations than the other ones. Compared to the average of the filter samples (without those obtained on the Whatman QM-A quartz fibre filters), the TEOM sampled only $(82 \pm 13.9)\%$ of the mass. Several studies on sampling artefacts of the TEOM are available that focus mainly on the underestimation of carbon mass determination (e. g. Eatough et al., 2003). The negative artefact is usually explained by the heating of the sample in the TEOM. As the instrument measures the mass concentration quasi-on-line, the deposited aerosol contains also an amount of water that is determined by the chemical composition of the aerosol and the ambient relative humidity. In order to remove this water, the sampling element is heated to 50°C . At this temperature, volatile organic carbon and other volatile aerosol species such as nitrate will be lost to the gas phase. The underestimation of mass concentration can be explained at least in part by this loss of volatile material (other than water).

The data set labelled “PM_{2.5}, quartz” in the PM_{2.5} plot was obtained with Whatman QM-A quartz fibre filters as sampling substrates using a filter face velocity of 0.216 m s^{-1} . The mass concentration is $1.38 (\pm 12.4\%)$ times the average concentration. Quartz fibre filters are known (e.g. Turpin et al., 2000; Maenhaut et al., 2001a) to have a positive sampling artefact caused by adsorption of gaseous organic carbon (which increases with decreasing face velocity) so the mass concentrations are also higher than those sampled on other substrates. The data obtained from the Digital samplers of IfT and BTU, which used a different type of quartz fibre filter (Munktell MK360) and a higher filter face velocity (0.5 m s^{-1}), fit very well to the data obtained with other non-quartz filter types.

In the case of the PM₁₀ filter samples, the mass concentrations obtained from the Whatman QM-A quartz fibre filters (face velocity 0.216 m s^{-1}) are also higher than those obtained on other sampling substrates, while the concentrations obtained with the Munktell MK 360 (face velocity 0.5 m s^{-1}) agree well with the average of all samplers. If all data are included, the concentrations agree within 12.2% . Without the Whatman QM-A quartz fibre filters, the PM₁₀ mass concentrations agree within 6.6% . Again, the positive artefact seems to be confined to the Whatman QM-A filters with the lower face velocities. Compared to the average of the mass concentrations obtained by the other filters, the concentrations on the SFU Whatman

QM-A quartz fibre filters were higher than the other concentrations by a factor of 1.22 and 1.23 (for the 12 and 24 h samples, respectively).

Whether the difference in the data obtained on quartz fibre filters is due to the face velocities (higher concentrations sampled with lower face velocities) or to the filter type (filter thickness, porosity, ease of handling) cannot be decided based on the data we have. More work is definitely needed on this subject, especially with regard to EU regulations requiring quartz fibre filters as sampling material.

3.2. Cascade impactors

Fig. 2 gives two examples of mass size distributions measured with the LPI30 impactor under conditions of low (7 April, daytime sample) and high pollution (10/11 April, night time sample). Under conditions of low pollution, the maximum of the fine-particle mode is found at smaller sizes, while the fine-particle mode of the polluted aerosol is centered at larger sizes. Under both conditions, very little mass is present in the size range below $0.1 \mu\text{m}$ and above $10 \mu\text{m}$. The least loaded stages (i.e. stages 1 and 8 on 7 April) have large errors due to the low sample mass, but the stages with high mass loadings are not unduly affected.

Figs. 3a and b show the comparison of the impactor samples as well as the average of the filter samples in the relevant size range. As the upper cut size of the ELPI was only $5.6 \mu\text{m}$, the data are not included in Fig. 3b (for PM10). The MOUDI and LPI impactors agree well with each other (fine size fraction: within 18.4%; coarse fraction: also within 18.4%) and with the filter samples.

In all PM_{2.5} cases, the ELPI gave mass concentrations in the range of $0.033\text{--}2.49 \mu\text{m}$ that were on average a factor of 1.92 higher than the average values obtained without the ELPI data. There are two reasons for this discrepancy. First, the ELPI size distribution measurements are carried out close to ambient relative humidity. Therefore the samples collected from ambient air obviously contain appreciable amounts of water. The influence of ambient humidity on the mass concentrations measured with the other impactor types is removed by weighing the foils under dry ($<50\%$) conditions. Without conditioning (drying) of the ELPI sample air it is difficult to calculate mass concentrations, which are comparable to those obtained with the gravimetric methods. The particle water content depends both on the chemical composition of particles and on the relative humidity changes during their lifetime. The latter (hysteresis effect in hygroscopic growth) is not easily modelled. During INTERCOMP2000, 24 h averages of relative humidity ranged from 64.1% to 86.7% with an absolute minimum of 25.2% and maximum of 100% so the particles nearly always contained at least some water. The second reason why the ELPI seems to

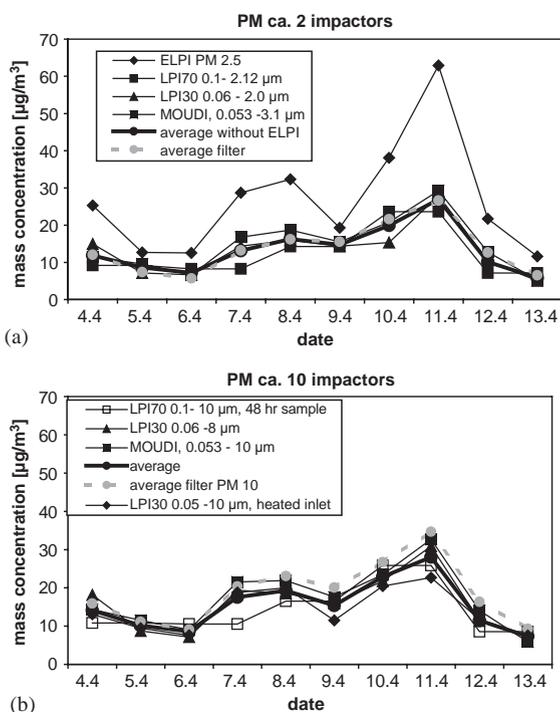


Fig. 3. (a) Mass concentrations collected by the cascade impactors in the given size range. The average of the PM 2.5 filter data is given for comparison. The average of the impactor data was calculated without including the ELPI data. Two points are plotted for each LPI70 measurement because of the different sampling schedule (see text). (b) Mass concentrations collected by the cascade impactors in the given size range. The average of the PM 10 filter data is given for comparison. Two points are plotted for each LPI70 sample because of the different sampling schedule.

overestimate the mass concentration when compared with the gravimetric methods is that the immediate detection of mass concentration minimizes the mass loss effect of semi-volatile material. Almost all data based on filter sampling and subsequent weighing suffer from mass loss of semi-volatile material like ammonium nitrate and organics.

It is difficult to convert the ELPI mass concentrations to values which are comparable to gravimetric methods. However, the water content of particles, also below the deliquescence points, alone could explain a large part of the differences between the ELPI and the gravimetric methods (Swietlicki et al., 1999; Tang and Munkelwitz, 1994).

3.3. Comparison of filter samplers and cascade impactors

The question often arises whether the mass concentrations measured with filter samplers and impactors are

comparable. Different sampling mechanisms, flow rates and substrates can influence this comparability. The lower and upper cut sizes as well as wall losses of impactors can lead to underestimations of mass concentrations, while non-ideal efficiency curves of some filter types could also give underestimations of mass concentrations. In this study, filter and impactor samples are very well comparable, if the instruments that give large deviations from the average mass concentration (i.e. SFU with Whatman QM-A quartz fibre filters, TEOM and ELPI) are excluded. In the PM_{2.5} range, the mass concentrations agree within $\pm 6.3\%$. For PM₁₀, the agreement is within $\pm 8.7\%$. The effect of slightly different cut sizes, which was discussed already in the sections above, seems to have been small.

4. Summary and conclusions

For the PM_{2.5} filter samples, mass concentrations agreed within 8.1% except for the samples collected with the SFU sampler (face velocity 0.216 m s^{-1}) on Whatman QM-A quartz fibre filters (38% higher than average of others) and with the TEOM, where concentrations were on average 18% lower. If all samples are considered, the mass concentrations agree within 18.1%. The higher concentrations collected by the SFU with Whatman QM-A quartz filters may have been caused by the known positive sampling artefact of these filters for gas phase components. Data sampled on another type of Quartz fibre filters (Munktell MK 360) with filter face velocities of 0.5 m s^{-1} agreed very well with the main data set. The lower concentrations collected by the TEOM can be at least partly ascribed to the evaporation of volatile aerosol components at the elevated temperature (50°C) of the sampling element. The differences in weighing protocols and sampler cut curves are not visible in the data set. For the PM₁₀ filter samples, findings were similar. The mass concentrations agreed within 12.1% (all filters) and within 6.6%, if the SFU Whatman QM-A quartz fibre filter samples were excluded. The mass concentrations collected on these filters were 22 and 23% higher (for the 12 and 24 h samples) than the average collected by all other filter types. A comparison of the average of the filter samples excluding the SFU samples on Whatman QM-A quartz fibre filters and TEOM to the mass concentrations obtained with the impactors (without ELPI) in the respective size ranges gave an agreement within $\pm 6.3\%$ and $\pm 8.7\%$ for the PM_{2.5} and PM₁₀ ranges. The positive bias in mass concentration obtained from low volume samplers equipped with quartz fibre filters should be kept in mind especially with regard to the EU regulations requiring quartz fibre filters as sampling substrate for PM considerations.

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