ON THE HORIZONTAL HOMOGENEITY OF MASS-RELATED AEROSOL PROPERTIES

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Abstract. We studied the mass-related aerosol properties, simultaneously at two sites at the urban roof top level in the same city. No systematic influence of the wind vector on the difference in the aerosol concentrations between the two locations could be found. These results are compared with results from a second, similar experiment over a larger distance including one urban and one rural site. Surprisingly, we could not detect a tendency which would indicate that sampling air at distance in the order of 1 km would be less affected by the heterogeneity than sampling distanced in the order of 10 km apart. On the contrary, the results suggest that mass-related properties at two sites in the same city are not necessarily more similar than at an urban and a rural site outside the city. These results stress the limited horizontal homogeneity of urban atmospheric aerosol. As a conclusion it is suggested that single-site measurements of mass-related aerosol properties should be considered to be representative for an area smaller than 1 km^2 on size.

Keywords: atmospheric aerosols, horizontal homogeneity, urban aerosol, PM_{10}

1. Introduction

Because of adverse effects to human health, fine particle fractions are criteria pollutants. Air quality standards are to be controlled based on airborne particulate matter measurements for particles less than a specified size, such as $PM_{2.5}$, i.e. particulate matter < 2.5 μm aerodynamic diameter (e.g. CEU, 1996). Threshold limits are expected to be exceeded in particular in urban areas. The spatial representativity of point measurements of mass related properties of the atmospheric aerosol at or near the ground is limited by the spatial variability. In the context of aerosol monitoring, essential information for network design can be expected from investigating the spatial variability of mass-related parameters. Through simultaneous measurements at two sites in one city and a control experiment with one extra-urban site we addressed this question for the so-called urban aerosol.

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2. Methods

2.1. SAMPLING

Samples were taken simultaneously at two locations in the city of Leipzig, Germany, 16.06.–08.07.1999, 2 and 4.5 km from the city center at a distance of Δs = 4.1 km (University Chemical Institute, Linnéstrasse, and Institute for Tropospheric Research, IfT, Permoserstrasse). The sampling sites were selected such as to exclude shielding or channeling of the advection by local structures and to minimise the direct influence of nearby sources: Sampling took place on the roof tops of campus buildings, 21 m and 14 m above ground. The roofs were somewhat higher than those of the closest other buildings and, in both cases, only one building in the surroundings exceeded its height. Traffic from secondary streets and parking and chimneys related to small-scale heating were the only emittors in the surroundings (> 60 m). Closest distance to supposedly major sources was 0.3 km (major streets in both cases).

Parallel sampling included a pair of low-pressure impactors (Berner type), covering 0.05–10 μm (5 stages with lower cutoffs at 0.05, 0.14, 0.42, 1.2 and 3.5 μm, 4.5 $m^3\ h^{-1}$) and 0.06–8 μm (8 stages analysed with lower cutoffs at 0.06, 0.13, 0.25, 0.5, 1.0, 2.0 and 4.0 μm, 1.5 $m^3\ h^{-1}$), respectively, and a pair of high-volume filter sampling devices (quartz fibre filters), one with a PM_{10} inlet (modified Sierra Andersen, 58 $m^3\ h^{-1}$) and the other without an upper cutoff (hence, addressing total suspended particulate matter, TSP; Digitel, 42 $m^3\ h^{-1}$). Sampling times were mostly 24 hours; 15 % were 11.5 h samples (day/night i.e., 18:30–06:00 h and 06:30–18:00 h). The results of these measurements are compared with a data set from a similar experiment performed simultaneously at one of the sites (IfT) and at Merseburg, 17.11.–07.12.1999. Merseburg is a small ciy at the western margin of the same, the Halle-Leipzig-Bitterfeld conurbation (ca. 1 million inhabitants). The sampling site there was on a roof top, too, of a building of the university campus directly adjacent to a rural area, 16 m above ground. With respect to the prevailing wind directions the building marked the beginning of an ensemble of similar buildings. Δs = 32.4 km in the Merseburg-Leipzig case. Wind, temperature and humidity were recorded continuously and directly on site (and at same height) at Leipzig-IfT and at Merseburg. Wind velocities were 2.2 ± 0.8 m s^{-1} during the summer campaign and 3.3 ± 1.8 m s^{-1} (Leipzig) and 4.4 ± 3.2 m s^{-1} (Merseburg) during the winter campaign (hourly data). Solar radiation was by far less (28 vs. 207 W m^{-2}) in the winter (mostly overcast), humidity was by average higher (73 vs. 62%) and precipitation events occurred more frequently (14 vs. 9 based on 12-h intervals) in the winter campaign than in the summer campaign.

2.2. MASS, CHEMICAL AND DATA ANALYSES

Mass (gravimetry), nitrate and sulfate (water soluble fractions; ion chromatography after aqueous extraction; Dionex) were determined from samples simultaneously

taken. For the filter samples, sulfate data are compared with total sulfur determined at one of the sites using x-ray fluorescence analysis (matrix-specific specification; Spectro A.I.). The mass of particulate matter sampled was determined with pre- and post-weighing of the substrates (quartz fibre filter membranes or and polyvinyl-fluoride or aluminium foils exposed in the impactors) at constant humidity and temperature using enclosed microbalances. Equilibration of the filter membranes to humidity was at least 16 h at rh = 50 ± 3%.

Impactor samples were taken during a few days (n = 6 and n = 4 during the two campaigns, cf. Table I) while filter samples were taken continuously during three weeks (n = 24 and n = 19 during the two campaigns, cf. Table I).

For the following data analysis we did not make use of the entire resolution of the mass size distributions, but discuss sub-micron and super-micron size fractions which are based on summing contributions of the respective impactor stages. The mass fraction of water in aerosol samples depends on chemical composition and is expected to account for 5–10% at rh = 50 ± 3% (Winkler, 1988). Therefore, the spatial variability of chemical composition introduces a corresponding uncertainty for the gravimetric determination.

The uncertainty is higher for the gravimetry of the impactor samples because of the addition of uncertainties of individual weighing processes (5 and 7 foils, respectively). Also, ion levels in individual impactor stages were below detection limits in some cases. The filter data time series addressed different size fractions, PM_{10} and TSP. Mass-related differences between these two should be related to particles > 10 μm. Also, the size fractions addressed by the two impactors, accumulation mode (AM) and coarse mode (CM), did not perfectly match (0.05–1.2 μm vs. 0.06–1.0 μm and 1.2–10 μm vs. 1.0–8.0 μm, respectively). Provided that the same aerosol was sampled by the pairs of samplers, these differences should albeit give rise to little deviations: Because of the respective mass-size distributions and based on numerous studies in polluted environments (Seinfeld and Pandis, 1998) we expect $c_i(PM_{10}) \approx c_i(TSP)$ for $i = SO_4^{2-}$. For i = m, particles > 10 μm could play a role and TSP could significantly exceed PM_{10}.

We quantify deviations between simultaneous measurements at sites 1 and 2 of the mass-related property i (i = m, NO_3^-, SO_4^{2-}) by $\Delta c_i/c_i = 2 * | c_{i1} - c_{i2} | / (c_{i1} + c_{i2})$. Criteria to judge upon the significance of $\Delta c_i/c_i$ regarding the uncertainties which result from the aforementioned experimental (sampling and analysis) errors, are chosen as follows: In accordance with the maximum analytical error, implications of water associated to particulate matter of different composition and as a consequence of the implications of the sampling techniques, differences in the ions and of mass from impactor samples are considered to be significant when larger than 15% i.e., for comparison of 2 concentrations, c_1 and c_2, the ranges $c_1 \pm 15\%$ and $c_2 \pm 15\%$ do not overlap). For mass from filter samples, a lack of overlap between the ranges $PM_{10} \pm 5\%$ and TSP + 5% / –15% are taken as criterium for significant deviations, because of the systematic difference $TSP \geq PM_{10}$.

TABLE I

Particulate mass and nitrate and sulfate concentrations for sub-micron (AM) and super-micron (CM) size ranges (impactor samples), PM_{10} and TSP (filter samples) and percentage of significant deviations between simultaneous data pairs (see text, Section 2). Concentration data are given as time weighted mean ± standard deviation ($\mu g\ m^{-3}$) (a) two sites in the same city (Δs = 4.1 km) and (b) one urban and one rural site (Δs = 32.4 km). n = number of samples, n.d. = no data

a.		Urban site Leipzig-IfT		Urban site Leipzig-University		Significant deviations (%)	
		AM	CM	AM	CM	AM vs.	CM vs.
		AM (0.05–1.2 μm)	(1.2–10 μm)	(0.06–1 μm)	(1–8 μ m)	AM	CM
Impactor	m	16.3 ± 5.9	7.6 ± 2.9	12.1 ± 4.1	9.7 ± 1.4	17	50
(n = 6)	NO_3^-	1.37 ± 0.69	0.71 ± 0.28	1.05 ± 0.70	0.77 ± 0.50	33	67
	SO_4^{2-}	3.3 ± 1.4	0.18 ± 0.07	3.1 ± 1.8	0.36 ± 0.24	0	67
Filter		PM_{10}		TSP		PM_{10} vs. TSP	
(n = 24)	m	29.1 ± 6.7		31.2 ± 6.7		54	
	SO_4^{2-}	3.6 ± 1.1		4.3 ± 1.6[a]		35	

b.		Urban site Leipzig-IfT		Rural site Merseburg		Significant deviations (%)	
		AM	CM	AM	CM	AM vs.	CM vs.
		AM (0.05–1.2 μm)	(1.2–10 μm)	(0.06–1 μm)	(1–8 μ m)	AM	CM
Impactor	m	12.6 ± 7.4	10.1 ± 7.1	n.d.	n.d.	n.d.	n.d.
(n = 4)	NO_3^-	2.6 ± 1.9	2.0 ± 1.9	3.4 ± 1.7	1.30 ± 0.26	25	25
	SO_4^{2-}	3.3 ± 1.3	1.2 ± 1.3	2.0 ± 0.9	0.46 ± 0.46	25	25
Filter		PM_{10}		TSP		PM_{10} vs. TSP	
(n = 19)	m	24.5 ± 10.7		22.4 ± 9.8		53	
	SO_4^{2-}	3.7 ± 1.6		3.6 ± 1.6[a]		16	

[a] based on the assumption that total S was present as SO_4^{2-} (hence, upper limit).

3. Results

At the city sites, the impactor data deviated 2% for mass (25% for the sub-micron fraction alone), 10% for nitrate (18% for the sub-micron fraction) and 5% for sulfate (0.6% for the sub-micron fraction) concentrations when averaged over all samples. These results are summarized in Table Ia. When considering simultaneous pairs of samples it is found that the deviations were insignificant with respect

TABLE II

Absolute and relative deviations of particulate mass concentrations, |dm| and dm/m, between PM_{10} and TSP (filter) samples from two sites (a.) in the city of Leipzig (Δs = 4.1 km, June-July 1999) and (b.) one Leipzig and one Merseburg site (Δs = 32.4 km, Nov–Dec 1999) as related to stability of the atmosphere (classes according to Pasquill, 1974). 12 h i.e., day-time or night-time samples only: Leipzig sampling intervals No. 7–8 and 16–19 (Fig. Ia) and Leipzig and Merseburg sampling intervals No. 13–13 (cf. Figure 1b). §= significant deviation of aerosol mass

		Day-time samples		Night-time samples	
a.	Stability class	|dm|	dm/m	|dm|	Dm/mB
	B	0.4	0.01		
		2.9	0.08		
		13.1	0.43§		
	F			2.1	0.06
				2.4	0.07
				1.4	0.09
b.	C	0.1	0.00		
		2.1	0.10	7.4	0.20
	E/F[a]			2.1	0.06

[a] E at Merseburg, F at Leipzig

to the inherent uncertainties in ca. 50% of the data pairs with a slightly higher frequency in the coarse mode. Further points to make is not supported by this small data set. The deviations in the filter data time series were 7% and 16% and these were significant in 54% and 35% of the individual data pairs of mass and sulfate concentrations, respectively. Both the mass and sulfate TSP data are somewhat higher than the PM_{10} values. These differences could be due to higher sub-micron particle concentrations (sulfate resided to > 90 % in the sub-micron size fraction; cf. impactor data), higher super-micron particle concentrations (as indicated by the impactor sample data) and as far as mass is regarded, possibly, also due to the different upper cut-offs (TSP vs. PM_{10}).

First we investigate the possible influence of atmospheric stability on the spatial variability of the mass-related aerosol properties. We expect, if any, more horizontal homogeneity at the ground under highly turbulent or unstable conditions and, vice versa, a more pronounced horizontal variability during stable conditions, e.g. nocturnal stratification, due to the higher significance of local sources. Stability classes were allocated to the 11.5 h (i.e., day-time or night-time) sampling intervals (sampling intervals No. 7–8 and No. 16–19) depending on wind velocity and insolation according to Pasquill, 1974. The data are listed in Table IIa. Insignificant

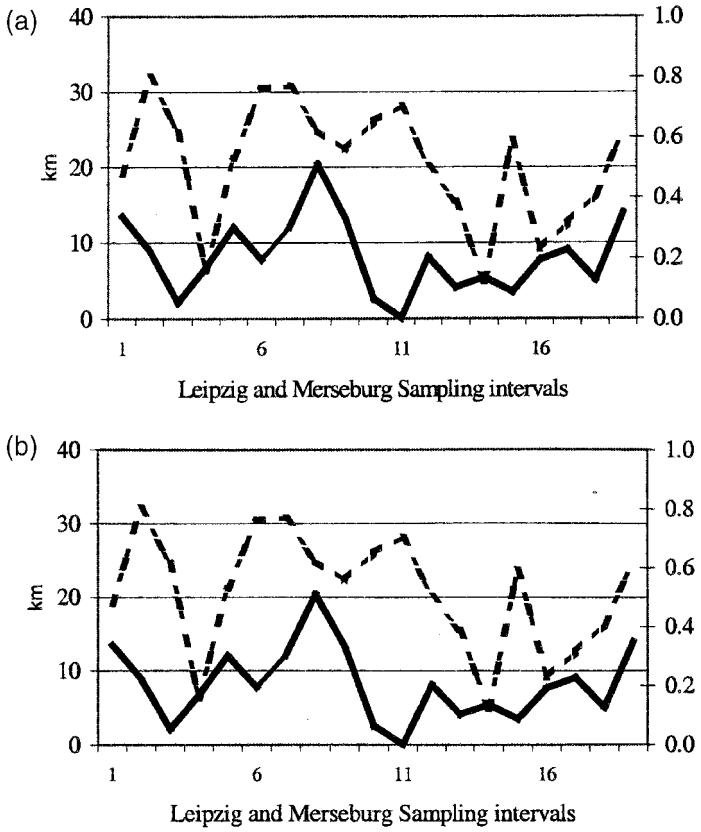

Figure 1. Time series of the deviation of particulate mass concentrations, dm/m, between two sites and of the angle between the horizontal wind direction and the line connecting the sites (expressed as the distance of air samples taken at both sites). (a.) Two sites in the city of Leipzig (Δs = 4.1 km, June-July 1999) and (b.) one Leipzig and one Merseburg site (Δs = 32.4 km, Nov-Dec 1999), 12-24 h samples.

mass deviations (dm/m = 0.01–0.09) were found during 2 day-time and 3 night-time measurements covering both unstable and very stable conditions (classes B and F) while the only significant deviation (dm/m = 0.43) occurred during one day-time measurement under unstable conditions (class B). These observations suggest that horizontal homogeneity on this spatial scale is at least not dominated by atmospheric stability. We tested also friction velocity, u_*, as a measure for near surface local atmospheric turbulence intensity and mixing. No correlation of u_* with the aerosol mass deviations was found. This finding is, however, not conclusive, because the effective range of the turbulent elements (eddies) is related to their characteristic size, which in most cases will be significantly smaller than Δs (4.1 km).

In any situation and in particular under stable conditions, advection will strongly influence the horizontal homogeneity of the near-ground atmosphere. An appropri-

ate indicator to address its influence is the effective distance between trajectories at the sites: Intuition suggests that the smaller the angle between the wind direction and the line connecting the two sites, the closer the results should match, because the trajectories which end at the sites then are close to each other. As the horizontal heterogeneity *in* wind direction should not play a role when sampling over hours, the distance of the trajectories provides an adequate indicator for the distance of the air samples taken and, hence, for horizontal homogeneity. Moreover, any aerosol source between the two sites should show up as an offset to the downwind results (which was not the case), while sinks should be negligible on such a short distance. However, we found that the horizontal variability of particulate mass concentration was *not* larger when the trajectories (air samples) were in maximum distance: the mass deviations were 18 ± 17% under conditions of wind direction perpendicular to the line connecting the sites (angle 90° ± 30°, distance between trajectories 3.8 ± 0.3 km), while these were 20 ± 16% when averaging over all wind directions. Moreover, the results suggest that the deviation is independent of the wind direction (Figure 1a): There is no systematic effect found, i.e. time series of deviation and distance between trajectories are apparently not in phase: The correlation are insignificant showing r = 0.13 and 0.21 for relative and absolute deviations, dm/m and |dm|, respectively.

What is the characteristic size of the horizontal variability? Is it significantly more pronounced when comparing more distanced sites? The degree of agreement between simultaneous samples from the experiment between an urban and a rural site and over a longer distance (Δs = 32.4 km) were essentially very similar to the intra-urban experiment: The impactor data deviate 2% for nitrate (24% for the sub-micron fraction) and 7% for sulfate (25% for the sub-micron fraction) concentrations when averaged over all samples (Table Ib). The filter data time series deviations are 9% for the mass concentrations and these are significant in 53% of the individual data pairs. Also over the longer distance, the horizontal variability of particulate mass concentration was not larger when the trajectories were in maximum distance: the mass deviations were 21 ± 13% when averaging over all wind directions and the time series of deviation and distance between the trajectories were not correlated, r = 0.12 and 0.02 for relative and absolute deviations, dm/m (Figure 1b) and |dm|, respectively. The deviations seemingly are, again, not corresponding to atmospheric stability: No significant mass deviations were observed during the 11.5 h sampling intervals which addressed various conditions of stability (2 nights classified E/F and D and 2 day-time measurements classified C and D; Table IIb).

The urban site is located west of the rural site. During these experiments southwesterly winds prevailed and wind directions at the sites deviated by 18 ± 13°. We note that the the comparability between these results and those of the intra-urban experiment is limited, because the measurements were not conducted simultaneously (different seasons). Moreover, there is only incomplete information about the wind field and the potential significance of sources and sinks during trans-

port over decades of km. Hence, any conclusion from this comparison is very preliminary.

4. Discussion and Conclusions

Significant deviations over $\Delta s = 4.1$ km have been observed which are indicative for inhomogeneity in the horizontal distribution of the aerosol. These were not determined by the effective distance of the trajectories at the sites. Although no direct comparison was made, preliminary results suggest that sampling at sites distanced on the order of 1 km would be less affected by the horizontal heterogeneity than sampling at sites distanced on the order of 10 km. Since the data set is small (measurements from only one season and only a small range of atmospheric conditions), only qualitative conclusions can be given: mass-related properties of two sites in the same city are not necessarily more similar than when compared with a rural site outside. Significant mass differences when averaging particulate matter concentrations over 12–24 h in the height of the canopy must be related to imperfect mixing – at least imperfect in the direction perpendicular to the flow over the distance studied (4.1 km) but also over shorter distances (as suggested by Figure 1a). This means a plume-like structure of the urban aerosol which will be determined by the spatial distribution of the sources and the atmospheric conditions (turbulence and stability). This effect might be even more visible when based on a higher sampling frequency.

The results stress the limited horizontal homogeneity of the urban atmospheric aerosol near the ground. In the area we sampled, fluctuations of the wind direction do not level out the spatial variability – even for 24 h samples. Local influences will certainly tend to decrease at higher altitudes and farther downwind in the urban plume. Airborne measurements, 300 m above ground, in the Los Angeles basin showed that PM_{10} and $PM_{2.5}$ horizontal variability can be significant within 1 km distance (hourly measurements; Collins *et al.*, 2000). What are adequate implications for the design of monitoring networks and episodic field studies, such as sampling frequency and location of instrumented sites? The results reported here suggest that significant discrepancies may be expected in data of mass-related aerosol properties at sites distanced 1 km or more from each other have to be expected in source areas and single-site measurements should be considered to be representative for an area smaller than 1 km^2 by size. Despite the smoothening effects of secondary aerosol formation, which occurs on a characteristic time scale of many hours to days, the spatial distribution of (primary) aerosol sources will limit the spatial homogeneity of the near-ground aerosol. The quantification of mass-related parameters at sites with various distances could be helpful to find an appropriate design of an aerosol monitoring network, adapted to the local situation.

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