Detailed Aerosol And Elemental Mass Size Distributions During Winter And Summer Campaigns In Ghent, Belgium

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Abstract. During 2004 winter, 2004 summer, and 2005 winter campaigns in Ghent, Belgium, 24-hour size-fractionated samples were collected with a 10-stage MOUDI and a 12-stage small deposit area low pressure impactor (SDI). The two devices were operated in parallel and between 30 and 35 samplings were made in each campaign. As impaction surfaces, aluminium foils were used in the MOUDI and Kimfol polycarbonate films in the SDI. The MOUDI samples were analysed for the particulate mass (PM) by weighing and the SDI samples were analysed for 27 elements (from Na to Pb) by PIXE. The average size distributions for the PM of winter and summer differed substantially from each other. In both seasons, two modes were present, but they had different relative intensities and the fine mode peaked at a different diameter. For the crustal elements (Al, Si, Ca, Ti, Fe), similar monomodal size distributions, which peaked at 3.3 μm aerodynamic diameter (AD), were obtained in both seasons. For several typical anthropogenic elements (e.g., S, V, Ni, Pb) or elements with an important anthropogenic contribution (K), two submicrometer modes and one coarse mode could be discerned. The submicrometer modes peaked at 0.3 and 0.7 μm AD. For V and Ni, which are attributable to residual oil burning, the lower submicrometer mode (i.e., the one with peak at 0.3 μm) was by far the major mode in both seasons. For K, the size distributions of winter and summer were very different. Whereas during summer most of the K mass was present in the coarse mode, during winter, the 0.3 μm mode was the major one, followed by the 0.7 μm mode. The large contribution of fine K during winter is attributed to biomass (wood) burning. In an earlier study, it was found that biomass burning can be quite important at Ghent during winter.

Keywords: atmospheric aerosols, mass size distribution, chemical composition, cascade impactor, Belgium.

INTRODUCTION

Aerosol particles play an important role in atmospheric chemistry and have effects on human health and climate. Since the effects of the particles depend on their size and chemical composition, it is of interest to measure the mass size distribution of the aerosol and its constituents in detail. Furthermore, the size distributions provide valuable information on the sources and source processes and on the transformation processes during atmospheric transport, and they are needed for estimating the dry deposition of the aerosol and its constituents. Detailed mass size distributions of the aerosol and its constituents for sites in Europe are rather rare. Examples of recent studies in urban areas of Europe are those by Pakkanen et al. for Helsinki [1] and of Salma et al. for Budapest [2]. As far as Belgium is concerned, a detailed study is available for Ghent for fall 1999 [3]. Here, we report on studies at the same Ghent site for two winter and one summer campaign in the years 2004 and 2005. The similarities and differences between the size distributions in winter and summer are discussed and some comparisons are made with the results for Helsinki [1] and Budapest [2]. In comparing the data from the three sites, it should be taken into account that our Ghent site is an urban background site, that the measurements were done at two sites (i.e., an urban and a rural site) in Helsinki and that the Budapest site was a kerbside. A particular feature of the latter site was the high proportion of resuspended road dust and of traffic-related elements.

EXPERIMENTAL

The samplings took place at the Institute for Nuclear Sciences of Ghent University (51°01′N, 03°44′E, 10 m a.s.l.) and the samplers were installed on the roof of a 3-story building at about 15 m above ground. Three sampling campaigns were conducted,

the first from 4 February to 26 March 2004 (winter 2004), the second from 14 June to 16 July 2004 (summer 2004), and the third from 10 January to 14 February 2005 (winter 2005). In each of these campaigns two cascade impactors were deployed in parallel for 24-hour collections (with start in the morning). The impactors were a 10-stage microorifice uniform deposit impactor (MOUDI) [4], which operates at a nominal flow rate of 30 L per min, and a 12-stage small deposit area low pressure impactor (SDI) [5], operating at 11 L per min. Upstream of the SDI was an inlet with cut-point of 15 μm aerodynamic diameter (AD). The collection surfaces in the MOUDI were 37-mm diameter aluminium foils (4 mg/cm^2) for the impaction stages and double Whatman QM-A quartz fibre filters for the back-up filter. The foils and filters had been pre-heated at 550°C to remove organic contaminants. Thin Kimfol polycarbonate films (1.5 μm thick) were used as collection surfaces in the SDI. A total of 35 parallel samples were taken in the 2004 winter campaign, 30 in 2004 summer, and 35 in 2005 winter. In parallel with the cascade impactors, various filter samplers were operated for different types of analyses, including for carbonaceous species. Results for some of the filter samples have been published elsewhere [6-9]. The median daily concentrations (and ranges) of the PM10 mass (in μg/m^3) during each of the campaigns, as derived from "Gent" PM10 stacked filter unit (SFU) samples, were 32 (16-72) in 2004 winter, 19 (14-26) in 2004 summer, and 24 (11-78) in 2005 winter.

The MOUDI samples were analysed for the particulate mass (PM) by weighing with a microbalance (at 20°C and 50% relative humidity) and the SDI samples were analysed for 27 elements (i.e., Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Zr, Nb, Mo, and Pb) by particle-induced X-ray emission spectrometry (PIXE) using a 2.4 MeV proton beam. Details on the PIXE procedures are given in Ref. [5] and in the references cited therein.

RESULTS AND DISCUSSION

Mass Size Distributions For The PM

Average mass size distributions were calculated for the PM and the various elements for each of the three campaigns. Fig. 1 shows the average size distributions for the PM. For each of the three campaigns there are clearly two modes present, a coarse mode which peaks at about 4 μm (all particle diameters reported in this manuscript are in AD) and a fine (submicrometer) mode, which has different features in winter and summer. In summer, the fine mode is narrower than in winter and it peaks at a lower diameter, i.e., at 0.4 μm

versus around 0.6 μm in winter. It should be noted that the size distributions varied substantially from sample to sample and for the individual winter samples, three types of fine modes could be discerned, with the first type equally broad as in Fig. 1 and peaking at around 0.6 μm and the other two types more narrow and peaking at 0.4 and 0.8 μm, respectively. Possible explanations for the shift in fine mode diameter will be indicated below, when discussing the size distributions of the elements (such as that for S). Another feature of Fig. 1 is that, on average, the coarse and fine modes are equally intense in summer, whereas in winter the fine mode is more pronounced, particularly in 2004 winter. Although there was quite some sample to sample variation for the relative intensities of the two modes, especially in winter, the difference between the overall average size distributions of summer and winter points to differences in contributions of major aerosol types. The difference in mode intensities was confirmed by the results from the SFU and other filter samples and it seems that it is at least in part due to the fact that there is much less fine nitrate in summer than in winter. In winter, fine nitrate (present as ammonium nitrate) was a major fine aerosol component (in 2004 winter its average concentration in PM2 was 6 μg/m^3 and it accounted for 25% of the average PM2 mass), whereas in the summer 2005 campaign nitrate was, on average, only 1.3 μg/m^3 and accounted for only 13% of the average PM2 mass. The lower fine nitrate levels (and lower nitrate percentages in PM2) in summer are attributed to the transfer of semi-volatile ammonium nitrate from the particulate to the vapour phase at the elevated temperatures [10], but volatilisation of ammonium nitrate from the collected aerosol during the 24-hour samplings may also have played a role. What could in principle also contribute to a relatively more pronounced coarse mode in summer is that there could be more primary coarse organic matter (OM) from the vegetation, but the data for OM from the filter samples did not seem to confirm this hypothesis.
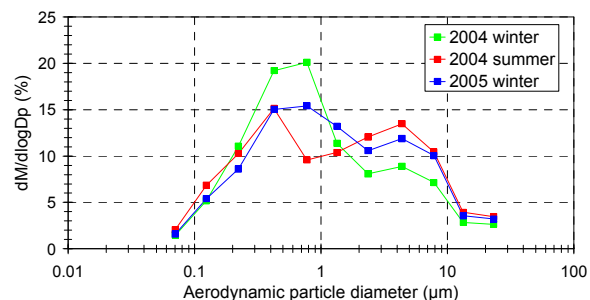

FIGURE 1. Average size distributions for the particulate mass in the three campaigns.

Mass Size Distributions For The Elements

The crustal elements (Al, Si, Ca, Ti, Fe) showed essentially a monomodal size distributions (with peak at 3.3 µm) in all campaigns. In Helsinki [1] and Budapest [2], these elements had also mainly monomodal distributions, but in addition to the major coarse mode, a minor intermediate mode was observed at the urban site in Helsinki and at the Budapest kerbside. Furthermore, the major coarse mode peaked at a larger diameter (around 8 µm) at the kerbside, because the crustal component originated from nearby road dust. For Mn a minor fine mode with center at about 0.9 µm was clearly also present at Ghent, particularly in winter. This fine Mn mode is most likely attributable to anthropogenic sources, in particular those in the industrial area to the north of Ghent [11].

For several typical anthropogenic elements (e.g., S, V, Ni, Pb) or elements with an important anthropogenic contribution (K), two submicrometer modes and one coarse mode could be discerned. The two submicrometer modes peaked at 0.3 and 0.7 µm and the coarse mode at 3.3 µm. Two submicrometer submodes were observed earlier for particulate sulphate, ammonium, and nitrate [12-14] and were labelled as "condensation" and "droplet modes"; the formation of the "droplet" mode is explained by activation of condensation mode particles to form fog or cloud drops followed by aqueous-phase chemistry and fog or cloud evaporation [15, 16]. The upper submicrometer mode for S and possibly also for other water-soluble or hygroscopic elements most likely corresponds to the "droplet" mode of the earlier studies and has the same formation process. However, cloud or fog processing can hardly be invoked for the upper submicrometer mode of the metallic elements, as these elements are less water-soluble and the sources are most likely more local (versus more regional for S), so that there is insufficient time for such processing. Multiple modes in the submicrometer size range for the metallic elements have also been seen in previous studies [e.g., 2, 17, 18]. The lower of our two submicrometer modes for the metallic elements is likely mainly due to condensation processes (as is also the case for S), whereas the upper probably originates from a variety of high-temperature dispersion and abrasion processes.

The relative intensities of the lower and upper submicrometer modes for S were quite different in winter and summer (see Fig. 2). Whereas in summer the lower one of the two was somewhat more pronounced, in winter the upper one was clearly more intense, suggesting more cloud or fog processing for this element in this season. Another feature in Fig. 2 is that the S coarse mode, although it is much weaker than the submicrometer modes, is more intense for the 2005 winter campaign than in the other two campaigns. This is due to the higher contribution from sea salt in that campaign, as was deduced from the analysis of the SFU and other filter samples.
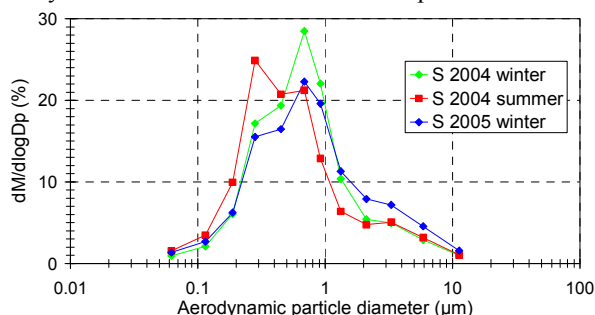

FIGURE 2. Average mass size distributions for S in the three campaigns.

For V and Ni, which are attributable to residual oil burning, the lower submicrometer mode was by far the major mode in both seasons (see Fig. 3). K, which has contributions from crustal material, sea salt, biomass burning, and municipal incinerators, exhibited two modes in the submicrometer size range and one in the coarse size range, but the relative intensities of the three modes were quite different between winter and summer. Whereas during summer most of the K mass was in the coarse mode, during winter, the lower submicrometer mode was the major mode, followed by the upper submicrometer mode. The large contribution of fine K during winter is attributed to biomass (wood) burning. In an earlier study, it was found that biomass burning can be quite important at Ghent during winter [19].
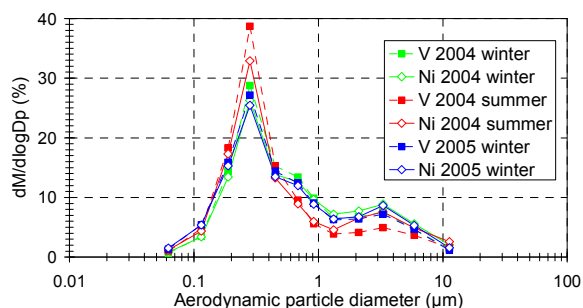

FIGURE 3. Average mass size distributions for V and Ni in the three campaigns.

Figs. 4 and 5 show the average size distributions for 6 mostly anthropogenic elements in the 2004 winter and summer campaigns. The distributions for the 2005 winter campaign were quite similar to those for the 2004 winter. The 6 elements have a trimodal size distribution, with most a their mass in the two submicrometer modes, but there are clearly differences in the relative intensities of these two modes between the various elements and for some of the elements also
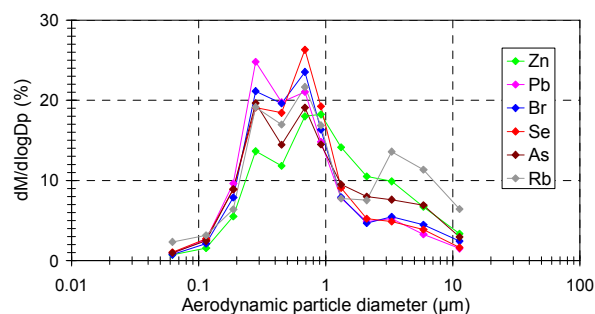
FIGURE 3. Average mass size distributions for 6 mostly anthropogenic elements in 2004 winter.
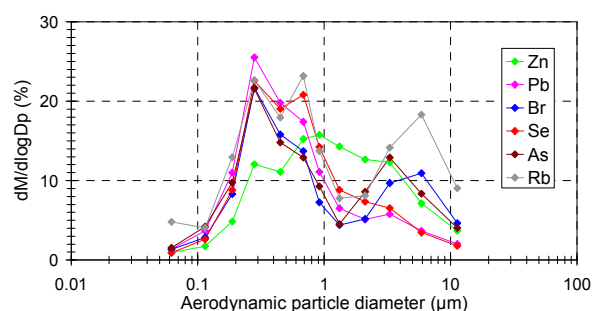

FIGURE 4. Average mass size distributions for 6 mostly anthropogenic elements in 2004 summer.

between the two seasons. Furthermore, for Zn, the upper submicrometer mode peaks at a clearly higher diameter (i.e., at 0.9 µm) than is the case for the other elements. The variability in mode diameters and relative intensities points to differences in sources and source processes for the anthropogenic elements. For 4 of the elements (i.e., Pb, Br, Se, and As), the upper submicrometer mode is relatively more pronounced in winter, as was also the case for S, and similarly as for S, more extensive cloud and fog processing in winter may be responsible for the more intense upper mode in winter. The 4 elements are water-soluble and some (i.e., Se and As) may to a large extent originate from the same major sources as S (i.e., fossil fuel combustion) and/or be present in the same sulphate particles. For Rb, which is chemically similar to K and has the same sources (including biomass burning), the difference between the winter and summer size distributions follows the same trend as for K, with the coarse mode becoming more intense in summer than in winter. As to the peculiar size distribution for Zn, this was in the submicrometer size range fairly similar to that for Mn, which could suggest similarity in the sources or source processes for Zn and noncrustal Mn, although this is actually rather unlikely. Also in Budapest [2], there was a clear difference between the size distributions of Zn and the other anthropogenic elements and also there, the upper submicrometer

mode peaked at 0.9 µm versus around 0.7 µm for the other anthropogenic elements. Most of the Zn was in the coarse mode in Budapest, though, and this Zn was attributed to mechanical wear of automobile tires. It is quite possible that such wear is also responsible for a substantial fraction of the coarse mode Zn in Ghent.

ACKNOWLEDGMENTS

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