



10th International Conference on
Particle Induced X-ray Emission and its Analytical Applications
PIXE 2004, Portorož, Slovenia, June 4-8, 2004
<http://pixe2004.ijs.si/>

Chemical Composition And Mass Closure For Fine And Coarse Aerosols At A Kerbside In Budapest, Hungary, In Spring 2002

Willy Maenhaut, Nico Raes, Xuguang Chi, Jan Cafmeyer, Wan Wang

Institute for Nuclear Sciences, Ghent University, Proeftuinstraat 86, B-9000 Gent, Belgium

Imre Salma

*Eötvös University, Department of Chemical Technology and Environmental Chemistry,
H-1518 Budapest, P.O. Box 32, Hungary*

ABSTRACT

A comprehensive chemical aerosol characterisation was carried out at a kerbside in downtown Budapest in spring 2002. Several filter samplers were deployed in parallel for day and night collections, and a total of 23 parallel collections were made. All samples were analysed for the particulate mass (PM) by weighing. Depending upon the sampler type and/or collection substrate, further analyses were done for up to 46 elements by a combination of PIXE and instrumental neutron activation analysis (INAA), for major anions and cations by ion chromatography, and for organic carbon and elemental carbon by a thermal-optical transmission technique. Aerosol chemical mass closure calculations were done for the separate fine (<2 µm) and coarse (2-10 µm) size fractions. For reconstituting the gravimetric PM, eight aerosol types were considered, whereby three aerosol types were deduced from the PIXE/INAA elemental data set. Organic matter (OM) and elemental carbon were the dominant aerosol types in the fine fraction; they explained on average 43 and 21% of the fine PM. The coarse PM consisted mainly of crustal matter (49%) and of OM (30%). The large contribution from crustal matter (road dust) to the coarse fraction is consistent with other data from kerbside sites in Europe.

Keywords: atmospheric aerosols, aerosol composition, chemical mass closure, kerbside, Budapest.

Corresponding author: W. Maenhaut, Institute for Nuclear Sciences, Ghent University, Proeftuinstraat 86, B-9000 Gent, Belgium; E-mail: Willy.Maenhaut@UGent.be

1. INTRODUCTION

Chemical analysis of atmospheric aerosols is needed to assess their effects on human health and climate and to get information that can be used for identifying the aerosol sources and for developing mitigation strategies. It is important to measure the major aerosol components and to examine to which extent the particulate mass (PM) can be explained by the measured components and thus aerosol chemical mass closure can be achieved. The aerosol components that are normally measured in mass closure studies are organic matter, elemental carbon, sulphate, nitrate, ammonium, crustal material, and sea salt. In this work we present results from a chemical aerosol characterisation and mass closure study at a kerbside in Budapest, Hungary, in spring 2002. The study is a follow-up and complement to our earlier investigations of the chemical composition of size-fractionated aerosols at various sites in Budapest [1, 2]. A detailed discussion of the carbonaceous aerosol data for the current study has been presented elsewhere [3].

2. EXPERIMENTAL

The aerosol collections and measurements at the kerbside in Budapest took place at 5, Rákoczi Street, in the downtown. The equipment was installed on the first-floor balcony at a height of about 7.5 m above the street level. The street can be characterised by width, height and length parameters of 30, 25-30 and 600 m, respectively. Several filter samplers were deployed at the site. They included (1) a PM_{2.5} filter holder with two pre-fired Whatman QM-A quartz fibre filters in series [PM_{2.5}(Q)], (2) a PM₁₀ filter holder, also with two pre-fired Whatman QM-A filters [PM₁₀(Q)], (3) a Gent PM₁₀ stacked filter unit (SFU) sampler, with coarse and fine Nuclepore polycarbonate filters (pore sizes: 8 µm and 0.4 µm, respectively) in series [PM₁₀(NN)], and (4) a second Gent PM₁₀ SFU sampler, with a coarse Nuclepore polycarbonate filter and a fine Pall Teflo filter (pore size 2 µm) [PM₁₀(NT)]. All filters had a diameter of

47 mm, and the four samplers operated at a flow rate of 17 L per min. The cut point (d_{50} -value) between the coarse and fine size fractions in the SFU sampler was 2 μm aerodynamic diameter (AD). The purpose of the second quartz fibre filter in the PM_{2.5}(Q) and PM₁₀(Q) filter holders was to assess artifacts (i.e., losses of semi-volatile compounds and/or adsorption of volatile organic compounds (VOCs)) in the collection of carbonaceous aerosols [4]. The campaign started in the evening of 23 April 2002 and lasted until the morning of 5 May. Separate day and night collections were done with the four filter samplers, starting at 7 am and 7:30 pm local time, respectively, and a total of 23 parallel collections were done.

The particulate mass (PM) was obtained from weighing each filter before and after sampling with a microbalance. All quartz filters were analysed for organic carbon (OC) and elemental carbon (EC) by a thermal-optical transmission (TOT) technique [5]. The coarse and fine Nuclepore filters from PM₁₀(NN) were subjected to particle-induced X-ray emission spectrometry (PIXE) and instrumental neutron activation analysis (INAA) [6, 7]. The combination of these two techniques provided concentration data for up to 46 elements (from Na to Th). The filters from PM₁₀(NT) were analysed for major anions and cations by ion chromatography (IC) [8].

3. RESULTS AND DISCUSSION

3.1 Concentrations and artifacts, and fine to PM₁₀ ratios

From the weights of the second quartz fibre filters in the PM_{2.5}(Q) and PM₁₀(Q) samplers, it was attempted to assess the extent of the artifacts for PM. However, the precision of the net weights was too low (30 μg) to conclude anything. The artifacts for OC and EC were assessed from the TOT analyses for these same samplers. The average ratio (2nd filter)/(1st filter) and associated standard deviation for OC were 0.15 ± 0.02 and 0.10 ± 0.02 for PM_{2.5}(Q) and PM₁₀(Q), respectively. EC was insignificant on the 2nd filter. The OC on the 2nd quartz fibre filter was assumed to be mainly due to adsorption of volatile organic compounds (VOCs) (positive artifact), and it was subtracted from the OC on the 1st filter in order to arrive at artifact-free particulate OC data. Median concentrations of the PM₁₀ mass concentration for several aerosol species and 18 elements (all elements with median > 10 ng/m^3) are given in Table 1. The PM₁₀ aerosol mass concentrations are higher for PM₁₀(Q) than for PM₁₀(NN). The mean Q/NN ratio is 1.10 ± 0.16 . That PM data from quartz fibre filters are higher than those from Nuclepore (or Teflon) filters is normally found in our studies [e.g., 8] and is mainly attributed to the adsorption of gaseous compounds by the quartz fibre filters.

On the basis of the available data, average fine (PM₂ or PM_{2.5}) to PM₁₀ ratios were calculated for the PM, OC, EC, ammonium, nitrate, sulphate, and the various elements. The average fine/PM₁₀ ratios and associated standard deviations for PM were 0.53 ± 0.14 for PM_{2.5}(Q)/PM₁₀(Q) and 0.38 ± 0.11 for PM₂(NN)/PM₁₀(NN). Low fine/PM₁₀ ratios for PM were found during polluted time periods, when resuspension of local coarse street dust was important. OC, EC, ammonium, sulphate (and S) were mainly present in the fine size fraction. In contrast, the crustal (Al, Si, Ca, Ti, Mn, Fe) and other (Na, Mg, P, Cl) elements were predominantly associated with the coarse size fraction.

Table 1. Median concentrations (in ng/m^3) in the PM₁₀ size fraction at the Rákoczi street site, Budapest, in the period 23 April – 5 May 2002. Ions were obtained from PM₁₀(NT), elements from PM₁₀(NN).

Species	Median	Species	Median	Species	Median
PM (NN)	48000	Al	1060	Fe	1930
PM (Q)	54000	Si	2600	Cu	61
OC (Q)	10600	P	66	Zn	84
EC (Q)	3400	S	1660	Br	10.3
Ammonium	1050	Cl	193	Sb	16.6
Nitrate	2400	K	420	Ba	52
Sulphate	4000	Ca	2600	Pb	24
Na	450	Ti	72		
Mg	480	Mn	30		

3.2 Chemical mass closure

Aerosol chemical mass closure calculations were done for the separate fine (PM₂) and coarse (2-10 µm AD) size fractions, and this for each of the 23 parallel samplings. As gravimetric PM data we used the values from the PM₁₀(NN) collections. For reconstituting this gravimetric PM, eight aerosol types (or components) were considered: (1) organic aerosol, which was estimated by multiplying the corrected OC by a factor of 1.4 [4]; (2) EC; (3) ammonium; (4) nitrate; (5) sulphate; (6) sea salt; (7) crustal matter; and (8) other elements. The OC and EC data were obtained from the PM_{2.5}(Q) and PM₁₀(Q) samplers, thereby applying a minor correction for converting from the PM_{2.5} to PM₂ size range. Ammonium, nitrate, and sulphate were obtained from the IC analyses of the PM₁₀(NT) samples. The last three aerosol types (components) were derived from the INAA and PIXE results for the PM₁₀(NN) samples, as described elsewhere [8]. The average percentage attributions of the gravimetric PM to each of the 8 aerosol types (components) are given in Table 2. The sums (in percent) of all included components are 104% and 94% for the fine and coarse size fractions. Considering the uncertainties in estimating some of the components, especially organic matter (the multiplication factor of 1.4 for OC), the difference from 100% is probably not significant. It should also be noted that water was not included, except for that associated with crustal matter. Organic matter (with 43%) and EC (21%) are the major components in the fine size fraction, while crustal matter (49%) and organic matter (30%) are the dominant components in the coarse size fraction. The large contribution from crustal matter (road dust) to the coarse size fraction is consistent with other data from kerbside sites [9].

Table 2. Average percentage attribution of the gravimetric aerosol mass (PM) to 8 aerosol types (components) for the fine and coarse size ranges (based on 23 samplings).

	Size fraction <2 µm AD	Size fraction 2-10 µm AD
Organic matter	43 ± 10	30 ± 6
Elemental carbon	21 ± 11	1.7 ± 0.8
Ammonium	5.7 ± 3.0	0.8 ± 0.6
Nitrate	5.8 ± 3.2	4.7 ± 2.0
Sulphate	13 ± 6	4.4 ± 2.0
Sea salt	0.9 ± 0.6	2.4 ± 1.3
Crustal matter	14 ± 4	49 ± 5
Other elements	0.5 ± 0.2	0.6 ± 0.3
Sum	104 ± 15	94 ± 8

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support from the Belgian Federal Science Policy Office, the FWO-Vlaanderen, the Special Research Fund of Ghent University, and the Ministry of Education, Hungary. We are also indebted to S. Dunphy for technical assistance.

REFERENCES

1. Salma, I., Maenhaut, W., Zemplén-Papp, É., and Zárny, G., *Atmos. Environ.* 35, 4367-4378 (2001).
2. Salma, I., Maenhaut, W., and Zárny, G., *J. Aerosol Sci.* 33, 339-356 (2002).
3. Salma, I., Chi, X., and Maenhaut, W., *Atmos. Environ.* 38, 27-36 (2004).
4. Turpin, B. J., Saxena, P., and Andrews, E., *Atmos. Environ.* 34, 2983-3013 (2000).
5. Birch, M. E., and Cary, R. A., *Aerosol Sci. Technol.* 25, 221-241 (1996).
6. Maenhaut, W., Salma, I., Cafmeyer, J., Annegarn, H. J., and Andreae, M. O., *J. Geophys. Res.* 101, 23631-23650 (1996).
7. Maenhaut, W., and Cafmeyer, J., *X-Ray Spectrom.* 27, 236-246 (1998).
8. Maenhaut, W., Schwarz, J., Cafmeyer, J., and Chi, X., *Nucl. Instr. and Meth.* B189, 233-237 (2002).
9. Putaud, J.-P., et al., *Atmos. Environ.* 38, 2579-2595 (2004).