

Chemical Composition And Mass Closure for PM_{2.5} And PM₁₀ Aerosols At K-pusztá, Hungary, in Summer 2006

W. Maenhaut, N. Raes, X. Chi, J. Cafmeyer and W. Wang

*Department of Analytical Chemistry, Institute for Nuclear Sciences, Ghent University,
Proeftuinstraat 86, B-9000 Gent, Belgium*

Abstract. A comprehensive chemical aerosol characterisation was carried out at the K-pusztá Supersite in Hungary from 24 May until 29 June 2006. Up to 11 June it was unusually cold at the site, but from 12 June onward it was warm. PM_{2.5} and PM₁₀ samplers with Nuclepore polycarbonate filters and quartz fibre filters were deployed in parallel for mostly day and night collections, and a total of 68 parallel collections were made. All samples were analysed for the particulate mass (PM) by weighing. The Nuclepore polycarbonate filters were analysed for up to 29 elements by PIXE and for major anions and cations by ion chromatography. The quartz fibre filters were analysed for organic and elemental carbon by a thermal-optical transmission technique. The atmospheric concentrations of the PM and most species and elements, in particular the crustal elements, were higher during the warm period than during the cold one. Aerosol chemical mass closure calculations were done for the PM_{2.5} and PM₁₀ aerosol. As gravimetric PM data we used the data from the Nuclepore polycarbonate filters. For reconstituting this PM, eight aerosol types (or components) were considered, whereby two aerosol types (including the important crustal matter component) were deduced from the PIXE data. Organic matter contributed by far the most to the PM_{2.5} and PM₁₀ PM; it was responsible for 40-50% of the average PM during both the cold and warm periods. Noteworthy were the much larger percentages of crustal matter during the warm period than during the cold one (both for PM_{2.5} and PM₁₀). In the PM_{2.5} aerosol, crustal matter accounted for 17% of the average PM during the warm period, but only for 3.1% during the cold period. For the PM₁₀ aerosol, the percentages were 28% in the warm period and 10% in the cold one.

Keywords: atmospheric aerosols, chemical composition, chemical mass closure, supersite, Hungary.

INTRODUCTION

Within the EU-funded project European Supersites for Atmospheric Aerosol Research (EUSAAR; <http://www.eusaar.net/>), 20 high-quality ground-based stations are available. The stations were identified based on the high level of implemented instrumentation for the study of atmospheric aerosols (chemical, physical, and optical properties) and on their atmospheric probing capacity in an identified environment. One of the 20 stations is that of K-pusztá in Hungary. This station is situated in a mixed coniferous/deciduous forest and is a good site for studying the formation and characteristics of biogenic secondary organic aerosol (SOA) that is formed from biogenic volatile organic compounds (BVOCs), such as isoprene and monoterpenes, that are emitted by the forest [e.g., 1]. It was therefore selected as a field study site for a 2006 summer campaign within the Belgian-funded project "Formation mechanisms,

marker compounds, and source apportionment for biogenic atmospheric aerosols" (BIOSOL). Although the emphasis in the campaign was thus on the organic aerosol, and in particular on biogenic SOA, it was felt that a complete chemical aerosol characterisation (including measurement of inorganic compounds, elements, and aerosol types) was also needed in order to be able to interpret the organic aerosol data. This paper focuses on the elemental composition of the aerosol and on the aerosol chemical mass closure. A similar study as presented here was performed at the same site during a 2003 summer campaign [2]. Therefore, the results of the 2006 campaign are compared with those from that earlier campaign.

EXPERIMENTAL

The K-pusztá station is located at 46°58'N, 19°35'E, at 136 m above sea level. It is about 15 km to the NW of the town of Kecskemét and about 80 km SE of

Budapest. Besides being an EUSAAR station, the K-pusztá station is also involved in the Global Atmospheric Watch (GAW) network and in the European Monitoring and Evaluation Programme (EMEP). The 2006 summer campaign at the station took place from 24 May until 29 June 2006. Whereas it was very hot and dry during the entire duration of the 2003 campaign, during the 2006 campaign there was substantial variation in weather conditions. From the start of the campaign until 11 June, it was unusually cold with daily maximum temperatures between 12 and 23°C, but from 12 June onward higher temperatures were noted with daily maxima from 24 to 36°C.

Several filter samplers were deployed in parallel, typically for separate day and night collections, and a total of 68 parallel collections were made. Among the samplers were two PM_{2.5} samplers (one [PM_{2.5}N] with a 0.4- μ m pore size Nuclepore polycarbonate filter, the other [PM_{2.5}Q] with two pre-fired Whatman QM-A quartz fibre filters in series) and two PM₁₀ samplers ([PM₁₀N] and [PM_{2.5}Q] with the same filter types as the PM_{2.5} samplers). All filters had a diameter of 47 mm, and the four samplers operated at a flow rate of 17 L per min. The purpose of the second quartz fibre filter was to assess artifacts (i.e., adsorption of volatile organic compounds and losses of semi-volatile organic compounds) in the collection of carbonaceous aerosols [3, 4].

The particulate mass (PM) was obtained from weighing each filter before and after sampling with a

microbalance. The weighings were done at 20°C and 50% relative humidity and the filters were pre-equilibrated at these conditions for at least 24 hours. All quartz fibre filters were analysed for organic carbon (OC) and elemental carbon (EC) by a thermal-optical transmission (TOT) technique. The Nuclepore filters were analysed for 29 elements (from Na to Pb) by particle-induced X-ray emission spectrometry (PIXE), and for major anions and cations by ion chromatography (IC). Details upon the various techniques used can be found in [5] and in the references therein. Particulate OC data were obtained as the difference between the OC on the front and back quartz fibre filters [6].

RESULTS AND DISCUSSION

Concentrations And PM_{2.5} To PM₁₀ Ratios

The concentrations of the PM and most species and elements followed the ambient temperature, with higher levels during the warm period. This is illustrated in Figure 1, which shows the medians (and interquartile ranges) of the PM₁₀ mass concentration for the PM, several aerosol species, and 15 elements in the separate cold (24 May – 11 June) and warm (12 – 29 June) periods.

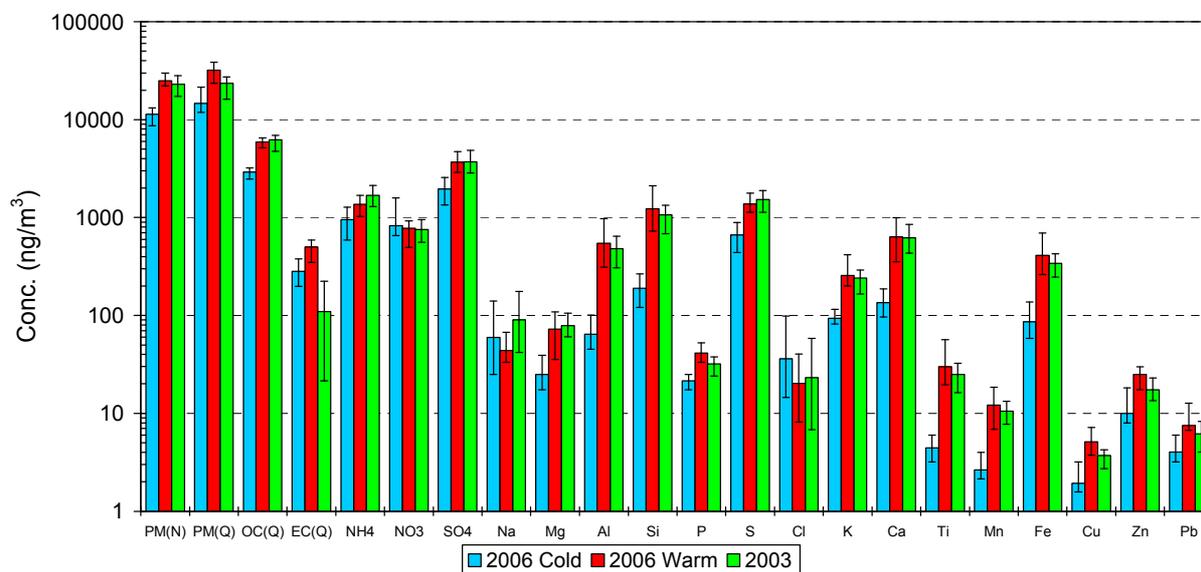


FIGURE 1. Medians (and interquartile ranges, denoted by the error bars) of the PM₁₀ mass concentration for the PM, several aerosol species, and 15 elements in the separate cold (24 May – 11 June) and warm (12 – 29 June) periods of the 2006 campaign at K-pusztá, Hungary and for the overall 2003 summer campaign at the same site. The data for Na, Mg, and Cl were obtained from IC, these for the other 12 elements from PIXE.

The higher levels for OC during the warm period are likely a consequence of both higher emissions of primary organic matter by the vegetation and of biogenic SOA precursors, such as isoprene and monoterpenes, at higher temperature. The increase from the cold to the warm period is especially pronounced for the crustal elements (i.e., Al, Si, Ca, Ti, Mn, Fe); the increase in their medians is about a factor of 5. This points to much more intense soil dust mobilisation during the warm period on the local and regional scale, probably because of the combination of a drier soil and increased agricultural activities. Of the species depicted in Figure 1, only nitrate, Na, and Cl exhibit lower levels in the warm period. The lower levels for nitrate are attributed to transfer of nitrate from the particulate to the vapour phase at elevated temperature, but volatilisation of nitrate from the aerosol collected on the filter may also play a role. For the sea-salt elements Na and Cl, changes in air mass origin are likely responsible. Figure 1 also shows overall medians (and interquartile ranges) for the 2003 summer campaign at the same site [2]. Overall, the atmospheric concentrations during that hot and dry 2003 campaign are similar or very similar to those observed during the warm period of the 2006 campaign. The major exceptions are EC, which had substantially lower levels in 2003, and Na, which showed higher levels then.

The PM and most species and elements were predominantly present in the PM_{2.5} size fraction of the PM₁₀ aerosol. For example, the average ratio PM_{2.5}N/PM₁₀N for the PM (average over all samples) was 0.67±0.08, and there was no difference in this ratio between the cold and warm periods. Of all

species and elements depicted in Figure 1, only the crustal elements (Al, Si, Ca, Ti, Mn, Fe) and Mg, P, and Cl had average PM_{2.5}/PM₁₀ ratios of less than 0.5 (for most of these elements: around 0.3-0.4).

Aerosol Chemical Mass Closure

Aerosol chemical mass closure calculations were done for the PM_{2.5} and PM₁₀ aerosol, and also for the coarse (PM_{10-2.5}) size fraction, and this for each individual sampling. As gravimetric PM data we used the data from the Nuclepore polycarbonate filters. For reconstituting this PM, eight aerosol types (or components) were considered, i.e., (1) organic aerosol (or organic matter, OM), which was estimated as 1.8 OC; (2) EC; (3) ammonium; (4) nitrate; (5) non-sea-salt (nss) sulphate; (6) sea salt, estimated as Cl + 1.4486 Na, whereby 1.4486 is the ratio of the concentration of all elements except Cl in sea water to the Na concentration in sea water (with Na and Cl obtained from IC); (7) crustal matter, derived from 5 elements measured by PIXE (i.e., Al, Si, Ca, Ti, and Fe); and (8) elements, which is the sum of the mass of all non-crustal/non-sea-salt elements measured by PIXE (S and K were excluded from this sum) [5]. The average concentrations of the various aerosol types (and of the unexplained gravimetric PM) are shown in Figure 2, and this separately for the PM_{2.5} and PM₁₀ aerosol and for the cold and warm periods. For 6 of the 8 components, higher average levels are observed in the warm period than in the cold one. The two exceptions are nitrate and sea salt. The reasons for this have been indicated above.

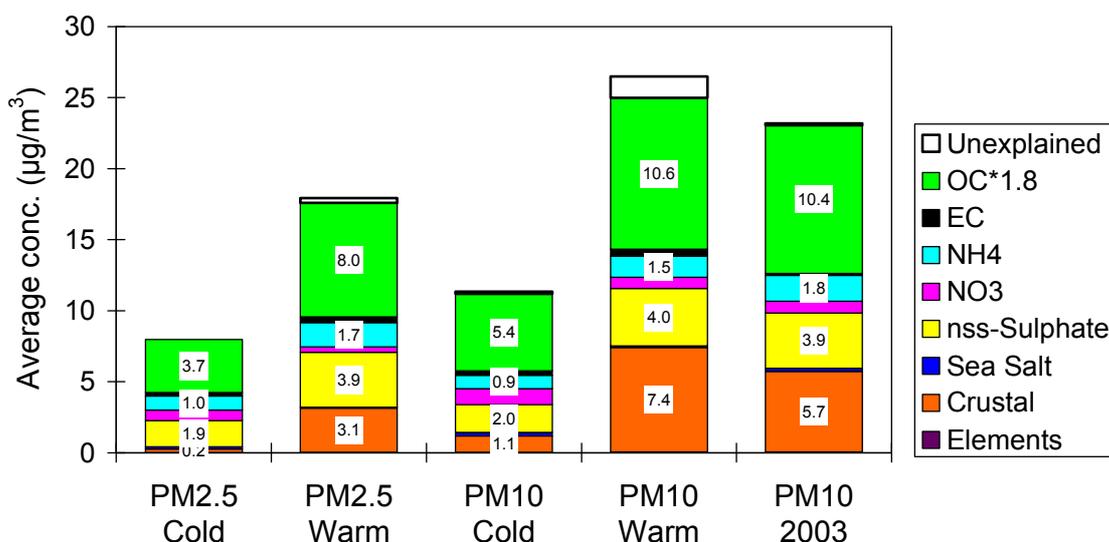


FIGURE 2. Average concentrations of 8 aerosol types during the 2006 summer campaign at K-pusztá, and this separately for the PM_{2.5} and PM₁₀ aerosol and for the cold and warm periods. The data for the PM₁₀ aerosol during the 2003 summer campaign at the same site are also shown.

The data for PM10 during the 2003 campaign are also shown in Figure 2. As was the case with the individual species and element concentrations, the data for most of the aerosol types in PM10 are quite similar for the overall 2003 campaign and the warm period of the 2006 campaign.

The percentage contributions of the various components to the average gravimetric PM were also calculated and are given in Table 1, together with the attribution of the average PM10 PM of the 2003 campaign to the same components. The sum of the 8 components is in all cases close to 100%, indicating that excellent mass closure was obtained. It should be indicated here that water is not included in our mass closure, except for that associated with crustal matter. The excellent mass closure also indicates that the OC-to-OM conversion factor of 1.8 used here is appropriate. In a 2001 review of such conversion

factors, Turpin and Lim [7] indicated that these factors are 1.6 ± 0.2 for urban PM2.5 aerosols and 2.1 ± 0.2 for nonurban aerosols, but they also recommended more measurements on this topic. The OM component contributed by far the most to the PM2.5 and PM10 PM; it was responsible for 40-50% of the average PM during both the cold and warm periods and also in the 2003 campaign. Noteworthy are the much larger percentages of crustal matter during the warm period than during the cold one (both for the PM2.5 and PM10 aerosol). In the PM2.5 aerosol, crustal matter accounted for 17% of the average PM during the warm period, but only for 3.1% during the cold period. For the PM10 aerosol, the percentages were 28% in the warm period and 10% in the cold one. The 25% for crustal matter in the 2003 campaign is quite similar to the 28% for the same component during the dry period of the 2006 campaign.

TABLE 1. Percentage attribution of the mean gravimetric PM to 8 aerosol types (components).

Component	PM2.5	PM2.5	PM10	PM10	PM10
	2006 summer, cold period	2006 summer, warm period	2006 summer, cold period	2006 summer, warm period	2003 summer campaign
Organic matter	49	45	48	40	45
Elemental carbon	3.3	2.3	2.7	1.8	0.6
Ammonium	13	9.5	8.3	5.6	7.9
Nitrate	9.9	2.1	10	3.0	3.5
nss-Sulphate	24	22	17	15	17
Sea salt	2.0	0.4	2.2	0.4	0.9
Crustal matter	3.1	17	10	28	25
Other elements	0.2	0.2	0.2	0.2	0.2
SUM	104	98	99	94	99

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support from the Belgian Federal Science Policy Office, the FWO-Vlaanderen, and the Special Research Fund of Ghent University. We are indebted to Prof. A. Gelencser and his team from the University of Pannonia (Veszprém) and to Prof. I. Salma from Eötvös University (Budapest) for assistance in the field campaign and for providing meteorological and atmospheric trace gas data. Thanks are also due to the BIOSOL partners and their teams from the Universities of Antwerp and of Helsinki. Furthermore, we are indebted to S. Dunphy for technical assistance.

REFERENCES

1. A. C. Ion, R. Vermeylen, I. Kourtchev, J. Cafmeyer, X. Chi, A. Gelencsér, W. Maenhaut and M. Claeys, *Atmos. Chem. Phys.* **5** (2005) 1805-1814.
2. W. Maenhaut, N. Raes, X. Chi, W. Wang, J. Cafmeyer, R. Ocskay and I. Salma, *J. Aerosol Sci.*, Abstracts of the European Aerosol Conference 2004 (2004) S799-S800.
3. B. J. Turpin, P. Saxena and E. Andrews, *Atmos. Environ.* **34** (2000) 2983-3013.

4. B. T. Mader, J. J. Schauer, J. H. Seinfeld, R. C. Flagan, J. Z. Yu, H. Yang, H. J. Lim, B. J. Turpin, J. T. Deminter, G. Heidemann, M. S. Bae, P. Quinn, T. Bates, D. J. Eatough, B. J. Huebert, T. Bertram and S. Howell, *Atmos. Environ.* **37** (2003) 1435-1449.
5. W. Maenhaut, N. Raes, X. Chi, J. Cafmeyer, W. Wang and I. Salma, *X-Ray Spectrom.* **34** (2005) 290-296.
6. M. Viana, X. Chi, W. Maenhaut, J. Cafmeyer, X. Querol, A. Alastuey, P. Mikuška and Z. Večera, *Aerosol Sci. Technol.* **40** (2006) 107-117.
7. B. J. Turpin and H. J. Lim, *Aerosol Sci. Technol.* **35** (2001) 602-610.