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Time and Size Resolved Elemental Component Study of Urban Aerosol in Debrecen, Hungary

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Abstract. With the use of accelerator based PIXE elemental analysis technique systematic investigation of aerosol samples have been performed in the Institute of Nuclear Research of the Hungarian Academy of Sciences for 15 years. In continuation of this research we observe the short-term time variation of the inorganic elemental components and the elemental mass size distributions in spring, 2007, at the end of the heating season. Aerosol sampling campaigns were carried out with a PIXE International continuous streaker sampler (PM_{10}) and a 9 stage PI cascade impactor in a downtown site of Debrecen. Meteorological data were recorded simultaneously with aerosol sampling. Another campaign was carried out with 2-stage nuclepore samplers ($PM_{2.5}$ and $PM_{2.5-10}$) in the same downtown and an outskirt site of the city.

The short-time variation of urban aerosol combined with meteorological data and with mass size distribution serves as a basis to reach a better understanding of the aerosol sources and receptor areas, to select single episodes, to follow the evolution of aerosol, and to make a better estimate on the health impact.

Keywords: Urban aerosol, inorganic elemental component, mass size distribution, hourly elemental concentration

INTRODUCTION

Debrecen is the second largest city of Hungary, situated in the Great Hungarian Plane surrounded by agricultural areas with increasing traffic and industry. The city of Debrecen situated in the meeting point of 3 different climate zones: the moist midlatitude, the dry midlatitude and the alpine [1]. The effect of the mediterranean zone was also detected through Saharan dust episodes [2]. In addition the borderline between the sand and loess soil types crosses the city almost in the middle in N-S direction. Due to its unique location, it is an ideal place for observing transport processes.

Although Debrecen has not a much stressed environment, with a population of about 200 000, air pollution presents significant health hazard. In order to evaluate the impact of aerosols on health, the knowledge of the particle size distribution, chemical composition and sources is needed.

With the use of accelerator based PIXE elemental analysis technique and statistical methods, systematic investigation of aerosol samples have been performed in the Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI) for 15 years determining the elemental composition, size distribution, seasonal and long term time variation, sources [3,4] and lung deposition probabilities of atmospheric aerosol characteristic to the east-Hungary region [5]. This study is based on the statistical evaluation of elemental concentration data measured on samples collected with 2-stage gent-type stacked filter units 2 times a week.

In the studies published in 1999 [3,4], four sources of the $PM_{10-2.5}$ course, and four sources of the fine $PM_{2.5}$ urban aerosol were identified: soil, traffic, oil and coal combustion and finally a mixed source of power generation and chemical industry.

Higher resolution in time and particle size would provide useful additional information for the source characterization and the estimation of the health impact. However, only a very limited amount of such data of the regional aerosol is available [6].

Therefore recently aerosol sampling campaigns have been started to determine the short term time variation and detailed size distribution of the Debrecen urban aerosol. In this paper the first results obtained from these campaigns are presented.

SAMPLING AND ANALYSIS

Aerosol Sampling

During the spring of 2007 several sampling campaigns were carried out. In the first campaign our intention was to make a comparison of the aerosol concentration in our usual sampling site (the garden of the Institute) situated in downtown and in an outskirt site near to the crossing of busy main roads. During a week time we collected coarse $PM_{10-2.5}$ ($2.5\mu m \leq d \geq 10\ \mu m$) and fine $PM_{2.5}$ ($d \leq 2.5\ \mu m$) samples every day from 9 am to 6 pm simultaneously on the two sites using Nuclepore 2-stage sampler units. The sampling was done 1.5 m above ground.

In the second campaign 48 hour samplings with a 9-stage PIXE International (PI) cascade impactor [7] were performed before, during and after the Easter holidays. From Easter Monday a continuous streaker sampler was also put to operation with which aerosol sampling was carried out in a period of 7 days. The sampling and the analysis provided a 2-h time resolution. The sampling location situated in the garden of our Institute, 4 m above ground, a few meters away from the regular aerosol sampling site.

The samples were collected on Nuclepore-Costar filters with 8μm and 0.4 μm pore diameter in the case of 2-stage sampling, and on kapton foil covered with paraffin in the case of impactor sampling. Although there is a possibility to use the streaker for bimodal sampling, our previous experiences showed, that using both stages results in not sufficient aerosol deposit. Therefore only the Nuclepore filter was used for PM10 sampling.

Parallel to the aerosol sampling meteorological parameters (temperature, humidity, air pressure, wind direction and wind strength) were recorded with a micrometeorological station in the downtown site.

Analysis

The PIXE analysis of the samples was carried out in the ATOMKI. A 2 MeV proton beam of the 5 MV VdG accelerator was used to irradiate the samples [8]. The accumulated charge on each sample was 40 μC.

The obtained X-ray spectra were evaluated with the PIXEKLM program package [9]. Concentrations of the following elements were determined: Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Co, Mn, Fe, Ni, Cu, Zn, Ba, Br and Pb. The detection limits (DL) of the elements in each sample are calculated with the concentration. The DL varies between 0.5 ng/m^3 and 20 ng/ m^3, depending on the element. In the case of samples collected with the 2-stage nuclepore sampler total mass was also determined by gravimetry on a Sartorius microbalance.

RESULTS AND DISCUSSION

As the previous studies of the Debrecen aerosol showed, one of the most interesting periods are the end and the beginning of the heating seasons. The heating season starts at 15th of October and ends at 15th of April. These are the dates when the district-heating is officially switched on/off. Therefore the sampling campaigns were timed to April, when the heating season finishes.

Comparison of Sampling Sites

Elemental concentration data as well as total particulate mass were determined on fine and course aerosol samples collected every day in a week's time in two different sampling sites of Debrecen. One site is situated in downtown, 1 km away from the city centre, the other is located in an outskirt area at the crossing of a new highway and a busy main road, 7 km from the centre.

As a representation of the results the concentration of Si in the coarse mode and the concentration of Zn in the fine mode is shown on figure 1. The tendency shown in the figure applies to all individual elemental concentration data too.

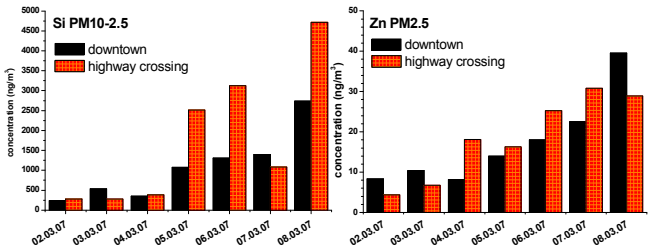

FIGURE 1. Sum concentration values of measured elements on fine and course aerosol samples collected in a downtown and an outskirt sampling sites, Debrecen, Hungary.

In the first 2 days of the sampling campaign, which was Friday and Saturday, every day 3 mm rain fell down. This explains the low aerosol concentration. From Monday there was a significant increase in the aerosol concentration.

In the case of elements of anthropogenic origin, like S, Cl, Cr, Ni, Cu, Zn and Pb, no differences were found in the concentration values either in the fine or in the coarse size fractions.

In the case of elements of predominantly soil origin - such as Al, Si, Ca, Ti, Fe, Ba - much higher concentrations were found in the outskirt site than in the downtown of Debrecen. The difference was higher in the coarse fraction. This difference can be

contributed to the much bigger traffic which passes nearby the sampling site.

The average aerosol mass concentrations obtained for the sampling sites and for weekend and weekdays are given in table 1.

Table 1. Average total mass concentrations on the two sampling sites for weekend and workdays (µg/m3)

	Weekend		working days	
	downtown	outskirt	downtown	outskirt
$PM_{10-2.5}$	13.4	5.3	18.5	25.7
$PM_{2.5}$	18.2	7.2	14.2	20.8

During the weekend much higher aerosol concentration was found in the downtown than in the outskirt site. In the case of working days the aerosol concentration was higher in the outskirt site.

Up to now we have data on aerosol concentrations only from working days, since the sampling can be solved easier then. These results show that more emphasis should be laid on the weekends too.

Size Distribution

Elemental mass size distributions were determined on samples collected with 9-stage PI cascade impactor, which separated the aerosol particles into 9 size fractions within the size range of 0.06 µm and 30 µm.

Basically two different kind of particles could be identified according to the size distribution. In the size distribution of Al, Si, Ca, Fe, Ba, Ti, Mn and Co one peak can be found around the 3µm aerodynamic diameter size range, as it is shown on Figure 2. These are the elements of predominantly natural origin.

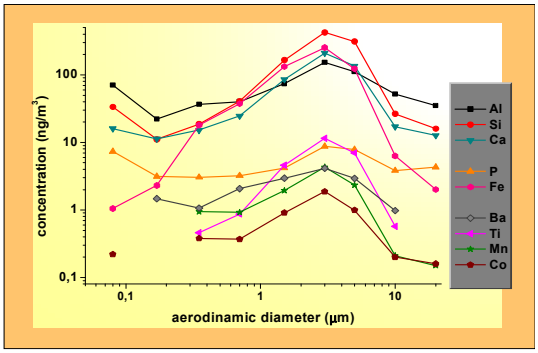

FIGURE 2. Mass size distribution of some elements measured on samples collected with a 9-stage PI cascade impactor on 7-8 April, 2007.

The size distribution of elements like S, Cl, K and Zn has a bimodial shape. One peak can be observed at 0.25-0.5 µm and an another at 2-4 µm size ranges, indicating different sources of these elements. However this second peak does not always exist, as is shown on Figure 3.

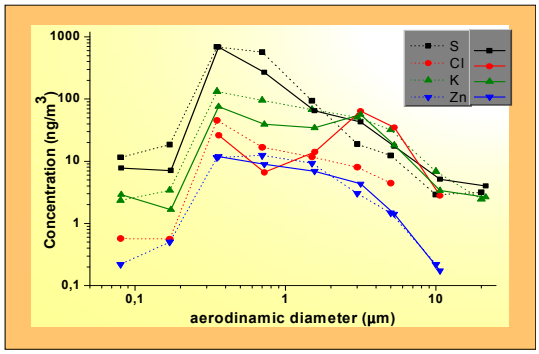

FIGURE 3. Mass size distribution of S, Cl, K and Zn measured on samples collected with a 9-stage PI cascade impactor. The dotted and continuous line corresponds to the samplings made on 4-5th and 7-8th April 2007, respectively.

Pb and Br could be found above DL in the 0.25-0.5 µm size range. Copper showed similar bimodial features on the 7-8th and 11-12th April sampling dates, with the difference that the peaks were shifted into the 0.12-0.25µm and the 8-16 µm size ranges, respectively. On 4-5th April the mass size distribution of Cu appeared to have a wide peak around 1µm, similar to the one can be observed in the case of Zn.

It can be also seen that concentration values are lower in the weekend than in the working days.

The obtained results are in good agreement with mass size distributions measured in other Hungarian and European cities [10-12]

Time Resolved Elemental Concentrations

Elemental concentration data with 2 hours time resolution were determined on samples collected with a PI streaker [7] in downtown Debrecen, between 9th and 14th of April, 2007. Unfortunately after a 5 days operation the membrane pump broke down, so we have no reliable data for the weekend. The meteorological data recorded paralelly showed, that this time period was a sunny, warm stable period with high air pressure. On Monday, 9th of April there was almost no wind. From 10th to 12th the ruling wind direction was S, S-W, whilst from 13th it changed to N.

Results obtained for S, Fe, Ca and Cl are shown on Figure 4.

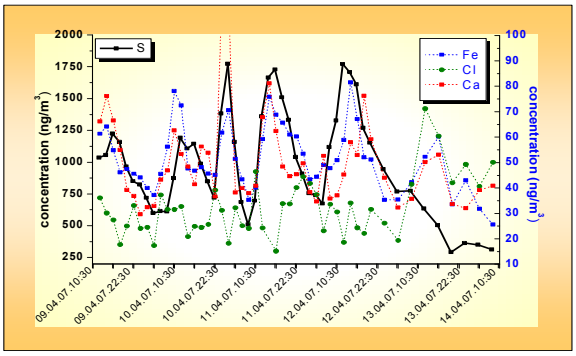

FIGURE 4. "Hourly" trends of PM10 S, Fe, Cl and Ca. Concentration scale on the left corresponds to S, on the right to the other elements.

In our previous studies [3,4] absolute principal component analysis gave four factors in the urban aerosol of Debrecen: soil (Al, Si, Ca, Fe, Ti), traffic (Cu, Zn, Pb), combustion of oil and coal (S, V) and an other enriched with Cl, presupposed as a mixed source of power generation and chemical industry.

In the time trend of Ca and Fe a periodicity can be observed with a higher peak in the morning and a lower in the evening, which fall together with traffic rush hours. The hourly evolution of these elements indicates their source as resuspended soil dust raised by traffic.

Although S has a similar pattern, its source supposed to be different. The change in the concentration correlated with the wind direction also indicates this. Further investigation based on more data and deeper statistical evaluation is needed to determine the source of S (which is supposed to be in the form of sulfate).

Up to now we have no explanation to the sharp peak appeared at the Ca, Fe and S concentration the night of 10th April. The shape of the peak suggests an industrial emission.

The change in Cl concentration with the change of the wind direction indicates its possible industrial origin.

In the case of K peaks appeared during evenings and nights, indicating that it originates from biomass burning for heating.

In the beginning of the sampling very high concentration of Si was measured, which decreased to one fifth when the wind blew from W. This strengthens the geological data that the borderline of loess and sand crosses the city in the N-S direction.

SUMMARY

In this paper we have investigated the mass size distribution and the short term time variation of the urban aerosol in the city of Debrecen, Hungary. Although the presented data are only preliminary results, it can be already seen, that such study gives a useful contribution to the ongoing atmospheric aerosol investigations carried out for 15 years in our PIXE Group. The elemental mass size distribution, with emphasis on the $PM_{2.5}$, serves as an input parameter for the determination of lung deposition probabilities by stochastic lung model calculation [13,14]. This calculation together with the short term time variation enables us to give a more precise estimation on the health impact of urban aerosol.

The higher resolution in time and particle size makes the source characterization more efficient and more accurate. It also allows the identification of long-range aerosol transport episodes [15].

The preliminary results already provided useful additional information. We'll continue this work, and complete with statistical analysis in order to integrate our knowledge about the nature of the regional aerosol.

ACKNOWLEDGEMENT

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