

## CHARACTERIZATION OF URBAN AEROSOL SOURCES IN DEBRECEN, HUNGARY

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### Abstract

Debrecen is an average middle European city from the point of view of aerosol pollution. Its location makes the city an ideal place for observing aerosol transport processes. Systematic investigation of atmospheric aerosol of the east-Hungarian region has been performed in the Institute of Nuclear Research of the Hungarian Academy of Sciences for 20 years by accelerator based elemental analytical technique. As a complementation of this research we observed the size distribution and short-term time variation of the elemental component of fine ( $PM_{2.5}$ ) and coarse ( $PM_{10}$ - $PM_{2.5}$ ) urban aerosol in the frame of sampling campaigns during 2007 and 2008 in a downtown site of Debrecen. Meteorological parameters were also recorded parallel to the aerosol sampling. Elemental concentrations ( $Z \geq 12$ ) were determined by particle induced X-ray emission (PIXE) analytical technique at the Laboratory of Ion Beam Applications (IBA) of the ATOMKI. On the obtained database six sources of the urban aerosol were identified: 2 types of soil, domestic heating, sulphate originating from long range transport processes, an unidentified source enriched with chlorine and traffic. Emission episodes were also observed. 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 in receptor areas, to select local emission and long range transport episodes, to follow the evolution of aerosol, and to make a better estimate on the health impact.

*Keywords:* urban aerosol, PIXE, elemental component, hourly variation, mass size distribution, aerosol sources

### 1. Introduction

Debrecen is the second largest city of Hungary, situated in the Great Hungarian Plane surrounded by agricultural areas without heavy industry. The city of Debrecen situated in the meeting point of 3 different climate zones: the moist midlatitude, the dry midlatitude and the alpine (Cartographia Világtalasz, 2001/2002, Peel et al. 2007). The effect of the mediterranean zone was also detected through Saharan dust episodes (Koltay et al. 2006). Thus, owing to its location, the city is an ideal place for observing long-range transport processes.

Although Debrecen has not a much stressed environment, with a population of about 200 000, due to the increasing traffic and industrial activity in the past 20 years, air pollution presents significant health hazard (Amann et al. 2005; air pollution maps on [www.idokep.hu/?oldal=legszeny](http://www.idokep.hu/?oldal=legszeny)). The level of  $PM_{2.5}$  aerosol pollution is on the European average, as we shown in our study (Dobos et al. 2007).

In order to evaluate the impact of aerosol particles on health, the knowledge of the particle size distribution, chemical composition, sources, and their change in time and space is needed.

In the Laboratory of Ion Beam Applications (IBA) of the ATOMKI systematic investigation of aerosol samples have been performed for 20 years. A continuously broadened data base has been created relating to the PM<sub>10</sub> (particles with aerodynamic diameter smaller than 10 µm), PM<sub>2.5</sub> (particles with aerodynamic diameter smaller than 2.5 µm) aerosol mass, black carbon content and main elemental components. On this basis the elemental composition, size distribution, seasonal and long term time variation, sources and lung deposition probabilities of atmospheric aerosol characteristic to the east-Hungary region is investigated (Borbély-Kiss I. et al. 1999a, 1999b). This study is based on the statistical evaluation of elemental concentration data measured on samples collected with a 2-stage Gent-type stacked filter unit 2 times a week.

Higher resolution in time and size would provide useful additional information for the source characterization and the estimation of health impact. However, only limited amount of such data of the regional aerosol is available (Kertész et al. 1999).

Therefore in 2007 aerosol sampling campaigns have been started to determine the short-term time variation and detailed size distribution of the Debrecen urban aerosol. We studied the changes in the elemental concentrations, their periodicity, correlation with other elements and meteorological parameters. Aerosol sources were determined by factor analysis. In this paper the results obtained from the first three campaigns are presented.

## 2. Methods

### 2.1. Sampling

Time resolved aerosol sampling was done with a two-stage sequential PIXE International streaker sampler (PIXE International Cooperation), which allows the study of the hourly evolution of atmospheric aerosol concentration. The sampling device collects the fine (PM<sub>2.5</sub>) and coarse (PM<sub>10</sub>-PM<sub>2.5</sub>) size fractions separately along a circle either continuously or sequentially. The coarse fraction was collected on a kapton foil coated with paraffin, while the fine fraction on a nuclepore polycarbonate filter with 0.3 µm pore diameter.

In order to determine the size distribution of urban aerosol samples were collected with a PIXE International cascade impactor. This device allows the separation of the aerosol particles in the 0.02-30 µm size range into the following ten size fractions: > 16, 16-8, 8-4, 4-2, 2-1, 1-0.5, 0.5-0.25, 0.25-0.12, 0.12-0.06 and < 0.06

$\mu\text{m}$  aerodynamic diameter. The samples were collected on paraffin coated kapton foils.

Sampling campaigns have been carried out since April, 2007 to study the hourly variation and size distribution of the Debrecen urban aerosol. The sampling location was in a downtown site, the garden of the ATOMKI, 50 m from our regular sampling site, 4 m above ground. The dates of the campaigns were the following: 9-16 April, 2007, 10-19 October, 2007 and 24-30 January, 2008. Most of the campaigns were timed around the beginning and end of heating season, since our previous experience showed that one of the most interesting dates are these periods from the point of view of urban aerosol studies.

Time-resolved samples were collected with 2 h time resolution, while sampling with cascade impactor lasted 48 hours. All sampling campaigns contained working days and weekends or holidays.

Parallel to the aerosol sampling local meteorological parameters (temperature, humidity, air pressure, wind direction, wind strength and rain) were recorded with a micrometeorological station installed on the roof of the highest building of the ATOMKI.

## 2.2. Analysis

The elemental composition of the samples was determined by particle induced X-ray emission (PIXE) analytical method. PIXE is based on the detection of characteristic X-rays induced by proton beam of 2-3 MeV energy. PIXE is a sensitive (0.1-100  $\mu\text{g/g}$  DL) multielemental analytical technique, which is widely used for the bulk analysis of atmospheric aerosol samples (Maenhaut and Malmquist, 2001).

The measurements were carried out at the PIXE chamber installed on the left 45° beamline of the 5 MV Van de Graaff accelerator of the IBA Lab. of the ATOMKI (Borbély-Kiss et al. 1985). The samples were irradiated with  $\text{H}^+$  beam of 2 MeV energy and of 35-40 nA current. The accumulated charge on each sample was 40  $\mu\text{C}$ .

The evaluation of the X-ray spectra was done with the PIXEKLM program code (Szabó and Borbély-Kiss, 1993). Concentrations of the following elements were determined: Al, Si, P, S, Cl, K, Ca, Ti, V, Sc, Co, Mn, Fe, Ni, Cu, Zn, As, Ba, Cd and Pb. The concentration values were given in  $\text{ng/m}^3$ . The detection limit varied between 0.5 and 20  $\text{ng/m}^3$  depending on the element, while the error of the determination of concentration was between 2 and 10%.

The statistical evaluation of the obtained data were carried out with the positive matrix factorisation model (Eberly, 2005) developed for aerosol source characterization by US EPA.

### 3. Results and discussion

#### 3.1. Mass size distribution

Size distribution is one of the basic properties of atmospheric aerosol. It is closely related to the origin, chemical composition and age of the aerosol particles, and it influences the optical properties, environmental effects and health impact of aerosol.

Mass size distribution of some elements measured in different seasons is shown on Fig. 1. Basically two different kinds 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 dominant peak can be found around the 3  $\mu\text{m}$  aerodynamic diameter size range. These are the elements of predominantly natural origin (Koltay, 2003, Borbély-Kiss et al. 1999a). Elements like S, Cl, K, Zn, Pb and Br appears with high frequency in the 0.25-0.5  $\mu\text{m}$  size range. These elements are originated mainly from anthropogenic sources.

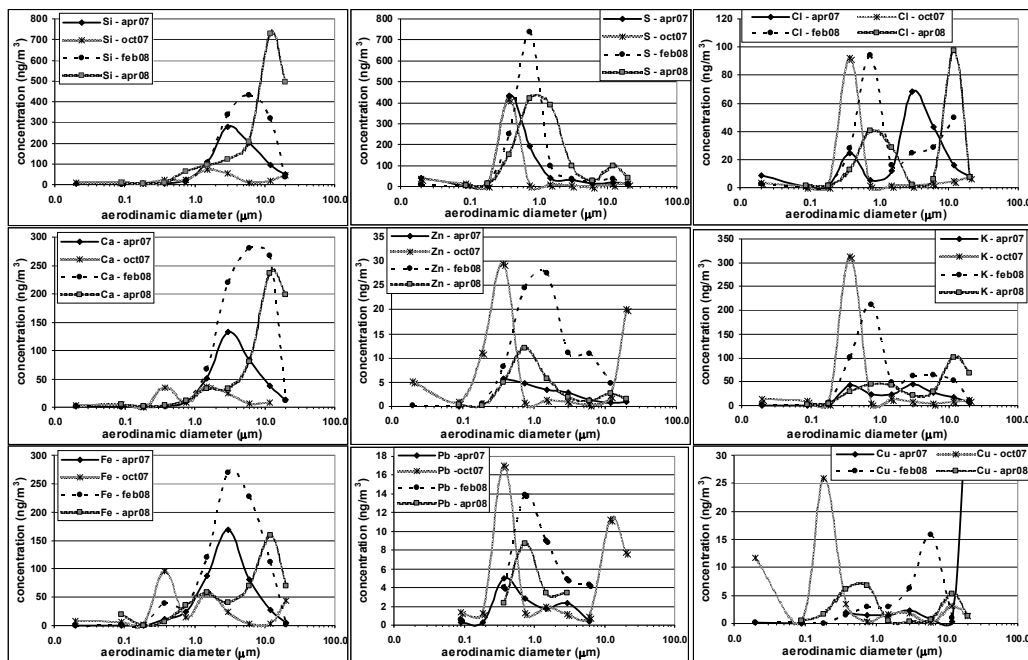


Fig. 1. Mass size distribution of some elements.

However the size distribution of some elements, e.g. K and Cl has a bimodal shape, indicating that these elements have at least two different sources. In the case of K the 0.25-0.5  $\mu\text{m}$  peak appears during winter (heating season), while in spring/summer the peak around 5  $\mu\text{m}$  is the dominant. K in the fine fraction

originates from biomass burning, thus K can be used as a tracer of domestic heating. K in the coarse fraction is of soil origin. S and Cu have also component of soil origin. Compounds of Pb, Zn, Cu and other anthropogenic elements can be found attached to mineral dust particles, which can explain their presence in the coarse mode. Cl appears more frequently in the fine fraction during winter and in the coarse fraction during summer. The possible sources of chlorine can be industry, agriculture, winter salting of streets, traffic, soil and seawater.

Differences were found between the size distribution of the spring and autumn/winter samples. In the case of elements of soil origin the size distribution was shifted towards smaller diameters in the autumn and winter samples and a second peak appeared around 0.5  $\mu\text{m}$ . A possible explanation to this phenomenon can be the different meteorological conditions (temperature, relative humidity). Elemental components of anthropogenic origin have higher concentration during winter, while in the case of natural (soil) origin it is the opposite: these components can be found in higher concentration during summer. This is in good agreement to our previous studies (Borbély-Kiss et al. 1999a, 1999b).

No differences were found between the weekend and working days in the size distribution, however the concentration values were smaller during the weekend than the other days.

The results obtained on the mass size distribution of the aerosol elemental components in Debrecen are in good agreement with the ones measured in other Hungarian or European cities (Horvath et al. 1996, Salma et al. 2002).

### *3.2. Time resolved elemental concentrations*

In order to get comparable data meteorologically similar periods were selected from weather forecast for the sampling campaigns to study the hourly evolution of urban aerosol in Debrecen. These periods were most of the time sunny, stable periods with high air pressure and no rain. Local meteorological data were recorded with a micrometeorological station, and the regional data was downloaded from the website of the Hungarian Meteorological Service ([www.met.hu](http://www.met.hu)).

In Table 1 average elemental concentrations measured in the coarse and fine size fraction, their standard deviation (SD), the enrichment factors calculated to the given element and detection limits are summarized for the samples collected during 10-19. October 2007. The concentration values were found to be similar to the ones measured in other European cities (Dobos et al. 2007).

Enrichment factor is a useful tool to identify soil derived and pollutant derived elements in the aerosol. It is the ratio of relative frequency of a certain element in

an aerosol sample to the relative frequency of the element in a natural source (e. g. Earth crust or seawater).

Table 1. Elemental concentration averages (and standard deviation), enrichment factors (EF) and detection limits (DL) obtained for samples collected by a bimodal streaker with 3 h time resolution between 10-19 October 2007.

	PM <sub>2,5</sub>		PM <sub>10</sub> -PM <sub>2,5</sub>		DL (ng/m <sup>3</sup> )
	conc. (SD) (ng/m <sup>3</sup> )	EF	conc. (SD) (ng/m <sup>3</sup> )	EF	
<b>Al</b>	73.5 (58.04)	0.67	57.9 (43.6)	0.46	16.3
<b>Si</b>	170.6 (207)	0.5	325.6 (168)	0.8	7.4
<b>P</b>	< DL		27.4 (5.5)	15	5.3
<b>S</b>	690.1 (380)	1966	41.1 (11.4)	103	4.05
<b>Cl</b>	11.5 (10.6)	65.3	31 (21.5)	155	3.4
<b>K</b>	211 (124)	6	44.7 (21)	1.1	3.4
<b>Ca</b>	90 (112)	1.8	101.9 (96.3)	1.8	4.9
<b>Ti</b>	5.9 (6.4)	1	6.8 (4.1)	1	1.5
<b>V</b>	1.6 (0.1)	8.9	1.9 (0.2)	9	1.3
<b>Mn</b>	4.7 (3.5)	3.2	3.0 (2.0)	2	1.2
<b>Fe</b>	133.1 (135.9)	2	106.6 (94.6)	1.4	6.4
<b>Ni</b>	1.2 (0.3)	11.6	2.3 (1.2)	20	0.8
<b>Cu</b>	6.4 (11.2)	86	4.0 (2.7)	47	0.84
<b>Zn</b>	27.2 (17.7)	289	5.6 (4.5)	55	1
<b>Ba</b>	9.9 (4.8)	14.8	7.5 (3.1)	9.8	5.7
<b>Pb</b>	21.8 (18.3)	1240	8.4 (3.5)	421.8	4.5

In this work Ti, an element of purely crust origin was used as reference. Values of enrichment factors around 1 indicates that this elemental component has natural origin, while in the case of anthropogenic components the value of the enrichment factor can exceed 1000. According to this analysis Al, Si, Ca, Ti, Mn, Fe and Ba can be considered as elements of soil origin, while S, K, Cl, Cu, Zn and Pb in the fine fraction originates from anthropogenic sources.

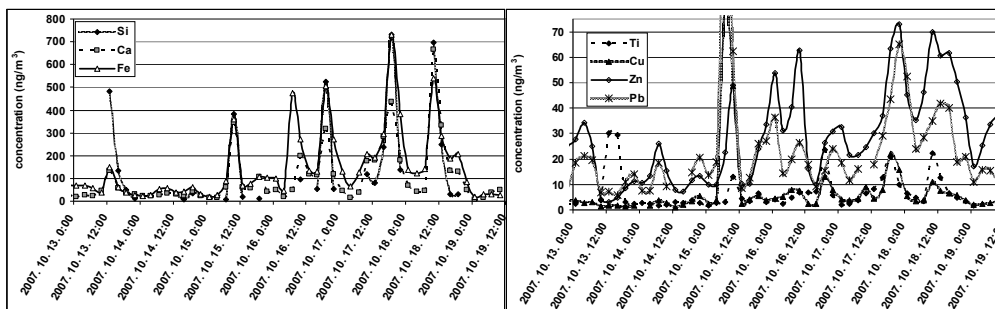


Fig. 2. Hourly variation of some elemental concentrations for the period 13-19 October, 2007

On Fig. 2 the evolution of some elemental concentrations are shown with 3h time resolution for the week 13-19 October, 2007. The period starts with a weekend (13-

14 October), and ends on a rainy Friday. In the time trend of Al, Si, Ca, Fe, and some metals like Ti, Mn, Cu, Zn, Pb similar periodicity can be observed. On working days two peaks appeared: one at morning and another in the evening hours. The behaviour of S, K and Cl was different.

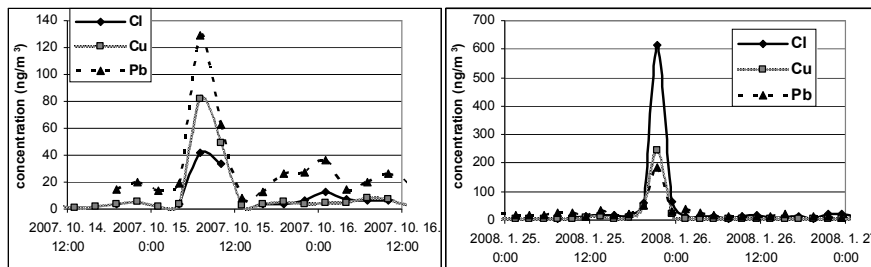


Fig. 3. Emission episodes observed in the increase of the concentrations of Cl, Cu and Pb on the fine size fraction between 14-16 October, 2007 and 25-27 January, 2008.

Several emission episodes were also detected. Such episodes are presented on Fig. 3 with a few-hours long increase in the concentration of Cu, Cl and Pb. These episodes were recorded during the campaigns in October 2007 and in January 2008 too. Other episodes with sharp increase in Ni or Ca, Fe and S were also observed. Sources of these episodes are unknown up to now, but the shape of the peaks suggests industrial origin (Almeida et al. 2006).

### 3.3. Aerosol sources

Sources of urban aerosol on the coarse and fine size fractions were determined separately by factor analysis using the positive mass factorisation model of the US EPA. Mass of species apportioned to factor, percentage of species apportioned to factors and contributions associated with factors were calculated. There were not enough data available to study the variability of contributions by year, season, and weekend/weekday.

On Fig. 4 and Fig. 5 percentage of elements apportioned to factors on the fine and coarse size fraction, respectively, is shown. On the fine fraction five sources were identified. Factor f2 had high Si and f3 had high Al, Ca, Ti, Mn and Fe content. These factors represent the soil dust. Factor f1 was characterized by high S concentration. Sulphur is supposed to be in form of sulphate, and its main source is the combustion of fossil fuel (oil, coal) and diesel engines. Sulphates are secondary aerosols, are created by oxidation of SO<sub>2</sub>, and are usually originated from long range transport processes. The contribution of local sources is small (Borbély-Kiss et al. 1999). The main component of factor f4 are metals like Cr, Mn, Fe, Cu, Zn, Pb and Cl. The source of f4 is presumably traffic. The fifth source, f5 is characterized by K. Potassium is emitted to the atmosphere by biomass burning,

e.g. forest fires. In our case the source of K is domestic heating, when wood is used as fuel in the ovens.

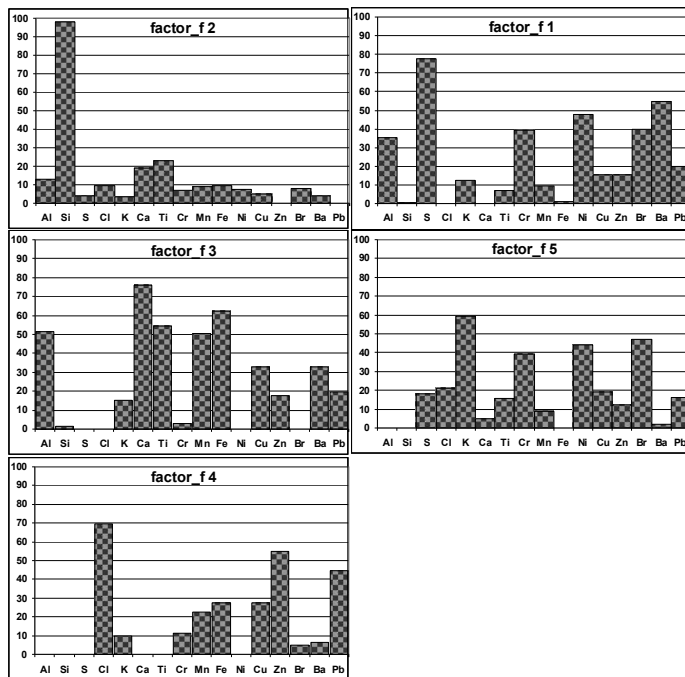


Fig. 4. Percentage of elements apportioned to factor, deduced from positive matrix factorization analysis for fine (PM<sub>2.5</sub>) size fraction

In the case of the coarse fraction four sources were identified. Factor c1 and c4 were similar to factor f2 and f3, representing the soil. Factor c2 is enriched with Cl, which source is not known yet. Factor c3 proved to be the less significant source, containing most metals and phosphorous.

The hourly contribution of some sources for the week 12-19 October is presented on Fig. 6. In the time trend of soil derived and heavy metals a periodicity can be observed: the peaks in the morning and in the evening of working days fall together with traffic rush hours. The hourly evolution of the soil derived elements indicates their source as resuspended dust raised by traffic. The source characterized by metals had a similar tendency, referring to its origin of traffic, too.



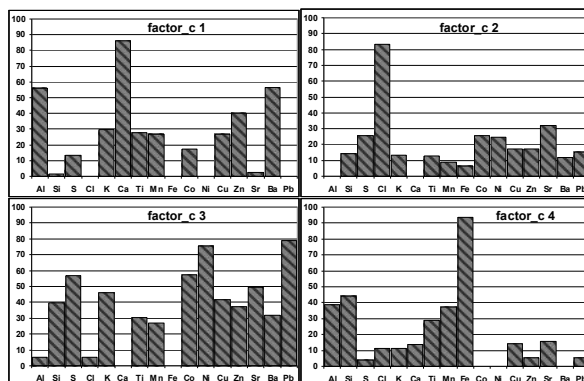


Fig. 5. Percentage of elements apportioned to factor, deduced from positive matrix factorization analysis for coarse (PM<sub>10</sub>-PM<sub>2.5</sub>) size fraction

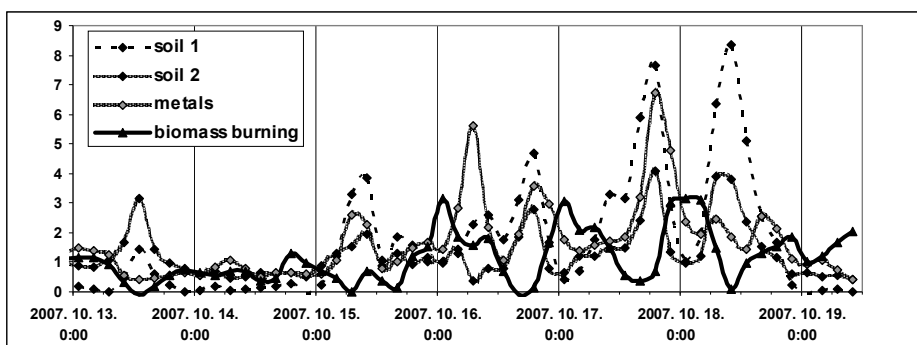


Fig.6. Contribution (average = 1) of sources for the time period 13-19. October, 2007.

The official heating season started on 15. October, 2007. On 15<sup>th</sup> October there was a significant fall in temperature: the average daily temperature decreased from 15°C to 7°C. The source characterized by K became significant only after the drop in the temperature. Peaks of this source appear during nights and mornings indicating its origin of domestic heating.

#### 4. Summary

In this paper we studied the sources of urban aerosol in the city of Debrecen by following the short term time variation of the elemental components and measuring the elemental mass size distribution.

Sources on both (PM<sub>10</sub>-PM<sub>2.5</sub> and PM<sub>2.5</sub>) size fractions were identified by observing the changes in the elemental concentrations, their periodicity, correlation with other elements and by statistical analysis. It turned out that the main sources of atmospheric aerosol in Debrecen are traffic through direct emission and

resuspended soil dust, sulfates originating from combustion, domestic heating and a yet unidentified source enriched with chlorine.

Although the presented data are only the first result of a sampling and measurement series, it can be already seen, that such study gives a useful contribution to the ongoing atmospheric aerosol investigations carried out for 20 years in the IBA Laboratory of the ATOMKI.

The higher resolution in time and size makes the source characterization more efficient and more accurate. It allows the identification of local emission and long-range transport episodes (Chiari et al. 2006). 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 in receptor areas, to follow the evolution of aerosol, and to make a better estimate on the health impact. 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 (Dobos et al. 2004).

This work will be continued in order to integrate our knowledge about the nature of the regional aerosol. Two more sampling campaigns have been already carried out in May and August 2008, and more are planned at the end of this year and in 2009. Our further intention is to investigate the dependence of concentration of aerosol and its component on meteorological parameters, follow the seasonal, weekly, daily, hourly variability of urban aerosol sources, and make further analysis on emission episodes and unidentified sources e.g. by single particle analysis.

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