

# CHARACTERIZATION OF URBAN AEROSOLS IN EAST-HUNGARY REGION FINAL REPORT 2009-2011

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## **Participants and FTE:**

Dr. Zsófia Kertész (MSc in Physics, PhD in Physical Sciences), chief investigator (FTE: 1.44)

Dr. Zita Szikszai (MSc in Physics, PhD in Medical Sciences), senior researcher (FTE: 0.4)

Anikó Angyal (MSc in environmental sciences), PhD student (FTE: 1.6)

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Enikő Furu (MSc in chemistry), young researcher (FTE: 1.265)

**Institution:** Laboratory of Ion Beam Applications, Institute of Nuclear Research of the Hungarian Academy of Sciences, H-4026 Debrecen, Bem tér 18/c, Hungary

## **Publications:**

The results obtained in the frame of the project were or are being published in 5 journal papers, 6 conference proceedings papers and 4 Atomki Annual Report papers. 3 more journal papers will be submitted in 2011. 2 MSc diploma works were prepared in the project, and 2 more will be submitted in May, 2011. All three young researchers and PhD students prepare their PhD thesis from the results achieved in this project.

The results were presented in 7 international and one national conferences in 13 talks and 6 posters. Below is the list of the conferences, the participants, the presenter of the results and the kind of presentation. All participants were co-author in each presentation.

19th International Conference on Ion Beam Analysis. Cambridge, UK, 7-11 Sept. 2009 (participants: Anikó Angyal – poster, Zsófia Kertész – poster, Zoltán Szoboszlai – talk, Zita Szikszai)

9. Magyar Aeroszol Konferencia. Balatonfüred, 2009. április 27-28. (participants: Anikó Angyal – talk, Zsófia Kertész – talk, Zoltán Szoboszlai – talk, Zita Szikszai)

European Research Course on Atmospheres, 11. January - 12. February 2010, Grenoble, France, 2010 (participant: Anikó Angyal - poster)

12th International Conference on Nuclear Microprobe Technology and Applications. Leipzig, Germany, 26-30 July, 2010 (participants: Anikó Angyal – talk, Zita Szikszai)

6. Kárpát-medencei Környezettudományi Konferencia. Nyíregyháza, 2010. április 22-24. (participants: Anikó Angyal – talk, Enikő Furu – talk)

Natural and Artificial Ecosystems in the Somes, Cris, Mures, Tisa River Basin. Arad, Romania, 7-8 May, 2010 (participants: Anikó Angyal – poster, Enikő Furu – poster, Zsófia Kertész – talk, Zoltán Szoboszlai - poster)

12th International Conference on Particle Induced X-Ray Emission and Its Analytical Applications. Guilford, UK, 27 June - 2 July, 2010 (participants: Zsófia Kertész – talk, Zoltán Szoboszlai – poster)

2010 International Aerosol Conference. Helsinki, Finland, 29 Aug. - 3 Sept., 2010 (participant: Zsófia Kertész – backup talk/poster)

7. Kárpát-medencei Környezettudományi Konferencia. Kolozsvár, 2011. március 24-27., (participants: Anikó Angyal – talk, Enikő Furu – talk)

Educational lectures were presented at schools and during the Fizikusnapok (Day of Physics) at the ATOMKI. We informed the regional environmental agency about the achievements of the project.

The detailed list of the publications and the conference presentations can be found at the end of the report. The support of the NFM and OTKA was indicated on all publications.

## 1. Introduction

The scope of the project was to study the properties of atmospheric aerosol in Debrecen and East-Hungary region using different sampling and analytical techniques.

Aerosol research based on nuclear analytical methods has been started in 1988 at the Laboratory of Ion Beam Applications of the Institute of Nuclear Research of the Hungarian Academy of Sciences. The main objectives of this project were to continue the ongoing aerosol research at the IBA Laboratory of the ATOMKI and to extend the aerosol research field with new and challenging studies. We focused on the environmental and health impact of urban aerosol through source characterization and investigation of indoor aerosol and personal exposure.

The work could be grouped around 3 main areas:

- Identification of urban aerosol sources by using time resolved sampling and/or single particle analysis.
- Study of indoor aerosol in workplaces and at schools.
- Study of long-term tendencies and variation of aerosol components and sources from 1988 to 2010.

## 2. Results

### 2.1. Characterization of urban aerosol sources

Sources of urban aerosol in the city of Debrecen were investigated by using time-resolved sampling, ion beam analytical methods and statistical analysis. Samples of fine ( $PM_{2.5}$ ) and coarse ( $PM_{2.5-10}$ ) urban particulate matter were collected with 2 hours time resolution in the frame of 8 sampling campaigns during 2007-2010 in different seasons in an urban background environment in Debrecen. Elemental concentrations of over 1000 samples were obtained by PIXE; concentrations of black carbon were determined with a smoke stain reflectometer. Source apportionment was carried out by using the positive matrix factorisation method.

Seven factors were identified for both size fractions by observing the changes in the elemental concentrations, their periodicity, and correlation with other elements and by PMF analysis. These sources were soil dust, traffic, secondary aerosol – sulphates, domestic heating, oil combustion, agriculture and an unknown factor enriched with chlorine. Seasonal and daily variation of the different factors was studied as well as their dependence on meteorological parameters. Other sources were also identified by detecting several emission episodes including a Saharan dust intrusion on 21<sup>st</sup> – 24<sup>th</sup> May, 2008. These episodes, however they bear little significance from the point of view of aerosol impact in the city, serve as a basis to reach a better understanding of short and long range aerosol transport.

Sources characterized by high chlorine content were found in both size fractions, which gave significant contribution to the aerosol concentration. However, the origin of these particles could not be identified on the available information. Thus further investigation of samples characterized with high Cl content were done on the ATOMKI Scanning Nuclear Microprobe Facility in order to determine the possible chemical composition of these particles and the potential sources. Morphology, size and elemental composition for  $Z \geq 6$  of around 1000 coarse mode particles were determined by using scanning transmission ion microscopy (STIM), light-element PIXE and PIXE analytical methods. Hierarchical cluster analysis was performed on the obtained dataset in order to group the particles; correlations between different elements were also calculated.

We found that in the fine fraction Cl appeared in emission episodes together with heavy metals such as Cu, Zn and Pb. These episodes had presumably industrial origin.

As a result of the nuclear microprobe study and statistical methods four possible sources of coarse mode Cl were identified. The main source was salting of streets during winter. Building was the most important source in summers, agriculture in autumn. Periodically sea-salt could be observed in spite of the fact that the nearest sea is situated at 1000 km distance. Sea-salt appears in the atmosphere of Debrecen as a result of long-range transport processes.

Aerosol deposits which could be connected to heavy metal pollution episodes and high aerosol pollution levels were studied by nuclear microscopy and scanning electron microscopy. Quantitative elemental composition and morphology of over 500 coarse mode aerosol particles were determined. Ion beam analytical methods (micro-PIXE and STIM) provided the elemental composition of coarse aerosols while the morphology of the different particle types was determined by SEM.

Through the elemental composition, elemental correlations and morphology different particle types were identified and attributed to different anthropogenic sources like biomass burning, oil combustion, traffic and industry.

From 15<sup>th</sup> April to 12<sup>th</sup> May 2010 an intensive aerosol sampling campaign took place, using 2-stage samplers with daily and hourly time resolution and 9-stage cascade impactors. Our intention was to trace the volcanic aerosol from the Icelandic Eyjafjöll eruption. We analysed over 500 samples. Despite the fact, that we couldn't identify the traces of the volcanic eruption, the obtained data set proved to be very useful in characterizing urban aerosol sources. More information were gained on the daily variation of sources and on emission episodes. Among others e.g. the effect of a car race (dragrace), which took place in the border of the city was detected. The change in the size distribution of some elements (Pb, Cu, Zn) could be attributed to different emission episodes.

#### *Relevant publications:*

- Kertész Zs., Szoboszlai Z., Angyal A., Dobos E., Borbély-Kiss I.: *Identification and characterization of fine and coarse particulate matter sources in a middle-European urban environment*. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 268 (2010)1:1924-1928.
- Angyal A., Kertész Zs., Szikszai Z., Szoboszlai Z.: *Study of Cl-containing urban aerosol particles by ion beam analytical methods*. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 268 (2010) 1:2211-2215.
- Angyal A., Szoboszlai Z., Furu E., Szikszai Z., Csedreki L., Kertész Zs.: *Study of emission episodes of urban aerosol by single particle analysis*, Nuclear Instruments and Methods in Phys. Res. B, article in press, DOI:10.1016/j.nimb.2011.02.057, 2011
- Angyal A., Kertész Zs., Szikszai Z., Szoboszlai Z., Furu E.: *Városi aeroszol emissziós epizódjainak vizsgálata ionnyaláb analitikai módszerekkel. (in Hung.)* 6. Kárpát-medencei Környezettudományi Konferencia. Nyíregyháza, 2010. április 22-24. Proceedings. Szer.: Szabó B., Tóth Cs. Nyíregyháza, Nyíregyházi Főiskola (2010) 1:277-282
- Angyal A., Kertész Zs., Szikszai Z., Szoboszlai Z., Furu E.: *Városi aeroszol forrásai*, 7. Kárpát-medencei Környezettudományi Konferencia. Kolozsvár, 2011. március 24-27.

#### **2.1.1. Radiocarbon determination of source contribution of carbonaceous aerosols by AMS**

In order to separate fossil and biomass contributions, parallel sampling of aerosols and high precision atmospheric CO<sub>2</sub> mixing ratio and <sup>14</sup>CO<sub>2</sub> observations in Debrecen has been started in September 2010. The first samples were measured in the Laboratory of Ion Beam Physics of Swiss Federal Institute of Technology Zurich (ETH) by accelerator mass spectrometry (AMS) on the MICADAS facility. We established a sampling and sample preparation protocol. Because there was only limited measurement capacity available and because at least 2 mg carbon is needed for one measurement, monthly samples were used.

According to the first results the fossil carbon ratio in the aerosols was much higher than in the CO<sub>2</sub> gas which was collected parallel at the same place. In the winter months the C-14 content of the urban aerosols increased. This means, that the contribution of biomass burning (e.g. soot) became more significant. With the cooling weather people used more and more wood for domestic heating, whilst the contribution of the increasing gas consumption had smaller effect on the C-14 content.

This work was done in cooperation with the Hertelendi Laboratory of Environmental Studies (HEKAL) of the ATOMKI and ETH.

The first results were presented on the 7<sup>th</sup> Conference of Environmental Sciences of the Carpathian Basin, in Kolozsvár, 24-27<sup>th</sup> March, 2011.

### **2.1.2. Source characterization by chemical speciation of elements**

It was planned, that samples originating from high pollution level episodes will be studied with “high resolution PIXE” method in order to find out the possible chemical composition and sources of such samples. Because the method is sensitive only to low-Z elements, at first we concentrate on Cl and S compounds. Although the samples were ready and we already prepared the adequate standards, the experiment couldn't be realised in the 24 months of the project due to the limited availability of the equipment (it is installed at the ESRF in Grenoble for most of the year). Finally this experiment is scheduled to 16-20. May 2011, which will be done in cooperation with the Jozef Stefan Institute in Ljubljana, Slovenia with the support of the SPIRIT EU7 Infrastructure program.

### **2.1.3. Study of high pollution level episodes in Hungarian cities**

The aerosol pollution level in bigger cities is highest during winters. Therefore a continuous sampling campaign was carried out in Debrecen from 7<sup>th</sup> December 2009 to 18<sup>th</sup> March 2010 to study the high pollution level episodes. Parallel to this a similar campaign in Budapest was also done in cooperation with the Pannon University, Veszprém and with the Hungarian Meteorological Service. During the campaigns several high pollution episodes were detected. So far all the samples were measured and elemental concentration values were determined, and a simple statistical analysis was made. From the point of view of reduction of air pollution the most important thing is to explore the sources of particulate matter. As a first step correlation analysis was carried out on the data set. Strong correlation was found between the PM10 mass and fine fraction S, K, Zn and Pb indicating that sulphates and biomass burning (heating) gives significant contribution to the high pollution level episodes. Furthermore, strong correlation was observed between the Debrecen and Budapest data for V, Ni and Ba ( $r > 0.75$ ,  $p < 0.01$ ), and somewhat weaker ( $r = 0.5$ ,  $p < 0.01$ ) correlation was found for S and Cl. This means that aerosols composed of these elements originate from regional or long range transport. Source characterization by PMF receptor modelling and by chemical mass balance analysis is on the way. Further evaluation of the data and comparison with data provided by the regional environmental protection agency (TIKÖTEVIFE) is in progress.

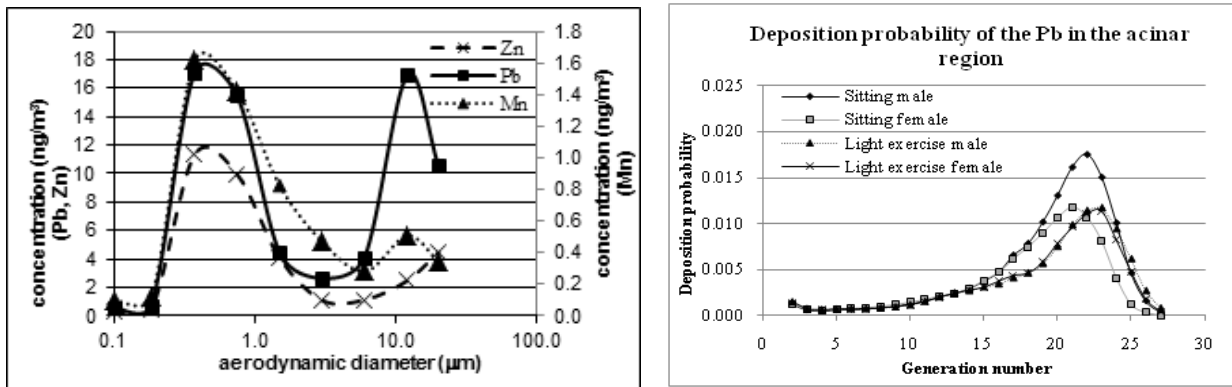
## **2.2. Indoor aerosols**

### **2.2.1. Workplace exposure**

In the frame of a case study elemental composition and size distribution of indoor aerosol were investigated in a working environment, where soldering of electronic devices takes place. During working hours for two days, outdoor air and the air in a large hall (where approx. 100 people works) were sampled with 2-stage filter units and 9-stage cascade impactors, which separated the aerosol into 10 size fractions in the 0.05-30  $\mu\text{m}$  range. Elemental composition (for  $Z \geq 13$ ) and elemental mass size distributions of aerosols were determined by PIXE analytical technique. Single particle analysis was carried out using light-element PIXE, PIXE and STIM to obtain more detailed and reliable data and also to estimate the emission sources. Some samples were further analysed by scanning electron microscopy.

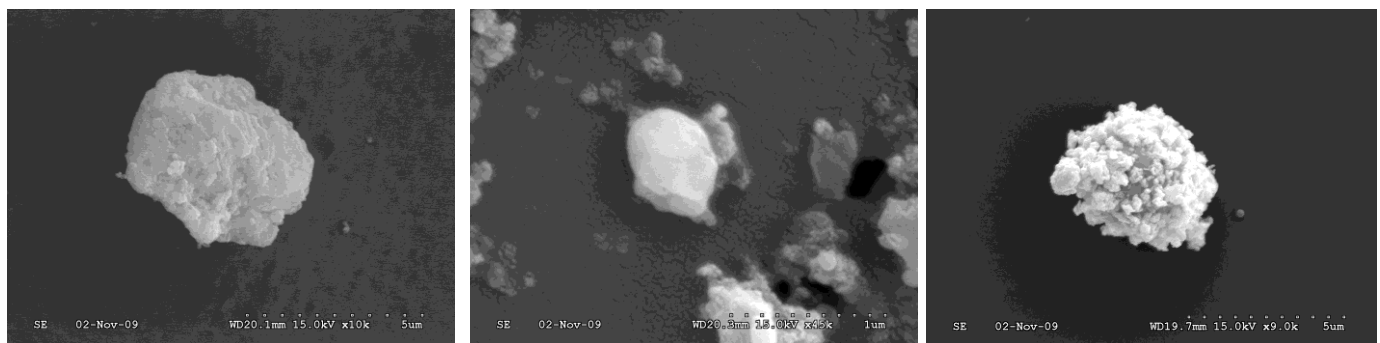
We utilized a stochastic lung model to calculate total and regional deposition efficiencies of the different types of particles along the human respiratory system (in case of different activities: sitting and manual working).

As an example size distribution of some heavy metals and deposition probability of Pb in case of different activities is shown in figure 1.



**Figure 1.** Mass size distribution of some heavy metals (left) and deposition probability of Pb-containing particles in the acinar region (right). The higher the generation number deeper in the lung.

It was confirmed by this study that relative to the outdoor atmosphere inside the working hall was clean. Despite of the air-filtering equipments, we were able to identify aerosol particles from outer origin in the working area: such as aluminium-silicates minerals, salt particles, and K from biomass burning, K-S, Ca-P from agriculture or industry. Internal sources related to the production were also identified: soldering and milling emitted significant amount of particles. These particles were characterized with high Sn, Pb and Cl content. Ag, Br, Cu, Zn and other heavy metals were used as tracers. Based on stochastic lung model calculations we found that particles with high heavy metal content were deposited deep in the lung with relative high probabilities.



**Figure 2.** Particle types: a big iron-chloride, a small lead-chloride and a tin-oxide particle (from left to right). On the surface of the tin-oxide sphere other aerosols were attached. The spherical shape indicates that this particle was created from the melt.

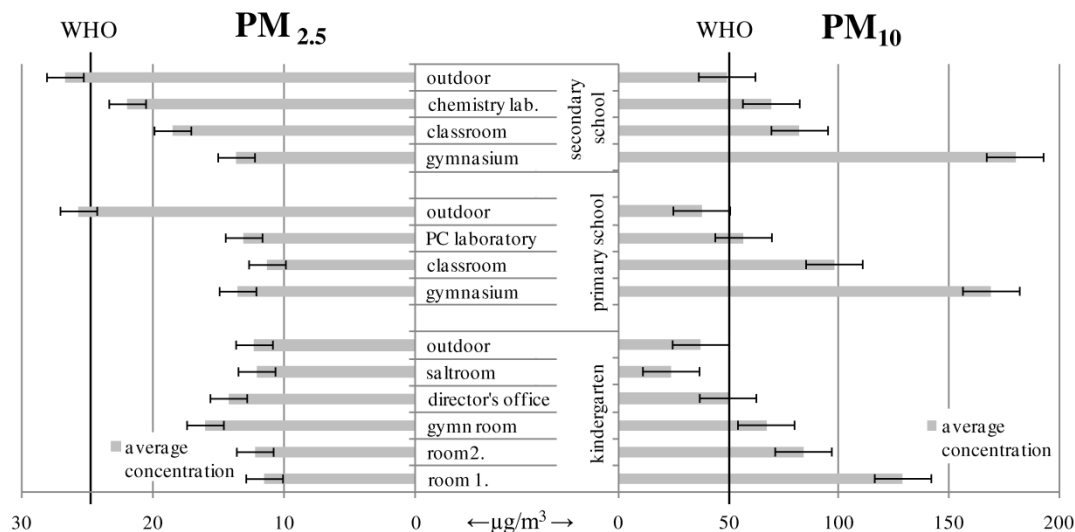
*Publication:*

- Z. Szoboszlai, Zs. Kertész, Z. Szikszai, A. Angyal, E. Furu, L. Daróczi, Á. Z. Kiss: Investigation of workplace aerosol particles by ion beam analytical methods, submitted for publication to Atmospheric Environment

**2.2.2. Aerosol pollution in schools**

In this study atmospheric aerosol concentration levels in two schools (a primary and a secondary grammar) and a kindergarten were investigated. The selected institutions are located close to the centre of Debrecen where the traffic density is rather high. Aerosol samples were collected with two-stage samplers in all cases and also with two 9 stage PI cascade impactors in the case of the kindergarten. Coarse and fine mass concentrations (PM), elemental composition and mass size distributions were determined in the selected microenvironments. These were different classrooms, school yards, gymnasiums, a computer lab, a chemical lab and a so-called salt-room. The elemental composition (for  $Z \geq 13$ ) was determined by PIXE. As expected, the PM concentrations were rather high in the studied areas. In most cases the indoor  $PM_{10}$  and the outdoor  $PM_{2.5}$  concentrations exceeded the WHO recommended 24-h values. We observed increased PM concentrations in the

lower educational levels. We did not observe big differences between the indoor and outdoor elemental compositions, but found differences in the elemental concentrations. The concentrations of the soil origin elements in the coarse fraction were significantly higher in the classrooms. Elemental concentrations in the fine fraction were similar outside and inside.



**Figure 3.** Average PM<sub>2.5</sub> and PM<sub>10</sub> concentrations in µg/m<sup>3</sup>.

Based on the mass size distribution values significant differences were found between the two rooms with different activity types. In the size distribution of the gymnastic room, where children made exercises and gymnastics throughout the day, higher concentration values and bigger particle sizes were detected in the coarse fraction than in the other room where children were allowed only to sit. Deposition probabilities along the respiratory system were also calculated using the obtained size distribution data. The lung deposition fraction was different in the two rooms. Both the total and the acinar deposition were higher for both a 5 year old child and an adult female in light exercise activity than in sitting.

Based on the elemental composition data we could identify the sources of the classroom pollution. These were the “usual” outdoor sources, like traffic, heating or sulphates. Cleaning proved to be the most significant internal source. Effects of the wall paints, the chemical experiments in the laboratories or the children’s play on carpets were also shown.

The high level of aerosol pollution in classrooms necessitates aerosol characterization studies in educational environments in order to identify the sources and the possible health effects of ambient aerosol and then to form mitigation strategies.

#### *Publications:*

- Szoboszlai Z., Furu E., Angyal A., Szikszai Z., Kertész Zs.: *Investigation of indoor aerosols collected at various educational institutions in Debrecen, Hungary.*, X-Ray Spectrometry, corrected proof, DOI: 10.1002/xrs.1323, 2011
- Furu E., Szoboszlai Z., Angyal A., Török Zs., Kertész Zs.: *Beltéri aeroszol vizsgálat debreceni oktatási intézményekben*, 7. Kárpát-medencei Környezettudományi Konferencia. Kolozsvár, Románia, 2011. március 24-27. Szerk.: Mócsy I. et al, Ábel Kiadó (2011)1: 95-98, 2011
- Furu E., Szoboszlai Z., Angyal A., Kertész Zs.: *Aerosol pollution in schools in Debrecen - Preliminary results*. International Conference: Natural and Artificial Ecosystems in the Somes, Cris, Mures, Tisa River Basin. Arad, Romania, 7-8 May, 2010, *conference abstract*

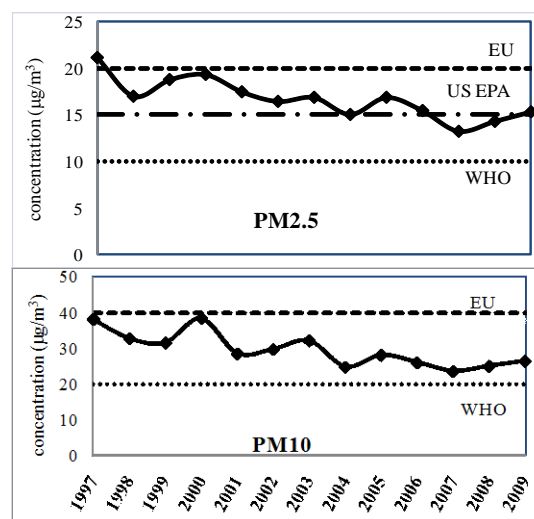
### 2.3. Long term tendencies and seasonal variation of fine and coarse particulate matter

In the IBA Laboratory of the ATOMKI properties of atmospheric aerosol have been studied since 1988. Size fractionated aerosol samples have been collected regularly twice a week in an urban background environment in Debrecen, East-Hungary since 1993. A continuously broadened data base has been created relating to the PM<sub>10</sub>, PM<sub>2.5</sub> and coarse aerosol mass, black carbon content and main elemental components ( $Z \geq 13$ ).

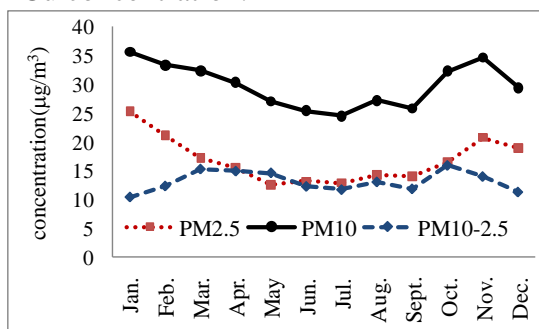
In the frame of this project we started the elaboration of the database for the period 1993-2010. Besides the long term tendencies and seasonal variation of the elemental concentrations and mass concentrations tendencies and variation of sources were also studied of the fine, coarse and PM10 fractions. Sources were determined with the PMF receptor model.

Yearly average concentrations of PM<sub>2.5</sub> and PM10 are presented in figure 2. The concentration of both size fractions decreased with time.

**Figure 4.** Yearly average concentration of PM<sub>2.5</sub> and PM10. EU, US EPA and WHO limit/target values are indicated.



The same decreasing tendency was observed in the case of most of the anthropogenic elements in both size fractions. The concentration of BC did not change, while there was a significant increase in Cu concentration.



**Figure 5.** Monthly average concentration of PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>10</sub>-PM<sub>2.5</sub> between 1996 and 2009.

The PM<sub>2.5</sub> concentration exceeded the PM<sub>10</sub>-PM<sub>2.5</sub> value. The PM<sub>2.5</sub>/PM<sub>10</sub> ratio varied between 0.7 (winter) and 0.5 (spring-summer), and it increased with time.

Comparing our data to the air quality standards set by the EU, we can conclude that the annual average PM<sub>10</sub> concentration did not exceed the limit value of 40 µg/m<sup>3</sup>, and the PM<sub>2.5</sub> concentration stayed under the target value of 20 µg/m<sup>3</sup> too. However the daily limit value (50 µg/m<sup>3</sup>) was regularly exceeded more than 35 times a year.

The first results showed that throughout the years there were significant changes in the concentration, enrichment factor, PM<sub>2.5</sub>/PM<sub>10</sub> ratios and sources of urban aerosol in Debrecen. The concentration of PM<sub>10</sub>, PM<sub>2.5</sub> and coarse aerosol decreased in Debrecen from 1993. Concentration of most elemental components decreased; the exceptions could be attributed to the increased traffic (abrasion of brake and tire wears). The PM<sub>2.5</sub>/PM<sub>10</sub> ratio was similar to those obtained in kerbsides and urban background sites in European cities: this means significant contribution of resuspended dust due to traffic. The seasonal variation of PM, its elemental components and sources are influenced by anthropogenic activity (heating, de-icing of streets, field burning, etc) and meteorological parameters. The change in enrichment factors indicated the change in emission sources and emission processes.

We used the elemental concentration data base to identify which source areas of Europe contributed to the PM concentration in Debrecen from 1993 to nowadays when high pollution levels were measured. According to the ruling wind directions Europe was divided to 5 sectors: western, southern, eastern, north-east and north-west. Backward trajectory modelling (NOAA-HYSPLIT) was applied to determine the spread of the aerosol particles, and correlation analysis and PMF modelling was employed to identify characteristic elements and sources of the 5 sectors of the continent.

In 70% of the high pollution level episodes air masses originated from Southern and Eastern Europe. Fingerprint elements and elemental ratios were found for all sectors. E.g. elemental fingerprints could be attributed to iron mining and metallurgy (N), plastic industry (E), chromium mining (S), and Saharan dust (S).

#### *Publications:*

- Furu E., Kertész Zs., Borbély-Kiss I., Dobos E., Szikszai Z., Angyal A., Szoboszlai Z.: *Változások és tendenciák a debreceni aeroszol (szálló por) koncentrációjában és összetételében*. 6. Kárpát-medencei Környezettudományi Konferencia. Nyíregyháza, 2010. április 22-24. Proceedings. Szer.: Szabó B., Tóth Cs. Nyíregyháza, Nyíregyházi Főiskola **0** (2010)1:283-288
- Kertész Zs., Borbély-Kiss I., Szikszai Z., Furu E., Dobos E., Angyal A., Szoboszlai Z., Szabó Gy., Koltay E.: *Long-term tendencies and seasonal variation of atmospheric aerosol and its elemental components in Debrecen, Hungary, between 1996 and 2009*. 12th International Conference on Particle Induced X-Ray Emission and Its Analytical Applications. Guilford, UK, 27 June - 2 July, 2010, *in press*
- Kertész Zs., Borbély-Kiss I., Szikszai Z., Furu E., Dobos E., Angyal A., Szoboszlai Z., Szabó Gy., Koltay E.: *Variation of fine and coarse particulate matter and its elemental components in a Central European city from 1996 to 2009*. 2010 International Aerosol Conference. Helsinki, Finland, 29 Aug. - 3 Sept., 2010 **0** (2010)0-X, *extended abstract*
- Török Zs., Kertész Zs., Szikszai Z., Szoboszlai Z., Angyal A., Furu E.: *Európa "aeroszol ujjlenyomata" Debrecen város légkörében*, 7. Kárpát-medencei Környezettudományi Konferencia. Kolozsvár, 2011. március 24-27., Szerk.: Mócsy I. et al, Ábel Kiadó (2011)1: 99-102, 2011

### **3. Summary**

The scope of the project was to study the properties of atmospheric aerosol in Debrecen and East-Hungary region using different sampling and analytical techniques.

We determined the urban aerosol sources by observing the short time changes in the elemental concentrations, their periodicity, and correlation with other elements and by receptor modelling. Seasonal, weekly, daily and hourly variation of the source contributions was studied as well as their dependence on meteorological parameters. Whenever this analysis didn't give satisfactory result, single particle analysis was done using ion and electron microscopy. As a result of the single particle analysis we were able to identify e.g. 4 different sources of coarse mode Cl. We showed that the combination of these methods gives excellent result in source characterization. In order to get a more complete picture of aerosol sources, new analytical techniques were introduced, like accelerator mass spectrometry to separate the fossil and biomass component of carbonaceous aerosol, or high-resolution PIXE for chemical speciation of the elemental components.

We have extended the aerosol research of the ATOMKI IBA Laboratory with indoor aerosol studies. In a frame of a case study we made a complex survey of the working environment of an electronic product company. It was found that aerosol particles originated from the production processes gave significant contribution to the air pollution inside the working hall, and thus to the workers' exposure. We have started a survey of indoor aerosols in schools and a kindergarten situated in the city centre near to busy traffic roads. Aerosol concentration, elemental composition and elemental mass size distribution were determined in several classrooms during teaching time in heating and non-heating seasons. We found, among others, that in almost all cases the indoor PM<sub>10</sub>



concentrations exceeded the WHO recommended 24-h values. Several outdoor and indoor sources gave contribution to the classroom pollution, the most significant of them were traffic, heating or sulphates (outdoor) and cleaning chemicals, wall paint, the children's play on the carpeted floor or the chemical experiments in the laboratories (indoor). In order to estimate the exposure due to indoor aerosols deposition probabilities of the different particle types along the human respiratory tract was calculated by a stochastic lung deposition model under different breathing conditions.

The elaboration of the data base comprising the PM<sub>10</sub>, PM<sub>2.5</sub> and coarse aerosol mass, black carbon content and main elemental components ( $Z \geq 13$ ) of Debrecen from 1993 to nowadays has been started. The long term tendencies and seasonal variation of the elemental concentrations, the mass concentrations and of sources were determined for the fine, coarse and PM10 size fractions. Decrease of concentration was the general tendency, however no change or increase was observed in the contribution of sources attributed to biomass burning (domestic heating) and to traffic. We found that the seasonal variation was influenced by human activity and meteorological conditions. Characteristic elemental compositions were identified for the different source areas of Europe using backward trajectory calculations, Spearman correlation analysis and PMF receptor modeling.

Since the recently published big European surveys lack data from Eastern Europe, our study will give a valuable contribution to the aerosol map of Europe.

During the 24 months of the project several aerosol sampling campaigns were carried out in different outdoor and indoor environments using various sampling techniques. The elemental composition of the samples was determined by particle induced X-ray emission (PIXE) analysis in the ATOMKI IBA Laboratory. Single particle analysis was done at the ATOMKI Scanning Nuclear Microprobe facility using different ion beam analytical techniques. Scanning electron microscopy was performed at the Department of Solid State Physics of the University of Debrecen. The radiocarbon determination by accelerator mass spectrometry was made in the Laboratory of Ion Beam Physics of Swiss Federal Institute of Technology, Zurich, Switzerland, and high-resolution PIXE studies will be carried out in the Microanalytical Centre of Jozef Stefan Institute, Ljubljana, Slovenia.

All together about 2500 samples were analysed by PIXE, quantitative elemental composition of ~ 1700 aerosol particles were determined by ion microscopy, 20 samples were analysed by SEM and the radiocarbon content of 5 monthly samples was determined. In order to evaluate the data statistical methods (e.g. correlation analysis, hierarchical cluster analysis, linear regression analysis) and model calculations (positive mass factorization receptor modelling, IDEAL stochastic lung deposition model, HYSPLIT trajectory model) were employed. During the statistical analysis over 80000 data were handled.

#### **4. Achievements of the project**

The research carried out in the frame of this project contributes to the knowledge of the basic properties of atmospheric aerosol. We investigated basic features of ambient aerosol particles like concentration, composition, size distribution, sources and their dependence on time (long and short scales) and on meteorological parameters. Our results contributed to the knowledge on the impact of urban aerosol on environment and on human health. Besides the basic research it provided useful information for the society, authorities and public health too. On the basis of the achieved results cooperation was already formed with the local environmental protection agency.

Despite the fact that the first journal papers were published less than one year ago there are already citations, showing the international interest about our results. Since there are very limited data available e.g. on workplace aerosol or about the aerosol impact of Eastern Europe, our results are valuable not only regionally, but on a global international scale too.

The obtained results were presented in national and international forums. All the young participants of this project had oral and poster presentations on prestigious forums of this research field. Our work was presented on the Hungarian Aerosol Conference, on the 19<sup>th</sup> International Conference on

Ion Beam Analysis, the 2010 International Aerosol Conference, the XII. International Conference on PIXE, the 12th International Conference on Nuclear Microprobes and the 6<sup>th</sup> and 7<sup>th</sup> Conference of Environmental Sciences of the Carpathian Basin. Anikó Angyal won the best poster award on the International Conference of Natural and Artificial Ecosystems in the Somes, Cris, Mures, Tisa River Basin.

Four journal papers are already published or accepted for publications. Another one is submitted to Atmospheric Environment. Three more journal papers are in preparation (about the long term tendencies and variation of Debrecen urban aerosol, about fingerprinting of Europe's source regions, and one about the high pollution level episodes in cities). These papers couldn't be submitted due to the short duration of the project, only the preliminary results were published in conference proceedings or presented on conferences.

In the project two PhD students and a young researcher, who will start to prepare her PhD were involved. Expected dates of PhD defence are the end of 2011 in the case of Zoltán Szoboszlai, and 2012 in the case of Anikó Angyal. Two more MSc students make their diploma work from parts of this project. Since part of the research was done at schools and there were increased interest among the teachers and students, we gave lectures about the basics of atmospheric research and about our most interesting results in schools and during the Days of Physics at the Institute.

Around this project a young multidisciplinary research team was formed, ensuring that this challenging research will be carried on on the highest level. In the frame of this project we have extended the ongoing aerosol research of the ATOMKI IBA Laboratory with introducing new analytical methods (electron microscopy, high-resolution PIXE and radiocarbon measurement by AMS) and new research areas (e.g. indoor studies).

The research carried out in this project (eg. aerosol source characterization and indoor studies) is a new and fast developing field of research which is available only in few laboratories of Europe. Thus the work started here might form a basis of successful new national and international projects in the future.

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