Short thesis for the degree of doctor of philosophy (PhD)

Characterization of urban aerosols pollution during the COVID-19 crisis by particle induced X-ray emission spectroscopy

by Shafa Aljboor

Supervisor: Dr. Zsófia Kertész

UNIVERSITY OF DEBRECEN

Doctoral School of Physics

Debrecen, 2024

Prepared at
The University of Debrecen
Doctoral School of Physics
and
the Institute for Nuclear Research, ATOMKI

Készült a
Debreceni Egyetem
Fizikai Tudományok Doktori Iskolában
és
az Atommagkutató Intézetben
(ATOMKI)

Introduction

Atmospheric aerosols have significant effects on many aspects of our lives. They affect the Earth's climate as strongly as greenhouse gases, and they influence the weather as well. Aerosols may also reduce visibility, which in many parts of the world results in haze. Aerosols have a considerable impact on the biosphere and the natural and built environments, too.

The importance and hazard of these particles originate from their tiny size, which means that they can penetrate deep into our lungs and pass into our bloodstream and could cause several health problems like lung cancer, heart disease, and stroke. Therefore, characterization of aerosol pollution and identification of sources of particulate matter are important issues for societies as well.

The COVID-19 pandemic caused by coronavirus (SARS-CoV-2) emerged at the end of 2019 and became a world pandemic in early 2020. The COVID-19 pandemic has reached almost every country in the world. The outbreak of the pandemic forced the governments to establish strict regulations in their countries in an effort to stop the spread of the virus. To establish social distance, 4 nationwide lockdowns were imposed in Hungary from March 2020 to February 2022 (March-May 2020, November 2020 – February 2021, March-May 2021 and December 2021 – February 2022). During lockdowns schools and institutions were closed, non-essential business and industrial activities were restricted, and leaving one's home was strictly prohibited.

These shutdowns around the world have given a precious window for researchers to study urban aerosol pollution changes under unique conditions.

We took advantage of this opportunity to study how the different measures introduced locally and globally affected urban aerosol pollution during the COVID crisis.

Objectives

The objective of my work was to characterize urban particulate matter pollution in Debrecen during the years of the COVID crisis and to compare it with the data from the previous two years. For this purpose, $PM_{2.5}$, PM_{coarse}, and PM_{10} aerosol samples were collected at an urban background site two times a week between March 2018 and Feb 2022. Concentration, elemental composition, and sources of APM pollution were determined, and the daily concentrations of NO_2, CO, NO_X, and PM_{10} were used from the Hungarian Air Quality Monitoring Network (OLM) stations as complementary data to our study. On this basis, changes in particulate matter pollution induced by lockdowns were studied. The elemental composition of the aerosol samples was determined by the particle-induced X-ray emission (PIXE) method at the new in-air millibeam PIXE setup of the ATOMKI Tandetron accelerator.

The characterization of this newly developed PIXE measurement setup was also part of my work.

Applied methods

$PM_{2.5}$ and PM_{coarse} aerosol samples were collected at the urban background site of the Institute for Nuclear Research (ATOMKI) in Debrecen two times a week between March 2018 and February 2022.

Mass concentration, black carbon (BC) content and elemental composition of the aerosol samples were determined. The mass concentration was determined by gravimetry using a microbalance with 1 μg sensitivity. BC measurements were preformed using a portable **M**ulti-Wavelength **A**bsorption **B**lack Carbon **I**nstrument (MABI). By measuring light absorption at different wavelengths, it becomes possible to distinguish between BC originating from biomass and fossil fuel burning. The elemental composition (Na – Pb) was measured by particle-induced X-ray emission (PIXE) analytical method. The PIXE technique is a widely used environmental analytical methods since it allows the simultaneous analysis of elements with $Z > 10$ in a single short measurement run without the need for sample preparation. For decades, this method has been widely used to detect and quantify trace elements. The PIXE measurements were carried out at the newly developed in-air millibeam PIXE setup installed at the left 45° beamline of the ATOMKI 2MV Tandetron accelerator. The obtained X-ray spectra were evaluated with the GUPIXWIN program code. Concentrations of 25 elements (O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, CR, MN, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Ba and Pb) were determined after blank correction.

On this basis, two databases containing 340 days and 27 variables each were created for the two size fractions. Basic and advanced statistical analysis including Spearman correlations and Mann-Whitney U test were carried out on the database.

Source apportionment was performed with the positive matrix factorization receptor model EPA PMF 5.0. Mass of species apportioned to factor, percentage of species apportioned to factors and contributions associated with factors were determined for the coarse and fine fractions separately.

In order to identify the origin of specific pollutants and to distinguish between local, regional, and remote contributions, trajectory statistical methods (TSM), including cluster analysis of backward trajectories, Potential Source Contribution Function (PSCF) and Concentration Weighted Trajectory (CWT) calculations were employed.

New scientific results

I have summarized the results of my PhD dissertation in the following thesis points:

1. Characterization of the new in-air millibeam PIXE setup

A novel external millibeam PIXE measurement system have been developed for the elemental characterization of thin and thick samples in a wide elemental range (N-U) with very good sensitivity. In this thesis point I present the results obtained concerning the characterization of this PIXE system.

1.1 In order to characterize the analytical performance of the new system, I determined the detection limits (LOD) for three commonly used aerosol filter materials, namely quartz, polycarbonate, and Teflon (PTFE), and compared them to the LODs achieved in the old in-vacuum PIXE setup of ATOMKI. I found that despite the reduced measurement time and the 50%–75% less collected charge on a sample, much better detection limit values were achieved. In the case of quartz and PTFE filters, LODs improved by several factors (e.g. for medium and high Z elements, the improvement was found to be a factor between 5 and 15).

1.2 In order to detect low energy X-rays, He flow have to be applied. I determined that He flow rate between 1.5 and 2.5 l/min was the optimal by performing a series of measurements on a Ni foil with changing He flux.

1.3 The effect of the level of He saturation on the quantification of light elements was also presented. Through model calculations within the GUPIXWIN program I showed that the change of the saturation level with only 1% (e.g. 99% instead of 100%) might lead to significant change in the calculated concentration of light elements. For elements with low-energy X-ray lines like O (0.525 keV) it can cause a difference up to 10 times. The smaller the atomic number the higher is this effect. For elements with Z >18 it has no influence.

2. Characterization of urban aerosol pollution before and during the COVID-19 crisis in Debrecen

In the second part the results concerning the aerosol pollution in Debrecen between 2018 and 2022 is presented. I studied the changes in the concentration of air pollutants (PM_{10}, NO_x, NO_2, and CO) measured at the 3 fixed monitoring stations of the Hungarian Air Quality Monitoring Network in Debrecen. Furthermore, concentration, elemental composition, and sources of $PM_{2.5}$ and PM_{coarse} were determined at the urban background site in ATOMKI. The variation of aerosol concentration, its elemental composition, and pollution sources were also determined between 2018 and 2022. This time interval included 4 lockdowns, 2 transition and 2 relaxation periods, which were studied individually, too.

2.1 The average concentrations of $PM_{2.5}$, PM_{coarse}, and PM_{10} were higher in the pre-COVID period than during COVID. Considering the whole 2-year period of COVID-19, a 20% reduction in average could be detected in the case of most gaseous and APM pollutants and in the components and sources of $PM_{2.5}$ and PM_{coarse} in Debrecen.

2.2 The yearly average concentrations for all pollutants and all sites were well below the EU limit values set in Directive 2008/50/EC (40 μg/m^3 for PM_{10} and NO_2, 70 μg/m^3 for NO_x, and 3000 μg/m^3 for CO). Only PM_{10} exceeded daily (24-hour) limit values. In the two years prior to the pandemic, exceedance was 51, 48, and 26 in traffic, UB and SUB sites, respectively. During the pandemic, the values were 23, 24, and 8, indicating a decrease of at least 50%. Most of the excesses happened in November and the winter months. In the case of PM2.5 the frequency of exceedances of the 24-h WHO guideline value of 15 μg/m^3 during the winter months dropped from 50% to 20% during the years of COVID-19.

2.3 In the coarse fraction, the main components were the mineral dust elements: Mg, Al, Si, Fe, Ca, and Cl. The contribution of mineral dust to PM_{coarse} mass was more than 30% on average for both periods. The highest contributions were measured in spring and autumn, and the lowest in winter. During COVID a significant decrease was observed in the concentration of almost all elemental components compared to the previous 2 years. In the case of mineral dust elements, the biggest drop in concentration occurred in autumn, while for elements related to anthropogenic activities like traffic (e.g., Pb, Zn, Cu, Ni), the highest level of decrease occurred in winter (Lockdown2 and 4). The smallest differences were in the summer, during the relaxation periods.

2.4 In the fine fraction, the main components were BC (14%–16%), SO_4^{2-} (17%–20%), and mineral dust (11.5%–14%). The smallest concentration of $PM_{2.5}$ was measured in the summer, the highest in the winter. BC, K, Cl, Zn and Pb have a strong association with household heating, which explains their increased occurrence throughout the heating season. The concentration of S showed little seasonal variation. Studying the differences in the components between the pre-COVID and COVID periods it turned out that only traffic-related elemental components such as Cu and Zn showed significant changes (-23%). In the cases of BC and S significant change occurred only throughout the summer periods (25% increase for BC and 35% decrease for S).

2.5 I have shown that chlorine had different sources during the investigated period. In 2018, a significant part of the coarse fraction Cl originated from construction because it showed a correlation with Ca. From 2019, it could be found in the form of NaCl, which mainly originated from sea-salt episodes. In the fine fraction the sources of Cl were sea salt and biomass burning.

2.6 I have shown that a large part of APM pollution of Debrecen comes from regional and long-range transport. The main source areas of secondary sulphate aerosols were the western Balkan countries and south-west Romania. The change in emission in these countries had a strong influence on the PM pollution level in the city of Debrecen.

2.7 Using Positive Matrix Factorization (PMF) receptor model analysis, the following sources were identified in the coarse fraction: traffic, two types of soil, two types of combustion, roadworks, a mixed source of construction and Cl salts, and biogenic emissions. Sources identified in the fine fraction were the two soil types, biomass burning, combustion, roadworks, traffic, sea salt, and secondary sulphates. In the coarse fraction, the contribution of soil was ~50% and biogenic emissions was 19%. Traffic gave ~6% and combustion 9% contribution. The two main contributors in the fine fraction were secondary aerosols and biomass burning with ~28%–30% and ~25%, respectively, while the traffic contribution varied around 12% and the soil ~18%. During the heating season the contribution of BB source was ~ 50%.

2.8 Considering the whole COVID-affected period, there was basically no change in the relative contribution of sources. Differences were found only in the case of temporary sources like construction, roadworks and sea-salt. In case of the absolute contribution of PM_{coarse} sources, soil factors were reduced by 30% on average. The reduction in traffic-related elements and sources was more than 40%. Biogenic emissions were also reduced by 30%, which could be attributed to the reduction in agricultural activity on the surrounding areas. For $PM_{2.5}$ the absolute source contributions decreased by 10%–30% on average, with the exception of the periodic sources. Contribution of sources related to energy production decreased the most. During Lockdown 1 and 3 (springs of 2020 and 2021) a significant increase of biomass burning from domestic heating was observed, which was attributed to the forced staying at home and colder weather conditions.

2.9 When studying the lockdown, transition, and relaxation periods individually, it was found that many factors other than the restrictions influenced the APM levels. I have demonstrated that long-range transport processes (e.g. Saharan dust episodes) as well as local and global meteorology, have a significant impact on the evolution of the APM pollution in the city on a shorter time scale like few weeks to few months. These parameters can cancel out, magnify or reverse the effects of the restrictions.

Publication related to the thesis:

In international journals

- **Aljboor, S**., Angyal, A., Baranyai, D., Papp, E., Szarka, M., Szikszai, Z., Rajta, I., Vajda, I., & Kertész, Z. (2023). Light-element sensitive in-air millibeam PIXE setup for fast measurement of atmospheric aerosol samples. Journal of Analytical Atomic Spectrometry, 38(1), 57–65. https://doi.org/10.1039/D2JA00291D
  IF:3.4 (Q2) (2022)

- Zsófia Kertész, **Shafa Aljboor**, Anikó Angyal, Enikő Papp, Enikő Furu, Máté Szarka, Sándor Bán, Zita Szikszai (2024). Characterization of urban aerosol pollution before and during the COVID-19 crisis in a central-eastern European urban environment,,Atmospheric Environment, 318, 120267. https://doi.org/10.1016/j.atmosenv.2023.120267
  IF:5.0 (Q1) (2022)

List of conference talks and posters

- **Shafa Aljboor**, Máté Szarka, Anikó Angyal, Dávid Baranyai, István Vajda, Zita Szikszai, István Rajta and Zsófia Kertész: The new in-air millibeam-PIXE setup at the ATOMKI Tandetron accelerator, 25th International Conference on Ion Beam Analysis & 17th International Conference on Particle Induce X-ray Emission & International Conference on Secondary Ion Mass Spectrometry, 11-15 October 2021. virtual conference
- **Aljboor, S**., Angyal, A., Papp, E., Furu, E., Török, Zs., Szikszai, Z., Kertész, Zs.: COVID-crisis induced changes in the atmospheric particulate matter pollution in Debrecen, Magyar Aeroszol Konferencia, September 21-23, 2022, Hévíz.
- **Shafa Aljboor**, Máté Szarka, Anikó Angyal, Dávid Baranyai, István Vajda, Zita Szikszai, István Rajta and Zsófia Kertész: The new in-air millibeam-PIXE setup at the ATOMKI Tandetron accelerator RADIATE Summer School 2022, 5-7 October 2022, Firenze, Italy.
- **Shafa Aljboor**, Anikó Angyal, Enikő Papp, Enikő Furu, Máté Szarka, Zita Szikszai, Zsófia Kertész: Variation of composition and sources of urban atmospheric particulate matter pollution during COVID-19 lockdowns in Debrecen, Hungary, 26th International Conference on Ion Beam Analysis & 18th

International Conference on Particle Induced X-ray Emission, 7 – 13. October, 2023, Toyama, Japan.

- Zsófia Kertész, **Shafa Aljboor**, Máté Szarka, Anikó Angyal, Enikő Papp, Zita Szikszai: The new in-air millibeam PIXE setup at ATOMKI: description, performance and some interesting aspects**,** 26th International Conference on Ion Beam Analysis & 18th International Conference on Particle Induced X-ray Emission, 7 – 13. October, 2023, Toyama, Japan.

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Registry number: DEENK/7/2024.PL
Subject: PhD Publication List

Candidate: Shafa Aljboor
Doctoral School: Doctoral School of Physics
MTMT ID: 10092741

List of publications related to the dissertation

Foreign language scientific articles in international journals (2)

1. Kertész, Z., **Aljboor, S.**, Angyal, A., Papp, E., Furu, E., Szarka, M., Bán, S., Szikszai, Z.: Characterization of urban aerosol pollution before and during the COVID-19 crisis in a central-eastern European urban environment.
   Atmos. Environ. 318, 1-18, 2024. ISSN: 1352-2310.
   DOI: http://dx.doi.org/10.1016/j.atmosenv.2023.120267
   IF: 5 (2022)

2. **Aljboor, S.**, Angyal, A., Baranyai, D., Papp, E., Szarka, M., Szikszai, Z., Rajta, I., Vajda, I., Kertész, Z.: Light-element sensitive in-air millibeam PIXE setup for fast measurement of atmospheric aerosol samples.
   J. Anal. At. Spectrom. 38 (1), 57-65, 2023. ISSN: 0267-9477.
   DOI: http://dx.doi.org/10.1039/D2JA00291D
   IF: 3.4 (2022)

Total IF of journals (all publications): 8,4
Total IF of journals (publications related to the dissertation): 8,4

The Candidate's publication data submitted to the iDEa Tudóstér have been validated by DEENK on the basis of the Journal Citation Report (Impact Factor) database.

11 January, 2024