Abstract

Air pollution is one of the greatest environmental threats to human. According to a research, air pollution contributes to the development of allergies, respiratory and cardiovascular system diseases, which consequently leads to premature deaths. The European Environment Agency estimated that in 2020 at least 238 000 people died prematurely in European Union due to exposure to $PM_{2.5}$ above the annual recommended level by World Health Organization. However, new legal regulations are limiting fuel combustion and influence social behaviour leading to changes in the characteristics of pollution emissions. Therefore there is a constant need to identify current sources of pollution and estimate their negative effect in order to prevent the harmful effects of pollution.

The aim, of the research conducted of this dissertation, was to assess the impact of the ban on using solid fuels introduced in Krakow on air quality in the city. This evaluation was prepared based on the comparison of research results obtained from the analysis of $PM_{2.5}$ samples collected in 2018/2019 (before the ban was introduced) with results obtained for $PM_{2.5}$ samples collected in 2020/2021 (after the ban introduction). Additionally, the impact of restrictions (lockdown) on air quality in Krakow was assessed. These restrictions included a reduction in car traffic and communication activity, switch of work and education to remote mode, which was associated with people staying at home as result of the COVID-19 pandemic.

Identification and assessment of contribution sources of air pollution fraction $PM_{2.5}$ and PM_{10} in Krakow was the specific aim of this project. To model emission sources, the receptor method Positive Matrix Factorization (PMF) was chosen. In this method, factors are determined based on positive concentrations and uncertainty of chemical components of dust at the place of immission, and next factors are assigned to sources of emission. Chemical elements, water-soluble ions and equivalent Black Carbon (eBC) were used as markers of pollution sources. Chemical elementals analysis was done by using X-ray fluorescence method and optical method was used for analysis of eBC. Ion composition was analyzed for $PM_{2.5}$ and PM_{10} with isocratic ion chromatography. For purposes of this study, Krakow was chosen as a sampling place in the period 2020/2021, which gave an opportunity to observe changes in characteristic of $PM_{2.5}$ and PM_{10} and their sources of pollution which were caused by two different events that occurred Krakow. The first was the ban on the use of coal and wood for heating purposes which was introduced in September 2019, and the second of them was lockdown which was caused by the COVID-19 pandemic in March 2020. Similar studies were carried out for the $PM_{2.5}$ fraction at the same sampling place in 2018/2019, so the results for these two periods were compared to assess the impact of the ban and the pandemic on air quality.

$PM_{2.5}$ and PM_{10} fractions of air pollutants were collected simultaneously from 2nd March 2020 to 28th February 2021 at background urban station in Krakow. Elemental composition of air particulate matter samples was determined by Energy Dispersive X-ray Fluorescence Technique (ED-XRF) with measurements conducted in air at atmospheric pressure. The usage of Ni and Mo secondary targets enabled extension of the method analytical range towards low-Z elements. The usage of a Ni secondary target made it possible to determine some other low-Z elements such as Al, Si, P, S, Cl. Next, the equivalent Black Carbon (eBC) was determined by optical method using Multi-Wavelength Absorption Black Carbon Instrument (MABI). The implementation of this method consequently allowed to determine the shares of eBC originating from incomplete combustion of fossil fuels and biomass. Enrichment factors were determined to identify the origin of the elements contained in dust, distinguishing between anthropogenic and natural sources. Ion composition was analyzed for $PM_{2.5}$ and

PM_{10} by using isocratic ion chromatography. Moreover, the ion analysis was done by ion chromatography. Identification and estimation of the contribution of pollution sources were performed using Positive Matrix Factorization (PMF).

Based on the conducted research was established that 63% of PM_{10} is the $PM_{2.5}$ fraction. The following elements were identified in the composition of the collected samples: Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Br, Rb, Sr, Pb. Over 80% of sulfur (S) and bromine (Br) occurred in the $PM_{2.5}$ fraction. About 10 % of silicon (Si), calcium (Ca) and iron (Fe) were presented in the $PM_{2.5}$ fraction. However, only in the PM_{10} fraction were detected the following elements: aluminum (Al), titanium (Ti), chromium (Cr), manganese (Mn), copper (Cu), rubidium (Rb), strontium (Sr). Seasonal variability was observed for chlorine (Cl), bromine (Br), sulfur (S), potassium (K), lead (Pb), with high concentrations in winter. For iron (Fe), calcium (Ca), aluminum (Al) and silicon (Si) were observed constant concentrations during the year. EBC concentrations showed seasonal variability, where the average in winter was 2,4 times higher than in summer for $PM_{2.5}$ fraction. Ion chromatography analysis showed, that ion concentrations of NH_4^+, NO_3^-, SO_4^{2-} were characterized by seasonal variability, with high values in winter. Based on elements, ion and eBC analysis; four factors were obtained from PMF modeling, and the following sources were attributed to them: solid fuel combustion, exhaust traffic, secondary inorganic aerosols, and road dust/construction work/industry/soil. A comparative analysis of data from before ban of solid fuel combustion showed a decrease in the concentrations of most of the identified air pollution components. It was estimated that the highest contribution had solid fuel combustion for $PM_{2.5}$, while for PM_{10} - road dust/construction work/industry/soil. It was observed that average contribution of solid fuel combustion declined about 53% in winter 2020/2021 in comparison to 2018/2019. This may be due to the ban of using solid fuel in the city of Krakow introduced in September 2019.

To sum up, results of the analysis confirmed the practically and usefulness of the ED-XRF method, the optical method, and ions chromatography in analyzing the composition of air pollution samples. It was shown that a comprehensive assessment of the composition of pollutants enables the identification and estimation of the contribution of pollution sources. It has been proven that with changing environmental factors and conditions, such as the ban on burning solid fuels and the lockdown caused by the COVID-19 pandemic, there is a constant need to identify sources and assess their impact on air quality that influence health conditions of local population.

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