Seasonal contribution of assessed sources to submicron and fine particulate matter in a Central European urban area[☆]

Lucyna Samek [a, *], Zdzislaw Stegowski [a], Katarzyna Styszko [b], Leszek Furman [a], Joanna Fiedor [a]

[a] Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059, Krakow, Poland
[b] Faculty of Energy and Fuels, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059, Krakow, Poland

ABSTRACT

This study presents the air pollution findings of the submicron (PM1) and fine (PM2.5) particulate matter. The submicron particles are entirely absorbed by the human body and they cause the greatest health risk. For the PM2.5 concentration, there are yearly and/or daily limit values regulations by the European Union (EU) and World Health Organization (WHO). There are no such regulations for PM1 but for health risk reason the knowledge of its concentration is important. This paper presents the seasonal concentration contribution of PM1 and PM2.5, their chemical composition and assessed three basic sources. Daily samples of both fractions were collected from 2nd July 2016 to 27th February 2017 in Krakow, Poland. Apart from PM1 and PM2.5 the concentration of 16 elements, 8 ions and BC for each samples were measured. Based on these chemical species the positive matrix factorization (PMF) receptor modeling was used for the determination of three main sources contribution to the PM1 and PM2.5 concentrations. Daily average concentrations of PM2.5 were 12 $\mu g/m^3$ in summer and 60 $\mu g/m^3$ in winter. For PM1 it was 6.9 $\mu g/m^3$ in summer and 17.3 $\mu g/m^3$ in winter. These data show a significant difference in percentage contribution of PM1 in PM2.5 in summer (58%) and in winter (29%).

For the combustion source, the concentrations calculated from PMF modeling in winter were 4.8 $\mu g/m^3$ for PM1 and 31 $\mu g/m^3$ for PM2.5. In summer, the concentrations were smaller than 1 $\mu g/m^3$ for both fractions. Secondary aerosols' concentration for PM1 was 3.4 $\mu g/m^3$ in summer and 11 $\mu g/m^3$ in winter - for PM2.5 these were 7.1 $\mu g/m^3$ and 17 $\mu g/m^3$ respectively. The third source - soil, industry and traffic together, had small seasonal variation: for PM1 it was from 1.4 to 1.8 $\mu g/m^3$ and for PM2.5 from 4.7 to 7.9 $\mu g/m^3$.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

In many urban areas in the World, the high concentrations of particulate matter are still observed (EEA, 2017; Amato et al., 2016; Rodriguez et al., 2007; Samek et al., 2017b). The exposure to ambient particulate matter can have adverse health effects (Zwozdziak et al., 2017; Styszko et al. 2017; Deng et al., 2013). PM10 enter the upper respiratory tract and deposit in a thoracic area of the respiratory tract. PM2.5 enter the lower respiratory system and can contribute to a cardiovascular disease. They penetrate to alveoli. PM1 is the most important in view of human health. The smaller particles can pass through the blood-air barrier in the lungs, entering the blood as toxins, causing cardiovascular diseases. Smaller particles can harm the regulation of the human nervous system. The smaller particles have higher surface area per mass coming into contact with tissues inside the human body. More research is needed on submicron (PM1) pollution. Air pollutants can have natural and anthropogenic origin. To natural sources belong: mineral dust, sea salts, volcanic eruption, forest fires - to anthropogenic sources: industry, combustion from vehicles, combustion from heating in houses during cold season, road dust and biomass burning (Jeong et al., 2011). In Krakow, PM10, PM2.5 have been already characterized and statistical methods were used for the determination of the sources (Samek et al., 2017a; Samek et al., 2017b; Samek, 2012; Samek et al., 2016a; Samek et al., 2016b). However, until now no such studies were performed for the submicron fraction. This work fill the gap and contains seasonal

---

characterization of PM1 fraction together with determination of the sources.

In this study samples of the submicron (PM1) and fine (PM2.5) fractions were collected at Krakow urban site from 2nd July 2016 to 27th February 2017 at every third day. Mass concentrations and chemical composition of the submicron and fine fractions were ascertained. Elemental concentrations were determined by X-ray fluorescence technique while concentrations of anions and cations - by the ion chromatography. In turn, black carbon concentrations were determined by measurements of the transmittance of samples. Seasonal variations of the above mentioned parameters for both fractions were estimated and presented in this paper. Based on the chemical concentrations (elements, ions, BC) three main sources of both fractions were estimated and their seasonal contribution are presented. The combustion and secondary aerosols proved to be the main sources of particulate matter pollution in winter season.

2. Materials and methods

2.1. Study area and sampling

The samples were collected in the urban district of Krakow (see map in Fig 1). Air quality of the area is affected by numerous small coal-fired, low efficiency boilers distributed over the city and the traffic through the city (Junninen et al., 2009). Additionally, there are several emitters of pollutants in Krakow: Huta Alcellor Mittal Steelworks in the northern part of the city, Cementownia cement factory, and EC Krakow coal-fired power plant.

Twenty-four hour PM1 and PM2.5 fractions were collected between 2nd July 2016 and 27th February 2017 utilizing low volume LV-3 air samplers with flow rate of 2.3m3/h. The samples were collected onto Teflon membrane filters PTEE (46.2 mm diameter). In total 72 samples of PM1 and 72 samples of PM2.5 were collected every 3rd day during the mentioned period covering three seasons: summer, autumn, and winter.

2.2. Chemical analyses

2.2.1. Elemental concentrations
Teflon filter samples were analyzed for the elements (Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, Rb, As, and Pb) and their concentrations quantified by energy dispersive X—Ray Fluorescence (XRF). PM1 and PM2.5 were analyzed as thin samples by XRF instrument equipped with 2 kW molybdenum tube as the source of X-rays, a capillary X-ray micro-beam optics, a broad X-ray beam

from a molybdenum secondary target for XRF analysis of bulk samples and a beam for total reflection X-ray technique. The excited X-rays are detected by a liquid nitrogen cooled Si(Li) detector (active area $30\,mm^2$, thickness 3 mm, Be window thickness 0.025 mm) with resolution of 170 eV at energy of 5.9 keV.

The measurements were carried out under the following conditions: voltage of 55 kV, current of 30 mA, measuring time of 10,000 s, under atmospheric air. In order to calculate concentrations of different elements, the spectrometer was calibrated using thin-film standards (Micromatter, USA) and verified by the analysis of NIST Standard Reference Material 2783 (Air particulate matter on filter media - Table 1). A proficiency exercise was carried out. It was confirmed that the results obtained for all the elements were very accurate. This exercise involved the analysis of the collected samples, performed by 16 different countries. The XRF spectra collected by the Canberra system (http://www.canberra.com) were quantitatively analyzed utilizing the QXAS package (Vekemans et al., 1994). Detection limit is presented elsewhere (Samek et al., 2017b).

2.3. Inorganic ions concentrations

Concentrations of inorganic anions and cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, NO_3^-, Cl^-, SO_4^{2-}) were analyzed with the isocratic ion chromatography: Two circular filter aliquots (ø 8 mm) per sample were extracted under ultrasonic agitation for 20 min, in either 1.5 mL of extra pure water or in 1.5 mL of the 12 mM methane sulfonic acid (MSA) in order to determine concentrations of anions and cations, respectively.

Ion chromatography (IC) analysis was performed on an ICS-1100 instrument (Thermo Scientific) equipped with an autosampler AS-DV and ion-exchange columns:

- Ion Pac AS22 ($4 \times 250\,mm$) for anions, mobile phase: 4.5 mM Na_2CO_3 + 1.4 mM $NaHCO_3$,
- CS16 ($5 \times 250\,mm$) for cations, mobile phase: 12 mM MSA.

After electrochemical suppression (AERS 500 (4 mm) and CERS 500 (4 mm) suppressors), quantification was performed with a conductivity detector (injection volume 25 μL, flow rate $1.2\,mL\,min^{-1}$).

Calibration was performed against external standards diluted from stock solutions supplied by Thermo Scientific. The limit of detection (defined as 3 x standard deviation for the field blank samples) of the method for atmospheric samples is presented in another paper (Samek et al., 2017b).

2.4. Concentrations of black carbon

Black Carbon was determined by the UV-VIS spectroscopy using Varian Cary 50-Bio UV-VIS spectrophotometer (Agilent). The transmittance was recorded at the 880 nm wavelength, in at least

Fig. 1. The sampling site.

Table 1
Measured and certified contents of elements in NIST SRM2783.

Element	Measured value [ng]	Certified value [ng]
K	6120 ± 4550	5280 ± 250
Ca	11,240 ± 3540	13,200 ± 1700
Ti	1400 ± 170	1490 ± 240
Cr	150 ± 85	135 ± 25
Mn	284 ± 50	320 ± 12
Fe	24,800 ± 1910	26,500 ± 1600
Cu	480 ± 70	404 ± 42
Zn	2350 ± 400	1790 ± 130
Pb	310 ± 64	317 ± 54