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Elemental and carbon isotope composition of total particulate matter in the urban atmosphere of Krakow, southern Poland: summer-winter contrast

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Deterioration of air quality in urban agglomerations is a growing problem of global significance [1]. This spurs research towards better understanding of parameters controlling air quality in urban environment (sources of particulate matter and gaseous contaminants, spatial and temporal variability of air quality, impact of atmospheric dynamics on the air quality, and several others).

Krakow belongs to four largest cities in Poland. With nearly one million inhabitants, rapidly growing car traffic and significant industrial activities, Krakow agglomeration represents a typical urban environment in the eastern Europe. Characteristic features of the local climate are generally weak winds (annual average around 2.7 m s^{-1}) and frequent inversions, extending sometimes over several days, particularly during winter seasons, favor accumulation of pollutants originating from surface emissions in the atmosphere over the city. Krakow ranks among the most polluted cities in Europe. There is an ongoing discussion on the role of different sources of total suspended particulate matter (TSPM) in the city's atmosphere, such as traffic, low- and high-level emissions related to burning of coal for heating purposes, resuspension of street dust, and some others.

The presented work was aimed at exploring possibilities of using carbon isotope composition of total particulate matter collected in Krakow atmosphere, for better characterization of TSPM sources in the city, with the focus on seasonal changes of the character and intensity of those sources. Archived samples of TSPM deposited on filters (sampling interval between 5 and 20 days) and spanning the period 2005 - 2010 [3] were used for this purpose. For each year one pair of filters representing summer and winter conditions was selected. The work comprised also multi-elemental analysis of available TSPM samples using EDXRF technique.

The measurements of ^{13}C and ^{14}C content in the total elemental carbon collected on filters revealed large seasonal variability of these two parameters. The mean fossil-fuel carbon fraction (pFF) derived from AMS radiocarbon analyses was 66.2 and 38.1%, for winter and summer samples, respectively. There was a strong positive correlation of pFF with $\delta^{13}C$, suggesting intensified burning of coal as the main source of fossil fuel derived carbon during winter in the city. Intensified burning of fossil fuels during winter was also reflected in larger percentage of fossil carbon in gaseous CO_2 present in the city atmosphere ($ffCO_2$) during winter. The linear relationship observed between pFF and $ffCO_2$, when extrapolated to $ffCO_2 = 0$ suggest that the main source of fossil carbon in TSPM during summer (extrapolated pFF value of ca. 30%) is related to transport (wearing of car tires and asphalt). The elemental composition of the analysed TSPM samples also showed distinct seasonal variability. This concerns mostly Cl, K, Zn, As, Br and Pb.

References:

[1] WHO's Urban Ambient Air Pollution database - Update 2016 (www.who.int/phe).

[2] M. Zimnoch, P. Wach, L. Chmura, Z. Gorczyca, K. Rozanski, J. Godlowska, J. Mazur, K. Kozak, A. Jeričević. Factors controlling temporal variability of near-ground atmospheric ^{222}Rn concentration over central Europe.Atmospheric Chemistry and Physics, **14** (2014) 9567-9581.