An 11 year study of multipollutant correlations of urban aerosols in Krakow, Poland

A.J. Włodarczyk[1], J. M. Arteaga-Salas[2], T. Jones[3], R. Zimmermann[2], and K. BéruBé[1]

[1]School of Biosciences, Cardiff University, Cardiff, Wales, CF10 3AX, UK
[2]Helmholtz Institute Complex Molecular Systems Environmental Health, Zentrum München, Germany
[3]School of Earth Sciences, Cardiff University, Cardiff, Wales, CF10 3AT, UK

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Presenting author email: wlodarczykaj@gmail.com

Krakow is the most polluted, as far as particulate matter (PM) is concerned, city in Poland. This is an important public concern as Krakow is also the second largest populated Polish city. The specific geomorphological localization of Krakow influences the atmospheric dynamics over the city, resulting in still- or weak-winds promoting air pollution accumulation, especially during the heating season.

Seasonal variability in concentrations and multipollutant correlations of gaseous pollutants (i.e. NO_2, NO, NO_x, SO_2) and PM_{10}, $_{2.5}$ measured over a period of January 2005 to December 2013 were investigated. Data for the study were obtained from reports published by the Voivodship Inspectorate for Environmental Protection in Krakow.

A strong seasonal variation in PM_{10} concentration revealed that during warm months the European Union annual limit value of 40 µg/m^3 was not exceeded, whereas during the heating season, it was exceeded more than twice (Figure 1).

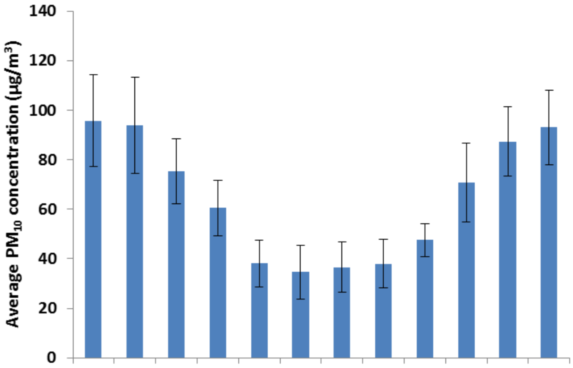

Figure 1. Average monthly PM_{10} over 11 years.

Normalized monthly concentration patterns of all investigated pollutants and temperatures revealed that NO_2 had the most consistent concentration pattern over the year. Conversely, SO_2, $PM_{2.5}$ and PM_{10} levels varied greatly (e.g. SO_2 concentrations in January were more than 100% greater and 54% lower than the monthly average in May). Moreover SO_2 had the strongest negative correlation (r = -0.64) with temperature.

Seasonal correlations between pairs of pollutants were the highest between NO and NO_x (0.99) and between PM_{10} and $PM_{2.5}$ in annual and seasonal terms. The non-heating season (May-August) was characterised by lower coefficients than the heating season (September-April), when coefficients were similar to the annual values. Additionally, the ratios between average concentrations of investigated pollutants were also higher in the heating season.

Transmission electron microscopy (TEM) images confirmed that particles were consistent with the known morphology of fly-ash (Brown *et al.*, 2011) and other combustion-derived PM (BéruBé *et al.*, 1999; Figure 2). For example, individual carbonaceous spheres' forming grape-like bunches of aggregates and agglomerates which are highly-respirable.

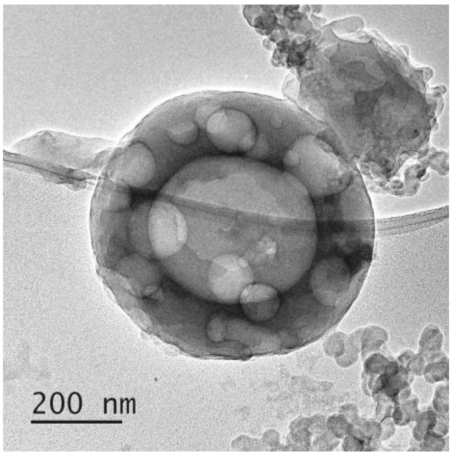

Figure 2. TEM micrograph of $PM_{2.5}$ particles.

Natural factors such as geomorphology, climate and weather conditions have been determined to be the perpetrators of air pollution accumulation over the city. The main source of elevated pollution levels were traffic emissions (i.e. nitrogen compounds) during warm months and residential coal-burning during the heating season.

In conclusion, high annual levels, especially for PM, are greatly affected by measurements from the heating season. This 'seasonality' in $PM_{2.5}$ concentrations should be taken into account when treating $PM_{2.5}$ as a proxy in epidemiological studies for Krakow; as people in colder months spend less time outdoors. Further analysis including *in vitro* toxicology of PM is required to assess its direct effects on human lung biology.

Brown, P., Jones, T. and BéruBé, K. (2011). *Environmental Pollution* 159 (12):3324-3333.

BéruBé, K., Williamson, B., Winters, C., *et al.*, (1999). *Atmospheric Environment*, 33(10):1599-1614.