Temporal variations of carbonaceous aerosol concentrations and sources in the metropolitan area of Kraków, Poland

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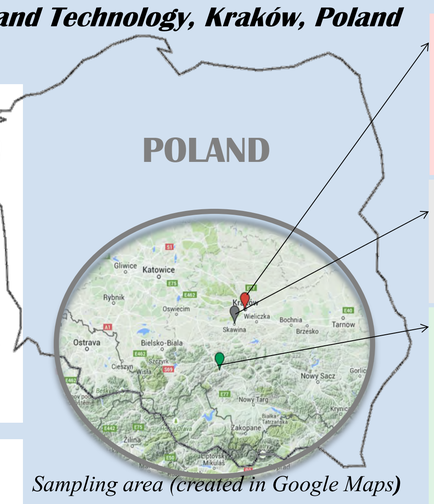
BACKGROUND

The study was launched in relation to repeating problems ambient air quality in Krakow, Poland (Samek, 2012). The concentrations of PM10 and PM2.5 as well as chemical composition (OC,EC, inorganic ions, saccharides, particulate Hg) of both fractions was investigated. This contribution shows the spatial and temporal variation of PM10/PM2.5 and EC/OC ratios, supported by selected tracer compounds in order to identify the most prominent PM sources in the region.



Sampling area (created in Google Maps)

KRAKOW – AGH University
- urban site in the city center
- influenced by mixed PM sources
- sampling at the roof of 3 stories building (~10 m a.g.l)

SKAWINA - AGH sampling point
- industrial town at SE Krakow suburbs
- strongly influenced by industry/energy production (coal)

BIALKA – private terrain
- small village, 60 km SE from Krakow
- rural background site in a private garden
- Sampling 1,5 m above the ground
- influenced by res. heating (coal, wood) and agriculture

METHODS

Sampling campaigns between 2013 and 2015 covered cold and warm periods. PM10 and PM2.5 was collected on quartz fiber filters (Pall Life Science, ø47mm) using low volume samplers of two types (DIGITEL A.G., Twin Dust Zambelli). Samples were taken at three sites, each representing a different environment type. Samples were taken in 24h-48h intervals (cumulated samples for weekends and during sampling campaigns IV and V in Krakow).

	KRAKOW - AGH					SKAWINA		BIALKA	
Period	5.02.-27.02. 2013	14.06.-29.07. 2013	27.01.-17.02. 2014 (18.02.-16.03.2014)	4.11.-21.12. 2014	5.02.-20.03 .2015	21.05.-8.06. 2013	28.12. 2013 – 9.01. 2014	2.03.-16.03. 2013	3.08.-18.08. 2013
Season	cold	warm	cold	cold	cold	warm	cold	cold	warm
Index	**K I**	**K II**	**K III**	**K IV**	**K V**	**S I**	**S II**	**B I**	**B II**

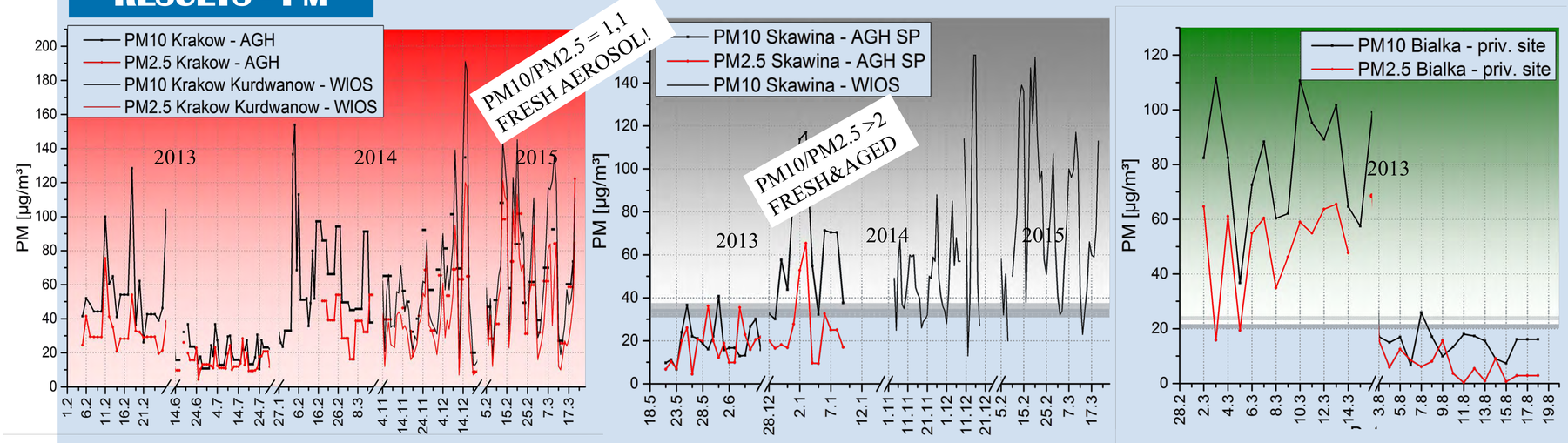
Mass was determined gravimetrically after 48 h conditioning at 20°C, and 50% relative humidity. Circular aliquots (Ø10mm) were cut out of the filters for analysis.

* OC and EC were determined with thermal-optical transmition method (TOT, Sunset Inc.) according to EUSAAR 2 protocol (Cavalli et al., 2010).

* Inorganic ions were analysed by isocratic ion chromatography (ICS 1100, ICS 3000).

* Particulate Hg was analysed by CV-AAS (Nippon, MA 3000).

RESULTS - PM



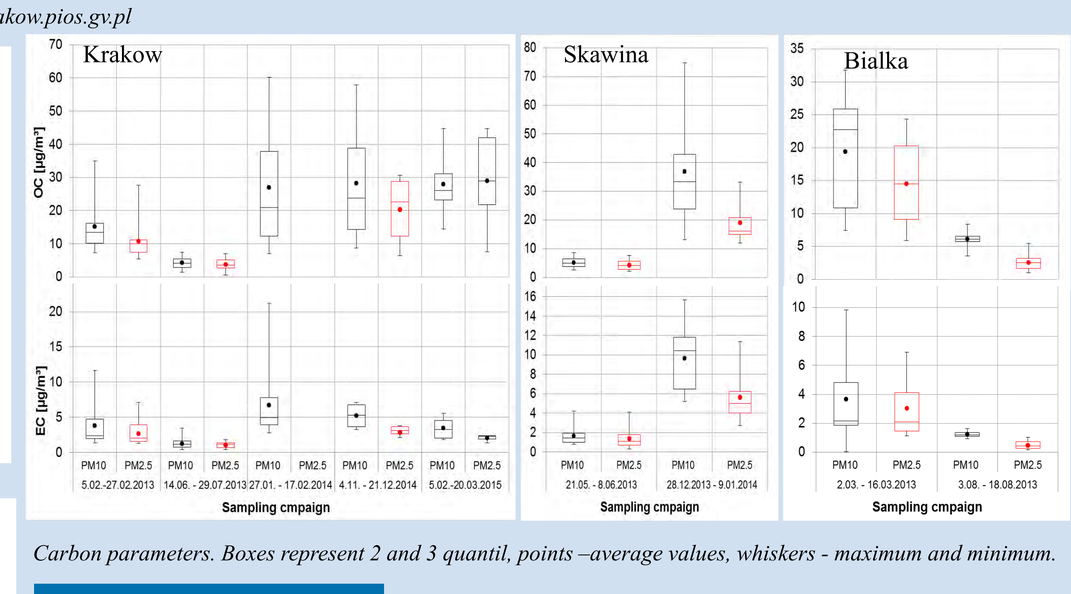
PM10 and PM2.5 concentration trends. Line without points were obtained from local monitoring network (WIOS): www.krakow.pios.gv.pl

Summer PM levels are 2 – 7 times lower than during winter. The highest difference was observed for PM2.5 in Bialka, the lowest for PM2.5 in Skawina. The PM10/PM2.5 ratios are variable. The highest average was obtained for cold season 2013/2014 in Skawina (2,7), which is much higher than the average for the summer period (1,4). The lowest value (1,1) was found for the cold period 2015 in Krakow.

RESULTS – Carbon

Carbonaceous aerosols follow the concentration trends of PM . TC shares are between 25% (K II, PM 10) and 95% (SII, PM2.5). The winter OC and EC concentrations vary tendientially stronger, than during summer. The highest OC concentrations were observed in Skawina and Krakow, while the concentrations in Bialka were lower.

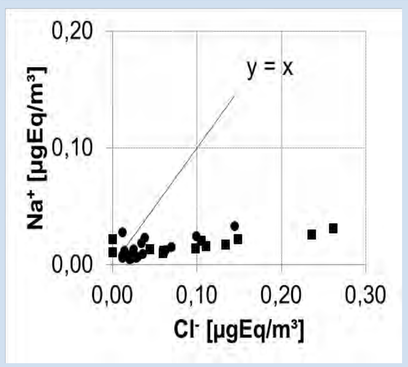
The OC/EC ratios in Skawina (3,1-3,8, for both fractions) is the lowest,. For Krakow and Bilaka the ratios vary between 3,4 – 5,4, only during winter period of 2015 in Krakow OC/EC was found to be extraordinary high (8,1 and 14,9 for PM10 and PM2.5).

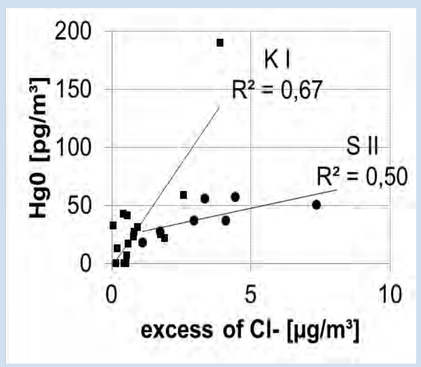


Carbon parameters. Boxes represent 2 and 3 quantil, points –average values, whiskers - maximum and minimum.

RESULTS – Ions & Hg_0

If the side is not under direct influence of marine aerosol, the winter sodium and chloride concentrations can be associated with de-icing salt (Jordan et al., 2015). As such, the molar equivalents of Cl^- and Na^+ are in balance. Here we observe a huge excess of Cl^- ions in winter samples (K I and S II depicted below). In Krakow and Skawina the excessive Cl^- correlate with particulate Hg, which can be associated with coal burning.





for Biaka (rural background):
less Cl^- excess, no distinct relation of Cl^- excess with Hg_0

in the summer period :
Cl^- levels at all sites up to order of magnitude lower, no Cl^- excees

Ionic balance and relation between Hg0 and the excess of Cl- ions . Dots for K I, rectangles for S II

CONCLUSIONS

- Variation of PM10/PM2.5 ratios during cold season points to bigger source variety and secondary aerosol formation related to winter meteorological conditions;
- Lowest OC/EC ratios at industrial site – presence of fresh combustion emissions. Higher ratios for big city; rural background with residential heating influence (mixture of various sources or influence of secondaries);
- Big excess of Cl^- ions, in relation to Na^+ correlate with Hg_0 concentrations and is a hint for coal combustion.

REFERENCES

* Samek, 2012, Nukleonika, 57(4):601−606, * Cavalli et al., 2010, Atmos. Meas. Tech. 3: 79–89
* Jordan et al., 2015, J. Geophys. Res.: Atmos., 120 (2): 678-694

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