

PARTICULATE MERCURY AND CARBON IN URBAN AND NON-URBAN SITES IN POLAND

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Introduction

Mercury is a trace component of ambient particulate matter (PM), carbon is a PM macro-component. However, their common origin (combustion of fuels, thermal processing of minerals and materials containing Hg and C) suggests that they should occur in PM in some association. In Poland, where PM comes mainly from hard and brown coal combustion (Rogula-Kozłowska et al., 2014), this association was supposed to be especially unequivocal.

In the paper, we substantiate the anticipated ties between the occurrences of PM-bound carbon (organic OC, and elemental EC) and both PM₁- and PM_{2.5}-bound mercury (particle-bound mercury, PBM) by applying statistical analysis to four long series of 24 h ambient concentrations of these substances measured at Godów, Złoty Potok, Zabrze, and Warsaw (Poland).

Methods

Three PM sampling sites, Godów, Złoty Potok, and Zabrze, were located in Silesia Province, a region of great impact of the industrial and municipal emissions on the PM (Rogula-Kozłowska et al., 2014). The fourth sampling site was located in Ursynów, a district of Warsaw, and was affected mainly by traffic emissions and air pollutants transported with air masses from southern Poland (Majewski and Rogula-Kozłowska, 2015). Godów and Złoty Potok are villages with relatively weak air pollution; Zabrze and Warsaw are strongly polluted big cities.

The measurements were carried out from January to December 2013 in Złoty Potok and Godów in parallel, and in June-August 2014 and January-March 2015 in Zabrze and Warsaw also in parallel. A high volume sampler was used in Godów (PM_{2.5}), and low volume samplers were used in Złoty Potok (PM_{2.5}), Zabrze (PM₁), and Warsaw (PM₁). The Hg content of PM was determined by applying cold-vapor atomic absorption spectrometry (CVAAS) to thermally decomposed PM samples; an MA-2 analyzer (Nippon Instr. Co, Tokyo, Japan) was used (Pyta and Rogula-Kozłowska, 2016). The OC and EC contents of PM were determined with the use of a Dual-Optical Carbonaceous Analyzer (Sunset Lab. Inc.) using the EUSAAR-2 protocol.

Results

The essential differences in the PM-bound mercury and carbon behaviors between the four sites were in the ambient concentrations (Table 1). This differentiation is due to the difference in the structure of the air pollutants emissions and in the impacts of variations in the sizes of these emissions on the concentrations of PBM, OC, and EC among the sites. However, at all sites, the ambient concentrations of PBM, OC and EC were much higher in the heating than in the non-heating periods. It is an effect of the intensification of the activity of secondary enrichment processes in the circumstances of intensified combustion of fuels and low air temperature, both favorable to condensation and sorption of mercury vapor and carbon compounds to fine PM particles (Rogula-Kozłowska et al., 2014). The scatterplots of the 24 h ambient concentrations of OC and EC against those of PBM (Fig. 1) suggested that the correlations between concentrations PBM and EC and OC exist. The values of the Spearman rank correlation coefficient (ρ_s) were high and positive, indicating the existence of strong correlations between the concentrations of PBM and OC and EC at all four sites. The lowest ρ_s were obtained for the concentrations of PBM and OC in the non-heating periods (Godów

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 $\rho_s < 0.7$, Złoty Potok $\rho_s < 0.5$, Zabrze and Warsaw $\rho_s < 0.4$). At all sites, the strongest correlations were those of the concentrations of PBM with the concentrations of EC, both in the whole measuring periods and in the heating periods (Godów $\rho_s < 0.9$, Złoty Potok and Zabrze $\rho_s < 0.8$, Warsaw $\rho_s < 0.7$).

Season Parameter Godów (PM _{2.5})				Złoty Potok (PM _{2.5})			Zabrze (PM ₁)			Warsaw (PM ₁)			
		PBM	DC	EC	PBM	C	EC	PBM	DC	EC	PBM	C	EC
on-heating*	Mean	46.4	7.7	1.5	40.0	4.9	0.9	17.3	3.3	1.0	5.0	3.1	0.9
	St.dev.	37.7	5.8	1.3	21.7	1.8	0.4	8.7	1.0	0.4	2.0	1.2	0.3
	No.	178	183	182	158	160	159	50	50	50	50	50	50
eating**	Mean	160.6	26.6	3.2	31.0	11.1	2.0	59.6	17	3.4	18.2	5.6	1.4
	St.dev.	100.9	20.7	2.4	51.7	5.6	1.1	47.8	13.6	2.1	11.0	3.7	0.6
	No.	161	164	164	173	179	179	50	50	50	50	50	50

Table 1. Ambient concentrations of PBM (pgm⁻³), EC and OC (µgm⁻³) in Godów, Złoty Potok, Zabrze, and Warsaw.

* January-March and October-December in Godów and Złoty Potok; January-March in Zabrze and Warsaw

** April-September in Godów and Złoty Potok; June-August in Zabrze and Warsaw

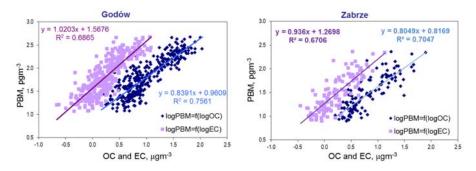


Figure 1. Linear correlation between the concentrations of OC, EC and PBM

Conclusion

The weak correlation between the concentrations of PM-bound OC and PBM in the non-heating periods in all the sites may be attributed to the coal combustion losing its importance as a PM source. The phenomenon could be most clearly seen in Złoty Potok, the site beyond any direct effect of any great permanent source releasing carbon and mercury to the air. However, there still exist quite strong relationships between PBM and the ambient concentrations of PM-bound EC and OC in Złoty Potok as well as in the rest of the sites. It may suggest that PM-bound (both PM₁- and PM_{2.5}-bound) carbon and mercury can be related to each other even within areas under relatively weak and indirect effect of coal combustion.

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