

Distribution of gaseous and particle-bound Hg concentrations at the sites representative for urban and non-urban zones of Silesia Province

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Abstract. The basic features of the distribution of total gaseous (TGM) and particle-bound mercury (PBM) concentrations were determined for a five locations representative for urban (Bielsko-Biała, Lubliniec, Zabrze) and rural areas (Godów, Złoty Potok) of Silesia Province. Gaseous mercury concentrations were measured (1) continuously - the automatic 1h TGM measurements in Złoty Potok and Zabrze and (2) non-continuously manual 24h TGM measurements with a pre-concentration of the Hg on gold traps (Bielsko-Biała, Lubliniec, Godów). The PBM concentrations were measured non-continuously by taking PM_{2.5} samples. The Hg content was determined by using a CVAAS method. The highest average concentration of TGM was recorded in Zabrze (2.8ng/m³), significantly lower (2.0ng/m³) in Bielsko-Biała and in the non-urban station in Godów, the lowest concentration (<2.0 ng/m³) was observed in Lubliniec and at the regional background station in Złoty Potok. The results obtained for TGM concentrations exceeded the European average level of 1.5 ng/m³ (AirBase, 2014). The highest average PBM concentration, associated with PM_{2.5}, was obtained in Zabrze (70pg/m³), more than 20% lower results were obtained in Bielsko-Biała and Godów, finally, the lowest one (lower by about 40% in comparison with Zabrze) were obtained in Lubliniec and Złoty Potok. Moreover, an enrichment of Hg concentration in PM was observed with the increasing of the PM content, during the heating season.

1 Introduction

Mercury (Hg) is a naturally occurring element found in the environment in metallic form (elemental mercury Hg⁰ in liquid or gaseous state) or in various inorganic (mercuric chloride HgCl₂, mercuric sulphide HgS, mercurous chloride HgCl) and organic compounds (methylmercury MeHg, ethylmercury EtHg). Mercury is a persistent substance that comes from natural and anthropogenic sources. It is a toxic pollutant, causing adverse health effects on humans and wildlife. Released to the atmosphere it can be transported over long distances and deposited on the Earth's surface, leading to contamination of aquatic and terrestrial ecosystems. Atmosphere is the main pathway for Hg distribution on a global and

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regional scale. Atmospheric Hg is dominated (95-99%) [1-2] by the gaseous elemental mercury (GEM, Hg^0) with the background concentrations in the Northern Hemisphere from 1.3 to 1.7 ng/m^3 [3]. Other forms of atmospheric Hg are operationally defined as reactive gaseous mercury (RGM) and particulate bound mercury (PBM). Their concentrations are much lower (expressed in pg/m^3). Despite this, RGM and PBM are essential for mercury removing from the air by wet and dry deposition [1].

Mercury can undergo methylation by aquatic biota and bioaccumulation in aquatic food chains including fish and shellfish. The consumption of contaminated seafood and rise is the main source of MeHg intoxication, which is known human neurotoxin, especially dangerous for foetus [4]. Organic and inorganic mercury exposure has also been proven to cause elevated risks for cardiovascular diseases and negative impacts to the reproductive and immune systems. Exposure to inorganic mercury by the general population and in occupational settings is primarily through inhaling elemental mercury vapours [5].

Over geological time, Hg existing naturally in the Earth's crust ($\sim 80 \mu\text{g}/\text{kg}$) has been released to the upper layer environment via the weathering of rocks, volcanic and geothermal activity, fires, movement of land water, and oceanic upwelling [5]. These are primary natural sources. Secondary natural sources redistribute mercury among ecosystems due to Hg historical emissions through the biomass burning, the land use changes, and the mechanisms of gaseous mercury exchange between the air and the water, top soil, or snow-ice pack surfaces [6]. There are several estimates on Hg emissions of natural origin in scientific literature, ranging from 3600 Mg/yr to 5300 Mg/yr [6]. In the EU GMOS project, the inventory of these emissions (primary and secondary) were assessed to be 5207 Mg/yr [7]. The major anthropogenic sources of global mercury emissions to the atmosphere are artisanal and small-scale gold mining, combustion of fossil fuels for power and heat generation, industry of non-ferrous metals, cement production and large-scale gold production [8]. According to the AMAP/UNEP inventory, the anthropogenic mercury emissions have been estimated to 1960 Mg/yr [8]. Therefore these emissions can be regarded as the main factor disrupting the natural (biogeochemical) mercury cycling. Due to anthropogenic emissions, current average mercury levels in the atmosphere are about 3–6 times higher than in the preindustrial atmosphere, resulting in a significant increase in human and wildlife exposure [9].

Monitoring of various forms of atmospheric mercury is a key factor in the assessment of the effectiveness of activities aimed at reducing the emission of mercury and assessing the health risk related to that problem. This applies in particular to inhabited areas, with a high Hg emissions levels. Poland, according to EEA data, is the country with the highest Hg emissions in the EU (Figure 1).

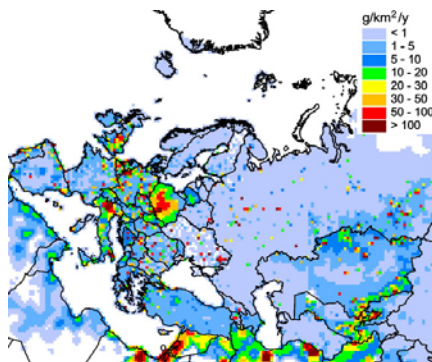


Fig. 1. Spatial distribution of Hg anthropogenic emissions over the EMEP domain in 2015 [10].

The amount of this emissions, according to the data from 2015 was estimated at 11 Mg, which consist 18.6% of the whole emission in the EU [11]. The results of the EMEP (European Monitoring and Evaluation Program) modelling show that the most polluted area of Poland is the Silesia Province [12]. These results become a reason for the launching in the period from January 2014 to December 2015 an extended atmospheric mercury research program in the Silesia Province. The project was realized in Institute of Environmental Engineering of the Polish Academy of Sciences (IEE PAS) in cooperation with the Regional Inspectorate for Environmental Protection (RIEP) in Katowice (measurements were carried out at the stations belonging to RIEP, PM samples were partially collected by the RIEP service). The results of TGM and PBM studies were presented in this paper.

2 Sampling sites

The measurements were conducted at five sites located in different parts of the Silesia Province, with a different topographical, emission and land use conditions. Three stations were located in a typical urban areas: (a) in Bielsko-Biała, at Kossak-Szcucka St., city with a population about 173 thousand people, located in the southern part of the Silesia Province, in the foothills of the Beskidy mountains; (b) in Lubliniec at Piaskowa St., city inhabited by a 24 thousand people, located in the western part of the province; (c) in Zabrze, at Skłodowska-Curie St., city with a 177 thousand inhabitants, located in the central part of the province, within the Upper Silesian Agglomeration, which is a densely populated and the most industrialized part of Poland. Zabrze, among all of the 14 cities of the Upper Silesian Agglomeration, has the least developed heating network. The other two measurement sites were located in a non-urban zones in a typical rural areas: (a) in Złoty Potok – a village inhabited by 1200 people, located in the north-western part of Silesia Province, about 20 km south-west of the city Częstochowa, and 45 km north west of the borders of the Upper Silesian Agglomeration; the station is surrounded by farmlands and arable land; and, being located at relatively weakly polluted area, it serves as regional background station for Silesia Province; (b) in Godów, at a Glinki St., a village inhabited by 2000 people, located in the southern part of Silesia Province, just near the Polish-Czech border and the Moravian-Silesian Region; the station is surrounded by meadows, farms and detached houses.

3 Measurement methods

3.1 Automatic measurements of gas-phase mercury

In Zabrze and Złoty Potok the concentration of gaseous mercury was measured continuously by using an automatic Tekran 2537B analyzer (Tekran Instr. Co.). The mercury present in the air was pre-concentrated with forming of Au-Hg amalgam onto a gold trap. After that, a thermal desorption and cold vapour atomic fluorescence spectrometry analysis (CVAFS), at wavelength $\lambda = 253.7$ nm was performed. Two Au sorbent tubes were working alternately in the analyzer, which ensured continuity of sampling. In Złoty Potok the TGM concentration was measured by Tekran 2537B, working as a separate module collecting results in every 5 minutes. However, in a RIEP data acquisition centre the measuring results were archived as 1-hour averages. On the other hand in Zabrze, Tekran 2537B is a module of much more advanced measuring system, allowing to the Hg speciation analysis, and it works in a 2 hours cycles (1 hour of sampling and an hour of both PBM and RGM forms desorption). Thus the frequency of results receiving in Zabrze is twice less. All the operational parameters of the analyzers –and their

calibration methods were the same. The analyzers were calibrated every day by using an internal Hg⁰ permeation tube and periodically by using an external gas standard. The detection limit of Hg⁰ for the measurement conditions in both cases was equal 0.06 ng/m³ and the precision of analysis was 2%.

3.2 Manual measurements of gas-phase mercury

Manual measurements of gaseous mercury in Bielsko-Biała, Godów, and Lubliniec were carried out in 24-h intervals with the frequency of minimum 7 measurements per month, equally distributed during the year. Air samples were collected using sorbent tubes (gold traps) and gas aspirators operating with a flow rate of 30 dm³/h. Besides the current samples, a blank transportation samples were also made. For the analysis, quartz tubes filled with gold-coated diatomite (M165 tubes by Nippon Instruments Co.) were used. The inlets of the tubes were protected with a quartz wool stoppers. MA-2 analyzer (Nippon Instruments Co.) was used for a chemical analysis of collected samples. The analysis was based on a thermal decomposition of samples in zero-air conditions (in temperature >600°C) and pre-concentration of the released Hg on the internal gold trap. After that, mercury in the form of Au-Hg amalgam was desorbed in a high temperature (>600°C) and analyzed by a cold vapour atomic fluorescence spectrometry analysis (CVAFS), at wavelength $\lambda = 253.7$ nm. The detection limit of a mentioned method for 24-h samples, at a flow rate equal 0.5 dm³/min was 0.15 ng/m³.

3.3 PM sampling and determination of particulate mercury

Particle mercury bound with the respirable fraction PM_{2.5} (24-h samples) were analyzed at all stations. In Lubliniec, PM₁₀- and PM₁-bound Hg were also determined. The measurements of PBM concentrations were performed with the frequency of minimum 7 measurements per month, equally distributed during the year, except for Godów and Złoty Potok, where the concentrations were determined every day. The samples of PM were collected onto quartz fiber filters using a low volume samplers (LVS) with automatic filters changers and the proper PM sampling heads. Mikro PNS samplers were used in all sites except Lubliniec, where 2-channel (PM₁, PM_{2.5}) Hydra Plus LVS (FAI Instruments s.r.l.) was installed and Godów with a high volume DHA-80 sampler (Digitel Elektronik AG) for PM_{2.5}. Immediately before and after sampling, the filters were conditioned and weighed. The procedures for conditioning, weighing, storage, and transport of the analysed samples and a blank sample preparation, were conducted according to the QA/QC procedures of the reference method for gravimetric measurements (PN-EN 12341:2014) and were described in detail in Pyta et al.[13]. The Hg content was determined by using CVAAS method, based on thermal decomposition of PM samples using the MA-2 analyzer [13]. The limits of detection and quantification were 0.094 and 0.283 ng, respectively. The average recovery of SRM was 96%. The repeatability was 3.9% for SRM and its average recovery was 96%.

4 Results

4.1 Gas-phase mercury

Statistical parameters of the measurement series of TGM concentrations were summarized in table 1, with a distinction on a summer season (a non-heating period from April to the end of October) and winter (heating) season (the other 6 months). Phrase “total” denotes a whole measurement period. At the station in Zabrze, a higher TGM concentrations were

recorded in summer season than in winter. This was due to the elevation of the air inlet (14 m a.g.l.), which allowed for the recording of concentrations caused by higher local emitters in summer season. In winter, the influence of higher emitters was undetectable due to the thermal inversion phenomenon, which prevents the pollutants to reach the ground level.

Table 1. Total gaseous mercury concentrations [ng/m³] – the descriptive statistics of 24-h and 1-h measurement series at urban and rural stations in Silesia Province, 2014-2015.

Statistical parameter	Urban stations			Rural stations	
	Bielsko Biala	Lubliniec*	Zabrze**	Godów*	Złoty Potok**
Summer season					
Mean ± SD [ng/m ³]	2.0 ± 0.4	1.9 ± 0.3	3.0 ± 5.0	2.0 ± 0.4	1.6 ± 0.4
Range [ng/m ³]	1.3 - 3.9	1.3 - 2.8	1.0 - 199.4	1.3 - 3.8	0.81 – 6.0
Winter season					
Mean ± SD [ng/m ³]	2.0 ± 0.4	2.0 ± 0.5	2.6 ± 1.4	2.0 ± 0.4	1.84 ± 0.5
Range [ng/m ³]	1.4 - 4.4	1.2 - 5.1	1.2 - 32.6	1.3 - 2.8	0.80 - 14.0
Total					
Mean ± SD [ng/m ³]	2.0 ± 0.4	1.9 ± 0.4	2.8 ± 3.6	2.0 ± 0.4	1.7 ± 0.5
Measur. No.	179	178	7739	180	15196

* 24-hour data;

** 1-hour data

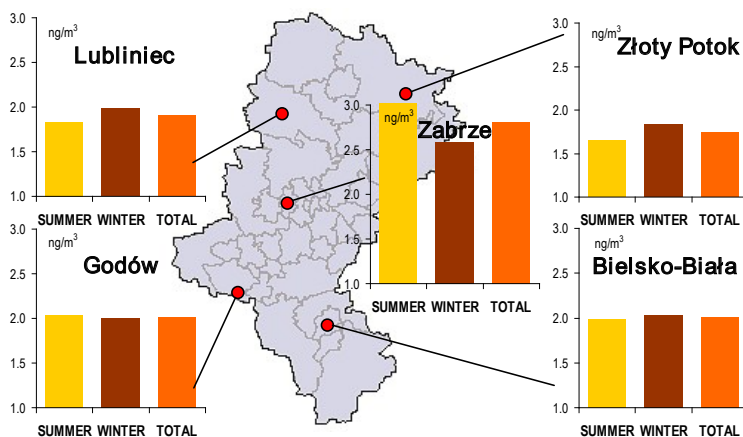


Fig. 2. Total gaseous mercury concentrations [ng/m³] averaged over summer and winter seasons, and the whole measurement period - Silesia Province, 2014-2015.

4.2 Particle-bound mercury

Table 2 summarizes the statistical parameters of the measurement series of ambient PM_{2.5}-bound Hg concentrations [pg/m³], and in Table 3 these concentrations were expressed as Hg contents in PM_{2.5} samples [ng/mg]. This allows to observe the phenomenon of enrichment of the PM samples in Hg in winter season and explains a higher increase in PM-Hg concentrations in this period than it should be resulted in seasonal variability of PM concentrations. The results of additional (simultaneous) measurements of Hg content in PM₁₀ and PM₁ samples in Lubliniec were summarized in Table 4.

Table 2. PM2.5-bound mercury concentrations [pg/m^3] – the descriptive statistics of 24-h measurement series at urban and rural stations in Silesia Province, 2014-2015.

Statistical parameter	Urban stations			Rural stations	
	Bielsko Biała	Lubliniec	Zabrze	Godów	Złoty Potok
Summer season					
Mean \pm SD [pg/m^3]	31.1 \pm 27.7	21.0 \pm 20.0	27.7 \pm 18.6	20.6 \pm 14.2	22.9 \pm 12.9
Range [pg/m^3]	6.4 – 147.0	6.5 - 152.4	7.6 - 121.06	6.0 - 121.2	7.4 - 82.5
Winter season					
Mean \pm SD [pg/m^3]	75.7 \pm 83.1	58.0 \pm 55.5	118.7 \pm 106.6	63.3 \pm 48.8	54.8 \pm 44.3
Range [pg/m^3]	8.9 - 517.5	11.0 - 306.9	18.8 - 565.7	8.4 - 431.7	7.7 - 281.7
Total					
Mean \pm SD [pg/m^3]	52.4 \pm 64.6	40.8 \pm 46.5	69.8 \pm 86.5	41.6 \pm 41.6	38.5 \pm 36.0
Measur.No.	291	245	255	709	652

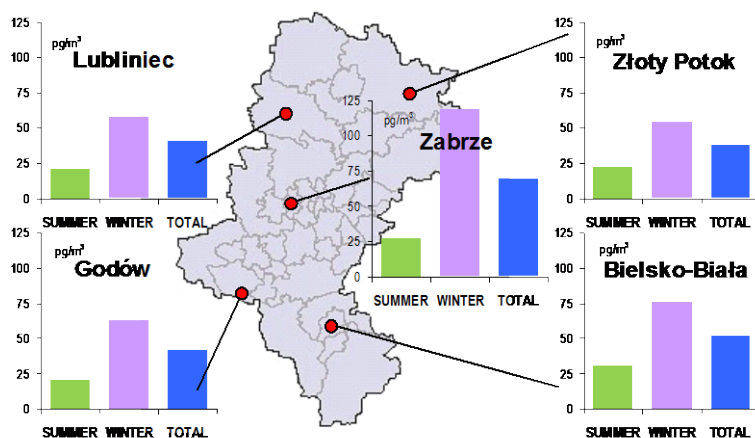


Fig. 3. PM2.5-bound mercury concentrations [pg/m^3] averaged over summer and winter seasons, and the whole measurement period - Silesia Province, 2014-2015.

Table 3. Mercury contents in PM2.5 samples [ng/mg] – the descriptive statistics of 24-h measurement series at urban and rural stations in Silesia Province, 2014-2015.

Statistical parameter	Urban stations			Rural stations	
	Bielsko Biała	Lubliniec	Zabrze	Godów	Złoty Potok
Summer season					
Mean \pm SD [ng/mg]	1.9 \pm 1.5	1.3 \pm 0.9	1.7 \pm 0.9	1.0 \pm 0.6	1.7 \pm 1.0
Range [ng/mg]	0.5 - 8.8	0.3 - 5.4	0.6 - 7.4	0.4 - 4.5	0.5 - 7.0
Winter season					
Mean \pm SD [ng/mg]	2.1 \pm 1.5	1.4 \pm 1.1	2.3 \pm 2.2	1.4 \pm 0.9	2.3 \pm 1.4
Range [ng/mg]	0.6 - 9.8	0.5 - 7.1	0.6 - 12.7	0.4 - 5.8	0.5 - 8.9
Total					
Mean \pm SD [ng/mg]	2.0 \pm 1.5	1.4 \pm 1.00	1.9 \pm 1.7	1.2 \pm 0.8	2.0 \pm 1.2

Table 4. PM10 and PM1-bound Hg concentrations [pg/m³] and Hg contents in these PM fractions [ng/mg] – the descriptive statistics of 24-h measurement series at the station in Lubliniec, 2014-2015.

Statistical parameter	PM10-bound Hg		PM1-bound Hg	
	Concentr. [pg/m ³]	Content [ng/mg]	Concentr. [pg/m ³]	Content [ng/mg]
Summer season				
Mean ± SD	26.99 ± 21.69	1.2 ± 0.8	12.42 ± 8.22	1.7 ± 1.1
Range	9.81-165.34	0.3 - 7.2	4.77-62.93	0.4 - 5.3
Winter season				
Mean ± SD	64.61 ± 61.76	1.4 ± 1.2	24.71 ± 17.32	1.6 ± 0.9
Range	9.5-432.84	0.4 - 8.2	7.6-97.46	0.6 - 5.2
Total				
Mean ± SD	45.99 ± 50.07	1.3 ± 1.00	18.60 ± 14.88	1.7 ± 1.0

5 Conclusions

The highest average TGM concentration in 2-years period between 2014-2015 was recorded in Zabrze, within the Upper Silesian Agglomeration (2.8 ng/m³). A characteristic feature of the TGM concentrations distribution at this station was a higher TGM level in summer months than in winter season. In winter, the impact of a numerous local emission sources, including high emitters related to commercial power industry, is hindered by the inversion layers. A clearly lower average concentration of TGM (2.0 ng/m³) was recorded at the second station of urban background in Bielsko-Biała and in the border village of Godów. In both cases, obtained average seasonal concentrations were the same, which may indicate on the other sources of Hg emissions than combustion of fuels for heating purposes, like eg. the advection of polluted air masses. The lowest TGM levels were observed in the suburbs of Lubliniec (1.9 ng/m³) and at the station of regional background in Złoty Potok (1.7 ng/m³). These were the only two locations wherein in the yearly distribution of TGM a higher share of the heating season was noted, probably as a result of Hg emissions from the local house furnaces (Lubliniec) or its advection from urban and industrial areas (Złoty Potok). The results obtained for TGM concentrations exceeded the European average level of 1.5 ng/m³ (AirBase, 2014).

The highest average concentration of PM2.5-Hg was observed in Zabrze (70 pg/m³) and it was 26% higher than in Bielsko-Biała (52 pg/m³). PM2.5-Hg concentrations at the other 3 sites were very similar and lower by about 40% than in Zabrze (Godów – 42 pg/m³, Lubliniec - 41 pg/m³, Złoty Potok - 39 pg/m³). Comparison of the obtained results with a literature data (for North America and Europe) shows that concentrations of particle-bound mercury in urban and suburban areas remained at the high level, as a result of higher PM2.5 concentrations in Silesia Province. In all of the analyzed locations, particle Hg concentrations were higher in winter season than in the summer, same as the PM2.5 concentrations. Nevertheless, it was noted that during the heating season there was an enrichment of PM by the mercury, significantly higher than it could be expected based on the proportion of the seasonal PM2.5 concentration changes. This is the result of a higher primary Hg emissions from the fuel combustion in this period, as well as lower air temperatures, which can favor the sorption of Hg on aerosol particles.

Measurement results of Hg content in PM10, PM2.5, and PM1 in Lubliniec showed that 77% of PM10-bound Hg mass was associated with the respirable particles (PM2.5) and nearly half mass of PM10-bound Hg was found in PM1 fraction (46%). This distribution of

Hg indicates that the dominant sources of local emissions are the solid fuel combustion processes. The high content of Hg in fine particles of aerosol, that can reach to the lungs (PM_{2.5}), and that, which can penetrate through the pulmonary alveolus to the bloodstream (PM₁) are particularly dangerous for health, by inhalation of PM-bound mercury.

The work was carried out thanks to the financial support of the Regional Environmental Protection Fund in Katowice, in cooperation with the RIEP Monitoring Department in Katowice and the RIEP Laboratory in Częstochowa. The TGM concentration data in Złoty Potok came from the RIEP air monitoring station (<http://powietrze.katowice.wios.gov.pl>).

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