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LONG-TERM MEASURMENTS

OF ATMOSPHERIC MERCURY SPECIES (TGM, TPM)

AND Hg DEPOSITION IN THE SILESIAN REGION, POLAND

– CONCEPT OF THE MERCURY DEPOSITION COEFFICIENT

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Astract: The aim of this work was to identify concentration levels of different chemical forms of mercury (TGM, TPM) in the ambient air in selected areas of the Silesian Region, characterized by low and high mercury emission. Based on the obtained data TGM and TPM concentration levels were determined. The project also focused on determination of dry and wet deposition of mercury compounds. Data concerning TGM and TPM flux rates in the ambient air and data on mercury deposition were used to determine a deposition coefficient. The coefficient was calculated as a share of mercury deposition on the land surface (dry and wet) to the amount of this contaminant transported with loads of air in the form of TGM and TPM in a given measurement station. At both monitoring stations the deposition coefficient did not exceed 0.2 %. The idea of calculating the deposition coefficient based on the analysis of TGM and TPM flux rate is a new solution. The proposed deposition coefficient allows to quantify information on a selected contaminant concentration and its potential impact resulting from deposition. Further studies on the deposition coefficient may contribute to the development of methods for estimating the impact of contaminants contained in the ambient air on other environmental components based on the analyses of the contaminant flux rate.

INTRODUCTION

For many years mercury in the atmospheric environment has been perceived as a global pollutant. Once released into the environment it remains there forever and does not disappear. The emitted mercury compounds can be transported over long distances. Mercury present in the atmosphere accumulates in the form of wet and dry deposition entering into the natural circulation and migrating among different ecosystems. In recent year's mercury release into the environment, its transformation and chemical reactions have evoked great interest, but despite numerous studies in this field many of these phenomena still remain unexplained, e.g. Higher TGM concentrations in summer in comparison to winter in Polish coastal zone and Silesia Region [1–4], which might be

caused by growing temperature and emission of mercury vapors from the earth surface to the atmosphere.

Generally mercury in the atmosphere occurs in three forms: Total Gaseous Mercury – (TGM) containing Hg^0, CH_3Hg, and $(CH_3)_2Hg$; Reactive Gaseous Mercury (RGM) with mercury compounds in a divalent ionic form (Hg(II)), and Total Particulate Mercury (TPM), i.e. mercury adsorbed on particles of dust. In uncontaminated areas the share of TGM in ambient air amounts to 95–99% of its total content. Other forms of mercury include: mercury vapor present in the divalent ionic form – RGM and TPM adsorbed on particles [5]. These three different forms of mercury have different physical and chemical properties and different residence time in the atmosphere. TGM, RGM and TPM both in a global and regional scale are deposited on the earth surface – dry and wet deposition [5, 6]. The main anthropogenic sources of mercury emissions to the air are: combustion of solid, liquid and gas fuels, cement production, steel and non-ferrous metals production, industrial processes using mercury and its compounds and waste incineration. TGM in ambient air is maintained for one or two years and is transported over long distances. However, RGM and TPM remain in the air for several days to several weeks and can be rapidly deposited both on a local and regional scale [5, 7].

Mercury and its compounds present both in a gaseous and liquid phase may enter into chemical reactions with many pollutants present in ambient air. In the liquid phase (drop of rain or fog), elemental mercury can react with ozone, hydroxyl ions, and halogens. Products obtained in these reactions are unstable and mercury in these products is converted to the form of Hg^{2+}. Such reaction products as HgO, $HgCl_2$, and $HgBr_2$ are usually embedded in a particle and referred to as TPM. The oxidized form of mercury may enter into further reactions with pollutants in the atmosphere. The most important one is the reaction of oxidized forms of mercury Hg^{2+} with SO_3^{2-}, derived from sulfur dioxide contained in the atmosphere [8, 9]. Both forms of mercury Hg^0 and Hg^{2+}, which are present in the liquid phase, may participate in a number of other reactions to form more or less stable products [10].

In the world, concentrations of TGM in ambient air vary quite significantly. In unpolluted areas of China, South Korea, Japan and the USA the TGM contents in ambient air range from 0.52 to 21.03 ng/m^3 [11–17]. Concentrations of TPM in ambient air also differ a lot. In the period of 2000–2003 the concentration of TPM was investigated in measurement stations located mainly in uninhabited areas of the USA. The obtained concentration values varied from 1 to 30 pg/m^3 [18–19]. In Seoul (South Korea), which is characterized by high traffic and high population density, in the period of 2005–2006 the average concentration of TPM in ambient air was 23.9 pg/m^3 [20]. In China, in the measurement campaign conducted in summer 2001, concentrations of TPM in ambient air ranged from 22 to 334 pg/m^3, whereas in the winter season the values varied from 148 to 1984 pg/m^3 [21]. In the period of 2005–2006, concentrations of TPM analyzed at the same measuring station ranged from 5.2 to 135.7 pg/m^3 [22]. In Table 1 TGM and TPM concentrations measurements made in Europe and Poland are presented.

As it can be seen from the data presented above, concentrations of different forms of mercury in the atmosphere are quite well recognized in the world, however, in Poland this issue is poorly identified. Most of the available research data are quite old, which can make them invalid. Current levels of mercury in the atmosphere may be significantly different from the data presented in the literature. This can be confirmed by the fact that the

Table 1. TGM and TPM concentrations measurements in Europe and Poland

Locations	Sampling period	TGM (ng m^{-3})	TPM (pg m^{-3})	Reference
Mace Head (Ireland)	1999–2003	1.65–1.79	-	[1]
Zingst (Germany)	1999–2003	1.59–1.66	-	
Mace Head (Ireland)	5 days in 1995	1.2–3.8	4.5–115	[25]
Ny-Alesund, Pallas (Finland)	1996	0.68–3.55	0.1–20	[6]
Göteborg (Sweden)	2005	1.37–1.97	3.89–20.26	[26]
Bratislava, Kosice, Zilina (Slovakia)	9 month 1996–1997	1.06–35.66	Nd – 4470	[27]
Pallas (Finland	1–2 samples per week – 1999	1.41	1.4	[28]
Rorvik Aspverten (Sweden)		1.37–1.52	7.6–8.7	
Neuglobsow, Zingst (Germany)		1.61–1.93	25.2–34.6	
Mace Head		1.66	-	
Lichwin (Poland)	August 2003––February 2004	1.20–7.02	20–1345	[29]
Hel Peninsula (Poland)	From June to August 1997 – from February to March 1998	0.8–7.5	-	[30]
Gliwice (Poland)	From October 2006 to April 2007	4.1–9.1	61–186 (PM10) and 53–141 (PM2.5)	[31]
Mazowieckie and Lubelskie Voivodeship (Poland)	2005	-	24–1918 (PM10)	[32]
Polish zone of the southern Baltic Sea	From December 2006 to December 2007	-	2–142	[33]
Coastal zone of the Gulf of Gdansk (Gdynia, Poland)	From December 2006 to December 2007	1.2	-	[34]
Gliwice (Poland)	November 2007, March 2008	4.1–9.1	-	[35]
Zabrze, Złoty Potok (Poland)	From August 2011 to July 2012	1.50–122.1	0.32–4786,0	[2]

total mercury emission in ambient air in 2005 in Europe was about 226.5 Mg [23]. Total mercury emission in ambient air in Poland in 2005 was about 21.2 Mg. The total emission of mercury into the atmosphere in Poland accounts for about 9% of its total emissions in Europe. According to the most optimistic scenarios mercury emissions to the atmosphere in 2020 may decrease by 40 to 60% [24], which will be reflected in the measured ambient concentrations of this metal. A similar situation can be observed in the case of mercury compound deposition. The content of mercury in the atmospheric precipitation or wet and dry deposition of mercury compounds is an issue poorly identified in the world. However, in such countries as Japan, Sweden and the United States there are (or were) special monitoring programs to organize mercury deposition studies in the whole country or in designated research areas. In Table 2 Hg concentrations in wet and dry deposition in Poland and in the world are presented.

Table 2. Hg concentrations in wet and dry deposition in Poland and in the world

Locations	Sampling period	Hg in wet deposition ($\mu g\ m^{-2}\cdot y^{-1}$)	Hg in dry deposition ($\mu g\ m^{-2}\cdot y^{-1}$)	Reference
10 sampling points in Japan	From December 2002 to November 2003	12.8	8.0	[36]
Northern East United States	2002	3.1–9.5	-	[37]
Underhill (United States)	1995–2006	0.25–2.5	-	[38]
5 sampling points in Guizhou, China	From January to December 2006	24.8–39.6	-	[39]
Sampling points located in Sweden, Finland, Deutschland and Northern Ireland	1995–1999	2.0–10.0	-	[28]
Katowice (Poland)	1996–1997	159	48	[40]
Zabrze (Poland)	2009	26.9–31.8	-	[41]

SAMPLING SITE

The measurement campaign was performed in the Upper Silesian Industrial Region (Southern Poland) – Katowice (X: 266466.68, Y: 498257.55, N: 50° 15' 55.37', E: 18° 58' 31.96') and Pszczyna (X: 233434.83, Y: 496924.94, N: 49° 58' 5.52'', E: 18° 57' 25.59') (see Fig. 1).

Upper Silesia is the biggest industrial region in Poland. In this area there are 21 mines, which belong to two mining holdings. There are also many mines that do not function nowadays, but which contributed to degradation of the natural environment in this region in the past. Many other industries, such as metallurgical, power, engineering and chemical industry, developed there as well. The first measurement station is Katowice, which is
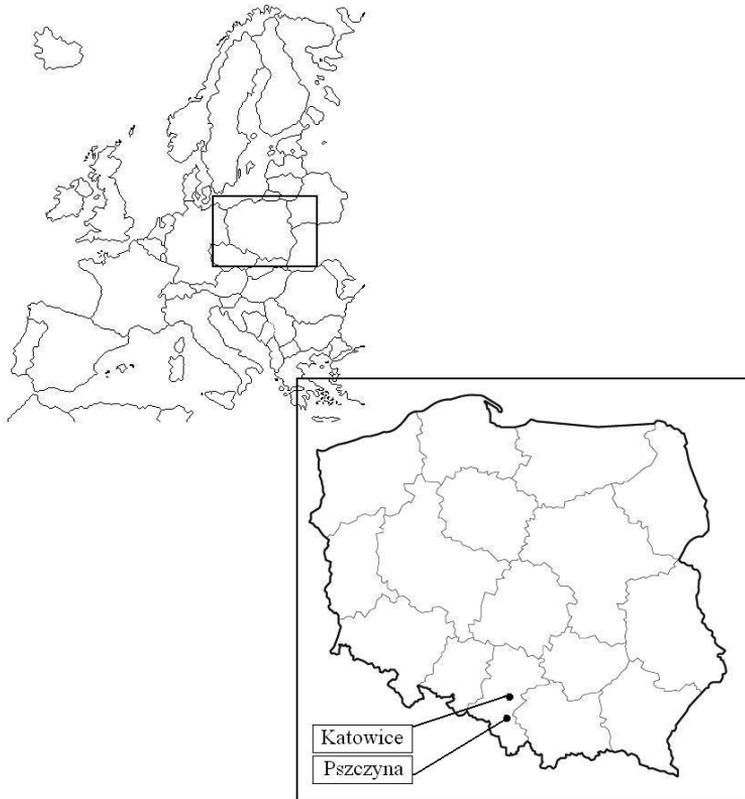
Fig. 1. Measurement stations in Katowice (X: 266466.68, Y: 498257.55, N: 50° 15' 55.37', E: 18° 58' 31.96')
and Pszczyna (X: 233434.83, Y: 496924.94, N: 49° 58' 5.52'', E: 18° 57' 25.59'), Poland

located in the central part of the Upper Silesian Industrial Region and which constitutes an urban background for a residential town of the population of 250–500 thousand of inhabitants. The second measurement station is Pszczyna with a population of about 26.5 thousand of inhabitants.

METHODS

Tgm measurements

For determining TGM concentration in ambient air the RA-915+ – LUMEX analyzer was used [42]. Its operation is based on differential Zeeman atomic absorption spectrometry technique, which is implemented using the direct Zeeman effect (Zeeman Atomic Absorption Spectrometry using High Frequency Modulation of Light Polarization ZAAS-HFM). A radiation source (mercury lamp) with a mercury resonance line l=254 nm was used. A multipath cell with an effective length of about 10 m was applied to enhance the sensitivity of the analysis. A sampling flow rate of 20 l min^{-1} was used. The analyzer was operated in a continuous mode (time of individual measurement

– 60 seconds). Air samples were collected at the level of 2.2 m above the ground. The TGM detection limit for this method is 0.24 ng·m^{-3}.

Tpm measurements

TPM samples for mercury analyses were collected on 47 mm Teflon filters (0.45 mm pore size) housed in acid cleaned Teflon filter packs at a nominal flow rate of 10 l min^{-1} [29]. After sampling the filters were placed into acid-cleaned Petri dishes and stored in a refrigerator. Upon completion of the measurement campaigns the filters were brought to the laboratory for analysis. The samples were transferred to Teflon vessels for mineralization in a microwave oven (*Multiwave 3000* – Anton Paar, Austria) using concentrated nitric acid and hydrochloric acid (1:1) (Hg≤ 0.000001%, pro analysis, Merck, Germany). Then the samples were heated in the microwave oven for 50 minutes at the temperature of 160°C and pressure 20 bars. Concentration of mercury was determined by the "cold vapor" atomic absorption spectrometry using the RA-915^{+} analyzer equipped with RP-91 attachment produced by Lumex Ltd. The attachment is equipped with 2 bubblers, in which the sample is placed together with a known volume of the reducing agent. The reducing agent ($SnCl_2$) changes Hg^{2+} to its atomic state. Mercury vapors are transported to the analytical cell where mercury atoms are directly detected. To check the operation of the analyzer the calibration solutions were prepared from the reference material in the concentration range from 0 to 500 ng L^{-1}. Linear correlation coefficient of the calibration curve was $R^2 = 0.97424$. The method detection limit for TPM is about 5 pg·m^{-3} for a 24 h sample at the applied flow rates.

Deposition measurements

Wet and dry deposition was collected to a bulk sampler with an acid-washed open borosilicate glass bottle and a 30 cm funnel made of an inert material. Funnel was supported in a thermostated housing system. In the summer season the samples are protected by the collecting system against solar radiation and high temperature. In winter this system allows to maintain the samples in a liquid state. On the days without wet deposition the particulate matter (dry deposition) deposited on the open collector and borosilicate glass bottle was washed with deionized water on the site. The obtained solution and precipitation were filtered using 47 mm Teflon filter (0.45 mm pore size). After sampling the filters with dry deposition were placed into acid-cleaned Petri dishes and stored in the refrigerator. The filters with dry deposition were analyzed following the same procedure as TPM filters [29, 41]. Wet deposition samples were preserved with 1 ml of stabilizing solution (nitric acid and potassium dichromate – 5 g $K_2Cr_2O_7$ + 500 ml HNO_3/1000 ml) and stored in a Teflon bottle in the refrigerator. After the completion of the measurement campaigns the solution samples were brought to the laboratory for analyses. In mineralization 20 ml of wet deposition samples and the following solutions were used: potassium permanganate – 0.2 ml (25 g·l^{-1}), nitric acid – 0.2 ml (concentrated) and potassium per(oxidi)sulfate – 0.5 ml (40 g·l^{-1}). Then the samples were heated in a water bath for 2 hours at the temperature of 95°C. After mineralization the samples were cooled down and then 100 g·l^{-1} of hydroxylamine hydrochloride was added dropwise to remove the excess of the oxidizer. The obtained solutions were placed in 25 ml flasks and deionized water was added up to the scale mark. All samples were analyzed twice. Concentration of mercury was determined by the "cold vapor" atomic absorption

spectrometry based on RA-915+ analyzer equipped with RP-91 attachment produced by Lumex Ltd. with ($SnCl_2$) as a reducing agent. To check the operation of the analyzer the calibration solutions were prepared from the reference material in the concentration range from 0 to 300 ng·l^{-1}. The linear correlation coefficient of the calibration curve was $R^2 = 0.97504$.

Meteorogical parameters

Meteorological parameters were determined at both measurement sites. The meteorological stations were equipped with ultrasonic anemometer (81000 YOUNG) used to measure wind speed along the three axes x, y and z, which allowed to determine two horizontal velocities and one vertical velocity, air temperature and humidity.

The measurements of TGM and TPM in the atmospheric air and mercury content in dry and wet atmospheric precipitation were carried out in ten measurement campaigns (each lasting 21 days) in summer and winter seasons. In Katowice, six measuring campaigns were conducted, three in the summer season (20.08.2008–09.09.2008, 14.07.2009–04.08.2009 and 19.05.2010–09.06.2010) and three in winter (01.12.2008––22.12.2008, 09.03.2009–30.03.2009 and 26.02.2010–18.03.2010). In Pszczyna four measurement campaigns were carried out, two in summer (18.05.2009–08.06.2009 and 02.07.2010–22.07.2010) and two in winter (20.10.2009–10.11.2009 and 08.10.2010––29.10.2010).

Quality control and quality assurance

TGM measurements: Lumex analyzer was calibrated before each measurement campaign. At the inlet of ambient air to the analyzer a Teflon filter was used to absorb all particles present in the air, so that pure TGM could be determined. To control blank signal for determination of TGM an effective absorber (activated carbon), which absorbed about 99.99% of mercury vapor, was used. The 900 sec interval between two blank line controls was employed to obtain a low detection limit of the analytical method (MDL).

Laboratory glass and other laboratory ware used in the analyses were etched with nitric acid (1:1) for 2 days and then washed in a laboratory washer (Miele G7883, Ontario). The solutions were prepared with highly deionized water of the conductivity of about 0,5 S/cm, Milli-Q (Millipore, Bedford, MA, USA). All reagents used in the analysis showed very low mercury content so that its impact on the final result could be neglected. The obtained results for TPM, wet and dry deposition were corrected using blank value. Blank samples for TPM and dry deposition were obtained by placing unused Teflon filters on Petri dishes. Afterwards, the blank samples were analyzed applying the same procedure as for TPM and dry deposition filters. A calibration curve for TPM and dry deposition ranged from 0 to 500 ng l^{-1}. A recovery rate for TPM and dry deposition was obtained by adding standard solutions into the Teflon vessels containing blank filters. The recovery rates were at a similar level and amounted to about 99.8%. The detection and quantification limits for determination of total mercury in wet deposition were measured using ten independently prepared blank samples. LOD and LOQ amounted to 2 and 5 ng l^{-1}, respectively. The repeatability of this method was expressed as the level of precision under the same conditions of measurement and amounted to 9.4%. The recovery of this method was determined by adding the appropriate amount of standard solution of mercury to the real samples, and subsequent analyses. The recoveries amounted to

100.4%. Blank tests were carried out for each measurement campaign in a similar way as with the samples but instead of the sample proper volume of deionized water was added.

Conception of the mercury deposition coefficient

The proposed conception of deposition coefficient can provide quantitative information on a selected pollutant and its potential impact resulting from deposition. To calculate the deposition coefficient (%) data concerning TGM and TPM stream intensity throughout the measurement campaign (see Table 4) and data on mercury wet and dry deposition in this time were used. The coefficient was calculated as a share of mercury deposition on the land surface (dry and wet) to the amount of the pollutant transported with loads of air in the form of TGM and TPM (stream intensity) at a given measurement station. To determine the TGM and TPM stream intensity in summer and winter seasons in each measuring location high resolution data on the concentration of TGM, TPM and meteorological data (wind speed, wind direction) were used. Stream intensity is defined as a product of pollutant concentrations and the vector opposite to the vector of wind speed. The length of the inflow vector is equal to the intensity of pollutant stream inflow through the surface perpendicular to the wind vector. The inflow vector at the same time indicates the direction of inflow of the pollutants (TGM and TPM) and their stream intensity. Values of the deposition coefficient were calculated based on the TGM and TPM stream intensity and values of mercury wet and dry deposition for each measurement campaign carried out in 2008–2010.

RESULTRS AND DISCUSSION

Seasonal variation of atmospheric mercury species

As shown in Fig. 2A and Fig. 2C, the average daily temperatures during the summer campaign in Katowice and Pszczyna amounted to 16.3 ± 4.18°C and 18.2 ± 5.29°C, respectively, whereas the average daily wind speed observed in this campaign amounted to 0.61 ± 0.28 m·s^{-1} and 1.53 ± 0.61 m·s^{-1}. As shown in Fig. 2B and Fig. 2D, the average daily temperature during the winter campaign in Katowice and Pszczyna amounted to 0.60 ± 3.96°C and 5.33 ± 2.60°C, respectively, but the average daily wind speed observed during this campaign amounted to 1.11 ± 0.61 m·s^{-1} and 1.27 ± 0.61 m·s^{-1}. During the summer campaigns conducted in 2008–2010, the hourly TGM concentrations in Katowice ranged from 1.20 to 38.4 ng·m^{-3}, mean value was 3.49 ± 1.12 ng·m^{-3} (Fig. 2a). But during the winter campaigns, the hourly TGM concentrations in Katowice ranged from 0.53 to 11.9 ng·m^{-3}, mean value was 2.70 ± 0.71 ng·m^{-3} (Fig. 2b). During the summer campaigns (2009–2010), the hourly TGM concentrations in Pszczyna ranged from 0.64 to 9.13 ng·m^{-3}, mean value was 2.53 ± 0.52 ng·m^{-3} (Fig. 2c). During the winter campaigns, hourly TGM concentrations in Pszczyna ranged from 0.84 to 5.66 ng·m^{-3}, and the mean value was 1.84 ± 0.41 ng·m^{-3} (Fig. 2d). In three consecutive years (2008–2010), about 30% highest concentrations of TGM were observed at Katowice monitoring station in comparison to Pszczyna. In the summer season in Katowice, the average daily concentration of TGM was about 28% higher than in Pszczyna, whereas in winter the TGM concentration was about 33% higher. The analyses of both measurement periods showed that in the summer season the mean TGM concentrations in ambient air in Katowice and Pszczyna were higher than in the winter season by 36% and 29%, respectively. Only in summer 2010 in Katowice the average daily TGM concentration was about 0.3 ng·m^{-3} (8%) lower than in winter.
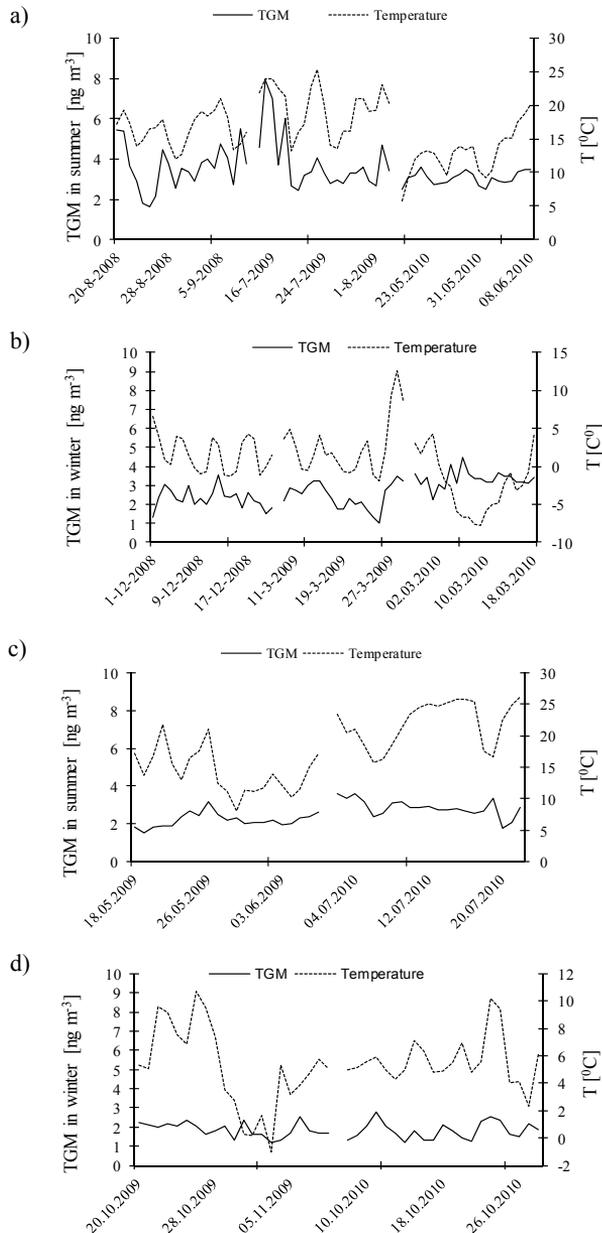
Fig. 2. Average hourly total gaseous mercury (TGM) concentration and temperature (T):
(a) Katowice, summer season 2008–2010; (b) Katowice, winter season 2008–2010;
(c) Pszczyna, summer season 2009–2010; (d) Pszczyna, winter season 2009–2010

Two types of correlation coefficients were calculated: TGM concentration vs. temperature and TGM concentration vs. wind speed. In all measuring sessions held in Katowice statistically significant correlation coefficients ($p < 0.005$) were observed

between TGM concentrations and wind speed. The correlations were as follows: $r = -0.38$ (2008), $r = -0.57$ (2009), $r = -0.47$ (2010) – in summer and $r = -0.43$ (2008), $r = -0.43$ (2009), $r = -0.54$ (2010) – in winter. A statistically significant positive correlation coefficient ($p < 0.005$) was recorded between TGM concentrations and temperature. These correlations obtained for the summer campaign were as follows: $r = 0.39$ (2008), $r = 0.64$ (2009), $r = 0.67$ (2010). During the winter season in Katowice the correlation coefficient $r = 0.64$ was obtained only for the measurement campaign conducted in 2009. In all measuring campaigns held in Pszczyna statistically significant positive correlation coefficients ($p < 0.005$) were observed between TGM concentrations vs. temperature. The correlation in the summer season was: $r = 0.21$ (2009), but in winter seasons the correlations were $r = 0.29$ (2009) and $r = 0.38$ (2010). In the measurement campaign conducted in summer 2010 no similar dependence was observed. Statistically significant negative correlation coefficients ($p < 0.005$) were observed between TGM concentrations and wind speed: $r = -0.36$ (2010), $r = -0.77$ (2009), $r = -0.45$ (2010). In the summer campaign conducted in 2009 this correlation was not recorded. The average values of TGM obtained in measurement stations located in the Silesian Region are very similar to average concentrations measured in Europe and worldwide [1, 6, 25–28]. Comparing the TGM concentrations at Upper Silesia with the data obtained in 2007 and 2008 over Polish Coastal Zone (see. Tab. 1), the received values in summer season are higher at Silesia Region from about 1 to 2 ng·m⁻³. TGM concentrations in the winter season are also higher at Silesia Region in comparison to the Polish coastal zone [34]. As in these studies, higher concentrations of mercury vapor are observed during the summer at the measuring stations located in Polish coastal zone [30, 34]. This phenomenon is translated as reemission of mercury vapor from the earth surface caused by increased of solar radiation. This process also occurs in Silesia, where long-term daily deposition of mercury adsorbed on the particles in the past, today causing the reemission of mercury during the summer months. Today this phenomenon is largely responsible for shaping concentration of mercury vapor in the air at the Silesia Region. These results support other studies conducted at stations located in Upper Silesia (Złoty Potok i Zabrze) [2].

During the summer campaigns conducted in 2008–2010 the daily TPM concentrations in Katowice ranged from 9.30 to 472.5 pg·m⁻³, mean concentration was 132.1 ± 107.8 pg·m⁻³ (Fig. 3a). But during the winter campaigns, the daily TPM concentrations in this measuring session ranged from 104.0 to 1368 pg·m⁻³, mean concentration was 531.7 ± 324.1 pg·m⁻³ (Fig. 3b). At Pszczyna monitoring station, during the summer campaigns conducted in 2009–2010, the daily TPM concentrations ranged from 7.81 to 288.6 pg·m⁻³, mean value was 97.18 ± 61.33 pg·m⁻³ (Fig. 3c). During the winter campaign the daily TPM concentrations ranged from 16.59 to 913.2 pg·m⁻³, mean value was 288.2 ± 165.2 pg·m⁻³ (Fig. 3d). In the winter season for each sampling station the daily average content of TPM in the atmospheric air was several times higher than its content in the summer season. The difference between the daily mean level of TPM in summer and winter seasons may result from the increased combustion of solid fuels in winter. In the winter season the consumption of coal significantly increases. This fact was also confirmed by the increase by about 50% of the average daily concentrations of PM10 in ambient air during the winter season in the Silesian Region. The Katowice monitoring station is located among a few combustion plants producing electricity for the city of Katowice and in the districts where houses are heated by coal-fired DHUs. Mean TPM/(TGM+TPM) ratios in the summer season (see Table 1) obtained for Katowice and Pszczyna were similar and

amounted to 3.14% and 3.71%, respectively. The same ratios in the winter season in Pszczyna were similar and amounted to 14%. At the measuring station in Katowice in the years 2008–2010, these ratios were higher: 24.4%, 21.3%, 8.3%, respectively.
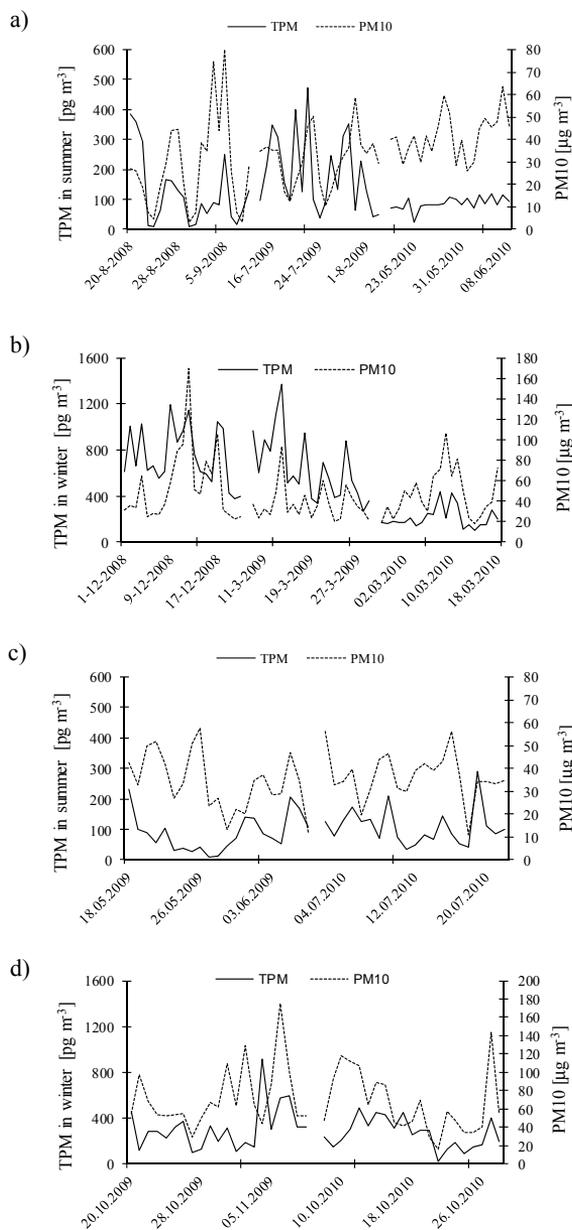

Fig. 3. Average daily TPM and PM10 concentrations: (a) Katowice, summer season 2008–2010;
(b) Katowice, winter season 2008–2010; (c) Pszczyna, summer season 2009–2010;
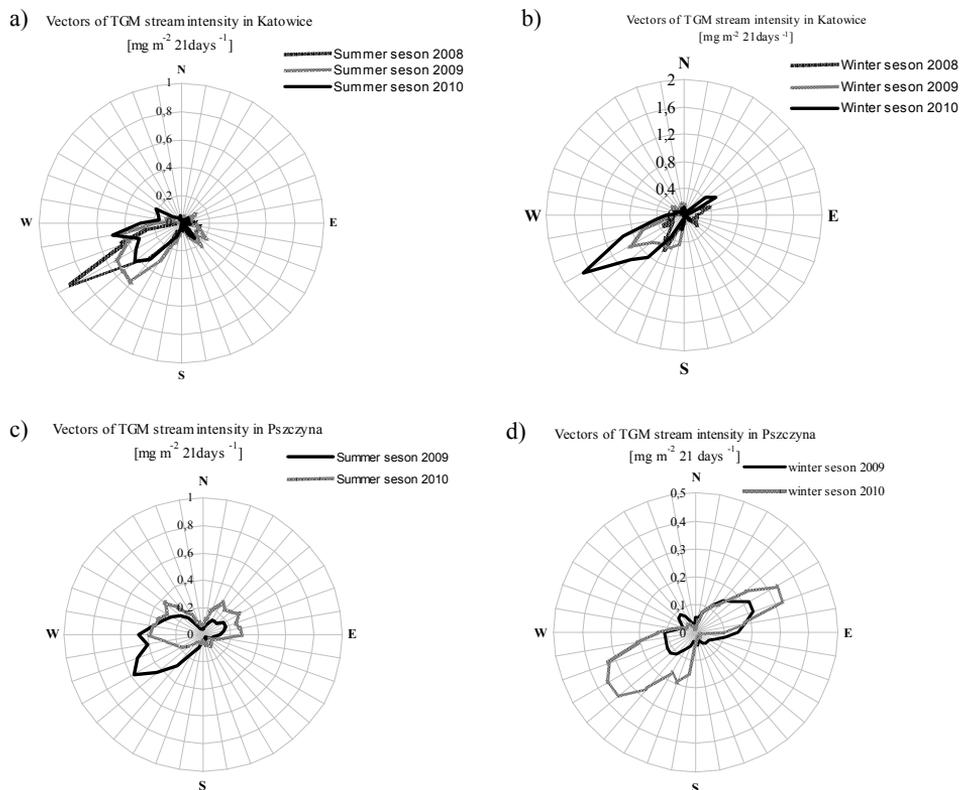(d) Pszczyna, winter season 2009–2010

Fig. 4. Roses of TGM stream intensity: (a) Katowice, summer season 2008–2010;
(b) Katowice, winter season 2008–2010; (c) Pszczyna, summer season 2009–2010;
(d) Pszczyna, winter season 2009–2010

Statistically significant positive correlation coefficients (p < 0.005) were obtained between TPM concentrations vs. PM10 concentration. These correlations obtained in the winter season in Katowice were as follows: r = 0.60 (2008), r = 0.74 (2009), r = 0.50 (2010). Statistically significant correlation coefficients between TPM concentrations and PM10 concentration in summer were not obtained. During summer and winter seasons in Pszczyna the statistically significant positive correlation coefficients (p < 0.005) were obtained between TPM concentrations and PM10 concentration. In winter campaign 2009–2010 correlation coefficients were r = 0.17 and r = 0.51, respectively. For the summer season the correlation coefficients were lower: r = 0.14 (2009) and r = 0.19 (2010). The average daily values of TPM obtained in Katowice and Pszczyna were much higher than the average concentrations measured in Europe and in the Polish Coastal Zone [6, 25–28, 33]. The difference between the average daily level of TPM in summer and winter seasons may result from the increased combustion of solid fuels in winter. In this season consumption of coal significantly increases. This fact is also confirmed by an increase by about 50% of the average daily concentrations of PM10 (50 μg/m³) in ambient air during the winter season in the Silesian Region. It was also noted that in

periods where precipitation were high, the TPM concentration is significantly lower than in the days when precipitation did not occur. This phenomenon is caused by washout of dust from the atmosphere by rainfall.

Wet and dry deposition of mercury

At the measuring station in Katowice (see Table 3) the daily wet deposition values measured in summer 2008–2010 ranged from 5.0 to 1530 ng·m^{-2}·d^{-1}, whereas in winter wet deposition varied from 8.0 to 1627 ng·m^{-2}·d^{-1}. The estimated daily dry deposition of mercury in summer ranged from 10.0 to 1613 ng·m^{-2}·d^{-1}, whereas in winter this value varied from 11.0 to 567 ng·m^{-2}·d^{-1}. In summer 2009–2010 in Pszczyna (see Table 3) the daily wet deposition ranged from 14.0 to 1416 ng·m^{-2}·d^{-1}, whereas in winter it varied from 11.0 to 164 ng·m^{-2}·d^{-1}. The estimated daily dry deposition of mercury in summer ranged from 20.0 to 918 ng·m^{-2}·d^{-1}, whereas in winter seasons this value varied from 7.1 to 287 ng·m^{-2}·d^{-1}.

Table 3. Daily wet and dry deposition of mercury (ng·m^{-2}·d^{-1}) and total precipitation value (mm) recorded in Katowice and Pszczyna in 2008–2010

Location	Katowice						Pszczyna			
Season	Summer			Winter			Summer		Winter	
Measurement period	August–September 2008	July–August 2009	May–June 2010	December 2008	March 2009	February–March 2010	May–June 2009	July 2010	October–November 2009	October 2010
Wet deposition [ng·m^{-2}·d^{-1}]	372±199	169±541	69±92	141±136	540±495	23±87	160±513	200±263	106±46	34±27
Dry deposition [ng·m^{-2}·d^{-1}]	341±353	93±59	58±19	159±139	57±21	56±16	285±249	50±17	175±71	85±79
Total precipitation [mm]	20.13	103.0	85.0	39.86	67.70	32.0	80.38	33.0	24.9	9.0

Based on the data on the average concentrations of mercury in wet and dry deposition determined in measurement campaigns 2008–2010 in Katowice and 2009–2010 in Pszczyna as well as on data concerning the total annual amount of precipitation in those locations assessment of the total annual mercury wet and dry deposition on the earth surface in the analyzed sampling stations was made. The total annual values of wet and dry deposition of mercury compounds measured in Katowice were as follows: 28.7 μg·m^{-2}·y^{-1} and 55.3 μg·m^{-2}·y^{-1} (2008), 31.8 μg·m^{-2}·y^{-1} and 15.7 μg·m^{-2}·y^{-1} (2009), 35.7 μg·m^{-2}·y^{-1} and

13.6 $\mu g \cdot m^{-2} \cdot y^{-1}$ (2010), respectively, whereas the total annual values of mercury wet and dry deposition measured in Pszczyna were: 12.2 $\mu g \cdot m^{-2} \cdot y^{-1}$ and 49.8 $\mu g \cdot m^{-2} \cdot y^{-1}$ (2009), and 10.3 $\mu g \cdot m^{-2} \cdot y^{-1}$ and 13.4 $\mu g \cdot m^{-2} \cdot y^{-1}$ (2010). The difference between the observed values of mercury deposition in 2008–2010 might be caused by such parameters as: temperature, wind speed and wind direction. The determined values of mercury wet and dry deposition are much higher than literature data [28, 36–38]. However, the obtained mercury wet deposition values are comparable to those values observed in China, where the estimated value of wet deposition in 2006 ranged from 24.8 to 39.6 $\mu g \cdot m^{-2} \cdot y^{-1}$ [39]. Emission of mercury compounds into the atmosphere from coal combustion in thermal processes caused an increase of mercury contribution associated with particulate matter, and consequently higher deposition of this element on the earth surface.

Mercury deposition coefficient

Values of the deposition coefficient (see Table 4) were calculated based on the TGM and TPM stream intensity and values of mercury wet and dry deposition for each measurement campaign carried out in 2008–2010.

Table 4. Seasonal TGM, TPM stream intensity (mg·m^{-2}·21 days^{-1}) and total wet and dry deposition of mercury (ng·m^{-2}·21 days^{-1}) in Katowice and Pszczyna for measurement campaigns 2008–2010

Location	Katowice						Pszczyna			
Season	Summer			Winter			Summer		Winter	
Measurement period	August–September 2008	July–August 2009	May–June 2010	December 2008	March 2009	February–March 2010	May–June 2009	July 2010	October–November 2009	October 2010
TGM stream intensity mg·m^{-2}·21 days^{-1}	3.98	4.82	4.12	4.85	6.83	8.11	6.01	6.35	3.14	4.16
TPM stream intensity mg·m^{-2}·21 days^{-1}	0.132	0.290	0.117	1.562	1.797	0.734	0.237	0.240	0.527	0.603
Wet deposition ng·m^{-2}·21 days^{-1}	1425	2408	1442	1929	9166	909	4667	1196	758	143
Dry deposition ng·m^{-2}·21 days^{-1}	6698	1230	375	1918	282	554	2809	826	2235	1528
Deposition coefficient %	0.198	0.071	0.043	0.060	0.110	0.017	0.120	0.031	0.082	0.035

Mercury inflow direction observed in both seasons was from the south-western sectors in Katowice and south-western, north-western and north-eastern sectors in Pszczyna. In the winter season the predominant direction of mercury inflow was from the north-east and south-west. The analysis of TGM stream inflow to the measuring point during 21 measurement days in all campaigns in Katowice showed that the observed average values were about 53% higher during the winter season. In Pszczyna an inverse relationship was recorded. At the measuring station in Pszczyna about 69% higher average values of TGM inflow streams were observed in summer. Deposition coefficient, calculated for measuring stations located in Katowice and Pszczyna in the summer season ranged from 0.043 to 0.190% and from 0.031 to 0.120%, respectively, whereas in the winter season these coefficients varied from 0.017 to 0.110% and from 0.035 to 0.082%, respectively. At both monitoring stations the deposition coefficient, which was defined as a share of mercury deposition on the land surface (dry and wet) to the amount of this pollutant transported with loads of air in the form of TGM and TPM (stream intensity) did not exceed 0.2%. Fluctuations of TPM concentrations between winter and summer seasons and variability of meteorological parameters between seasons contributed to the differences in the obtained results.

CONCLUSION

The idea of calculating the deposition coefficient based on the analysis of TGM and TPM stream intensity is a new solution. The idea of deposition coefficient based on analyzing of streams intensity of TGM and TPM is a new solution. This is especially important when mercury deposition process is realized into the soil, vegetation and water. The proposed deposition coefficient allows to quantify information on a selected pollutant concentration and its potential impact resulting from deposition. Further studies on the deposition coefficient may contribute to the development of methods for estimating the impact of pollutants contained in ambient air on other environmental components based on the analyses of the pollutant stream intensity. What is more, we have the possibility to determine the direction from which the pollutant (risk) is derived. Further development of this method may allow for the identification of mercury emission sources.

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DŁUGOTERMINOWE OZNACZANIE SPECJACYJNYCH FORM RTĘCI (TGM, TPM)
W POWIETRZU ATMOSFERYCZNYM ORAZ DEPOZYCJI RTĘCI NA OBSZARZE
WOJEWÓDZTWA ŚLĄSKIEGO – KONCEPCJA WSPÓŁCZYNNIKA DEPOZYCJI RTĘCI

Głównym celem tego projektu było określenie poziomów stężeń specjacyjnych form rtęci (TGM, TPM) w powietrzu atmosferycznym na wybranych obszarach Województwa Śląskiego charakteryzujących się zróżnicowanym oddziaływaniu źródeł emisji zanieczyszczeń powietrza. Na podstawie uzyskanych danych pomiarowych określono poziomy stężeń TGM i TPM jakie występują na badanym obszarze oraz wyznaczono wielkości suchej i mokrej depozycji związków rtęci. Na podstawie otrzymanych danych dotyczących natężeń strumieni TGM i TPM a także danych o wielkości depozycji związków rtęci wyznaczono wartość współczynnika depozy-

cji rtęci. Współczynnik ten można scharakteryzować jako udział natężeń strumieni TGM i TPM napływającymi z masami powietrza do punktu pomiarowego w stosunku do suchej i mokrej depozycji rtęci w danym punkcie pomiarowym. Rozwiązanie dotyczące wyznaczenia współczynnika depozycji, które opiera się na analizie przepływów rtęci w powietrzu jest podjęte po raz pierwszy zarówno na świecie, jak i w Polsce. W przeprowadzonych badaniach wartości współczynnika depozycji rtęci nie przekroczyła 0,2%. Zaproponowany współczynnik depozycji daje możliwość powiązania w sposób ilościowy informacji o poziomach stężeń analizowanego zanieczyszczenia w powietrzu atmosferycznym z możliwością jego oddziaływania w wyniku depozycji. Rozwój idei współczynnika depozycji może w przyszłości prowadzić do stworzenia systemu oceny oddziaływania zanieczyszczeń zwartych w powietrzu atmosferycznym na inne komponenty środowiska poprzez analizę strumieni napływu tych zanieczyszczeń.