



## Temporal variability of particulate mercury in the air over the urbanized zone of the southern Baltic

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### ABSTRACT

Mercury concentrations in fine (TPM<sub>0.7</sub>) and coarse (TPM<sub>2.2</sub>) aerosols were measured over an urbanized and industrialized region of the southern Baltic Sea, during the period of April 2008 – April 2009. Concentrations ranged between 0.3 – 151.5 pg m<sup>-3</sup> (TPM<sub>2.2</sub>) and 0.2 – 39.9 pg m<sup>-3</sup> (TPM<sub>0.7</sub>). Higher variability and range of TPM concentrations over the southern Baltic were observed during months of both low or below 0 °C temperature and strong turbulence. Elevated concentrations of Hg in aerosols were the result of emission from local sources (mainly fossil fuel burning in domestic furnaces and boiler-rooms). The autumn–winter season was the period of the highest Hg concentrations in fine and coarse aerosols.

### Keywords:

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### 1. Introduction

Mercury is a natural component of continental crust. Due to its toxic properties and the ability to bioaccumulate, it is included in the group of harmful substances. In the atmospheric cycle of this element, both natural and anthropogenic emission sources are important (Schroeder and Munthe, 1998; Lin and Pehkonen, 1999). However, the role of industrial and production processes is of crucial importance. It was proved that mercury is present in the atmosphere in a gaseous form as elemental mercury – Hg<sup>0</sup> (generally, over 95%) and as bivalent reactive gaseous mercury (RGM), in a particulate form (TPM) and in organic compounds (methyl mercury). Mercury undergoes different chemical and photochemical transformations which influence the concentrations of its forms in the atmosphere. As a result of such transformations, the properties (reactivity, solubility, bioavailability and toxicity) of mercury and its influence on the environment are modified, which can be revealed, for example, in the processes of atmospheric dispersion, transport, and deposition (Lin and Pehkonen, 1999). In the atmosphere, elemental mercury has the longest lifetime (0.5 – 1 year), whereas reactive and particulate forms have much shorter residence time. Hg<sup>0</sup> can be transported over long distances, whilst the range of RGM and TPM transport is often limited to source areas, where these forms are quickly scavenged of the air by the processes of dry and wet deposition (Poissant et al., 2005). When the substances with high oxidizing potential (e.g. ozone, hydroxyl and nitric radicals, reactive halogens) are present in the air, the cycle of Hg<sup>0</sup> can be shortened. As a consequence of photochemical and chemical reactions as well as by dry deposition, mercury is removed from the atmosphere (Schroeder and Munthe, 1998; Lin et al., 2006; Lindberg et al., 2007).

Previous studies showed that deposition of particulate mercury is closely connected with the vicinity and activity of natural and anthropogenic emission sources. The emission changes with seasons and meteorological conditions. Wang et al. (2006) observed a high variability of Hg concentrations in different size aerosols over China which influenced TPM deposition. Exceptionally high concentrations of TPM in the air were measured over industrial centers (Pyta et al., 2009) and over areas remote to anthropogenic sources (the result of transport and dispersion of atmospheric Hg).

The objective of the present study, carried out in urbanized and industrialized coastal zone of the southern Baltic, was to analyze the temporal variability of particulate mercury concentrations and to verify the hypothesis that concentrations of TPM in the air in winter and autumn – seasons when fossil fuel burning is intensified – are elevated. In Poland, the main source of atmospheric mercury is the emission from power plants, power and heat generating stations and boiler houses during combustion of fossil fuels (Zielonka et al., 2005; Beldowska et al., 2003). The authors paid special attention to the variation (in the following seasons) in levels and amplitudes of concentrations of Hg in aerosols. That variability was dependent on the temperature and local circulation of the air.

### 2. Methodology

#### 2.1. Measurement site

The measurements of TPM concentration were carried out every 48 and 72 hours, in the period from April 2008 to April 2009,

in the coastal zone of the Gulf of Gdansk. The measurement station was located in the Institute of Oceanography, Gdansk University, in the city of Gdynia (population of about 300 000), about 1 km from the coastline (Figure 1a). For the measurements of Hg aerosol fraction, the filter-pack technique was applied. The measurement system was placed on the roof of the Institute building (20 m over ground level, 3 m above the tree-tops). It consisted of an oil-free vacuum pump, an air flow gauge connected with filters put in cascade and closed in a Teflon case. The average air flow was  $16 \text{ L min}^{-1}$ . Aerosols were collected using two types of filters: (1) Teflon filters, Whatman QMA with an effective pore diameter of  $2.2 \mu\text{m}$  and (2) glass fiber filters, Whatman GF/F, the effective pore diameter of  $0.7 \mu\text{m}$ . The sampled air first passed through the Teflon filter ( $2.2 \mu\text{m}$  pore size), which collected mainly the large suspended particles ( $\geq 2.2 \mu\text{m}$  but also some fraction of smaller aerosols) and next through the GF/F filter ( $0.7 \mu\text{m}$  pore size) which absorbed fine particles ( $< 2.2 \mu\text{m}$  and  $\geq 0.7 \mu\text{m}$ ) and gaseous fraction of mercury.

The adopted sampling approach was one of the conventional techniques for collecting aerosols (Lu and Schroeder, 1999). Due to lack of attaching KCl denuder in our aerosol sampling set, it was not possible to estimate what percentage of gaseous species of Hg (RGM) was retained during measurements. Landis et al. (2002), indicated that the simplest method overestimates the results of particulate-mercury measurements, mainly by the adsorption of divalent inorganic reactive gaseous mercury on particles. Some authors suggest that in urban environment, the production of reactive gaseous mercury in KI or KCl-coated denuder system during the long-term measurements is possible (Lynam and Keeler, 2005). In our research a comparison of two techniques (with and without denuder-based system) has not been tested and we could not discuss about the uncertainty in the estimate. The lack of measurements with denuder-based system is potentially a source of unknown amount of RGM in each sample. It will be developed using an advanced system in future research.

## 2.2. QC/QA and laboratory analysis

Prior to fieldworks, the filters were pre-treated at  $500 \text{ }^\circ\text{C}$  for 8 hours and Teflon parts of the filter-pack were digested in nitric acid (Merck Suprapure) for 24 hours. The filters were changed in the laminar air flow clean bench (ALPINA). In order to check the contamination of samples during filter changing, a series of analyses was conducted. Hg concentrations for filters placed and

not placed in the filter-pack were similar. The possibility of contamination during preparing the filters for further levels of analysis was excluded. An AMA 254 atomic absorption spectrometer was used to determine Hg concentrations in aerosols. The detection limit was estimated to be  $0.03 \text{ ng}$ . The standard deviation of the blank results ( $n = 5$ ) for QMA filters (diameter  $47 \text{ mm}$ ) and GFF filters was  $0.0004 \text{ ng}$  and  $0.0014 \text{ ng}$ , respectively. The sampling method detection limit was established as  $6 \text{ pg m}^{-3}$ . The environmental blank (test for contamination during the exposure for environmental conditions: placing a filter in the filter-pack without passing the air through it) was checked and taken into account during calculations. About 300 filters were collected for further analyses. The following abbreviations have been used in the present study:  $\text{TPM}_{2.2}$  for particles larger than  $2.2 \mu\text{m}$  as well as some fraction of smaller aerosols collected on filters with pore diameter of  $2.2 \mu\text{m}$  and  $\text{TPM}_{0.7}$  for fine particles ( $< 2.2 \mu\text{m}$  and  $\geq 0.7 \mu\text{m}$ ) collected on filters with pore diameter of  $0.7 \mu\text{m}$ .

Meteorological data, i.e. temperature, air pressure, relative humidity, height of precipitation, direction and velocity of wind, were recorded continuously during the period of measurements. Trajectories of air masses moving over the measurement site were retrieved from the HYSPLIT model based on GDAS (global, 2005-present) (Draxler and Rolph, 2003). End-points of trajectories were established on the basis of the number of hours from the time of starting the exposition to the time of collecting the aerosols, in relation to the stable point in space, with a standard time step of 48 or 72 hours. Despite the fact that trajectories were calculated for each case, only one example has been chosen to illustrate the procedure for the determination of trajectory map (Figure 1b). The starting height was established as 20 m.

## 2.3. Statistical procedures

Multidimensional methods of environmental data analysis were applied previously (Yawei et al., 2005). Principal Component Analysis (PCA) can be used as one of the chemometric approaches to handle environmental data. It is possible to detect several factors which describe the greatest variation of results in the set of data, on the basis of a mathematical transformation of matrices of mutually correlated input data. In a multivariate PCA analysis, new variables (i.e. principal components) are a weighted linear combination of original variables. Those, which have eigen-values from  $0.8 - 1$  or above  $1$ , provide a statistically important

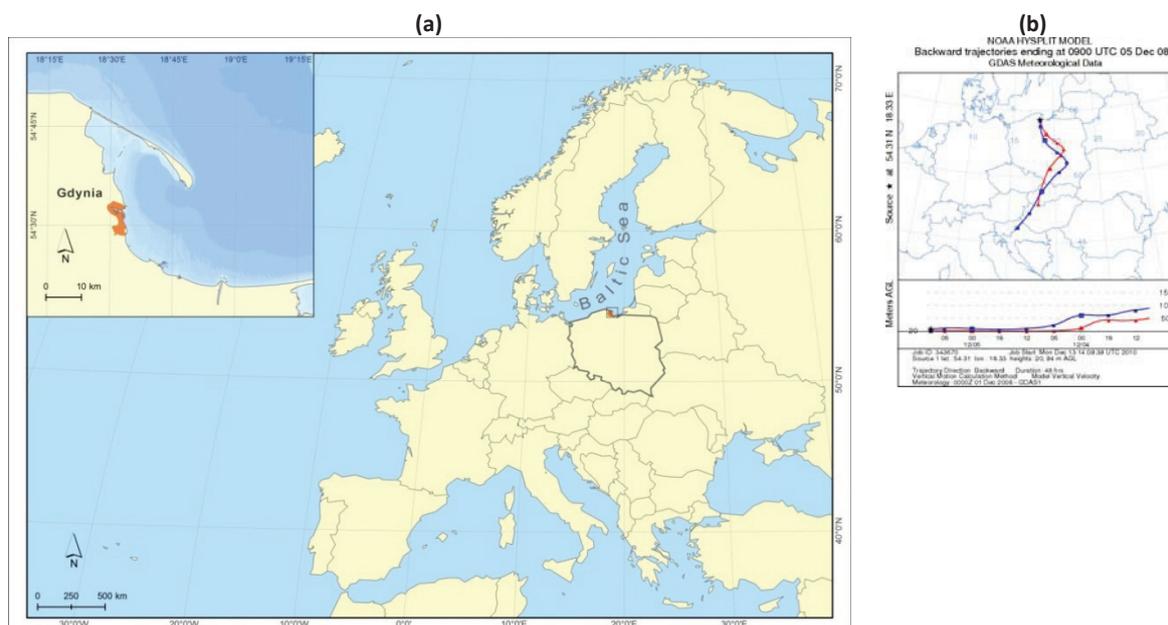


Figure 1. (a) The measurement site location at Gdynia ( $54^\circ 30' \text{N}$ ,  $18^\circ 32' \text{E}$ ) and (b) back trajectory of air mass flowing to the southern Baltic.

information. The Varimax algorithm is proposed for obtaining principal components in a PCA analysis. The aim of the normalized Varimax rotation is a change of coordinates in order to allow the variables to be closer to the axes and enable to reveal factors that correspond to a source or origin of the variables.

A multivariate analysis with the normalized Varimax rotation was applied in the present study in order to achieve interrelationships between the measured chemical variables (Hg in fine and coarse aerosols:  $TPM_{0.7}$  and  $TPM_{2.2}$ ) and meteorological data (temperature, air pressure and velocity of wind) in different measurement seasons (spring, summer, autumn, and winter) over the coastal zone of the southern Baltic. The seasons were as follows: spring (March–May), summer (June–August), autumn (September–November) and winter (December–February). The program Statistica v 8.0. was used for PCA analysis.

### 3. Results and Discussion

#### 3.1. Mercury in aerosols over the coastal zone of the southern Baltic

Concentration of mercury in aerosols over the coastal zone of the southern Baltic during the measurement period April 2008 – April 2009 was within a wide range of 0.3 to 151.5  $\mu\text{g m}^{-3}$  for  $TPM_{2.2}$  and 0.2 to 39.9  $\mu\text{g m}^{-3}$  for  $TPM_{0.7}$ .

Both  $TPM_{2.2}$  and  $TPM_{0.7}$  were dependent on the influence of local anthropogenic emission sources and the measurement season. Similar variations in concentrations of Hg in aerosols were observed in the air over coastal area of the Mediterranean Sea, where TPM concentrations were influenced mainly by the distance of the measurement site from local and regional sources of Hg located on land (Wangberg et al., 2008). High concentrations of Hg in aerosols at measurement stations in Thau Lagoon (France) – 1 160  $\mu\text{g m}^{-3}$  and in Haifa (Israel) – 700  $\mu\text{g m}^{-3}$  were caused mainly by emissions from medical waste incineration units and other industrial sources (Wangberg et al., 2008). Relatively low concentrations of TPM in the marine air (between 0 and 36  $\mu\text{g m}^{-3}$ ), in comparison with those over the southern Baltic, were recorded at background stations: Capo de Creus (Spain), Piran (Slovenia) and St. Lucido (Italy) (Wangberg et al., 2008). The average TPM concentration at the measurement station in Gdynia was similar to that observed in Detroit  $20.8 \pm 30.0 \mu\text{g m}^{-3}$  (Liu et al., 2007). Kim et al. (2009), during measurements in Seoul (Korea), obtained similar values. The average diurnal concentration of Hg in aerosols equaled  $23.9 \pm 19.6 \mu\text{g m}^{-3}$ . Those values constituted, on average, 0.2 – 3.2% of total gaseous mercury and were comparable with the results from other parts of the world (Lindberg and Stratton, 1998; Han et al., 2004; Feng et al., 2004; Gabriel et al., 2005; Poissant et al., 2005). In Seoul, higher concentrations of TPM in the air were observed in winter, which was probably the result of condensation of water vapor on particles, favored by low temperature (Kim et al., 2009). Concentrations of mercury in aerosols over the southern Baltic were lower than those measured by Xiu et al. (2009) in the area distant from the industrial sources, however, being under the influence of mobile sources (main road in the city; 20 000 vehicles per hour during rush hour) in Shanghai (China). The average concentrations of TPM, recorded at the station located in that area, were within the following range: 70  $\mu\text{g m}^{-3}$  – 1 450  $\mu\text{g m}^{-3}$  and were close to the values from other Chinese cities, i.e. Beijing (Wang et al., 2006), Changchun (Fang et al., 2001). Results of the Hg measurements in aerosols over Baltic were considerably lower than over China or Slovakia and southern Poland (Hladikova et al., 2001, Zielonka et al., 2005, Pyta et al., 2009). Hladikova et al. (2001) found that 34% of the measured samples ( $n = 160$ ) had TPM concentration over 500  $\mu\text{g m}^{-3}$ . The maximum value of Hg in aerosols (4 250  $\mu\text{g m}^{-3}$ ) was measured in Krompachy, while concentrations in Bratislava were between 200 and 600  $\mu\text{g m}^{-3}$ .

#### 3.2. Influence of meteorological conditions on temporal variation of mercury in aerosols over the coastal zone of the southern Baltic

It should be stressed that TPM concentrations over the coastal zone of the southern Baltic are lower than those observed in other industrial areas, however, they are under a noticeable influence of meteorological conditions. The factors which stimulated or decreased  $TPM_{2.2}$  and  $TPM_{0.7}$  concentrations over Gdynia were obtained by PCA analysis (Table 1).

During spring 2008, the greatest variation in the results of  $TPM_{0.7}$  concentrations was caused by meteorological factors, particularly by wind velocity (–0.856) and temperature (0.770). Moreover, the increase in  $TPM_{0.7}$  concentration was reported to occur in the conditions of high pressure – supported by a linear dependence (0.951 Factor 3, Table 1 and Figure 2a). Similar dependences were observed during the following spring 2009 (36% of the variance, Factor 1, Table 1), namely dependence on the atmospheric pressure (–0.751) and temperature (–0.809). Description of the variability in Hg concentration over the southern Baltic in spring 2009 was additionally presented by Factor 2 indicating 30% of the variance in the results. An increase in  $TPM_{2.2}$  concentration (0.842) together with a decrease in wind velocity (–0.828), particularly from the W and NW sectors, could be the result of strong Hg dispersion over the area of the measurement site. Elevated concentrations of mercury in small aerosols ( $>7 \mu\text{g m}^{-3}$ ) were observed when winds with the speed of  $>5 \text{ m s}^{-1}$  were blowing from the south (the area where local emission sources of the Tricity agglomeration are located, e.g. the refinery, power and heat generating plants, etc., Figure 3a). The increase of suspended mercury concentration in fine aerosols was statistically significant (significance level:  $p < 0.05$ , U Mann–Whitney test).

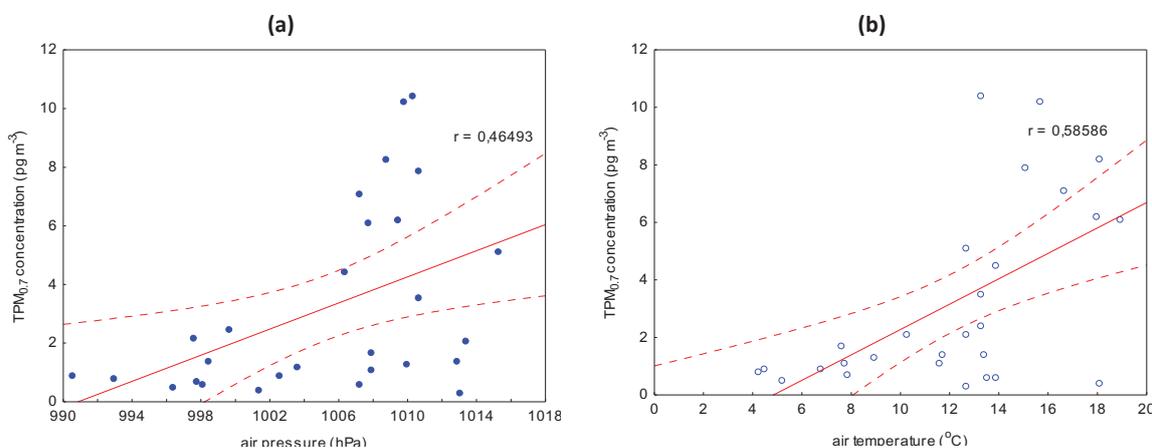
High temperatures of the air greatly impacted transformations of particulate mercury during the whole vegetation season. In warm months, transformations of gaseous mercury to its reactive form (in the presence of ozone and other oxidants such as  $\text{Cl}^-$ , formaldehyde, acrylic aldehyde) and the following adsorption on aerosol particles could occur (Han et al. 2004). It was illustrated in Figure 2b –  $TPM_{0.7}$  was directly proportionally correlated with temperature in warm months of 2008. Such dependence can be regarded as a complex combination of atmospheric/chemical processes, and it reflects the important role of solar radiation in mercury transformations.

Evasion of the elemental mercury from the sea and land surface to the atmosphere increases in summer. GEM can be transformed into particulate species in a short period of time (Poissant et al., 2005). Photochemical reactions are then sustained by the increased solar radiation, which causes the reduction of Hg complex compounds in surface waters of the Baltic and reemission of  $\text{Hg}^0$  to the atmosphere layer over the sea (Beldowska et al., 2008).

Factor 1 of the PCA analysis, describing variability of mercury in aerosols over Gdynia, revealed that in summer an increase in Hg concentration in airborne particles occurred when the temperature was increasing (0.797, Table 1). In summer 2008, Hg concentrations in  $TPM_{0.7}$  and  $TPM_{2.2}$  were similar, which suggests the influence of the same sources (Figure 4a, 4b). The greatest variability was determined by dynamic conditions in the atmosphere. Fine aerosols had the highest Hg concentration when winds were the weakest (wind speed  $<1 \text{ m s}^{-1}$ ). The substantial increase in  $TPM_{0.7}$  concentration was coincident with a decrease in the speed of wind from the NW direction, which suggested the transport of Hg from the biggest anthropogenic sources (i.e. harbors, shipyards, factories, power and heat generating plants) located near the measurement station (Figure 4a). Hg in coarse aerosols ( $TPM_{2.2}$ ) had concentration levels  $>11 \mu\text{g m}^{-3}$  when the air

**Table 1.** Results from principal component analysis (PCA) with normalized Varimax rotation

Season	Variables	Factor 1	Factor 2	Factor 3
SPRING 2008	Atmospheric pressure (hPa)	0.123	-0.087	<b>0.951</b>
	Velocity of wind ( $\text{m s}^{-1}$ )	<b>-0.856</b>	0.280	0.244
	Temperature ( $^{\circ}\text{C}$ )	<b>0.770</b>	0.280	0.313
	TPM <sub>2.2</sub> ( $\mu\text{g m}^{-3}$ )	-0.067	<b>-0.964</b>	0.078
	TPM <sub>0.7</sub> ( $\mu\text{g m}^{-3}$ )	<b>0.785</b>	0.199	0.343
	% of variance explained	44	22	20
SUMMER 2008	Atmospheric pressure (hPa)	-0.086	<b>0.881</b>	-
	Velocity of wind ( $\text{m s}^{-1}$ )	-0.062	<b>-0.835</b>	-
	Temperature ( $^{\circ}\text{C}$ )	<b>0.797</b>	-0.441	-
	TPM <sub>2.2</sub> ( $\mu\text{g m}^{-3}$ )	<b>0.774</b>	-0.018	-
	TPM <sub>0.7</sub> ( $\mu\text{g m}^{-3}$ )	<b>0.753</b>	0.391	-
	% of variance explained	38	25	-
AUTUMN 2008	Atmospheric pressure (hPa)	<b>0.872</b>	-0.232	-
	Velocity of wind ( $\text{m s}^{-1}$ )	<b>-0.754</b>	-0.360	-
	Temperature ( $^{\circ}\text{C}$ )	<b>0.754</b>	0.038	-
	TPM <sub>2.2</sub> ( $\mu\text{g m}^{-3}$ )	0.200	<b>0.775</b>	-
	TPM <sub>0.7</sub> ( $\mu\text{g m}^{-3}$ )	0.154	<b>-0.828</b>	-
	% of variance explained	40	29	-
WINTER 2008/2009	Atmospheric pressure (hPa)	0.245	<b>-0.803</b>	0.246
	Velocity of wind ( $\text{m s}^{-1}$ )	0.080	0.015	<b>-0.950</b>
	Temperature ( $^{\circ}\text{C}$ )	0.192	<b>0.845</b>	0.177
	TPM <sub>2.2</sub> ( $\mu\text{g m}^{-3}$ )	<b>-0.804</b>	-0.136	0.222
	TPM <sub>0.7</sub> ( $\mu\text{g m}^{-3}$ )	<b>-0.872</b>	0.146	-0.111
	% of variance explained	31	29	20
SPRING 2009	Atmospheric pressure (hPa)	<b>-0.751</b>	0.112	-
	Velocity of wind ( $\text{m s}^{-1}$ )	0.090	<b>-0.828</b>	-
	Temperature ( $^{\circ}\text{C}$ )	<b>-0.809</b>	0.132	-
	TPM <sub>2.2</sub> ( $\mu\text{g m}^{-3}$ )	0.056	<b>0.842</b>	-
	TPM <sub>0.7</sub> ( $\mu\text{g m}^{-3}$ )	<b>-0.758</b>	-0.297	-
	% of variance explained	36	30	-

**Figure 2.** Linear correlation between TPM<sub>0.7</sub> concentration ( $\mu\text{g m}^{-3}$ ) and (a) atmospheric pressure (hPa) (b) air temperature ( $^{\circ}\text{C}$ ) over the coastal zone of the Gulf of Gdansk in spring 2008.

was flowing from all the adjacent areas, which proves the equivalent role of land and marine mercury sources in summer (Figure 4b).

In autumn 2008, mercury concentrations in aerosols over the southern Baltic were changing due to a decrease in the wind speed ( $-0.754$ ) or an increase in the temperature of the air ( $0.754$ ) and atmospheric pressure ( $0.872$ ). Factor 2 of the PCA analysis, responsible for 29% variance of data, showed that TPM<sub>0.7</sub> and TPM<sub>2.2</sub> could originate from different sources (Table 1). A gradual decrease of Hg concentration in aerosols was mainly observed when  $T > 9^{\circ}\text{C}$ , what can be supported by the inversely proportional correlation of TPM<sub>2.2</sub> concentrations and air temperature

( $r = -0.442$ ,  $p < 0.05$ ). That dependence is probably the effect of the mercury loss from aerosols and the increase in  $\text{Hg}^{\circ}$  concentration at the expense of TPM.

In winter, when photochemical production of compounds oxidizing  $\text{Hg}^{\circ}$  to RGM and TPM is inhibited, industrial emissions are the main factor responsible for the increase in concentration of particulate forms of mercury in the air. It is assumed that low temperature of the air reduces to minimum the loss of mercury caused by evaporation from aerosols and favors the condensation of volatile compounds onto the particle surface (Liu et al., 2007). In winter 2008/2009, the strongest influence on fluctuations in TPM<sub>2.2</sub> and TPM<sub>0.7</sub> concentrations were caused by atmospheric

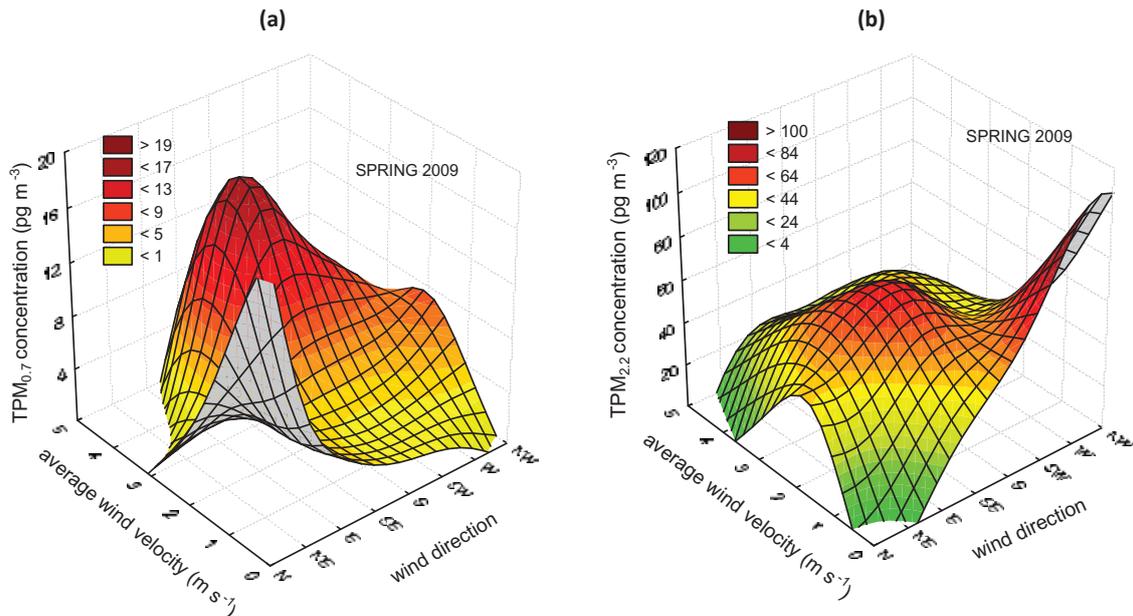


Figure 3. Surface graph demonstrating dependences between concentration of (a)  $TPM_{0.7}$  ( $pg\ m^{-3}$ ) and (b)  $TPM_{2.2}$  ( $pg\ m^{-3}$ ), the average wind velocity ( $m\ s^{-1}$ ) and the predominant wind direction in the coastal zone of the southern Baltic in spring 2009, made using the method of distance weighted least squares.

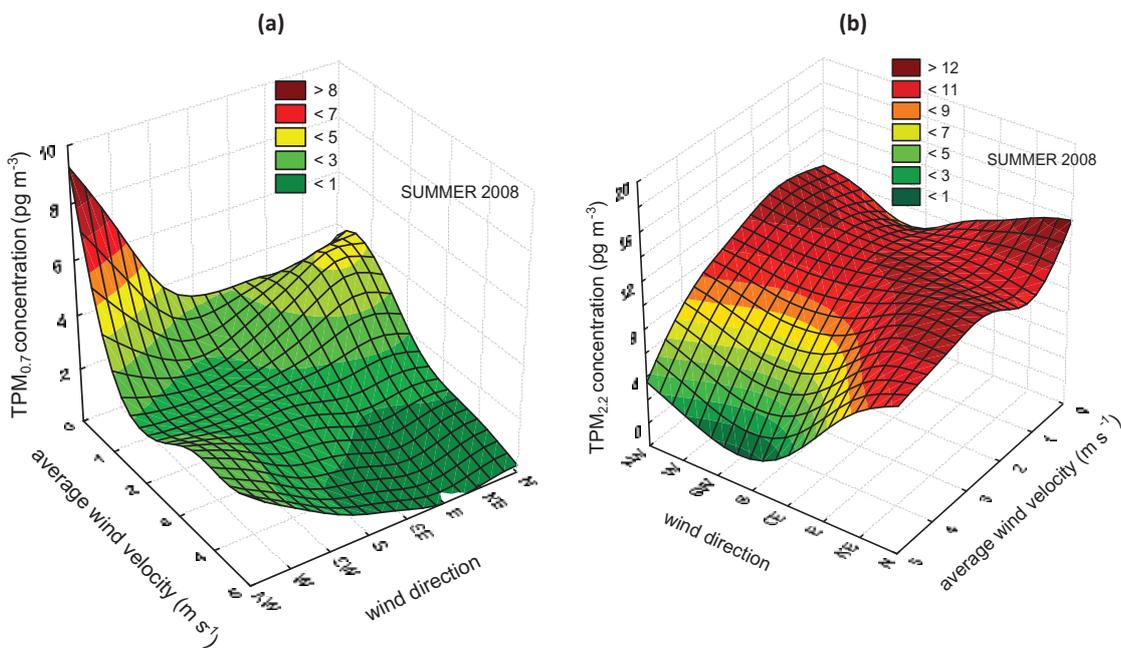
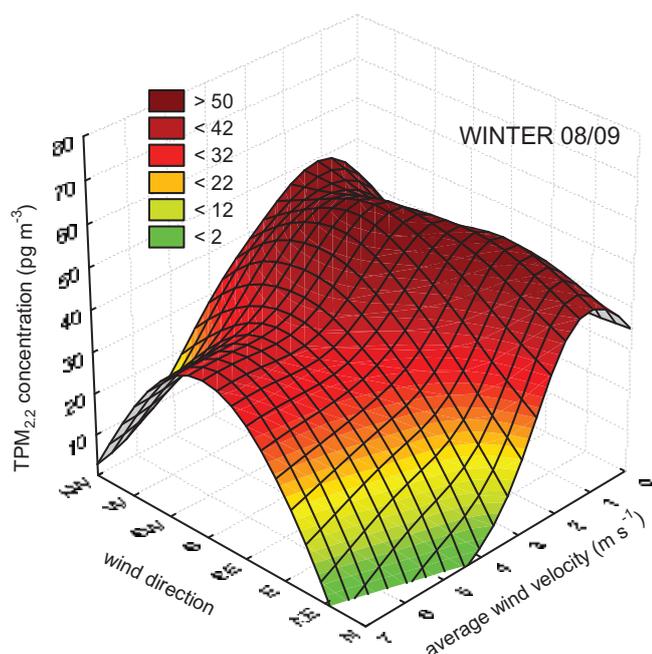


Figure 4. Surface graph demonstrating dependences between concentration of (a)  $TPM_{0.7}$  ( $pg\ m^{-3}$ ) and (b)  $TPM_{2.2}$  ( $pg\ m^{-3}$ ), the average wind velocity ( $m\ s^{-1}$ ) and the predominant wind direction in the coastal zone of the southern Baltic in summer 2008, made using the method of distance weighted least squares.

pressure and temperature (29% of variance, Factor 2, Table 1) as well as by velocity of wind (20% of variance, Factor 3, Table 1). When winds were blowing with the speed over  $4\ m\ s^{-1}$ , the variability in concentration of coarse particles ( $TPM_{2.2}$ ) was connected with the inflow of mercury to the coastal area from the south, where the biggest industrial point sources are situated (Figure 5). The situation was similar in spring 2008.

To sum up, concentrations of  $TPM_{2.2}$  and  $TPM_{0.7}$  were clearly higher during the heating season, which includes autumn and winter, than during the non-heating season (spring and summer). It was a consequence of intensive coal combustion processes in the coastal zone of the Gulf of Gdansk. However, those high concentrations were not as high as the values from the southern Poland (Zielonka et al., 2005). In winter, they were reported to be  $1\ 050 \pm 180\ pg\ m^{-3}$  (Zielonka et al., 2005). The influence of thermal

conditions on the differences in Hg concentration in fine and coarse particles in the atmosphere over the Gulf of Gdansk was verified on the basis of the U Mann–Whitney test. Statistically significant differences were found for  $TPM_{2.2}$  concentrations (level of significance:  $p < 10^{-6}$ ), unlike  $TPM_{0.7}$  ( $p = 0.333$ ), in the chosen seasons. Similar observations were made by Liu et al. (2007) in the air over Detroit (USA) during their measurements of HgP ( $< 2.5\ \mu m$ ). The authors noticed statistically important differences in the average concentration of particulate mercury for four measurement seasons at several stations ( $p < 0.001$ , Kruskal–Wallis test). They frequently reported elevated concentrations of mercury in winter and spring, and gave the following explanations for that: the winter peak in TPM was due to the gas–particle conversion caused by low temperature of the air and a decrease in solar radiation, especially UV.



**Figure 5.** Surface graph demonstrating dependences between  $TPM_{2.2}$  concentration ( $\text{pg m}^{-3}$ ), the average wind velocity ( $\text{m s}^{-1}$ ) and predominant wind direction in the coastal zone of the southern Baltic in winter 2008/2009, made using the method of distance weighted least squares.

Furthermore, the peak in HgP concentration observed in warm season can be the result of photochemical processes in the presence of atmospheric substances (elevated concentration) with high oxidizing potential as reported by Poissant et al. (2005). Analogical dependencies were also obtained by Wang et al. (2006) and Xiu et al. (2009). TPM concentrations over Gdynia in summer were less diversified than in winter, when Hg concentrations in fine particles were twice and five times lower than in coarse particles, respectively for  $TPM_{0.7}$  and  $TPM_{2.2}$ . In summer, the average ( $\pm$ SD) concentration of fine particulate mercury was  $2.8 \pm 3.1 \text{ pg m}^{-3}$ , whereas in winter –  $4.1 \pm 6.7 \text{ pg m}^{-3}$ . For coarse particulate mercury, the average concentrations were established at  $12.7 \pm 5.1 \text{ pg m}^{-3}$  (summer) and  $35.5 \pm 28.5 \text{ pg m}^{-3}$  (winter). Different situation was observed in the industrial region of the southern Poland by Zielonka et al. (2005). Diurnal concentrations of TPM measured in August were much more diversified than over the coastal zone of the southern Baltic. In this one of the most polluted regions of Poland, far from our sampling site about 500 km, minimum concentration of Hg in aerosols was reported to be  $20 \text{ pg m}^{-3}$ , while the maximum value was one order of magnitude higher,  $200 \text{ pg m}^{-3}$  (Zielonka et al., 2005). This comparison demonstrates how the urban pollution impact is significant on a local scale.

When analyzing Hg concentrations over the coastal zone of the southern Baltic, it is important to take under consideration local emission sources as well as those located in the whole area of Poland and abroad. Due to transboundary transport of Hg, such approach was suggested in the studies by Poissant et al. (2005), Jaffe et al. (2005), Weiss–Penzias et al. (2007), Beldowska et al. (2003). Poissant et al. (2005) noticed that during lowering the height of a flowing air mass – in the planetary boundary layer – to dozens of meters over ground level, that air mass is enriched in mercury of the local origin. It was observed that RGM concentration could increase from 50 to  $320 \text{ pg m}^{-3}$  in nearly 48 hours, when the air mass lowered from 2 000 to 500 m (Poissant et al., 2005). Additionally, on the basis of short measurement series, it was proved that the oxidation of gaseous mercury by ozone and hydroxyl radicals leads to production of TPM and an increase in its concentration by  $52 \text{ pg m}^{-3}$  in 4 hours (Poissant et al., 2005). Analyzing 96 hour back trajectories of the

air inflowing to the Polish coastal zone from remote areas in Europe, we observed the increase in Hg concentration in local precipitation, which suggested the additional contribution of mercury from distant sources.

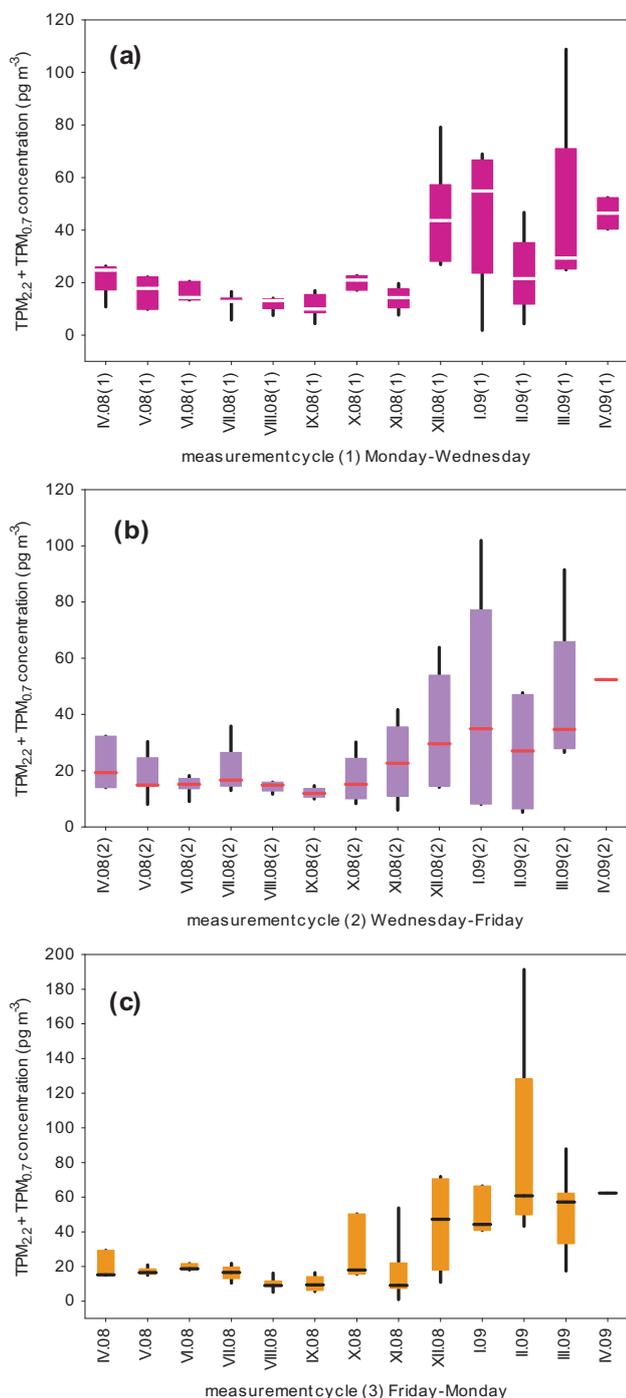
Water vapor content in the air mass contributes to the changes in distribution of atmospheric mercury, which is manifested as a high variability in TPM concentrations. Maximum concentrations of  $TPM_{2.2}$  (on average:  $28.2 \text{ pg m}^{-3}$ ) over the coastal zone of the southern Baltic were reported when the relative humidity of the air was high (80–89%), and  $TPM_{0.7}$  ( $5.4 \text{ pg m}^{-3}$ ) when RH was within the range of 60–69%. Those observations prove that if there is more moisture in the air, the process of hydration and coagulation of  $0.7\text{--}2.2 \mu\text{m}$  particles is more effective than  $<0.7 \mu\text{m}$  particles. The lowest average concentration of  $TPM_{2.2}$  and  $TPM_{0.7}$  was observed when the relative humidity was below 50%. The results of field studies carried out by Xiu et al. (2009) showed that fog had an important influence on the increase in Hg concentration in aerosols. As a consequence of that, TPM concentration was as follows: high cloudiness > rain > sunny weather > weather after rain. The authors emphasized that in hydrometeors with slightly acid reaction, gaseous forms of Hg can react with  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{HS}^-$ ,  $\text{S}^{2-}$ ,  $\text{H}_2\text{O}_2$ , which results in the increase of particulate Hg concentration.

### 3.3. Variation of TPM concentration in measurement cycle

The variability in TPM concentration over the coastal zone of the southern Baltic is caused by the activity of natural and industrial emission sources as well as by chemical and photochemical transformations of mercury in the air. Previous studies demonstrated that 2–3 day series of measurement revealed statistically significant differences in TPM concentrations (Beldowska et al., 2003). The measurements presented in this study were conducted in 3 cycles: (a) from Monday to Wednesday (b) Wednesday–Friday (c) Friday–Saturday, and they revealed low and high concentrations of the sum of Hg in fine ( $TPM_{0.7}$ ) and coarse ( $TPM_{2.2}$ ) aerosols (Figure 6). TPM concentrations in the following measurement cycles were statistically different ( $p = 0.6827$ ).

Regardless of the time step (a, b or c), small variability and very similar concentrations of mercury in fine and coarse aerosols over the coastal zone of the southern Baltic were observed during first eight months of the measurements, i.e. April 2008–November 2008 (Figure 6). That tendency changed in November 2008, when an increase in Hg concentration in aerosols was reported together with bigger amplitude of concentrations in autumn and winter (Figure 6a, 6b, 6c). The situation was caused by the increased demand for heating energy, which was the reason for higher emission of dust containing mercury from power and heat generating plants, factories, domestic furnaces and boiler-rooms in Tricity. Burning of fossil fuels was more intensive than in warmer seasons. Similar dependences over the same area were observed by Beldowska et al. (2007) in 2005–2006. The highest average concentrations of  $TPM_{0.7} + TPM_{2.2}$  in the air over Gdynia were reported in the first and second measurement cycle in January 2009. The value of TPM median for the days from Monday to Wednesday was  $54.9 \pm 30.7 \text{ pg m}^{-3}$  and from Wednesday to Friday it was  $34.9 \pm 42.1 \text{ pg m}^{-3}$ . The maximum median of  $TPM_{2.2} + TPM_{0.7}$  concentration in the days free of work (third cycle) was noticed in February and equaled  $60.8 \pm 68.8 \text{ pg m}^{-3}$ . The highest concentrations of mercury in aerosols over the coastal zone of the southern Baltic occur in February, due to the lowest monthly precipitation. Nevertheless, concentration of Hg in aerosols is also dependent on the air temperature, which was presented in Table 1. When temperatures were relatively high during the 2008/2009 winter, concentrations of TPM were low ( $TPM_{0.7}$ ,  $39.9 \text{ pg m}^{-3}$  and  $TPM_{2.2}$ ,  $151.5 \text{ pg m}^{-3}$ ) in relation to the results obtained by Beldowska et al. (2003) during previous measurements. In February 2006, when winter was very frosty, the

exceptional value of TPM was observed ( $1\,964\text{ }\mu\text{g m}^{-3}$ ) (Beldowska et al., 2007). This value was several times greater than one determined in the present study. Such high anthropogenic emission of Hg to the atmosphere is a consequence of the demand for heating energy during frosty winters and the intensified processes of burning fossil fuels.



**Figure 6.** Concentration of  $\Sigma\text{TPM}_{2.2} + \text{TPM}_{0.7}$  ( $\mu\text{g m}^{-3}$ ) in the air over the coastal zone of the southern Baltic in 3 measurement cycles: (a) Monday–Wednesday (b) Wednesday–Friday (c) Friday–Monday in the period April 2008 – April 2009 (statistical differences were proved by Kruskal-Wallis test  $p = 0.6827$ ).

#### 4. Conclusions

Mercury in aerosols over the coastal zone of the southern Baltic originates mainly from anthropogenic sources (the Tricity agglomeration, the refinery, power and heat generating plants,

waste incineration units, domestic furnaces and boiler rooms, sewage treatment plants etc.) and from photochemical transformations of Hg in air masses inflowing from remote areas to the coastal zone. The second important source of Hg<sup>0</sup> in the air is the Gulf of Gdansk.

Temperature and local circulation of the air were the factors which influenced TPM concentration the most. That was manifested in greater variability and the range of Hg concentrations in fine and coarse aerosols during months when temperatures were below zero and the turbulence was strong.

The autumn–winter season was the period of the highest concentrations of Hg in fine and coarse aerosols over the coastal zone of the southern Baltic (the average  $\text{TPM}_{0.7}$  concentration was  $4.1 \pm 6.7\text{ }\mu\text{g m}^{-3}$  while  $\text{TPM}_{2.2}$  was  $35.5 \pm 28.5\text{ }\mu\text{g m}^{-3}$ ).

Higher emissions of Hg were commonly reported in winter. Observations of TPM concentrations in the particular days of a week in winter revealed elevated emissions during weekends, when the demand for heating energy for individual consumers is the highest.

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