



Mercury loads into the sea associated with extreme flood



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ABSTRACT

Floods are an important factor determining riverine pollution loads, including toxic mercury (Hg). The impact of the Vistula River flood in 2010, which was the biggest one recorded in 160 years and its influence on marine environment was studied. Mercury concentration was analyzed in river and sea water, suspended matter, phytoplankton and sea surface sediment. Flood and gulf water contained several times higher concentration of Hg (exceeded reference values safe for aquatic organisms) than before or after the flood. In 2010 the Vistula introduced into the Baltic ca. 1576 kg of Hg, of which 75% can be attributed to the flood water. Increase of water temperature, decrease of oxygen content contended increasing of dissolved mercury concentration, which was transported far into the Baltic. This phenomenon led to an increase of Hg concentration in phytoplankton and during many months in surface sediments. It is a potential threat to marine organisms.

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1. Introduction

Mercury (Hg) is a highly toxic pollutant found in terrestrial and aquatic systems all around the globe. Ubiquity of mercury all over the world constitutes significant threat to wildlife and human health, as well as to socioeconomy worldwide (Mergler et al., 2007; Swain et al., 2007). Particularly sensitive to Hg contamination is the aquatic environment, where the metal bioaccumulates and biomagnifies with increasing trophic level. Consequently, Hg concentration in tissues of fish, birds and water mammals can be even 10 000–100 000 times higher than in the surrounding water (Boening, 2000). The most common intake route in human Hg poisoning is the consumption of fish and seafood with high levels of this metal in the tissues.

Mercury emissions have both natural and anthropogenic components but most of these sources emit Hg directly to the atmosphere (Pacyna et al., 2010; Pirrone et al., 2010). Therefore in a global scale, main transport route of Hg from land to oceans is the atmosphere, whereas Hg load by rivers is substantially smaller. However in the coastal zone, the rivers are the main Hg source. The rivers in turn receive a major mercury portion from land erosion.

Mercury on the land mainly comes from atmospheric deposition (Grigal, 2002). Also, soil ability to accumulate metals, caused catchments to become an important source of Hg for aquatic systems. The rate of Hg remobilization from land and its transport to the sea depends on many factors, including: physical characteristics of catchment (e.g. land cover or soil type) and biogeochemical controls (organic and inorganic ligands) (Grigal, 2002). Also land use in catchment (arable lands or urban area with the impermeable surfaces) can short-circuit hydrologic pathways of Hg in river basins and thus reduce retention (increase yield) of atmospherically derived Hg (Lyons et al., 2006). This enhances the rate of elution of pollutants from land and together with surface outflow, magnitude of transport to the sea. Seasonal dynamics (storm events, draughts and snowmelt) also play an important role in mercury transport, because concentration and dissolved/particulate partitioning of Hg depend on the water flow in the river (Mason and Sullivan, 1998). Therefore floods are the important factor controlling riverine pollution loads. During those events, water flow increases dramatically, which is usually connected with an increased load of contaminants eluted from inundated areas. In such events, during relatively short time, a large mass of contaminants reaches the sea, which may create a risk not only for estuaries, but also for offshore areas. This phenomenon is particularly important in areas where the estuary is directly connected to the sea (like in the Gulf of Gdańsk). The risk of sea contamination decreases in places, where

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river discharges to an inner coastal lagoon. In such scenarios, a major portion of contaminated sediments within confined area, and in consequence only a fraction of their riverine load enters the sea. Such situation was observed in 1997 in the Oder estuary. After the major flood, Pohl et al. (2002) did not observe adverse effects in the Baltic Sea ecosystem. The major part of transported metals was associated with SPM and precipitated out of the water column, accumulating in the sediments of the lagoon.

Mercury is now listed as a priority element in a large number of international agreements and conventions aimed at protecting the environment (Ebinghaus et al., 1999). Also the Baltic States are obliged to control emissions of this metal (HELCOM, 2010). The largest load of mercury, especially in the coastal zone of the Baltic Sea is delivered by rivers (HELCOM, 2010; Saniewska, 2013). For many years the input of this metal into the Baltic Sea has been monitored based on few measurements extrapolated by models (HELCOM, 2010). It appears that these estimates are insufficient, because they do not take into account anomalous meteorological and hydrological events. More frequent changes in the hydrological cycle, which result in heavy rain and flooding, significantly increase the input of pollutants washed out of the atmosphere and soil into surface water.

Presently, in many parts of the world, the climate change is causing extreme floods that are the more frequent phenomenon. The flood in 2010 was one of the biggest observed in Poland and culmination of the flood wave was the biggest recorded for 160 years (Maciejewski et al., 2011). This created an opportunity to answer some important research questions. Can the extreme flood become a significant source of toxic mercury and the threat for the marine environment? At what distance from the river mouth are adverse effects noticeable? How long can the impact of the flood persist in the marine environment?

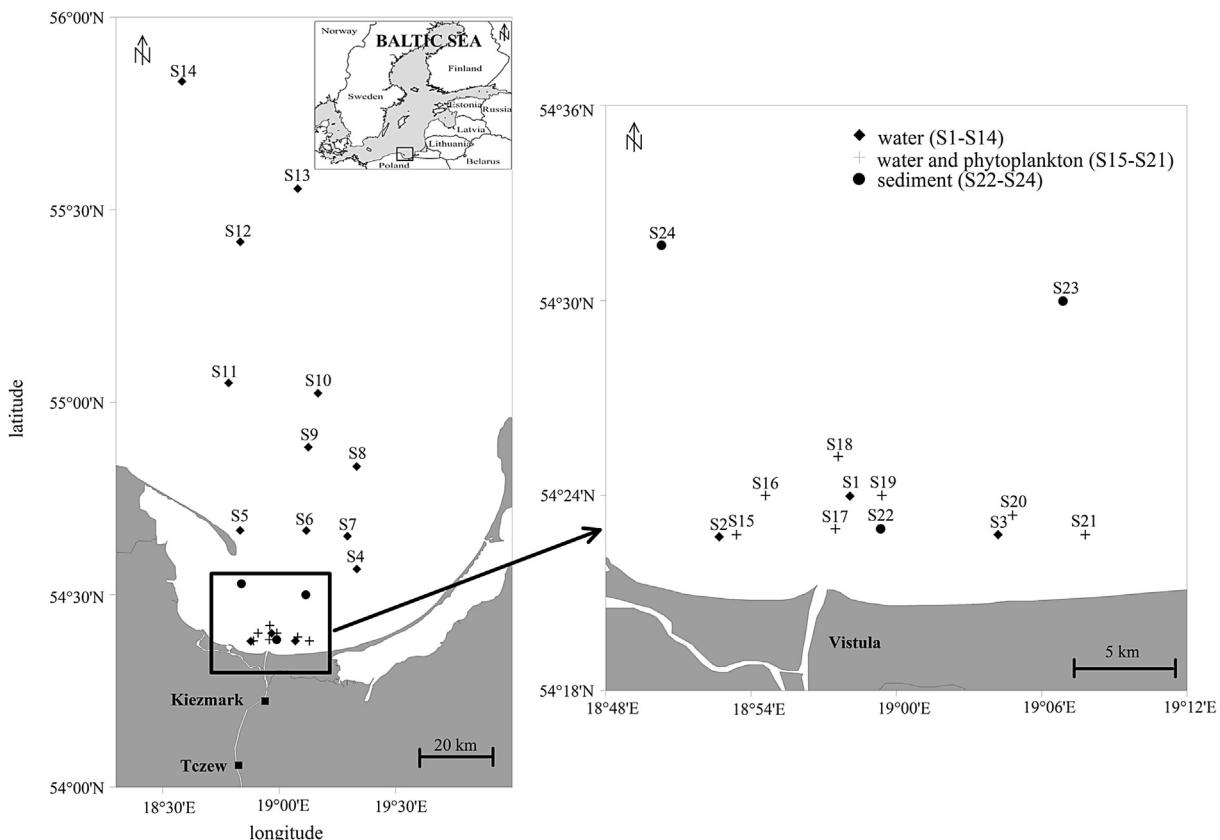


Fig. 1. Sampling sites location.

2. Materials and methods

2.1. Study area

Study area is located in the mouth of the second largest river (after Neva) discharging into the Baltic Sea—the Vistula (catchment area is 194 000 km²) and the Gulf of Gdańsk, for which the Vistula is the most important source of contaminants. In mid-May 2010 in the southern Poland massive rainfall occurred (max 200 mm per day), whose magnitude, intensity and duration exceeded all monthly sums for May for 160 years of recorded measurements. This has caused an increase of water levels in the upper Vistula catchment and formation of the first flood wave (20 May–4 June). The flood wave was characterized by rapid increase and after reaching a plateau a slow decrease. Since 19 May water level near-mouth profile in Tczew (35 km from the mouth) started to increase and culmination of the flood wave occurred on 25 May and lasted for 2–3 days. The flood wave reached the Baltic Sea on 26 May. On the first days of June another wave of precipitation occurred in the upper Vistula, which induced a rise of water levels and formation of second flood wave (9–19 June). Small retention capability of the watershed, already saturated with previous flood, caused that the second flood wave level exceeded the first one. Since 9 June another water level rise was observed in Tczew and the peak of flood wave was observed on 12 June. On the next day flood wave reached the Baltic (Śmiech, 2011). As a result of the flood 706 thousands of hectares were inundated in 2157 towns. 14 565 persons had to be evacuated and 101 288 farms were severely damaged (Biedroń et al., 2011).

2.2. Sample collection

Subsurface water samples were collected from the Vistula River at Kiezmak (12 km from the mouth) (Fig. 1). During the flood (26 May–19 June) samples were collected daily ($n = 24$), in the remaining period of 2010 – monthly. Additionally, on 1, 8, 14 and 21 June sea water samples ($n = 8$) were collected from the Gulf of Gdańsk: at point S1, located 5 km north from the mouth and S2, located 5 km west from the mouth (Fig. 1). Surface water samples ($n = 19$) were also collected from 19 locations (S3–S21) in the southern Baltic during the monitoring cruise of the Institute of Meteorology and Water Management – National Research Institute from aboard R/V Baltica (7–15 June). At this time samples of phytoplankton ($n = 7$) from surface water of the Gulf of Gdańsk were collected (S15–S21) with a 50 µm mesh net (Fig. 1). Additionally, surface sediment samples ($n = 7$) were collected in the years 2010–2013 Institute from aboard the R/V Oceania, at 2 stations situated in a region under the influence of the Vistula water (Majewski, 1990): S22 (depth 16 m;

November 2011, March 2012), S23 (depth 69 m; June 2010, April 2011, March 2012, February 2013) and one away from Vistula influence – S24 (depth 39 m; September 2011) with Van Veen Grab sampler (Fig. 1).

Water samples for the analysis of the total mercury were collected directly into acid washed borosilicate vials with Teflon screw cap. Samples were stored at 4 °C until analysis. Water samples collected for the analysis of suspended mercury were taken directly to 1 dm³ bottles of dark borosilicate glass. Samples, after being transported to the lab, were filtered through ignited, preweighted glass fiber filters with pore size of 0.7 µm (Whatman GF/F). Filtration was carried out immediately after the return from the sampling station in the lab under the laminar flow hood (HEPA class 100). Blanks were collected during filtration. Filters were freeze dried and then stored at -20 °C, in acid digested polycarbonate boxes. Sediments and phytoplankton samples were stored in zip bags at -20 °C. Sediments samples were homogenized in a ball mill with agate milling chamber.

2.3. Analysis

According to an accepted methodology (Method 1631, USEPA, 2002), Hg_{tot} in the water samples was oxidized by BrCl and pre-reduced with solution of hydroxylamine hydrochloride. Analyses were performed by the use of Tekran 2600 mercury analyzer (CV-AFS). Quality control procedures for water samples included blanks and water spiked with Hg nitrate in the range of 0.5–25 ng dm⁻³ and produced adequate precision (1% RSD) and recovery (98%–99%).

Sediments and suspended matter samples were freeze dried and homogenized. Samples were then analyzed with AMA 254 advanced mercury analyzer (AAS), after thermal decomposition in pure oxygen. Quality control procedures (triple repetition, BCR-414; GBW 07314) showed that average error did not exceed 5%. Detection limit for water samples was 0.05 ng dm⁻³, and for suspended matter 5 ng kg⁻¹.

In the same water sample Hg_{tot} and Hg_{SPM} concentrations were measured. Colloidal material exhibits similar ability to transport as dissolved fraction, therefore dissolved mercury (Hg_{dis}) was estimated as a difference between Hg_{tot} and Hg_{SPM} concentrations.

2.4. Additional parameters

Additionally, in the Vistula River in Kiezmak (12 km from the mouth) water temperature, suspended particulate matter (SPM) concentration and dissolved oxygen concentrations were measured. Those measurements were performed according to the Polish National Environmental Monitoring standards (WIOŚ, 2011). The average daily flows of the Vistula were measured at the Tczew profil (35 km from the mouth) with ADCP (Acoustic Doppler Current Profiler). The reception area rise below Tczew is small and it can be assumed that the data presented here determine the amount of water flowing into the sea (Pempkowiak and Kupryszecki, 1980). Those measurements were done by Institute of the Meteorology and Water Management – National Research Institute. Based on the mercury concentration and daily flow of the Vistula, daily load was determined. Both monthly and annual Hg load was calculated assuming linear variability in time periods between two measurements (HELCOM, 2010; Niemirycz, 2011). This method of estimating the load of pollutants is applied by HELCOM and the other Baltic countries:

$$L_r = \sum_{i=1}^n C_i Q_i \quad (1)$$

where: L_r – annual load (kg a⁻¹); n – number of measurements; C_i – discrete concentration of constituent in the i -th measurement (µg m⁻³); Q_i – discrete (daily) flow corresponding to the concentration C_i (m³ s⁻¹).

The flood began on 20 May 2010, however, samples were collected from 26 May 2010. Load of the metal transported in the first days of the flood (20 May–26 May)

was estimated in a similar way as annual Hg load according to formula 1 (HELCOM, 2010; Niemirycz, 2011).

Fine fraction content of sediments ($\varphi < 0.0063$ mm) was determined by sieving.

2.5. Statistical analysis

Statistical tests were performed using the computer software Statistica 9. Pearson correlation coefficient was used to describe relationship. As significance level an $\alpha = 0.05$ was used.

3. Results

3.1. Hg in the Vistula River

Total mercury concentration (Hg_{tot}) measured in the Vistula in 2010, with a median value of 6.3 ng dm⁻³ (average 7.3 ng dm⁻³) outside of flood period, were slightly higher than global average in unpolluted rivers (5.0 ng dm⁻³) (Mason et al., 1994) (Table 1). Before the flood, median and average Hg concentration were equal 5.6 ng dm⁻³ and after the flood median achieved 6.7 ng dm⁻³ and average 7.3 ng dm⁻³. At the same time no values exceeding 12 ng Hg dm⁻³, which are supposed to have chronic toxic effects on aquatic organisms, were observed (USEPA, 1992). Outside of the flood period, Hg occurred in the water mostly as particulate matter bound (Hg_{SPM-V}) (89% Hg_{tot}) (Table 1). This value is typical for river water, in which dissolved mercury (Hg_{dis}) contribution usually does not exceed 10% Hg_{tot} (Mason and Sullivan, 1998). Only the content of Hg in suspended particulate matter (Hg_{SPM-M}) (median 334 µg kg⁻¹ d.w.) was higher than in unpolluted or relatively free of anthropogenic pressure areas (50–200 µg kg⁻¹ d.w.) (Mason and Sullivan, 1998).

During the Vistula flood, river water was significantly more polluted with all Hg forms than before and after the flood (Table 1). In the entire flood period values exceeded 12 ng Hg dm⁻³, which indicated negative influence on aquatic organisms (USEPA, 1992). Median value of Hg_{tot} (41.3 ng dm⁻³) calculated for 25 days of flood was seven fold higher than in the remaining period (11 months of 2010) and eight times higher than in the same period (May–June) of years 2008–2009 (Saniewska, 2013). During flood, median Hg_{SPM-M} concentration was calculated to be 34 times higher than outside of flood period. Whereas concentrations of suspended matter during flood (21.6 mg dm⁻³) and outside of flood period (20.1 mg dm⁻³) were comparable (Table 1). The highest Hg_{tot} concentrations were observed on: 26 May: 299.1 ng dm⁻³, 27 May: 230.9 ng dm⁻³, 28 May: 227.8 ng dm⁻³ (Fig. 2). In this period, also Hg_{SPM-M} concentration was very high, reaching 7227 µg kg⁻¹ d.w. on the second day. In this day concentration of SPM was low – 24 mg dm⁻³. During the following days Hg_{tot} concentration was rapidly falling and the lowest values for the entire flood period (<30 ng dm⁻³) were observed between the two flood waves (5.06–

Table 1
Descriptive statistics of measured parameters in the Vistula River in 2010.

Estimator	Hg _{tot} ng dm ⁻³	Hg _{SPM-V}	Hg _{dis}	Hg _{SPM-M} µg kg ⁻¹ d.w.	SPM mg dm ⁻³	T °C	O ₂ mg dm ⁻³	Q m ³ s ⁻¹
Outside of flood period								
N	6	6	6	6	6	6	6	325
M	6.3	5.8	0.7	334	18.8	8.8	10.6	1474
Av	7.3	6.5	0.5	539	20.1	11.7	9.6	1425
Min–Max	4.7–11.7	4.5–9.6	0.2–2.1	157–1749	3.6–35.0	4.5–9.6	5.8–11.2	502–4020
Flood								
N	24	24	24	24	24	24	24	31
M	41.3	10.2	24.0	1145	11.3	19	7.2	4423
Av	59.2	33.3	25.9	1694	21.6	18	8.0	4144
Min–Max	20.8–299.1	3.4–206.2	11.8–55.9	152–7227	1.4–102.9	14–22	6.1–9.3	2130–6360

N – number of measurements. M – median. Av – average. Min–Max – range.

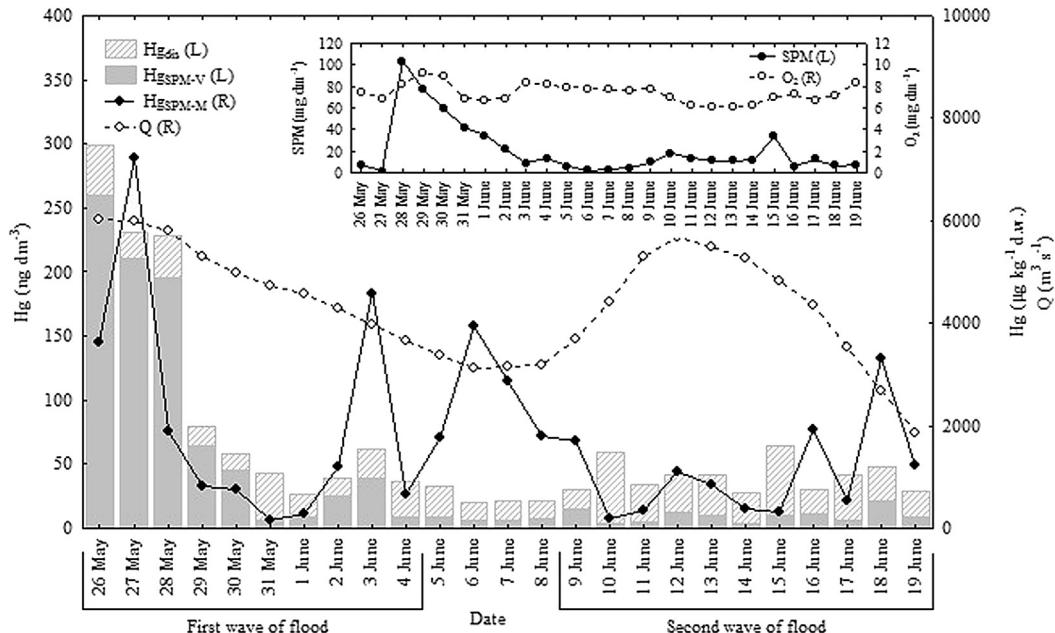


Fig. 2. Temporal variability of Hg_{tot}; Hg_{dis} and Hg_{SPM} concentration in Vistula water during the flood in 2010.

8.06). Those values were ten times smaller than those observed during the first days of the flood (Fig. 2).

During the flood in 2010, Hg occurred in Vistula mostly as dissolved form (Hg_{SPM-V} contributed to 42% of Hg_{tot}), which is not atypical situation (Mason and Sullivan, 1998). Outside of the flood period Hg_{SPM-V} contributed to 89% of Hg_{tot}. During the flood, the proportion of Hg_{SPM-V} decreased (Fig. 2). During the first flood wave, Hg_{SPM-V} contributed to 83% of Hg_{tot}, and the smallest proportions occurred during the second flood wave (average 25% of Hg_{tot}), amounting to a minimum value – 6% of Hg_{tot}: on the 17th day of the flood (11.06) (Fig. 2).

3.2. Additional parameters measured in Vistula

Multiannual (1951–2005) average flow of the Vistula was equal to 1047 m³ s⁻¹ (IMGW, 2011), while the average flow in 2010 amounted to 1729 m³ s⁻¹. Flood period was characterized by three times higher flow (4423 m³ s⁻¹) than outside the flood (1474 m³ s⁻¹). During one month of the flood (20.05–19.06) 12 km³ of water were transported into the gulf, which amounted to 21% of the water transported into the Gulf of Gdańsk in 2010.

During the flood water temperature varied between 14.1 °C and 22.0 °C (Table 1). Measured dissolved oxygen concentrations were from 7.8 mg dm⁻³ to 8.3 mg dm⁻³. SPM concentration was in the range from 1.4 to 102.9 mg dm⁻³ (Table 1).

3.3. Hg and additional parameters in the Gdańsk Basin

Hg concentration in surface water of the Gdańsk Basin measured during the flood at 21 marine stations varied from 2 ng dm⁻³ (at S14 station) to 103.6 ng dm⁻³ (at S1 station) (Fig. 1). Hg concentration in phytoplankton measured at 7 stations in Gulf of Gdańsk varied in the range from 115 µg kg⁻¹ d.w. (S18 station) to 326 µg kg⁻¹ d.w. (S21 station). Sediments at 3 sampled stations were characterized with Hg concentrations from 9.4 µg kg⁻¹ d.w. (S22 station, March 2012) to 288.8 µg kg⁻¹ d.w. (S23 station, June 2010). At station S22 content of fine fraction was about 1–2%, at S23 varied between 19% and 23% and at S24 was about 13%.

4. Discussion

4.1. The flood as a source of toxic mercury into the sea

In 2010 the Vistula's load of Hg into the Gulf of Gdańsk was estimated to be 1576 kg (Fig. 3). During the one month flood, 75% of that load was delivered (1197 kg). The load of the metal transported with the flood wave in relatively short time, was over two times higher than combined annual load of Hg transported from all municipal sources to the Baltic (HELCOM, 2004).

During five days (24–28 May) 53% of the flood Hg load reached the Baltic Sea, which translates into 636 kg Hg. The biggest single day input of this metal was recorded in 26 May 2010—156 kg Hg. In this day SPM concentration itself was low, but it was substantially

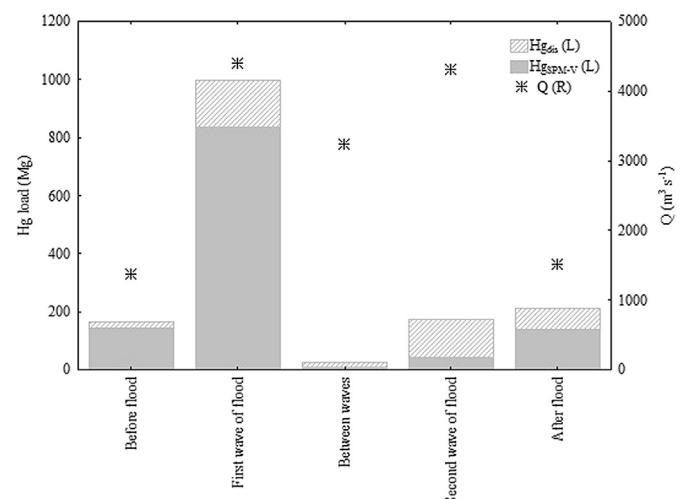


Fig. 3. The sum of Hg load introduced to the Baltic Sea with Vistula River water in 2010: before the flood (January–April), during the first wave of the flood (20 May–4 June), between waves (5–8 June), during second wave of the flood (9–19 June) and after the flood (July–December); * – Average discharge rates measured at lower profile.

enriched in mercury (Fig. 2). High values of Hg concentrations in Vistula River during the flood resulted not only from enhanced water transport. Flood waters transported pollutants eluted from inundated buildings, septic tanks, graveyards, sewage treatment plants etc. In total, during the first flood wave (20 May–4 June 2010), 998 kg Hg mainly associated with SPM, reached the Baltic, including 163 kg Hg_{dis}, while during the second wave (9–19 June 2010) 172 kg Hg, including 132 kg Hg_{dis} (Fig. 3). Despite the fact, that Hg_{tot} load was almost six times lower during the second flood wave (11 days) than during the first flood wave (16 days), the mass of introduced Hg_{dis} was comparable (Fig. 3), which is important for aquatic organisms. During the flood, the increase of Hg_{dis} contribution in Hg_{tot} (and simultaneous decrease of Hg_{SPM-V} in Hg_{tot}) was observed in Vistula water (Fig. 2). Riverine Hg_{SPM} to Hg_{tot} ratio correlated to water temperature ($r = -0.65$, $p < 0.001$) and to dissolved oxygen concentration ($r = 0.59$, $p < 0.001$). Water temperature reflected the duration for which the flood water remained on inundated areas, which in turn impacted mercury partitioning. With sustained high water levels, SPM was a subject to sedimentation (Fig. 2). Decrease of dissolved oxygen concentration was most probably caused by the degradation of sedimenting organic matter. Those processes led on one hand to a decrease of Hg_{SPM} concentration and on the other hand to a release of dissolved reactive mercury to the water (Bonzongo and Donkor, 2003; Ravichandran, 2004). In time when water temperature was the highest (>20 °C) and oxygen concentration was the lowest (7.8 mg dm⁻³), the lowest concentration of Hg_{SPM-V}, Hg_{SPM-M} and the highest concentration of Hg_{dis} were measured, which constituted 94% of Hg_{tot}. These parameters (high water temperature, low oxygen concentration) caused the concentrations of Hg_{SPM-V} and Hg_{SPM-M} during flood to be lower than during outside of flood time period (Fig. 2; Table 1). Observed decrease of Hg_{SPM-V} and increase of Hg_{dis} concentration were caused by prolonged flood duration (31 days), which caused an increase of water temperature, decrease of oxygen content and in consequents elution of Hg(II) from sedimented SPM and additionally from inundated areas, where it accumulated for decades. Those processes led to an increase of dissolved Hg concentration, which could be a substrate for methylation. Process of deposition of suspended matter in times of flood was also observed in River Nura in Kazakhstan, which caused increase of mercury input in dissolved form (Heaven et al., 2000b; Ullrich et al., 2007). It is most probable that Hg released from the sediment and flood plains could be moving downstream during new seasonal inundation (for example during the snowmelt). Deposition of Hg_{SPM} is the serious problem, because subsequent remobilization of Hg occurs mainly in the toxic form of MeHg (Jackson, 1991; Heaven et al., 2000a).

4.2. Hg associated with the flood along the distance gradient from the mouth of the river into the sea

In the surface waters of the Gulf of Gdańsk, 5 km north from the Vistula mouth (S1), seven days after the arrival of the flood wave (1 June 2010), Hg_{tot} concentration was 103.6 ng dm⁻³ (Fig. 4). This value was almost hundred times higher than values usually observed in this area (Saniewska et al., 2010) and eight times higher than a reference safe value for aquatic organisms (USEPA, 1992). Determining factors for high concentrations of pollutants in the coastal zone, in addition to flooding, are the strength and direction of the wind (Covelli et al., 2007). Sustained high concentrations of pollutants recorded in subsequent days of June 2010 in the gulf near the river mouth (Fig. 4) were additionally stimulated by high winds blowing inland (on average 11 m s⁻¹), causing the Vistula water level rise in the mouth area. This phenomena is widely described by Sztobryn et al. (2011). Change of wind speed during the following

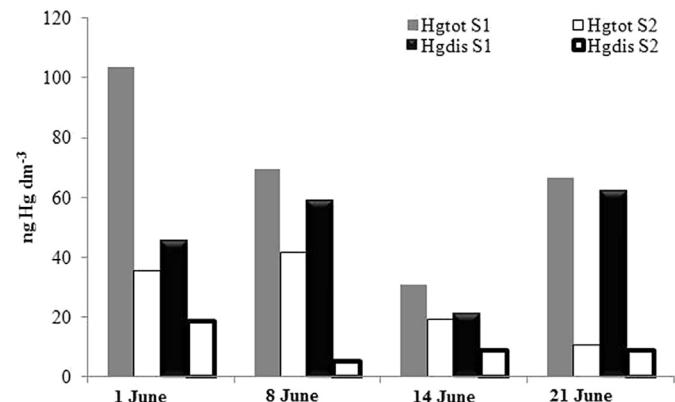


Fig. 4. Concentrations of Hg_{tot} and Hg_{dis} in surface sea water at stations S1 and S2 in the Gulf of Gdańsk, during the first wave of the flood (1 June), between waves (8 June), during the second wave of the flood (14 June) and two days after the flood (21 June).

days (14 June 2010) caused dispersion of Hg and the decrease of this metal concentration. The direction of currents and wind (N, NE) (Sztobryn et al., 2011; Zajaczkowski et al., 2010) caused the concentration of Hg 5 km NW from the river mouth (S2) to be lower than those recorded directly north of the mouth (S1) (Fig. 4). In the gulf water, similar to river water, Hg_{dis} content has risen and Hg_{SPM-V} has dropped through the flood. On 21 June Hg_{SPM-V} contribution to Hg_{tot} went down to 7% (Fig. 4). Outside of the flood period, this contribution was a lot higher – ca. 72% (Saniewska et al., 2010). Similar Hg_{SPM-V} to Hg_{tot} ratios trends were observed in 1997 during the Odra river flood (Pohl et al., 2002).

With increasing distance from the Vistula mouth towards the Gdańsk Basin, Hg concentration, during the period 7–15 June 2010, was dispersed in “cleaner” Baltic water. On the transition zone between the Gulf of Gdańsk and offshore waters, at the station (S7) 22 NM (40 km) away from the Vistula mouth, Hg_{tot} concentration was still elevated (9.9 ng dm⁻³) (Fig. 1). Hg entered the gulf mostly in the dissolved form (Fig. 4) and bound to fine particles. Those forms could be transported in the surface water layer. Prevalence of these forms of Hg made possible its migration to open southern Baltic waters. At S12 station, 67 NM (120 km) from the Vistula mouth (Fig. 1), Hg concentration was still elevated up to 6.5 ng dm⁻³. Such a long range of flood mercury transport resulted most probably from the fact that Vistula discharges directly into the gulf, as opposite i.e. to Odra river, discharging first to an enclosed lagoon, where flood associated mercury transport in 1997 was much shorter reaching (Pohl et al., 2002). Hg_{tot} concentrations in the Baltic Sea after the flood 2010 were several times higher than previously observed (Bełdowski et al., 2009; Murawiec et al., 2007; Pempkowiak et al., 1998; Saniewska et al., 2010; Wurl et al., 2001). Mercury concentrations in sea water observed in the years 1998–2009 were comparable, so the increase of concentration in 2010 may be attributed to the flood effect.

4.3. Hg associated with the flood in marine sediments in the scale time

Exceptionally strong current associated with the flood leads to an enhanced transport of mercury rich suspended matter, which can be partially composed with silt originating from bed and shores erosion. Similar phenomenon was reported in Idrijca–Isozno River drainage basin, where contaminated sediment transport from mining region contributed to enhanced mercury load, during seasonal floods (Covelli et al., 2007). In the catchment of the Vistula, there are not as significant sources of Hg, but the scale of

the event had made that an extremely large load of Hg, together with the strong current of the river, was introduced into southern Baltic Sea. Hg deposition at the bottom of the Gulf of Gdańsk led to an increase of Hg concentration in the surface sediments (Fig. 5). Similarly as in case of sea water contamination, the scale of contamination of marine sediments depends on sea currents and wind speed and direction (Covelli et al., 2007). During Vistula flood, the effect was enhanced by strong inland blowing winds, which prevailed for few days at the peak of flood (Sztobryn et al., 2011; Zajączkowski et al., 2010). They caused the flood waters to remain in the gulf, which in consequence lead to sedimentation of flood transported material within this area. This has reduced the area of the flood impact, but at the same time increased its magnitude. Total Hg concentrations in sediments at sampling stations situated in a region under the influence of the Vistula water (Majewski, 1990) were higher after the flood as compared to the year 2000 (Biedowski and Pempkowiak, 2007) (Fig. 5). Although Hg_{tot} concentration increase was not especially pronounced (from 40% at S24 to 500% at S22), values normalized to the fine sediment fraction Hg_ϕ show several fold differences (from 45% at S24 to 1500% at S23) as compared to concentrations recorded in the year 2000. There, a longer time series demonstrates a peak of Hg_ϕ concentrations after the flood, and gradual decrease towards 2013, reaching levels comparable to that observed in the year 2000. This suggests that observed increase was caused mostly by the transport of Hg rich fine suspended matter, contained in flood surge. It was especially visible in the Gulf of Gdańsk, north east from the Vistula mouth (S23). This suggests that the site was a transport area – in which sedimentation is balanced by erosion, where deposited material undergoes periodic resuspension and is transported to other areas of the sea. Damrat et al. (2013) confirmed that sedimentary material, discharged by the Vistula River, was transported to deeper areas. Sediment deposition/accumulation in this region (S23) is controlled by a range of processes, inter alia: the magnitude and

the dynamics of the riverine supply of terrigenous matter, water mixing, waves on the sea, gravity and wave induced sediment remobilization on the slopes of the upper prodelta and extreme phenomena, such as severe winter storms (Damrat et al., 2013).

Smaller Hg_ϕ concentration difference, between the year 2000 and 2011, was observed in the immediate vicinity of the mouth (S22) (Fig. 5). This suggests that majority of fine SPM from the Vistula River was transported to deeper areas of the gulf, as described for non-flood situation by Biedowski and Pempkowiak (2007). The smallest increase was observed at S24 station, which is neither under direct influence of Vistula plume, nor located on the source/sink pathway of Vistula material (Fig. 5).

4.4. Hg associated with the flood in marine organisms

The impact of the Vistula River on Gulf of Gdańsk waters is manifested in an increase in production rate, i.e. the biomass of phytoplankton (Wielgat-Rychert et al., 2013). Hg introduced with flood waters into the Gulf of Gdańsk was adsorbed by the phytoplankton. In consequence, its concentrations in algae, between first and second flood wave (14.06.2010) in more than half of results (57%) were higher than $200 \mu\text{g kg}^{-1}$ d.w. The average concentration ($204 \mu\text{g kg}^{-1}$ d.w.) was four times higher than usually observed in this area in June (Biedowska et al., 2013). The increase of Hg concentration in phytoplankton and surface sediments (especially Hg_ϕ) after the flood in 2010 could lead to an introduction of higher Hg load into the food chain of the Gdańsk Basin. Measured by Woroń and Danowska (2012) concentration of Hg in female herring muscles, fished in the Gulf of Gdańsk in 2011, increased by 67% in comparison to average value for years 1998–2010 and was the highest recorded during this period (Woroń and Danowska, 2012). Similar increase (60%) was observed in blue mussels (Woroń and Danowska, 2012). That increase of Hg concentrations in marine organisms was most probably associated with input of contaminants with the Vistula flood. Influence of flood on trace metals

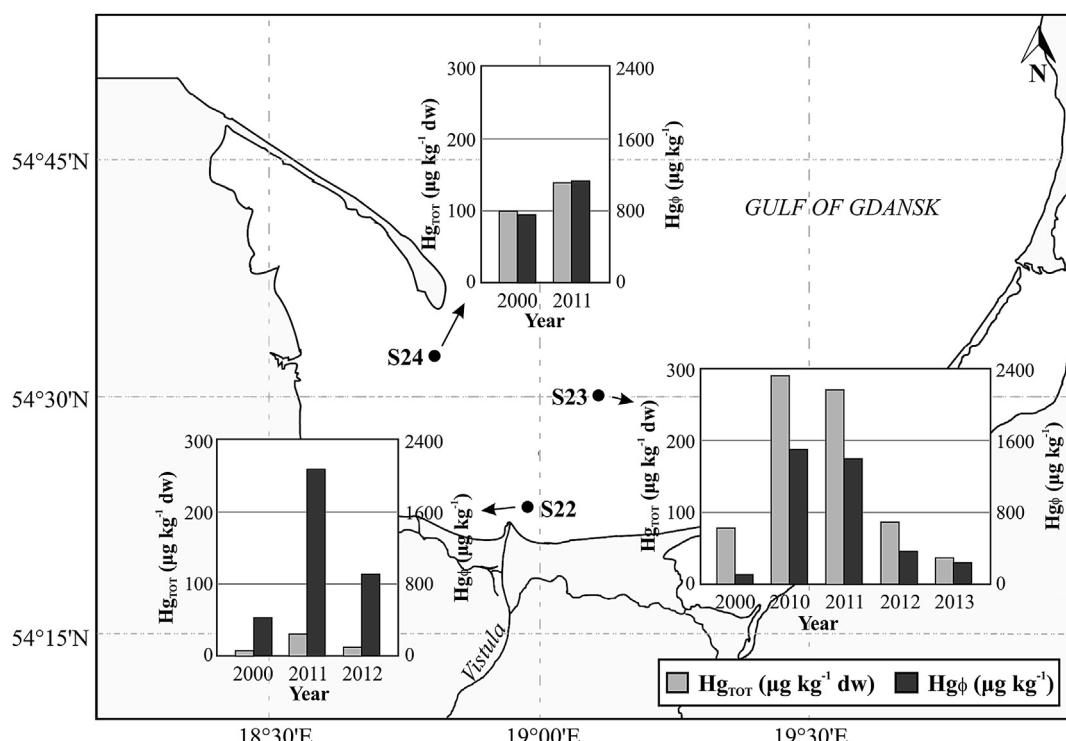


Fig. 5. Concentration of Hg_{tot} and Hg_ϕ in surface sediments at S22–S24 stations.

concentrations in fish was observed also after Odra River flood in 1997 (Polak-Juszczak, 2009).

5. Conclusions

In relatively short time (31 days), the extreme flood (12 km³ of water – 21% of the annual Vistula inflow), caused several fold increase of concentrations of both total and particulate Hg forms in the Vistula waters as compared to situation outside the flood period. During the culmination of the first flood wave Hg_{tot} concentrations reached values higher than 200 ng dm⁻³. In the receiving area of the Gulf of Gdańsk close to the river mouth, strong winds blowing towards the shore (Sztobryn et al., 2011; Zajączkowski et al., 2010) caused an additional accumulation of pollutants, which influenced Hg_{tot} concentrations (104 ng dm⁻³) during the first weeks of the flood. Hg concentrations in the river and in the gulf water close to the mouth exceeded reference values safe for aquatic organisms.

During the one month flood 1197 kg Hg (75% of annual mercury load) reached the southern Baltic Sea. Such a large load of the contaminant introduced in such a short period of time to the coastal zone could have a negative impact on aquatic organisms living in that region. Prolonged flood duration favored an increase of water temperature, decrease of oxygen content and in consequence increase of Hg_{dis} concentration. Hg_{dis} content had risen through the flood, which led to an atypical situation during the second flood wave, when dissolved mercury constituted the majority of Hg_{tot} (average 75%). In that form, mercury was transported for large distances into the sea, leading to elevated Hg concentration in the water even as far as 67 NM (120 km) from the Vistula mouth. Elevated concentration of Hg in the sea water led to an increase of Hg concentration in plankton and in consequence in surface sediments. High mercury concentration in sediments sustained for several dozen months. Increase of Hg concentration, especially of Hg_d, in sediments, was observed not only in the coastal zone itself, but also in the offshore region, from where it was further transported to the deeper region of the sea, which lasted several months. Metal input associated with the flood was able to enter the marine food chain, as confirmed by the elevated concentration of this metal in tissues of herrings and blue mussels (Woron and Danowska, 2012).

According to future climate scenarios, precipitation patterns change, and prolonged draughts, which make the soil hydrophobic, followed by downpours, may cause increase both frequency and magnitude of floods (HELCOM, 2013). Precipitation is projected to increase in the entire Baltic Sea catchment, especially during winter. Some projections for the Baltic region show an increased probability and frequency of very extreme precipitation, from single rain events to long-lasting precipitation (HELCOM, 2013). If those floods enhance mercury load to the sea by the factor of 3, as observed in this study, we may face a substantial remobilization of historical mercury deposits, to the Baltic. This represents a major threat to the rich ecosystems situated in coastal areas and in consequences for consumers of contaminated fish.

It appears that floods are important source of pollution for a long-term scale (even years). In consequence, the level of contaminants in consumed fish and seafood should be monitored at least 2 years after the flood. Due to long-range transport of toxic substances in the sea, floods are potential transboundary problems. Toxic substances, which they introduce to the sea, are deposited not only in the coastal zone but can travel to distant areas, where they can remain elevated even for years. Therefore, flood protection measures, and level of contaminants in potentially inundated areas should be a subject of international concern, similarly to pollutant loads.

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