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Watershed characteristics and climate factors effect on the temporal variability of mercury in the southern Baltic Sea rivers

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ABSTRACT

Mercury (Hg) is a neurotoxic metal which can enter into the human organism mainly by fish consumption, skin and transpiration. In the coastal zone of the southern Baltic Sea, rivers are the main source of Hg. The Polish region represents the largest proportion of the Baltic Sea catchment and this research included four rivers of the Baltic watershed: the Reda, Zagórska Struga, Kacza and Gizdekpa. The samples were collected in the years 2011–2013. Total and particulate Hg concentration in these rivers were measured. Due to intensive rain, deposited mercury on the catchment area was washed out into the riverines water and introduced into the Baltic Sea. Consequently, the load of Hg increased three times. Additionally, the intensive dry atmospheric deposition during heating season caused the increase of the concentration of particulate Hg in the river water even by 85%. The research confirmed the role of the river flow magnitude in the load of mercury introduced into the sea by rivers. Moreover, a high variability of mercury concentration was connected to the additional sources such as the chemicals containing Hg and no municipal sewage system. The analysis of stable isotopes indicated that the SPM contained terrestrial organic matter; however, there was no clear correlation between Hg_{tot} , C_{org} and N_{tot} concentrations and $\delta^{13}C$, $\delta^{15}N$, C/N in particulate matter.

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Introduction

Mercury (Hg) is recognized as one of the most dangerous heavy metals found in terrestrial and aquatic systems throughout the world. 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 times higher than in the surrounding water (Boeing, 2000; Schurz et al., 2000). Therefore, our understanding

of mercury cycling in the terrestrial and aquatic environments is of fundamental importance, especially in areas where the population depends heavily on food from the sea (Gerstenberger, 2004). Hg enters a human organism mainly during the consumption of food and also through the respiratory system and skin (Boeing, 2000). A methylmercury has the most significant impact on human health, because of its bioavailability and potential for biomagnification (Kibria, 2014). Numerous studies for years have proved that such health effects were resulting from mercury exposure, which in some

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cases were lethal (Boeing, 2000; Zahir et al., 2005; Bose-O'Reilly et al., 2010), and has a large, direct impact on human health.

On a global scale, the atmospheric deposition is the main source of mercury into sea water. The main anthropogenic sources of mercury into the atmosphere in the Polish coastal zone are the combustion of coal for energy and heat production (Bartnicki et al., 2010, 2011; Beldowska et al., 2012; Beldowska et al., 2014). Despite restrictions requiring the reduction of emission of Hg into the environment, the concentration of this metal in the Baltic Sea had not decreased in the same proportions (HELCOM, 2010). The load of mercury introduced into the sea by rivers is relatively small compared to other sources in the global ocean, where the atmospheric deposition plays a main role. A different situation was noticed in smaller bays/coastal zones where rivers deliver the majority of the total mercury input (Saniewska et al., 2010, 2014a, 2014b). They are the main areas where organic matter delivered by rivers accumulates. It is significant, because Hg can be adsorbed onto the suspended particulate matter (SPM) in the water environment. Besides this adsorption, heavy metals can be connected with organic matter by a complexation process. SPM can remove many contaminants (e.g., mercury) from the water column due to sorption and its sedimentation and burial in the bottom sediments (IAEA, 2000). Moreover, organic matter can transport mercury into a trophic chain. Many factors have an impact on the quality and quantity of SPM in aquatic ecosystems. The most important factors are as follows: autochthonous production, allochthonous materials such as humic and fulvic substances, dust and mineral particles, and the amount of re-suspended material. SPM is a complex mix of finely divided solids and liquids with different origins and properties like a capacity to bind pollutants (Ostapenia, 1989; Velimorov, 1991; Boulion, 1994). The main allochthonous source of this matter in the marine environment is an inflow of river water. It can also introduce pollutants like mercury into the marine environment. The increase in the concentration of suspended particulate Hg causes the rise of contamination in a trophic chain (Salot et al., 2002). The coastal regions are mostly exposed to anthropogenic inputs of different contamination such as heavy metals and nutrients.

Stable isotopes of carbon and nitrogen are commonly used to identify provenance of organic matter in the environment as well as to study structure and functioning (Kidd et al., 1995; Al-Reasi et al., 2007; Ikemoto et al., 2008; Evers et al., 2009; Senn et al., 2010). Thus, isotopic composition may help to investigate the bioaccumulation and biomagnification of different contaminants in marine organisms (Cabana and Rasmussen, 1996). The origin of the SPM has an impact on transformation of adsorbed mercury. Hg^{2+} reacts with organic carbon by bacteria in the sediment causing a conversion into MeHg. After that, MeHg can be bioaccumulated into marine species through the trophic chain.

Organic matter, both particulate (POM) and dissolved (DOM) originates from various sources. Generally two basic sources can be distinguished: marine and terrigenous. Both differ significantly in terms of elemental and isotopic composition. Hence the variables such as: C/N molar ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are often used as tools to distinguish organic matter provenance (Emerson and Hedges, 2008). The C/N ratio of marine organic matter is usually found between 4 and 10, while that of terrigenous origin is most often above 14. This is

due to the fact that terrestrial organic matter is predominated by material from higher vascular plants, which contain a lot of polysaccharides (cellulose) and relatively little proteins (N source) (Orem et al., 1991; Tyson, 1995; Meyers, 1997). For both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ higher values are observed for the marine organic matter, while lower indicate terrigenous origin. $\delta^{13}\text{C}$ for marine organic matter is usually found in the range from -22‰ to -17‰ . The terrestrial one is isotopically lighter and its $\delta^{13}\text{C}$ oscillates between -30‰ and -25‰ (Schultz and Zabel, 2006). Both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ increase also stepwise in the consecutive links of the food pyramid. The change is especially pronounced for $\delta^{15}\text{N}$, for which amounts to 3.4‰ on average (Hobson and Welch, 1992). Additionally, it was reported that POM in sewage contains higher $\delta^{15}\text{N}$ values (Fogg et al., 1998; Rožič et al., 2015).

The rivers are the complicated system. Every part of this water body has a various type of soil, geological structure and the land use along the entire river length can be different. All land use changes can contribute to the change of mercury form and interactions of mercury with other components (Hurley et al., 1995; Lacerda et al., 2012). Due to the drastic reduction of forest area, the soil denudation and run-off increases soil Hg transfer into the rivers (Lacerda et al., 2012). Depending on the type of catchment, different amounts of mercury are introduced into the marine coastal zone (Saniewska et al., 2014b). The aim of this work was to recognize impact of the air temperature, precipitation, river water flow and origin of organic matter on the Hg concentration in SPM and in consequence the load of riverine mercury to the southern Baltic Sea.

1. Material and methods

The water samples were collected from the four rivers of the Gulf of Gdansk (Baltic Sea) catchment area: Reda, Zagórska Struga, Kacza and Gizdepka (Fig. 1). These rivers differ in the length, size and the type of catchment area (Table 1). The heating (October–April) and non-heating seasons (May–September) have been chosen basing on the meteorological data and information when the heat and power plants starts and ends (Beldowska et al., 2012).

Water samples were collected in the acid-cleaned borosilicate vials about 200 m from the river mouth. Those samples were taken once a month from January 2012 to December 2013 at a station located in the Reda river, from December 2011 until November 2012 in the Zagórska Struga and the Kacza river, from December 2011 to October 2013 at a station in the Gizdepka river. The salinity value was measured every time and it was 0 PSU. After sampling, the water samples were kept in a fridge in 5°C. The data of the water flow was measured by the Institute of Meteorology and Water Management - National Research Institute (IMGW-PIB).

1.1. Rivers description

The Reda river is the longest river included in this study. Most of its catchment is covered by forest area, arable land, pastures and meadows. Major parts of this river basin are agricultural land (51.2% of catchment area). The upper part of the river represents urbanized area, because of the Reda city

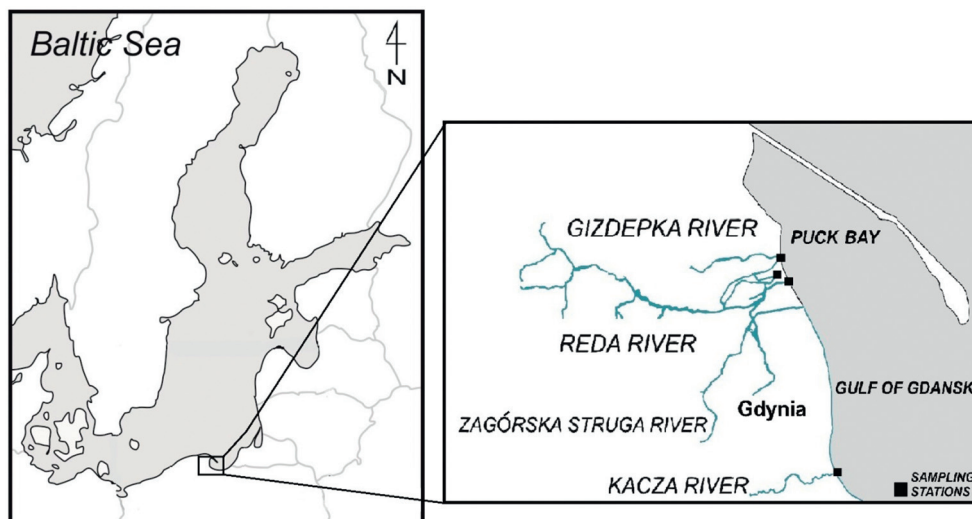


Fig. 1 – Sampling location.

situated along its shores. The outflow of this river varied through the year, with mean value being 4.3 m³/sec. The Reda flows to the Puck Bay.

Some parts of Zagórska Struga river are the mountain streams, though the upper part of its catchment is covered by fields and forest area. This river flows by Rumia city and in this part the Zagórska Struga was transformed and in this part, the river bed is laid with concrete. The zagórska Struga flows to the Puck Bay as well. The mean outflow for Zagórska Struga was 1.5 m³/sec.

The Kacza river is flowing through the city of Gdynia and flows to the Gulf of Gdansk (Baltic Sea). This river is urbanized and the storm water enters into the Kacza river. However the source of the Kacza river is in a small village so the catchment is covered by forest and peatlands as well. The mean outflow of the Kacza river was 0.2 m³/sec (Krajewska and Bogdanowicz, 2009).

The Gizdepka is the smallest river out of the other studied rivers, and the source is in a forest area; however, some part of this river is surrounded by meadows and fields. The mean outflow of Gizdepka into the Puck Bay (Baltic Sea) was 0.2 m³/sec.

1.2. Chemical analyses of Hg

The water samples for total mercury (Hg_{tot}) analysis were oxidized by adding BrCl. These samples were pre-reduced with hydroxylamine and hydrochloride solution for 1 hr before the

analysis by CVAFS (TEKRAN 2600, Canada). This method was adopted from the U.S. Environmental Protection Agency, 1992, 2002 (USEPA method 1631). The quality of the analytical procedure was controlled by using blanks and water spiked with Hg nitrate within the range from 0.5 to 25 ng/dm³ and produced adequate precision (1% RSD) and recovered (98%–99%). The reference material was used as well (BCR-579- coastal sea water). The limit of detection was 0.05 ng/dm³.

To obtain the suspended particles for Hg analyses, the water samples were filtered through ignited, pre-weighed glass fiber filters Whatman GF/F (pores size 0.7 µm) as fast as possible after sampling. The samples were frozen at –20°C. Before chemical analysis all materials were freeze-dried. Samples of particulate matter were analyzed using thermal desorption automatic mercury analyzer AMA 245. The analysis included triplicates to control the quality and reproducibility results (reference material - offshore marine sediment GBW 07314). The limit of detection was 0.005 ng/g and RSD 5%. The results of the particulate mercury concentration were expressed as the mass of SPM (Hg_{SPM}).

In this study, the concentration of mercury in the river water was used to calculate annual load of Hg transported into the Gdansk Basin (Baltic Sea) by Reda river, assuming linear variability in time periods between measurements (Niemirycz, 2011):

$$Lr = \sum_{i=1}^n C_i Q_i$$

where Lr—annual load (kg/year); n—number of measurements; C_i—discrete concentration of constituent in the ith measurement (µg/m³); Q_i—discrete (daily) flow corresponding to the concentration C_i (m³/sec).

1.3. Elemental and isotopic analysis

Elemental and isotopic analysis were done according to the method adapted by Kuliński et al. (2014). The freeze-dried samples were homogenized and weighed into the silver capsules, where they were soaked in 2 mol/L HCl in order to

Table 1 – The description of rivers.

River	The size of catchment area (km ²)	The length of river (km)	The average flow of the river water (m ³ /sec)
Reda	485.5	51.0	4.3 **
Zagórska Struga	105.2	28.0	1.5 *
Kacza	53.8	14.8	0.2 *
Gizdepka	37.2	11.8	0.2 *

* Krajewska and Bogdanowicz, 2009.

** IMGW-PIB.

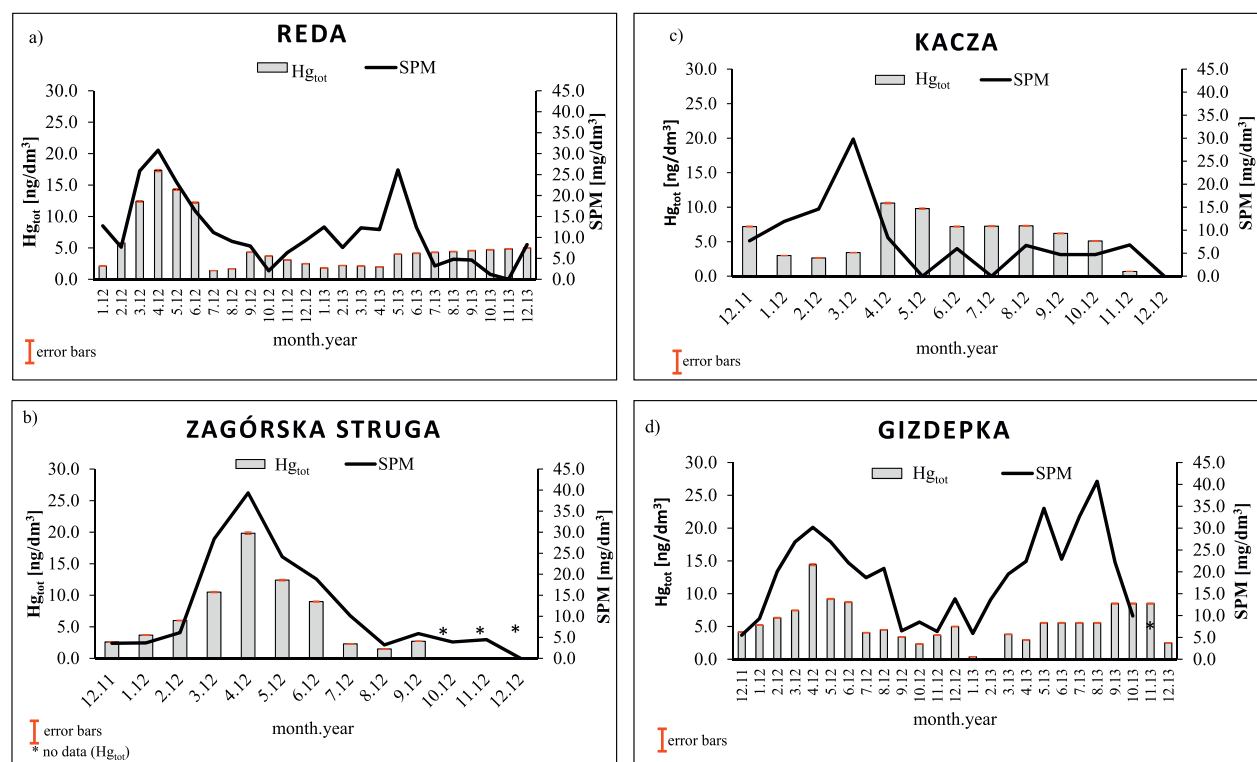


Fig. 2 – The concentration of Hg_{tot} and SPM] in the water of the Reda (a), Zagórska Struga (b), Kacza (c) and Gizdeпка river (d).

remove carbonates. Afterwards, samples were dried at 60°C for 24 hr. In such, prepared sample concentrations of organic carbon (C_{org}) and total nitrogen (N_{tot}) were measured together with isotopic composition ($\delta^{13}C$ and $\delta^{15}N$) with an Elemental Analyzer Flash EA 1112 Series combined with an Isotopic Ratio Mass Spectrometer (IRMS) Delta V Advantage (Thermo Electron Corp., Germany). The measurements of $\delta^{13}C$ and $\delta^{15}N$ were calibrated against certified reference materials (Fluβsediment, HekaTech GmbH). For both C_{org} and N_{tot} satisfactory precision was obtained: 0.03% for C_{org} and 0.11% for N_{tot} . The quality of isotopic measurements ($\delta^{15}N$ and $\delta^{13}C$) was guaranteed by using the laboratory working pure nitrogen (N_2) and carbon dioxide (CO_2) calibrated against IAEA standards (CO-8 and USGS40 for $\delta^{13}C$, N-1 and USGS40 for $\delta^{15}N$). Values of $\delta^{15}N$ and $\delta^{13}C$ were given in parts per thousand (‰) with reference to the standard Pee Dee Belemnite for $\delta^{13}C$ and to air for $\delta^{15}N$.

$$\delta X = \left[\frac{R(\text{sample})}{R(\text{reference})} - 1 \right] * 1000\text{‰}$$

where X is the stable isotope ratio of $\delta^{13}C$ or $\delta^{15}N$; R is the ratio of $^{13}C/^{12}C$ or $^{15}N/^{14}N$ (Rumolo et al., 2011; Khan et al., 2015; Koziorowska et al., 2016).

1.4. Statistical analysis

Statistical tests were conducted using STATISTICA 12 software. To check the normality of all data the Kolomogorov–Smirnov test was used. The Spearman’s co-efficient was used

to verify the dependencies between the analyzed data. The significance level was 0.05.

2. Results

The median concentration of total mercury (Hg_{tot}) in the Reda river (4.1 ng/dm^3) and Zagórska Struga (4.9 ng/dm^3) was similar to the global riverine concentration of total mercury, which was calculated at about 5.0 ng/dm^3 (Mason et al., 1994) (Fig. 2a, b). The Kacza river was characterized by a higher median of total mercury than global riverine concentration of Hg_{tot} amounting to 6.7 ng/dm^3 and in the Gizdeпка about 5.2 ng/dm^3 (Fig. 2c,d).

The concentration of total mercury (Hg_{tot}) in the Reda river, the longest river in the studied area, was variable and ranged from 1.4 to 17.3 ng/dm^3 (Fig. 2a). The Reda river was characterized by the widest range of the concentration of mercury in SPM (Hg_{SPM}) among studied rivers (49.3–1116.3 ng/g) (Fig. 3a). However, the median value was 103.4 ng/g , which was much lower than in the Zagórska Struga and Kacza river (Fig. 3a, b, c). The concentration of SPM in the Reda river varied from 1.2 to 30.8 mg/dm^3 (median: 12.3 mg/dm^3) (Fig. 2a). However, suspended matter was not characterized by the wide range of carbon and nitrogen stable isotopes ratios ($\delta^{13}C$ median: –29.3‰; $\delta^{15}N$ median: 2.9‰) (Fig. 4b). The organic matter contained the total nitrogen (N_{tot}) in range from 3.8 to 31.2 mg/g (median: 11.7 mg/g) and organic carbon (C_{org}) from 54.4 to 419.1 mg/g (median: 154.3 mg/g). The median of C/N ratio was 14.2 (Fig. 4a).

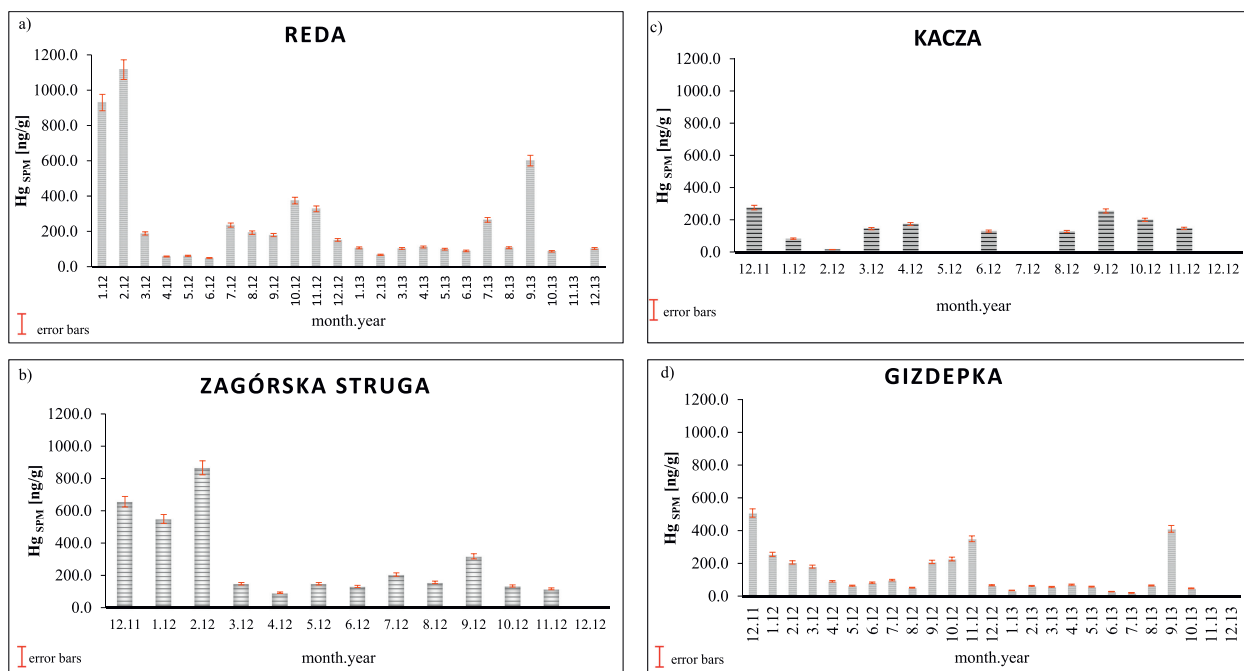


Fig. 3 – The concentration of Hg_{SPM} in the water of the Reda (a), Zagórska Struga (b), Kacza (c) and Gizdepka river (d).

Similar to the Reda river, the wide range of concentration of Hg_{tot} was detected in the Zagórska Struga river ($1.2\text{--}19.8\text{ ng/dm}^3$) (Fig. 2b). The concentration of Hg_{SPM} was not as wide as in the Reda river and it ranged from 92.4 to 866.2 ng/g (median: 176.6 ng/g) (Fig. 3b). The concentration of SPM in Zagórska Struga varied from 3.2 to 39.3 mg/dm^3 (median: 8.0 mg/dm^3) (Fig. 2b). The median values of $\delta^{13}C$ and $\delta^{15}N$ at the station located in the Zagórska Struga were respectively -28.9‰ and 4.2‰ (Fig. 4b). The content of the total nitrogen in the SPM was in the range from 4.1 to 42.4 mg/g (median: 13.7 mg/g). The SPM organic carbon content ranged from 59.2 to 744.1 mg/g (median: 158.0 mg/g). The C/N ratio was similar to the Reda river and amounted to 15.5 (Fig. 4a).

The range of the concentration of Hg_{tot} in the Kacza river was not as wide as in the Reda and Zagórska Struga river and varied from 0.7 to 10.6 ng/dm^3 (Fig. 2c). The maximum concentration of Hg_{SPM} in the Kacza river was the lowest compared to the maximum value of other studied rivers (range: $15.1\text{--}276\text{ ng/g}$, median: 146.6 ng/g) (Fig. 3c). The concentration of SPM ranged from 4.7 to 29.8 mg/dm^3 (median: 6.8 mg/dm^3) (Fig. 2c). The Kacza river was characterized by the highest median of $\delta^{13}C$ compared to the other studied rivers (-28.2‰). However, the median of $\delta^{15}N$ was lower (2.2‰) (Fig. 4b). The content of N_{tot} was similar to the Zagórska Struga ($7.0\text{--}42.9\text{ mg/g}$) (median: 9.7 mg/g), and the range of the concentration of organic carbon was not as wide as in the other rivers ($68.6\text{--}219.4\text{ mg/g}$). The C/N ratio in that river was the lowest (12.7) (Fig. 4a).

In the smallest river out of all studied rivers (Gizdepka), the concentration of total mercury varied from 0.1 to 14.4 ng/dm^3 (Fig. 2d). That river was characterized by the variable concentration of Hg_{SPM} as well (range: $19.8\text{--}507.6\text{ ng/g}$, median: 66.5 ng/g) (Fig. 3d), and SPM has been changing through the year and ranged from 5.5 to 40.7 mg/dm^3 (median: 13.8 mg/dm^3) (Fig. 2d). The stable isotopes ratios in the Gizdepka were similar to the rest

of the studied rivers ($\delta^{13}C$ median: -29.3‰ ; $\delta^{15}N$ median: 4.5‰) (Fig. 4b). The content of the total nitrogen in the SPM ranged from 3.0 to 30.9 mg/g (median: 9.9 mg/g), and it was comparable to the Reda, Zagórska and Kacza rivers. The concentration of organic carbon ranged from 32.4 to 630.8 mg/g . That high value of C_{org} was observed only once, in December 2011 (median: 131.4 mg/g). The ratio of C/N was similar to the other rivers (median: 13.4) (Fig. 4a).

3. Discussion

3.1. The supply of Hg by rivers

In the southern Baltic Sea, rivers are the main source of Hg. According to HELCOM reports, from the 90s, Hg riverine input into the Baltic Sea has decreased by almost 50% (HELCOM, 2010). Presently, the mercury riverine input into the southern Baltic displays seasonal and inter-annual variability (Fig. 5) (Beldowska et al., 2014; Saniewska et al., 2014). A lower load (0.8 kg Hg/year and 0.5 kg Hg/year) was introduced into the marine environment in the year 2012 and 2013 via the Reda river compared to the year 2010 (1.3 kg Hg/year) (Fig. 5) (Saniewska, 2013). In some cases, the reason for Hg input increase was higher riverine inflow. The example was observed in February 2012. The maximum flow was detected in the second part of that month ($12.5\text{ m}^3/\text{sec}$). That value was about two times higher than the mean flow in the year 2012 ($6.7\text{ m}^3/\text{sec}$) and remained high for several days, which was associated with the snow melting in the second half of February (Fig. 5). The maximum duration of continuous snow cover lasted 25 days with the average thickness in the 20's. The maximum temperature in the second week of February amounted to 10°C (ARMAAG, 2012; IMGW, 2012). After taking into consideration the value of

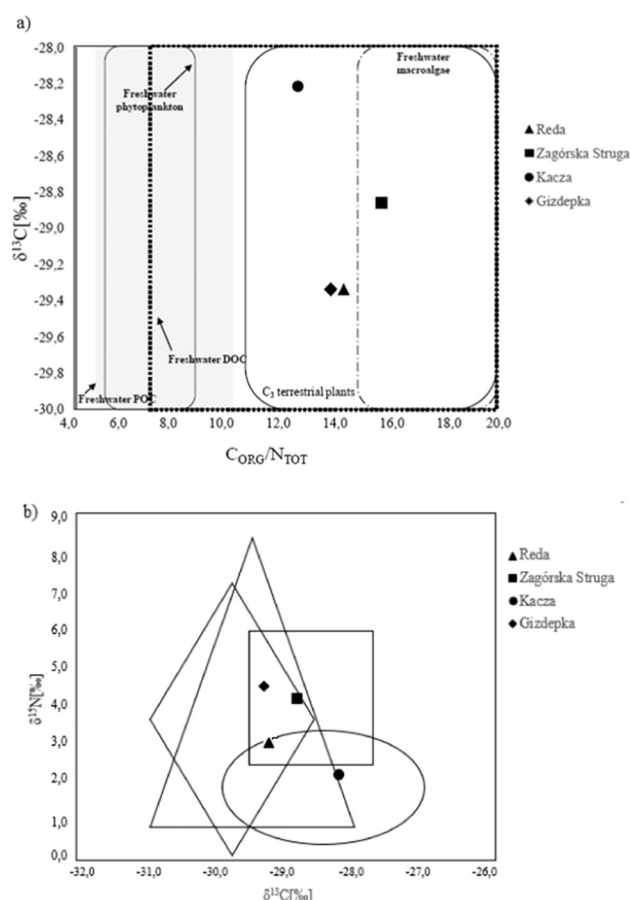


Fig. 4 – The median values of $\delta^{13}\text{C}$ [‰] and $\text{C}_{\text{org}}/\text{N}_{\text{tot}}$ (a) and median values of isotopes composition ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) (b) in suspended particulate matter (SPM) in the Reda, Zagórska Struga, Kacza and Gizdepka rivers, compared to the typical ranges reported for coastal environment (Raymond and Bauer, 2001; Cloern et al., 2002; Goñi et al., 2003; Lamb et al., 2006).

maximum flow of the water, the Reda river transported almost three times a higher load of Hg (19 g Hg/day) into the Sea compared to the average flow (7 g Hg/day) (Fig. 5).

There was no statistical correlation between the Hg load and the water flow: $r = 0.2$; $p = 0.4$. The magnitude of mercury load transported into the sea hence depended on other factors than the flow of the river. The supply of the total mercury in the sea was dependent on the concentration of this metal in the river water as well. The high monthly values of Hg concentration in the Reda river continued from February to June 2012, with a simultaneous decrease of the water flow (Fig. 5). In this term, the average load of Hg was 126.8 g Hg/m, which was almost twice as high as the average load in the year 2012 (71.5 g Hg/m). Moreover, the much lower amount of Hg was introduced into the southern Baltic Sea in the year 2013 in the same term (average: 43.5 g Hg/m). The flow of river water was measured only in the Reda river. However, taking into account that this river is the longest of the studied rivers, there was a probability that the flow rose also in the other stations. The similar situation was observed in the Zagórska

Struga and Gizdepka. The highest concentration of Hg_{tot} was observed in the Zagórska Struga river, and it was 19.8 ng/dm³ compared to the Reda river (17.3 ng/dm³), and the Gizdepka river (14.4 ng/dm³) in April 2012. The high concentration of Hg_{tot} was detected also in March (12.4 ng/dm³), May (14.3 ng/dm³) and June 2012 (12.2 ng/dm³) in the Reda river (Fig. 2a, b, d). Observed Hg_{tot} concentration increase was caused mainly by dissolved mercury (subtraction of the result of the Hg_{tot} and Hg_{SPM}) (Saniewska et al., 2014). Increase of the concentration of this form was probably a consequence of its elution from the surface of the catchment, where Hg was deposited during the heating season (October–April). However, atmospheric deposition can be a source of both dissolved and particulate mercury in the river. It was observed in December–February in the year 2012 in the studied rivers. The lower the temperature of the air, the more intensive the combustion of fossil fuels for heating buildings were. As follows, the Hg dry deposition is greater in the heating season (October–April) than in the non-heating season (May–September). Due to the lower temperature in the year 2012 (in particular in February: -2.8°C (in the year 2012); 0.5°C (in the year 2013) (ARMAAG, 2012, 2013), more coal was burned and this caused the higher emission of mercury into the atmosphere from this source. Due to this, more Hg could be deposited on the catchment surface and then could be washed out together with adsorbed mercury from the catchment area, and then transported into the sea via river water.

SPM plays an important role in biogeochemical cycle of Hg (Bełdowski and Bełdowska, 2008). During winter season of 2012, the SPM was much enriched in mercury: in the Reda river the highest concentration of Hg_{SPM} was 1116.3 ng/g (February 2012); in the Zagórska Struga 866.2 ng/g (February 2012) and in the Gizdepka 507.6 ng/g (December 2011). The concentration of the Hg_{SPM} in February 2012 was 85% higher in the Reda river and about 75% in the Gizdepka, than in February in the following year (Fig. 3a, b, d). Probably it was caused by the atmospheric deposition, which more effectively washed out Hg from the atmosphere in the year 2012 as compared to the year 2013. In February 2012, the solar radiation was higher than in February 2013 (in February 2012: 80 hr; in the February 2013: 30 hr) (IMGW, 2012; IMGW, 2013). Also in February 2012 the marine air masses were dominant in Gdynia. These conditions stimulated transformation of atmospheric gaseous mercury (Hg^0) to the reactive form (Hg^{2+}) (Malcolm et al., 2003; Poissant et al., 2005). The reactive gaseous mercury was directly washed out by precipitation. This process has a great importance in mercury transformations in winter in the coastal zone of the Baltic Sea (Saniewska et al., 2014; Bełdowska et al., 2015). This suggests that during the winter 2012, conditions were more favorable to change the form of Hg in the atmosphere to more reactive/soluble, compared to the year 2013. In the consequence, more effective atmospheric deposition of mercury in the year 2012 caused the increase of Hg concentration in SPM.

Furthermore, in the year 2012 the dominant wind speed was $1 \leq V_w < 3$ m/sec. These values play an important role in the wet deposition of Hg and indicated the importance of regional sources of this metal (land and marine) (Bełdowska et al., 2014). Along these lines, the increase of the mercury

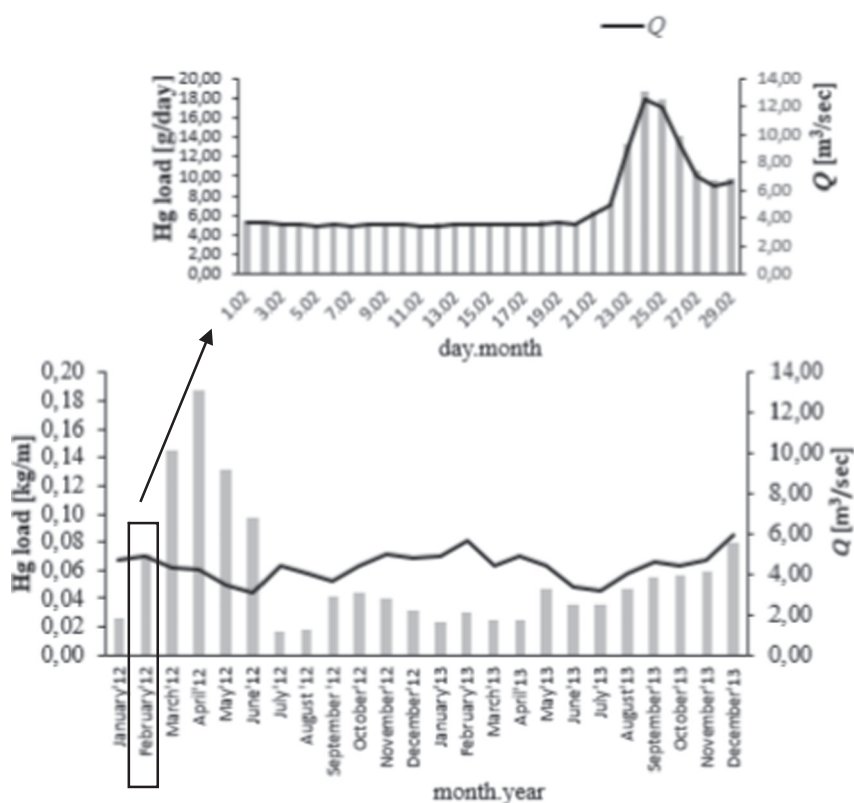


Fig. 5 – The Hg load introduced into the Gulf of Gdansk (Baltic Sea) by the Reda river and the flow of river water (Q) during individual months in the years 2012–2013 and days of February 2012 (the flow of the river water was measured by IMGW-PIB).

concentration in SPM in river water can be connected with the load of Hg from the atmospheric deposition especially by the precipitation. An increase of the precipitation, retention capacities of the catchment area of the river and anthropogenic impact cause the change of the concentration of Hg_{tot} in the river water (Saniewska et al., 2014).

The influence of intense precipitation on the concentration of Hg_{tot} in the rivers was observed in the September 2013. Higher concentration of particulate mercury was recorded in September 2013 (5.6 ng/dm^3) than in September 2012 (1.3 ng/dm^3) in the Gizdepa (Fig. 2d). Two times more rain had fallen in September 2013 than in the year 2012, and it could have caused enhanced re-mobilization of mercury from surrounding areas, as compared to 2012 (ARMAAG, 2012, 2013).

Additionally, the influence of the SPM amount on the concentration of Hg was detected in May 2013. During days with non-intensive rain or without rain, the dry atmospheric deposition is more intense than re-mobilization of mercury from the land. The intensive rain in May 2013 (52.9 mm), after the period of low rainfall (March 2013: 0.1 mm and April 2013: 13.0 mm) (ARMAAG, 2013) caused the re-mobilization of the accumulated Hg_{SPM} from the catchment area of the rivers. As a consequence, the concentration of Hg_{SPM} in May 2013 in the Reda river was a substantial part of total form of mercury (63% of Hg_{tot}) compared to the same month one year before (9% of Hg_{tot}).

Due to this phenomenon, a higher Hg load was introduced into the Baltic Sea (Fig. 5). A similar process was noticed by Saniewska et al. (2014), in the years 2008–2009 in the Kacza river and Oliwski Stream.

The dissolved Hg can be transported over the long distances, which leads to the absorption of Hg by the phytoplankton (Beldowska and Kobos, 2016). However, Hg_{SPM} riverine input to the coastal zone is also significant, especially in small bays and estuaries where it is a food source for both benthic and planktonic fauna. Nowadays, when climate change affects the length of the winter season, this causes elongation of the vegetation season (HELCOM, 2013). As a consequence, the greater load of mercury enters to the trophic chain.

The increase of the water flow did not cause the rise of Hg load every time. If it was caused by the intense rainfall, then it could make the concentration of mercury in the river water more diluted as well. The result of these processes depends on the concentration of Hg in the surrounding areas and the type of river catchment. If the catchment of the river consists of a high concentration of mercury, an intensive precipitation can cause the direct transport of mercury from the whole catchment. If the areas are rich in the organic matter and fine grains, mercury can be absorbed and it will not be directly delivered into the sea during intensive precipitation. This process was detected in this study. In July in the year 2012, an intensive precipitation (170 mm) was detected as well (it was

about 37% of an annual precipitation) (ARMAAG, 2012). However, it caused the “dilution” of the river water and decrease of total mercury concentration in the Reda river almost nine times, the Zagórska Struga about four times and in the Gizdepka about two times compared to June 2012 (Fig. 2a, b, d).

3.2. The additional source of Hg

The Kacza river is a specific water body. This river flows through the area with many parcel gardens. Taking into account that the parcel gardens are additional sources of pollution, cultivation of these places can cause an increase of the mercury concentration in the river. There is a probability that in the allotment, gardens, seed dressings and pesticides containing mercury (which are banned nowadays) were used in the past. Probably, these fertilizers are still used; however, this information was not confirmed by the appropriate organizations. There is no trend connected to the concentration of mercury in the heating and non-heating season like it was observed in the other studied rivers. The highest concentration of Hg_{SPM} was in both cold and warm months (Fig. 3c). The high concentration of Hg_{tot} was observed from March to October 2012 (Fig. 2c). The monthly measurement indicated that the fluctuations of Hg load are not proportional to the concentration of SPM. Equally significant is the concentration of mercury. It could be caused by a lot of buildings in the villages and allotments which are not connected to the municipal sewage system or even if they are, the plumbing is old and leaking. As a consequence, the Kacza river was characterized by the highest median value of the concentration of Hg_{tot} (6.7 ng/dm^3) among studied rivers. The much lower median of total mercury was detected by Saniewska et al., 2014 in the years 2008–2009, and it was 2.9 ng/dm^3 . However, the range of the concentration of Hg_{tot} in the Kacza river was similar to this study, and it was respectively $0.2\text{--}14.7 \text{ ng/dm}^3$ and $1.0\text{--}10.6 \text{ ng/dm}^3$ in this research (Fig. 2c). The slight changes of the concentration of Hg_{tot} and Hg_{SPM} indicated the constant increase in concentration of mercury (Figs. 2c, 3c).

3.3. The connection between origin of suspended matter and Hg concentration

SPM in all investigated rivers contained typical terrestrial organic matter irrespective of the sampling season. This is confirmed by the similarity of the median values of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N ratios in all rivers (Fig. 4a, b). The results also did not exclude freshwater macroalgae as a source of POM, while relatively high C/N ratios suggested rather low contribution of freshwater phytoplankton (Fig. 4a). This is contrary to findings reported for the Vistula River by Maksymowska et al. (2000) and Jędruch et al. (in press). They both found that fresh production by phytoplankton is an important (sometimes even predominant) source of POM in the Vistula. The Vistula is, however, a relatively slow flowing river – a feature favoring primary production. The rivers investigated in our study are much shorter, and the residence times of water in those rivers do not foster phytoplankton growth.

No clear correlation was found between Hg_{tot} concentrations and parameters describing both quantity (C_{org} and N_{tot} concentrations) and quality ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C/N) of POM. This suggests that organic matter is not a main carrier of Hg_{tot} in the investigated rivers. This indicates that studied catchment could be important sources of Hg_{dis} in rivers.

4. Summary

The supply of mercury by rivers is the main source of this metal in the Baltic Sea, in particular in the south part (Saniewska et al., 2010, 2014a, 2014b). After the introduction of regulations, the amount of mercury released into the environment has been reduced and controlled. Nevertheless, the Hg load introduced into the Baltic Sea displayed both monthly and inter-annual variability. The changes were connected to the water flow and the concentration of mercury in the catchment area. If the soil of the area of the river was more polluted by mercury, then the flow of the river water could remove more Hg into the water than in the area of low mercury concentration. These parameters lead to a five time daily increase of Hg load into the Gulf of Gdansk compared to the average load. One of the potentially important sources of Hg was the atmospheric deposition associated with a combustion of fossil fuels in the heating season. Moreover, the meteorological conditions such as increase of temperature, humidity, solar radiation and presence of halogen-rich marine masses affected the transformation of mercury from Hg^0 to Hg^{2+} . In consequence, reactive mercury was washed out from the atmosphere by precipitation. It affected an increase of Hg concentration on the land and then re-mobilization of this metal adsorbed on the organic matter (OM) into the river water by the thaws or intensive rain. It is important, due to an increase frequency of the intense precipitation events caused by climate change (HELCOM, 2013; IMGW, 2013). OM can transport mercury into the Gulf of Gdansk; however, the elemental and isotopic analysis have not defined which type of organic matter can be a best transfer of Hg. Moreover, the correlation between Hg_{tot} , C_{org} and N_{tot} concentrations and $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C/N in particulate matter has not been found.

The variability of mercury concentration in the rivers was affected by seasonal changes, meteorological conditions but also by additional sources. It was found in the Kacza river. A lot of small villages have no municipal sewage system in the area of this river. Additionally, the higher concentration of Hg was caused by chemicals containing mercury using in the parcel gardens. Because of these sources the concentration of Hg is not stable even over the months, or it is on a high level all the time.

In order to assess the influence of climate factors on mercury re-mobilization and its input to the rivers, and further to the sea and marine food chain, studies of labile mercury forms have to be conducted in SPM and in the catchment soil. Land use and rainfall magnitude as well as various hydrological conditions in particular seasons have to also be taken into consideration. This study was focused on the four rivers of the southern Baltic Sea catchment area, which can be a good reference to the different gulfs in the temperate latitude.

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