JOURNAL OF ENVIRONMENTAL SCIENCES XX (2018) XXX–XXX

Available online at www.sciencedirect.com

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www.elsevier.com/locate/jes

JES JOURNAL OF ENVIRONMENTAL SCIENCES

www.jesc.ac.cn

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

Karolina Gębka[1], *Magdalena Bełdowska*[1,*], *Dominika Saniewska*[1], *Karol Kuliński*[2], *Jacek Bełdowski*[2]

1. *The Institute of Oceanography, University of Gdansk, Marszałka Piłsudskiego Alley 46, 81-378 Gdynia, Poland*
2. *The Institute of Oceanology of The Polish Academy of Sciences, Powstańców Warszawy Street 55, 81-712 Sopot, Poland*

ARTICLE INFO

Article history:
Received 28 April 2017
Revised 5 September 2017
Accepted 9 November 2017
Available online xxxx

Keywords:
Hg
Suspended particulate matter
Stable isotopes
Atmospheric deposition
Rivers

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 Gizdepka. 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.

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 biomagnificates with increasing trophic level. Consequently, Hg concentration in tissues off ish, 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

* *Corresponding author. E-mail:* m.beldowska@ug.edu.pl (Magdalena Bełdowska).

https://doi.org/10.1016/j.jes.2017.11.030
1001-0742

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; Bełdowska et al., 2012; Bełdowska 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 adsorbtion, 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 allochtonic 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 (Saliot 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, $\delta^{13}C$ and $\delta^{15}N$ are often used as tolls 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 $\delta^{13}C$ and $\delta^{15}N$ higher values are observed for the marine organic matter, while lower indicate terrigenous origin. $\delta^{13}C$ for marine organic matter is usually found in the range from −22‰ to −17‰. The terrestrial one is isotopically lighter and its $\delta^{13}C$ osscilates between −30‰ and −25‰ (Schultz and Zabel, 2006). Both $\delta^{13}C$ and $\delta^{15}N$ increase also stepwise in the consecutive links of the food pyramid. The change is especially pronounced for $\delta^{15}N$, for which amounts to 3.4‰ on average (Hobson and Welch, 1992). Additionally, it was reported that POM in sewage contains higher $\delta^{15}N$ 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 Sturga, 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 (Bełdowska 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