

Mercury fractionation in sediments of the Lower Vistula River (Poland)

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Abstract

The Vistula is the second largest river in the Baltic Sea catchment area and provides one of the main inputs to the Baltic. The river and its tributaries flow through some of the major industrialized and urbanised regions of Poland, making it one of the most highly human-impacted rivers in Europe. Although the river status is monitored routinely, little is known about mercury forms in the sediments. This study examines mercury fractionation in the sediments of the lower part of the Vistula River. The results show that the cities along this stretch of river have a relatively low impact on both the mercury forms found in the sediment and its bioavailability in the floodplain soils. The mean concentration of total mercury in the sediments was 65 ± 14 ng g⁻¹ dry mass (range 54–92), calculated as the sum of mercury concentrations in the individual fractions. The most abundantly represented of these fractions were mercury bound to sulphides

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(68 ±11%, range 55–82%) and humic matter (19 ±10%, range 10–35%), with lower fractions of water-soluble mercury (6.9 ±2.9%, range 5.1–13%) and organomercury compounds (6.4 ±5.3%, range 0.6–13%). The least abundant fraction observed was acid-soluble mercury (0.3 ±0.2%, range 0.1–0.6%). Similar concentrations and fractionation were observed in floodplain soils from Kieźmark, collected 1, 10 and 50 meters from the riverbed.

INTRODUCTION

Much of the mercury released into surface waters is deposited in sediments. The concentration of mercury in sediments, where it can undergo various transformations, is a very good indicator of water pollution with this element. Mercury both accumulates in bottom sediments as a result of sedimentation, and is released from the sediments, becoming available to further biogeochemical transformations (Boszke et al. 2003). The rates of these two processes depend significantly on the specific environmental conditions in a given aquatic system. As a result of complex chemical, physical and biological transformations, some mercury species can convert into more toxic ones, e.g. methylmercury (Boszke et al. 2003). Tragic examples of the toxicity of methylmercury and dimethylmercury were seen in Japan, where these mercury species were responsible for the lethal poisoning of people who had eaten contaminated fish (Kurland et al. 1960). This episode aroused great interest in the problems of mercury speciation in the natural environment, including sediments.

Direct measurements of the concentration of particular mercury species in soils and sediments are usually difficult or even impossible (Gustin et al. 2002, Hesterberg et al. 2001, Kim et al. 2000, Sladek et al. 2002). One of the methods that can be applied for this purpose is to subject solid-state matrices, such as environment solids, to sequential extraction by solutions of increasing complexing ability (Calmano and Förstner 1983, Hall et al. 1996, Lechler et al. 1997, Tessier et al. 1979). This approach is based on the assumption that a given solution causes extraction of a certain operationally defined fraction of mercury species. None of the solutions are completely selective, so the fraction includes a number of different but similar chemical species. Although the extraction methods are based on chemical interactions in complex matrices, and therefore yield results that are strongly influenced by the matrix effect, they have the advantage of permitting determination of mercury species at relatively low concentrations (Biester and Scholz 1997, Biester et al. 2002, Gustin et al. 2002, Sladek et al. 2002, Sladek and Gustin 2003).

The sediments of the Vistula River are known to be contaminated with heavy metals (Buszewski et al. 2005, Buszewski and Kowalkowski 2003), but little work has been carried out on the identification of mercury species along the lower course of the river. The aim of this study is to identify mercury species in sediments of the lower Vistula River by sequential extraction, and to

assess mercury bioavailability and mobility in these sediments. The results of this study may be used to estimate the discharge of mercury when the river is in flood. Of central importance is the question of whether flooding is responsible for elevated mercury levels in Southern Baltic waters.

STUDY AREA

The basin of the Vistula River (in Polish - Wisła) covers an area of 194 424 km², 87% of which is located within Poland, and a total of 13% in the Ukraine, Belarus and Slovakia. The Vistula is the longest river in Poland at 1068 km, its source being in the south of the country, at Barania Góra (1220 m high) in the Beskidy Mountains. From there it flows over the vast Polish plains, passing several large cities along its way, in its lower course including Płock, Włocławek, Toruń, Świecie, Tczew and Gdańsk. Via a delta and several branches it empties into the Vistula Lagoon and Gdańsk Bay of the Baltic Sea. The annual water discharge into Gdańsk Bay is 34.5 km³, of which the Vistula contributes approximately 30 km³ (Majewski 1990). The Vistula River suffers heavy pollution from multiple origins. In the upper course metallic and chlorine pollution originates from the mining and industrial region of Upper Silesia. Downstream from there, urban and industrial sewage from the large urban agglomerations add more metallic and organic contaminants (Buszewski and Kowalkowski 2003, Buszewski et al. 2005).

MATERIALS AND METHODS

Samples of sediments were collected from the shore at six different sites along the lower Vistula River in 2004 (Fig. 1, Table 1). At each site one sediment sample was collected (0-20 cm), and the depth of water at the collecting site varied from 50 to 100 cm, and at Kiezmark additional soil samples were collected at distances of about 1, 10 and 50 metres from the riverbank (0-20 cm). The samples, about 2 kg, were manually collected using a stainless steel scoop. The samples were placed in plastic vessels and transported to the lab where they were dried in a dust-free room, at room temperature, to constant mass (a few weeks). The samples were then gently crushed in an agate mortar, but not so as to damage the structure of the grains. A subsample of 250 g was collected from each sample and sifted through a copper sieve (0.15 mm mesh size).

The analytical agents used for mercury determination were of highest available purity, made by Merck (Darmstadt, Germany). All dilutions were made with deionised water from Milli-Q system (Millipore, France). Laboratory vessels used were made of boron-silica glass of the highest quality. Details of

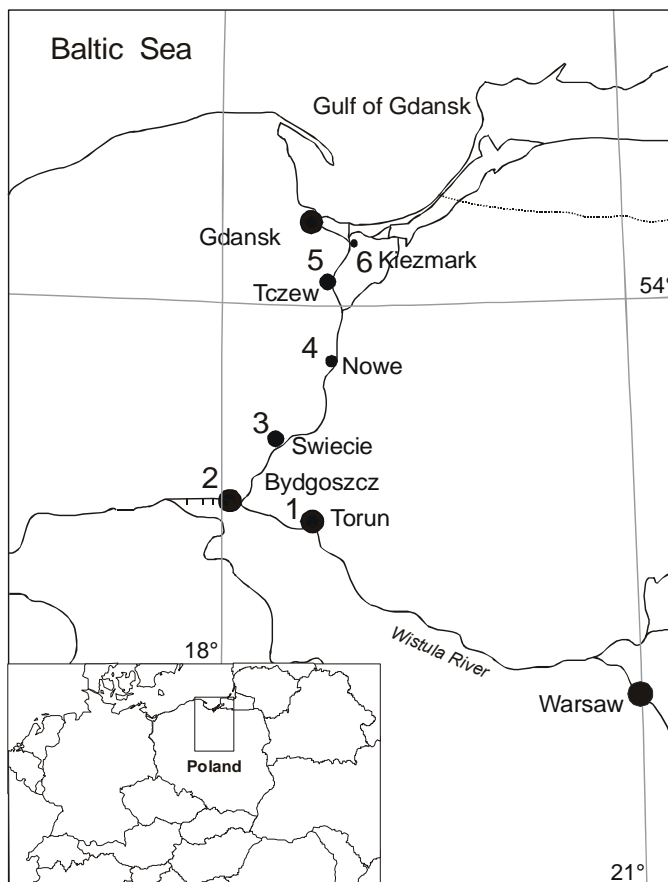


Fig. 1. Map showing sampling sites.

Table 1

The contribution of mercury from particular fractions in the total content of mercury in the samples of the river Vistula sediments and its floodplain soil

Site number	Description of sampling site	Geographical coordinates		LOI (%)	Fractions (%)					Σ Fractions (ng g ⁻¹)
		Latitude N	Longitude E		F1	F2	F3	F4	F5	
1	Toruń – sediment	53° 00'14.16"	18°36'32.02"	1.35	1.8	5.1	0.6	35	57	54
2	Bydgoszcz – sediment	53° 08'41.06"	18°10'14.40"	1.03	12	5.1	0.3	12	70	65
3	Świecie – sediment	53° 23'58.94"	18°28'12.09"	0.77	6.3	6.1	0.1	10	77	92
4	Nowe – sediment	53° 38'52.69"	18°44'17.48"	1.09	4.4	7.2	0.3	23	65	57
5	Tczew – sediment	54° 05'34.44"	18°48'16.16"	0.96	13	13	0.5	19	55	63
6	Kieźmark – sediment	54° 15'21.62"	18°56'37.75"	0.46	0.6	5.2	0.3	12	82	62
	soil – 1 m			0.47	4.7	13	0.4	13	69	69
	soil – 10 m			0.75	5.1	4.0	0.3	13	78	86
	soil – 50 m			1.25	3.1	4.9	0.7	27	65	67

preparation of reagents and apparatus are described in Boszke et al. (2006, 2007).

After a review of the literature on determination of various species of mercury in solid samples, a sequential extraction method was proposed [based partially on the work of Wallschläger et al. (1996a,b), Lechler et al. (1997), Bloom et al. (2003), Renneberg and Dudas (2001)]. The scheme of the sequential extraction procedure is presented in Fig. 2 and details of the procedure are described in Boszke et al. (2007). Organic matter was determined as a loss on ignition at 550°C for 12 hours to constant weight.

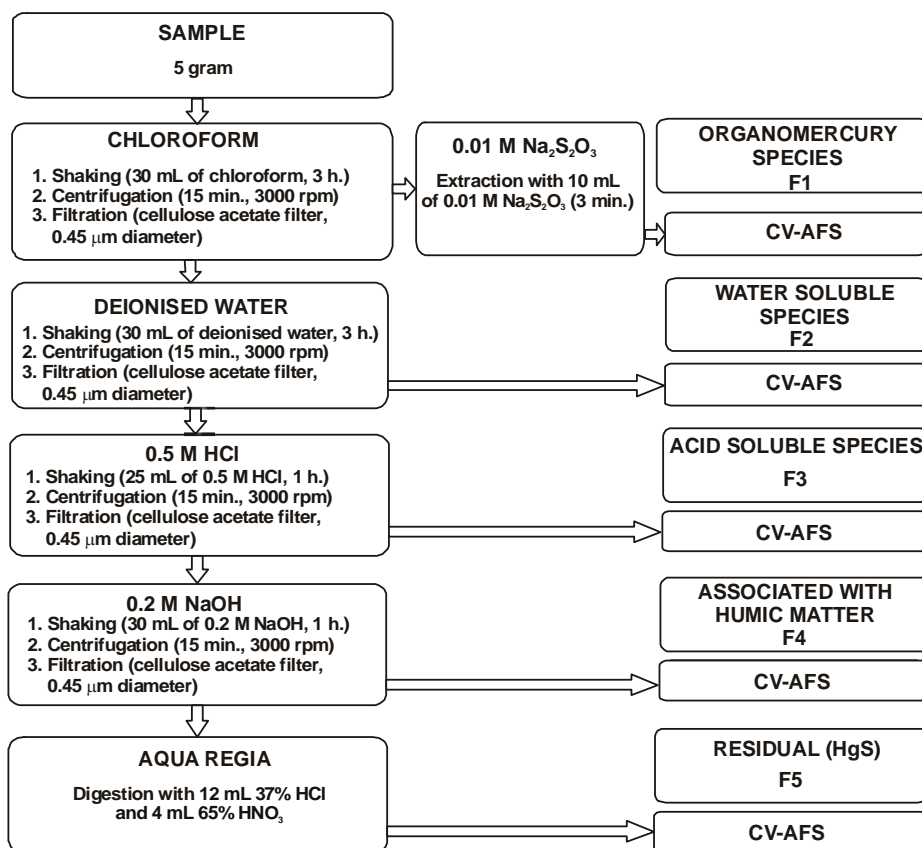


Fig. 2. Scheme of sequential extraction process.

Mercury was determined by the method of cold-vapour atomic fluorescence spectroscopy (CV-AFS) on Millennium Merlin (PS Analytical, England). The calibration was performed with the mercury standard $\text{Hg}(\text{NO}_3)_2$ (Merck) with the nominal mercury content of $980 \pm 20 \text{ ng dm}^{-1}$. The limit of detection and quantification of the method depend on the purity of the reagents used. The value of the limit of quantification (LOQ) of the method reached $0.8 \text{ ng Hg dm}^{-1}$ and was calculated according to the formulas presented by Konieczka et al. (2004).

Along with determination of total mercury, routine analyses were made of certified materials, including: SRM 2711 (Montana Soil), SRM 2709 (San Joaquin Soil) and LGC 6137 (Estuarine Sediment). The total mercury concentrations obtained in our study, taking into consideration the values of expanded uncertainty (Konieczka et al. 2004) were $6060 \pm 351 \text{ ng g}^{-1}$ (SRM 2711, $n = 5$), $1440 \pm 98 \text{ ng g}^{-1}$ (SRM 2709, $n = 6$), $370 \pm 21 \text{ ng g}^{-1}$ (LGC 6137, $n = 7$), which correspond well with those obtained for the certified materials, being $6250 \pm 190 \text{ ng g}^{-1}$, $1400 \pm 80 \text{ ng g}^{-1}$ and $340 \pm 50 \text{ } \mu\text{g g}^{-1}$, respectively (Kowalski 2006).

For comparison with the results of sequential extraction, one certified sample LGC 6137 was used. The sum of mercury concentrations obtained from particular fractions was 373 ng g^{-1} dry mass, while the corresponding sum obtained for the certified material was 340 ng g^{-1} dry mass. The method of sequential extraction is thus characterised by a recovery of about 110% (range 108–112%) and good reproducibility (Boszke et al. 2007).

RESULTS

The total mercury concentrations and the contributions of particular fractions are shown in Table 1. The mean concentration of total mercury was $65 \pm 14 \text{ ng g}^{-1}$ dry mass (range 54–92) in sediments and $74 \pm 10 \text{ ng g}^{-1}$ (range 67–86) in floodplain soils, calculated as a sum of mercury concentrations in individual fractions. The content of organic matter (calculated as loss on ignition) was $0.9 \pm 0.3\%$ (range 0.5–1.4) in river sediments and $0.8 \pm 0.4\%$ (range 0.5–1.3) in floodplain soils. The average mercury concentration normalised to organic matter content was $7.9 \pm 3.9 \text{ } \mu\text{g g}^{-1}$ (range 4.0–13.5) in sediments and $10.5 \pm 4.8 \text{ } \mu\text{g g}^{-1}$ (range 5.4–14.8) in floodplain soils.

The fraction contributing the most to the total mercury concentration in the river sediments and floodplain soils was the mercury bound to sulphides $68 \pm 11\%$ (range 55–82) and $70 \pm 6\%$ (range 65–78), respectively. The fraction bound to humic matter also contributed highly, with $19 \pm 10\%$ (range 10–35) and $17 \pm 8\%$ (range 13–27) of total mercury respectively. The water-soluble mercury (contributing $6.9 \pm 2.9\%$ (range 5.1–12.5) and $7.4 \pm 5.1\%$ (range 4.0–

13.2), respectively) and organomercury compounds (contributing $6.4 \pm 5.3\%$ (range 0.6–13.3) and $4.3 \pm 1.0\%$ (range 3.1–5.1), respectively) were the next most abundant mercury fractions. The fraction that contributed least to the total mercury content was the acid-soluble mercury, with $0.3 \pm 0.2\%$ (range 0.1–0.6) and $0.5 \pm 0.2\%$ (range 0.3–0.7) respectively.

DISCUSSION

Distribution of total mercury

The concentrations of total mercury in sediment samples collected from sites along the Vistula River show relatively low variation ($54 - 92 \text{ ng g}^{-1}$) (Table 1). The total mercury concentration was well below 200 ng g^{-1} in all of the sediments examined, which is accepted as the upper limit of geochemical background (Kabata Pendias and Pendias 1999). In other studies, sediments of the lower Vistula River were reported to contain comparable or higher mercury concentrations than those observed in this study (Table 2).

Table 2

Total mercury concentrations in the sediments of the lower Vistula River

Sampling site	Number of samples	Hg concentration (ng g^{-1} d. w.)		Reference
		Mean	Range	
Włocławek				
Weir reservoir	13	28	3-54	Wyrzykowska and Falandysz (2003)
Down stream weir	16	18	6-36	Wyrzykowska and Falandysz (2003)
	2	25	21-39	Falandysz et al (1996)
	1	2.3		Kannan and Falandysz (1998)
Toruń				
City area	1	54		This study
Downstream the city	21	120	33-600	Wyrzykowska and Falandysz (2003)
City area	18	220	68-460	Wyrzykowska and Falandysz (2003)
Upstream the city	18	150	54-310	Wyrzykowska and Falandysz (2003)
	1	140		Falandysz et al (1996)
Bydgoszcz				
City area	1	65		This study
	19	86	14-210	Wyrzykowska and Falandysz (2003)
Świecie				
City area	1	92		This study
Grudziądz				
	16	29	10-80	Wyrzykowska and Falandysz (2003)
Nowe				
City area	1	57		This study
Gniew				
	10	27	10-40	Wyrzykowska and Falandysz (2003)
Tczew				
City area	1	63		This study
	14	370	73-730	Wyrzykowska and Falandysz (2003)
Kieźmark				
	1	62		This study
	2	400	110-690	Falandysz et al (1996)
Gdańsk				
Ptasi Raj -waterbird sanctuary area	20	40	10-150	Wyrzykowska and Falandysz (2003)
Dead Vistula Channel	20	62	3-550	Wyrzykowska and Falandysz (2003)
Dead Vistula Channel	18	500	44-1800	Falandysz et al (1996)
Przegalina – ferry boat port	10	200	28-720	Wyrzykowska and Falandysz (2003)
Shipyard area	44	190	7-1300	Wyrzykowska and Falandysz (2003)

The mercury concentrations observed in this study are lower than those reported in the sediments of the Rhine ($400 \pm 300 \text{ ng g}^{-1}$) and Neckar ($300 \pm 200 \text{ ng g}^{-1}$) rivers (Germany), the Scheldt river (Belgium) (460 ng g^{-1}) and the Warta river (Poland) ($57 - 340 \text{ ng g}^{-1}$) (Boszke et al. 2007, vide Papina et al. 2000, Pilz and Yahya 2000, Prange et al. 2002). Much higher concentrations of mercury have been reported in other European rivers, such as the Odra river (Poland) ($120 - 2999 \text{ ng g}^{-1}$) (Boszke et al. 2004a,b), the Elbe river (Germany) ($3700 \pm 2800 \text{ ng g}^{-1}$) (Prange et al. 2002) and the Yare river (UK) ($100 - 8130 \text{ ng g}^{-1}$) (Birkett et al. 2002). In the Elbe river (Germany) total mercury has been detected in concentrations of up to $12,000 \text{ ng g}^{-1}$ (Hintelmann and Wilken 1995).

Organomercury species

Organomercury compounds are those in which mercury is bonded directly to the carbon atom (e.g. $\text{CH}_3\text{Hg(I)}$, $\text{C}_2\text{H}_5\text{Hg(I)}$). They are at least an order of magnitude more mobile than inorganic mercury species, and thus are more toxic and more readily bioaccumulated (Stein et al. 1996; Ullrich et al. 2001; Boszke et al. 2002, 2003). The concentration of methylmercury in sediments usually comprises 1–1.5% of total mercury, and less than 0.5% in marine and estuarine sediments (Ullrich et al. 2001). In bottom sediments of the Gdańsk Bay (Poland), the South China Sea (Malaysia) and the Bering Sea (Russia), the contributions of methylmercury to total mercury were 0.02–2.27%, 0.02–0.27% and 0.02–0.7%, respectively (Kannan and Falandysz 1998). Higher contributions were found in the bottom sediments of the harbour in Hamburg, where its value varied from 2.5 to 8.1 (Wilken and Hintelmann 1991) and in the sediments from Kagoshima Bay (Japan) where the contribution of the organomercury compounds varied from 7% to 37% (Sakamoto et al. 1995, Egushi and Tomiyasu 2002).

The relatively high contributions of the organomercury fraction to total mercury observed in this study, $6.4 \pm 5.3\%$ (range 0.6–13%) (Table 1), may be partly explained by lack of selectivity of the organic solvents, extracting not only the organomercury species but also part of the mercury bound to organic matter (Egushi and Tomiyasu 2002). The highest organomercury contributions were found in sediment samples collected from Tczew (13%) and Bydgoszcz (12%), with lower proportions in samples from Świecie (6.3%) and Nowe (4.4%) and the lowest in sediments from Toruń (1.8%) and Kiezmark (0.6%). The absolute concentration of organomercury species was statistically significantly ($p < 0.05$) correlated to the contribution of mercury in this fraction (Table 3). In the floodplain soil samples collected from Kiezmark the contribution of organomercury species was higher (3.1–

5.1%) than in the sediment collected from that part of the river (0.6%), and the absolute concentration of organomercury species in the sediment was lower (0.38 ng g^{-1}) than in the floodplain soils ($3.2 \pm 1.1 \text{ ng g}^{-1}$, range 2.1–4.4). As a result it seems that the floodplain soils near the Vistula River in the Kiezmark area may be potential source of organomercury species for the river, especially at times of high water levels. In contrast to this situation, the absolute concentrations of organomercury species were higher in the sediments of the Warta River (Boszke et al. 2007) than in the floodplain soils of that river (Boszke and Kowalski, in press).

Comparisons to reported results of contributions by certain mercury fractions in other sediments may be only semiquantitative as a result of differences in fractionation methods. The same extraction method was used in this study as was used for analyses of freshwater sediment samples from the Warta River (Boszke et al. 2007), post-tsunami sediments (Thailand) (Boszke et al. 2006) and estuarine sediment (Boszke et al. 2007). The total mercury concentrations in these sediments, calculated as a sum of mercury concentrations in individual fractions, were $130 \pm 71 \text{ ng g}^{-1}$ dry mass (range 51–307), $119 \pm 50 \text{ ng g}^{-1}$ dry mass (range 66–230) and 373 ng g^{-1} for river, post-tsunami and estuarine sediments, respectively. In the Warta River sediments the contribution of mercury bound with organomercury species was higher $17 \pm 18\%$ (range 0.03–65) than in those of the Vistula River. The contribution of the organomercury fraction in the Warta River was even higher ($12 \pm 9\%$, range 0.08–32) when the sample with the maximum (65%) contribution of organomercury fraction was excluded from the calculations (Boszke et al. 2007). In comparison to the Vistula River sediments, a higher contribution of organomercury fraction was found in the post-tsunami sediments, $14 \pm 7\%$ (range 4–26) (Boszke et al. 2006), and lower in the estuarine sediment, 2.2% (Boszke et al. 2007). However, of all these sediments the absolute concentration of organomercury species in the Vistula River was observed to be the lowest. Higher concentrations were seen in the Warta River sediments ($17 \pm 18 \text{ ng g}^{-1}$, range 0.08–64) (Boszke et al. 2007), post-tsunami sediments ($15 \pm 7 \text{ ng g}^{-1}$, range 6–32) (Boszke et al. 2006) and estuarine sediment (8.3 ng g^{-1}) (Boszke et al. 2007).

Water soluble fraction

The fraction called water-soluble mercury includes mercury species present in pore water. Usually mercury is not present in the form of water soluble ionic species in the water phase, but as species bound to organic matter (without a Hg-carbon bond) or suspended mineral particles (Biester and Scholz 1997; Wallschläger et al. 1998a,b; Wasay et al. 1998; Renneberg

and Dudas 2001). Mercury species extracted by water may be easily transported by natural processes and serve as the substrate for mercury methylation process (Stein et al. 1996; Ullrich et al. 2001; Boszke et al. 2003). In general, the contribution of the water-soluble mercury species is very small, and often below the detection limit (Kot et al. 2002; Kot and Matyuskina 2002). For example, in the sediments of the river Ji Yun in China this fraction constituted 0.05–1.22% of the total mercury (Ching and Hongxio 1985), and in the marine sediments of Gdańsk Bay in Poland it was less than 4% (Beldowski and Pempkowiak 2003).

Contributions of water-soluble mercury in the Vistula River sediments were $6.9 \pm 2.9\%$ (range 5.1–13), being relatively uniform except in sediments collected from Tczew, where the contribution of water-soluble mercury was higher (13%). Absolute concentrations of water-soluble mercury species were $4.5 \pm 1.9 \text{ ng g}^{-1}$ (range 2.8–7.9), and were statistically significantly ($p < 0.05$) correlated with the proportional contribution to mercury by this fraction (Table 3). The contribution of the water-soluble mercury was also significantly correlated with the sum of the contributions of the water-soluble and the acid-soluble mercury (Table 3). In the floodplain soils collected from Kiezmark the contribution of water-soluble mercury was higher in the sample collected at 1 meter from the riverside (13%), than in the soil samples collected at 10 (4.0%) and 50 (4.9%) meters from the riverside. The concentration of water-soluble mercury in the sediment sample collected from Kiezmark was (at 3.2 ng g^{-1}), lower than in the floodplain sample collected 1 meter from the riverside (9.2 ng g^{-1}), but comparable to the soil samples collected at 10 and 50 meters from the riverside (3.4 and 3.3 ng g^{-1} , respectively). As a result it seems there is no high risk of contamination of the river sediments with water-soluble mercury from floodplain soils in the Kiezmark area. Similar concentrations were found in sediments and floodplain soil samples near the Warta River (Boszke and Kowalski, in press).

Lower contributions of the water-soluble mercury fraction, compared to those in the Vistula River sediments, were recorded in the sediments of the Warta river ($2.1 \pm 0.9\%$ (range 1.1–3.8)) (Boszke et al. 2007), post-tsunami sediments ($0.8 \pm 1.0\%$ (range 0.1–3.6)) (Boszke et al. 2006) and estuarine sediment (0.3%) (Boszke et al. 2007). The absolute concentrations of water-soluble mercury were also lower than those observed in the Vistula River samples ($2.7 \pm 2.4 \text{ ng g}^{-1}$ (range 1.3–9.7) in the Warta River sediments (Boszke et al. 2007), $0.9 \pm 0.9 \text{ ng g}^{-1}$ (range 0.1–3.4) in the post-tsunami sediments (Boszke et al. 2006) and 0.95 ng g^{-1} in the estuarine sediment (Boszke et al. 2007).

Acid soluble fraction

The fraction of acid-soluble mercury species includes strongly-bound Hg species extracted using acids, e.g. HCl (Ching and Hongxiao 1985, Lechler et al. 1997). Acid solution extracts are operationally defined as “reactive mercury species” or “bioavailable inorganic mercury” bound to iron monosulfides (i.e., AVS), iron and manganese hydroxides and carbonates. They can also include the species bound to organic matter and adsorbed on the surface of minerals (Lechler et al. 1997, Bloom et al. 2003, Shi et al. 2005).

In the Vistula River sediments the contribution of acid-soluble mercury is low and uniform $0.3 \pm 0.2\%$ (range 0.1–0.6). The absolute concentration of acid-soluble mercury species was statistically significantly ($p < 0.05$) correlated with the contribution of mercury in this fraction (Table 3). The contribution of acid-soluble mercury was also positively correlated with the contribution of mercury bound to humic matter and the sum of contributions of organomercury species and mercury bound to humic matter (Table 3). The contribution of acid-soluble mercury in the floodplain soil samples collected from Kiezmark was $0.5 \pm 0.2\%$ (range 0.3–0.7) and in the sediment sample collected there was 0.3%. The absolute concentration of the acid-soluble mercury in the sediments and floodplain soils was very low and comparable: $0.2 \pm 0.1 \text{ ng g}^{-1}$ and $0.3 \pm 0.1 \text{ ng g}^{-1}$, respectively. There is no high risk of contamination of the river sediments with acid-soluble mercury from the floodplain soils of the Vistula river in the Kiezmark area. By comparison the absolute concentration of acid-soluble mercury was eight-fold lower in floodplain soils than in the sediments of the Warta River (Boszke and Kowalski, in press).

Similar contributions of acid-soluble mercury were seen in Warta river sediments ($0.4 \pm 0.1\%$, range 0.2–0.7) and in estuarine sediment (0.2%) (Boszke et al. 2007) as in the Vistula River sediments, whereas higher contributions were observed in post-tsunami sediments $0.9 \pm 0.5\%$ (range 0.2–2.1) (Boszke et al. 2006). The absolute concentrations of acid-soluble mercury in Vistula River sediments were lower ($0.2 \pm 0.1 \text{ ng g}^{-1}$, range 0.1–0.4) than in the Warta river sediments ($0.6 \pm 0.5 \text{ ng g}^{-1}$, range 0.2–2.0) (Boszke et al. 2007), post-tsunami sediments ($0.9 \pm 0.4 \text{ ng g}^{-1}$, range 0.3–1.7) (Boszke et al. 200) and estuarine sediment (0.63 ng g^{-1}) (Boszke et al. 2007).

Comparable or higher acid-soluble mercury fraction values have been obtained using similar extraction methods for both freshwater and marine sediments. In Ji Yun river sediments (China) the contribution was from 0.34 % to 1.55% (Ching and Hongxio 1985). According to Peng and Wang (1985) the mean contribution of mercury in the acid-soluble fraction in Ji

Yun and Zijan River sediments (China) was 3.4%, and the maximum contribution of this fraction (13.1%) was found in the vicinity of a waste outflow, with an absolute concentration of 262,000 ng g⁻¹.

Humic matter fraction

Organic matter is an important component of sediments and soils and is responsible for significant binding of metals. The organic mercury fraction includes mercury Hg(II) complexes with organic ligands e.g. humic, fulvic and amino acids (but without a Hg-carbon bond). Binding of mercury in organic matter is mainly due to the reduced sulphur species in such functional groups as thiol (R-SH), disulphide (R-SS-R) or disulphane (R-SSH) (Xia et al. 1999). Besides sulphur, some mercury in organic matter is also bound by oxygen and nitrogen atoms, but in much lower amounts (Hesterberg et al. 2001). It has been indicated that organic matter can bind up to 95% of divalent mercury species (Meili 1997). A significant component of organic matter is the humic matter whose contribution in the total organic matter is ~25% in the bottom sediments, 20% in marine water, 60% in river water and 70% in marsh areas of river catchments (Weber 1993).

In the Vistula River sediments, the contribution of the mercury bound to humic matter was 19 ±10% (range 10–35). The highest contribution of the mercury bound to humic matter was found in the sediment samples collected at Toruń (35%), lower in the samples collected at Nowe (23%) and Tczew (19%), and the lowest in sediments at Bydgoszcz (12%), Kiezmark (12%) and Świecie (10%). The absolute concentration of the mercury bound to humic matter was statistically significantly ($p < 0.05$) correlated with the contribution of mercury in this fraction (Table 3). The contribution of the mercury bound to humic matter was also positively correlated with the sum of the contributions of the organomercury species and the mercury bound to humic matter (Table 3). In the samples of floodplain soils collected near Kiezmark the contribution of the mercury bound to humic matter (17 ±8%, range 13–27) was similar as in the sediment collected from this part of river (12%). In the soil samples collected at 1 and 10 meters from the riverside, the contribution of the mercury bound to humic matter was 13%, and much higher in the sample collected at 50 meters from the riverside, at 27%. The absolute concentrations of the mercury bound to humic matter in the sediments and floodplain soils were comparable: 11.4 ±4.3 ng g⁻¹ (range 7.6–19.1) and 12.6 ±4.7 ng g⁻¹ (range 8.7–17.8), respectively. These imply that there is a relatively low risk of contamination of the river sediments by

the mercury bound to humic mater from floodplain soils in the Kieźmark area.

Reported proportional contributions of the humic-bound mercury fraction to total mercury in Warta River sediments ($23 \pm 9\%$, range 4–36) (Boszke et al. 2007) were comparable to those reported here, but were lower in post-tsunami sediments ($9 \pm 7\%$, range 1–27) (Boszke et al. 2006) and estuarine sediment (4.6%) (Boszke et al. 2007). The absolute concentrations of mercury bound to humic matter observed in this study was lower than reported in Warta River sediments ($30.5 \pm 19.6 \text{ ng g}^{-1}$, range 4.3–63.5) (Boszke et al. 2007) and estuarine sediment (17.0 ng g^{-1}) (Boszke et al. 2007), and comparable to those in post-tsunami sediments ($12.0 \pm 14.4 \text{ ng g}^{-1}$, range 0.8–45.9) (Boszke et al. 2006).

The use of similar fractionation methods by other authors has resulted in a wide range of values being reported for the proportional contribution to total mercury of species bound to humic matter. In the bottom sediments of the rivers Ji Yun and Zijan (China) the humic matter fractions contributed 2.7% to 77.4% (Peng and Wang 1985) of total mercury. The lowest proportion of contribution of this fraction was found in a sample taken close to a waste release from a plant producing chlorine alkaline compounds. In that sample the concentration of mercury bound to organic matter was $54,000 \text{ ng g}^{-1}$. The concentration of mercury in the sample with the greatest proportion of contribution of the organic matter bound mercury was 4400 ng g^{-1} (Peng and Wang 1985). Other authors (Ching and Hongxiao 1985) reported the contribution of the humic acid bound mercury in the bottom sediments from the same river Ji Yun as varying from 6.52% to 23.7% ($800\text{--}46,650 \text{ ng g}^{-1}$). In marine sediments the proportion of fulvic acid bound mercury is small and does not exceed a few percent (9% at maximum), while the contribution of the humic acid bound mercury is much greater, about 20% (reaching 54%) (Beldowski and Pempkowiak 1998). In general, greater contributions of the mercury bound to organic matter are found in the sediments from non-polluted rivers and smaller in highly polluted ones. For example the contribution of the fraction containing mercury bound to humic matter in bottom sediments from the Carson river (USA) was a few percent in the region flowing through mill tailings (and hence highly polluted with mercury) and increased to $< 40\%$ in less polluted areas (Lechler et al. 1997).

Sulphide mercury fraction

In the presence of sulphides the mercuric ion becomes tightly bound as insoluble HgS and is not available for methylation. Sulphide activity may be the main factor influencing the availability of Hg(II) and the concentration

of methylmercury in the sediment. If conditions become aerobic, due to a decrease in the organic load or seasonal turnover, sulphide can be oxidized to sulfate, releasing the mercury in the ionic form Hg(II), which is then available for methylation (Stein et al. 1996, Ullrich et al. 2001, Boszke et al. 2003).

In the Vistula River sediments the contribution of mercury bound to sulphides was $68 \pm 11\%$ (range 55–82). Higher contributions of mercury in this fraction were found in the sediments collected at Kiezmark (82%) and Świecie (77%), lower in the samples collected at Bydgoszcz (70%), Nowe (65%), and lowest in those collected at Toruń (57%) and Tczew (55%). These results suggest that the main factor influencing the bioavailability and mobility of mercury in the Vistula River sediments are sulphides. The contribution of the mercury bound to sulphides was significantly ($p < 0.05$) negatively correlated with the sum of the contributions of the organomercury species and mercury bound to humic matter. The contribution of the mercury bound to sulphides was also negatively correlated ($p < 0.05$) with that of the non-residual mercury (the sum of fractions F1, F2, F3 and F4) (Table 3).

In the floodplain soil samples collected from Kiezmark the proportional contribution of the mercury bound to sulphides was lower $70 \pm 6\%$ (range 65–78) than in the associated river sediment sample (82%). However, the absolute concentrations of mercury in these samples were comparable at $52.7 \pm 12.4 \text{ ng g}^{-1}$ (range 43.3–66.8) in the floodplain soil, and $45.0 \pm 14.8 \text{ ng g}^{-1}$ (range 30.9–71.3) in the river sediment. This implies that there is relatively low risk of contamination of the river sediments by the mercury bound to sulphides in these floodplain soils. In Warta River samples the proportional contribution of the sulphide mercury in floodplain soil was higher than in the sediments, but the absolute concentration of mercury in this form was about twice as high in the sediments as in the floodplain soil (Boszke and Kowalski, in press).

Lower proportional contributions of the fraction containing mercury bound to sulphides were found in Warta River sediments ($58 \pm 17\%$, range 20–81%) (Boszke et al. 2007) than in those of the Vistula River, but higher in post-tsunami sediments ($75 \pm 6\%$, range 62–86) (Boszke et al. 2006) and in estuarine sediment (93%) (Boszke et al. 2007). Despite the lower proportion of this fraction in Warta River sediments the absolute mercury concentrations were higher ($79.5 \pm 59.2 \text{ ng g}^{-1}$, range 20–232) (Boszke et al. 2007) than those of the Vistula River. Much higher concentrations of mercury bound to sulphides were found in post-tsunami sediments ($90 \pm 40 \text{ ng g}^{-1}$, range 47–177) (Boszke et al. 2006) and estuarine sediment (346 ng g^{-1}) (Boszke et al. 2007) than in the Vistula samples.

The contribution of mercury bound to sulphides is greater in sediments and soils characterised by reducing properties (Lechler et al. 1997, Bełdowski and Pempkowiak 2003). For example, the proportional contribution of mercury bound to sulphides in the bottom sediments of Gdańsk Bay (Poland), which are characterised by reducing properties, was close to 40%, with a maximum value of 96% (Bełdowski and Pempkowiak 2003). In the soil profile the contribution of residual mercury was found to increase with the depth of the profile, from 8.1% in the surface layer (0-30 cm) to 69% at 50-80 cm (Lechler et al. 1997). High contributions of mercury bound to sulphides, mean 71.4% (range 38–96), were found in bottom sediments from the Kogushima Bay (Japan), where mercury sulphide is formed from H₂S and mercury chloride is liberated from fumarole gasses released from the sea bottom (Sakamoto et al. 1995).

Estimation of mercury load to water of Gulf of Gdańsk

The Vistula River is the main inflow of freshwater to the Gulf of Gdańsk and with an average annual water discharge reaching 32×10^{12} t it comprises about 10% of the total volume of the Gulf (Majewski 1990). The riverine waters spread out in the form a 3-5 km long tongue (Tarnowska and Zeider 1980), which extends during flooding (in spring flows increase up to ca $5000 \text{ m}^3 \text{ s}^{-1}$) so that the border of the low salinity region can be detected even 30 km from the river mouth (Bojanowski 1981). The concentration of suspended particle matter in water at the mouth of the Vistula River, in a period from April to September, ranged from 6.85 to 23.73 mg dm^{-1} , with a mean of $12.5 \pm 6.78 \text{ mg dm}^{-1}$ (Sokołowski et al. 2001).

In order to estimate the load of mercury into the water of the Gulf of Gdańsk it was assumed that the concentration of mercury forms, and their proportional contributions to total mercury, in the suspended particulate matter of the lower Vistula river was the same as in sediments (own study). Further it was assumed that the concentration of suspended particulate matter was the same as reported by Sokołowski et al. (2001) and the annual load of Vistula River water is 32×10^{12} t (Majewski 1990). These assumptions result in the load into the Baltic of mercury bound to suspended matter to the Baltic water being estimated as 26 t y^{-1} (range 9–81). The load of the mercury has been estimated as 1.7 t y^{-1} (range 0.08–6.4) for organomercury species, 1.8 t y^{-1} (range 0.6–6) for water-soluble mercury, 0.08 t y^{-1} (range 0.02–0.3) for acid-soluble mercury, 4.6 t y^{-1} (range 1.7–15) for mercury bound to humic matter and 18 t y^{-1} (range 7–54) for mercury bound to sulphide.

The amounts of mercury entering the Baltic Sea from the atmosphere and with river waters were estimated as 20 and 50 t y^{-1} respectively. As much as

93% of the mercury load introduced into the Baltic comes from anthropogenic sources, with the most important natural contributions derived from the atmosphere (ca. 0.1 t y⁻¹), and from the rivers (ca. 4.9 t y⁻¹) (Matschullat 1997).

CONCLUSIONS

In the sediments of the lower Vistula River, mercury occurs primarily in the form of mercury sulphide, which is relatively insoluble and not readily bioavailable, and in forms bound to humic matter (up to 82% and 35%, respectively). Perhaps surprisingly, however, it seems that the main factor influencing the bioavailability and mobility of mercury in these sediments is the concentration of these intractable mercury sulphides. As changes in the conditions of the sediments occur, a significant portion of mercury bound to these sulphides may become available for biotic and abiotic methylation. The proportion of organomercury species in the samples studied was seen to be low (up to 6.3%), but these species may pose a real threat to man and other organisms because of their extreme toxicity and the potential of bioaccumulation and biomagnification in trophic chains. Water-soluble mercury and acid-soluble mercury (exchangeable mercury) can easily enter the aquatic system and may accumulate in organisms. It is possible that heavy floods of the Vistula River area would cause dilution and removal up to 13% of the total (exchangeable) mercury from the river sediments.

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