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Original Research

Distribution of Mercury and Other Heavy Metals in Bottom Sediments of the Middle Odra River (Germany/Poland)

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Abstract

The Odra is the second largest river in Poland, running from the Czech Republic through a large part of Poland before entering the Baltic Sea. Its catchment area has been heavily polluted by anthropogenic emissions. Our data document an intensive anthropogenic impact on the abundance of heavy metals in bottom sediments of the middle part of the Odra. Normalized heavy metal concentrations in sediments and indices of geoaccumulation (I_{geo}) indicate that this area is polluted by various metals, especially mercury, cadmium and zinc. The ranges of their concentrations vary as follows: Hg 0.12-2.99 mg/kg, Cd 2.93-7.87 mg/kg, Pb 21.2-163 mg/kg, Cu 11.5-88.3 mg/kg, Zn 28.0-471 mg/kg, Cr 1.57-47.5 mg/kg, Ni 5.10-19.1 mg/kg, Fe 1493-37972 mg/kg and Mn 47.6-1242 mg/kg.

Keywords: mercury, heavy metals, bottom sediments, Odra River

Introduction

The Odra, as one of the five longest rivers in Europe, is a system transporting and collecting a large number of substances from natural and anthropogenic sources. The Odra River Basin has a catchment area of 118.861 km^2. The basin is situated in the industrialized and highly populated centre of Europe, shared by Poland (89 %), the Czech Republic (6 %) and Germany (5 %). The Odra has its sources in the Odra Mountains (the Czech Republic, 632m above sea level), and after 854.3 km the river flows into the Szczeciński Lagoon and through Pomeranian Bay into the Baltic Sea. The Odra is one of the largest rivers entering Baltic. Over a distance of 176 km the Odra forms the state border between Poland and Germany. At present, 15.4 million people live in the catchment area: 13 million in Poland, 1.4 million in the Czech Republic and 1 million in Germany [1, 2].

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The Odra River basin is divided into the upper course (source - Wroclaw, 21.4% of total area), the mid-altitude course (Wroclaw-Warta, 54.6% of total area), and the lower course (Warta-Szczecinski Lagoon, 24% of the total area). In the upper part of the Odra catchment, pollution comes from mining of coal, copper, lead and zinc and sulphur as well as heavy industry. In the middle part and the underflow the sources of pollution are agriculture, oil industry and communal waste. In the middle part of the river urban and industrial agglomerations localized directly on the river impact the quality of its water: Wrocław, Brzeg Dolny, Malczyce, Głogów, Nowa Sól and Krosno Odrzańskie. In the border part the river also collects wastes from Germany, and via the Nysa Łużycka river also from the Czech Republic. On the Polish side the main sources of pollution are Kostrzyń and Słubice, while on the German side Eisenhuttenstadt and Frankfurt/Oder [1, 3-5].

The objective of this study was to estimate the contamination of the Odra river bottom sediments by mercury and other heavy metals in the middle of its course and to identify potential sources of heavy metal pollution in this part of the Odra river and its drainage area.

Materials and Methods

Sediment Sampling

Bottom sediments were collected from 7 sites in the middle part of the Odra in 2002 (Figure 1). The samples from German (A) and/or Polish (C) banks, and/or from the middle part of the river-bed (B) were collected at each site. Generally, the sediment samples were taken with a hand corer made of stainless steel. They were placed in plastic boxes of 1000 cm^3 volume and transported to the laboratory where they were dried at room temperature to constant weight.

Sediment Fractionation

The sediment samples, homogenized in an agate mortar, were dry sieved to separate the required fractions from ~250 g bulk sediment. In order to avoid sample contamination, nylon sieves were used. Geochemical analyses of mercury were performed for the grain-size fraction of < 0.2 mm. The other heavy metals were analyzed from the fraction of < 0.8 mm.

Analytical Procedure

Total mercury concentration was determined by cold-vapour atomic fluorescence spectroscopy (CV-AFS) using a Millenium Merlin Analyzer (PS Analytical) after sample digestion with aqua regia. The total content of heavy metals was determined after sample digestion with concentrated HNO_3 and 30% H_2O_2. Heavy metals were determined by flame atomic absorption spectrometry (AAS) on a Varian spectrometer Spectr AA 20 plus. Cadmium was determined by the graphite furnace technique. Organic matter was determined as a loss on ignition at 550^0C in 12 hours to obtain constant weight.

Analytical Methods

Standard Reference Materials were analysed routinely as laboratory reference materials: SRM 2711 (Montana Soil - agricultural soil) for mercury and LKSD-2 (Canadian Lake Sediment) for other heavy metals. Recoveries of heavy metals were: Hg-97%, Cu-88%, Pb-86%, Ni-82%, Cr-79%, Mn-85%, Zn-88%, Fe-79%.

Indicator of Sediment Contamination (Geoaccumulation Index)

In order to classify local anthropogenic sources of heavy metal pollution, the I_{geo} index (geoaccumulation

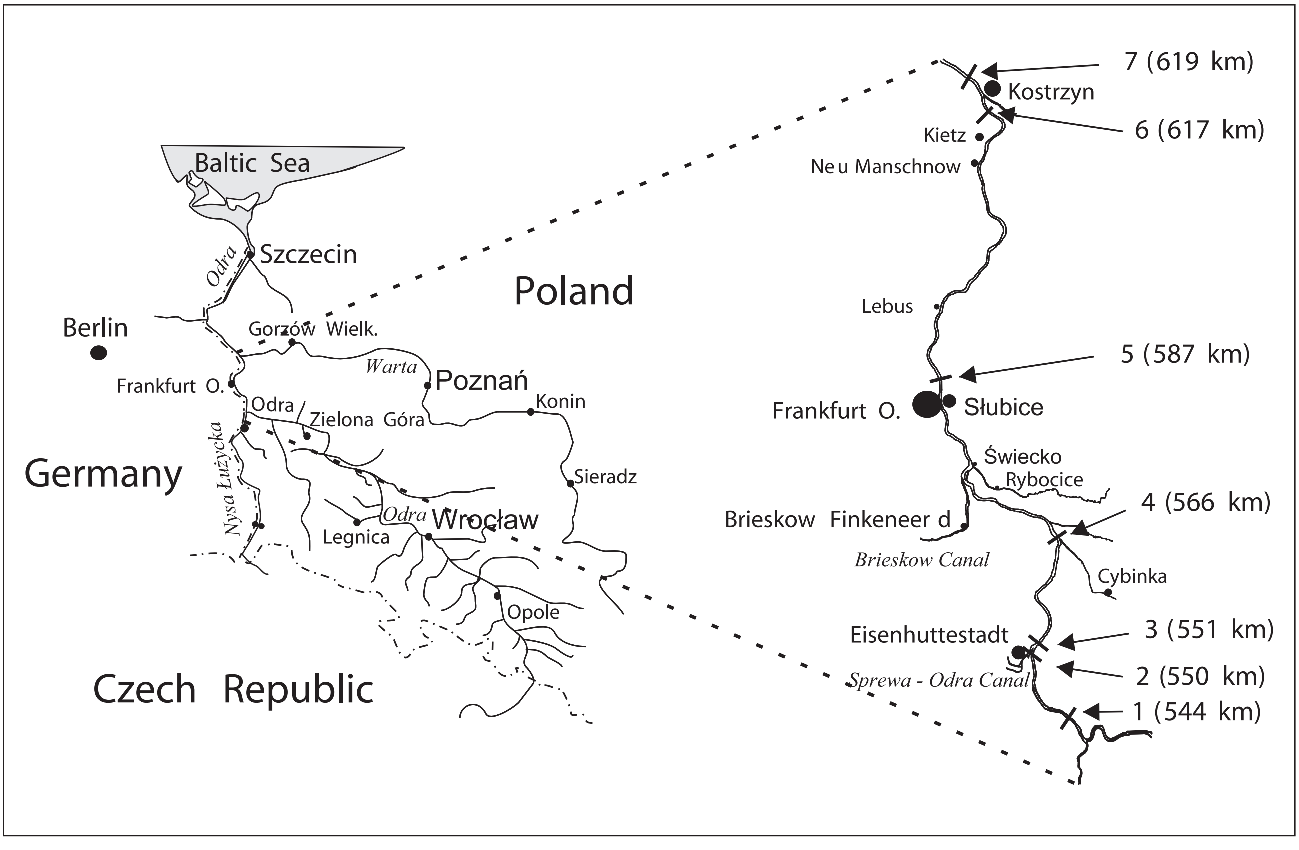

Fig. 1. Map of study area.

Table 1. Concentrations of heavy metals (mg/kg dry weight) in bottom sediments of the Odra.

Sampling site	River bank	LOI (%)	Fe (%)	I_{geo}	Mn	I_{geo}	Hg	I_{geo}	Cd	I_{geo}	Pb	I_{geo}	Cu	I_{geo}	Zn	I_{geo}	Cr	I_{geo}	Ni	I_{geo}
1	A	4.9	1.5	1	418	1	1.78	3	4.7	3	91.1	1	51.7	1	323	1	47.6	1	19.2	1
	B	0.2	2.0	1	284	1	-	-	4.48	3	60.3	1	11.5	1	59.2	1	2.37	1	13.6	1
	C	0.5	2.0	1	47.6	1	0.28	0	3.69	3	28.8	1	14.2	1	47.4	1	2.98	1	13.3	1
2	A	6.3	17.3	1	711	1	1.36	2	7.87	4	163.3	1	88.3	1	471	1	44.2	1	31.0	1
3	A	1.1	2.9	1	95.7	1	0.35	0	3.36	3	33.5	1	14.8	1	70.0	1	3.39	1	17.6	1
	B	0.3	1.9	1	263	1	-	-	3.36	3	38.4	1	13.4	1	56.5	1	2.03	1	19.0	1
	C	0.8	2.8	1	100	1	1.32	2	3.27	3	31.0	1	15.2	1	61.9	1	3.04	1	14.1	1
4	A	0.7	2.6	1	138	1	0.51	0	3.44	3	30.8	1	16.2	1	92.0	1	4.33	1	11.5	1
	B	0.4	2.0	1	257	1	-	-	3.34	3	31.8	1	14.8	1	71.0	1	1.57	1	8.23	1
	C	2.8	8.9	1	324	1	2.99	6	4.18	3	83.3	1	64.5	1	225.3	1	20.6	1	14.0	1
5	A	4.1	37.9	1	1242	1	0.12	0	3.86	3	42.8	1	25.1	1	71.0	1	13.5	1	18.0	1
	B	0.6	2.1	1	248	1	-	-	2.93	3	23.9	1	13.3	1	68.8	1	2.33	1	12.0	1
	C	0.7	3.4	1	110	1	0.21	0	3.90	3	38.5	1	16.4	1	57.5	1	7.51	1	7.57	1
6	A	2.4	5.5	1	205	1	1.49	2	4.35	3	42.8	1	30.6	1	303	1	12.6	1	14.1	1
	B	0.5	1.8	1	222	1	0.25	0	4.62	3	33.6	1	13.9	1	72.2	1	2.32	1	11.7	1
	C	0.4	1.9	1	109	1	0.28	0	3.73	3	21.2	1	12.5	1	55.6	1	2.00	1	5.11	1
7	A	1.0	2.1	1	79.4	1	0.42	0	3.88	3	27.3	1	16.2	1	62.0	1	4.15	1	9.59	1
	B	0.5	1.6	1	284	1	0.89	0	4.33	3	30.0	1	13.5	1	47.1	1	2.64	1	12.12	1
	C	0.6	1.5	1	51	1	0.18	0	4.37	3	28.7	1	11.7	1	28.1	1	2.03	1	10.49	1
Background			1.3[a]		140[a]		0.2[b]		<0.5[c]		10[c]		6[c]		48[c]		5[c]		5[c]	
			4.67[d]		850[d]				0.3[d]		20[d]		45[d]		95[d]		90[d]		68[d]	
					960[e]				0.3[e]		30[e]		51[e]		115[e]				46[e]	

[a] Background values for Fe and Mn in Vistula river (Poland) (fraction < 0.060 mm) [*vide* 16], [b] For worldwide river sediments [21, 22], [c] Background for rivers sediments in Poland (fraction < 0.2 mm) [10], [d] For worldwide river sediments (fraction < 0.002 mm) [23], [e] Background for Rhine river sediments (Germany) [7]

index) was calculated and classification in I_{geo} classes was carried out [6]:

$$I_{geo} = \log_2 C_n / 1.5 B_n$$

Cn is the concentration of the element 'n' in the fraction < 0.002 mm (clay) and Bn is the background value for this element for this fraction of river sediments. The factor 1.5 is used to take into account possible variations in the background data. Heavy metals concentrations in the grain fraction < 0.075 mm [7, 8] and < 0.02 mm [9] were used in the calculations of Igeo characterizing bottom sediments. In this study, the values of Igeo were calculated for mercury from using grain-size fraction of < 0.2 mm and for other heavy metals from using < 0.8 mm. The background concentration values for bottom sediments in Polish rivers were assessed for grain fraction < 0.2 mm [10].

Hence, the value I_{geo} in class 0 indicates the absence of contamination, and the value I_{geo} in class 6 represents the upper limit of maximum contamination. The following classification was used: I_{geo}: < 0 = practically unpolluted; 0-1 = unpolluted to moderately polluted; 1-2 = moderately polluted; 2-3 = moderately to strongly polluted; 3-4 = strongly polluted; 4-5 = strongly to very strongly polluted; and > 5 very strongly polluted. The highest grades 6 (very strong contamination) reflects 100-fold enrichment of the metals relative to their background values.

Results

The concentrations of heavy metals in bottom sediments of the middle Odra river are given in Table 1. The mean values of the heavy metals concentrations are (mg/kg): Hg – 0.83±0.81 (0.12-2.99), Cd – 4.09±1.05 (2.93-7.87), Pb – 46.4±34.0 (21.2-163), Cu – 24.1±21,1 (11.5-88.3), Zn - 118±121 (28.0-471), Cr – 9.4±13.8

(1.57-47.5), Ni – 13.8±5.7 (5.10-19.1), Fe - 6096±8960 (1493-37972) and Mn - 273±282 (47.6-1242).

Variance analysis (ANOVA) has not revealed any significant differences ($p>0.05$) in the mean concentration of heavy metals in the cross-section of the bottom sediments studied, but statistically significant have been the differences in the organic concentration ($F(2,19) = 5.520688$; $p=0.0150$). The mean concentration of organic matter (%) was highest for samples collected on the German side 2.94±2.22, lower in samples collected on the Polish bank 0.94±0.90, and lowest in samples collected from the central riverbed 0.43±0.15.

Except for mercury, the mean concentrations of heavy metals found in the samples collected from the German bank (mg/kg): Cd - 4.50±1.56, Pb – 61.7±49.7, Cu – 34.7±26.9, Zn - 199±165, Cr – 18.5±19.1, Ni – 17.3±7.0, Fe - 11934±13045 and Mn - 413±429 were higher than the mean concentrations of heavy metals in sediments collected from the Polish bank (mg/kg): Cd – 3.86±0.39, Pb - 38.6±22.6, Cu - 22.4±20.7, Zn - 79.3±72.5, Cr – 6.4±7.3, Ni – 10.8±3.8, Fe - 3460±2780 and Mn - 124±102. The mean concentration of mercury in the samples collected from the Polish bank 0.88±1.12 mg/kg, was higher than in the samples collected from the German bank 0.86±0.66 mg/kg. The concentrations of the majority of the heavy metals studied in the samples collected from the central riverbed (except for nickel) were the lowest; (mg/kg): Hg – 0.57±0.46, Cd – 3.84±0.72, Pb – 36.3±12.7, Cu - 13.4±1.1, Zn – 62.4±9.9, Cr – 2.2±0.37, Fe - 1920±158 and Mn - 13.4±1.1. The mean concentration of nickel in the samples from the central riverbed 12.8±3.6 mg/kg was higher than in the samples from the Polish bank but lower than in those from the German bank. The ranges of the relative standard deviations (RDS) of the heavy metals concentrations determined in the sediments from the Polish and German banks were (%): Hg (77-128), Cd (10-35), Pb (59-81), Cu (78-92), Zn (83-91), Cr (103-114), Ni (35-41), Fe (80-109) and Mn (83-104). For the bottom sediment samples from the central riverbed the RDS values were (%): Hg (80), Cd (19), Pb (35), Cu (8), Zn (16), Cr (17), Ni (28), Fe (8) and Mn (9).

The samples collected below the outlet of the Sprewa-Odra canal (2A) were characterized by the highest concentrations of such metals as: Cd (7.87 mg/kg), Pb (163.3 mg/kg), Cu (88.3 mg/kg), Zn (471 mg/kg) and Ni (31.03 mg/kg). These samples also contained the greatest amount of organic matter 6.34%, and high concentrations of Fe (17399 mg/kg), Mn (711 mg/kg) Hg (1.36 mg/kg) and Cr (44.21 mg/kg). The highest concentration of Cr was found in the sample collected below the outlet of the Nysa Łużycka river on the German bank (1A). The samples from this site were also characterised by high contents of Fe (14916 mg/kg), Mn (416 mg/kg), Hg (1.78 mg/kg), Cd (4.74 mg/kg), Pb (90.06 mg/kg), Cu (51.66 mg/kg), Zn (323 mg/kg) and Ni (19.15 mg/kg) and a high content of organic matter 4.93%. The highest concentration of Fe (37973 mg/kg) and Mn (1242 mg/kg) was found in the sample collected near Frankfurt/Oder on the German bank (5A). The samples collected at the same site also contained a high concentration of nickel (18.03 mg/kg) and organic matter (4.1%). In the sample collected near the outlet of the Pliszka river on the Polish bank (4C) mercury was found in the highest concentration (2.99 mg/kg). The same sample also contained high concentrations of other heavy metals such as: Fe (8958 mg/kg), Mn (324 mg/kg), Pb (83.3 mg/kg), Cu (64.5 mg/kg), Zn (224 mg/kg) and Cr (20.6 mg/kg). Elevated concentrations of mercury were also determined in the samples collected above the outlet of the Warta river, on the German bank (7A) (1.49 mg/kg) and below the outlet of the Sprewa-Odra canal on the Polish bank (1.32 mg/kg) (3C).

Discussion

Heavy Metals Distribution

Among the heavy metals studied, the concentrations of mercury have been found the most diverse. This situation can be a result of the inflow of mercury from point sources of contamination such as municipal and industrial waste from towns and cities located directly on the Odra river or in the area of its catchment. The catchment area contains mainly arable land, so mercury can also be released from soil on which cultivations have been treated with pesticides or herbicides containing this element. The level of cadmium in the bottom sediments in the section studied is relatively uniform, and the main source of this metal is the industry in the region of Silesia, although it can also come from some point sources. In the conditions of normal water level, the content of heavy metals in the bottom sediments over the section studied decreased from Frankfurt/Oder to the town of Schwedt, which has been explained by a dilution effect [11]. The only exception was Cd, whose mean concentration increased from 6.2 mg/kg near Frankfurt/Oder to 7.7 mg/kg near Schwedt [11], so that a source for this metal was suggested down the river from Frankfurt/Oder [11]. In the conditions of elevated water level, the concentration of heavy metals in the bottom sediments can be even twice higher, and in the time of flooding (e.g. the flooding of 1997) it can be 3-4 times higher than at the normal water level, which was explained by the increased influx of metals bound to the particulate matter from the industrial region of Silesia [11].

It has been established that Cu, Cr, Ni and Zn are mainly transported in bulk river water and Cd, Pb, Fe and Al in the river water suspension [12]. In general, the concentration of cadmium in the dissolved phase (in bulk water) shows little diversity over the whole section of the Odra river studied and in its tributaries. The concentrations of other metals are higher in the upper part of the Odra river and in its tributaries than in the lower part of the Odra river and in the Warta river [4]. In the fraction of suspended matter the concentration of lead shows small changes, while greater regional changes are noted in the concentrations of cadmium, copper and chromium. The highest concentrations of these metals were determined in the suspended matter from the Warta river, lower in the upper and the lowest in the lower part of the Odra [4]. The highest concentrations of nickel and zinc were found in the suspension from the upper Odra and its tributaries [4]. During the flooding of 1997 the water of the Odra at the mouth to the Baltic carried greater heavy metals in higher concentrations (ng/L): Hg <210, Cd < 98, Pb <3300 [13]. During the flooding of 1997, in the lower Odra the concentrations of the heavy metals in suspended matter phase were as follows (mg/kg): Cd 2.3-7.5, Pb 91-537, Cr 79-129, Ni 42-117, Cu 95-775, Zn 778-2260 [14]. At the same time, the concentrations of heavy metals in the suspended matter in the upper and middle Odra were (mg/kg): Cd - 18,41, Cr - 174, Cu - 173 and Pb – 185 [12].

River bottom sediments in Poland (fraction <0.2 mm) have lower mean concentrations of Hg (0.31 mg/kg), Cd (2.3 mg/kg) and Pb (27 mg/kg), and higher mean concentrations of Zn (209 mg/kg), Cu (58 mg/kg), Cr (56 mg/kg) and Ni (17 mg/kg) [10] than the concentrations determined in the Odra river sediment in this study. High concentrations of heavy metals were also established in bottom sediments of the Wisła river (Cd – 25.6 mg/kg, Cu – 152 mg/kg, Hg – 0.67 mg/kg) and its tributaries: Przemsza (flows through the Industrial Centre of Upper Silesia) (Cd – 24.4 mg/kg, Zn – 5390 mg/kg, Pb – 302 mg/kg, Ni – 70 mg/kg, Hg – 1.19 mg/kg), Radomka (Cr – 469 mg/kg), Dunajec (Hg – 1.54 mg/kg), Bzura (Hg – 0.74 mg/kg), Liwa (Cu – 264 mg/kg, Cr – 530 mg/kg, 0.58 mg/kg, Ni – 46 mg/kg, Zn – 924 mg/kg) [10]. High concentrations of heavy metals were also determined in the rivers: Ner (Cd – 10.8 mg/kg, 316 mg/kg, Hg – 0.78 mg/kg), Wieprza (Cd – 15.6 mg/kg), Ślęża (Cd – 11.2 mg/kg, Cr – 239 mg/kg) and Prosna (Cr – 235 mg/kg) [10].

After the flooding of 1997, the mean concentrations of heavy metals in non-sifted sediments were (mg/kg): Cd – 2.7 (<1.0 – 8.9), Zn - 403 (24-3335), Pb - 78 (22-463), Cu - 47 (4-568), Cr – 18.9 (<5–90.3), Ni - 25,8 (<5.9–50.8), Mn - 465 (133–2539) and Fe - 15557 (2308-52904) and in the fraction <0.02 mm of the sediments collected from different sites in the upper and middle Odra: Hg – 1.31 (0.2-3.71), Cd – 5.0 (1.7-10.6), Zn - 1096 (274-3656), Pb - 172 (79-1773), Cu – 112 (38-2244), Cr - 68 (26-136), 43 (30.4–68.9), Mn - 1124 (556-5737) and Fe - 38429 (20802–56509) [15].

Very high concentrations of heavy metals were found in the bottom sediments of Odra tributaries. In the sediments of the Kaczawa river flowing through the industrial region of Lower Silesia they were the highest (Cu – 711 mg/kg, Cr - 1780 mg/kg, Ni – 164 mg/kg, 400 mg/kg) [10]. Only slightly lower concentrations (Zn – 1540 mg/kg, Cu-297 mg/kg, Pb –145 mg/kg, Ni - 52 mg/kg) were determined in the sediments of the Bystrzyca river (joining the Odra in Wrocław), Nysa Łużycka river (Cu - 176 mg/kg, Pb – 119 mg/kg), Nysa Kłodzka river (Cr – 226 mg/kg) [10]. The mean concentrations of heavy metals in the Warta river, being the main tributary of the Odra, were (mg/kg): Hg – 1.55 (0.18-5.75), Cd - 14,9 (0.13-87.9), Zn - 1396 (170-6772), Pb - 236 (30.6-1074), Cu - 170 (25.4-559), Cr – 271 (27.7-1948), Ni – 57.4 (15.0-272), Mn - 3771 (253-10025) and Fe – 58411 (24633-119038) [4]. In general, in the bottom sediments of the Odra tributaries in the fraction <0.02 mm, the mean concentrations of heavy metals were (mg/kg): Hg – 3.23 (0.22-29.78), Cd – 9.12 (0.01-91.7), Zn - 770 (122-2197), Pb - 136 (27.2-746), Cu - 189 (14.8-1276), Cr – 85.8 (3.64-535), Ni – 49.6 (11.0-125), Mn - 2020 (408-12900) and Fe - 50362 (20607-119044) [4].

Relative to the mean concentrations of heavy metals in the bottom sediments of the Rhine, Neckar, Elbe and Scheldt rivers, the mean concentrations determined in the Odra sediments in this study were usually lower. In the bottom sediments of the Rhine and Neckar the mean concentrations of Cd and Hg were smaller than in the Odra , while those of Pb and Zn were comparable to those in the Odra. In the bottom sediments of the rivers Elbe and Scheldt, the mean concentrations of Cd were of the same order of magnitude as in the Odra, while the mean concentrations of Hg were higher. The heavy metals concentrations in bottom sediments from the world's most polluted rivers were much higher (Table 2).

Interelemental Correlations

The interelemental correlation coefficients of heavy metals and organic matter in bottom sediments are given in Table 3. There are significant ($p < 0.05$) positive correlations between organic matter and heavy elements. Positive correlation of the metal concentrations with organic matter infers that organic matter present in sediments provides active sites for sorption of these metals. There are some positive significant correlations between trace elements themselves, suggesting their "similar behaviour" in bottom sediments.

Anthropogenic Contribution

To clarify the extent of heavy metals contamination associated with the sediments, the I_{geo} of heavy metals were calculated, as shown in Table 1. According to the classification of I_{geo} suggested by Müller [6], the content of Hg in the sediment taken from the Polish bank at 4 sites can be regarded as representing a very strong contamination level (6th grade). The content of mercury in the sediment from the German bank at point 1A can be regarded as representing a level of moderate to strong contamination (3rd grade) and from the German bank at sites 2A and 6A, and from the Polish bank at point 3C, can be regarded as representing a level of moderate contamination (2nd grade). Sediments from the other sites can be regarded as practically unpolluted with mercury (0 grade). The sediment contamination with Cd can be regarded as a moderate to strong, level (3 grade) but the sediment from the German bank at sites 2A can be regarded as strongly contaminated with Cd (4 grade). The sediment contamination with Pb, Cu, Zn, Cr, Ni, Fe and

Table 2. Heavy metal concentrations in bottom sediments from various sites in the world (mg/kg).

	Warta river[a] (Poland)	Elbe river[b] (Germany)	Rhine river[b] (Germany)	Neckar river[b] (Germany)	Scheldt river[c] (Belgium)	Ganga river[d] (India)	Ob river[e] (Russia)	Waterways in New Jersey[f] (USA)	River system[g] (Brazil)
Hg	1.55	3.7±2.8	0.4±0.3	0.3±0.2	0.46		0.02	0.38-29.6	
Cd	14.9	5.0±2.0	0.5±0.5	1.8±2.8	4.8	0.1-18.4	0.06	0.38-45.4	
Pb	236	170±110	70±40	74±26		27-549		4.4-3000	
Cu	170	170±180	48±22	110±110	35	43-445	5.5	3-3850	< 354±2
Zn	1396	1100±470	180±150	370±250	230	50-7485	20	10.2-10200	
Cr	271	160±40	40±14	120±150		76-49937		76-49937	< 235±14
Ni	57.4	66±12	39±6	44±16		21-502		6.4-269	
Fe	58411				10400	17000-78000	3100		
Mn	3771				343	76-49937	180		<235±14

[a] [4], [b] *vide* [4], [c] *vide* [18], [d] [24], [e] [18], [f] [25], [g] [26]

Table 3. Correlation matrix of various metals and organic matter (loss on ignition, LOI) in river sediments ($p < 0.05$; N=15).

	LOI (%)	Fe	Mn	Hg	Cd	Pb	Cu	Zn	Cr	Ni
LOI (%)	1									
Fe	**0.76**	1								
Mn	**0.74**	**0.97**	1							
Hg	0,48	0.10	0.10	1						
Cd	**0.72**	0.30	0.41	0.27	1					
Pb	**0.88**	0.44	0.48	**0.57**	**0.88**	1				
Cu	**0.87**	0.45	0.48	**0.71**	**0.79**	**0.97**	1			
Zn	**0.86**	0.36	0.37	**0.65**	**0.78**	**0.90**	**0.91**	1		
Cr	**0.93**	**0.53**	0.50	**0.58**	**0.72**	**0.90**	**0.89**	**0.89**	1	
Ni	**0.85**	**0.56**	**0.60**	0.36	**0.74**	**0.85**	**0.77**	**0.76**	**0.76**	1

Mn can be classified as belonging to the unpolluted to moderately polluted class (1 grade).

The values of I_{geo} significantly depend on the fraction for which they were determined. The values of I_{geo} for heavy metals in bottom sediments of the Odra were much higher for the fraction < 0.002 mm [16]. The values of this index for Cd in sediments from the Odra river collected near Chałupki, Brzeg Dolny, Słubice and Kołbaskowo, were classified in grades 5, 6, 5 and 5. The values of the index for Cu in sediments from the same sites were classified in grades 4, 3, 4, 3 and 3, those for Pb in grades 4, 4, 5 and 6, and those for Zn in grades 5, 6, 5 and 4 [16]. The bottom sediments from the Rhine (Germany) can be classified as belonging to classes 6 in the concentration of Cd, 2-3 in the concentration of Pb and Zn and 2 in the concentration of Cu, while the sediments from the Neckar river to classes: 3-6 (Cd), 2-3 (Pb, Zn), 2 (Cu) and 0-2 (Ni) [*vide* 16].

In order to minimize trace metal variability caused by grain size as well as by mineralogy, and hence to provide a more precise identification and quantification of anthropogenic heavy metal, geochemical normalization of trace metal data of conservative elements, such as Fe or Al has been used [17, 18]. Normalisation of the specific heavy metal concentrations in the bottom sediments under aerobic conditions to iron can be used as a correction factor for comparative assessment of simple sites and river basin contamination by heavy metals [17, 18]. Iron was chosen as the conservative element in this study because it had been measured in all data sets included. Iron was chosen as a element of normalization because natural sources (98%) vastly dominate its input [19]. Using this procedure it is possible to factor out the natural trace variability and identify environmental contamination and frequently also its sources, even where the overall level of contamination is low [20]. Investigations show that iron has a great ef-

Table 4. Normalized contents of heavy metals in different bottom sediments under aerobic conditions.

	Odra river (this study)	Ob river[a]	Danube river[b]	Scheldt river[b]	Haifa Bay[c]	Amazon rivers[d]	Back-ground river
Hg/Fe x 10^3	0.086±0.043 (0.002-0.142)	0.012	-	0.033		0.0013-0.0038	0.008[b]
Mn/Fe x 10^3	68±49 (24-170)	48	30	30			17[b]
Cd/Fe x 10^3	1.45±0.81 (0.10-2.93)	0.02	0.09	0.3			0.006[b]
Cu/Fe x 10^3	6.01±1.79 (0.66-8.06)	1.3	1.2	3.1	0.91±0.24		1.1[b]
Zn/Fe x 10^3	27.5±10.5 (1.9-54.5)	5.2	5.6	22.0	4.60±1.44		1.5[b]
Pb/Fe x 10^3	13.1±6.3 (1.1-30.2)				3.39±0.93		4.3[e]
Cr/Fe x 10^3	1.55±0.69 (0.36-3.18)						19.1[e]
Ni/Fe x 10^3	4.53±2.56 (0.47-10.15)						14.5[e]

[a] [18], [b] *vide* [18], [c] [17], [d] [27], [e] [23]

fect on heavy metals content in bottom sediments of the Odra (Table 4). The background values normalized with respect to iron were most exceeded by the concentrations of cadmium – 242 times, zinc – 18 times and mercury – 11 times, while for copper the background value was exceeded 5 times, for manganese – 4 times and for lead – 3 times. The concentrations of chromium and nickel did not exceed the background values (Table 4). The same table also presents the normalized concentrations of heavy metals in bottom sediments of other rivers in various parts of the world.

Conclusions

The present data document an intense anthropogenic impact on the abundance of heavy metals in bottom sediments of the middle part of the Odra. Normalized heavy metals concentration in sediments and their geoaccumulation indices (I_{geo}) indicate that this area is polluted by various metals, especially mercury, cadmium and zinc.

Potential sources of pollution are municipal wastes of such large cities as Frankfurt/Oder, Eisenhuttestadt, Słubice, Kostrzyn and smaller towns on the Odra. The most threatening source of pollution from among large cities seems to be Eisenhuttestadt, which hosts metallurgic plants, a shipyard, and a construction material production plant (cement and concrete). Moreover, a significant source of the bottom sediments of middle Odra contamination with heavy metals seems to be the influx of heavy metals bound to suspended matter from the Lower Silesia industrial region.

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