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Original Research

Total Mercury in Floodplain Soils of the Warta River, Poland

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Abstract

The aim of this study was to determine spatial distribution of mercury in floodplain soils of the middle Warta river with special regard to the polluting influence of the city of Poznań (capital of the Wielkopolska District) and high water levels and floods. Total mercury concentration was determined in samples collected from eleven sampling sites located above, below and in the area of Poznań agglomeration. From each site three soil samples were collected at distances of 1, 10 and 50 meters from riverside. The method used for the determinations was cold vapour atomic fluorescence spectrometry (CV–AFS). The results of the study have shown that mercury distribution in the samples of floodplain soil of Warta river was relatively uniform. However, higher mercury concentrations were found in the floodplain soils collected below of Poznań (median 300 ng g^{-1}, range 75–884), lower in soil samples above of Poznań (228 ng g^{-1}, range 54–754) and from the city area (183 ng g^{-1}, range 72–303).

Keywords: mercury, floodplain soil, Warta river, Poland

Introduction

The considerable attention focused on environmental pollution by mercury (Hg) is a consequence of the high toxicity and stability of its chemical species (mainly methylmercury and the vapours of elemental Hg), its prevalence resulting from the large number of its sources and the ease of its dispersal [1-4]. Moreover, in view of the fact that bioaccumulation of Hg occurs especially in fish and aquatic mammals, the migration of this element in the natural environment has been studied for many years.

Most anthropogenic mercury emissions are released to the air as by-products of various industrial processes, including coal combustion, fossil fuel combustion, mercury vapour lights and chloroalkali production [5]. The total mass of mercury emitted to the atmosphere from industrial sources in Poland has been estimated at 40 tons per year [6]. The main source of mercury emissions to the atmosphere is fuel combustion. As a consequence of this process, about 26 tons of mercury is emitted to the atmosphere per year. Processes of combustion of hard coal and lignite are responsible for the release of 44% and 18.3% of total mercury emitted to the atmosphere. Other sources of mercury, such as the cement production process and used fluorescent lamps are responsible for the release of 16.6% and 6.4%, respectively [6]. The main sources of mercury in urban areas are combustion facilities, including coal-fired power plants, municipal solid waste incineration and hospital incineration. Other sources of mercury contamination in urban areas are hazardous waste and sewage sludge [7]. Mercury is generally primarily emitted to air and water.

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Eventually, mercury accumulates in soils and, as cities often are located at rivers, also in bottom sediments. The soils and sediments can therefore provide time-integrated fingerprints of environment pollution, at least for mercury that has a reasonably strong affinity to natural particles [8-11].

The aim of this study was to determine the distribution of mercury in floodplain soils of Warta river and to identify the effect of Poznań agglomeration as a source of mercury pollution. Possible relation of floods on mercury accumulation/mobilization to/from soil in aspects of cultivation safety of vegetables and fruits in this area is also discussed.

Materials and Methods

Characteristics of Study Area

The Warta river in west-central Poland is the principal tributary of the Oder river. Its source lies 380 meters above sea level in Kromołow, near Zawierec. With a length of approximately 808 kilometers it is the third longest river in Poland. The Warta basin's 55,193 km^2 covers approximately one-sixth of Poland. Its main tributaries are: Prosna, Obra, Widawka, Ner and Noteć rivers. It is connected to the Vistula river by the Noteć river and the Bydgoszcz Canal. The main city on the Warta River is the capital of Wielkopolska, Poznań. Within the boundaries of the city itself the river runs for 20 kilometers. Poznań is a city with 578,900 inhabitants and is the fourth biggest industrial centre in Poland with domination by the food, mechanical, electrotechnical, pharmaceutical and chemical industries.

Soil Sampling and Preparation for Analysis

Samples of soils were collected from different sites along the Warta river in 2004 (Fig. 1). In each site three samples were collected (0-20 cm), at a distance of about 1, 10 and 50 metres from the riverside. Soil samples weighting about 2 kg were collected from the shore using a manual scoop of stainless steel from each site. The samples were placed in a plastic vessel and transported to the lab where they were dried for a few weeks at room temperature in a dust-free room to constant mass. The samples were then gently crushed in an agate mortar but not to damage the structure of the grains. From such samples portions of 250 g of uniform mass were collected and sieved through a copper sieve of the mesh size 0.15 mm. In samples of soils organic matter was determined as a loss on ignition at 550^0C for 12 hours to obtain constant weight.

Analytical Procedure

For determination of mercury, sediment and soil subsamples (~1 g) were wet digested with aqua regia in a glass apparatus consisting of a round-bottom flask, partial condenser (30-cm long) and water cooler. 17 mL of aqua regia were added to the samples and the mixture was allowed to stand for 16 h. The flask was then gently heated for 2.0 h at boiling temperature. After cooling, the water cooler and condenser were rinsed with 5 mL of redistilled water. The digest was filtered by blotting paper and diluted with redistilled water up to 100 mL. Finally the mercury content was determined by cold vapour atomic fluorescence spectroscopy (CV-AFS) using Millenium Merlin Analyzer (PS Analytical).

Analytical Method

Standard Reference Materials: SRM 2711 – Montana Soil, SRM 2709 – San Joaquin Soil and LGC 6137 – Estuarine Sediment were analyzed routinely as laboratory reference materials. The values for total mercury 6.06 ±0.07 μg g^{-1} (SRM 2711, n=3), 1.44±0.03 μg g^{-1} (SRM 2709, n=4) and 0.37±0.01 μg g^{-1} (LGC 6137, n=4) were in agreement with the certified concentrations of 6.25±0.19 μg g^{-1}, 1.40±0.08 μg g^{-1} and 0.34±0.05 μg g^{-1}, respectively. Procedural blanks were run with each set of sample analyses.

Results

The concentrations of total mercury and organic matter content (as a loss on ignition) in floodplain soils of Warta river are shown in Table 1. The median of concentration of total mercury was 198 ng g^{-1} dry mass (range 54–884) in bulk soils. The Kruskal-Wallis test (nonparametric ANOVA) did not show statistical differences in mercury concentrations between the soil samples collected above, below and in the area of Poznań ($H(2.33) = 2.522$, $p = 0.283$). However, higher concentrations of mercury were found in the floodplain soil samples collected below Poznań (median 300 ng g^{-1}, range 75–884), lower in the soil samples above Poznań city (228 ng g^{-1}, range 54–754) and from the city area (183 ng g^{-1}, range 72–303). Total mercury concentrations in the floodplain soil samples collected at different distances from the riverside were uniform ($H(2.33) = 0.405$; $p = 0.812$). Relatively higher average mercury concentration was found in the samples collected at 1 meter from the riverside (228 ng g^{-1}, range 72–637), lower in those collected at 50 meters from the riverside (190 ng g^{-1}, range 54–884) and the lowest in the samples collected at 10 meters from the riverside (185 ng g^{-1}, range 80–754). In the samples of floodplain soil collected at 1 meter from the riverside the average mercury concentration was the highest in those collected below the city (609 ng g^{-1}), lower above the city (214 ng g^{-1}) and the lowest in the city area (140 ng g^{-1}). From among the floodplain soil samples collected at 10 meters from the riverside, the highest mercury concentration was noted below the city (202 ng g^{-1}), lower in Poznań city (185 ng g^{-1}), and the lowest above the city

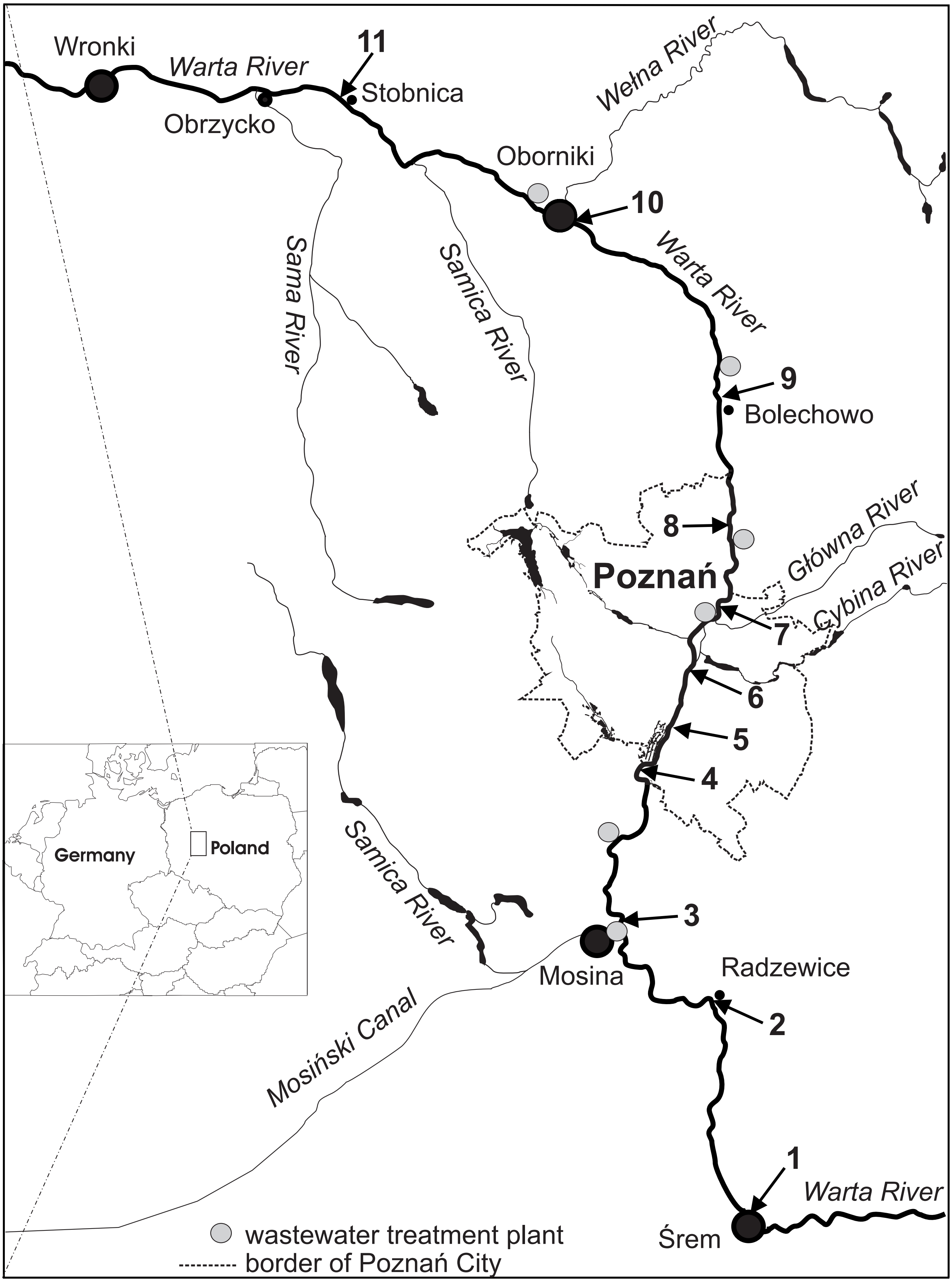

Fig. 1. Sampling sites.

Table 1. The contribution of mercury from particular fractions in the total content of mercury in samples of the Warta River floodplain soil.

Site number	Geographical coordinates	Distance from riverside (m)	LOI (%)	Total mercury in bulk soils (ng g^{-1})	Total mercury in bulk sediment[a] (ng g^{-1}) and LOI[b] (%)	Water[a] (ng L^{-1})
1	N 52^0 05’ 34.3” E 17^0 01’ 02.9”	1	4.9	72	103 (1.3)	17
		10	10.2	283		
		50	28.4	291		
2	N 52^0 13’ 01.1” N 52^0 13’ 01.1”	1	2.6	214	138 (4.4)	13
		10	3.8	127		
		50	7.0	303		
3	N 52^0 15’ 20.6” N 52^0 15’ 20.6”	1	4.0	228	165 (3.2)	27
		10	10.4	80		
		50	9.6	236		
4	N 52^0 22’ 25.3” N 52^0 22’ 25.3”	1	5.7	241	60 (1.7)	26
		10	3.5	122		
		50	2.0	54		
5	N 52^0 21’ 56.3” N 52^0 21’ 56.3”	1	1.6	121	80 (2.9)	20
		10	4.1	161		
		50	6.6	124		
6	N 52^0 23’ 58.0” N 52^0 23’ 58.0”	1	2.3	140	47 (1.5)	22
		10	6.7	185		
		50	6.9	190		
7	N 52^0 25’ 52.1” N 52^0 25’ 52.1”	1	1.2	113	121 (1.3)	32
		10	2.5	198		
		50	8.3	313		
8	N 52^0 28’ 29.6” N 52^0 28’ 29.6”	1	1.9	375	310 (1.8)	36
		10	13.9	754		
		50	5.7	183		
9	N 52^0 32’ 26.0” N 52^0 32’ 26.0”	1	5.4	637	105 (1.0)	15
		10	4.2	202		
		50	4.6	75		
10	N 52^0 38’ 35.1” N 52^0 38’ 35.1”	1	5.5	426	203 (2.8)	13
		10	13.3	152		
		50	6.8	884		
11	N 52^0 42’ 48.4” N 52^0 42’ 48.4”	1	11.2	609	162 (2.2)	12
		10	10.6	300		
		50	1.6	131		

a) Mercury concentration from Boszke et al. [12]

b) LOI – Loss On Ignition

Table 2. Median, mean and standard deviation mercury, LOI and normalized concentrations and enrichment factors in floodplain soils and sediments of the Warta river.

			Floodplain soil			Sediment[a]	Enrichment (floodplain/sediment)		
			1 m	10 m	50 m		1 m	10 m	50 m
All samples N = 11	Hg (ng g^{-1} d.w.)	Median	228	185	190	121	1.6	1.9	1.6
		Mean	289	233	253	136	2.4	1.9	2.0
		S.D.	197	185	228	74	1.7	1.0	1.3
	LOI (µg g^{-1})	Median	40	67	68	18	1.5	4.3	3.0
		Mean	42	76	80	22	2.3	3.9	4.7
		S.D.	29	42	72	10	1.8	2.3	5.7
	Hg (µg g^{-1} LOI)	Median	7.7	3.3	2.7	7.2	1.1	0.4	0.7
		Mean	8.0	3.6	4.1	7.0	1.4	0.6	0.7
		S.D.	4.8	2.0	3.6	4.4	0.8	0.4	0.5
Above Poznań n = 3	Hg (ng g^{-1} d.w.)	Median	214	127	291	138	1.4	0.9	2.2
		Mean	171	163	277	135	1.2	1.4	2.2
		S.D.	86	106	36	31	0.5	1.2	0.7
	LOI (µg g^{-1})	Median	40	102	96	32	1.2	3.3	3.0
		Mean	38	81	150	30	1.8	3.9	8.6
		S.D.	11	37	116	15	1.6	3.4	10.9
	Hg (µg g^{-1} LOI)	Median	5.8	2.8	2.5	5.2	1.1	0.4	0.5
		Mean	5.1	2.3	2.6	5.3	1.3	0.5	0.7
		S.D.	3.4	1.3	1.6	2.3	1.2	0.5	0.6
Area of Poznań n = 5	Hg (ng g^{-1} d.w.)	Median	140	185	183	80	1.5	2.0	1.6
		Mean	198	284	173	124	2.1	2.4	1.9
		S.D.	111	265	96	108	1.3	0.9	1.4
	LOI (µg g^{-1})	Median	19	41	66	17	1.1	2.0	3.2
		Mean	25	61	59	19	1.5	3.5	3.5
		S.D.	18	46	24	6	1.1	2.7	2.0
	Hg (µg g^{-1} LOI)	Median	7.7	4.0	2.7	3.5	1.2	0.9	0.7
		Mean	9.5	4.7	2.9	7.2	1.6	0.9	0.6
		S.D.	6.1	2.1	0.7	6.3	0.8	0.4	0.3
Below Poznań n = 3	Hg (ng g^{-1} d.w.)	Median	609	202	131	162	3.8	1.9	0.8
		Mean	557	218	363	157	4.0	1.5	2.0
		S.D.	115	75	452	49	2.0	0.7	2.1
	LOI (µg g^{-1})	Median	55	106	46	22	5.0	4.7	2.4
		Mean	74	93	43	20	4.2	4.6	2.6
		S.D.	33	47	2.6	9	2.0	0.2	2.1
	Hg (µg g^{-1} LOI)	Median	7.8	2.8	8.5	7.3	1.1	0.4	1.2
		Mean	8.3	2.9	7.7	8.4	1.0	0.3	1.0
		S.D.	3.2	1.8	5.7	2.1	0.2	0.2	0.8

[a]) from Boszke et al. [12]

(127 ng g^{-1}). From among the floodplain soil samples collected at 50 meters from the riverside, the lowest mercury concentration was found below the city (131 ng g^{-1}), higher in the Poznań city area (183 ng g^{-1}) and the highest above the city (291 ng g^{-1}).

The median content of organic matter was 5.2% (range 1.2–28.4). When the mercury concentration was normalized to organic matter content, median mercury concentration was 4.0 µg g^{-1} (range 0.8–19.8). The Kruskal-Wallis test (nonparametric ANOVA) did not show statistically significant differences in the normalized mercury concentrations between the soil samples collected above, below and in the area of Poznań ($H(2.33) = 1.455$; $p = 0.249$). Relatively higher normalized mercury concentration was in the soil samples below the city (5.4 µg g^{-1}, range 1.1–13.0) and in the city (4.0 µg g^{-1}, range 1.9–19.8), lower in the samples collected above the city (2.8 µg g^{-1}, range 0.8–8.1). The Kruskal-Wallis test showed the same differences in the distribution of the normalised mercury concentrations in the soil samples collected at different distances from the riverside ($H(2.33) = 8.665$; $p = 0.013$). In the floodplain soil samples collected at 1 meter from the riverside the normalized mercury concentration was found higher (8.7 µg g^{-1}) than in the samples collected at 10 and at 50 meters from the riverside: 3.3 and 4.1 µg Hg g^{-1} organic matter, respectively.

Discussion

Median mercury concentration in the samples of the floodplain soils collected below Poznań was higher than that in the samples collected above and in the area of the city, so it seems that the Poznań agglomeration is a source of mercury to the Warta river. It becomes more evident after analyzing the distribution of mercury in the soil samples collected at different distances from the riverside.

In the samples of floodplain soils collected at 1 meter from the riverside the median mercury concentration was abound 3-4 times higher below the city than above and in area of Poznań. It may be explained by the influence of the Warta River water on washing out mercury from the Poznań area and accumulating it below the city. For samples collected at 1 meter from riverside statistically significant Spearman nonparametric correlation (no Gaussian assumptions) between the mercury concentration in the floodplain soil and organic matter content was found ($r = 0.63$; $p = 0.044$). It seems that organic matter is the main factor bounding mercury in the soil samples collected at these distances. From among the samples of floodplain soils collected at 10 meters from the riverside, the higher mercury concentration was found below and in the area of city, but relatively lower above the city. In soils collected at this distance from riverside correlation between mercury concentration and organic matter content was not statistically significant (Spearman correlation: $r = 0.38$; $p = 0.248$). It seems that organic matter is not the only factor causing enrichment in mercury of the floodplain soil samples collected at this distance from the riverside. From among the floodplain soil samples collected at 50 meters from the riverside, the lowest mercury concentration was noted in those below the city, higher in those from the city area and the highest in those above the city. Higher mercury concentrations in the soil samples collected at this distance in an area above of the city may be caused by the inflow of mercury from agriculture. The catchment area contains mainly agricultural land, so mercury can also be released from soil on which cultivations have been treated with pesticides or herbicides containing this element. For samples collected at 50 meters from riverside, statistically significant Spearman nonparametric correlation between the mercury concentration in the sediments and the floodplain soil was found ($r = 0.72$; $p = 0.016$).

Floodplain soils of the Warta river have much higher total mercury content (median 198 ng g^{-1}, range 54–884) than the corresponding river sediments (median 121 ng g^{-1}, range 47–340, [12]). Correlations between mercury concentration in the Warta river sediments and mercury concentrations in floodplain soils collected at different distances from riverside were not statistically significant ($p > 0.05$). Floodplain soils of the Warta river have higher content of organic matter than the river sediments but in many cases a lower ratio of mercury concentration to the organic matter content (Tables 1 and 2). Lower ratio of mercury concentration to organic matter in the floodplain soils than in the sediments may be explained by biodilution. Deposited contaminated organic matter in floodplain soil is mixed with freshly produced organic matter less contaminated with mercury. Enrichment factors as a ratio of mercury concentration in the soil to that in the sediment were higher below the city (up to 3.8), lower above the city (up to 2.2) and in area of the Poznań city (up to 2.0). When mercury concentrations were normalized to organic matter content, the enrichment factors were generally higher for the soil samples collected at 1 meter from the riverside (Table 2). A similar situation when the floodplain soils had higher mercury concentrations than the river sediments was observed by other authors [13]. For example, the mercury concentrations in the floodplain soils of Elbe river (3560 ± 3050 ng g^{-1}) was higher than in the sediments of this river (340 ± 300 ng g^{-1}) [13].

In general, the values of total mercury concentration obtained in this study are relatively higher than the total mercury established in the urban soil of Poznań [14] and in the other studies where uncontaminated soils were studied [15, 16]. For example, mercury concentration in the urban soil from Poznań was 146 ± 130 ng g^{-1} (17–746) [14]. Relatively higher average concentrations of mercury were found in the soil samples taken from lawns and meadows 183±184 ng g^{-1} d.w. (range 31–749), lower in the soil collected from the urban forests 151±129 ng g^{-1} d.w. (range 17–469) and in the soil samples of no current agricultural use 136±85 ng g^{-1} d.w. (range 50–378). The lowest average mercury concentration was determined in the samples of soils of current agricultural use 84±52 ng g^{-1} d.w. (range 31–207) [14]. The average concentration of mercury in the soil samples from farmlands under direct effect of anthropopressure in Poland was 130 ng g^{-1} dry mass (range 2.3–450) [16]. In the soil samples from typical villages near industrial centres in Poland much higher mercury concentrations were determined [17]. In the soil samples from these areas the mercury concentrations was between 150 and 3700 ng g^{-1} [17]. The average mercury concentration in different soil samples from agricultural areas in Poland was 61 ng g^{-1} (range 7.3–250) [16]. The mean mercury concentration reported for European agricultural soils is very close to 100 ng g^{-1} d.w., the results vary in the range 70–120 ng g^{-1} [15]. European forest soils contain much less mercury than agricultural soils, usually 50–150 ng g^{-1} [15]. In Poland, the forest soils contained, on average, 95 ng Hg g^{-1} (range 38–250) [16].

Conclusion

The study results show that the distribution of the total mercury in the samples of floodplain soils of collected from the middle part of the Warta river is relatively uniform but the influence of the Poznań agglomeration on this distribution is observed. The concentration of total mercury in the floodplain soils are relatively low and the there is a relatively low risk from mercury contained in floodplain soils in the study area on the cultivation safety of vegetables and fruit. Although the concentration of total mercury in the floodplain soils is relatively low, but higher in the river bottom sediments, it is possible that heavy flooding would cause dilution and removal of a significant portion of mercury that can enter into the aquatic system of the Warta River.

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