Application of neural-based modeling in an assessment of pollution with mercury in the middle part of the Warta River

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Abstract The level of pollution with various mercury species (organomercury, water- and acid-soluble mercury, mercury bound to humic matter and to sulphides) of the floodplain soils and sediments from middle part of the Warta River has been assessed using self-organizing maps (SOM). Chemometric evaluation allowed identification of moderately (median 173–187 ng g^{-1}, range 54–375 ng g^{-1} in soil and 130 ng g^{-1}, range 47–310 ng g^{-1} in sediment) and heavily polluted samples (662 ng g^{-1}, range 426–884 ng g^{-1}). Heavily polluted were located mainly below and in the area of the Poznań city. Statistical comparison of mercury species distribution in floodplain soils of the Warta River shows different patterns for moderately and heavily polluted samples. In heavily polluted soils the contribution of mobile mercury (sum of organomercury species, water- and acid soluble species) is lower (4.2%) than in moderately polluted soils (6.1%). Higher contribution of mobile mercury was observed in sediments of the Warta River (12%). In case of moderately polluted samples, statistical differences in the contribution of mercury species are relatively low and thus the environmental risk from mercury deposited in aquatic system of the Warta River is relatively low. However, higher water levels and heavy floods may incite remobilisation of some organomercuries (2.2–2.9 ng g^{-1} in soil and 10 ng g^{-1} in sediment) and acid-soluble species of mercury (2.6–2.9 ng g^{-1} in soil and 0.5 ng g^{-1} in sediment).

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Introduction

Regarding mercury contamination, sediments and soils are critical environment compartments because they are important sites in which inorganic mercury is methylated to the most toxic methylmercury. Depending on the redox conditions in the environment, mercury occurs in three different valence states: Hg(0), Hg(I) and Hg(II). Besides the oxidation potential, also pH, Cl^- and organic matter concentration are important factors influencing the speciation of mercury in soils and sediments (Stein et al. 1996; Ullrich

et al. 2001; Ravichandran 2004). The presence of sulphides is also important due the formation of highly insoluble HgS. In addition to chemical reactions, transformations may also be mediated by microbial activity such as methylation (Stein et al. 1996; Morel et al. 1998; Ullrich et al. 2001). The knowledge of mercury speciation and reactions is important in order to explain the mobility and bioavailability. Mentioned aspect seems to be important in determining the risk of exposition to mercury and in selecting appropriate remediation technologies.

In order to determine various species of mercury in the sediment samples, a sequential extraction procedure was proposed (Boszke et al. 2006, 2007, 2008; Boszke and Kowalski 2007a,b, 2008). This procedure permits determination of organomercury species, water-soluble mercury, acid-soluble mercury, mercury bound to humic matter and mercury bound to sulphides. The organomercury species such as methylmercury are at least an order of magnitude more mobile than inorganic mercury species, and thus are more toxic and posses higher ability to be bioaccumulated. These extractable organomercury species and extractable inorganic species are mainly responsible for the potential toxicity of mercury in the sediments and soils (Stein et al. 1996; Ullrich et al. 2001). The water-soluble mercury includes mercury species present in pore water and the mercury species extractable by water that may be easily transported by natural processes and serve as substrates for mercury methylation process (Stein et al. 1996; Ullrich et al. 2001). In the water phase of soils and sediments, mercury is not usually present in the form of ionic mercury but rather bound to organic matter or as suspended mineral particles (Wallschläger et al. 1996, 1998; Renneberg and Dudas 2001; Biester et al. 2002). The acid-soluble fraction includes strongly bound mercury species extractable by solutions of acids and includes the mercury species strongly bound to iron and manganese hydroxides and carbonates (Ching and Hongxiao 1985; Lechler et al. 1997). It can also include the species bound to organic matter and adsorbed on minerals' surface (Bloom et al. 2003; Shi et al. 2005). The fraction of mercury species bound to humic matter includes Hg(II) complexes with humic matter. Organic matter is an important component of sediments and soils. It is also, to a significant degree, responsible for binding metals. Binding of mercury in organic matter is

mainly realized by the reduced sulphur species as well as by oxygen and nitrogen atoms but their significance is lower (Hesterberg et al. 2001). The fraction of mercury bound to sulphides is the most biounavailable and thus, the least toxic. Sulphide activity may be the main factor influencing the availability of Hg(II) and the concentration of methylmercury in sediments and soils. If conditions become aerobic due to a decrease in the organic load or seasonal turnover, sulphide can be oxidized to sulphate, releasing mercury in the ionic form Hg(II), which is available for methylation (Stein et al. 1996; Ullrich et al. 2001).

The aim of presented study is to assess a level of contamination with mercury of sediment and floodplain soil samples of the Warta River using neural network-based modeling. Two major hypothesis have been verified: (1) Poznań agglomeration may play a significant role as a substantial source of mercury introduced to the river ecosystem, (2) relation between floods and mercury accumulation and/or mobility in the soil exists and can be discussed in the aspect of safety of vegetables and fruits cultivation in the area of interest.

Characterisation of the study area

The Warta River, located in western-central Poland, is the principal tributary of the Oder River. With a length of approximately 808 km it is the third longest river in Poland after the Vistula and the Oder. Major tributaries of the Warta include the Noteć (388.4 km long), Prosna (216.8 km), Drawa (185.9 km), Obra (163.8 km), Gwda (145.1 km), Ner (125.9 km), and Wełna (117.8 km) rivers. The Warta basin, equal to 55,193 km^2 covers approximately one-sixth of Poland area. The basin is divisible into three major subbasins: the Upper Warta sub-basin (including the Prosna River watershed) which covers about 20,825.6 km^2; the Middle and Lower Warta sub-basin (to the river mouth at the confluence with the Oder) which covers about 17,033.5 km^2; and the Upper and Lower Noteć sub-basin which covers 17,333.9 km^2.

Land use in the basin is 70% agriculture and forestry, 30% urban and industrial. The basin's population is about 6,770,000 over 34% of which live in cities. By far the largest city in the region is Poznań, the capital city of Wielkopolska District, with

a population of approximately 600,000 is the fourth biggest industrial centre in Poland with domination of food, mechanical, electrotechnical, pharmaceutical and chemical industry (Statistical Yearbook of Poznań City 2003).

Materials and methods

Sampling and analytical procedures

Details of sampling, preparation of reagents and vessels prior to analyses, sequential extraction procedure and determination of mercury species are presented in Boszke et al. (2006, 2007, 2008) and Boszke and Kowalski (2007a, b, 2008). Samples of sediments from the Warta River labelled as: W1–W11 and those from the floodplain soil of the Warta River labelled as: WS1–WS11 were collected in 2004 (Fig. 1). In each site three floodplain soil samples were collected, at a distance of about 1, 10 and 50 meters from the riverside (WSX-1, WSX-10 and WSX-50, where X represents the number of the sampling site and ranges between 1 and 11).

In order to determine various species of mercury in the sediment samples, a sequential extraction procedure was applied which permits determination of organomercury species, water-soluble mercury, acid soluble mercury, mercury bound to humic matter and mercury bound to sulphides. Mercury was determined by the cold-vapour atomic fluorescence spectroscopy (CV-AFS) on Millenium Merlin (PS Analytical,

Fig. 1 Sampling sites located at the Warta River's basin area
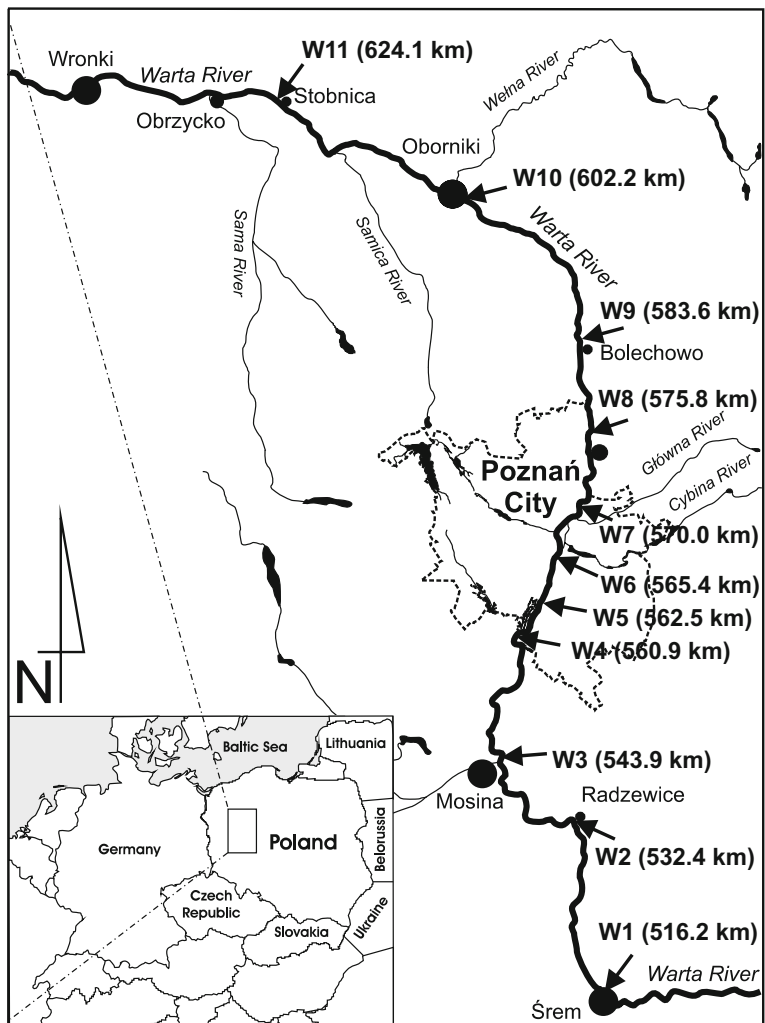
England). The limit of quantification (LOQ) of the method reached 0.8 ng Hg dm^{-3} and was calculated according to the formulas presented by Konieczka et al. (2004). For comparison with the results of sequential extraction, one certified sample LGC 6137 was used. The sum of mercury concentrations obtained from particular fractions in the certified sample studied was 373 ng g^{-1} dry mass ($n=6$), while the corresponding sum obtained for the certified material was 340 ng g^{-1} dry mass. The method of sequential extraction is thus characterized by a recovery of about 110% (range 108–112%) and by the reproducibility (Relative Standard Deviation) from 1% to 7% (Boszke et al. 2007). Highly significant correlation between the bulk mercury concentration and the total mercury understood as a sum of mercury concentrations in particular fractions in sediments and soils of the Warta River was observed (Fig. 2).

Statistical methods and software

Self-organizing map (SOM) algorithm has been proposed by Kohonen (1995) and is a neural-network model that implements a characteristic non-linear projection from the high-dimensional space of sensory or other input signals onto a low-dimensional array of neurons (Kohonen et al. 1996). The term "self-organizing" refers to the ability to acquire and organize information without being given the associated-dependent output values for the input pattern (Mukherjee 1997). SOM shares with the conventional ordination methods the basic idea of displaying a high-dimensional signal manifold onto a much lower dimensional network in an orderly fashion (usually a two dimensional space). A SOM consists of neurons organized on a regular low-dimensional grid. The number of neurons may vary from a few dozen up to several thousands. The neurons are connected to adjacent neurons by a neighbourhood relation, which determines the topology, or structure of the Kohonen map and thus similar objects (in our case sampling sites) should be mapped close together on the grid. During the test phase the algorithm constructs the nodes in SOM in order to represent the whole data set and their weights optimised at each iteration step. In each step, one sample vector x from the input data set is chosen randomly and the distances between it and all the weight vectors of the SOM are calculated using some distance measure. Thus, the optimal topology is
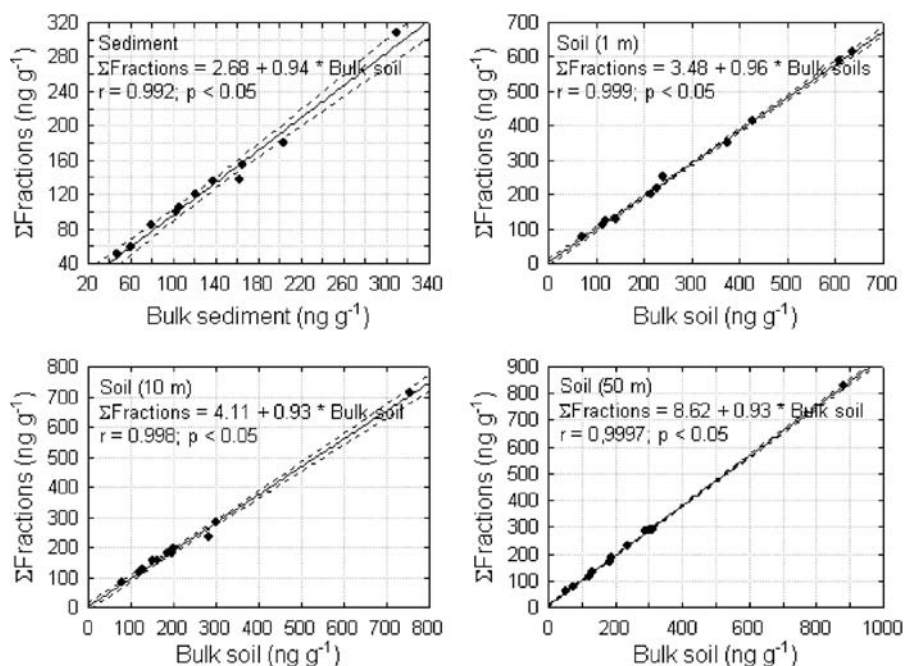

Fig. 2 Correlation between bulk mercury concentration and total mercury as a sum of mercury concentration in particular fraction in soils and sediments of the Warta River

expected. In our study the non-hierarchical K-means classification algorithm was applied. Different values of k (predefined number of clusters) were tested and the sum of squares for each run was calculated. Finally, the best classification with the lowest Davies–Bouldin index was chosen (Davies and Bouldin 1979). The network organises itself by adjusting the synaptic weights as the input patterns are introduced to it; hence, discovery of a new pattern is possible at any instant. Moreover, SOM is noise tolerant; this property is highly desirable when site-measured data are used. Interesting SOM applications have been reported in mainly three fields: exploratory data analysis or data mining, the identification and monitoring of complex process states, and pattern classification (Kohonen 1995).

A commercial statistics software package, Statistica 6.0 (StatSoft, Inc.) for MS Windows was used for chemometric testing such as Shapiro–Wilk's, Kruskal–Wallis's and U Mann–Whitney's and Matlab 6.5 (MathWorks, Inc.) for MS Windows was used to the self-organising mapping.

Results

Raw data on mercury species in sediments and floodplain soils of the Warta River are presented in Table 1. Sediment samples as well as floodplain soil samples were tested for homogeneity. In order to obtain more homogenous distribution, the result of fractionation of sediment sample labelled as W1 was excluded from statistical analysis. In the excluded sample the pattern of the percent contribution of mercury in the analyzed fractions was meaningfully different (Boszke et al. 2007). Results of mercury fractionation of floodplain soil samples were evaluated with neural network-based SOM technique and the results of self-organising mapping are presented in Fig. 3. The U-matrix shows the distances between neighbouring map units, and helps identify the cluster structure of the map: high values of the U-matrix indicate a cluster border; uniform areas of low values indicate the clusters (Ultsch and Siemon 1990), while each component plane shows the values of one variable in each map unit. In other words the U-matrix expresses semiquantitative information concerning to distribution of a complete set of variables for a complete set of the floodplain soil

samples, while separate component planes visualize the distribution of a particular variable for a complete set of the floodplain soil samples. This suggests, that an analysis of U-matrix connected with an analysis of component planes can be effectively applied for assessment of inter-variable and inter-site interdependences. The sample classification according to sampling sites was based on the K-nearest neighbour classification technique offered by SOM. Different values of k (predefined number of clusters) were tested and the sum of squares for each run was calculated. Finally, the best classification was found for two clusters with the lowest Davies–Bouldin index value (Fig. 4). Clustering pattern indicates the lack of homogeneity in the set of floodplain soil samples and suggests the existence of two subpopulations in the data set. Samples WS8–10, WS9–1, WS10–50, WS10–1, WS11–1 were classified as cluster I in SOM, while the others as cluster II. All the above-mentioned five samples were collected mainly below Poznań area. In case of these samples large mercury concentration was determined both in bulk soil and as a sum of fractions (Fig. 5). Because high mercury concentration was not observed at every distance from the riverside the cluster I samples were classified as "heavily polluted", while appropriate sampling locations were recognized as "site-specific" polluted locations. Samples classified as cluster II show high homogeneity and are referred to "moderately polluted". Results of the fractionation of mercury in sediment and floodplain soil samples taken from different sites together with basic descriptive statistics with and without "site-specific" polluted samples are presented in Table 1. Differences in the median mercury concentration and the median mercury contribution between the moderately and heavily polluted samples were tested statistically by applying of U Mann–Whitney's test (Table 2).

A comparison of the mercury mobility and bioavailability in the investigated sediments and floodplain soils of the Warta River as well as the contributions of mercury species in particular fractions were taken into consideration. To assess the normality of the data distribution the Shapiro–Wilk's (S–W) test was applied and results show abnormal distribution. The differences between the percent contributions of different bioavailable forms of mercury were assessed with the non-parametric Kruskal–Wallis's (K–W) test because majority of data

Fig. 3 SOM's for mercury concentration values for bulk floodplain soils, fractions as a sum of fraction for sampling sites divided as above, in the area and below Poznań agglomeration (each component plane shows the values of one variable in each map unit; both grey-tone pattern and grey-tone bar labeled as "d" delivers information regarding to species abundance calculated through SOM learning process)
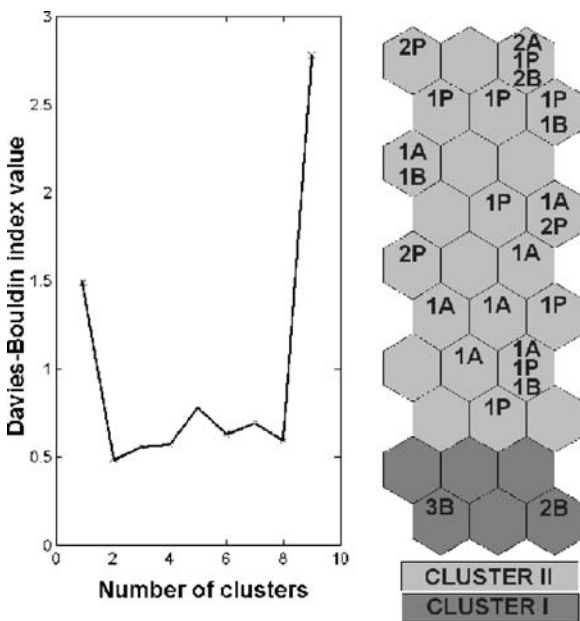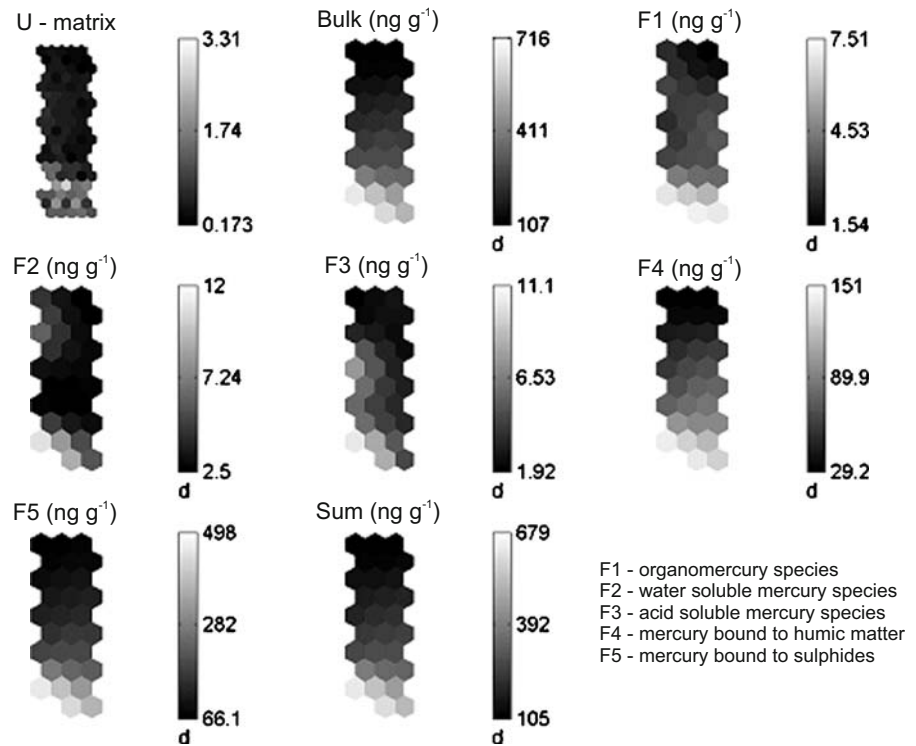

F1 - organomercury species
F2 - water soluble mercury species
F3 - acid soluble mercury species
F4 - mercury bound to humic matter
F5 - mercury bound to sulphides

Fig. 4 SOM clustering pattern according to the Davies–Bouldin index minimum value and classification of sampling locations with division to samples collected chemical above (*A*), in area (*P*) and below (*B*) of the Poznań city

were abnormally distributed. K–W's test does not indicate unequivocally between which pair of sampling location statistically significant differences in percentage contribution (expressed by median values) of various bioavailable form of mercury appears. This is why, the U Mann–Whitney's test was applied simultaneously. Table 3 gives the results of Kruskal–Wallis and U Mann–Whitney tests for mercury concentrations as well as for percent contributions of mercury in sediments and floodplain soils of the Warta River. Statistical differences appears only for F1 and F3 and this is why on Fig. 6 mean, minimum and maximum concentration and contribution of organomercury and acid-soluble species, only for F1 and F3, are presented.

Discussion

Total mercury in floodplain soils and sediments of the Warta River

In case of moderately polluted sediment and floodplain soils of the Warta River, the concentration of total mercury is relatively uniform and does not show

Fig. 5 Mercury concentrations in heavily (*I*) and moderately polluted (*II*) samples of floodplain soils of the Warta River (bars present mean value while *whiskers* present standard deviation)
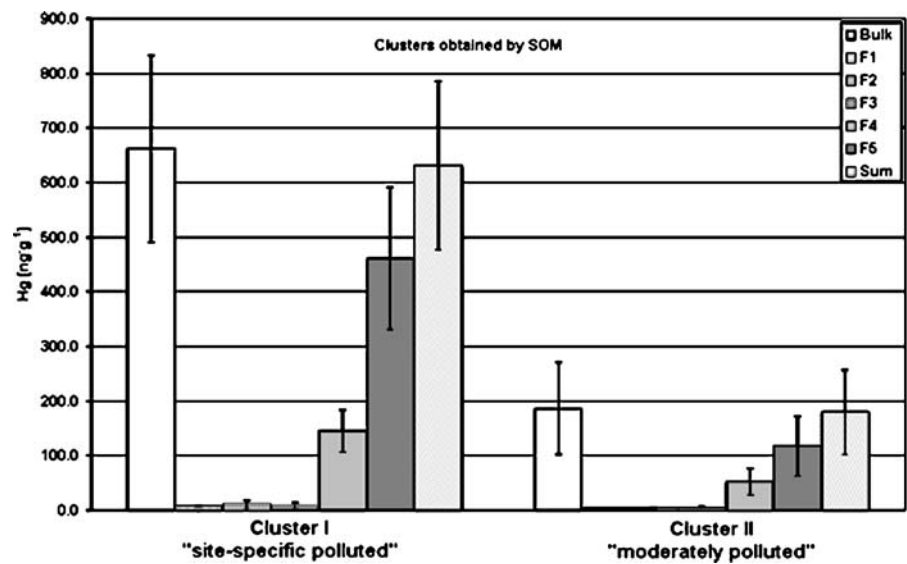
statistically significant differences (*U* M–W test; $p > 0.05$) between the sediment (median 130 ng g^{-1}, range 47–310 ng g^{-1}) and floodplain soil samples taken at different distances from riverbed (173–187 ng g^{-1}, range 54–375 ng g^{-1}; Table 1). In case of "site-specific" polluted floodplain soils of the Warta River the mercury concentration was 662 ng g^{-1}, range 426–884 ng g^{-1} (Table 2, Fig. 5). These samples were taken below the city area, and they show that Poznań agglomeration is substantial source of mercury in the Warta River system. The total mercury concentration for heavily polluted soils significantly exceed the level of 200 ng g^{-1}, which is assumed to be the upper limit of global geochemical background (Fergusson 1990; Kabata-Pendias and Pendias 1999). The value of total mercury concentration in moderately polluted floodplain soils of the Poznań city is comparable to the total mercury determined in the urban soil of the Poznań city (Boszke and Kowalski 2006) and much higher in the uncontaminated soils and sediments studied by other authors (Falandysz et al. 1996a, b).

The highest contribution to the emission of anthropogenic sources in Poznań comes from the products of coal combustion, municipal large coal fired plants and many local coal-fired sources located in Poznań region. This conclusion is indirectly supported by the temporary concentration of mercury in wet deposition and the spatial distribution of mercury in the soil. Average mercury concentration in the samples of wet precipitation was 38±62 ng

dm^{-3} and the values ranged from 0.9 to 340 ng g^{-3} (Kowalski et al. 2005). Higher mercury concentration was determined in samples of snowfall 140± 145 (range 31–340), than in those of rainfall 26±30 (range 0.9–116). The mercury concentration in the urban soil from the Poznań city was 146±130 ng g^{-1} dry weight (range 17–746 ng g^{-1}) and the soil samples from the city centre contained mercury at higher concentrations (Boszke and Kowalski 2006). In contrast to the above, the distribution of mercury in the samples of sediments (97±70 ng g^{-1} dry weight, range 29–283 ng g^{-1}; Boszke and Kowalski 2006), ground water 1.3±0.7 ng dm^{-3} (range 0.8–4.1 ng dm^{-3}; Kowalski et al. 2007), and surface water (20± 8 ng dm^{-3}, range 8–40 ng dm^{-3}; Kowalski et al. 2007) collected from various sites in the Poznań were relatively uniform.

Contribution of mercury species in moderately polluted sediments and floodplain soils of the Warta River

For the moderately polluted floodplain soils two categories of mercury species content pattern can be distinguished. The first includes these fractions of mercury species for which the differences in the concentrations and contributions in the total concentrations between the bottom sediments and floodplain soil are statistically significant ($p < 0.05$), i.e. organo-mercury species and acid-soluble species (Table 3). In

Table 1 Descriptive statistics for mercury concentration as well as percentage contribution in sediments and floodplain soils of the Warta River with excluded sample identified as outlier (In parenthesis raw data including all samples are presented; Boszke et al. 2007; Boszke and Kowalski 2008)

Location	Contribution (%)	N	Mean	Median	Min	Max	SD
Warta sediments							
F1		10[a]	12 (17)	9.0 (9.3)	0.03 (0.03)	32 (65)	9.4 (18)
F2			2.1 (2.1)	2.1 (2.0)	1.1 (1.1)	3.8 (3.8)	0.9 (0.9)
F3			0.4 (0.4)	0.4 (0.4)	0.2 (0.2)	0.7 (0.7)	0.2 (0.9)
F4			24 (23)	25 (24)	4.1 (4.1)	36 (36)	9.1 (9.2)
F5			61 (58)	60 (60)	44 (20)	81 (81)	13 (18)
Σ Fractions	(ng g^{-1})		134 (130)	128 (121)	51 (51)	307 (307)	74 (71)
Bulk sediment	(ng g^{-1})		139 (136)	130 (121)	47 (47)	310 (310)	78 (74)
Warta floodplain soils (1 m from river side)							
F1		8[b]	1.5 (1.5)	1.5 (1.4)	0.8 (0.8)	2.2 (2.2)	0.5 (0.5)
F2			2.1 (2.0)	2.1 (2.0)	0.8 (0.7)	3.5 (3.5)	1.0 (1.0)
F3			1.7 (1.6)	1.3 (1.2)	0.8 (0.5)	3.1 (3.1)	0.9 (0.9)
F4			30 (28)	28 (28)	21 (17)	42 (42)	6.7 (7.5)
F5			65 (67)	66 (66)	53 (53)	76 (77)	7.0 (7.8)
Σ Fractions	(ng g^{-1})		183 (280)	166 (129)	77 (77)	352 (616)	90 (189)
Bulk soil	(ng g^{-1})		188 (289)	177 (228)	72 (72)	375 (637)	97 (197)
Warta floodplain soils (10 m from river side)							
F1		10[c]	1.7 (1.7)	1.6 (1.5)	0.8 (0.8)	3.5 (3.5)	0.8 (0.8)
F2			2.4 (2.4)	1.5 (1.7)	0.3 (0.3)	6.0 (6.0)	2.0 (1.9)
F3			2.8 (2.8)	2.0 (2.2)	0.8 (0.8)	10 (10)	2.7 (2.6)
F4			28 (28)	28 (27)	21 (21)	35 (35)	4.6 (4.5)
F5			65 (65)	67 (67)	54 (54)	74 (74)	6.5 (6.3)
Σ Fractions	(ng g^{-1})		171 (221)	168 (179)	83 (83)	285 (711)	59 (172)
Bulk soil	(ng g^{-1})		181 (233)	173 (185)	80 (80)	300 (754)	69 (185)
Warta floodplain soils (50 m from river side)							
F1		10[d]	1.8 (1.7)	1.3 (1.3)	1.0 (0.9)	4.8 (4.8)	1.2 (1.1)
F2			2.3 (2.2)	1.3 (1.1)	0.5 (0.5)	7.8 (7.8)	2.3 (2.3)
F3			1.8 (1.7)	1.6 (1.6)	0.9 (5.0)	5.0 (5.0)	1.2 (1.2)
F4			30 (29)	32 (31)	21 (21)	35 (35)	5.3 (5.5)
F5			64 (65)	63 (64)	52 (52)	75 (75)	6.3 (6.8)
Σ Fractions	(ng g^{-1})		185 (224)	181 (189)	58 (58)	293 (829)	89 (212)
Bulk soil	(ng g^{-1})		190 (253)	187 (190)	54 (54)	313 (884)	94 (228)

[a] Without sample from site W1

[b] without samples from site WS9–1, WS10–1 and WS11–1

[c] Without sample from site WS8–10

[d] without sample from site WS10–50

this case the contribution of organomercury species was almost six times higher in the sediments than in the floodplain soil samples. In the contrary to the organomercury species, the contribution of acid-soluble mercury was three to three and a half times lower in the sediments than in the floodplain soil of the Warta River. Taking into consideration the total concentration of mercury in the fractions of organomercury and acid-soluble mercury the enrichment factors are 0.2–0.3 and 5.2–5.8, respectively, which means that elevated water level may affect the remobilisation of organomercury compounds in the sediments and their possible deposition in soils. It may cause a relative risk of toxic effect on vegetables, fruits and humans, but on the other hand, it may lead to reduction of the amount of methylmercury species in the aquatic biota of the Warta River. It is possible that some part of acid-soluble mercury may be

Table 2 Result of U Mann–Whitney's test (p values) for sub-divided data set on moderately and heavily polluted soils

	Concentration (ng g^{-1})		U M–W Test	Contribution (%)		U M–W Test
	Moderately polluted	Heavily polluted	P	Moderately polluted	Heavily polluted	p
F1	2.8	7.6	0.0005***	1.7	1.3	0.248
F2	3.2	9.7	0.003**	2.3	1.6	0.393
F3	3.4	8.7	0.031*	2.1	1.3	0.228
F4	53	145	0.0005***	29	24	0.050*
F5	118	461	0.0004***	65	72	0.024*
Σ Fractions	180	632	0.0004***			
Bulk	186	662	0.0004***			

*$p<0.05$

**$p<0.01$

***$p<0.001$

remobilised from the floodplain soil and be accumulated in aquatic system of the Warta River at higher level of water or upon heavy floods.

The second group of mercury species comprises those for which percent contribution in sediments and soils does not show statistically significant differences (K–W; p>0.05), i.e. water-soluble mercury, mercury bound to humic matter and mercury bound to sulphides (Table 3). Among them, the mercury bound to sulphides in the sediments occurred in the highest contribution: 60% (range 44–81%) in the sediments and 64–67% (range 52–76%) in the floodplain soils.

The sum of the contributions of mercury bound to humic matter and mercury bound to sulphides may be estimated as 88% (range 66–96%) in the sediments and 94–96% (range 86–97%) in the floodplain soils. It shows that in both sediments and floodplain soils of the Warta River, the major contribution of mercury is relatively immobile and biounavailable. For the total concentration of mercury bound to sulphides, mercury bound to humic matter, water soluble mercury, the enrichment factors are around: 1.2–1.3, 1.5–1.8, 0.9–1.6, respectively. The risk of increased mobility and the following migration of the fractions of mercury

Table 3 Results of Kruskall–Wallis, U Mann–Whitney tests and correlation (values of Spearman r in parentheses) for mercury concentrations as well as for percentage contribution in sediments and floodplain soils of the Warta River

	Sediment–soils	Sediment–soil (1 m)		Sediment–soil (10 m)		Sediments–soil (50 m)	
	K–W test	U M–W test	Correlation	U M–W test	Correlation	U M–W test	Correlation
F1 (ng g^{-1})	0.004**	0.008**	0.383 (0.39)	0.003**	0.460 (0.28)	0.002**	0.865 (−0.07)
(%)	0.003**	0.004**	0.215 (0.54)	0.002**	0.013 (0.78)*	0.002**	0.516 (0.25)
F2 (ng g^{-1})	0.361	0.051	0.432 (0.36)	0.226	0.125 (0.55)	0.496	0.865 (0.07)
(%)	0.845	0.790	0.294 (0.46)	0.821	0.154 (0.52)	0.326	0.139 (0.53)
F3 (ng g^{-1})	0.0002***	0.0007***	0.939 (−0.04)	0.0003***	0.188 (0.48)	0.0005***	0.077 (0.62)
(%)	0.0001***	0.0004***	0.760 (−0.14)	0.0002***	0.966 (−0.02)	0.0002***	0.668 (−0.17)
F4 (ng g^{-1})	0.173	0.092	0.432 (0.36)	0.096	0.460 (−0.28)	0.070	0.139 (0.53)
(%)	0.369	0.248	0.432 (−0.36)	0.326	0.576 (0.22)	0.096	0.088 (0.60)
F5 (ng g^{-1})	0.423	0.286	0.645 (0.21)	0.174	0.187 (0.48)	0.131	0.356 (0.35)
(%)	0.864	0.534	0.535 (0.29)	0.545	0.139 (0.53)	0.496	0.042 (0.68)*
Σ Fractions (ng g^{-1})	0.446	0.248	0.337 (0.43	0.112	0.732 (−0.13)	0.257	0.332 (0.37)
Bulk (ng g^{-1})	0.503	0.230	0.337 (0.43)	0.212	0.932 (−0.03)	0.226	0.332 (0.37)

* $p<0.05$; **$p<0.01$;*** $p<0.001$

Fig. 6 The values of concentration and contribution of organomercury and acid-soluble species in sediments and floodplain soils collected at different distances from riverbed
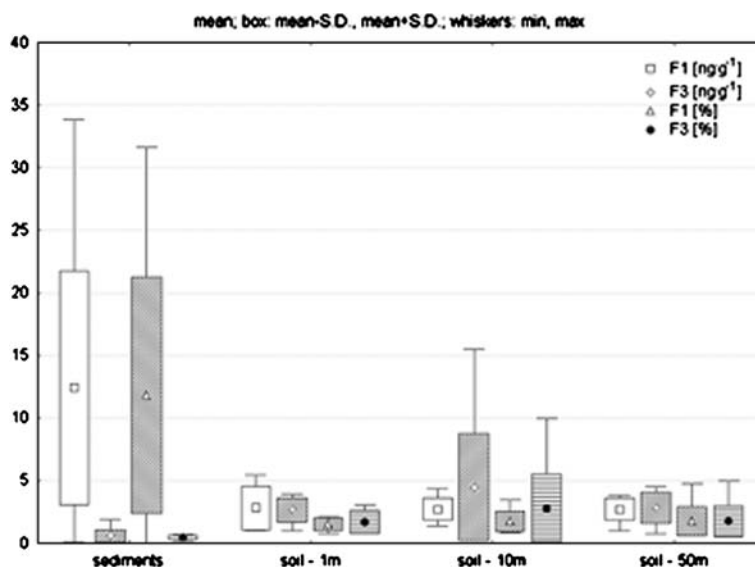
species bound to sulphides, bound to humic matter and water-soluble mercury as a consequence of elevated water levels or flooding is relatively low.

The impact of the Poznań city on the distribution of mercury species in heavily polluted sediments and floodplain soils of the Warta River

Table 2 presents results of statistical analysis of the moderately and heavily polluted floodplain soil samples from the Warta River. Heavily polluted samples have statistically significantly ($p < 0.05$) higher mercury concentration in all fractions. Statistically significant differences in the contribution of mercury species between moderately and heavily polluted soils appear only for mercury bound to humic matter and mercury bound to sulphides (Table 2). However, the sum of contributions of the most mobile mercury species, i.e. organomercury species, water- and acid-soluble species, is higher in moderately polluted samples (6.1%) than in heavily polluted samples (4.2%).

For relatively low mobile species, as mercury bound to organic matter and mercury bound to sulphides, the sum of contributions is comparable both for moderately and heavily polluted samples: 94% and 96%, respectively. In case of heavily polluted samples the contribution of mercury bound to sulphides is higher, while in case of mercury bound

to humic matter lower than in the moderately polluted samples (Table 2). As was mentioned above only five from thirty three samples collected were heavily polluted. However they were collected below and in an area of city, which indicates a substantial impact of the city on distribution of mercury in sediments and soils. When only moderately polluted samples are analysed, the conclusions are less informative. In this case, relatively low impact of the Poznań city on the distribution of total mercury concentration and mercury species in floodplain soil in the investigated area was observed. The concentrations of mercury species in floodplain soil samples collected above, in the area of the city and below the city are relatively uniform (K–W test; $p > 0.05$). Higher differences are observed only for contribution of immobile mercury species, i.e. the sum of contributions of mercury bound to humic matter and mercury bound to sulphides (Table 4). Floodplain soil samples collected from the area of Poznań are characterised by higher contribution of mercury bound to humic matter (30%) than in case of samples collected below the city (U M–W test; $p < 0.05$; 21%). There were no differences between the soil samples collected above and in the area of the city discovered. In the contrary to the mercury bound to humic matter, the contribution of the mercury bound to sulphides was lower in the soil samples from the Poznań city (64%) than in the samples collected below the city (69%).

Table 4 Results of Kruskall −Wallis' and U Mann–Whitney's tests for mercury concentrations as well as for percentage contribution in sediments and floodplain soils of the Warta River

	K–W Test	U M–W Test		
		City area – Above of city	City area – Below of city	Above of city – Below of city
F1 (ng g^{-1})	0.351	0.900	0.195	0.181
(%)	0.218	0.257	0.116	0.463
F2 (ng g^{-1})	0.989	0.900	0.781	0.947
(%)	0.566	0.284	0.926	0.549
F3 (ng g^{-1})	0.844	0.614	0.711	0.739
(%)	0.837	0.614	0.643	0.947
F4 (ng g^{-1})	0.351	0.659	0.165	0.257
(%)	0.019*	0.571	0.003**	0.072
F5 (ng g^{-1})	0.792	0.571	0.610	0.739
(%)	0.021*	0.284	0.005**	0.096
Σ Fractions (ng g^{-1})	0.737	0.450	0.643	0.947
Bulk (ng g^{-1})	0.267	0.131	0.355	0.549

*$p<0.05$
**$p<0.01$
***$p<0.001$

Comparison of the mercury content in the sediment samples of the Warta River system and other sediments and soils

The contribution of mercury in particular fractions can be only semiquantitatively compared with the analogous data reported by other authors because of the slightly differences in the methods of fractionation. Statistical assessment of differences in percent contribution of mercury between samples of different types, using the same analytical scheme, both uncontaminated and highly polluted, was accomplished by various chemometric techniques in previous works (Boszke and Astel 2007; Boszke et al. 2008). However, in the present study not the percent contributions of particular fractions but those of the mobile and immobile contributions of the fractions were analysed.

As was mentioned above, contribution of mobile and immobile mercury species in moderately and highly polluted samples of the floodplain soil of the Poznań city area, shows different pattern. Higher contribution of mobile mercury was observed in moderately (6.1%) than heavily (4.2%) polluted samples. These observations were supported by results of other studies where similar patter was observed. In relatively uncontaminated floodplain soils of the Vistula River, the contribution of mobile mercury was 10% (Boszke and Kowalski 2008). In case of highly polluted soils, the contribution

of mobile mercury was only 3.7% (Boszke et al. 2008).

The contribution of mobile mercury in sediments of the Warta River is much higher (12%) than in floodplain soil collected in the vicinity of this river (Boszke et al. 2007; Boszke and Kowalski 2008). Comparing to the sediments of the Warta River, similar contribution of mobile mercury equal to 12%, was observed also in the sediments of the Vistula River (Boszke and Kowalski 2007a, b) as well as in the deposit from the coastal zone inundated by the 26th December 2004 tsunami in Thailand – 15% (Boszke et al. 2006). In the estuarine sediment the contribution of mobile mercury was only 2.7% (Boszke et al. 2007). Lower contribution of mobile mercury was observed also in the coastal sediment taken from the area out of reach of the tsunami wave 6% (Boszke et al. 2006). It seems that lower contribution of mobile mercury in marine and estuarine sediments is rather specific for this kind of environmental samples, than is related with higher contamination of these sediments.

Correlation analysis

Some significant correlations ($p<0.05$) between the mercury concentrations and contributions of the total mercury and its species in the floodplain soils and sediments appear (Table 5). Among them an interesting one is that, between the contribution of the

Table 5 The list of statistical correlations (Spearman's *r*) of Hg contribution and concentration between sediments and floodplain soils with division to three distances form the riverbed

	N	Spearman's r	t(N−2)	p
Contribution				
F1% (Sediment) and F1% (10 m)	9	0.78	3.33	0.013*
F1% (Sediment) and F2% (10 m)	9	0.78	3.33	0.013*
F1% (10 m) and F2% (10 m)	9	0.72	2.72	0.030*
F1% (10 m) and F4% (50 m)	8	0.71	2.50	0.047*
F1% (50 m) and F5% (50 m)	9	−0.83	−3.99	0.005**
F2% (1 m) and F3% (1 m)	7	0.86	3.72	0.014*
F2% (Sediment) and F5% (10 m)	9	−0.70	−2.60	0.036*
F2% (1 m) and F5% (10 m)	6	−0.89	−3.82	0.019*
F3% (Sediment) and F4% (Sediment)	10	−0.65	−2.41	0.043*
F3% (50 m) and F4% (10 m)	8	−0.76	−2.88	0.028*
F4% (Sediment) and F5% (Sediment)	10	−0.67	−2.57	0.033*
F4% (1 m) and F5% (1 m)	7	−0.96	−8.14	0.0005***
F4% (10 m) and F5% (10 m)	9	−0.83	−3.99	0.005**
F4% (50 m) and F5% (50 m)	9	−0.73	−2.85	0.046*
F5% (Sediment) and F4% (50 m)	9	−0.80	−3.53	0.010**
F5% (Sediment) and F5% (50 m)	9	0.68	2.48	0.042*
Concentrations				
Bulk (1 m) and Bulk (10 m)	6	−0.89	−3.82	0.019*
Bulk (1 m) and F1 (1 m)	7	0.79	2.84	0.036*
Bulk (50 m) and F1 (50 m)	9	0.72	2.72	0.030*
Bulk (Sediment) and F2 (50 m)	9	−0.70	−2.60	0.036*
Bulk (Sediment) and F4 (Sediment)	10	0.88	5.21	0.0008***
Bulk (10 m) and F4 (10 m)	9	0.87	4.60	0.002**
Bulk (50 m) and F4 (50 m)	9	0.95	8.05	0.00009***
Bulk (Sediment) and F5 (Sediment)	10	0.90	5.95	0.0003***
Bulk (1 m) and F5 (1 m)	7	0.96	8.14	0.0005***
Bulk (10 m) and F5 (1 m)	6	−0.94	−5.66	0.005**
Bulk (10 m) and F5 (10 m)	9	0.93	6.88	0.0002***
Bulk (1 m) and ΣFractions (10 m)	6	−0.89	−3.82	0.019*
Bulk (10 m) and ΣFractions (1 m)	6	−0.89	−3.82	0.019*
Bulk (10 m) and ΣFractions (10 m)	9	0.98	14.3	0.000002***
F1 (10 m) and F3 (10 m)	9	−0.67	−2.37	0.050*
F1 (Sediment) and F4 (10 m)	9	−0.73	−2.85	0.025*
F1 (1 m) and F4 (1 m)	7	0.82	3.22	0.023*
F1 (50 m) and F4 (50 m)	9	0.80	3.53	0.010**
F1 (50 m) and F5 (50 m)	9	0.72	2.72	0.030*
F1 (1 m) and ΣFractions (1 m)	7	0.79	2.84	0.036*
F1 (50 m) and ΣFractions (50 m)	9	0.72	2.72	0.030*
F2 (1 m) and F2 (10 m)	6	0.89	3.82	0.019*
F2 (50 m) and F5 (Sediment)	9	−0.82	−3.74	0.007**
F2 (50 m) and ΣFractions (Sediment)	9	−0.70	−2.59	0.036*
F4 (Sediment) and F5 (Sediment)	10	0.71	2.84	0.022*
F4 (10 m) and F5 (1 m)	6	−0.83	−2.96	0.042*
F4 (10 m) and F5 (10 m)	9	0.70	2.59	0.036*
F4 (50 m) and F5 (50 m)	9	0.95	8.05	0.00009***
F4 (Sediment) and ΣFractions (Sediment)	10	0.88	5.21	0.0008***
F4 (10 m) and ΣFractions (10 m)	9	0.82	3.74	0.007**
F4 (50 m) and ΣFractions (50 m)	9	0.95	8.05	0.00009***
F5 (1 m) and F5 (10 m)	6	−0.89	−3.82	0.019*
F5 (Sediment) and ΣFractions (Sediment)	10	0.90	5.95	0.0003***

Table 5 (continued)

	N	Spearman's r	t(N−2)	p
F5 (1 m) and ΣFractions (1 m)	7	0.96	8.14	0.0005***
F5 (1 m) and ΣFractions (10 m)	6	−0.94	−5.66	0.005**
F5 (10 m) and ΣFractions (10 m)	9	0.97	9.99	0.00002***
ΣFractions (1 m) and ΣFractions (10 m)	6	−0.89	−3.82	0.019*

*$p<0.05$
**$p<0.01$
***$p<0.001$

mercury bound to humic mater and the mercury bond to sulphides in the sediments and floodplain soils (Table 5). These correlations show that the mercury bound to humic matter may be released in the process of degradation of organic matter, in more anoxic conditions in which the forming H_2S may bind mercury in the form of HgS. In case of highly contaminated soils, a significant correlation between the concentration of the mercury bound to humic matter and the mercury sulphide concentration ($r=0.76$) was observed (Boszke et al. 2008).

From ecotoxicological point of view, the negative correlation ($p<0.05$) between the contribution of organomercury compounds and that of mercury bound to sulphides in the floodplain soil samples collected at 50 m from riverbed are particularly interesting. However, in case of sediments from the Gulf of Thailand, a strong positive correlation was found between the contribution of methylmercury and mercury sulphide (Bloom et al. 2003). Moreover, in these sediments, a strong positive correlation between the contribution of methylmercury and the organic matter fraction was also found (Bloom et al. 2003). A significant negative correlation between the contribution of the organomercury species and mercury bound to humic matter was observed in post-tsunami sediments (Boszke et al. 2006). Significant correlation between the contribution of the acid-soluble mercury and that bound to organic matter ($r=−0.65$) for sediments of the Warta River was also discovered.

These correlations show that divalent mercury released from organic matter, may be bound not only to sulphides, but also to Fe/Mn hydro(oxide) and/or carbonates (acid-soluble mercury). Some portion of mercury bound to sulphides may be oxidized and converted, e.g. by biotic transformations, to extremely toxic organomercury species. It seems the main factor in this processes plays the organic matter, as observed also in other studies (Waples et al. 2005). It is also known that organic matter may also dissolve some mercury bound to sulphides (Ravichandran 2004; Waples et al. 2005).

Conclusions

The studies with using neural network-based modelling confirmed the usefulness of the chemometric techniques in interpretation of environmental data. Self-organising maps may be helpful in identification of "site-specific" polluted locations and for estimation of the contamination level. The most important conclusions are related to different patterns of contributions of mobile and immobile mercury species in moderately polluted and heavily polluted samples. In case of moderately polluted samples the contribution of mobile mercury is higher and that of immobile mercury lower than in the heavily polluted samples. Also, in case of moderately polluted samples the statistical differences in the contribution of mercury species are relatively low and thus the environmental risk from mercury deposited in aquatic system of the Warta River is relatively low. However, higher water levels and heavy floods may incite remobilisation of some organomercuries and acid-soluble species of mercury.

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