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TRACE ELEMENTS IN A VALLEY OF UPPER RIVER NAREW AND ITS SELECTED TRIBUTARIES, NE POLAND

The catchment of the upper river Narew (NE Poland) was studied. Investigations were carried out in March, May, August, and October 2006. The study was aimed at evaluating total cadmium, lead, zinc, chromium, nickel, and cobalt content as well as their forms dissolved in bottom sediments of the upper river Narew and its selected tributaries. Also the attempts to recognize the influence of the catchment management on concentration of the elements studied in bottom sediments of the upper river Narew were undertaken by using the neural networks. Metal concentrations were determined by means of AAS technique. Human economic and household activities, along with a surface runoff, are responsible for the metals deposited in sediments of the rivers under analysis, which was confirmed by statistical computations. The sediments were described as not contaminated (I class) with nickel, zinc, copper, chromium, cobalt, and lead, whereas cadmium concentration slightly exceeded that typical of the I geochemical class in about 20% of the samples studied. Contents of other elements under investigation occurred at the level of geochemical background. The highest metal concentrations were recorded in the alluvia of the river Horodnianka that flows through the area situated near municipal waste dump in Hryniewicze. Studies using artificial neural networks gave the opportunity and efficiency to predict the heavy metals contents in bottom sediments of the river Narew and allowed us to assess its efficiency taking into account many parameters at the same time.

1. INTRODUCTION

River ecosystems are one of the natural environment elements. Quality of every river greatly depends on the pollution load, e.g. heavy metals supplied. It is associated among others with urbanization, intensive agricultural and forest management as well as dust and gases emissions (SING et al. 2002). Bottom sediments are main receivers of various pollutants deposited in rivers, including heavy metals (TAM and WONG 2000; XIANGDONG et al. 2001; VILLARES et al. 2003; EL-SIKAILY et al. 2004). They are the center of accumulation, chemical processes, periodical deactivation, and decomposition of many toxic compounds reaching the aqueous environment (VAN DEN BERG et al. 1999; COBELO-GARCIA and PREGO 2003). Therefore, the status of water

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contamination due to trace elements is often determined on the basis of their contents in sediments (KABATA-PENDIAS and PENDIAS 1999; WARDAS 2001; TSAIL et al. 2003; AHMED et al. 2006). Recognition of heavy metals concentrations in bottom sediments may serve for more detailed chemical learning the aqueous environment, directions of pollutants spreading, identifying their origins, and as an indicator of natural geochemical situation within a catchment.

Present investigations were aimed at evaluating the total cadmium, lead, zinc, chromium, nickel, copper, and cobalt contents as well as their forms dissolved in bottom sediments of upper river Narew and its selected tributaries. Also the attempts to recognize the influence of catchment management on concentrations of studied elements in bottom sediments of upper river Narew were undertaken by using the neural networks.

2. MATERIAL AND METHODS

Catchment of upper river Narew (NE Poland) was the studied object). The largest area is covered by lessive and brown soils there, then rusty and podzolic developed from different-origin sands, which occur mainly on sander areas and moraine heights. River valleys are filled with the youngest Holocene forms: silt, peat, gytia, loam, and dune sands. North-eastern Poland is counted to “The Green Polish Lungs” as a unique landscape. That area is slightly industrialized, and green area cover huge territories.

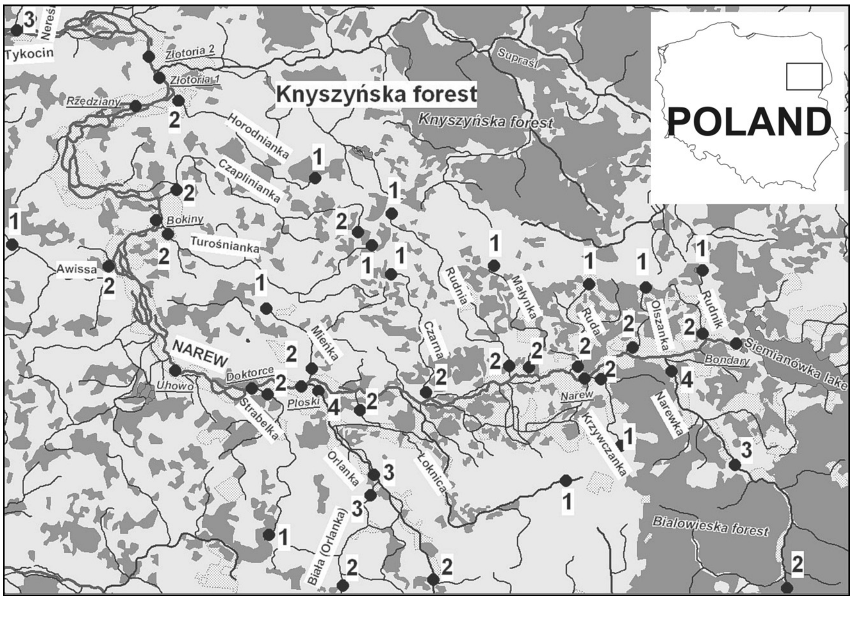


Fig. 1. Sediments sampling points, river Narew – not-numbered points river Narew tributaries (1 – river’s springs, 2 – river’s estuary)

Ten sampling points were set on river Narew (6270 km^2 of catchment area): Bondary, Narew, Ploski, Doktorce, Uhowo, Bokiny, Rzędziany, Złotoria, Złotoria weir, and Tykocin, along with its twenty tributaries (figure 1) that were divided into two groups. The first group included: Jaskranka, Biała (river Orlanka tributary), Awissa, Czaplinianka, Czarna, Horodnianka, Krzywczanka, Łoknica, Małynka, Mieńka, Ruda, Rudnia, Rudnik, Olszanka, Targonka, Strabelka, and Turośnianka catchment areas of which are from 20 to 175 km^2; these flows formed "small rivers group". Other rivers: Narewka (711 km^2 of catchment area), Orlanka (520 km^2 of catchment area), and Nereśl (283 km^2 of catchment area) constituted "larger rivers group". Selection of bottom sediments sampling points in larger rivers group was based on the presence of aqueous environment pollution foci with heavy metals. Number of such delimited points was from 3 to 4. Number of sampling points in smaller rivers group was maximum 2 (spring and mouth) or only one (mouth) due to their length (from 7 to 26.2 km).

Investigations of upper river Narew and its tributaries were carried out in March, May, August, and October 2006. Bottom sediments, in which total contents of cadmium, nickel, zinc, chromium, cobalt, and lead along with their soluble forms were determined, were studied object. Collecting the representative sample is often difficult moment in analytical procedure (SIEPAK 1997). River-bed processes determine the size and character of sediments, contamination of which depends on parameters governing the metals distribution within river environment (LADD et al. 1998, WARDAS 2001). Higher metal accumulation in sediments of shore than active zone is considered as a feature of lowland rivers under moderate climate (BUBB et al. 1991). The bottom sediment was collected in shore zone where suspended material is deposited (BOJAKOWSKA 2001). A representative sample of sediment for every sampling point was achieved by mixing several primary samples collected from different shore sites in river beds (to 10 cm of thickness) from beneath the water and no more than 0.5 kg. Samples were air-dried and passed through 0.2 mm mesh polyethylene sieve. Fraction <200 µm was subjected to analyses, because it is present most often in studied sediments (SKORBIŁOWICZ 2007) and is applied in works associated with geochemical mapping (THALMANN et al. 1989, LIS and PASIECZNA 1995). This fraction quite well reflects the alluvia composition, because it does not contain random mechanical contaminants and mineral particles. Then, the bottom sediments were digested in nitric acid in microwave system CEM Mars-5. Aliquots of 0.5 g sample were closed in microwave vessels and 8 ml of concentrated HNO_3 + 2 ml 30% H_2O_2 were added. After filtration, samples were quantitatively transferred to measure flasks of 50 ml capacity each. Simultaneously, soluble metal forms were extracted from bottom sediments using 1 $mol \cdot dm^{-3}$ HCl (DEMBSKA et al. 2001, VILLARES et al. 2003, SNAPE et al. 2004, PARAFINIUK et al. 2005). Such procedure makes possible to extract mobile fractions of heavy metals from sediments, which is important in evaluating the level of environmental pollution. DEMSKA et al. (2001) proposed that labile form of metals is taken into account (extraction with 1 $M \cdot dm^{-3}$HCl), instead of the total content, because it better reflects the real metal concentration in sediments originating from anthropogenic activity. CARRAL et al. (1994) also reported that soluble forms give clues on anthropogenic origin of the metals. The sequential extraction was not applied in present experiments, because of low total metal contents in majority of studied samples: their concentrations in extracts corresponding to particular fractions were often below AAS detection limits. The metals concentrations were determined using spectrometer Varian SpectraAA-100. The method correctness was verified on a base of analysis of reference material NCS DC73312 (table 1). The reference material was analyzed at first and after each sample series. Method precision and accuracy was determined on a basis of analyte reflux from 5 model samples at different concentrations of studied metals (table 2). The sediment acidity in water suspension was estimated by potentiometric measuring the pH value.

Table 1

Result for reference material NCSDC 73312 by means of ASA, (n = 4, p = 95%)

Metal	Certified value for NCSDC 73312 [mg·kg^{-1}]	ASA [mg·kg^{-1}]
Cr	12	13±4
Ni	5.5	6.0±1.5
Cu	4.9	5.0±0.6
Co	2.6	2.9±0.9
Cd	0.065	0.070±0.012
Pb	32	31±5.0
Zn	44	45±6

Table 2

Conditions and parameters of AAS sediments determinations

Item	Detection range	Precision	Accuracy	Wavelength	Gap width
	[mg·dm^{-3}]	%		nm	nm
Cr	0.06–15	10	20	357.9	0.2
Ni	0.1–20	10	20	232.0	0.2
Cu	0.03–10	10	20	324.7	0.5
Co	0.05–15	10	20	240.7	0.2
Cd	0.02–3	10	20	228.8	0.5
Pb	0.1–30	10	20	217.0	1.0
Zn	0.01–2	10	20	213.9	1.0

Achieved results related to contents of studied metals were given in reference to air-dried sediments and compared with literature data and median values for these metals in bottom sediments for Poland (fraction <0.2 mm) (LIS, PASIECZNA 1995) and for Europe (fraction <0.15 mm) [Foregs]. Proposition of aqueous sediments classification (table 3) on a base of geochemical criteria was used to evaluate the level of sediments contamination with heavy metals (BOJAKOWSKA 2001). There are no legal regulations on aqueous sediments classification in Poland. Geochemical monitoring of bottom sediments in aqueous reservoirs is based on the classification proposed by National Geological Institute (PIG) (BOJAKOWSKA and SOKOŁOWSKA 1998, BOJAKOWSKA 2001) that distinguishes four classes of sediment quality: I class – not-contaminated sediments, II class – slightly contaminated sediments, III class – moderately contaminated sediments, and IV class – very contaminated sediments. The threshold limits for particular classes (table 3) were defined taking into account the harmful influence of contaminants accumulated in bottom sediments towards aqueous organisms.

Table 3

Proposition of aqueous sediments classification in Poland on a base of geochemical criteria (BOJAKOWSKA 2001)

Component	I	II	III	IV
	$mg \cdot kg^{-1}$ DM			
Cadmium	0.7	3.5	6	>6
Chromium	50	100	400	>400
Copper	20	100	300	>300
Nickel	16	40	50	>50
Lead	30	100	200	>200
Zinc	125	300	1000	>1000

3. STATISTICAL COMPUTATIONS

Following items were calculated for studied bottom sediments from river Narew and two tributaries groups: minimum and maximum values, arithmetic mean, median, and standard deviation. In total, 3180 results were analyzed in present study. Factorial analysis (FA) that is multi-dimensional one and is applied to describe and explore the large sets of data, was used for statistical computations. To isolate factors, main components method was applied, which uses a primary correlation matrix for calculations. It is used in hydrochemistry to investigate processes occurring in underground waters and to identify the supplying and origin sources shaping the chemical composition of waters (SIMEONOVA et al. 2003, SIMEONOV et al. 2004). In order to interpret the factorial analysis results, it was assumed that associations of primary variable with a factor are strong when absolute values of its charges are greater than 0.70 (EVANS et al. 1996, PUCKET, BRICKER 1992). Analyses also involved cluster analysis (CA) – Ward agglomeration method that is based on the notion of the distance of objects or variables in multi-dimensional space. Achieved results were also subjected to analysis using neural networks to confirm the influence of catchment management on concentration of studied elements in bottom sediments of upper river Narew as well as to predict their concentrations changes.

4. ARTIFICIAL NEURAL NETWORKS

Artificial neural networks are the mathematical model consisting of the calculation nodes net called neurons along with their bindings. This model simulates the human brain action. Adjusting the neural network to solve particular task is realized by means of its teaching using typical stimuli and corresponding desired reactions, not by defining the algorithm and writing it in a form of a program, as in the case of traditional modeling methods (EINAX, TRUCKENBRODT, KAMPE 1998, HAZAKI et al. 2001).

Fitting the model's elements is due to network's teaching. It consists in the selection of variable parameters of the model so that the dependence input-output showed high interrelations expressed by Pearson's coefficient. Algorithm with reciprocal error propagation is the best known method for neural networks teaching. Pearson's coefficient r between calculated and real output values, is also quite good measure of ANN network quality (TADEUSIEWICZ 1993, 1998; FAUSETT 1994; BISHOP 1995; PATTERSON, 1996).

5. RESULTS AND DISCUSSION

Results on contents of studied heavy metals and other indices in bottom sediments from river Narew and its tributaries are presented in tables 4, 5, and 6.

Table 4

Results from determinations of grain fraction (<200 μm) of bottom sediments in river Narew for the whole experimental period

Statistical data River Narew	Bottom sediments n = 40														
	pH in H_20	mg·kg^{-1} DM													
		Cd		Pb		Zn		Cr		Ni		Cu		Co	
		tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.
Minimum	6.7	0.49	0.08	6.3	0.6	8.7	3.0	0.8	0.2	3.8	0.1	0.8	0.2	1.6	0.2
Maximum	7.5	1.78	0.71	58.2	26.3	198.6	98.1	31.2	14.7	13.6	4.6	17.3	11.0	15.6	10.8
Arithmetic mean	–	0.80	0.25	22.9	8.8	48.9	22.7	6.7	1.9	8.1	1.3	5.2	2.8	4.0	1.4
Median	–	0.77	0.19	17.0	4.2	36.8	16.2	4.7	0.9	7.6	1.1	4.0	2.1	3.2	0.8
Standard deviation	–	0.29	0.15	15.14	8.28	42.74	20.99	7.00	3.03	2.33	1.01	3.94	2.52	2.79	1.95

Remarks: tot. – total content, sol. – soluble content.

Table 5

Results from determinations of grain fraction (<200 μm) of bottom sediments in smaller rivers group for the whole experimental period

Statistical data River Narew tributaries	Bottom sediments *n* = 128														
	pH in H_2O	mg·kg^{-1} DM													
		Cd		Pb		Zn		Cr		Ni		Cu		Co	
		tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.
Minimum	5.3	0.33	0.05	1.5	0.4	5.2	2.4	1.3	0.3	3.8	0.2	0.9	0.4	1.9	0.3
Maximum	7.9	2.33	1.33	50.6	21.6	140.8	57.3	67.2	27.9	94.2	18.1	88.1	41.9	29.5	10.7
Arithmetic mean	–	0.74	0.23	13.1	3.3	33.7	15.5	5.9	1.4	9.9	1.8	5.2	2.6	4.2	1.5
Median	–	0.71	0.21	11.4	2.2	26.2	11.6	4.3	0.9	8.1	1.2	3.7	1.6	3.8	1.4
Standard deviation	–	0.27	0.16	7.14	3.18	22.29	11.06	7.39	2.81	8.75	2.16	8.08	3.98	2.58	1.11

Remarks: tot. – total content, sol. – soluble content

Table 6

Results from determinations of grain fraction (<200 μm) of bottom sediments in larger rivers group for the whole experimental period

Statistical data River Narew tributaries	Bottom sediments *n* = 44														
	pH in H_2O	mg·kg^{-1} DM													
		Cd		Pb		Zn		Cr		Ni		Cu		Co	
		tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.
Minimum	6.4	0.49	0.08	2.5	0.3	11.5	3.1	1.3	0.3	2.1	0.1	0.7	0.2	1.9	0.4
Maximum	8.8	1.11	0.45	27.5	14.4	59.9	23.9	10.2	1.9	15.5	4.3	10.0	5.6	8.3	4.2
Arithmetic mean	–	0.76	0.21	10.4	2.8	24.1	10.1	4.5	0.8	8.1	1.3	3.6	1.8	3.6	1.3
Median	–	0.79	0.21	9.1	2.1	22.4	8.4	4.8	0.7	7.5	1.0	3.1	1.4	3.3	1.1
Standard deviation	–	0.16	0.09	4.84	2.81	9.74	4.85	1.97	0.46	2.71	0.99	2.56	1.41	1.31	0.82

Remarks: tot. – total content, sol. – soluble content

In majority of cases, the pH value was neutral or slightly basic. Statistical processing did not reveal any significant correlation between acidity vs. total and easily soluble contents of studied elements in bottom sediments.

Amount of total cadmium in sediments from investigated rivers was within the range from 0.33 mg·kg^{-1} to 2.33 mg·kg^{-1} (tables 4, 5, 6). Its concentration mainly remained at the level from 0.4 mg·kg^{-1} to 1.0 mg·kg^{-1}, which made up about 94% of tested sediment samples. Median value in river Narew and its tributaries exceeded 0.70 mg·kg^{-1} (tables 4, 5, 6). Data achieved for cadmium content in sediments of investigated rivers were much lower than those in upper Vistula (WARDAS 2000) and comparable or slightly higher to river Dunajec (WIŚNIOWSKA-KIELIAN and NIEMIEC 2005). From a point of view of environmental protection, it is important if metals concentrations – cadmium in this case – is dangerous. Therefore, the question is: is it "natural level" for the metal? It means the amount that corresponds to geochemical background level that is determined for a particular region and also varies within a single environmental component (RUIZ et al. 1998). However, more often "natural" samples are rare, because the effects of contemporary pollution on "a background" that should represent "pre-industrial" situation cannot be avoided (MATSCHULLAT et al. 2000). Therefore, older layers in flooded valleys, samples from not polluted areas, or rock samples from mines that are built of similar material and similar grain size may be the geochemical background (MÜLLER 1981). Loamy rocks are the most suitable as petrified fossils for comparisons. They were used by TUREKIAN and WEDEPHOL (1961) to set the geochemical background often applied as a global basis for contaminated river sediments. Considering bottom sediments from upper river Narew and its tributaries, it was found that 21% samples did not exceed that limiting level for cadmium according to BOJAKOWSKA and SOKOŁOWSKA (1998). Within analyzed period, bottom sediments from river Narew and its tributaries were not contaminated or slightly contaminated (up to the level of II class) according to PIG classification. Median values for studied sediments were slightly higher than those for cadmium in sediments for Europe and for Poland.

When recognizing the status of river environment, determination of total metals content accumulated in bottom sediments does not supply with the information on their mobility. A labile part of metals is greatly of anthropogenic and biochemical origin. From a point of environmental pollution view, that part of metals is very important, because – due to labile character – they can be desorbed from sediments to a water as well as get accumulated in benthos organisms (DEMBSKA et al. 2001). Concentration of soluble cadmium in studied alluvia ranged from 0.05 $mg \cdot kg^{-1}$ to 1.33 $mg \cdot kg^{-1}$. The percentage of its soluble in total form was about 27%, on average.

Lead supplied to aqueous wastes is quickly bonded by various minerals and organic compounds present in bottom sediments, thus its contents in these materials can be a pollution indicator (KABATA-PENDIAS and PENDIAS 1999). Investigations upon the lead content in bottom sediments from river Narew and its tributaries revealed levels of 1.5–58.2 $mg \cdot kg^{-1}$. Much higher contents were found in river Odra and its tributaries (Poland) (from 19.2 to 418 $mg \cdot kg^{-1}$) (HELIOS-RYBICKA et al. 2001) as well as in river Gomti (India) (from 4.86 to 156 $mg \cdot kg^{-1}$) (KUNWAR et al. 2005). Median of lead I bottom sediments for Poland amounts to 13 $mg \cdot kg^{-1}$, while for Europe 14 $mg \cdot kg^{-1}$; similar values were achieved in present study. Taking into account all investigated rivers, it can be concluded that 87.3% of sediments samples did not exceed the geochemical background level for lead according to TUREKIANA and WEDEPHOL (1961). Amounts of soluble lead in studied bottom sediments were from 0.3 $mg \cdot kg^{-1}$ to 26.3 $mg \cdot kg^{-1}$. In most cases, the percentage of soluble Pb in total lead content remained at constant level of 7–36% with mean value of about 22%.

KABATA-PENDIAS and PENDIAS (1999) claim that lead is less active in geochemical environments, which was confirmed in present study.

Studied sediments can be considered as not contaminated with zinc, because geochemical background is accepted to be 48 mg·kg^{-1} (BAJAKOWSKA and SOKOŁOWSKA 1998) and 98 mg·kg^{-1} (TUREKIAN and WEDEPHOL 1961), whereas determined zinc amounts were within the range between 10 mg·kg^{-1} and 40 mg·kg^{-1}. Median of zinc for bottom sediments in Poland is 73 mg·kg^{-1}, while in Europe 60 mg·kg^{-1}; lower values were recorded in present study. Content of soluble zinc in sediments ranged from 2.4 to 98.1 mg·kg^{-1}. Relatively high level of soluble form proves its great mobility. Such dependence is also indicated by the percentage of soluble in total zinc content that in majority of cases ranged from 35% to 60%.

Chromium concentration in river Narew and its tributaries at selected sampling points was from 0.8 to 67.2 mg·kg^{-1} with median above 4.0 mg·kg^{-1} (tables 4, 5, 6). Chromium contents in bottom sediments do not exceed 10 mg·kg^{-1} in not polluted Polish rivers (BOJAKOWSKA and SOKOŁOWSKA 1998). About 95% of samples contained chromium at the level close to natural one or slightly above 10 mg·kg^{-1} (BOJAKOWSKA and SOKOŁOWSKA, 1998). Median values achieved for total chromium were lower than that for sediments in Europe (22 mg Cr·kg^{-1}) and in Poland (5 mg Cr·kg^{-1}). Content of soluble chromium forms in most cases ranged from 0.2 to 27.9 mg·kg^{-1} and only 13 studied samples revealed concentrations above 2.0 mg Cr·kg^{-1}. Relatively low level of soluble chromium may prove its poor mobility, which is also indicated by the percentage of its soluble in total content that was about 18%, on average.

In the case of nickel, median values of sediments from river Narew and its tributaries were as follows: 7.6 mg·kg^{-1}, 8.1 mg·kg^{-1}, and 7.5 mg·kg^{-1} (tables 4, 5, 6), which were lower than median for Europe (16 mg Ni·kg^{-1}) and higher than median for Poland (6 mg Ni·kg^{-1}). Analyzed nickel concentrations did not exceed the I class (BOJAKOWSKA 2001). Percentage of soluble in total forms of nickel – in majority of studied samples – was within 10–25%. This metal easy forms quite durable chelate compounds as well as complex cations and anions.

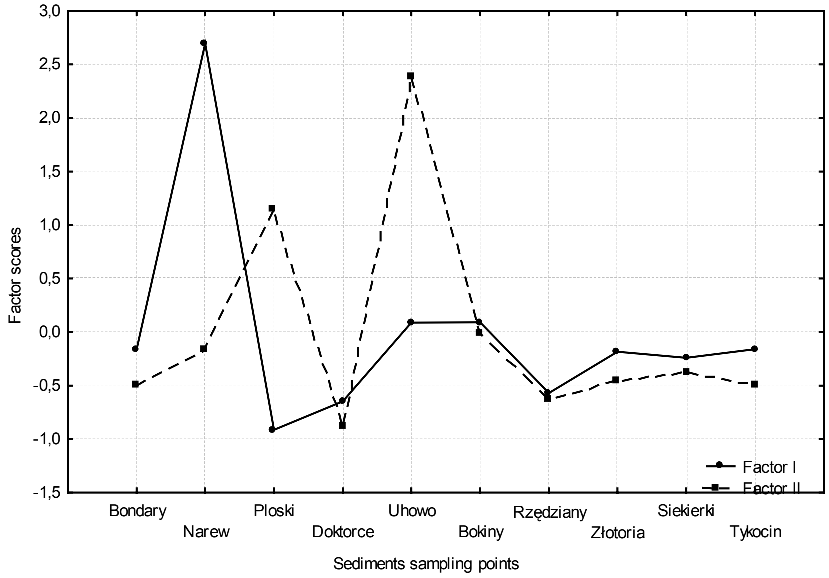
When comparing the values of median in river Narew (4.0 mg·kg^{-1}) with smaller rivers (3.7 mg·kg^{-1}) and larger rivers group (3.1 mg·kg^{-1}), a slight difference is apparent. Referring to those contents, copper can be considered as at the level of geochemical background (TUREKIAN and WEDEPHAL 1961, BOJAKOWSKA and SOKOŁOWSKA 1998). Therefore, such amounts can be accepted as not contaminated. The percentage of soluble copper forms in its total content was about 45%, on average.

Achieved results for bottom sediments indicate the lack of pollution of aqueous environment with cobalt (TUREKIAN and WEDEPHAL 1961, BOJAKOWSKA and SOKOŁOWSKA 1998). Content of soluble cobalt in studied sediments was most often at the level of 0.5–2.0 mg·kg^{-1}, which was made up by about 90% of analyzed samples. The percentage of soluble Co in total cobalt amount was about 35%.

As expected, dependencies between total contents of cadmium, cobalt, lead, zinc, chromium, copper, and nickel vs. their soluble forms were found. Correlation coefficients were as follows: $R_{Cd} = 0.767$, $R_{Co} = 0.891$ (at $p < 0.001$); $R_{Pb} = 0.897$, $R_{Zn} = 0.933$, $R_{Cr} = 0.909$, $R_{Cu} = 0.967$ (at $p < 0.01$), and $R_{Ni} = 0.824$ (at $p < 0.05$).

Table 7

Factorial analysis results (rotation method – normalized varimax; determined loads are >0.7) and dynamics of factorial values changes at measurement points on river Supraśl



Variables	Factor I	Factor II
Cd (total form)	0.29	0.05
Cd (soluble form)	**0.70**	0.11
Pb (total form)	0.04	**0.96**
Pb (soluble form)	0.06	**0.95**
Zn (total form)	–0.02	**0.92**
Zn (soluble form)	0.05	**0.91**
Cr (total form)	**0.76**	–0.34
Cr (soluble form)	**0.90**	–0.02
Ni (total form)	0.63	0.52
Ni (soluble form)	**0.88**	0.37
Cu (total form)	0.49	0.69
Cu (soluble form)	0.27	**0.81**
Co (total form)	**0.95**	0.20
Co (soluble form)	**0.93**	0.16
Variance explained [%]	48	27

The multidimensional data analysis methods are becoming very popular in environmental studies dealing with measurements and monitoring (SIMEONOV et al. 2002, KRAFT et al. 2003, ASTEL et al. 2004. The correlation matrix of variables was generated and factors extracted by the Centroid method, rotated by Varimax rotation (AHMED et al. 2005).

The main components method that uses a primary correlation matrix for calculations was applied in FA in order to separate factors. It is used in hydrochemistry to investigate processes occurring in underground surface and waters and to identify the supplying and origin sources shaping the compounds shaping the aqueous environment chemical composition (SIMEONOVA et al. 2003, SIMEONOV et al. 2004). In order to interpret the factorial analysis results in FA, it was assumed that associations of primary variable with a factor are strong when absolute values of its charges are greater than 0.70 (EVANS et al. 1996, PUCKET, BRICKER 1992).

Analyses also involved cluster analysis (CA) – Ward agglomeration method that is based on the notion of the distance of objects or variables in multi-dimensional space. Normalized Euclidean distances and the Ward's methods were used to obtain dendrograms (EINAX et al. 1997).

Achieved results on bottom sediments from river Narew were subjected to multifactorial analysis based on "rubble criterion" and "Kaiser's criterion"; two explaining factors were selected: PC1 48% and PC2 27% (75%) of global phenomena variability in analyzed system (table 7). Factor I explains the variability of chemical composition of bottom sediments in river Narew in 48%. Positive factorial charges being "correlation coefficients" were obtained between following variables: cadmium, chromium, nickel, and cobalt vs. Factor I, including its highest share at sampling point Narew. It was also affected by interaction with Narew village that disposed purified and non-purified sewage (municipal and industrial) along with storm water and agricultural wastes. Factor II explains processes making supply analyzed sediments with lead, zinc, and copper. It explains in 27% the chemical composition variability of bottom sediments in river Narew. The maximum share of the factor is at two sampling points: Ploski and Uhowo (table 7). Road and railroad are localized near those points. They are national tracts where the traffic is continuous and intensive. Thus, lead is emitted along with exhausting gases from various vehicles. Other elements are released due to friction of break covers and dusting of different products transported by trucks or trains. Studies by OSMÓLSKA-MRÓZ and SADOWSKI (1992) revealed that pollution from rainfalls and thawing snow depends on the intensity and quality of road traffic. Analysis of data referring to surface runoff from road No E-77 (Poland) revealed that zinc and lead dominated in determined sum of heavy metals (71.5% and 18.7%, respectively).

Dendrogram (figure 2) resulting from cluster analysis can be some kind of a confirmation of above theses. There are two main groups: I including points Ploski and Uhowo, and II including points seemed to be exposed to other interactions than transportation. Arrangement III – Rzędziany, Doktorce, Złotoria (influences being a result of agricultural activity), arrangement IV – Narew, Siekierki, Bokiny, Tykocin, Bondary (other effects with apparent surplus of sewage treatment plant and reservoir Siemianówka near Bondary).

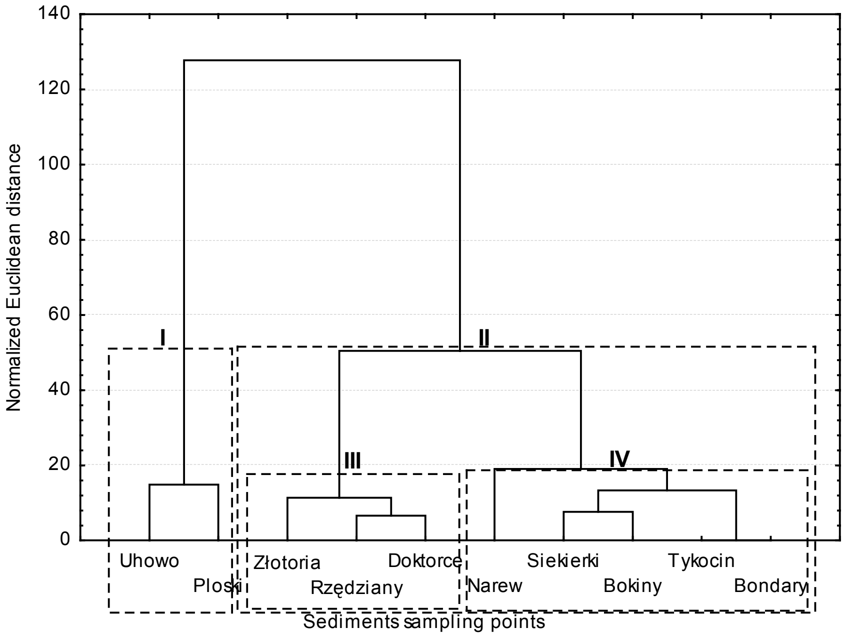


Fig. 2. Dendrogram of the CA according to Ward.
Monitoring locations of the Narew river

Another dendrogram (figure 3) groups particular rivers – river Narew tributaries on a base of studied parameters in their bottom sediments. Arrangement I includes rivers (Targonka, Horodnianka, Biała – Orlanka tributary) directly exposed to influences of non-purified or insufficiently purified sewage from municipal treatment plants localized near their catchments. Moreover, in Bielsk Podlaski (Biała of Orlanka tributary) and Mońki (Targonka), there are localized fruit and vegetable processing works, dairy, meat, building, and metallurgic works; river Horodnianka flows through the area that is influenced by the municipal wastes dump in Hryniewicze. Arrangement II groups rivers that are exposed to various influences of agricultural activity (organic fertilization, plant protection means, mechanization).

Results of bottom sediments were subjected to analysis using artificial neural networks (ANN). ANN is in the "black-box" class of models. These models do not require detailed knowledge of the internal functions of a system in order to recognize relationships between inputs and outputs (EL-DIN and SMITH 2002). The application of ANN algorithms to sediment load data started recently (ABRAHART and

WHITE 2001; JAIN 2001; CIGIZOGLU 2002a,b,c; NAGY et al. 2002; TAYFUR 2002; ALP 2003; CIGIZOGLU and Alp 2003; MERRITT et al. 2003; YITIAN and GU 2003; CIGIZOGLU 2004; KISI 2004; AGARWAL et al. 2005). Artificial neural networks with properly selected structure allow for solving non-linear and multi-dimensional problems, that are often impossible to solve in conventional manner (ŁOZOWICKA-STUPNICKA 2000).

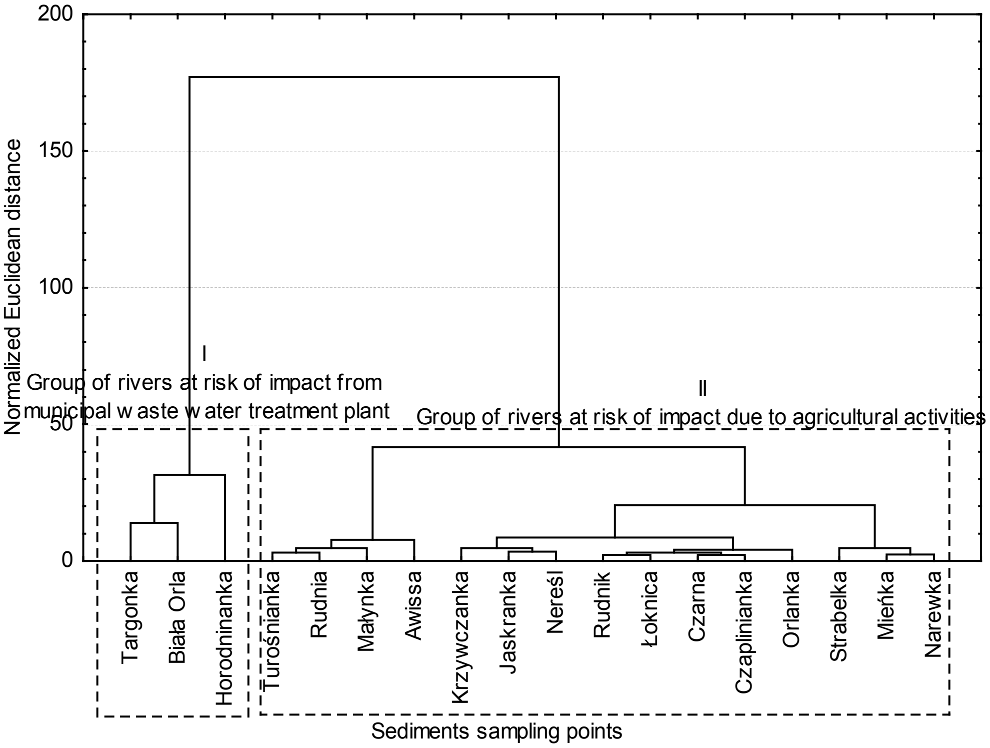


Fig. 3. Dendrogram of the CA according to Ward,
Tributaries of Narew river

A three-layer network structure (including one hidden layer) with back-propagation algorithm) was proposed for model building (figure 4). It is so-called multi-layer perceptron (MELESSE and HANLEY 2005). Back-propagation algorithm was used to teach the network and licensed Statistica 7.1 software was applied for analyses. Artificial neural network applied had a following structure: 3 neuron layers, one hidden layer, 53 neurons in the first input layer and 14 neurons in output layer. The first layer is represented by: soil acidity within the catchment (in KCl and H_2O), content of organic matter in soils of river Narew catchment, concentrations of total and soluble forms of heavy metals in soils (Cd, Pb, Cr, Ni, Zn, Co, and Cu), length of river Narew, catchment surface, arable lands, green lands, forests, population, loads of heavy metals in rainfalls (Zn, Cu, Pb, Ni), sum of atmospheric precipitations, fertilization (P), flow speed of river Narew at sampling points, concentrations of soluble forms of heavy metals in river Narew water (Pb, Cd, Zn, Cu, Cr, Co, Ni), and specific conductivity of river Narew water. The output layer is represented by total and soluble heavy metals concentrations (Pb, Cd, Zn, Cu, Cr, Co, Ni) in bottom sediments from river Narew. The network has following parameters: learning quality = 0.397436, validation quality = 0.511349, test quality = 0.481983.

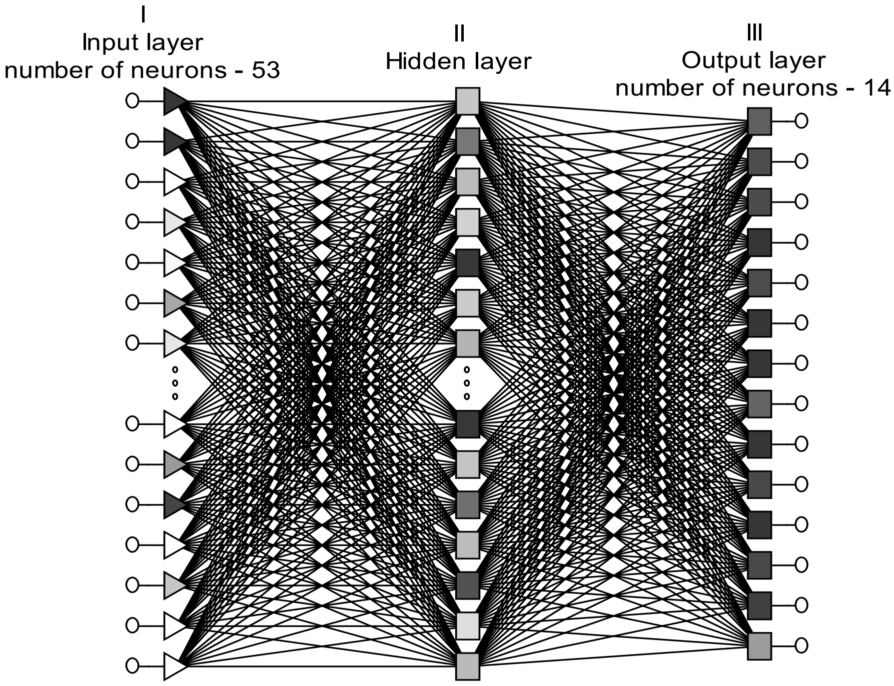
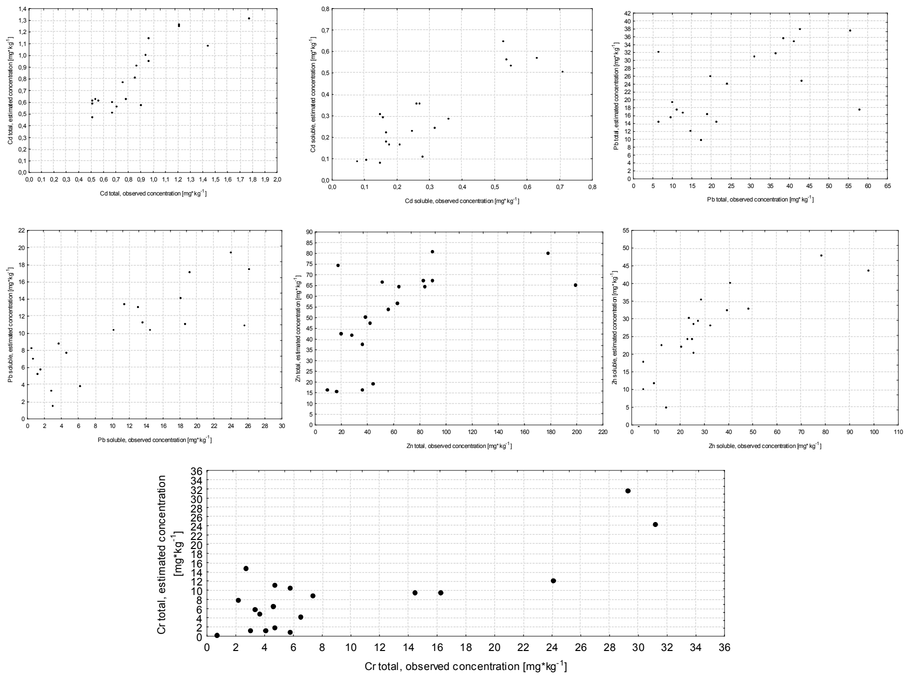


Fig. 4. Structure of neural network applied.
Network type: multi-layer perceptron

Such constructed model of ANN network was tested and verified by means of "back" method that consisted in network's putting the predictions covering with the real results. These predictions not always agreed in 100%, which resulted from the error of a given model. In this case, the model is considered as right and suitable for "forward" parameters prediction on a base of given new input variables.

The tests revealed dependencies between real and calculated values expressed with the Pearson's coefficients *r* (table 8), (figure 5a, 5b).

a



b

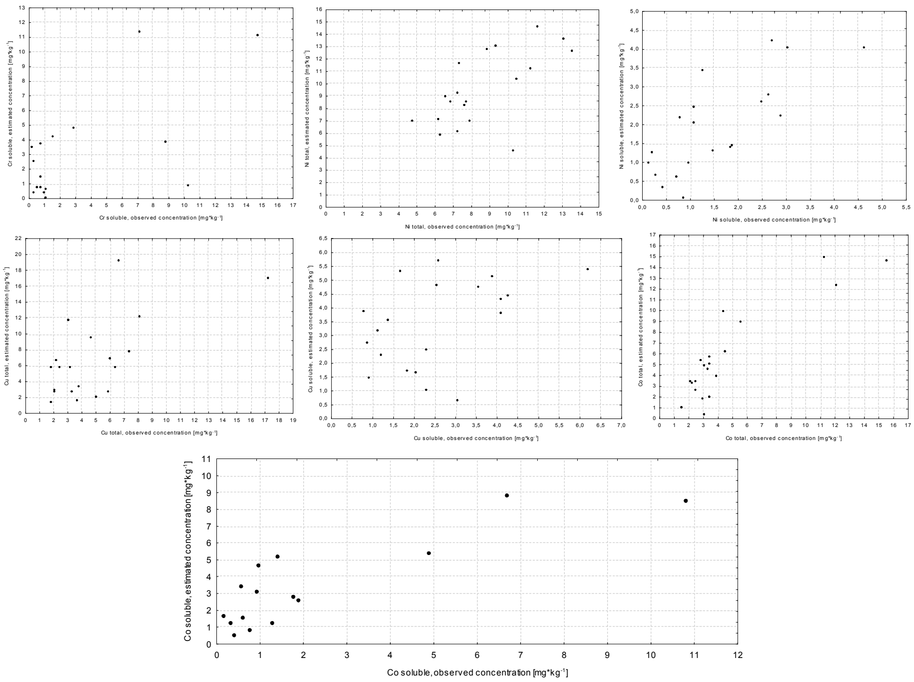


Fig. 5. Results from artificial neural network tests

The most significant predictions of heavy metals content in investigated bottom sediments were achieved for cadmium.

Table 8

Regression – correlation values from neural network tests

Metal	Cd tot	Cd sol	Pb tot	Pb sol	Zn tot	Zn sol	Cr tot	Cr sol	Ni tot	Ni sol	Cu tot	Cu sol	Co tot	Co sol
Correlation	0.86	0.87	0.57	0.83	0.60	0.83	0.80	0.65	0.66	0.76	0.64	0.46	0.89	0.72

6. CONCLUSIONS

1. Studies upon upper river Narew and its tributaries revealed that bottom sediments were characterized by low contents of potentially harmful elements. Trace elements concentrations were at the level of geochemical background in most cases for zinc and copper (BOJAKOWSKA, SOKOŁOWSKA 1998). The sediments were characterized as not contaminated (I class) with nickel, zinc, copper, chromium, cobalt, and lead, whereas little exceeding of the I geochemical class referring to cadmium was recorded in about 20% of examined samples (BOJAKOWSKA 2001).

2. Analysis of labile metal forms (1M HCl) also seems to be reasonable at evaluating the level of bottom sediments contamination, because it reflects more precisely the real metals contents originating from human activity. Labile part of metals has greatly anthropogenic and biochemical origin. From a point of view of environmental pollution, that part of metals is considered as important, because due to its lability, these metals can be desorbed from sediments into the water, as well as be accumulated in benthos organisms.

3. A positive linear correlation between total contents of analyzed metals and their soluble forms was found.

4. Human activity, including local transport, as well as surface runoff, are the sources of studied metals deposited in bottom sediments of examined rivers.

5.The highest metals concentrations were recorded in alluvia of stream Horodnianka in small rivers group (Cd – 2.33 mg·kg^{-1}, Cr – 67.2 mg·kg^{-1}, Ni – 94.2 mg·kg^{-1}, Cu – 88.1 mg·kg^{-1}, and Co – 29.5 mg·kg^{-1}). Horodnianka flows through the area adjacent to municipal waste dump in Hryniewicze and municipal sewage from Choroszcz has also significant influence of its water quality.

6. The attempts to combine selected catchment, hydrological, contamination sources, and climatic parameters on the area the river Narew flows through, with trace elements contents in its bottom sediments, were undertaken. Due to a difficult nature of these data associations, the system of artificial neural networks was applied. Proposition of such solution is one of the possible and permissible procedures at modeling generalized environmental relations. It allowed for predicting the heavy metals con-

centrations in studied sediments on a base of varied input variables. The most significant predictions of heavy metals contents in examined bottom sediments were achieved for cadmium.

7. Determinations of heavy metals content in bottom sediments from river Narew and its tributaries contributed to the existing knowledge on the quality of the aqueous environment in north-eastern Poland that belongs to functional area of "Green Polish Lungs". They can also be helpful for comparisons of metal-contaminated areas.

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