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ASSESSMENT OF HEAVY METAL CONTENT IN BOTTOM SEDIMENTS OF RIVER SUPRAŚL AND ITS TRIBUTARIES

The catchment of the river Supraśl was studied. The investigations were carried out in March, May, August, and October 2006. The aim of the study was to evaluate and predict the total content of cadmium, lead, zinc, chromium, nickel, copper, and cobalt, as well as their soluble forms in the bottom sediments of the river Supraśl and its tributaries. Concentrations of heavy metals were determined by means of AAS technique. Bottom sediments from the river Supraśl and its tributaries proved to be slightly contaminated with cadmium. Content of other metals investigated was usually at the geochemical background level. The highest concentration of the heavy metals were found in the bottom sediments of the river Supraśl at the sampling point Fasty and the river Biała that is a receiver of municipal and industrial sewage from Białystok, which was confirmed by statistical analyses. Differences in metal contents in the river Supraśl tributaries resulted mainly from the character of the surrounding catchment.

1. INTRODUCTION

Recently, many studies upon the aqueous environment pollution associated with the programs for protecting and screening the natural environment status, have been conducted (RAY and WHITE 1979; BOJAKOWSKA et al. 2001). Much attention has been paid to heavy metals (HELIOS-RYBICKA 1991; BOJAKOWSKA and SOKOŁOWSKA 1992; WARDAS 2001; BUDEK et al. 2004). Enrichment of aqueous environment in heavy metals first of all results from a man's activity: sewage disposal (ANAWAR et al. 2000; KOLDEMAN et al. 2000), industrial gases and dust emission (FANG et al. 2000) or vehicles exhausting gases (XIANNGDONG et al. 2001; CHARLESWORTH et al., 2003; SEZGIN et al. 2004), accumulation of municipal and industrial wastes as well as applying the artificial fertilizers and plant protection means in agriculture (TESSIER and HARE 1996; KABATA-PENDIAS and PENDIAS 1999; KLAVINS et al. 2000). Quality of bottom sediments is a good indicator of aqueous environment contamination as

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well as the amount of pollution emission within a catchment area (WIŚNIOWSKA-KIELIAN and NIEMIEC 2005).

The study was aimed at evaluating, assessing, and predicting the total cadmium, lead, zinc, chromium, nickel, copper, and cobalt contents in bottom sediments of river Supraśl and its tributaries.

2. MATERIAL AND METHODS

The catchment of river Supraśl (figure 1) flowing through non-industrial area was the object for study. River Supraśl (93.8 km length and 1844.4 km^2 of catchment area) is a right-side tributary of river Narew reaching it at 299.8 km. Podzolic and red soils developed from weak loam, loam, and loose sands dominate within the catchment of analyzed river. A peat fills mainly wide fragments of Upper and Lower Supraśl valley. There is a Set of Landscape Parks of Knyszyńska Forest in the river catchment. The river is the source of drinking water supply for Białystok agglomeration (surface intake); its catchment is within indirect protective zone. Localization of sampling points was selected to evaluate the influence and range of disposed sewage from villages and main tributaries within the catchment area. Six sampling and measuring points were localized at river Supraśl: Topolany, Michałowo, Gródek, Supraśl, Nowodworce, and Fasty. Also smaller flows in river Supraśl catchment were included in studies: Biała, Płoska, and Czarna, where three sampling points at each river were situated, two at river Słoja, and four at river Sokołda.

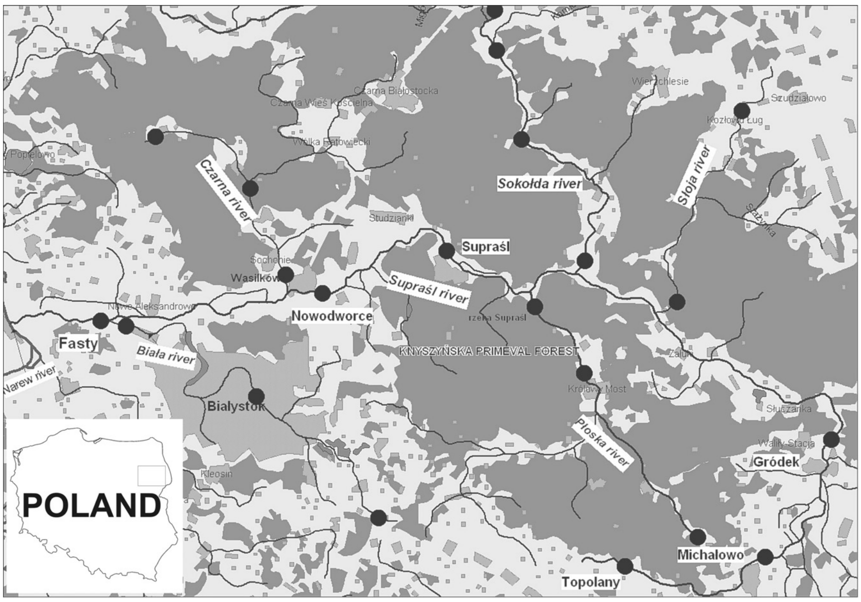


Fig. 1. Sediment sampling points

Investigations of river Supraśl and its tributaries were carried out in March, May, August, and October 2006. CARVALHO et al. (1999) claim that the sampling should made at least in two seasons (dry and wet) to verify study and make results more credible. Bottom sediments were collected in the shore zone, where the sedimentation of suspended material takes place. The sediment representative sample for each point was achieved by mixing several primary samples collected from different shore sites within the river bed from the layer of 0.05 m thickness and at the amounts not less than 0.5 kg. Bottom sediment samples were air-dried and sieved through a polyethylene sieve (0.2 mm mesh). Fraction <200 μm was subjected to analysis, because of its most frequent occurrence in studied sediments (SKORBILOWICZ 2007), and most often applied at works associated with geochemical mapping (THALMANN et al. 1989; LIS and PASIECZNA 1995). According to FÖRSTNER (1981), fractions between 20 and 200 μm are suitable for evaluating the pollution influence. Total contents of Cd, Pb, Zn, Cr, Ni, Cu, and Co were determined in sediment samples after their previous digestion in nitric acid in closed microwave system MARS 5. At the same time, soluble forms of metals contained in bottom sediments were extracted using cool 1 M HCl (DEMBSKA et al. 2001; SNAPE et al. 2004). Incomplete sample digestion with hydrochloric acid makes possible to extract only a mobile part of heavy metals from the sediments, which is important for evaluating the level of environmental contamination (PARAFINIUK et al. 2005). DEMSKA et al. (2001) proposed a labile form of the metals (extraction with 1 $M\cdot dm^{-3}$HCl) instead of the total content, for the sediments contamination extent, because it better reflects the real metal concentration originating from the human activity. No sequential extraction was applied in present study due to low total metals contents in majority of samples; their concentrations in extracts corresponding to particular fractions were often below detection limits at AAS determinations. Metal concentrations were analyzed on spectrometer Varian SpectraAA-100. The method correctness was confirmed on a basis of reference material (NCSDC 73312) analysis (table 1).

Table 1

Results for reference material NCSDC 73312 from AAS technique, ($n = 4$, $p = 95\%$)

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

The method precision and accuracy was estimated by determining the reflux of 5 model samples at different concentrations of studied metals (table 2). The acidity of sediments in water suspension was determined by potentiometric measuring the pH value.

Table 2

Conditions and parameters of AAS sediments and plants determinations

Item	Detection range [mg·dm^{-3}]	Precision	Accuracy	Wavelength	Gap width
		%		nm	nm
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
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

Achieved results of studied metals contents were presented in reference to air-dried bottom sediments and compared to literature data. Geochemical background level (TUREKIAN and WEDEPHOL 1961; LIS and PIASECZNA 1995; BOJAKOWSKA and SOKOŁOWSKA 1998) and accumulation index (MÜLLER, 1981) were used to evaluate the level of sediment contamination with heavy metals.

Statistical computations. Following values were calculated for studied bottom sediments from river Supraśl and its tributaries: minimum and maximum, arithmetic mean, median, and standard deviation in accordance to recommendations of SPAHR and WYNN (1997) as well as JOHNES and BURT (1993). In total, 1350 results were computed in present investigations. Factorial analysis (FA), that is a multi-dimensional one and is applied to describe and explore large number of data, was used for statistical analysis. In order to separate factors, main components method was applied, which uses a primary correlation matrix for calculations. It is used in hydrochemical research to describe processes occurring in surface and underground waters as well as to identify the supplying sources and origin of substances shaping the chemical composition of an aqueous environment (SIMEONOVA et al. 2003; SIMEONOV et al. 2004). To interpret results from factorial analysis, it was accepted that associations of primary variable with a factor are strong when the absolute values of its charges are greater than 0.70 (EVANS et al. 1996; PUCKET and BRICKER 1992). Also cluster analysis (CA) – Ward agglomeration method – that is based on the notion of object's or variable's distance in a multi-dimensional space, was applied in result analysis. Achieved results of bottom sediments determinations were also subjected to analysis using neuron networks to estimate the influence of particular river Supraśl tributaries on heavy metals contents in its bottom sediments as well as to predict the their concentrations changes.

3. RESULTS AND DISCUSSION

Results related to heavy metals and other indices determined in bottom sediments of river Supraśl and its tributaries are presented in tables 3 and 4.

Table 3

Results for grain fraction (<200 μm) of bottom sediments from river Supraśl collected during the whole study period

Statistical data	pH in H_2O	Cd		Pb		Zn		Cr		Ni		Cu		Co	
		Bottom sediments $n = 24$, $mg \cdot kg^{-1}$ DM													
		tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.
Minimum	6.19	0.43	0.07	3.5	0.4	10.2	4.3	1.8	0.5	5.4	0.1	0.8	0.1	2.1	0.6
Maximum	7.55	1.14	0.51	35.5	15.6	67.3	30.8	15.7	5.1	17.9	3.9	16.4	10.1	8.9	5.2
Arithmetic mean	–	0.81	0.25	16.3	4.5	34.6	16.7	7.3	1.4	9.9	1.6	6.8	3.2	4.7	1.6
Median	–	0.83	0.26	15.0	3.6	34.3	15.5	6.4	1.1	9.5	1.4	5.9	2.8	4.4	1.6
Standard deviation	–	0.22	0.13	8.55	3.81	16.93	3.40	3.41	1.03	3.24	0.95	4.43	2.40	1.64	0.95

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

Table 4

Results for grain fraction (<200 μm) of bottom sediments from river Supraśl tributaries collected during the whole study period

Statistical data	pH in H_20	Cd		Pb		Zn		Cr		Ni		Cu		Co	
		Bottom sediments $n = 66$, $mg \cdot kg^{-1}$ DM													
		tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.	tot.	sol.
Minimum	6.81	0.12	0.03	2.2	0.2	11.8	5.2	1.2	0.4	3.9	0.4	1.3	0.1	1.8	0.6
Maximum	7.52	1.89	0.67	57.2	32.4	187.2	87.3	42.1	19.5	17.8	5.1	33.9	21.9	7.3	3.6
Arithmetic mean	–	0.71	0.21	15.6	4.6	42.9	21.1	8.4	2.4	8.9	1.5	6.3	3.1	3.9	1.7
Median	–	0.61	0.15	12.3	2.4	29.1	13.2	6.1	1.3	8.3	1.3	3.8	1.5	3.7	1.5
Standard deviation	–	0.36	0.18	10.84	6.20	36.32	18.24	9.06	3.68	3.44	1.04	6.94	3.94	1.36	0.77

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

The acidity of sediments for majority cases was neutral. Statistical analysis of bottom sediments did not reveal significant correlation between the acidity and total and soluble fractions of studied elements contained.

Total cadmium amounts in analyzed fraction from bottom sediments collected in river Supraśl were within the range of 0.43–1.14 $mg \cdot kg^{-1}$ DM (median 0.83 $mg \cdot kg^{-1}$), while in tributaries 0.12–1.89 mg·kg^{-1} DM (median 0.61 mg·kg^{-1}). The geochemical background values for cadmium were accepted for aqueous sediments in Poland as <0.5 mg·kg^{-1} DM (LIS and PASIECZNA 1995; BOJAKOWSKA and SOKOŁOWSKA 1998). A concentration not exceeding 1 mg·kg^{-1} DM was proposed for sediments of the 1st quality class (BOJAKOWSKA and SOKOŁOWSKA 1998). For < 200 μm fraction, only at two points at river Supraśl (Fasty) and river Biała (Białystok), cadmium concentration was greater than 1 mg·kg^{-1} DM. Contents of cadmium in sediments of studied rivers were much lower than in upper Vistula (WARDAS 2000), and comparable or slightly higher to those found in river Dunajec (WIŚNIOWSKA-KIELIAN and NIEMIEC 2005). Levels of soluble cadmium for all investigated rivers were low ranging from 0.03 up to 0.67 mg·kg^{-1}. As expected, the dependence between total cadmium content and its soluble form was detected; the correlation coefficient was $r = 0.7589$ significant at $p < 0.01$. Also dependence between total cadmium concentration and soluble forms of zinc, chromium, and lead in sediments were observed ($r_{Zn} = 0.684$, $r_{Zn} = 0.712$ at $p < 0.01$; $r_{Cr} = 0.533$, $r_{Cr} = 0.539$, as well as $r_{Pb} = 0.514$, and $r_{Pb} = 0.586$ at $p < 0.001$).

Median for lead content in bottom sediments of river Supraśl and its tributaries were 15.0 mg·kg^{-1} DM and 12.3 mg·kg^{-1} DM, respectively. Value of geochemical background for lead is 10 mg·kg^{-1} DM, and its content for the 1st quality class should not exceed 50 mg·kg^{-1} DM (BOJAKOWSKA and SOKOŁOWSKA 1998). About 45% of sediment samples contained more lead than geochemical background, while all of them were within the 1st quality class with the exception of those collected in August 2006 from river Biała in Białystok, where lead concentration was 57.2 mg·kg^{-1} DM. Studies upon bottom sediments in river Odra and its tributaries in 1997–2000 revealed values from 19.2 up to 418 mg·kg^{-1} (HELIOS-RYBICKA et al. 2001). Content of soluble lead in bottom sediment of investigated rivers was from 0.2 to 32.4 mg·kg^{-1}. The share of soluble forms in total lead content ranged from 20% to 30%. The highest lead amounts were found in sediment samples from river Biała that is a receiver of sewage from Białystok. The dependence between total lead content and its soluble form was confirmed at correlation coefficient $r = 0.874$ significant at $p < 0.01$.

Studied sediments may be considered as not contaminated with zinc, because values of 48 mg·kg^{-1} (BAJAKOWSKA and SOKOŁOWSKA 1998) and 98 mg·kg^{-1} (TUREKIAN and WEDEPHOL, 1961) are commonly accepted as geochemical background, while achieved results in majority of cases are within the range of 10 to 45 mg·kg^{-1}. Elevated zinc levels occurred only in river Supraśl in Fasty (67.3 mg·kg^{-1} in March and 59.6 mg·kg^{-1} in October), whereas the highest zinc concentrations were recorded in river Biała (111.5 mg·kg^{-1} in March, 162.2 mg·kg^{-1} in August, and 187.2 mg·kg^{-1} in October). Much higher zinc concentrations were found by VICENTE-BECKETT (1992) in rivers on Luzon Island (Philippines), where median for zinc was 95 mg·kg^{-1}. Content of soluble zinc in sediments oscillated from 4.3 to 87.3 mg·kg^{-1}. Relatively high level of soluble form proves great zinc mobility. Such dependence is also indicated by the share of soluble in total zinc form that ranged from 45% to 55%. It was found that there was very strong dependence between total and labile zinc form content; correlated coefficient was $r = 0.977$ at significance level of $p < 0.01$. Also dependence between total zinc concentration and copper and chromium soluble forms amounts in sediments was observed ($r_{Cu} = 0.798$, $r_{Cu} = 0.816$ at $p < 0.05$; $r_{Cr} = 0.795$, $r_{Cr} = 0.831$ at $p < 0.01$).

Concentration of total chromium in studied bottom sediments was from 1.2 to 42.1 $mg \cdot kg^{-1}$. Taking the results in a view of geochemical background for chromium given by BOJAKOWSKA and SOKOŁOWSKA (1998) and amounting to 5 $mg \cdot kg^{-1}$, it should be stated that the element amounts were not exceeded at 37 sampling points (about 41%). TUREKIAN and WEDEPHOL (1961) found that natural chromium concentration in bottom sediments reached 90 $mg \cdot kg^{-1}$. The highest recorded concentration of the metal was observed in river Biała (42.1 $mg \cdot kg^{-1}$) and it was not higher than 90 $mg \cdot kg^{-1}$. Chromium contents in sediments of studied rivers were comparable to those in river Dunajec (KIELIAN-WIŚNIOWSKA and NIEMIEC 2005), while lower than found in river Wilga (WARDAS et al. 2004). Content of soluble chromium forms ranged from 0.4 to 19.5 $mg \cdot kg^{-1}$. Relatively low content of its soluble fraction may prove the poor chromium mobility, which is also indicated by the percentage of soluble in total form that in majority of investigated rivers was from 10% to 25%. In reference to chromium content in bottom sediments, statistically significant correlation between total and soluble chromium forms was found ($r = 0.936$ at $p < 0.01$).

Studies revealed that nickel concentration ranged from 3.9 to 17.9 $mg \cdot kg^{-1}$ at median for river Supraśl amounting to 9.5 $mg \cdot kg^{-1}$, and 8.3 $mg \cdot kg^{-1}$ for tributaries. LIS and PASIECZNA (1995) gave median value for nickel as 6 $mg \cdot kg^{-1}$ for sediments in Polish surface waters. However, it should be noticed that even the highest recorded contents were lower than 68 $mg \cdot kg^{-1}$, which TUREKIAN and WEDEPHOL (1961) consider as geochemical background value. Share of soluble in total nickel forms in majority of studied bottom sediments was about 10–20%. The metal easily forms quite durable chelates and complex cations and anions. As similar as above described metals, the dependence between total and soluble form concentrations occurred ($r = 0.864$ at $p < 0.05$).

Median for copper in studied sediments from river Supraśl was 5.9 $mg \cdot kg^{-1}$, while in tributaries it was 3.8 $mg \cdot kg^{-1}$. Referring to natural geochemical copper level given by BOJAKOWSKA and SOKOŁOWSKA (1998) amounting to 6 $mg \cdot kg^{-1}$, it should be concluded that the element limit was not exceeded. Similarly as in the case of other metals, the highest copper amounts were found in river Biała. Studies upon the bottom sediments in river Odra and its tributaries in 1997–2000 revealed much higher copper levels from 15.0 up to 1276 $mg \cdot kg^{-1}$ (HELIOS-RYBICKA et al. 2001). The percentage of soluble in total copper forms, in majority of studied sediments, was within the range of 20–50%. Statistically significant difference between total and soluble copper was present ($r = 0.932$ at $p < 0.05$).

Cobalt concentration in bottom sediment oscillated within the range of 1.8–8.9 mg·kg^{-1}. According to TUREKIAN and WEDEPHOL (1961), the geochemical background value is 19 mg·kg^{-1}. Taking into account such level, studied samples can be considered as not contaminated by cobalt. Content of soluble cobalt forms was relatively low ranging from 0.3 to 5.2 mg·kg^{-1}. Also very strong dependence between total and soluble cobalt forms was observed; the correlation coefficient was $r = 0.932$ at $p < 0.05$.

Contamination changes of bottom sediments in river Supraśl and its tributaries is present using geochemical classification using index I_{geo} proposed by MÜLLER (1981) for loamy river bottom sediments. Studied sediments were characterized as:

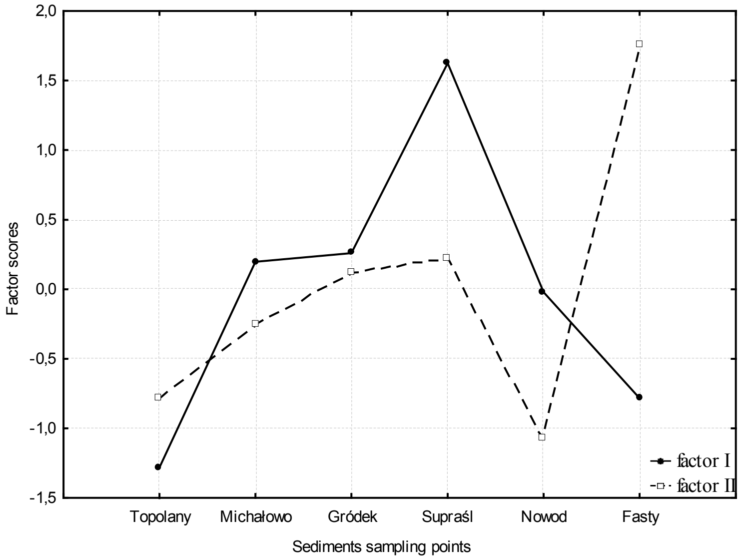
– non-contaminated to moderately contaminated with cadmium – surplus of 1st class;

– non-contaminated with: nickel, zinc, copper, chromium, cobalt, and lead – class 0.

Achieved results from determinations of bottom sediments in river Supraśl were subjected to multi-factorial analysis on a base of „osypiska criterion" and „Kaiser criterion"; two factors: PC1 63% and PC2 17% (80%) explaining the global variability of phenomena in analyzed system were selected (table 5).

Table 5

Results from factorial analysis (rotational method – normalized varimax, determined charges are > 0.7) and dynamics of factorial values changes at sampling points at river Supraśl



Variables	Factor I	Factor II
Cd (total forms)	0.14	**0.97**
Cd (soluble forms)	0.29	0.52
Pb (total forms)	0.68	0.59
Pb (soluble forms)	0.67	0.45
Zn (total forms)	0.39	**0.87**
Zn (soluble forms)	0.41	**0.86**
Cr (total forms)	0.46	**0.81**
Cr (soluble forms)	–0.05	**0.93**
Ni (total forms)	**0.96**	0.10
Ni (soluble forms)	**0.77**	0.12
Cu (total forms)	**0.88**	0.35
Cu (soluble forms)	**0.76**	0.25
Co (total forms)	**0.92**	0.32
Co (soluble forms)	**0.89**	0.21
Variance explained [%]	63	17

Factor I explains the variability of chemical composition in bottom sediments of river Supraśl in 63%. Positive factorial charges being „correlation coefficients" between variables (nickel, copper, and cobalt) and Factor I, including the highest share of the factor in sampling point Supraśl, were calculated. The interaction of Supraśl town that dispose purified and not treated municipal and farming, along with industrial sewage and water from storm drainage system, as well as river Sokołda, is the greatest in this case. Factor II explains processes making the supply of analyzed sediments in zinc and chromium. It explains in 17% the variability of chemical composition in bottom sediments of river Supraśl. Its maximum share is recorded at sampling point Fasty. Outlet of river Biała flowing through Białystok is localized above that point. It receives all municipal and household, motorization and industrial wastes containing zinc and chromium from the city.

Analysis of a dendrogram achieved from the cluster analysis can be the confirmation of above theses. Dendrogram in figure 2 presents on X axis 5 sampling points localized at river Supraśl. There are 2 main arrangements apparent. It is also seen large distance, at which arrangement II is joined with a group I, which significantly differentiates these two bundles. Arrangement I is formed from sampling points Nowodworce, Topolany included 2 points where the lowest levels of studied metals were recorded, which was confirmed due to multi-factorial analysis. Group II joins points exposed to anthropogenical influences, to their point sources in majority. That arrangement is apparently divided into 2 separate ones, among which III describes points exposed to pollution from Białystok, and IV to pollutions from sewage treatment plant and municipal and farming wastes from two small cities of rural character. There are wrong operating sewage treatment plants in those towns; they are one of the major sources of pollution in that region. Bundle forming arrangement V contains only one object called isolated point. The sampling point Supraśl is localized on a wide forest area (Knyszyńska Forest). There is also the sewage treatment plant in Supraśl town. The fact that the point is isolated is a confirmation of multi-factorial analysis (share of the highest value of Factor I at that point).

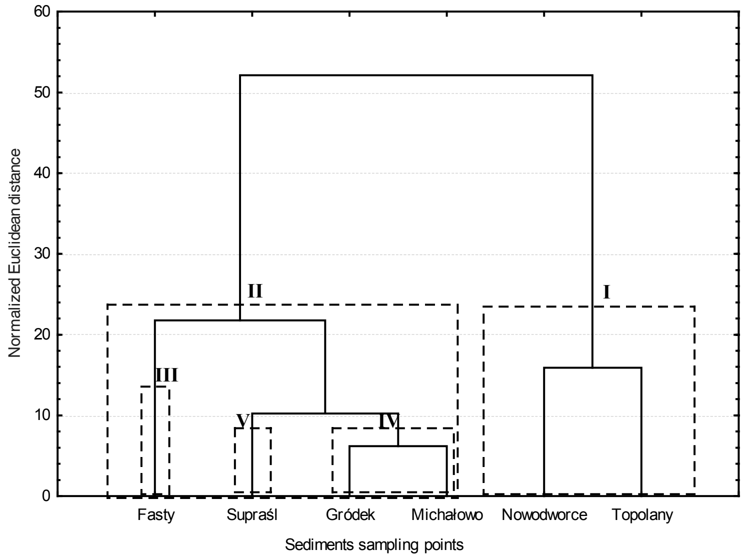


Fig. 2. Dendrogram of the CA according to Ward. Monitoring locations of river Supraśl

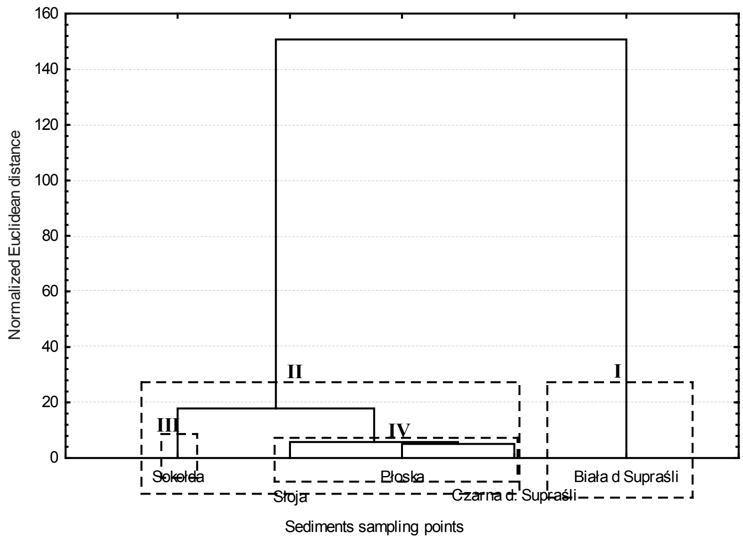


Fig. 3. Dendrogram of the CA according to Ward, tributaries of river Supraśl

Analysis of results from river Supraśl and its tributaries allowed for separating two bundles that are apparently differentiated due to large distance of the binding between them (figure 3). Therefore, point I being isolated presents Biała – river Supraśl tributary. As mentioned, that river carries high loads of pollution from Białystok. A single bundle III is contained in arrangement II: it is river Sokołda flowing almost completely through woody areas and being a receiver of purified sewage from Sokółka town, thus probably that fact determined the localization of the point on a dendrogram. Other rivers characterizing by uniform concentrations of studied metals in bottom sediments form arrangement IV.

Present study was also aimed at the evaluating of the influence of selected river Supraśl tributaries on heavy metals concentrations in its bottom sediments applying artificial neuron networks. CLAIR and EHERMAN (1998) as well as LISCHEID (2001) also applied similar methods. Proposition of such solution is one of possible and permissible procedures at modeling such generalized environmental interactions. A three-layer network structure (with one hidden layer) and reciprocal error propagation was proposed for a model building (figure 4); it is so-called multilayer perceptrone (MELESSE and HANLEY 2005). Reciprocal error propagation was used to the network learning, and analyses were performed using licensed software Statistica ver. 7.1. An artificial neuron network was accepted: 3 neuron layers, one hidden layer, 5 neurons in the first input layer, and 1 neuron in output layer. The first layer is represented by 5 tributaries of river Supraśl: Biała, Czarna, Płoska, Słoja, and Sokołda. The output layer is represented by river Supraśl. The network has the following parameters: learning quality = 0.064294, validation quality = 0.366807, test quality = 0.473552. Analysis of particular input neurons sensitivity revealed that river Biała (rank 5), then Sokołda (rank 4), Płoska (rank 3), Słoja (rank 2), and Czarna (rank 1) had the greatest influence on heavy metals concentrations in bottom sediments of river Supraśl.

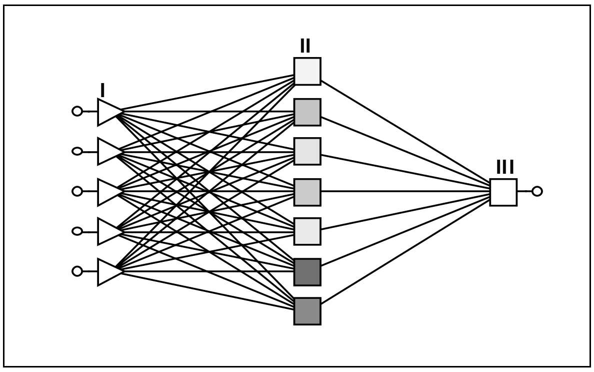


Fig. 4. Structure of applied neuron network:
I – input neuron layer; II – hidden neuron layer; III – output neuron layer

4. CONCLUSIONS

Wastes disposed from larger towns and cities are the anthropogenic foci of river Supraśl and its tributaries pollution. Białystok, then Supraśl, Sokółka, Gródeka, and Michałowo are such cities. Pollution carried from Białystok had significant influence on the increase of heavy metals in bottom sediments in rivers Biała and Supraśl at sampling point Fasty (55 000 inhabitants). There are also two transportation tracts (road and railroad) at the point where river Biała flows into the river Supraśl that may affect the concentrations of studied elements. It should be taken into account that larger part of river Biała catchment is covered by urbanized area, therefore water is exposed to a continuous disposal of wastes supplied through the storm drainage system and purified sewage. Foodstuff and agricultural processing works, factories of building materials, metallurgic industry and electric plants, textile, spirit, and brewery works are localized in Białystok. Difference of metals contents in river Supraśl tributaries resulted mainly from the character of the surrounding catchment. Metals in rivers: Słoja, Płoska, and Czarna, are characterized by low levels close to geochemical background, which is determined by geochemical structure of that area as well as its management status. It seems that sediments from those flows are genetically closely associated with the material of direct catchment of studied rivers.

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