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AQUATIC PLANTS AS BIOINDICATORS OF CONTAMINATION OF UPPER NAREW RIVER AND SOME OF ITS TRIBUTARIES WITH HEAVY METALS

In this study, the contents of cadmium, nickel, zinc, copper, chromium, cobalt and lead were analysed in the roots of *Glyceria aquatica, Phragmites australis* and *Acorus calamus*, living in the upper Narew River and some of its tributaries as well as in bottom sediments of those watercourses. The concentrations of the above chemical elements were determined by means of atomic absorption spectrometry (AAS). Anthropogenic, economic and municipal activities as well as traffic and run-offs are responsible for heavy metal accumulation in bottom sediments and aquatic plant roots. The study performed revealed that plant material and bottom sediments of the Narew River and its tributaries are mostly contaminated with cadmium.

1. INTRODUCTION

Heavy metals are the most troublesome and widely investigated contaminants of rivers (CALMANO et al. [2]). Various pollutants, including heavy metals, are mainly accumulated in river bottom sediments (XIANDONG et al. [10], VILLARES et al. [9]). An assessment of aquatic environment conditions is based on the determination of heavy metal concentrations in flora and fauna living in water reservoirs or watercourses. This can be a valuable source of information on qualitative and quantitative changes occurring in aquatic ecosystems.

The aim of this study was to determine the content of cadmium, nickel, zinc, copper, cobalt, chromium and lead in bottom sediments and in the roots of *Glyceria aquatica, Phragmites australis* and *Acorus calamus* in the upper Narew River and its tributaries.

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2. MATERIALS AND METHODS

The investigation was performed in early summer and late autumn 2007 at 8 intersections located at the Narew River and 18 of its tributaries (table 1, figure 1). The total content as well as soluble forms of cadmium, nickel, zinc, copper, chromium, cobalt and lead were analysed in the plant material (reed manna grass (*Glyceria aquatica*), common reed (*Phragmites australis*) and calamus (*Acorus calamus*)) and in bottom sediments. The species investigated occurred at all the sampling sites. Bottom sediment samples were taken near riverbanks, where suspended material settles. Prior to analyses, the samples were air-dried and sieved through a nylon sieve of 0.2 mm mesh size (LIS and PASIECZNA [6]). Simultaneously with bottom sediment sampling, at the same sites the roots of reed manna grass, common reed and calamus were collected and air-dried as well. Then, dry bottom sediments and plant material were mineralized in nitric acid in the CEM Mars-5 microwave system. Simultaneously, the soluble forms of metals were extracted from bottom sediments using cold 1 mol·dm^{-3} HCl (SNAPE et al. [7]). The concentrations of heavy metals were determined by means

Table 1

List of sampling sites at Narew River and its tributaries

Sampling site no.	River	Adjacent place	Sampling site no.	River	Adjacent place
1	Narew	Bondary	21	Orlanka	Orla
2	Narew	Ploski	22	Sokołda	Bogusze
3	Narew	Doktorce	23	Sokołda	Sokółka
4	Narew	Uhowo	24	Sokołda	Straż
5	Narew	Rzędziany	25	Sokołda	Sokołda
6	Narew	Złotoria	26	Awisa	Lapy
7	Narew	Siekierki	27	Czaplinianka	Niewodnica
8	Narew	Tykocin	28	Horodnianka	Choroszcz
9	Supraśl	Mościska	29	Loknica	Stupniki
10	Supraśl	Michałowo	30	Małynka	Folwarki
11	Supraśl	Supraśl	31	Mieńka	Kożany
12	Supraśl	Nowodworce	32	Ruda	Narew
13	Supraśl	Fasty	33	Rudnia	Trześcianka
14	Narewka	Eliaszuki	34	Rudnik	Barszczewo
15	Narewka	Lewkowo	35	Turośnianka	Stoczki
16	Narewka	Bialowieża	36	Biała	Białystok
17	Nereśl	Piaski	37	Biała	Białystok
18	Nereśl	Czechowizna	38	Biała	Białystok
19	Orlanka	Chraboły	39	Słoja	Lipowy Mst.
20	Orlanka	Kotly	40	Ploska	Przychody

of AAS (atomic absorption spectrometry) technique using the Varian SpectraAA-100 spectrometer. The correctness of the method was confirmed by the analyses of reference material NCSDC 73312. The reaction of bottom sediments in a suspension was measured by potentiometric method.

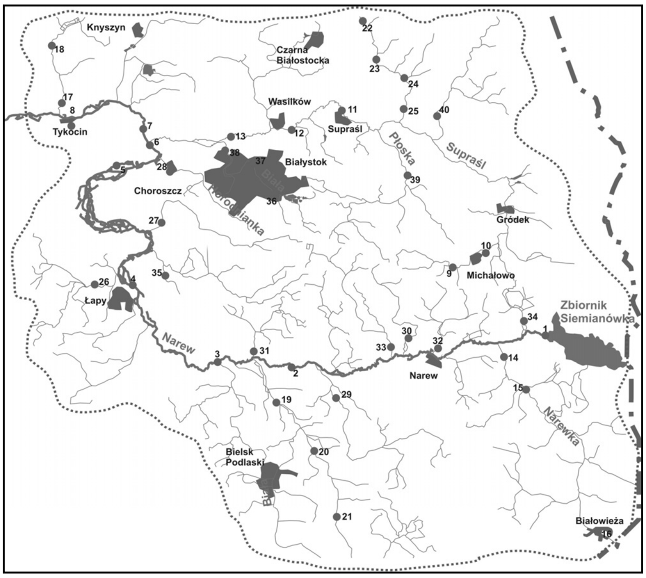

Fig. 1. Sampling area

The contamination of bottom sediments with heavy metals was assessed using the classification of aquatic sediments in Poland based on geochemical criteria (BOJAKOWSKA and SOKOŁOWSKA [1]). The physiological standard of metal content in plants was given by KABATA-PENDIAS and PENDIAS [5]. The statistical analyses of the data obtained included principal component analysis (PCA) and Ward's cluster analysis (CA), which determine the distance of objects or variables in a multidimensional space. All the calculations were performed using Statistica 7.1 software.

3. RESULTS AND DISCUSSION

The concentrations of metals in the bottom sediment samples of the upper Narew River and its tributaries are given in table 2. They revealed a considerable variability, depending on the grain-size distribution as well as on location of a sampling site, both for total and labile forms. Medians of total concentrations of particular elements in summer and autumn, respectively, were equal to: 0.5 and 1.3 mg·kg^{-1} for cadmium, 11.4 and 14.0 mg·kg^{-1} for lead, 24.2 and 32.6 mg·kg^{-1} for zinc, 9.0 and 7.5 mg·kg^{-1} for chromium, 7.1 and 7.6 mg·kg^{-1} for nickel, 11.3 and 3.3 mg·kg^{-1} for copper, and 2.8 and 5.9 mg·kg^{-1} for cobalt. Mean total contents of heavy metals in the grain fraction investigated can be arranged in the following descending order: Zn > Pb > Cr > Cu > Ni > Co > Cd. The analysis of only total metal concentrations accumulated in bottom sediments does not allow us to properly assess the conditions of a riverine environment, since it does not give any information about metal mobility. Labile forms are mostly of anthropogenic and biochemical origin. In the environment, those fractions are of great importance because they can be desorped from bottom sediments to water and later accumulated in benthic organisms (DEMBSKA et al. [3]). Our study indicated that medians for labile forms (table 2) reached the following values: 0.22 and 0.23 mg·kg^{-1} for cadmium, 2.6 and 3.3 mg·kg^{-1} for lead, 13.1 and 14.4 mg·kg^{-1} for zinc, 1.1 and 1.9 mg·kg^{-1} for chromium, 1.1 and 1.3 mg·kg^{-1} for nickel, 1.5 and 2.1 mg·kg^{-1} for copper, 0.9 and 1.1 mg·kg^{-1} for cobalt. The average concentrations of labile metal forms can be arranged in the following descending order: Zn > Pb > Cu > Cr > Ni > Co > Cd. Both cadmium and cobalt occurred in the highest total and labile

Table 2

Results of chemical analysis of bottom sediment grain fraction of <0.2 mm from Narew River and its tributaries

Statistical parameters	Summer, n = 40														
	pH in H_2O	(mg·kg^{-1}d.m.)													
		Cd		Pb		Zn		Cr		Ni		Cu		Co	
		Total	Labile	Total	Labile	Total	Labile	Total	Labile	Total	Labile	Total	Labile	Total	Labile
Minimum	6.54	0.25	0.08	3.5	0.2	14.2	4.8	4.1	0.4	4.5	0.4	6.6	0.5	1.4	0.5
Maximum	7.80	1.49	0.78	39.7	26.2	189.3	89.5	47.6	10.4	13.9	6.6	33.1	12.1	6.9	1.7
Arithmetic mean	–	0.64	0.26	15.0	5.8	36.9	19.0	11.2	1.8	7.6	1.3	12.1	2.7	3.0	0.9
Median	–	0.5	0.22	11.4	2.6	24.4	13.1	9.0	1.1	7.1	1.1	11.3	1.5	2.8	0.9
Standard deviation	–	0.29	0.16	10.11	6.94	32.40	18.25	8.08	2.37	2.18	1.11	5.16	2.75	0.99	0.28
Autumn, n = 40															
Minimum	6.62	0.8	0.05	4.9	0.2	12.7	6.7	1.9	0.4	5.5	0.4	0.9	0.6	3.3	0.4
Maximum	7.91	3.1	0.65	47.0	23.1	198.3	104.2	54.1	10.9	26.1	8.7	21.1	10.9	10.1	2.6
Arithmetic mean	–	1.45	0.24	17.8	5.3	48.5	23.2	11.1	2.7	8.7	1.4	5.2	2.9	6.0	1.2
Median	–	1.3	0.23	14.0	3.3	32.6	14.4	7.5	1.9	7.6	1.3	3.3	2.1	5.9	1.1
Standard deviation	–	0.57	0.14	11.13	5.67	52.9	24.08	11.08	2.53	3.68	1.29	5.02	2.74	1.69	0.55

form concentrations in bottom sediments. The ratios of labile to total form contents, expressed in per cent, may be arranged in descending order: Zn > Pb > Cu > Co > Cd > Ni > Cr. This reflects the mobility of those heavy metals as well as their anthropogenic origin.

Our investigation revealed a relatively low content of a labile form of chromium in its total content. In most of the samples, this species ranged from 15 to 20%. KABATA-PENDIAS and PENDIAS [5] reported that chromium is one of the least mobile trace metals in the environment. In non-contaminated bottom sediments, it occurs in a durable form which makes 84% at the maximum (ŚWIETLIK [8]). Zinc, in contrast to chromium, is one of the most mobile metals, which was confirmed by our study. The percentage of its labile form in the total species content in most of the bottom sediments studied varied between 40 and 70%. The labile forms of lead and copper constituted on average 30–40% of their total concentrations, in the case of cadmium and cobalt it was 20–30%, while for nickel – from 15 to 25%, since that metal is the component of rather stable chelates as well as of cation and anion complex compounds. Taking into account the geochemical background of zinc and copper (BOJAKOWSKA and SOKOŁOWSKA [1]), the bottom sediments of interest proved to be free of those metals. The contents of the remaining metals allow bottom sediments to be classified into class I – non-contaminated (table 3). The only exception was cadmium, whose concentration in autumn in ca. 50% of samples slightly exceeded that of the geochemical class I. Such anthropogenic activities as run-off from inappropriately fertilized agricultural areas or discharges from sewage treatment plants were mostly responsible for that high cadmium content. The other important source of cadmium in the environment is also exhaust gas.

Table 3

Geochemical classification of bottom sediments from upper Narew River and its tributaries [2]

Sampling season	Cd	Pb	Zn	Cr	Ni	Cu	Co
Summer 2007	I	I	background	I	I	I	I
Autumn 2007	II	I	background	I	I	background	I

The other indicator, which determines the influence of anthropopression on natural ecosystems, is the content of heavy metals in aquatic plants. It reflects the amount of bioavailable forms of metals in the environment and is a valuable completion of bottom sediment investigation. The contents of cadmium, lead, zinc, chromium, nickel, copper and cobalt measured in the roots of reed manna grass (*Glyceria aquatica*), common reed (*Phragmites australis*) and calamus (*Acorus calamus*) are given in table 4 and figures 2–8.

Table 4

Results of chemical analysis of vascular plant roots from upper Narew River and its tributaries

Statistical parameters	Cd		Pb		Zn		Cr		Ni		Cu		Co	
	Summer	Autumn	Summer	Autumn	Summer	Autumn	Summer	Autumn	Summer	Autumn	Summer	Autumn	Summer	Autumn
Reed manna grass (*Glyceria aquatica)* (mg·kg^{-1}d.m.), *n* = 40														
Minimum	0.9	0.7	1.8	1.4	9.7	12.4	1.7	3.1	3.7	3.1	8.2	2.6	0.4	0.4
Maximum	2.9	4.9	27.5	24.0	421.2	345.1	26	31.9	58.9	48.2	141.3	33.7	19.0	10.2
Arithmetic mean	2.0	1.8	10.6	6.9	62.9	53.4	11.5	7.9	12.6	10.5	23.4	8.0	2.6	2.2
Median	2.0	1.8	9.4	5.5	37.4	35.2	9.5	7.7	8.9	8.2	14.6	5.8	1.9	1.8
Standard deviation	0.55	0.77	6.58	5.62	79.26	62.70	6.58	4.46	10.31	8.53	23.8	7.48	3.09	1.91
Calamus (*Acorus calamus*) (mg·kg^{-1}d.m.), *n* = 40														
Minimum	1.2	0.95	2.5	1.5	6.4	5.9	2.7	1.2	2.9	1.1	6.9	2.2	0.7	0.5
Maximum	4.1	3.8	26.2	23.4	159.3	145.1	25.3	16.8	31.2	25.6	132.4	82.1	12.4	10.4
Arithmetic mean	2.1	1.7	14.9	11.3	40.8	33.5	11.5	7.4	9.6	7.8	26.4	13.4	2.8	2.2
Median	2.0	1.6	16.9	12.3	27.2	26.6	11.4	7.9	7.4	6.2	17.3	6.8	1.8	1.5
Standard deviation	35.75	0.56	6.16	6.03	34.14	27.84	5.52	3.20	6.73	5.74	24.10	17.13	2.38	1.94
Common reed (*Phragmites australis*) (mg·kg^{-1}d.m.), *n* = 40														
Minimum	1.17	0.97	1.14	1.0	11.9	10.2	1.9	1.3	1.2	1.1	7.8	2.6	0.3	0.3
Maximum	3.65	3.21	28.1	21.3	463.6	34.8	76.9	49.7	167.3	147.7	147.9	92.1	14.0	13.0
Arithmetic mean	2.2	1.0	12.5	9.8	71.1	54.7	14.5	9.2	14.3	11.9	24.0	10.5	2.7	2.3
Median	2.2	1.7	13.2	9.5	46.8	41.2	10.7	7.3	8.6	8.0	17.4	6.8	2.2	1.5
Standard deviation	0.61	0.58	8.2	6.9	86.5	64.5	13.2	8.4	25.3	22.3	23.8	14.7	2.5	2.2

The metals studied were accumulated by the above plants in the following desceding orders:

- reed manna grass (*Glyceria aquatica*): Zn > Cu > Cr > Ni > Pb > Cd > Co,
- common reed (*Phragmites australis*): Zn > Cu> Pb> Cr > Ni > Cd > Co,
- calamus (*Acorus calamus*): Zn > Cu> Pb> Cr > Ni > Cd > Co.

The coefficients of bioaccumulation in the roots of aquatic plants were arranged as follows (table 5):

- reed manna grass (*Glyceria aquatica*): Cd > Cu > Zn > Ni > Cr > Pb > Co,
- common reed (*Phragmites australis*): Cd > Cu> Zn> Cr > Ni > Pb > Co,
- calamus (*Acorus calamus*): Cd > Cu> Ni> Cr > Zn > Pb > Co.

Table 5

Bioaccumulation coefficients for plants grown in Narew River and its tributaries

Statistical parameters	Cd		Pb		Zn		Cr		Ni		Cu		Co	
	Summer	Autumn	Summer	Autumn	Summer	Autumn	Summer	Autumn	Summer	Autumn	Summer	Autumn	Summer	Autumn
Reed manna grass (*Glyceria aquatica*) (mg·kg^{-1}d.m.), n = 40														
Minimum	1.2	0.6	0.2	0.2	0.5	0.3	0.2	0.2	0.5	0.4	0.6	0.2	0.2	0.2
Maximum	11.5	2.8	2.9	2.6	5.5	4.6	2.5	4.3	4.8	2.3	5.9	5.4	9.1	1.2
Arithmetic mean	3.7	1.3	0.9	0.5	1.7	1.4	1.1	1.1	1.6	1.1	1.8	1.9	0.9	0.4
Median	3.4	1.4	0.8	0.4	1.3	1.1	1.0	0.8	1.3	1.0	1.5	1.7	0.6	0.3
Standard deviation	2.04	0.41	0.71	0.52	1.14	0.91	0.63	0.78	0.9	0.44	1.07	1.18	1.49	0.22
Calamus (*Acorus calamus*) (mg·kg^{-1}d.m.), n = 40														
Minimum	1.2	0.51	0.3	0.2	0.3	0.2	0.2	0.2	0.4	0.2	0.6	0.7	0.2	0.2
Maximum	3.0	3.2	3.5	1.7	5.4	2.5	2.5	4.1	2.8	1.3	4.0	9.3	6.0	1.8
Arithmetic mean	3.9	1.3	1.3	0.7	1.2	0.9	1.2	1.1	1.2	0.9	2.1	2.9	1.0	0.4
Median	3.4	1.3	1.1	0.6	1.0	0.7	1.2	0.8	1.9	0.8	1.9	2.6	0.7	0.3
Standard deviation	1.95	0.50	0.78	0.44	0.87	0.63	0.56	0.87	0.63	0.49	0.97	1.82	1.09	0.31
Common reed (*Phragmites australis*) (mg·kg^{-1}d.m.), n = 40														
Minimum	1.2	0.7	0.2	0.2	0.4	0.2	0.3	0.2	0.2	0.2	0.8	0.2	0.2	0.2
Maximum	7.9	2.2	7.3	2.7	5.7	3.2	3.1	7.1	13.5	5.7	4.5	5.5	6.7	1.5
Arithmetic mean	3.9	1.3	1.1	0.7	1.9	1.5	1.3	1.2	1.7	1.2	1.8	2.3	1.0	0.4
Median	3.7	1.2	0.7	0.4	1.8	1.3	1.2	1.1	1.1	1.0	1.7	2.1	0.7	0.3
Standard deviation	1.73	0.35	1.36	0.65	1.22	0.87	0.72	1.16	2.03	0.86	0.84	1.08	1.19	0.28

Habitat conditions, the type of local emission as well as sampling time influence the diversification of metal co-occurrence in roots and bottom sediments. In the roots of the plants studied, zinc and copper occurred in the highest concentration, while cobalt and cadmium – in the lowest one. According to KABATA-PENDIAS [4] the content of cadmium in plants varies considerably and most often ranges from 0.05 to 0.2 mg Cd·kg^{-1}. In all the root samples studied, it exceeded 0.2 mg·kg^{-1}. Cadmium bioaccumulation coefficient reached the highest values in summer. Our study showed that common reed and calamus accumulated metals in a similar way. The concentrations of lead, zinc, chromium, nickel, copper and cobalt in roots proved that the environment investigated was not contaminated with those chemical elements. Moreover, the metal concentrations in roots in most cases were comparable to those in bottom sediments – they were only slightly higher in summer and lower in autumn.

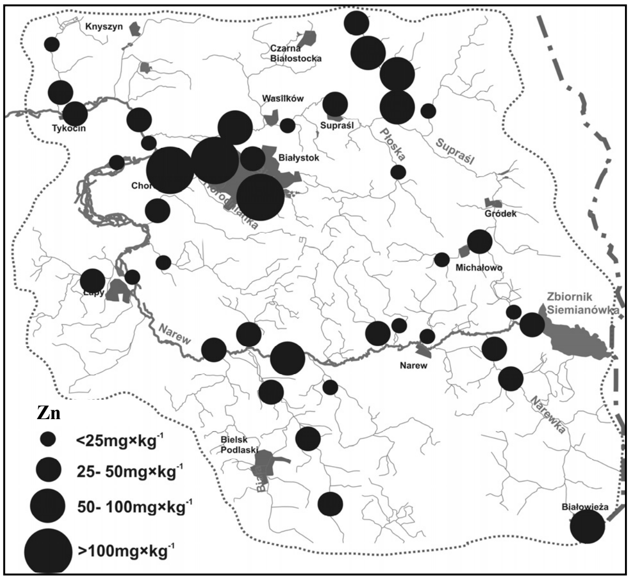

Fig. 2 Average content of zinc in plants

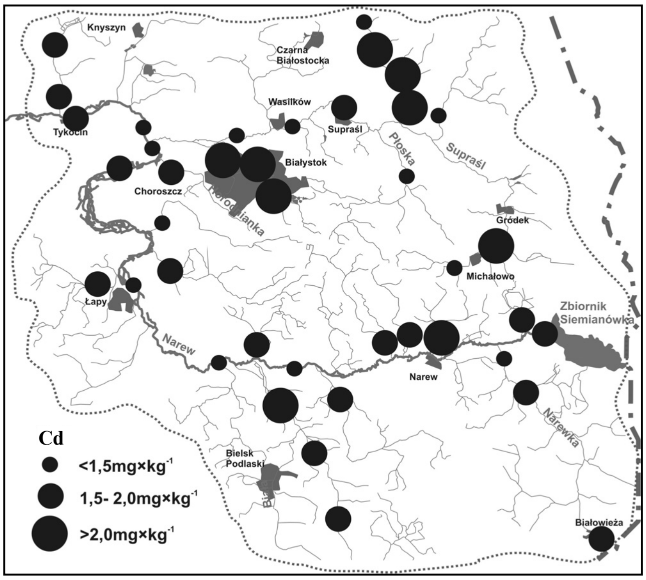

Fig. 3. Average content of cadmium in plants

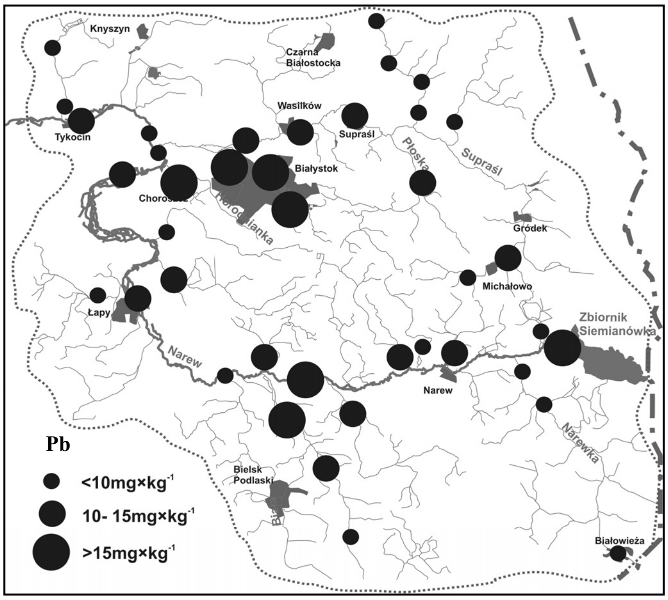

Fig. 4. Average content of lead in plants

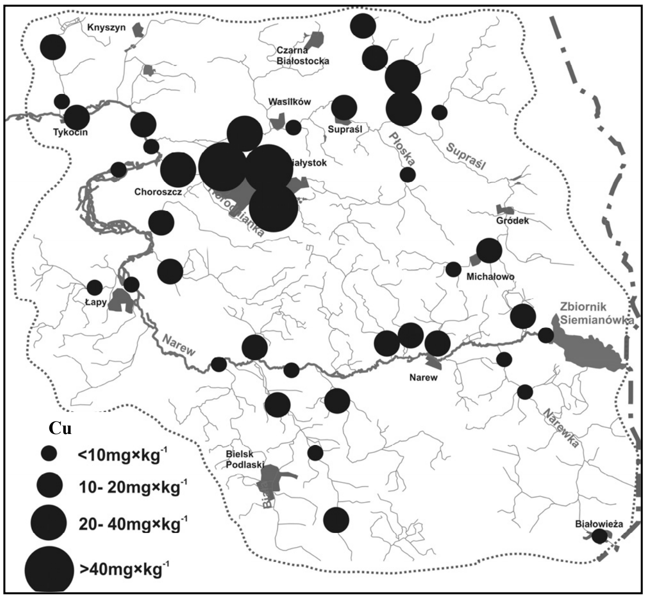

Fig. 5. Average content of copper in plants

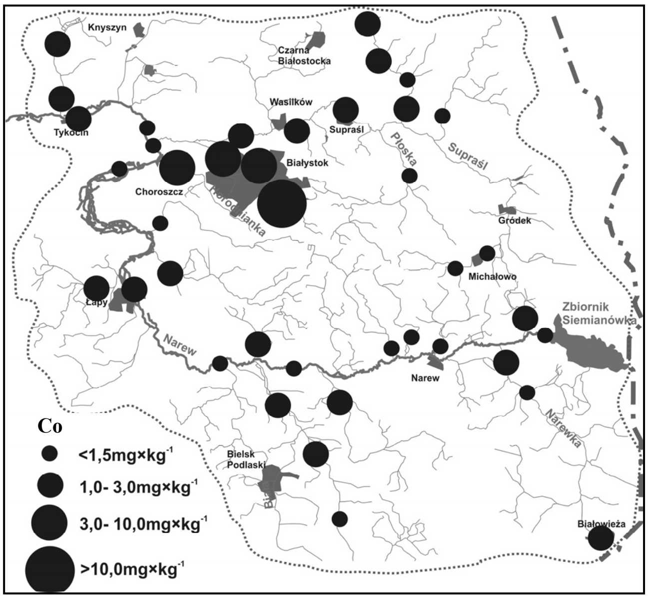

Fig. 6. Average content of cobalt in plants

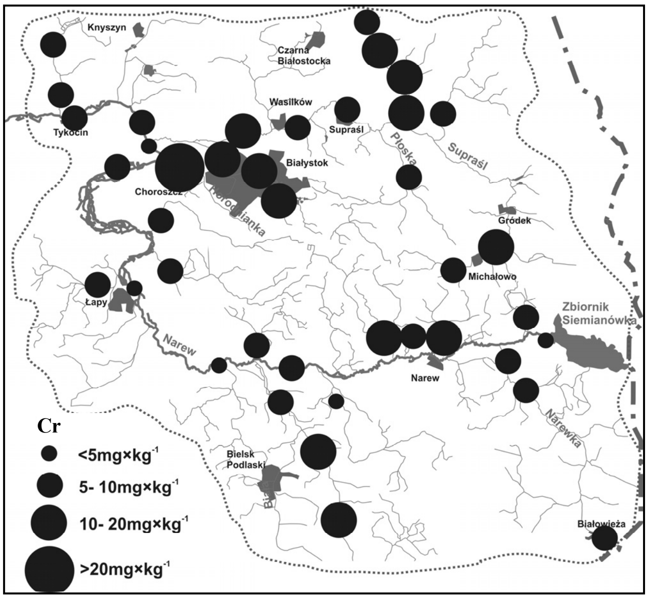

Fig. 7. Average content of chromium in plants

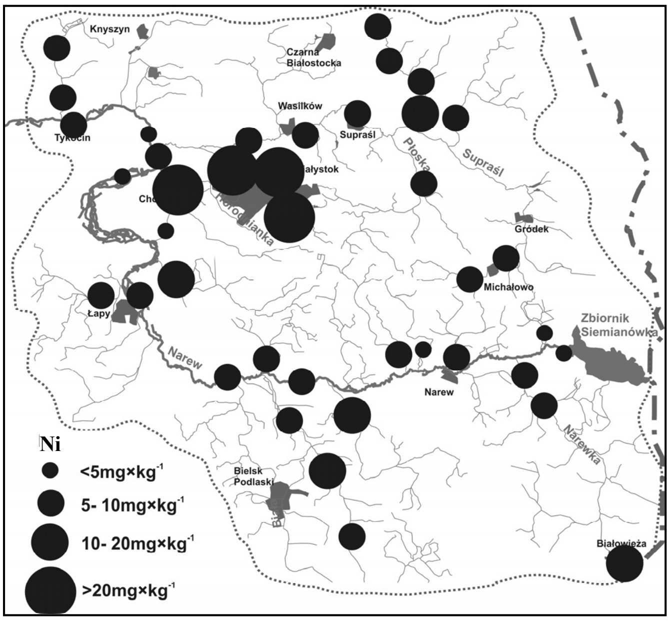

Fig. 8. Average content of nickel in plants

An anthropogenic source of river pollution in the Narew River catchment area is sewage of domestic and industrial origin, mostly coming from Białystok that lies on the Biała River (figures 2–8). The economy in Białystok (33000 inhabitants) is based on food-processing, power plants, building and metal industry as well as brewing and spirit industry. Higher concentrations of the metals analysed were also observed in bottom sediments and plant roots of the Supraśl River at the site Fasty (figures 2–8). In the area, where the Biała and the Supraśl Rivers join, there are two arterial roads, which can also contribute to an increase in the contents of the metals studied. The highest heavy metal concentrations were observed in the Horodnianka River at the sampling site no. 28 (figures 2–8). It flows near the municipal waste dump in Hryniewicze and is also influenced by municipal sewage from Choroszcz. Additional sources of pollution in the area studied are also run-offs from arable land. The lack of sewage systems in many villages and also traffic do not improve the water purity either.

The statistical analyses performed, i.e., principal component analysis (PCA) and cluster analysis (CA), showed similarities between the rivers studied in all the parameters investigated. Comparing the results of both methods one can conclude that the contents of metals in bottom sediments and in plant roots were similar in the Biała and the Horodnianka Rivers (figure 9). It was also statistically confirmed that the concentrations of heavy metals in plant roots depend on their contents in bottom sediments (correlation coefficient range of 0.315–0.913). The only exception was chromium because it is one of the least mobile trace metals in the environment.

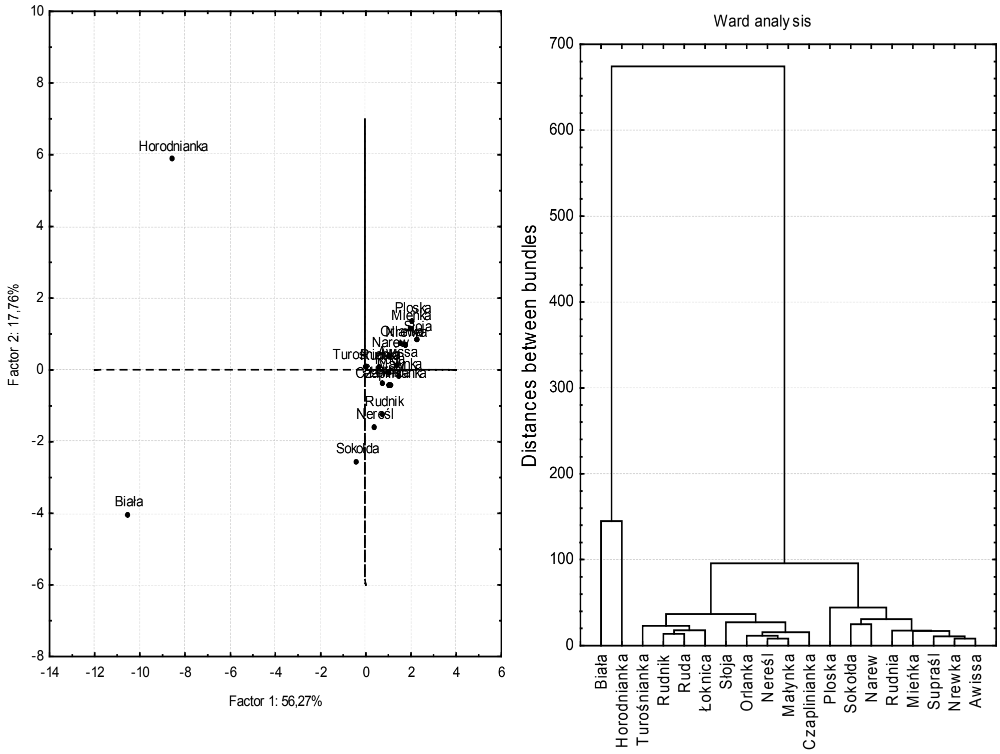

Fig. 9. Results of principal components analysis (PCA) and Ward's cluster analysis (CA) for rivers studied

4. CONCLUSIONS

1. The most probable sources of heavy metals accumulated in bottom sediments and plant roots in the upper Narew River and its tributaries are economic and municipal activities, including local transport and run-offs. The highest metal concentrations were observed in the Biała River (the tributary of the Supraśl River) and the Horodnianka River.

2. The plant material and bottom sediments in the Narew River and its tributaries were mainly contaminated with cadmium.

3. The concentrations of the metals under study revealed seasonal character. In summer, their concentrations in roots were in most cases higher, while in autumn–lower.

4. Our study revealed positive linear correlation between the contents of cadmium, nickel, zinc, copper, cobalt and lead in bottom sediments and their contents in the roots of aquatic plants, both for their total and labile forms.

5. Heavy metal concentrations in the material studied depended on a sampling site location.

6. Investigation of heavy metal contents in the roots of vascular plants proved to be a valuable source of information on the contamination of aquatic ecosystems and adjacent land ecosystems.

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ROŚLINY WODNE JAKO BIOINDYKATORY SKAŻENIA METALAMI CIĘŻKIMI WÓD GÓRNEJ NARWI I JEJ NIEKTÓRYCH DOPŁYWÓW

Oznaczono zawartość kadmu, niklu, cynku, miedzi, chromu, kobaltu i ołowiu w korzeniach: *Glyceria aquatica*, *Phragmites australis*, *Acorus calamus* oraz w osadach dennych wybranych rzek w dorzeczu górnej Narwi. Zawartość metali oznaczono metodą ASA. Źródłem metali w osadach dennych i korzeniach roślin wodnych badanych rzek i górnej Narwi jest działalność gospodarcza i bytowa człowieka, w tym wpływ lokalnej komunikacji, oraz spływy powierzchniowe. Badany materiał roślinny i osady denne Narwi i jej dopływów są zanieczyszczone głównie kadmem.