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MACROPHYTES AS INDICATORS OF HEAVY METALS BIO-ACCUMULATION IN UPPER NAREW RIVER

MAKROFITY JAKO WSKAŻNIKI BIOPRZYSWAJALNOŚCI **METALI CIĘŻKICH W GÓRNEJ NARWI**

Abstract: The study aimed at evaluating the cadmium, nickel, zinc, copper, cobalt, chromium and lead contents in bottom sediments, as well as roots and above ground parts of *Carex elata* and *Acorus calamus* in upper Narew River. Studies were carried out in summer 2008 at 10 measurement points localized on Narew River (Bondary, Ploski, Doktorce, Rzedziany, Uhowo, Bokiny Zlotoria, Siekierki and Tykocin). The metal concentrations were determined by means of AAS technique. Calculated bio-accumulation coefficients for roots of examined plants were following: *Carex elata* Co > Cu > Zn > Cd > Ni > Pb = Cr while for *Acorus calamus* $Co > Cu > Zn > Cd > Ni > Cr > Pb$. It can be supposed that household activity, including influences of a local transport and surface runoffs, were the main sources of examined metals deposited in bottom sediments and aquatic plants of upper Narew River. Studied plant material and bottom sediments were only slightly contaminated with cadmium.

Keywords: heavy metals, macrophytes, Narew River

Introduction

The problem of aquatic environment contamination with heavy metals is still serious despite of numerous activities associated with limitations of anthropogenic emission of these elements [1–4]. Evaluation of the aquatic environment quality includes monitoring of heavy metals contents in bottom sediments, as well as in flora and fauna living in water reservoirs or flows [5–10]. They may be a valuable source of information on qualitative and quantitative changes within rivers [11–13].

The aim of present study was to evaluate the cadmium, nickel, zinc, copper, cobalt, chromium and lead contents in bottom sediments, as well as roots and above ground parts of *Carex elata* and *Acorus calamus* in upper Narew River.

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Material and methods

The study was performed in summer 2008 at 10 measurement points localized on Narew River (Bondary, Ploski, Doktorce, Rzedziany, Uhowo, Bokiny Zlotoria, Siekierki and Tykocin). Plant material and bottom sediments were experimental material subjected to determinations of total contents of cadmium, nickel, zinc, copper, chromium, cobalt and lead, as well as their soluble forms. Tussock sedge (*Carex elata*) and sweet flag (*Acorus calamus*) grew at all studied points were test plants. The bottom sediment was collected from the shore zone where the sedimentation of suspended material occurs. Samples were air-dried and sieved through a polyethylene screen (0.2 material occurs. Samples were an area and steved amodge a perjodified several (σ . applied in works associated with geochemical mapping [14]. At the same time, roots and above ground parts of tussock sedge and sweet flag were collected. After drying, each sample (roots and above ground parts) were ground using agate mill. Then, bottom sediments and plant material was digested in nitric acid in a hermetic microwave system CEM Mars-5. The bottom sediments samples were also subjected to extraction of metals soluble forms in cool 1 mol \cdot dm⁻³ HCl solution [15]. Applied hydrochloric acid is one of the most commonly used to isolate the non-residual metal fraction from solid samples [16]. In addition, according to Sutherland [17] and Frankowski et al [16], diluted HCl is the most suitable eluent for determination of anthropogenic sources of metals in solid samples. The metals concentrations were determined by means of AAS technique (spectrophotometer Varian SpectraAA-100).

Classification of water sediments in Poland on a base of geochemical criteria was applied to evaluate the level of sediment contamination with heavy metals [18] and threshold values taking into account the detrimental effect of pollutants accumulated in sediments on aquatic organisms [19]. The results on the content of tested metals in the upright sedge (*Carex elata*) and sweet flag (*Acorus calamus*) are based on the dry weight of plants and compared to the literature data relating to a dry weight of plants. The physiological norm of metals contents for plants was quoted after data presented by [20].

Statistica 7.1 software was used for statistical analysis of test results: arithmetic mean, standard deviation, median and also Spearman correlation coefficients between content of metals in the bottom sediments and plants, were calculated.

Results and discussion

Concentrations of studied metals in collected bottom sediments samples from upper Narew River revealed variability due to the level of the sediment dispersion, as well as the localization of the measure point. It referred both to the total and labile forms of analyzed heavy metals. Sediments were characterized by following arithmetic mean and standard deviation (Table 1) values of their total contents: 1.52 ± 0.07 mgCd $\cdot \text{ kg}^{-1}$, 14.2 ± 1.45 mgPb \cdot kg⁻¹, 47.5 \pm 15.36 mgZn \cdot kg⁻¹, 14.8 \pm 3.99 mgCr \cdot kg⁻¹, 11.9 \pm 0.99 mgNi \cdot kg⁻¹, 3.5 \pm 1.12 mgCu \cdot kg⁻¹ and 2.6 \pm 0.18 mgCo \cdot kg⁻¹ d.m. From a point of view of the environmental pollution, the soluble portion of metals is very important,

Table 1

Heavy metals contents in bottom sediments Heavy metals contents in bottom sediments

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 $* A - decomposition in HNO₃ and H$

because due to their mobility, metals can be desorbed from sediments to water, as well as be accumulated in benthos organisms [15, 20]. Performed study revealed following arithmetic mean and standard deviation (Table 1) values for labile forms: cadmium – 0.40 ± 0.32 mgCd \cdot kg⁻¹, 5.6 \pm 1.25 mgPb \cdot kg⁻¹, 18.9 \pm 2.00 mgZn \cdot kg⁻¹, 1.2 ± 1.22 mgCr \cdot kg⁻¹, 1.3 ± 0.52 mgNi \cdot kg⁻¹, 1.1 ± 0.50 mgCu \cdot kg⁻¹ and 0.8 ± 0.17 $mgCo \cdot kg^{-1}$ d.m.

Result analysis indicated that the highest level of total contents and labile forms was found for zinc and lead, whereas the lowest concentrations were determined in the case of cadmium and cobalt. The ratios of labile to total forms of heavy metals concentrations in studied bottom sediments and expressed as a percentage could be lined up in the following sequence: $Zn > Pb > Cu > Co > Cd > Ni > Cr$. It illustrates the mobility of examined metals as well as their anthropogenic origin. Studies revealed relatively low share of chromium soluble form in its total content that in majority of examined samples, was from 4 to 10 %. Kabata-Pendias [21] reported that chromium is one of the least mobile trace elements in a natural environment. In not contaminated bottom sediments, it occurs in a stable form in 84 %. Zinc is one of the most mobile metals in a natural environment, which was also confirmed by numerous studies; its soluble form share in the total content of the bottom sediments ranged from 30 % to 80 %. The lead and copper labile forms in their total contents made up about 30 % to 40 % in examined sediments, while those of cobalt and cadmium from 25 % to 30 %, and nickel from 8 % to 18 %, because it readily forms quite durable chelate and compounds, as well as complex cations and anions. Analysis of study results from bottom sediments in upper Narew River and their comparison to sediment classification in Poland on a base of geochemical criteria [18, 19], it was found that copper and zinc contents in Zlotoria, Rzedziany, Doktorce, Ploski, Narew and Bondary localities were at the level of geochemical background, while other metals (lead, nickel, chromium and cobalt) should be classified to the I class as not contaminated sediments (Table 2).

Table 2

Nearest locality	Classification of metal content in sediments						
	C _d	Ph	Zn	Cr	Ni	Cu	Co
Tykocin	H					Background	
Siekierki	П					Background	
Złotoria	П		Background			Background	
Rzedziany	П		Background			Background	
Bokiny	П					Background	
Uchowo	П					Background	
Doktorce	П		Background			Background	
Ploski	П		Background			Background	
Narew	П		Background			Background	
Bondary	П		Background			Background	

Geochemical classification of sediments from upper Narew River

Source: own work based on the Bojakowska and Sokołowska [18] and Bojakowska [19].

Cadmium was the exception, because a slight exceeding the I geochemical class occurred (Table 2). Such concentrations result mainly from the anthropogenic factors, due to which it penetrates along with the surface runoff from cultivated fields with wrong phosphorus fertilizing management [20], as well as along with the sewage; transport is also a significant source of cadmium contamination [18]. Koc et al [22] and Skorbilowicz [23] argue that the modification of chemical composition of water flowing within the catchment of Narew River results primarily from structure of agricultural performance of its surface. In addition, water of Narew River is enriched in contaminants from urban settlements and storm waters from both rural and urban areas. Mioduszewski [24] and Banaszuk [25] note that relatively intensive agriculture carried out in the vicinity of the valley, meadow management on part of the bogs, and processes of organic formations decay that take place in the upper Narew River cause significant changes in migration processes within the landscape.

Contents of heavy metals at aquatic plants can be one of the indicators of anthropopresure influences on natural environment. Heavy metal contents at aquatic plants reflect their bio-available forms concentrations in a natural environment as well as valuable complement of bottom sediments studies. Values of metal arithmetic mean and standard deviation in roots of *Carex elata* (Table 3) were: 1.9 ± 0.25 mgCd \cdot kg⁻¹, 7.6 ± 1.04 mgPb \cdot kg⁻¹, 78.2 ± 12.79 mgZn \cdot kg⁻¹, 7.1 ± 3.66 mgCr \cdot kg⁻¹, 8.6 ± 0.98 mgNi \cdot kg⁻¹, 6.2 \pm 1.98 mgCu \cdot kg⁻¹ and 9.2 \pm 0.69 mgCo \cdot kg⁻¹ d.m., while in roots of *Acorus calamus*: 2.1 ± 0.07 mgCd \cdot kg⁻¹, 7.7 ± 1.17 mgPb \cdot kg⁻¹, 67.4 ± 15.23 mgZn \cdot kg⁻¹, 8.9 ± 3.9 mgCr \cdot kg⁻¹, 9.0 ± 1.67 mgNi \cdot kg⁻¹, 5.4 ± 1.72 mgCu \cdot kg⁻¹ and 9.0 \pm 0.93 mgCo \cdot kg⁻¹ d.m. (Table 4). Values of arithmetic mean and standard deviation for studied metals at above ground parts of test plants were slightly different: *Carex elata* (Table 3): $1.4 \pm 0.28 \text{ mgCd} \cdot \text{kg}^{-1}$, $6.8 \pm 0.96 \text{ mgPb} \cdot \text{kg}^{-1}$, 38.7 ± 5.94 mgZn \cdot kg⁻¹, 4.8 \pm 0.92 mgCr \cdot kg⁻¹, 5.6 \pm 1.31 mgNi \cdot kg⁻¹, 3.1 \pm 0.64 mgCu \cdot kg⁻¹ and 6.3 ± 0.75 mgCo \cdot kg⁻¹ d.m., whereas *Acorus calamus*: 1.4 ± 0.29 mgCd \cdot kg⁻¹, 7.8 ± 1.13 mgPb \cdot kg⁻¹, 56.8 \pm 17.83 mgZn \cdot kg⁻¹, 5.6 \pm 3.33 mgCr \cdot kg⁻¹, 4.4 \pm 0.67 mgNi \cdot kg⁻¹, 3.8 \pm 0.98 mgCu \cdot kg⁻¹ and 6.7 \pm 0.85 mgCo \cdot kg⁻¹ d.m. (Table 4).

Cadmium and lead are dangerous and toxic to most of life forms and more available to aquatic organisms. Distribution of these metals within the plant depends on a number of factors, including the form of the metal (ion, complex), presence of other metals, as well as the species and individual characteristics, and even a plant organ. The root usually has a higher content than shoot [26, 27]. In majority of analyzed cases, studies upon Cd and Pb confirmed that fact. According to Kabata-Pendias [28], the Cd contents in plants are very diverse and most often are in the range of $0.05-0.2$ mg \cdot kg⁻¹. The toxicity symptoms occur at amounts around $5-10$ mg \cdot kg⁻¹ for sensitive plants, and 10–30 mg \cdot kg⁻¹ for resistant plants. In all samples, it was found that concentration of a given metal in the test plants amounted to over $0.2 \text{ mg} \cdot \text{kg}^{-1}$.

The average value of bioaccumulation coefficient for studied plants in the case of Cd was 1.3 ± 0.29 (Table 5).

Contents of Pb found in *Carex elata* and *Acorus calamus* did not exceed 15 mg \cdot kg⁻¹ (Table 3 and 4), while toxic content according to Kabata-Pendias and Pendias [20] is 30

* P – Heavy metals contents in above ground parts; ** R – Heavy metals contents in roots.

Heavy metals contents in *Carex elata* J. $\vec{\zeta}$ \overline{a} ł,

Table 3

Contents of heavy metals in Acorus calamus Contents of heavy metals in *Acorus calamus*

Table 4

* P - Heavy metals contents in above ground parts; ** R - Heavy metals contents in roots. * P – Heavy metals contents in above ground parts; ** R – Heavy metals contents in roots.

Table 5

Bio-accumulation coefficientin *Carex elata* and *Acorus calamusi* in Narew River

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 $mg \cdot kg^{-1}$. Lead is hardly mobile and hardly available to plants in bottom sediments, which was confirmed by the bioaccumulation coefficient that averaged to 0.5 (Table 5).

Zinc is an element that is essential for the proper functioning of living organisms, and its excess can be harmful. It is one of the more active metals in the environment [27]. Results of the plant material analysis indicate that there is not the issue of water environment contamination by this element. Average zinc contents in two analyzed plants of *Carex elata* and *Acorus calamus* were in the range of 38.75 ± 5.94 to 78.2 \pm 12.79 mg \cdot kg⁻¹, respectively, which according to Kabata-Pendias and Pendias [20] indicates its physiological content. The most common zinc bioaccumulation coefficient is about 1, although studies have shown its higher values: 1.7 ± 0.52 and 1.6 ± 0.70 (Table 5).

Like for zinc, there was no contamination of the environment of upper Narew River with chrome. It is generally accepted that for highly sensitive plants, Cr is harmful if present in an amount of larger than $2 \text{ mg} \cdot \text{kg}^{-1}$, while medium-resistant plants tolerate content up to ≤ 20 mg \cdot kg⁻¹ [20]. Baker and Chesnin [29] claim that concentrations above 10 mgCr \cdot kg⁻¹ in plants is excessive. Only in four samples were found excessive chromium content (one sample of *Carex elata*, 3 samples of *Acorus calamus*). The average value of bioaccumulation coefficient for Cr oscillated between 0.5 and 0.6.

Kabata-Pendias and Pendias [20] as well as Baker and Chesnin [29] report that the nickel concentration above 10 mg \cdot kg⁻¹ in the plant is excessive. All test plant samples had natural Ni content. The bioaccumulation coefficient for *Carex elata* and *Acorus calamus* varied from weak accumulation typical for nickel to moderate one. The intensive accumulation expressed above 1, was reported in a single case at *Acorus calamus*.

Copper shows a high susceptibility to bioaccumulation from the aquatic environment [27]. In a plant, this element is accumulated mainly in roots [30], as confirmed in present study. Physiological standard for copper content in plants is $5-50$ mg \cdot kg⁻¹ according to Kabata-Pendias and Pendias $[20]$ or 2–20 mg \cdot kg⁻¹ in opinion of Market [31]. The copper content in analyzed plant material ranged from 1.6 to 9.9 mg \cdot kg⁻¹ and most often it remained at a level of 3.1–6.7 mg \cdot kg⁻¹. The range of bioaccumulation coefficient for copper was high ranging from 0.5 to 3.1.

The cobalt content in tested plants from the upper Narew River ranged 4.9 to 10.4 mg \cdot kg⁻¹ (with mean values from 6.3 \pm 0.75 and 9.2 \pm 0.69 mg \cdot kg⁻¹). The toxic effects related to cobalt occur at its content range about $15-50$ mg \cdot kg⁻¹. The bioaccumulation coefficients for cobalt in *Carex elata* and *Acorus calamus* were high and amounted to 3.5 and 3.3, respectively. The results of analyzes indicate the lack of contamination due to cobalt.

Studies performed upon the chemistry at plants of two Polish lowland rivers Ołobok and Pilawa showed higher metal contents than those in the present work; mean values were: 6.2–23.0 mgPb, 255–303 mgZn, 23–55 mgCr.0, 6.6–21.4 mgNi, 12.9–78 mgCu and $4.0-23.0$ mgCo \cdot kg⁻¹ [13].

Studied metals in the roots were accumulated in the following order: in *Carex elata* $Zn > Co > Ni > Pb > Cr > Cu > Cd$, and in *Acorus calamus* $Zn > Co > Ni > Pb > Cr >$ $Cu > Cd$. In contrast, in the above ground parts, metals occurred in the following

sequence: in *Carex elata* Zn > Co > Pb > Cr > Ni > Cu > Cd, and in *Acorus calamus* Zn $> Pb > Co > Ni > Cr > Cu > Cd$. The lowest concentrations were observed for copper and cadmium in the roots and above ground parts, while the highest ones for zinc.

Calculated bioaccumulation coefficients were as follows in roots of the examined aquatic plants: for *Carex elata* $Co > Cu > Zn > Cd > Ni > Pb = Cr$, and for *Acorus calamus* $Co > Cu > Zn > Cd > Ni > Cr > Pb$. Overall, the largest bioaccumulation coefficients in studied plants were recorded for Co and Cu, whereas the lowest for Cr and Pb. It can be also concluded that upright sedge and sweet flag in most cases accumulate examined metals in similar ways.

Studied material in the form of numerical data on metal contents was statistically analyzed. The analyses performed showed significant statistical correlations within bottom sediments between total contents of Cr and Cu and soluble forms of these elements (Table 6). It was also statistically confirmed that the Co content in *Acorus calamus* roots depends on the concentration of Co in sediments (HCl extraction). Significant correlations between the content of Pb, Zn and Cr in the roots of aquatic plants and their contents in above ground parts were recorded as well (Table 6).

Table 6

Dependencies between heavy metals contents in bottom sediments *vs* plants

^a Total content in bottom sediments; \overline{b} soluble forms content in bottom sediments; \overline{b} *Acorus calamus* roots; \overline{b} *Acorus calamus* above ground parts; ^{Sk} *Carex elata* roots; ^{Sn} *Carex elata* above ground parts.

Conclusions

1. Studies upon bottom sediments of the upper Narew River showed low contents of studied metals with an exception of cadmium. The copper content and in most cases zinc, occurred at the level of geochemical background. Lead, chromium, nickel and cobalt ranged within the $1st$ geochemical class, while cadmium in the $2nd$ class.

2. The achieved results from nickel, zinc, copper, cobalt, chromium and lead analysis in plant material indicate the lack of aquatic environment contamination with these elements; the only exception was cadmium, which exceeded the natural level.

3. It has been proven that aquatic plants are characterized by a greater tendency for metals accumulating than bottom sediments with an exception of lead and chromium.

4. It has been shown that the metal contents in most of tested plants were higher in the roots than in above ground parts.

5. Elevated cadmium content may be caused by anthropogenic activities, due to which the element passes along with the surface runoff from agricultural fields, where bad economy related to phosphorus fertilizers is run and wastewaters from sewage treatment plants; transport is also a major source of cadmium.

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MAKROFITY JAKO WSKAŻNIKI BIOPRZYSWAJALNOŚCI **METALI CIĘŻKICH W GÓRNEJ NARWI**

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Abstrakt: Celem przeprowadzonych badań było określenie zawartości kadmu, niklu, cynku, miedzi, kobaltu, chromu i ołowiu w osadach dennych oraz korzeniach i częściach nadziemnych roślin: *Carex elata* i *Acorus calamus* w górnej Narwi. Badania wykonano latem w 2008 r. w 10 przekrojach pomiarowych zlokalizowanych na rzece Narew (Bandary, Ploski, Doktorce, Rzędziany, Uhowo, Bokiny Złotoria, Siekierki i Tykocin). Steżenie metali oznaczano metoda ASA. Obliczone współczynniki bioakumulacji w korzeniach badanych roślin wodnych kształtowały się w następujący sposób: *Carex elata* Co > Cu > Zn > Cd > Ni > Pb = Cr i *Acorus calamus* Co > Cu > Zn > Cd > Ni > Cr > Pb. Można sądzić, że źródłem badanych metali zdeponowanych w osadach dennych i badanych roślinach wodnych w górnej Narwi jest działalność gospodarcza i bytowa człowieka, w tym wpływ lokalnej komunikacji oraz spływy powierzchniowe. Badany materiał roślinny i osady denne rzeki Narew sa w niewielkim stopniu zanieczyszczone kadmem.

Słowa kluczowe: metale ciężkie, makrofity, rzeka Narew