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THE CONTENT OF HEAVY METALS IN LEAVES OF *PHRAGMITES AUSTRALIS* (CAV.) TRIN.EX STEUD. AND BOTTOM SEDIMENTS FROM LAKES OF POJEZIERZE LESZCZYŃSKIE

ZAWARTOŚĆ METALI CIĘŻKICH W LIŚCIACH *PHRAGMITES AUSTRALIS* (CAV.) TRIN.EX STEUD.I OSADACH DENNYCH JEZIOR POJEZIERZA LESZCZYŃSKIEGO

Key words: common reed, accumulation of heavy metals, bioindication.
Słowa kluczowe: trzcina pospolita, akumulacja metali ciężkich, bioindykacja.

W przeprowadzonych badaniach określono zawartość Fe, Zn, Mn, Cu, Ni, Pb, Cd, Co i Cr w osadach dennych oraz liściach Phragmites australis (Cav.) Trin.ex Steud, zebranych z 10 stanowisk badawczych, zlokalizowanych w 5 jeziorach Pojezierza Leszczyńskiego (woj. wielkopolskie). Zawartości badanych metali w osadach dennych i liściach trzciny pospolitej z jezior Pojezierza Leszczyńskiego były stosunkowo małe i nie przekraczały wartości tła biogeochemicznego. Jedynie zawartości Mn i Cr w badanych makrohydrofitach wyraźnie przekraczały poziom fizjologiczny i mieściły się w zakresie toksycznym dla większości roślin. Pomimo dużych zawartości Cr w liściach trzciny nie obserwowano żadnych objawów toksyczności u tego gatunku, co świadczy o wysokich zdolnościach kumulacyjnych Phragmites australis w stosunku do Cr. Wysokie zdolności trzciny pospolitej do pobierania i gromadzenia Cr potwierdza wysoki współczynnik kumulacji dla tego metalu (średnio 14,9). Również współczynniki kumulacji Ni i Mn były istotnie wyższe od współczynników wyznaczonych dla pozostałych metali. Stwierdzono istotne statystycznie, dodatnie korelacje między zawartością Cu i Pb w liściach Phragmites australis, a ich zawartością w osadach dennych, co świadczy o możliwości wykorzystania trzciny pospolitej w bioindykacji skażenia środowiska tymi metalami ciężkimi.

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1. INTRODUCTION

The quality of water determines growth and distribution of various high aquatic plants [Carbiener *et al*. 1990, Romero and Onaindia 1995]. Macrohydrophytes demonstrate great ability to accumulate macro- and microelements [Nogueira et al. 1996] and show selective absorption of certain metals and therefore can be employed to ascertain levels of heavy metals in waters and bottom sediments, as demonstrated by Aksoy et al. [2005]. In waters affected by accidental discharges of wastes where pollutants are easily diluted, chemical analysis of plant material allows integrated assessment of pollution levels in the environmental [Baldantoni et al. 2005]. According to Jones [1985] chemical analysis of plant tissues could be considered more effective in biomonitoring of water pollution than water or sediment analysis.

The aim of this paper was to determine chemical characteristics of *Phragmites australis* and bottom sediments from lakes of Pojezierze Leszczyńskie (West Poland) with different levels of some nutrients and heavy metals and to investigate bioindicative value of this species.

2. MATERIALS AND METHODS

Ten study sites chosen within five lakes of Pojezierze Leszczyńskie (in West Poland – Poznań Province) (15º47’ – 17º8’ East, 51º51’ – 52º6’ North) have been analysed (Table 1).

Table 1. Morphometric features of studied lakes (Choiński 1995, Joachimiak 1995)
Tabela 1. Cechy morfometryczne badanych jezior [Choiński 1995, Joachimiak 1995]

Lake	Surface [ha]	Average depth [m]	Maximum depth [m]	Surrounding	Study sites
Dominickie	343.9	6.5	17.1	pine forest; numerous resorts and campings	1, 2
Boszkowskie	29.4	1.2	2.2	meadows; agricultural fields	3, 4
Olejnickie	243.4	1.6	5.0	pine forest	5
Górskie	-	1.6	3.0	pine forest; numerous resorts and campings	6, 7, 8
Osłonińskie	-	1.6	2.0	meadows; agricultural fields	9, 10

In July samples of bottom sediment from the superficial layer (5 – 20 cm), together with leaves of *Phragmites australis,* were collected in triplicate from each of the study sites. Leaves from 5 randomly selected plants represented a plant sample for further analysis. Prior to analysis, bottom sediment samples were air dried and ground in a mortar to pass a 2 mm sieve and were then homogenised. The plant leaves were washed thoroughly in distilled water, dried at 60°C and pulverised prior the analysis.

Sediment and plant material (200 mg) were digested in an open system with concentrated nitric acid and hydrogen peroxide (30%) during which temperatures were raised to about 95°C until evolution of nitrous gas stopped and the digest became clear. The total concentrations of Fe, Zn, Mn, Cu and Pb were determined by atomic absorption spectrometry with flame atomization, whereas Ni, Cd, Co and Cr were with electrothermal atomization (AVANTA PM by GBC Scientific Equipment). All elements were measured against standards by SIGMA.

The precision of the measurements was determined by comparing the results of heavy metal content in the solutions made from three separate weighted portions of each sample, being analysed using an identical method. The reproducibility of the methods used were compared to the results of an inter-laboratory study by digesting and analysing reference material GBW 07604 Poplar Leaves (Institute of Geophysical and Geochemical Exploration Lanfang China), and RTH 907 Dutch Anthropogenic Soil (Wageningen Evaluating Programms for Analytical Laboratories, WEPAL). Values were found to be 98±3% (percent ± standard deviation) for soil material and 100±1% for plant material.

Differentiation between study sites with respect to mean concentrations of elements in bottom sediments and plants were evaluated by analysis of variance with the F Snedecor test. The least significant difference (LSD) were calculated [Parker 1983]. Pearson regressions and correlation coefficients ($n=72$ and $p<0.05$) were calculated to examine the relationships between the concentrations of elements in soil and plants [Parker 1983]. All calculations were carried out using the CSS-Statistica Statsoft© [StatSoft Inc. 2008].

3. RESULTS AND DISCUSSION

The average concentrations of the elements in the bottom sediments and in the leaves of *Phragmites australis* as well as differentiation in their content between the study sites are shown in table 2 and 3.

The analysis revealed that the metal concentrations in the lakes of Pojezierze Leszczyńskie were within the background values given by Woitke et al. [2003], Polýak and Hlavay [2005] and hence can be considered relatively low. The mean concentrations of majority of the studied metals in leaves of *Phragmites australis* were not higher than the biogeochemical values according to Markert [1992] as well as Kabata-Pendias and Pendias [1993] and they were also within the concentration range for plants from uncontaminated waters studied by Manny et al. [1991] and Deng et al. [2004]. Nonetheless, the levels of Mn and Cr significantly exceeded the physiological thresholds and were within the toxic ranges proposed by Kabata-Pendias and Pendias [1993] for most plant species (400–1000 $mg \cdot kg^{-1}$ for Mn, 5 – 20 $mg \cdot kg^{-1}$ for Cr). The concentrations of Cd in the studied plant samples were found to be below the detection limit like $3 \cdot 10^{-6}$ $mg \cdot kg^{-1}$.

Table 2. Mean concentration of elements in bottom sediments (mg·kg^{-1}; n=90, $F_{tab\ 0.05}$ = 2.39)

Tabela 2. Średnie zawartości pierwiastków w osadach dennych (mg·kg^{-1}; n=90, $F_{tab\ 0,05}$ = 2,39)

Study sites	pH	Fe	Zn	Mn	Cu	Ni	Pb	Co	Cr
1	7.10	1781	18.1	489	15.3	0.95	8.85	1.06	3.84
2	7.13	1557	17.3	521	8.47	0.84	7.93	0.96	2.86
3	7.02	1636	7.44	345	9.40	0.77	4.12	0.45	0.34
4	7.10	1164	10.9	113	8.60	1.39	3.34	0.33	0.61
5	7.32	1114	4.97	342	3.10	0.72	6.56	0.20	0.23
6	7.10	1796	26.0	607	38.2	4.66	11.6	1.51	3.64
7	7.05	1249	30.4	397	28.6	3.24	13.4	1.10	1.89
8	7.45	5622	8.05	110	5.60	1.38	6.96	0.76	0.47
9	6.88	4571	27.1	356	36.3	5.02	11.6	0.86	2.97
10	7.00	2742	19.7	533	25.8	3.33	8.41	0.45	1.06
LSD	0.07	96.5	0.27	6.21	1.05	0.01	0.10	0.01	0.05
F_{est}	42.7	2253	9659	6381	1363	186383	9121	8880	6440

F_{tab} – F tabular,
F_{est} – F estimated,
LSD –least significant difference.

Table 3. Mean concentration of elements in leaves of *Phragmites australis* (mg·kg^{-1}; n=90, $F_{tab0.05}$ = 2.39)

Tabela 3. Średnie zawartości pierwiastków w liściach *Phragmites australis* (mg·kg^{-1}; n=90, $F_{tab\ 0,05}$ = 2,39)

Study sites	Fe	Zn	Mn	Cu	Ni	Pb	Co	Cr
1	48.7	9.80	221	1.56	2.23	0.352	0.035	8.37
2	84.6	9.25	450	1.25	2.12	0.315	0.063	10.0
3	65.4	10.80	775	1.28	2.12	0.656	0.080	8.92
4	64.1	11.80	665	1.04	3.73	0.497	0.058	17.3
5	95.8	4.03	717	1.28	2.38	1.224	0.023	9.60
6	76.6	10.45	376	2.88	2.48	0.870	0.054	5.64
7	85.7	11.40	446	1.31	2.84	1.374	0.026	9.87
8	93.6	8.20	196	1.35	2.90	1.050	0.045	13.7
9	56.0	5.45	490	1.60	2.50	1.384	0.042	8.62
10	65.4	7.15	423	1.81	2.17	0.435	0.059	8.04
LSD	3.04	0.32	16.4	0.18	0.17	0.06	0.002	0.30
F_{est}	242	584	1217	76.7	73.6	465	507	1051

F_{tab} – F tabular,
F_{est} – F estimated,
LSD –least significant difference.

The concentrations of Mn in leaves of the reed from the Pojezierze Leszczyńskie were found to be within the ranges published by other authors [Kurilenko and Osmolovskaya 2006, Demerizen and Aksoy 2006]. According to Kabata-Pendias and Pendias [1993] the accurate iron to manganese ratio ensuring enzymatic equilibrium in plants ranges from 1.5 to 2.5. The analysis herein show the Fe to Mn ratio to be significantly lower in the macrohydrophytes studied. This ranged form 0.08 to 0.48 (average 0.18) revealing high manganese content in tissues of reed from the sampled areas. Nonetheless, no toxicity symptoms were noted on the plant organs. Extraordinary accumulation of Mn in the reed analysed seems to support findings of other authors [Demerizen and Aksoy 2006] who reported elevated amounts of manganese in reed species.

The levels of Cr in leaves of *Phragmites australis* from lakes under investigation were found to be higher than those reported in the current literature. For example concentrations of Cr in leaves of common reed sampled during vegetation growing season by Windham et al. [2003] and Aksoy et al. [2005] amounted 0.44 mg·kg^{-1} and 1.65 mg·kg^{-1} respectively. Lower concentrations of Cr in the reed leaves compared to these presented here, were also reported by Kurilenko and Osmolovskaya [2006]. While Vymazal et al. [2007], who studied heavy metals accumulation in leaves of *Phragmites australis* and *Phalaris arundinacea,* found the average concentration of Cr to be as low as 0.27 mgCr·kg^{-1}.

Although leaves of the reed from the studied lakes were found to be high in Cr no plant toxicity symptoms were observed. This finding seems to confirm extraordinary accumulation capacity for Cr exhibited by *Phragmites australis* as well as potential use of this species in phytoremediation of sites contaminated with Cr. According to Mant et al. [2006] healthy plants, exhibiting high accumulation potential of metals could be considered for metal phytoremediation. Both high biomass production and fast growth, typical to emergent macrophytes, make them efficient potential phytoremadiators [Bragato et al. 2006].

High values of accumulation coefficients calculated for the reed analysed (average 14.9) (Table 4) show high accumulation abilities of the reed in respect of Cr. These values exceed significantly Cr accumulation coefficients proposed by Kabata-Pendias and Pendias [1993] and Duman et al. [2007]. The accumulation coefficients established for Ni and Mn were also high and they exceeded those calculated for the remaining metals considered in this study (Table 4).

Table 4. Enrichment ratios of heavy metal concentrations between leaves of *Phragmites australis* and bottom sediments ($F_{tab0.05}$ = 2.39)

Tabela 4. Współczynniki kumulacji metali ciężkich z osadów dennych (stosunek zawartości metalu w liściach *Phragmites australis* do jego zawartości w osadach dennych ($F_{tab\ 0,05}$ = 2.39)

Study sites	Fe	Zn	Mn	Cu	Ni	Pb	Co	Cr
1	0.027	0.54	0.45	0.10	2.35	0.040	0.033	2.18
2	0.054	0.53	0.86	0.15	2.52	0.040	0.065	3.51
3	0.040	1.45	2.25	0.14	2.75	0.159	0.178	26.25
4	0.055	1.08	5.88	0.12	2.68	0.149	0.175	28.33
5	0.086	0.81	2.09	0.41	3.30	0.187	0.115	41.76
6	0.043	0.40	0.62	0.08	0.53	0.075	0.036	1.55
7	0.069	0.37	1.12	0.05	0.88	0.103	0.023	5.22
8	0.017	1.02	1.78	0.24	2.10	0.151	0.060	29.21
9	0.012	0.20	1.38	0.04	0.50	0.119	0.049	2.90
10	0.024	0.36	0.79	0.07	0.65	0.052	0.131	7.59
LSD	0.005	0.035	0.070	0.025	0.17	0.007	0.005	1.07
F_{est}	200	1109	4478	170	332	510	1078	1671

F_{tab} – F tabular,
F_{est} – F estimated,
LSD –least significant difference.

The heavy metal accumulation sequence in the leaves of the reed is as follows: Mn > Fe > Cr > Zn > Ni > Cu > Pb > Co. This sequence corresponds to that noted by Klink et al [2004] for water plants: Mn > Zn > Cu > Pb > Ni > Cd.

The significant positive correlations between concentration of Cu (r=0.70, p=0.000) and Pb (r=0.49, p=0.006) in the leaves of *Phragmites australis* and the sediments suggest that the investigated macrohydrophytes should be employed for bioindication of environmental contamination with Cu and Pb [Frazin and McFarlane 1980, Jones 1985].

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