Nauka Przyroda Technologie

2013
Tom 7
Zeszyt 4
#66

ISSN 1897-7820 http://www.npt.up-poznan.net

Dział: Melioracje i Inżynieria Środowiska

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ACCUMULATION OF HEAVY METALS (Co, Cr, Cu, Mn, Zn) IN THE FRESHWATER ALGA *ULVA* TYPE, SEDIMENTS AND WATER OF THE WIELKOPOLSKA REGION, POLAND*

AKUMULACJA METALI CIĘŻKICH (Co, Cr, Cu, Mn, Zn) W PLECHACH ZIELENIC RODZAJU *ULVA*, OSADACH ORAZ WODZIE NA TERENIE WIELKOPOLSKI, POLSKA

Summary. The concentration of five trace elements: cobalt (Co), chrome (Cr), copper (Cu), manganese (Mn) and zinc (Zn) was determined in the *Ulva* thalli, in the water and sediment collection from several inland sites (lakes, stream and river) from the Wielkopolska region during summer 2010. The multielemental analysis of the heavy metal concentration was carried out with the use of ICP-OES method. The aim of this study was to determine the role of tubular forms as biomonitoring species. The relative abundance of metals in sediment decreased in the order: Mn > Zn > Cu > Cr > Co and in the water: Cr > Mn > Zn > Cu > Co. In *Ulva* thalli the distribution order from higher to lower was Mn > Zn > Cr > Cu > Co. The results indicate that the concentration changes of heavy metals in thallus, water and sediment have some differences, but concentration distribution tends to be similar, because among the analysed heavy metals Mn has the highest concentrations while Co the lowest abundance in the thalli and sediment of all the sites. Possibility to use freshwater species from *Ulva* genus as bioindicators of water pollution by manganese requires further study.

Key words: bioaccumulation, freshwater *Ulva*, *Enteromorpha*, heavy metals, bioindicator

*This project was supported by funds from the Polish Ministry of Science and Higher Education, grant No. N N 304 013 437. Co-author Andrzej Rybak is a grant holder within the framework of Measure 8.2 of the Operational Program Human Capital (OP HC) co-financed by the European Social Fund of the European Union.

Rybak A., Messyasz B., Pikosz M., Szendzina L., Łęska B., 2013. Accumulation of heavy metals (Co, Cr, Cu, Mn, Zn) in the freshwater alga *Ulva* type, sediments and water of the Wielkopolska region, Poland. Nauka Przyr. Technol. 7, 4, #66.

Introduction

In biological and in environmental studies the term "heavy metals" is often used with connotations of pollution and toxicity (DUFFUS 2002). For metals, which occur in low concentration (in mass fractions of ppm or less) in the water, sediments or thalli in studies term "trace metals" (DUFFUS 2002) is used. Heavy metals are introduced into the environments as a result of natural processes occurring in nature and anthropogenic sources, mainly by industrial activities (HARITONIDIS and MALEA 1995). Some of metals such as Cu, Mn, Cr and Zn are essential micronutrients, but can become toxic in case of exceeding the limit values required for normal algae growth (LOBBAN and HARRISON 1994, GLEDHILL et AL. 1997, NIES 1999). To the main negative effects of heavy metals on algae belong: inhibition of growth, photosynthesis and fertility, disruption of development and chlorosis (GLEDHILL et AL. 1997, BROWN and NEWMAN 2003, HAN et AL. 2008). Mechanism of accumulation of metals by the algae is composed of two processes, first stage lies on adsorption on the exterior surface and next intracellular uptake (GARNHAM et AL. 1992, FAVERO et AL. 1996).

Macroalgae are used as bioindicators to measure heavy metal pollution in the water because they show the high degree of accumulation of dissolved metals in their cell walls (FAVERO et AL. 1996, SALGADO et AL. 2005, JI et AL. 2011). Many studies show that seaweed such as *Ulva*, *Cladophora*, *Padina*, *Cystoseira* are very common as biomonitoring species (AKCALI and KUCUKSEZGIN 2011). For the first time AL-HOMAIDAN et AL. (2011) used filamentous green alga *Enteromorpha intestinalis* (syn. *Ulva intestinalis* L.) as indicator of heavy metals pollution for inland waters – Wadi Hanifah Stream, which runs through the city of Riyadh in the central region of Saudi Arabia. Due to the anthropogenic activities in this area water in the stream showed high levels of total dissolved solids (TDS was 1.25-2.71 $mg \cdot l^{-1}$) and nutrients (AL-HOMAIDAN et AL. 2011). To comprehensively evaluate the environmental contamination with heavy metals, both abiotic factors like water and sediment and biotic elements such as bioindicator organisms should be investigated (VILLARES et AL. 2001).

According to PHILLIPS (1990), good indicator should be wide spread, show significant tolerance to high concentrations of contamination, should be easy to identify and collect and metals concentration recorded in the organisms should show simple correlation with the concentration of these metals in the environment. Species of the genus *Ulva* (Ulvophyceae, Chlorophyta) comply with Phillips requirements of the indicator. Thus, research to confirm the indicative role of *Ulva* species has been carried out for many years. TALBOT and CHEGWIDDEN (1982) complete that *Ulva lactuca* could be an indicator for Cd, Fe, Mn and Pb, while *Ulva rigida* – for Pb, Zn and Cd (HARITONIDIS and MALEA 1999, BOUBONARI et AL. 2008). Also *Ulva clathrata*, *U. linza* and *U. flexuosa* could be good indicators of Cd, Cu, Pb and Zn contaminations (SEELIGER and WALLNER 1988).

Species of the *Ulva* genus are cosmopolitan (KIRCHHOFF and PFLUGMACHER 2000, MESSYASZ and RYBAK 2009). They prefer salty water, but recently more and more frequently are recorded in freshwater ecosystems. In Poland freshwater populations of *Ulva* were found in flowing ecosystems from drainage ditches, streams to rivers, and in stagnat ecosystems: from ponds by reservoirs and lakes (LIEBIETANZ 1925, PLIŃSKI

1971, STARMACH 1972, KOWALSKI 1975, GOŁDYN 2000, ENDLER et AL. 2006, MESSYASZ and RYBAK 2009). A wide range of occurrence (cosmopolitan nature) and also the presence of this species in contaminated waters gives the possibility to use the species of *Ulva* taxa as an indicator of water pollution by heavy metals (HO 1990, MALEA and HARITONIDIS 2000, VILLARES et AL. 2001).

In Poland since XIX century eight freshwater species have been found: *Ulva compress*a L., *Ulva intestinalis* L., *Ulva paradoxa* (C. Agardh) M.J. Wynne, *Ulva prolifera* O.F. Müller, *Ulva flexuosa* Wulfen, *Ulva flexuosa* subsp. *pilifera* (Kützing) M.J. Wynne, *Ulva tubulosa* (Kützing) Kützing and *Ulva plumosa* Hudson (LIEBETANZ 1925, MARCZEK 1954, PLIŃSKI 1971, KOWALSKI 1975, MESSYASZ and RYBAK 2009). In our study, *Ulva flexuosa*, *Ulva compressa* and some specimens from the *Ulva* genus were collected at six different sites from the Wielkopolska region.

In biomonitoring studies, there are lots of data about the use of aquatic species as pollution indicators, such as *Ulva* species – there are definitely more documents about marine than freshwater forms. And due to the little knowledge about the ability to accumulate heavy metals in freshwater *Ulva* thalli is very important to examine this group of macroalgae as a potential biomonitor.

The aim of this study was to describe the differences of Co, Cr, Cu, Mn and Zn concentrations in the *Ulva* thalli growing in freshwater ecosystems and contamination levels of these metals in sediments and in water. We also wanted to know if freshwater *Ulva* such as marine forms can be used as indicators of heavy metal pollution. And also which trace metal is preferably accumulated by this green algae in the Wielkopolska region. To determine the ability of *Ulva* thalli to accumulate heavy metals the BCF (bioconcentration factor) was assessed.

Materials and methods

The study was carried out during the summer of 2010. Populations of freshwater *Ulva* were in their optimal phase of development at the time. Samples of *Ulva* thalli were taken from the Wielkopolska region (Poland) from six sites (Fig. 1). The sampling sites were located in a stream (the Dworski Rów), lakes (Gosławskie, Pątnowskie, Lednica, Malta) and river (the Nielba) (Table 1).

The thalli specimens that were taken from sampling sites were identified as *Ulva flexuosa* Wulfen, *Ulva intestinalis* L., *Ulva compressa* L. and some were identified only as *Ulva* sp. The reason is a complex taxonomy of the genus and the high morphological similarity between the species (VILLARES et AL. 2001).

During the collection of *Ulva* thalli, also water and sediment samples were taken. Then, samples were put in a plastic container, refrigerated at 4°C, and transported to the laboratory. To clean thalli from any adhering algae, vascular plants (lemnids) and snails, they were washed several times in distilled water. Next, the thalli and also sediments were dried (2 h, the temperature of 105°C), then put into 100-ml plastic containers. Next the samples were preserved with 15% nitric acid (HNO_3) and placed in a freezer (–20°C). All glassware which was used in the procedures was washed with acid (with 15% nitric acid).

Rybak A., Messyasz B., Pikosz M., Szendzina L., Łęska B., 2013. Accumulation of heavy metals (Co, Cr, Cu, Mn, Zn) in the freshwater alga *Ulva* type, sediments and water of the Wielkopolska region, Poland. Nauka Przyr. Technol. 7, 4, #66.

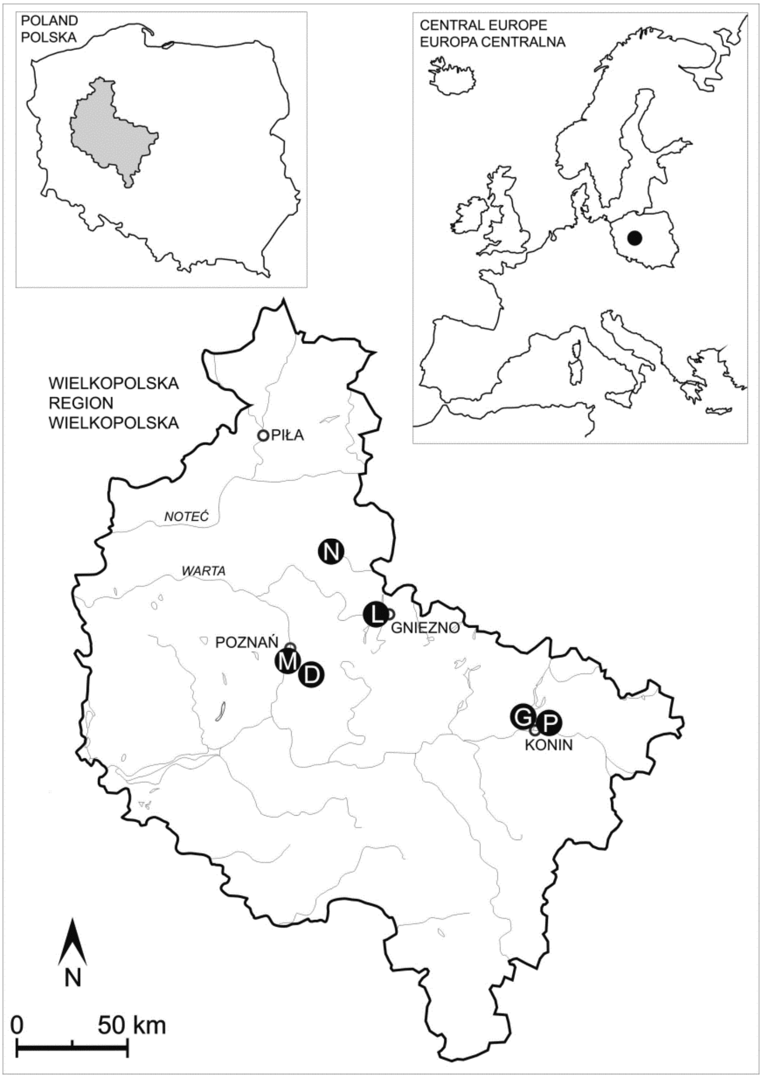

Fig. 1. Location of sampling sites in the Wielkopolska region: L – Lednica Lake, P – Pątnowskie Lake, G – Gosławskie Lake, D – Dworski Rów Stream, N – Nielba River, M – Malta Lake

Rys. 1. Rozmieszczenie stanowisk poboru prób w Wielkopolsce: L – jezioro Lednica, P – Jezioro Pątnowskie, G – Jezioro Gosławskie, D – strumień Dworski Rów, N – rzeka Nielba, M – jezioro Malta

The basic physico-chemical parameters of the water (temperature, concentrations of oxygen, Cl^{-}, pH and conductivity) were measured at the sampling sites with a YSI--Professional Plus-meter.

Rybak A., Messyasz B., Pikosz M., Szendzina L., Łęska B., 2013. Accumulation of heavy metals (Co, Cr, Cu, Mn, Zn) in the freshwater alga *Ulva* type, sediments and water of the Wielkopolska region, Poland. Nauka Przyr. Technol. 7, 4, #66.

Table 1. Basic information on the examined freshwater ecosystems (fractions: *Ulva* thalli, water and sediments)
Tabela 1. Podstawowe informacje o badanych ekosystemach wodnych (frakcje: plechy *Ulva*, woda i osady)

Site Stanowisko	Site code Kod stanowiska	Date Data	Taxon Takson	Coordinates Współrzędne
Lednica Lake Jezioro Lednica	L	8.07.2010	*Ulva* sp.	N 52°30'40.2"; E 17°22'30.5"
Pątnowskie Lake Jezioro Pątnowskie	P1 P2	9.07.2010	*Ulva* sp.	N 52°18'05.6"; E 18°16'34.9" N 52°18'05.8"; E 18°17'04.8"
Gosławskie Lake Jezioro Gosławskie	G1 G2	7.07.2010	*Ulva* sp.	N 52°17'17.9"; E 18°12'45.2" N 52°18'12.1"; E 18°14'49.5"
Dworski Rów Stream Strumień Dworski Rów	D1 D2	4.07.2010	*Ulva compressa*	N 52°20'32.3"; E 17°02'29.5" N 52°20'33.6"; E 17°02'30.3"
Nielba River Rzeka Nielba	N1 N2	1.08.2010	*Ulva intestinalis*	N 52°48'27.5"; E 17°12'59.0" N 52°48'11.3"; E 17°12'34.9"
Malta Lake Jezioro Malta	M1 M2	1.07.2010	*Ulva flexuosa*	N 52°24'16.9"; E 16°57'50.0" N 52°24'01.0"; E 16°58'25.9"

Extraction of metals from *Ulva* thalli was carried out by digesting 0.5 g of algae with a mixture of 15 ml of 65% HNO_3 and 5 ml of 30% H_2O_2 in teflon bombs in a MarsX5 microwave oven. All samples were mineralised in two steps: I – 300 s and 400 W, II – 300 s and 800 W.

The labile fraction of sediment was extracted with 1 M HCl. The samples were stored overnight to allow the complete removal of generated CO_2. Subsequently, the samples were shaken mechanically at room temperature for 1 h. The extract was centrifuged at 5000 rpm for 2 min. Metal extraction was carried out by digesting 0.4 g of the sediment. The other steps followed the procedure for macroalgae mineralization (see above).

Metal extraction from water was carried out by digesting 25 ml and following the same protocol as described for thalli and sediment.

The content of Co, Cr, Cu, Mn and Zn ions in the investigated samples were determined, after previous mineralization in a microwave oven Mars Xpress, on an inductively-coupled plasma emission spectrometer Vista-MPX produced by Varian ICP. Calibration was performed using aqueous standard solutions. After the mineralization, the samples were quantitatively transferred into 10-ml flasks, filled up with redistilled water and then, the content of Co, Cr, Cu, Mn and Zn ions was determined.

The bioconcentration factor (BCF) is a ratio, which gives information about the ability of the plants or algae to accumulate metal in their tissue. The BCFs were calculated according to ZAYED et AL. (1998) solution:

$$\text{BFC} = \frac{\text{mean concentration of metal in plant tissue } (\mu g \cdot g^{-1} \text{ dry wt})}{\text{mean concentration of metal in the water } (\mu g \cdot ml^{-1}) \text{ or sediment } (\mu g \cdot g^{-1})}$$

Results and discussion

The presence of cosmopolitan taxa of *Ulva* genus in inland waters is strongly related to several environmental factors (MESSYASZ and RYBAK 2010). The most significant parameters for development of *Ulva* populations are concentrations of nutrients and chlorides, this group of macroalgae develops in the fertile waters (SITKOWSKA 1999, MESSYASZ and RYBAK 2008, 2010). Concentrations of phosphates, ammonium nitrate and nitrite in the water at examined sites show high levels of fertility (Table 2). Among the researched ecosystems the highest nutrients content was in the Gosławskie Lake, where values of $N\text{-}NH_4^+$, $N\text{-}NO_3^-$ and $P\text{-}PO_4^{3-}$ were 1.64, 1.27 and 0.073 $mg \cdot l^{-1}$, respectively.

Table 2. Measured physico-chemical parameters of the water from the examined sites
Tabela 2. Wartości parametrów fizyczno-chemicznych wody z badanych stanowisk

Site Stanowisko	Temp. (°C)	Conductivity Przewodnictwo ($\mu S \cdot cm^{-1}$)	O_2 (%)	pH	Cl^- ($mg \cdot l^{-1}$)	$N\text{-}NH_4^+$ ($mg \cdot l^{-1}$)	$N\text{-}NO_3^-$ ($mg \cdot l^{-1}$)	$P\text{-}PO_4^{3-}$ ($mg \cdot l^{-1}$)	Fe_{tot} Fe_{og} ($mg \cdot l^{-1}$)
Lednica Lake (L) Jezioro Lednica (L)	27.3	604	117.1	8.84	65.1	0.82	0.63	0.03	0.03
Pątnowskie Lake (P1) Jezioro Pątnowskie (P1)	24.2	565	95.1	8.77	70.9	0.09	1.42	0.01	0.02
Pątnowskie Lake (P2) Jezioro Pątnowskie (P2)	24.7	577	82.3	8.55	72.5	0.08	10.96	0.02	0.02
Gosławskie Lake (G1) Jezioro Gosławskie (G1)	22.0	485	106.9	8.76	64.6	0.43	0.33	0.02	0.01
Gosławskie Lake (G2) Jezioro Gosławskie (G2)	23.8	551	131.9	8.91	60.8	1.64	1.27	0.07	0.22
Malta Lake (M1) Jezioro Malta (M1)	24.1	627	102.7	8.64	171.6	0.37	1.17	0.01	0.03
Malta Lake (M2) Jezioro Malta (M2)	25.4	648	100.3	8.57	160.8	0.44	0.67	0.03	0.02
Dworski Rów Stream (D1) Strumień Dworski Rów (D1)	18.4	889	32.5	7.66	316.9	0.39	2.75	0.03	0.00
Dworski Rów Stream (D2) Strumień Dworski Rów (D2)	17.7	934	20.6	7.75	340.0	0.28	3.58	0.04	0.00
Nielba River (N1) Rzeka Nielba (N1)	19.4	727	99.7	8.39	930.0	0.85	n.d.[a]	0.02	0.29
Nielba River (N2) Rzeka Nielba (N2)	20.0	733	119.0	8.56	1 025.0	0.22	n.d.	0.03	0.12

n.d. – no data.
n.d. – brak danych.

Rybak A., Messyasz B., Pikosz M., Szendzina L., Łęska B., 2013. Accumulation of heavy metals (Co, Cr, Cu, Mn, Zn) in the freshwater alga *Ulva* type, sediments and water of the Wielkopolska region, Poland. Nauka Przyr. Technol. 7, 4, #66.

Representatives of the green algae may occur in different freshwater ecosystems, such as lakes or rivers; these habitats differ significantly due to the physical and chemical parameters. Their occurrence is a result of a wide range tolerance for changes salinity, temperature and light conditions by some *Ulva* species (MESSYASZ 2009). During the research the samples of thalli were collected from sunny places, where water temperature was near 20°C (17.7-27.3). Limnic ecosystems were characterized by a lower chlorides concentration (60.08-171.6 $mg \cdot l^{-1}$) than in flowing waters (316.9-1025.0 $mg \cdot l^{-1}$). Data recorded in Table 2 showed also values of pH, alkaline was always from 7.75 to 8.91, in the limnic waters pH values were higher than 8.5 while in flowing ecosystems a value below 8 was received. These results are similar to previous data where freshwater *Ulva* developed at a pH of about 8 (MESSYASZ and RYBAK 2010). Values of water pH have a significant impact on bioavailability of metals and at low pH a higher bioavailability of metals ions is observed (PETERSON et AL. 1984).

There are numerous factors, which have an impact on the abundance of metals in the algae, e.g. biological processes, levels of metals in the sediment and in the water (HARITONIDIS and MALEA 1999). There are a lot of data on heavy metal contamination in the marine *Ulva* species (HARITONIDIS and MALEA 1995, 1999, VILLARES et AL. 2001, CALICETI et AL. 2002, AKCALI and KUCUKSEZGIN 2011) and on heavy metals in water, sediment and macroalgae (KAMALA-KANNAN et AL. 2008). Until now, only one study has been published about accumulation of heavy metals (Mn, Cu, Zn, As, Cd and Pb) by freshwater *Enteromorpha intestinalis* (syn. *Ulva intestinalis*) (AL-HOMAIDAN et AL. 2011).

Concentration of five metals: Co, Cr, Cu, Mn and Zn in thalli, water and sediments is provided in Table 3. The maximum uptake capacity for cobalt (Co), chrome (Cr), copper (Cu), manganese (Mn) and zinc (Zn) were 4.65, 340.61, 54.44, 2577.50 and 1203.08 $\mu g \cdot g^{-1}$ of dry weight for freshwater *Ulva* from Wielkopolska region, respectively. The observation for the same heavy metals concentrations in *Ulva* thalli was made in the past (Table 4). In *Enteromorpha linza* (L.) J. Agardh and *Ulva rigida* C. Agardh from Thermaikos Gulf (Greece) average value of Co was in both 0.28 $\mu g \cdot g^{-1}$ of dry weight and Cr concentrations was 3.73 and 2.60 $\mu g \cdot g^{-1}$ of dry weight, respectively (HARITONIDIS and MALEA 1995). The highest value for Co concentration noted up to now has been only for *Ulva lactuca* L. (4-40 $\mu g \cdot g^{-1}$ dry wt.) (BOYDEN 1975). The maxima in metal concentrations in *Ulva* thalli were found in algae collected from the most fertilized water among the studied ecosystems. A similar incident occurred in the Harbour, where higher Cr content in *Enteromorpha linza* (L.) J. Agardh was in station with a lot of sewage (HARITONIDIS and MALEA 1995). In connection with higher heavy metals content in water and other ecological variables some of green algae show higher resistance to metals (KNAUER et AL. 1997). For example, *Enteromorpha compressa* (L.) Nees, which occurs in water enrich in Cu, was more resistant to Cu than the same species from unpolluted water (CORREA et AL. 1996). Among the analysed metals the highest values belong to manganese, such as in *Enteromorpha intestinalis* from Wadi Hanifah Stream in Saudi Arabia, where mean concentrations of manganese ranged from 84.49 to 339.29 $\mu g \cdot g^{-1}$ of dry weight (AL-HOMAIDAN et AL. 2011). Also in the same taxa from Assateague (Delaware) and also *Ulva lactuca* from Assateague Mn had the highest values from examined metals (CHAUDHURI et AL. 2007). Such high values

Table 3. Heavy metal concentration in *Ulva* thalli, water and sediments from the examined sites (μg·g^{-1} of dry weight of thalli and the sediments, μg·ml^{-1} of water)
Tabela 3. Zawartość metali ciężkich w plechach *Ulva*, wodzie i osadach z badanych stanowisk (μg·g^{-1} suchej masy plech i osadów, μg·ml^{-1} wody)

Metal	Fraction Frakcja	Site – Stanowisko										
		L	P1	P2	G1	G2	D1	D2	N1	N2	M1	M2
Co	T	0.63	3.31	0.89	0.63	4.65	0.90	0.72	1.45	1.26	1.31	1.81
	W	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	S	3.38	0.75	5.21	2.03	1.54	3.81	4.71	4.84	2.25	1.37	1.03
Cr	T	35.69	215.65	42.90	39.37	340.61	41.21	40.40	39.99	39.42	114.63	125.10
	W	0.16	0.16	0.15	0.15	0.15	0.15	0.16	0.12	0.15	0.16	0.13
	S	14.68	33.87	52.29	36.56	7.46	48.61	45.79	20.85	8.95	5.41	5.50
Cu	T	15.37	44.37	39.84	9.41	54.44	5.55	5.42	11.22	10.10	11.81	11.56
	W	0.027	0.023	0.019	0.006	0.006	0.012	0.014	0.02	0.006	0.02	0.02
	S	38.89	34.14	28.61	262.21	243.94	20.467	33.20	51.98	24.65	22.39	11.35
Mn	T	110.77	1 445.69	699.44	380.73	2 577.50	868.88	392.16	330.49	285.22	356.14	464.14
	W	0.056	0.027	0.043	0.164	0.087	0.023	0.027	0.118	0.023	0.112	0.075
	S	103.42	147.78	348.02	485.62	449.51	559.36	1 914.63	162.41	134.74	302.34	71.49
Zn	T	7.55	1 203.08	220.26	40.72	422.94	20.87	15.82	71.47	65.67	19.03	13.82
	W	0.056	0.043	0.029	0.019	0.014	0.021	0.023	0.048	0.014	0.021	0.052
	S	147.59	15.44	90.44	43.68	43.54	61.80	95.63	233.40	100.46	38.07	16.86

T – *Ulva* thalli, W – water, S – sediments, BDL – below detection limit.
T – plechy *Ulva*, W – woda, S – osady, BDL – poniżej progu wykrywalności.

of Mn concentration in thalli were reported previously in *Ulva fasciata* Delile (to 1076.0 μg·g^{-1} dry wt.) and in *Ulva reticulate* Forsskal (1721.04 μg·g^{-1} dry wt.) (HÄGERHÄLL 1973, AGARDI et AL. 1978). High concentration of manganese (Table 3) in thalli can be explained by use of it in the process of photosynthesis (HALL and RAO 1999). This metal (in the form of ions) is necessary in the reaction of oxygen secretion. Ions of manganese (are located in photosystem II) form a matrix which joins two coordinative molecules of water, creating a connection between the oxygen atoms. Then the oxidation reaction occurs, but the mechanism is not completely understood (HALL and RAO 1999). High concentration of Mn may limit the development of two species of green algae from the *Ulotrix* genus (PAWLIK-SKOWROŃSKA 2002). According to AL-HOMAIDAN et AL. (2011) high concentration of Mn in the algae is a reason of high degree of pollution. Overall, Cr, Cu, Mn and Zn concentrations from water were low and Co content in the water at all stations was below the detection limit (BDL > 0.000001). In seawater in Thermaikos Gulf cobalt concentration ranged between 0.06-0.84 μg·l^{-1} (HARITONIDIS and MALEA 1995). The low concentration of metals in polluted

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Table 4. Comparison of heavy metal concentration at different *Ulva* (syn. *Enteromorpha*) species ($\mu g \cdot g^{-1}$ of dry weight)
Tabela 4. Porównanie zawartości metali ciężkich u różnych gatunków rodzaju *Ulva* (syn. *Enteromorpha*) ($\mu g \cdot g^{-1}$ suchej masy)

Taxon Takson	Site Stanowisko	Co	Cr	Cu	Mn	Zn	Reference Źródło
Ulva lactuca	Chincoteague Island (Virginia) Wyspa Chincoteague (Wirginia)	7.54	9.35	0.69	50.45	12.95	CHAUDHURI et AL. (2007) CHAUDHURI i IN. (2007)
Ulva lactuca	Assateague Island (Maryland) Wyspa Assateague (Maryland)	2.30	6.43	0.65	22.4	6.86	CHAUDHURI et AL. (2007) CHAUDHURI i IN. (2007)
Enteromorpha intestinalis	Assateague Island (Maryland) Wyspa Assateague (Maryland)	3.5	24.2	16.9	41.7	27.5	CHAUDHURI et AL. (2007) CHAUDHURI i IN. (2007)
Enteromorpha intestinalis	Marina River (Delaware) Rzeka Marina (Delaware)	9.8	8.8	0.69	42.15	13.4	CHAUDHURI et AL. (2007) CHAUDHURI i IN. (2007)
Ulva compressa	Dworski Rów Stream (Poland) Strumień Dworski Rów (Polska)	0.81	40.8	5.48	630.5	18.34	Present study Niniejsze badanie
Ulva intestinalis	Nielba River (Poland) Rzeka Nielba (Polska)	1.35	39.7	10.66	307.8	68.6	Present study Niniejsze badanie
Ulva flexuosa subsp. *pilifera*	Malta Lake (Poland) Jezioro Malta (Polska)	1.56	119.9	11.68	410.1	16.4	Present study Niniejsze badanie

water may be due to their accumulation by biota, e.i. *Ulva* thalli. Values of all examined metals in the sediment are lower than in the thalli but higher than in the water. The same was observed by DAVIES et AL. (2006) who describe sediments as the main place of metals deposition. Comparison of metal composition of *Ulva* (syn. *Enteromorpha*) species was done by HARITONIDIS and MALEA (1995), they recorded in the sediment of Gulf of Greek the concentration of Cr at the level of 2.33 to 14.49 $\mu g \cdot g^{-1}$ of dry weight, while in inland ecosystems in the Wielkopolska region the values reach up to 52.9 $\mu g \cdot g^{-1}$ of dry weight.

In most of the sites metal concentrations in *Ulva* thalli decreased in the order: Mn > Zn > Cr > Cu > Co and other stations differed only a little (Table 5). This result is very similar to concentration of trace metals in marine *Ulva rigida* C. Agardh populations (FAVERO et AL. 1996), where they decrease in the order: Al > Fe > Mn > Zn > Cu > Ni > Pb > Cr > Co > Cd. And also this result was true to order of three metals underlined: Mn > As > Zn > Cu > Pb > Cd of freshwater *Enteromorpha intestinalis* L. (AL--HOMAIDAN et AL. 2011). The most similar view of metal series occurred in the water samples and followed: Cr > Mn > Zn > Cu > Co. The abundance of metals in the sediment was similar in comparison to the concentration in the *Ulva* thalli.

Table 5. Capacity of heavy metals uptake in *Ulva* thalli, water and sediments from the examined sites
Tabela 5. Zdolność kumulacji metali ciężkich w plechach *Ulva*, wodzie i osadach z badanych stanowisk

Site Stanowisko	*Ulva* thalli Plechy *Ulva*	Water Woda	Sediments Osady
Lednica Lake (L) Jezioro Lednica (L)	Mn > Cr > Cu > Zn > Co	Cr > Mn > Zn > Cu > Co	Zn > Mn > Cu > Cr > Co
Pątnowskie Lake (P1) Jezioro Pątnowskie (P1)	Mn > Zn > Cr > Cu > Co	Cr > Zn > Mn > Cu > Co	Mn > Cu > Cr > Zn > Co
Pątnowskie Lake (P2) Jezioro Pątnowskie (P2)	Mn > Zn > Cr > Cu > Co	Cr > Mn > Zn > Cu > Co	Mn > Zn > Cr > Cu > Co
Gosławskie Lake (G1) Jezioro Gosławskie (G1)	Mn > Zn > Cr > Cu > Co	Mn > Cr > Zn > Cu > Co	Mn > Cu > Zn > Cr > Co
Gosławskie Lake (G2) Jezioro Gosławskie (G2)	Mn > Zn > Cr > Cu > Co	Cr > Mn > Zn > Cu > Co	Mn > Cu > Zn > Cr > Co
Dworski Rów Stream (D1) Strumień Dworski Rów (D1)	Mn > Cr > Zn > Cu > Co	Cr > Mn > Zn > Cu > Co	Mn > Zn > Cr > Cu > Co
Dworski Rów Stream (D2) Strumień Dworski Rów (D2)	Mn > Cr > Zn > Cu > Co	Cr > Mn > Zn > Cu > Co	Mn > Zn > Cr > Cu > Co
Nielba River (N1) Rzeka Nielba (N1)	Mn > Zn > Cr > Cu > Co	Cr > Mn > Zn > Cu > Co	Zn > Mn > Cu > Cr > Co
Nielba River (N2) Rzeka Nielba (N2)	Mn > Zn > Cr > Cu > Co	Cr > Mn > Zn > Cu > Co	Mn > Zn > Cu > Cr > Co
Malta Lake (M1) Jezioro Malta (M1)	Mn > Cr > Zn > Cu > Co	Cr > Mn > Zn > Cu > Co	Mn > Zn > Cu > Cr > Co
Malta Lake (M2) Jezioro Malta (M2)	Mn > Cr > Zn > Cu > Co	Cr > Mn > Zn > Cu > Co	Mn > Zn > Cu > Cr > Co

Useful tool to check the possibility of using species as a bioindicator is bioconcentration factor (BCF). This is a ratio which describes the relation between the concentration of metals in thalli, water and sediment (ZAYED et AL. 1998). Analysis of obtained result allows to determine "hiperaccumulators" – species, for which value of bioconcetration factor is more than 1000.

Bioconcentration factor between the concentration of metals in thalli and water is presented in Table 6. Cobalt was not included in BCF thalli-water ($BCF_{t\text{-}w}$) analysis due to very low (below the limit of detection) concentration of metals in water. In this study, $BCF_{t\text{-}w}$ refers to the concentration of heavy metals in a thalli per content of these metals in the water. The high values (> 1000) of bioconcentration factor for freshwater populations of *Ulva* were noted for all metals. BCFs for manganese in each position were higher than 1000, from 19.8×10^2 to 53.7×10^3, probably because of utilization of the metal in photosynthesis (HALL and RAO 1999). In studies on metal accumulation by *Enteromorpha intestinalis* conducted by CHAUDHURI et AL. (2007) the highest BCF for Mn was also determined. *Ulva rigida* and *Enteromorpha linza* show high values of concentration factors for Co: 1566 and 1500 respectively and for Cr: 1171 and 1404 respectively (HARITONIDIS and MALEA 1995).

Table 6. Ratio of heavy metals concentration in *Ulva* thalli to that in water ($BCF_{t\text{-}w}$) and in sediments ($BCF_{t\text{-}s}$) from the examined sites (in bold: BCF > 1000)
Tabela 6. Stosunek zawartości metali ciężkich w plechach *Ulva* do ich zawartości w wodzie ($BCF_{t\text{-}w}$) i osadach ($BCF_{t\text{-}s}$) z badanych stanowisk (bold: BCF > 1000)

Metal	L	P1	P2	G1	G2	D1	D2	N1	N2	M1	M2
	$BCF_{t\text{-}w}$										
Cr	2.2×10^2	**1.3×10^3**	2.8×10^2	2.6×10^2	**2.3×10^3**	2.8×10^2	2.6×10^2	3.2×10^2	2.5×10^2	7.2×10^2	9.2×10^2
Cu	5.7×10^2	**1.9×10^3**	**2.1×10^3**	**1.5×10^3**	**8.8×10^3**	4.5×10^2	3.7×10^2	5.4×10^2	**1.6×10^3**	6.3×10^2	5.6×10^2
Mn	**1.9×10^3**	**5.4×10^4**	**1.6×10^4**	**2.3×10^3**	**2.9×10^4**	**3.8×10^4**	**1.4×10^4**	**2.8×10^3**	**1.2×10^4**	**3.2×10^3**	**6.2×10^3**
Zn	1.3×10^2	**2.7×10^4**	**7.5×10^3**	**2.2×10^3**	**2.9×10^4**	1.0×10^3	6.9×10^2	1.5×10^3	**4.5×10^3**	9.2×10^2	2.7×10^2
	$BCF_{t\text{-}s}$										
Co	0.18	4.43	0.17	0.31	3.01	0.24	0.15	0.30	0.56	0.96	1.76
Cr	2.43	6.37	0.82	1.08	45.68	0.84	0.88	1.92	4.41	21.19	22.73
Cu	0.39	1.30	1.39	0.04	0.22	0.27	0.16	0.22	0.41	0.52	1.02
Mn	1.07	9.78	2.01	0.78	5.73	1.55	0.20	2.03	2.11	1.18	6.49
Zn	0.05	77.93	2.43	0.93	9.71	0.33	0.16	0.31	0.65	0.49	0.82

BCF thalli-sediment ($BCF_{t\text{-}s}$) is defined as the ratio of metals concentration in the thalli to that in the sediment. BCFs calculated for the thallus and sediment were very low, never exceeding 1000. The highest values of $BCF_{t\text{-}s}$ were recorded for Zn: 77.93.

Rybak A., Messyasz B., Pikosz M., Szendzina L., Łęska B., 2013. Accumulation of heavy metals (Co, Cr, Cu, Mn, Zn) in the freshwater alga *Ulva* type, sediments and water of the Wielkopolska region, Poland. Nauka Przyr. Technol. 7, 4, #66.

Conclusions

1. The relative abundance of metals in freshwater *Ulva* thalli decreased in the order: Mn > Zn > Cr > Cu > Co and in the water: Cr > Mn > Zn > Cu > Co, whereas in the sediment was the same as in thalli except Cu > Cr.

2. Concentrations of metals were generally similar to other studies with different species from freshwater *Ulva* genera.

3. High levels of heavy metals in the Pątnowskie Lake and Gosławskie Lake are a result of very polluted waters.

4. Freshwater *Ulva* from the Wielkopolska region exhibited the highest contamination for Mn among the studied metals (Co, Cr, Cu, Mn and Zn).

5. More data is needed in order to draw conclusions concerning the possible utilization of freshwater forms of *Ulva* as an indicator for Mn contamination.

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AKUMULACJA METALI CIĘŻKICH (Co, Cr, Cu, Mn, Zn) W PLECHACH ZIELENIC RODZAJU *ULVA*, OSADACH ORAZ WODZIE NA TERENIE WIELKOPOLSKI, POLSKA

Streszczenie. Badano stężenie pięciu pierwiastków śladowych: kobaltu (Co), chromu (Cr), miedzi (Cu), manganu (Mn) i cynku (Zn) w plechach *Ulva*, wodzie i osadach pobranych z różnych stanowisk śródlądowych (jeziora, strumień i rzeka) na terenie Wielkopolski w okresie letnim 2010 roku. Wieloelementową analizę zawartości metali ciężkich przeprowadzono za pomocą metody ICP-OES. Celem badań było określenie możliwości zastosowania tubokształtnych zielenic rodzaju *Ulva* w biomonitoringu. Względna zawartość badanych metali w osadach malała w następujący sposób: Mn > Zn > Cu > Cr > Co, a w wodzie: Cr > Mn > Zn > Cu > Co. Zielenice rodzaju *Ulva* kumulowały badane pierwiastki w następującej kolejności: Mn > Zn > Cr > Cu > Co. Wyniki wskazują, że zmiany stężenia metali ciężkich w plechach makroglonu, wodzie i osadach wykazują niewielkie różnice, jednak ogólny układ koncentracji wydaje się podobny, ponieważ Mn występuje zawsze w największym stężeniu, a Co – w najmniejszym. Możliwość zastosowania gatunków rodzaju *Ulva* jako biowskaźników zanieczyszczenia wód manganem wymaga dalszych badań.

Słowa kluczowe: bioakumulacja, *Ulva*, *Enteromorpha*, metale ciężkie, bioindykator

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Accepted for publication – Zaakceptowano do opublikowania:
6.11.2013

For citation – Do cytowania:
Rybak A., Messyasz B., Pikosz M., Szendzina L., Łęska B., 2013. Accumulation of heavy metals (Co, Cr, Cu, Mn, Zn) in the freshwater alga Ulva *type, sediments and water of the Wielkopolska region, Poland. Nauka Przyr. Technol. 7, 4, #66.*