



Cadmium and Lead Accumulation in Water and Macrophytes in an Artificial Lake

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1. Introduction

Heavy metals are one of the main pollutants of the environment, especially in urban areas. Cadmium and lead concentrations in environmental elements are dependent on anthropogenic sources; hence we can suspect higher concentrations in urban areas. Water reservoirs can play the role of a specific natural sink for trace elements (Birch et al. 1996) or even may have a function of natural filters for the abatement of heavy metals (Weiss & Weiss 2004). Wetland plant species, such as *Typha latifolia* (L.), *Typha angustifolia* (L.) and *Phragmites australis* (Cav. Trin ex Steudel), have been found to be important for trace elements' accumulation in freshwater ecosystems (Bragato et al. 2006, Drzewiecka et al. 2010, Fediuc & Erdei 2002). Although these plants are not hyperaccumulators, they can play an important role as removers of trace elements, due to fast growth, high biomass production, a deep root system, and high tolerance and/or accumulation of a wide range of trace elements (Cooper & Green 1995).

Heavy metal concentrations can change during the year in the ecosystem, and plant uptake possibilities can also change during the growing season (Drzewiecka et al. 2010). Trace element concentrations in wetland plants collected from natural ecosystems can also be a type of monitoring system for the level of environment pollution by these pollutants (Demirezen & Aksoy 2004). Uptake and accumulation of elements by plants may follow two different paths – the root system and the foliar

surface (Sawidis et al. 2001). In artificial lakes and rivers, plants mainly absorb metals from the water, not from the sediments (Lewander et al. 1996). Moreover, the pattern of accumulation is different in different elements. Some authors have reported a major role of roots as Cd and Pb filters for other plant organs (Mazej & Germ 2009), while others recorded transport to above-ground plant parts (Pevery et al. 1995).

The aims of this study were as follows: (i) to determine changes in concentrations of cadmium and lead in water and two macrophyte species during the growing season; (ii) to determine the differences of elements' location in plant organs of two plants; (iii) to examine Pb and Cd bioaccumulation by two littoral plant species in natural conditions and contamination in water ecosystem.

2. Materials and methods

According to the physical and geographical classification of Poland, the Cybina river lies in Wielkopolska Lakeland (Kondracki 2009). This river is a third order river, and the right tributary of the Warta river. The river catchment area is 190.61 km² (Fig. 1). According to the code system of the European Union, the river received the code 1858 (Czarnecka 2005). From the source, which is Lake Ósemka at altitude 119.9 m a.s.l., to the mouth to the Warta river at altitude 51.8 m a.s.l. the Cybina river across 43 km, which gives a river slope of about 1.6‰.

Land use of the catchment is mainly agricultural (approx. 60% of the area), while forestry area covers about 31%. There is a high lake ratio, about 3.4% of its area. The catchment area is located in the lowest precipitation zone (approx. 550 mm), with the highest number of sunny days (more than 50 days) and the lowest number of cloudy days (less than 130). Mean annual air temperature is 8°C, and the growing season varies between 210 and 220 days.

Malta Lake is located in the lower part of the Cybina catchment. This artificial reservoir was built in and is located on the right bank of the Warta river. The reservoir covers a maximal area of 65.5 ha, with a length of 2.2 km (circuit 5.6 km), which makes it the biggest artificial water reservoir in the city of Poznan. The mean depth is over 3.13 m, while the maximum is 5 m (Maluškiewicz 2000). This water reservoir was built for water sports, active and passive recreation and fire-protection purposes (Bogucki & Staniewska-Zątek 1996). Once every

four years the water is drained and the lake is deepened together with conservation activities.

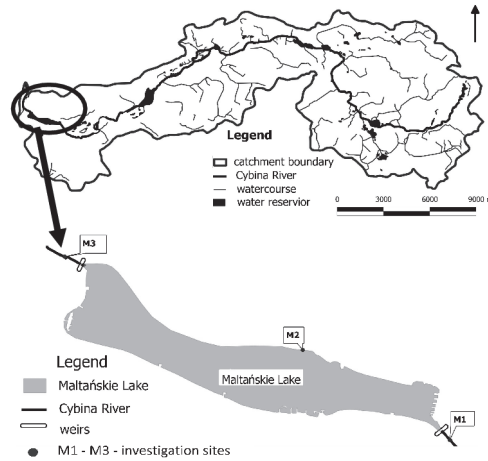


Fig. 1. Cybina river catchment with labeled investigation sites

Rys. 1. Zlewnia rzeki Cybiny wraz z zaznaczonymi punktami pomiarowo-kontrolnymi

Samples of water and plants were collected for further laboratory analyses. The water was collected from three sites – along the Cybina river course (before and after Malta Lake) and from Malta Lake (Fig. 1). Water was sampled five times in the growing season of 2012, every month from April to September, excluding July. Samples of water were placed in polypropylene bottles and acidified with nitric acid to obtain cation-exchangeable forms.

Plants were collected only from the lake area at the beginning and at the end of the growing season – in May and September. Common reed (*Phragmites australis* Cav. Trin ex. Steudel) and narrow-leaved cattail (*Typha angustifolia* L.) were chosen for heavy metal concentration investigations. Five plants of each species were selected, and divided into plant organs. In the case of *P. australis* three plant organs, rhizomes, stem and leaves, while from *T. angustifolia* rhizomes and leaves were collected.

The samples of analysed materials after collection were washed with distilled water (Milli-Q Academic System (non-TOC) – with the

exception of soils – and dried in an electric drier (SLW 53 STD, Pol-Eko) at $105 \pm 1^\circ\text{C}$ for 72 h (analysis of plant/soil dry weight). Dry samples were ground to a powder for 2 min in a laboratory cutting boll mill. The material as three representative samples (0.5 g each) was mineralized in a CEM Mars 5 Xpress microwave mineralization system (CEM, Matthews, NC) in a closed system (55 mL vessels) using 65% HNO_3 (5 mL) and 30% H_2O_2 (1 mL). Digestion of the plant materials was performed according to a microwave program composed of three stages: first stage – power 600 W, time 4 min, temperature 120°C ; second stage – power 600 W, time 5 min, temperature 200°C ; third stage – power 1200 W, time 6 min, temperature 200°C . Materials after digestion were filtered through 45 mm filters (Qualitative Filter Papers Whatman, Grade 595: 4-7 μm) and whole contents were made up to a final volume of 50 mL.

Analysis of contents of Pb and Cd in plant materials was conducted by flame atomic absorption spectrometry (FAAS), and in lake waters by electrothermal atomic absorption spectrometry (ETAAS) using an Agilent Technologies AA Duo – AA280FS/AA280Z spectrometer (Mulgrave, Victoria, Australia). All analyses used hollow-cathode lamps (HCL) (Varian and Perkin Elmer); lamps were used for one element. The results were validated by analyses of randomly selected samples by inductively coupled plasma optical emission spectrometry (ICP-OES) with a Vista MPX instrument (Varian), additionally the standard additions has been applying for the accuracy testing, the recoveries have been in the range 80-120%. The limits of determination were 0.1 mg kg^{-1} and 0.001 mg L^{-1} respectively for solid and water samples for both elements determined. Precision has been on the level 3% for FAAS and 1.5% for ETAAS.

The obtained results were the basis for evaluation of the degree of water and plant pollution. The contamination factor was calculated as follows:

$$C_{fi} = \frac{C^i}{C_{ni}} \quad (1)$$

where C^i is the mean concentration of substance in water, and C_{ni} is the reference level for the substance. The following criteria are used to describe the values of the contamination factor: $C_f^i < 1$, low contamination factor (LCF); $1 \leq C_f^i < 3$ moderate contamination factors (MCF); $3 \leq C_f^i < 6$, considerable

contamination factors (CCF); and $C_f^i \geq 6$, very high contamination factor (VHCF) (Zarei et al., 2014). The pollution load index (PLI) was calculated based on equation:

$$PLI = \frac{C_{fi}(1) \cdot C_{fi}(2) \cdot \dots \cdot C_{fi}(n)}{n} \quad (2)$$

where n is the number of metals and $C_{fi}^i(n)$ is the contamination factor analyzed metals. The following criteria are used to describe the values of the pollution load index: $PLI < 1$, no pollution (NP); $1 \leq PLI < 2$, moderate pollution (MP); $2 \leq PLI < 3$, heavy pollution (HP); and $PLI \geq 3$, extremely heavy pollution (EHP) (Banerjee and Gupta, 2012). The accumulation efficiency of analysed trace elements in plant organs was described using bioaccumulation factor (BAF) values calculated according to Cohen et al. (1998) as the ratio of a trace element concentration in individual plant (rhizomes, stems and leaves) organs and trace element concentrations in water. BAF values greater than 1 indicate accumulation, while those lower than one indicate a lack of accumulation. Additionally, in order to describe trace elements' transport from water to the plants, the translocation factor (TF) was calculated according to Yu & Zhou (2009). Wherein $TF > 1$ indicates that the plant translocates metals effectively.

Statistical analyses employed STATISTICA 9.1. Results were analyzed with factorial ANOVA, with period, site and plant species as fixed factors. Tukey's test was used to analyze the differences between measured parameters. For determination of structure and rules in the relations between variables, principal component analysis (PCA) was used. In this analysis, the orthogonal transformation of observed variables to a new set of non-correlated variables (components) is performed.

3. Results and discussion

Heavy metal concentration in water

Two-way ANOVA revealed a highly significant ($\alpha \leq 0.001$) effect of site and date of sampling on all measured heavy metal concentrations in water (Table 1).

Table 1. Two-way analysis of variance results (F test statistics and significance levels) of Cd and Pb concentrations in water and plant organs with period of measurement and site of measurement or period of measurement and plant organ fixed factors ($***\alpha \leq 0.001$; $**\alpha \leq 0.01$; $*\alpha \leq 0.05$; ns – not significant)

Tabela 1. Wyniki dwuczynnikowej analizy wariancji (statystyki testowe F i poziomy istotności) stężenia Cd i Pb w wodzie i organach roślin z okresem oraz miejscem pomiarowym albo okresem pomiarowym i organem rośliny jako czynnikami wpływającymi na badany parametr ($***\alpha \leq 0.001$; $**\alpha \leq 0.01$; $*\alpha \leq 0.05$; ns – nieistotne statystycznie)

Heavy metal	Term of measurement	Site of measurement	Interaction
Water concentrations			
Cd	74.3***	323.6***	4.9***
Pb	6.9***	1690.9***	1.5ns
Accumulation in plants			
	Term of measurement	Plant's organ	Interaction
<i>Phragmites australis</i>			
Cd	7.3*	169.7***	0.03ns
Pb	829.4***	2273.3***	177.8***
<i>Typha angustifolia</i>			
Cd	15.3**	339.3***	0.03ns
Pb	776.5***	5166.5***	147.2***

Cadmium concentrations did not reveal levels considering as polluted water, which is $0.2 \mu\text{l l}^{-1}$ (Samecka-Cymerma & Kampers 2001). The highest level was observed in April at the site located below Malta Lake, and did not reach a value of $0.15 \mu\text{l l}^{-1}$. Cadmium concentrations increased along the Cybina river's course. Moreover, a higher level of this element's concentration was noted at the beginning of the growing season and in July. The latter one was probably connected with human activity along Malta Lake. We can also observe that this increase was the highest in samples collected from the Malta reservoir.

Similar levels of Pb concentrations were recorded in samples collected from the Malta inflow and the lake itself during the whole sample collection period. However, similarly as in the case of Cd, an increase of Pb concentrations (although not statistically significant between measurement periods) was observed in July at these two sites. Three times higher Pb concentrations were noted in the stream below Malta Lake during the whole growing season. Moreover, we can again note higher levels during the July sampling time and elevated values in the last two

periods. The higher Pb concentration in water of Cybina river in Malta Lake outflow could be caused with Pb release from lake sediments, as well as from surface water flow of near roads and it is also another possible source from near located industry (Fig. 2). Similarly as in the case of cadmium, the level of Pb was very low, and at the last site did not even reach 1/5 of the value which is treated as polluted water (Samecka-Cymerman & Kampers 2001).

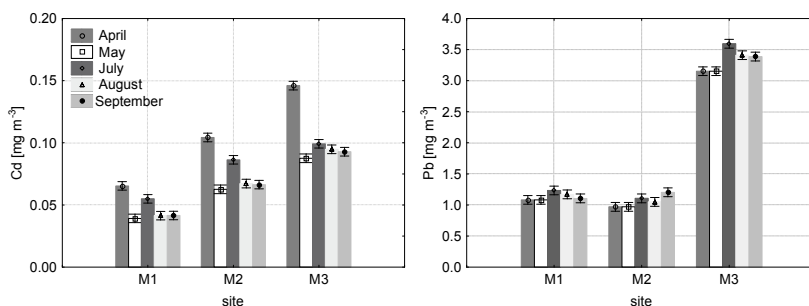


Fig. 2. Cd and Pb concentrations in water collected from three sites within five periods

Rys. 2. Stężenia kadmu i ołowiu w wodzie pobranej z trzech stanowisk pomiarowych w pięciu terminach

The contamination factor (C_{fi}) indicated a low level of contamination for cadmium during the whole season at all measurement points. In the case of lead a low level of C_{fi} was noted at the first two measurement points and an increase to a medium level was noted in the outflow of Malta Lake (Table 2).

The contamination factors of Cd and Pb were at relatively low levels in comparison to the industrial area of river water collected near to the industrial area of Kosovo (Ferati et al. 2015). The pollution load index was three times lower than that recorded by Ferati et al. (2015), although in both cases the pollution level was not reached. Higher levels of C_{fi} for Cd and Pb were also recorded in water collected from a coastal port area of Malaysia (Sany et al. 2013) and the Maharlu saline lake in Iran (Moore et al. 2009) in comparison to our results.

Table 2. Contamination factor of both measured trace elements and Pollution Load Index of water in measurement sites and terms

Tabela 2. Współczynnik zanieczyszczenia obu badanych pierwiastków śladowych oraz Indeks Ładunku Zanieczyszczeń w wodzie we wszystkich punktach i terminach badawczych

Month	site	Cd	Pb	Pollution load index (PLI)
April	M1	1.934 (LCF)	0.361 (LCF)	0.392 (NP)
May		1.934 (LCF)	0.361 (LCF)	0.235 (NP)
July		2.172 (LCF)	0.411 (LCF)	0.485 (NP)
August		2.053 (LCF)	0.390 (LCF)	0.302 (NP)
September		2.025 (LCF)	0.369 (LCF)	0.279 (NP)
April	M2	1.683 (LCF)	0.324 (LCF)	0.370 (NP)
May		1.683 (LCF)	0.324 (LCF)	0.222 (NP)
July		1.891 (LCF)	0.369 (LCF)	0.463 (NP)
August		1.787 (LCF)	0.350 (LCF)	0.290 (NP)
September		1.763 (LCF)	0.401 (LCF)	0.320 (NP)
April	M3	1.056 (LCF)	1.051 (MCF)	0.883 (NP)
May		1.056 (LCF)	1.051 (MCF)	0.530 (NP)
July		1.186 (LCF)	1.198 (MCF)	0.927 (NP)
August		1.121 (LCF)	1.137 (MCF)	0.698 (NP)
September		1.106 (LCF)	1.129 (MCF)	0.662 (NP)

Accumulation of trace elements in plant organs

Two-way ANOVA revealed a highly ($\alpha \leq 0.001$) significant effect of plant organ on concentrations of all elements in plants, similarly as the period of sampling, with the exception of cadmium (Table 1).

An increase of both elements during the growing season in all plant organs of both plant species was recorded. An increase of trace element concentrations in plant organs has previously been found by many authors in a constructed wetland (Vymazal et al. 2007) and in natural ecosystems (Drzewiecka et al. 2010, Duman et al. 2007). Cd accumulation in rhizomes was noted at a similar level for both plant species. Moreover, a comparable level of this element's translocation to above-ground plant organs was found. In the case of Pb, slightly higher accumulation was observed in *Typha angustifolia* rhizomes and leaves, and higher transport of this trace element was observed in this plant species (Fig. 3).

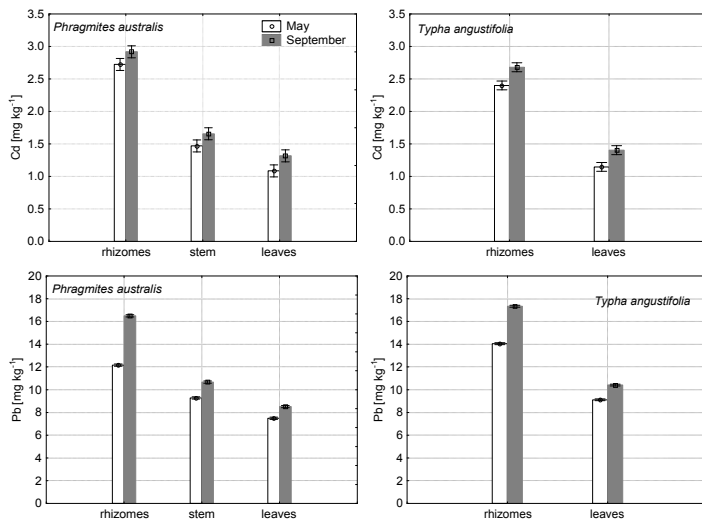


Fig. 3. Cd and Pb accumulation in *Phragmites australis* and *Typha angustifolia* organs collected from Malta Lake within two periods

Rys. 3. Poziom akumulacji Cd i Pb w organach *Phragmites australis* i *Typha angustifolia* zebranych z Jeziora Malta w dwóch terminach badawczych

Our results concerning higher concentrations of Pb and Cd in belowground plant organs are in agreement with many previous investigations conducted in constructed wetlands as well as in natural ecosystems with such plant species as *Phragmites australis*, *Phalaris arundinacea* (Vymazal et al. 2007), *T. angustifolia*, *Potamogeton pectinatus* (Demirezen & Askoy 2004), *Carex rostrata* (Stozl & Greger 2002), *Nuphar lutea* and *Potamogeton nodosus* (Mazej & Germ 2009), *Hydrocharis morsus-ranae* (Gałczyńska & Bednarz 2012), and *Ceratophyllum demersum* L. (Senze et al. 2009). On the other hand, some authors have recorded transport of Pb to the upper parts of plants, for example in *P.* (Liu et al. 2007, Peverly et al. 1995) and *Eriophorum angustifolium* (Stoltz & Greger 2002). The bioaccumulation factor for cadmium increase was also noted for growing season in all plant organs of both analysed species. In the case of Pb an increase of BAF was only recorded for rhizomes of *P. australis* (Table 3).

Table 3. Bioaccumulation factor (BAF) values for plant organs of *P. australis* and *T. angustifolia* from water in two measurement terms

Tabela 3. Wskaźnik bioakumulacji (BAF) pierwiastków pobranych z wody odniesione do organów roślin *P. australis* i *T. angustifolia* w dwóch terminach badawczych

Term of measurement	BAF values					
	Cd	Pb	Cd	Pb	Cd	Pb
<i>P. australis</i>						
	rhizomes		stems		leaves	
May	43.68	12.57	23.68	9.59	17.46	7.75
September	44.08	13.71	25.00	8.87	19.94	7.08
<i>T. angustifolia</i>						
	rhizomes		stems		leaves	
May	38.50	14.53	–	–	18.33	9.44
September	40.53	14.41	–	–	21.22	8.66

However, the highest translocation factor values were noted for *P. australis* from rhizomes to stems for Pb. Moreover, Pb revealed the highest level of translocation from rhizomes to leaves in both plant species (Table 4).

Table 4. Translocation factor (TF) values for plant organs

Tabela 4. Wartości wskaźnika translokacji (TF) dla organów roślin

Term of measurement	Plant organs	Translocation factors	
		Cd	Pb
<i>P. australis</i>			
May	rhizomes → stems	0.54	0.76
September		0.57	0.65
May	rhizomes → leaves	0.40	0.62
September		0.45	0.52
<i>T. angustifolia</i>			
May	rhizomes → leaves	0.48	0.65
September		0.52	0.65

Relations between parameters

A positive linear correlation was observed between water Cd and Pb content and plant organs of both species. However, for Pb these relations were highly statistically significant ($p \leq 0.001$) (Fig. 4). Anyway,

these relations suggest the positive role of chosen plant species in removing both elements from water. Our results are in agreement with investigation of Lewander et al. (1996), who found a positive relation between water heavy metal content and plant accumulation in a river. Usually, this relation is more evident for sediment in lakes (Weiss, & Weiss, 2004). However, in our case the sediment is moved every 4th year; hence more relevant information should be obtained from water heavy metal contents in relation to plant concentrations.

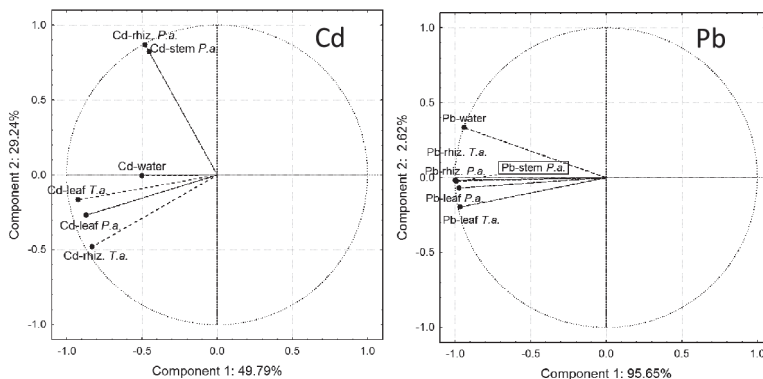


Fig. 4. Principal component analysis of Cd and Pb concentrations in plant organs and water (*Rhiz.* – rhizomes; *P.a.* – *P. australis*; *T.a.* – *T. angustifolia*)

Rys. 4. Analiza składowych głównych dla ołowiu i kadmu zakumulowanych w roślinach i wodzie

4. Conclusions

The levels of cadmium and lead were relatively low in water and in plant organs. Our investigations revealed an increase of Pb and Cd along the Cybina river. This was especially valid for Pb, which might suggest the effect of urban sources. There was also evidence for an increase of both elements during July, when a high number of tourists is usually recorded in this area. Moreover, higher concentrations of both elements were noted in belowground plant organs of both examined plant species, as well as accumulation during the growing season. This makes it possible to treat these species as good indicators of Pb and Cd contents in artificial lakes located in an urban area and possible heavy metal removers even when there are relatively low concentrations in water. Both

elements revealed a high level of BAF, especially Pb. Moreover, Pb revealed the higher translocation to upper parts of plants of both analysed species in comparison to Cd. Uptake and transport to upper parts of plants of both elements was positively correlated with water concentration.

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Akumulacja kadmu i ołowiu w wodzie i makrofitach w sztucznym zbiorniku wodnym

Streszczenie

Celem przeprowadzonych badań była ocena poziomu stężenia kadmu i ołowiu w wodzie i roślinach jeziora Malta oraz na jego dopływie i odpływie. Badano dwa gatunki roślin (trzcina pospolita, palka wąskolistna) jako potencjalne wskaźniki albo akumulatory pierwiastków śladowych w zbiorniku wodnym zlokalizowanym na terenie miejskim. Wyższe stężenia kadmu zanotowano w jeziorze oraz w rzece poniżej jeziora zwłaszcza w kwietniu. Natomiast w przypadku ołowiu wyższe stężenia tego pierwiastka notowano w rzece poniżej jeziora, co spowodowane mogłoby być uwalnianiem ołowiu z osadów dennych oraz z dopływu ze szlaków komunikacyjnych i terenów produkcyjnych położonych w dolnej części jeziora. Współczynnik zanieczyszczenia wykazał niski lub średni poziom dla obu badanych pierwiastków. Wykazano akumulację obu pierwiastków we wszystkich organach obu gatunków roślin w ciągu sezonu wegetacyjnego. Wyższe poziomy stwierdzono w organach podziemnych roślin, co może sugerować, że ich źródłem jest głównie woda. Wskaźnik translokacji informuje jednak, że ołów był w większych ilościach transportowany do części nadziemnych niż kadm.

Abstract

The aim of the present study was to evaluate Cd and Pb concentrations in water and plants of Malta Lake and its inflow and outflow. We evaluated two water plant species (common reed, narrow-leaved cattail) as potential indicators or accumulators of trace elements in water reservoirs in city areas. Higher cadmium concentration was noted in the lake and lake outflow, especially in April. While in the case of lead higher concentrations were recorded in the river on the lake outflow, which can be caused by lead release from lake sediments and water surface flow roads and industry area located nearby the lake. The contamination factor indicated a low or medium level for both elements. Accumulation of both heavy metals in plant materials was observed during the growing season in all plant organs. Higher levels of both heavy metals were noted for below-ground organs, which may suggest water as a main source of these elements. However, the translocation factor indicated that Pb were transported in the highest amounts to the above-ground parts of plants.

Słowa kluczowe:

Jeziro Malta, kadm, ołów, rośliny wodne

Keywords:

Malta Lake, cadmium, lead, water plants