Kragujevac J. Sci. 41 (2019) 169-180. UDC 581.5:582.542.11:546.72/711/56/47/815(497.11)
Original scientific paper

SEASONAL DYNAMICS OF HEAVY METAL BIOACCUMULATION (Fe, Mn, Cu, Zn and Pb) IN *Phragmites australis* (Cav.) Trin. ex Steud. IN BARDAČA FISHPOND

Tanja Maksimović[a], Srđan Rončević[b] and Biljana Kukavica*

[a]*University of Banja Luka, Faculty of Sciences and Mathematics, Mladena Stojanovića 2, 78000 Banja Luka, Republic of Srpska, Bosnia and Hercegovina*
[b]*University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića 2, 21000 Novi Sad, Serbia*

* Corresponding author; E-mail: biljana.kukavica@pmf.unibl.org

(Received January 2th, 2019; Accepted February 10th, 2019)

ABSTRACT. Paper monitors seasonal dynamics of heavy metals bioaccumulation (Fe, Mn, Cu, Zn and Pb) of emerged plant *Phragmites australis* (Cav.) Trin. ex Steud. on two localities (Necik and Sinjak) in the area of Bardača fishpond (BiH-Republic of Srpska). Dynamics of heavy metals bioaccumulation varied depending on sampling period, locality and plant organ. Concentration, transfer (transport) and accumulation of metals from sediment to rhizome above ground plant part was evaluated based on biological concentration factor (BCF), translocation ability (TA) and bioaccumulation factor (BAC). The highest average BCF value in researched species was determined for Fe (0.87) and the lowest for Zn (0.18). Bioaccumulation coefficient was the highest for Mn (0.82) and the lowest for Fe (0.20) whereas TA was the highest for Zn (2.28) and Mn (2.70). For Fe, it was significantly lower (0.24). Based on values for BCF, TA and BAC, *Phragmites australis* (Cav.) Trin. ex Steud. could be identified as accumulator for Mn and indicator for metals Fe, Zn and Cu and it has good potential for application in phytoremediation techniques, especially in phytostabilization and phytoextraction of polluted land. Considering the fact that higher degree of bioaccumulation was recorded in the period at the end of season, we could take this period as a signal for their removal from water ecosystems.

Keywords: water macrophytes, *Phragmites australis* (Cav.) Trin. ex Steud., sediment, heavy metal, accumulation

INTRODUCTION

Water macrophytes, being very important components of water ecosystems, have a key role in heavy metal bioaccumulation from water systems, hence are more often used for evaluation of pollution level and removal of heavy metals from environment (ZUBCOV *et al.*, 2003; BALDANTONI *et al.*, 2005; ŠTRBAC *et al.*, 2014). Different water macrophytes adopt and accumulate metals with different intensity where degree of bioaccumulation varies depending on species, metal concentration in a species, sediment, physical-chemical characteristics of water and abiotic environmental factors (SAMECKA-CYMERMAN *et al.*, 2001; MAZEJ and GERM, 2009; GRUDNIK, 2010; MILOŠKOVIĆ *et al.*, 2013). Differences are especially evident in species growing on anthropogenic habitats or those naturally rich in heavy metals (SAMECKA-CYMERMAN *et al.*, 2001; RAVERA, 2001; MARCHAND *et al.*, 2010). Contents of heavy metals in emerged plants varies in relation to researched organ and type of element (LARSEN and SCHIERUP, 1981; WEIS *et al.*, 2003; WEIS and WEIS, 2004) which significantly depends on seasonal dynamics of plant growth as well as on decreased rate of transport from root towards organs for storage and detoxification (aboveground plant parts) (BALDANTANONI *et al.*, 2005; BAI *et al.*, 2014). Rooted macrophyte such as *Ph. australis* is more affected by heavy metals originating from sediment rather than those originating from water and hence, bioaccumulation degree increases especially if sediment is loaded by heavy metals (ZWOLSMAN *et al.*, 1993). Some studies showed that heavy metals could be accumulated and kept in swamp land for longer period not differentiating significantly during season. Numerous studies (BONANO and GIUDICE, 2010; BONANO, 2011; BAI *et al.*, 2014; ESMA-EILZADEH *et al.*, 2016) indicate to positive correlation among metals in sediment and their accumulation in reed organs as well as that metals remain longer in underground organs and hence protect aboveground parts from exceeded bioaccumulation (BALDANTONI *et al.*, 2005).

Numerous experimental studies showed that emerged plants with large biomass, *Ph. australis*, are able to accumulate heavy metals in high concentrations and releasing them during aging (WEIS *et al.*, 2003; WEIS and WEIS, 2004; BRAGATO *et al.*, 2009; GRUDNIK, 2010; EID *et al.*, 2012; BAI *et al.*, 2014; BOROWIAK *et al.*, 2016; KANCLERZ *et al.*, 2016). Taking this fact into consideration, these plants are very often used in phytoremediation techniques in order to decrease heavy metal concentration in sediment and water of polluted water ecosystems (BRAGATO *et al.*, 2009). Being a good bioaccumulator of heavy metals (DUMAN *et al.*, 2007; BRAGATO *et al.*, 2009; BOROWIAK *et al.*, 2016) reed found a broad application in cleaning municipal and industrial waste waters loaded by heavy metals.

In previous researches we pointed out changes in concentration and loading of heavy metals in water and sediment in the area of Bardača fishpond (MAKSIMOVIĆ *et al.*, 2016a; MAKSIMOVIĆ *et al.*, 2016b). In those studies, comparison in bioaccumulation of heavy metals between various water macrophytes, where we considered aboveground reed part was also made. In this research, we wanted to point out differences in bioaccumulation among reed organs, as emerged plant, in vegetation season. One of the aims also was to establish in which period heavy metal accumulation had been the best, in order to determine mutual relation and made evaluations of reed application in phytoremediation techniques.

MATERIALS AND METHODS

Analyzed area is Bardača fishpond. Geographic location of Bardača fishpond is in the middle of temperate climate (450 08' North latitude and 170 25' East longitude), at about 100 m elevation, in the foothill of Motajica Mountain. Bardača covering 2810 ha (810 ha water and 2000 ha land ecosystems) existed under state ownership. In 1969, Bardača was accepted as special natural reserve and since then it had served for production of cyprinids. Since 2007, area of Bardača fishpond was included in the list of worlds protected swamp areas (Ramsar site), which designated it as Important Bird Area and confirmed its international importance. However, after acquiring this status, under strong anthropogenic influence, there was major devastation and ruining this sensitive ecosystem. The following systems fall into composition of Bardača fishpond: Dugo polje I, Dugo polje II, Dugopoljski Lug, Ljetni basen, Sinjak, Necik, Rakitovac, Prevlaka, Veliki Dajkovac, Mali Dajkovac and Brzajski (ĐURIĆ *et al.*, 2004). Researches were performed on the localities Necik and Sinjak, which were active fish basins during research period.

Sampling was performed in coastal area of fish basins each month (May-October) on the same profile points on selected localities. Plant material was washed with tap water and distilled water afterwards and was further prepared for chemical analysis applied for water and water plant described in APHA (1995). Concentrations of heavy metals were defined by atomic absorption spectrophotometer Aanalyst 700, produced by Perkin Elmer, USA, using flame technique, standard method EPA 7000B. All the analyses were performed in three independent repetitions, and analyzed parameters were processed by variance method (ANOVA) factorial experiment.

Concentration, translocation and accumulation of metal from sediments to roots and aboveground part was estimated based on Bioconcentration factor (BCF) (YOON *et al.*, 2006), translocation ability (TA) and bioaccumulation coefficient (BAC). Factors are used for evaluation of potential species in phytoremediation techniques (CUI *et al.*, 2007; LI *et al.*, 2007).

Compared to contents of metal in sediment, BCF was calculated based on following formula:

$$BCF = \frac{[Metal]_{root}}{[Metal]_{sediment}}$$

Greater ratio of BCF indicates bigger bioaccumulation ability.

Plants' ability to relocate metals from root to aboveground part was estimated through translocation ability (TA). TA was calculated as ratio of metal concentrations in root and aboveground part of the plant:

$$TA = \frac{[Metal]_{aboveground\ part}}{[Metal]_{root}}$$

Bioaccumulation coefficient (BAC) was calculated as ration of heavy metals in aboveground part to the one in sediment as described in procedure LI *et al.* (2007).

$$BAC = \frac{[Metal]_{aboveground\ part}}{[Metal\ ]_{sediment}}$$

where [Metal] refers to measured concentration of given metal in root, aboveground part of the plant and sediment.

RESULTS AND DISCUSSION

In the area of Bardača fishpond, presence of heavy metals is a result of anthropogenic influence in the first place due to inflow of household and agricultural waste waters. Heavy metal accumulation in sediment is a result of its long-term deposition and containment, whereas concentrations of microelements in water are mostly indictors of recent pollution (BALDANTONI *et al.*, 2005; MAZEJ and GERM, 2009; MAZEJ *et al.*, 2010). Heavy metal concentration in sediment of researched localities presented in papers MAKSIMOVIĆ *et al.*

(2016a; 2016b) were as follows: Fe 617-620 mg/kg; Mn 189-628 mg/kg; Zn 51-71 mg/kg; Cu 2.8-17.72 mg/kg and Pb in detection limits (<51 mg/kg), which had been significantly lower compared to other similar researches (MILOŠKOVIĆ *et al.,* 2013; ŠTRBAC *et al.,* 2014; KUCAJ and ABAZI, 2015).

Results presented in paper MAKSIMOVIĆ *et al.* (2016b) point out that levels of Fe and Mn in sediment of researched area were higher than allowed concentrations in relation to the results presented in the paper KABATA-PENDIAS (2001). Compared to earlier researches of this area (MAKSIMOVIĆ *et al.,* 2007, MAKISMOVIĆ and ILIĆ, 2008), concentration values of Mn in sediments increased 2-5 times in 7 years (MAKSIMOVIĆ *et al.,* 2016b). Generally, seasonal variations were recorded in concentration of heavy metals in sediment for Mn, Zn and Cu, whereas Fe concentration remained quite constant during research period (MAKSIMOVIĆ *et al.,* 2016a; 2016b). Pollution of aquatic ecosystems with heavy metals is the most evident in high levels of metals in sediment and macrophytes rather than in increased concentrations of metal in water (RAI, 2009; BONANNO and GIUDICE, 2010; MAZEJ *et al.,* 2010; EID *et al.,* 2012; BOROWIAK *et al.,* 2016). Total concentrations of heavy metals in water for both researched localities of Bardača fishpond (MAKSIMOVIĆ *et al.,* 2016a; MAKSIMOVIĆ *et al.,* 2016b) were significantly lower compared to sediment, which probably was consequence of bigger containment and deposition of heavy metals in sediment, which could have been connected to results of researches by DUMAN *et al.,* 2007; EID *et al.,* 2012; MILOŠKOVIĆ et al., 2013; ŠTRBAC *et al.,* 2014.

Contents of heavy metals in researched organs of *Ph. australis* significantly varied with metal, sampling period and locality. In paper of MAKSIMOVIĆ *et al.* (2016a; 2016b), heavy metals in reed aboveground part were presented. Authors showed that concentration of Fe during research period in reed aboveground part varied 76-347 mg/kg, and Mn 116-300 mg/kg, zinc 11-50 mg/kg, whereas for Cu and Pb were in detection limits.

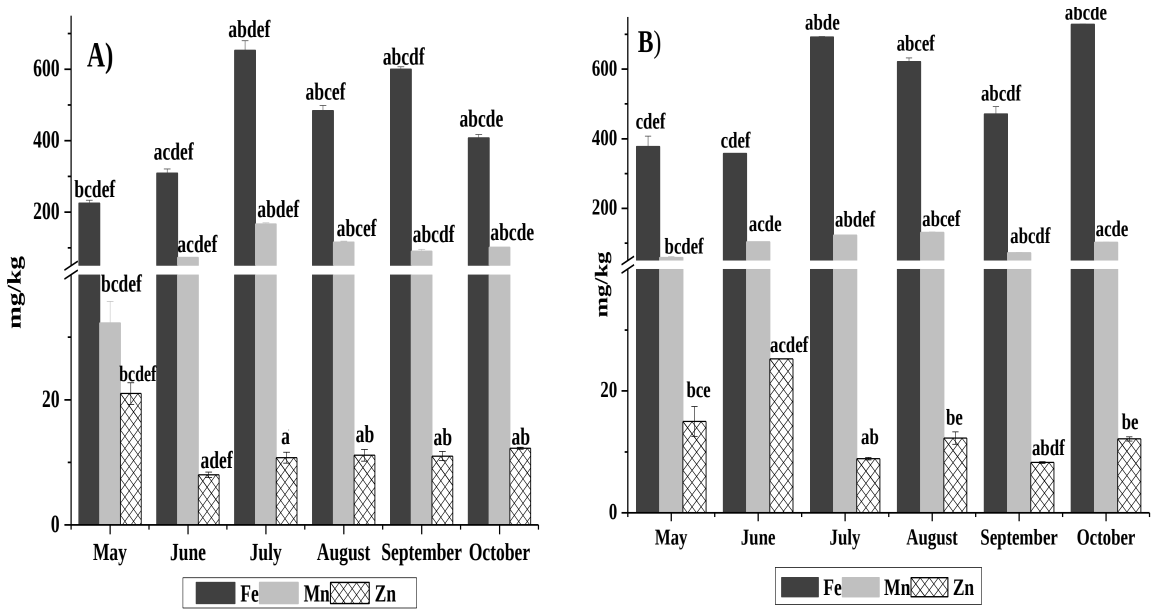

Figure 1. Heavy metals concentration (Fe, Mn and Zn) in rhizome of *Ph. australis* on researched localitis (A-Necik; B- Sinjak)
- different small letters denote values in research period (a-May, b-June, c-July, d-August, e-September; – statistically significantly different for importance level $p<0.05$)

According to KABATA-PENDIAS and PENDIAS (2001), Fe is an element of low mobility so it is not easy to translocate it to aboveground parts and is mostly accumulated in its underground parts (BALDATONI *et al.*, 2005; BABOVIĆ *et al.*, 2010; BONANNO and GIUDICE, 2010; EID *et al.*, 2012; KLINK *et al.*, 2013; ŠTRBAC et al., 2014; KUCAJ, 2015; ESMAEILZADEH *et al.*, 2016; BOROWIAK *et al.*, 2016) which was in accordance with results acquired in this paper. In this paper, rhizome showed as target organ of bioaccumulation, which also was in accordance with researches of other authors (BALDANTONI *et al.*, 2009; ŠTRBAC *et al.*, 2014; ESMAEILZADEH *et al.*, 2016) (Figure 1).

Researches on *Ph. australis* in Lake Averno, showed that heavy metal concentration (Cr, Cu, Ni, Pb, V, Zn except for Mn) in rhizome were lower than in root for almost two times (BALDANTONI *et al.*, 2009). It is well-known that plants tolerant to heavy metals, such as reed, are able to move heavy metals to a root cortex part, as well as how to prevent or decrease translocation in other parts of the plants (VERKLEIJ and SCHAT, 1990). Immobilization of toxic elements in reed root is an important form of rhizome protection, which is the only permanent part of a plant. When it comes to locality, higher Fe values were defined for Sinjak. Reason for that probably lies in different inflow of waste waters and physical–chemical environmental conditions.

Degree of heavy metal translocation of researched species at localities Sinjak and Necik was monitored and based on BCF, TA and BAC factors, which varied depending on season, plant organ, researched metal and researched locality (Table 1).

Table 1. Factors BCF, BAC and TA for Fe, Mn and Zn for *Ph. australis* on locality Necik in the area of Bardača fishpond in the period May-October 2010

Period (month)	**Fe**	**Mn**	**Zn**	**Fe**	**Mn**	**Zn**	**Fe**	**Mn**	**Zn**
	BCF			**BAC**			**TA**		
May	0.36	0.15	0.31	0.17	0.93	0.41	0.47	5.97	1.29
June	0.50	0.28	0.12	0.22	0.45	0.79	0.44	1.59	6.26
July	1.05	0.73	0.15	0.32	1	0.26	0.30	1.37	1.71
August	0.78	0.60	0.15	0.56	1.04	0.19	0.71	1.71	1.29
September	0.96	0.40	0.15	0.44	1.04	0.23	0.46	2.57	1.46
October	0.65	0.16	0.18	0.24	0.48	0.29	0.36	2.96	1.65

Researched species mostly had BCF<1 or BCF~1. Generally, BCF values were higher for Fe and exceeded during July (1.05) on locality Necik and during October (1.17) on locality Sinjak. Concentration of iron in sediment is not correlated to its presence in plant organs, and mobility through tissue of *Ph. australis* is low (BONANNO, 2011), which was also confirmed in this study. Mobility of elements varied in a great deal, so that Fe was most mobile whereas Mn and Zn, based on BCF, were of very low mobility. Low translocation could be caused by sequestration of most metals in cell vacuoles of root, which could be natural answer for mitigation of possible toxic effects of heavy metals (MARCHAND *et al.*, 2010), and the same case is with Fe. KUCAJ (2015), in the area of Tirana, for *Ph. australis* recorded BCF values (for Fe, Mn, Cr, Ni, Cu, Zn) significantly under 1 contrary to results we got in this paper.
Researched species mostly had TA>1, except for Fe and Zn in June (Sinjak), whose values had been significantly lower, which pointed out to lower translocation from root to aboveground part. Values of TA varied 0.19-0.71 and were higher on locality Necik. BAC for Fe went from 0.12 to 0.44 and was lower compared to Mn and Zn. ZHAO *et al.* (2002) pointed out the fact that TA is lower than 1, this is about decreased ability for metal transport, probably due to weaker translocation, which is recorded in this paper of ZHAO *et al.* (2002).

GHOSH and SINGH (2005) emphasize that species with high BCF and low TF can be used for phytostabilization of polluted land, and that these species retain metals in the root hence limiting metal mobility from root to aboveground part (CUI *et al.*, 2007), such is the case with reed in this paper.
Different authors monitored seasonal distribution of heavy metals in aquatic plants (WEIS *et al.*, 2003; WEIS and WEIS, 2004; BAI *et al.*, 2014; BALDATONI *et al.*, 2009; GRUDNIK, 2010; EID *et al.*, 2012) and, recorded that heavy metals show significant seasonal variations depending on growth and development phase and results are their changes in concentration and bio-availability in immediate environment (LARSEN and SCHIERUP, 1981; ŠTRBAC *et al.*, 2014), which can be connected to results stated in this paper.

Some publications by GRUDNIK (2010) and BAI *et al.* (2014) showed that heavy metal concentrations increase in growing season (summer) and then decrease with the plants aging. However, BALDATONI *et al. (*2009) stated increase of Cr, Cu, Fe, K, Mg, Mn, N, Ni, Pb, S, V and Zn for reed by the end of season.

Concentration of Mn in *Ph. australis* rhizome went from 32 to 130 mg/kg (Figure 1), where no toxic concentration of Mn, according to KABATA-PENDIAS and PENDIAS (2001), were recorded. Researches by some authors MAKSIMOVIĆ *et al.*, 2007; MAKSIMOVIĆ and ILIĆ, 2008; KLINK *et al.*, 2013; ŠTRBAC *et al.*, 2014 showed that Mn accumulates more in aboveground part compared to rhizome, and this was showed by coefficient analysis in this paper. It was proven that mobility of Mn is slow, still higher than Fe and Cu, and it significantly went up with mononucleotide plants (KABATA-PENDIAS and PENDIAS, 2001) so higher concentration could be supported by this fact i.e. better translocation of Mn in underground part as well as by higher mobility of Mn from sediments (Table 1). Different results were showed by NIKOLIĆ *et al.*, 2003; BONANNO and GIUDICE, 2010; KUCAJ, 2015; ESMAEILZADEH *et al.*, 2016 were higher concentration of Mn were recorded in rhizome compared to aboveground part of *Ph. australis*. In the relation to locality, increased content of Mn was recorded in locality Necik (Table 1 and Table 2) which was consequence of influence of surrounding agricultural surfaces, influence of waste waters from channels supplying this basin.

Table 2. Factors BCF, BAC and TA for Fe, Mn and Zn for *Ph. australis* on locality Sinjak in the area of Bardača fishpond in the period May-October 2010

Period (month)	Fe	Mn	Zn	Fe	Mn	Zn	Fe	Mn	Zn
	BCF			BAC			TA		
May	0.60	0.16	0.22	0.16	0.35	0.52	0.27	2.14	2.35
June	0.58	0.29	0.42	0.12	0.55	0.35	0.21	1.84	0.84
July	1.12	0.48	0.16	0.17	0.66	0.20	0.16	1.35	1.26
August	1	0.63	0.23	0.19	1.07	0.36	0.19	1.67	1.53
September	0.76	0.24	0.13	0.25	1.16	0.47	0.33	4.71	3.42
October	1.17	0.34	0.21	0.33	1	0.33	0.28	2.94	1.56

BCF values for Mn significantly varied during season (0.15-0.73) and were twice lower compared to Fe. Highest BCF was during maximum growth (July-August) on both researches' localities. BCF values were significantly lower compared to researche acquired by KASTRATOVIĆ *et al.* (2013) for the same species in the area of Skadar Lake.

BAC is used as indicator of high potential in accumulation of heavy metals for those plant species usually associated with well-developed cell mechanism for detoxification and tolerance in heavy metals (GHOSH and SINGH, 2005). Researched species mostly had BAC<1, and for Mn it went from 0.35 to 1.16 and was twice higher compared to Fe and Zn for both researched localities. Based on acquired values, it could be stated that researched species did not have hyper accumulation characteristics.

KUCAJ (2015), in the area of Tirana for *Ph. australis*, got BCF values that were significantly under 1 and TA a bit higher than 1 for Fe, Mn, Cr, Ni, Cu, Zn, which was opposite to results we have recorded in this paper. Compared to Fe and Zn, TA values for Mn in average were the highest (1.35-5.97), which pointed out to high mobility from underground to the aboveground part. High accumulation of metal can be associated with well-developed mechanism of detoxification based on ion sequestration of heavy metals in vacuoles, connecting them to appropriate ligands (CUI *et al.*, 2007).

During May, the value of TA was the highest, followed by the significantly decreased and by the end of research period re-increase was determined. YOON *et al.* (2006) stated that species with high TA values were appropriate for phytoextraction and relocation of heavy metals in aboveground parts, which can be connected to *Ph. australis*. TA values for Mn in this paper were higher to GRISEY *et al.* (2012) or similar to those SASMAZ *et al.* (2008) recorded for *Typha latifolia* and *Ph. australis*.

According to earlier researches of MAKSIMOVIĆ *et al.* (2016a) contents of zinc in aboveground part and rhizome of was not correlated to concentrations of Zn in sediment, even when values were high in sediment, which led to weaker translocation. According to MAKSIMOVIĆ *et al.* (2016a), zinc concentrations in aboveground part of *Ph. australis* went from 11 to 50 mg/kg. Zn concentration in rhizome was twice lower (8-25 mg/kg), and higher concentration was recorded on locality Necik (Figure 1). Some studies showed that Zn is better in translocation to aboveground organs (AKSOY *et al.*, 2005; BALDANTONI *et al.*, 2009; KASTRATOVIĆ *et al.*, 2013) while other indicated that rhizome and root were the same hyper-accumulators of Zn (WEIS *et al.*, 2003; BRAGATO *et al.*, 2009; BALDATONI *et al.*, 2009; KLINK *et al.*, 2013; ŠTRBAC *et al.*, 2014; KUCAJ, 2015; KANCLERZ *et al.*, 2016; ESMAEILZADEH *et al.*, 2016). KANCLERZ *et al.* (2016) recorded that concentration of Zn increased at the beginning of season, and concentration of Cu increased at the end of season through monitoring of zinc and copper with *Ph. australis*. In earlier researches of MAKSIMOVIĆ et al. (2014) higher concentration of Zn in researched reed organs was determined compared to results obtained in this paper. Likewise, obtained values of researched reed organs were lower compared to researches performed by BRAGATO *et al.* (2009) and BONANNO and GIUDICE (2010). However, compared to research performed by KUCAJ (2015) in the area of Tirana, Zn values were increased in researched reed organs in the area of Bardača. As for locality, slightly higher concentration of Zn was recorded on locality Necik.

BCF values for Zn went from 0.13-0.42 and were significantly lower compared to Fe and Mn. Highest BCF values were recorded at the beginning of season (May), whereas twice lower were acquired by the end of research period. KASTRATOVIĆ *et al.* (2013) recorded BCF value >1, which was contrary to results acquired in this paper. Based on defined TA values, Zn appeared to be element that was easily relocated from root to aboveground part. TA value for Zn was highest during June (6.26) on locality Necik, whereas in the rest of period, TA was up to three times lower. Reason for this probably lies in the fact of faster translocation of Zn to aboveground parts, which can also be connected with changes of physical-chemical environmental conditions. TA values for Zn in this paper were higher than those recorded in the researches of *Typha latifolia* and *Ph. australis* (SASMAZ *et al.*, 2008; GRISEY, 2012; KANCLERZ, 2016; KUCAJ, 2015). High transport of Zn to aboveground parts of the plant was recorded by LESAGE *et al.* (2007) for *Ph. australis* in artificial swamps using for waste waters filter. According to WEIS et al. (2004), plants having TA values above 1, are considered to be accumulator species, which points out to high ability of transport and storage in aboveground plants, which is, again, important in selecting plants for removal of heavy metals. The highest

TA values in this paper were recorded for Zn and Mn, which pointed out the fact that researched species could serve as bioaccumulators in phytoremediation techniques.

BAC for Zn significantly varied during season (0.19-0.79) and was higher on locality Necik. Highest BAC values were recorded in May and June on both researched localities. In researching seasonal distribution, LARSEN and SCHIERUP (1981) discovered that zinc in leaves and stems of *Ph. australis* from freshwater lake had been maximal in growing season, then it had fallen, whereas copper in leaves had remained relatively constant, which could be connected to results recorded in this paper.

Obtained coefficient BCF, TA and BAC values for researched elements were significantly lower compared to values recorded by KASTRATOVIĆ *et al.* (2013). Research results highlight that *Ph. australis* is not hyper accumulator for any of researched metals since measured metal concentrations in reed organs had been lower than 1000 mg/kg. We could say that researched localities compared to previous researched performed in this area by MAKSIMOVIĆ and ILIĆ (2008); MAKSIMOVIĆ *et al.* (2014) were not loaded by these pollutants dangerous for ecosystem.

CONCLUSION

Based on evaluation of BCF, TA and BAC values (for Fe, Mn, Zn), reed has capacity for phytostabilization and phytoextraction of polluted land and can be considered a bioaccumulator of Zn and Mn. However, obtained results pointed out that *Ph. australis*, based on contents of heavy metals Fe, Mn, Zn, Cu and Pb is not hyper accumulator. Rhizom of *Ph. australis* is the preferred site of Fe accumulation, while Mn and Zn are translocated into the above-ground parts

Generally, all analyzed metals did not show same seasonal trend i.e. the highest contents of Fe and Mn were determined at the end of vegetation season (August-September-October); Zn follows – during spring (May-June). According to this paper, there were accumulations of Fe and Mn with aging as much as 20-50 % compared to spring period. Considering this, the best period for removing biomass of *Ph. australis* would be at the end of growing season. Results of this study emphasize an important role of macrophyte vegetation in water ecosystem, and that we can acquire data for realistic image of ecological situation of researched water ecosystem in the aim of revitalization of the same through monitoring of chemical composition.

Acknowledgments

This work was partially funded by the Foundation "Dr Milan Jelic" within the Ministry of Science and Technology of the Republic of Srpska (grant number 01-2-473-1/10).

References:

[1] AKSOY, A., DEMIREZEN, D., DUMAN, F. (2005): Bioaccumulation, Detection and Analyses of Heavy Metal Pollution in Sultan Marsh and its Environment. *Water Air and Soil Pollution* **164**: 241-255. doi: 10.1007/s11270-005-3538-x

[2] AMERICAN PUBLIC HEALTH ASSOCIATION (APHA) (1995): Standard Methods for the Examinations of Water and Wasterwater. Franson, M.H. (ed), 19th ed. Washington DC 20005.

[3] BABOVIĆ, N., DRAZIC, G., DJORDJEVIĆ, A., MIHAILOVIC, N. (2010): Heavy and toxic metal accumulation in six macrophythe species from fish pond Ecka. *The Fourth International Scientific Conference* BALWOIS. Ohrid, Rebublic of Macedonia, 25-29 May.

[4] BAI, J., XIAO, R., ZHAO, Q., LU, Q., WANG, J., REDDY, K.R. (2014): Seasonal Dynamics of Trace Elements in Tidal Salt Marsh Soils as Affected by the Flow-Sediment Regulation Regime. *Plos One* **9**(9): 1-11. doi: 10.1371/journal.pone.0107738

[5] BALDANTONI, D., LIGRONE, R., ALFANI, A. (2009): Macro-and trace-element concentrations in leaves and roots of *Phragmites australis* in a volcanic lake in Southern Italy. *Journal of Geochem Exploration* **101**(2): 166-174. doi: 10.1016/j.gexplo.2008.06.007

[6] BALDANTONI, D., MAISTO, G., BARTOLI, G., ALFANI, A. (2005): Analyses of three native aquatic plant species to assess spatial gradient of lake heavy metal contamination. *Aquatic Botany* **83**(1): 48–60. doi: 10.1016/j.aquabot.2005.05.006

[7] BONANNO, G. (2011): Trace element accumulation and distribution in the organs of *Phragmites australis* (common reed) an biomonitoring applications. *Ecotoxicology and Environmental Safety* **74**(4): 1057-1064. doi: 10.1016/j.ecoenv.2011.01.018

[8] BONANNO, G., GIUDICE, R.L. (2010): Heavy metal bioaccumulation by the organs of *Phragmites australis* (common reed) and their potential use as contamination indicators. *Ecological Indicators* **10**(3): 639-645. doi: 10.1016/j.ecolind.2009.11.002

[9] BOROWIAK, K., KANCLERZ, J., MLECZEK, M., LISIAK, M., DRZEWIECKA, K. (2016): Accumulation of Cd and Pb in water, sediment and two littoral plants (*Phragmites australis, Typha angustifolia*) of freshwater ecosystem. *Archives of Environmental Protection* **42**(3): 47-57.

[10] BRAGATO, C., BRIX, H., MALAGOLI, M. (2009): Accumulation of nutrients and heavy metals in *Phragmites australis* (Cav.) Trin. ex Steudel and *Bolboschoenus maritimus* (L.) Palla in a constructed wetland of the Venice lagoon watershed. – *Environmental Pollution* **144**: 967– 975. doi: 10.1016/j.envpol.2006.01.046

[11] CUI, S., ZHOU, Q., CHAO, L. (2007): Potential hyper-accumulation of Pb, Zn, Cu and Cd in endurant plants distributed in an old smeltery, northeast, China. *Environmental Geology* **51**: 1043-1045. doi: 10.1007/s00254-006-0373-3

[12] DUMAN, F., CICEK, M., SEZEN, G. (2007): Seasonal changes of metal accumulation and distribution in common club rush (*Schoenoplectus lacustris*) and common reed (*Phragmites australis*). *Ecotoxicology* **16**(6): 457–463. doi: 10.1007/s10646-007-0150-4

[13] ĐURIĆ, D., SOPIĆ, D., TRIFKOVIĆ, A., JANDRIĆ, B. (2004): Hidrotehnički radovi u području močvare Bardača. U: Šarić Ž, Stanković M, Butler D, (urednici), Život u močvari, Urbanistički zavod Republike Srpske, a.d. Banja Luka, pp: 17-27.

[14] EID, E.M., SHALTOUT, K.H., EL-SHEIKH, M.A., ASAEDA, T. (2012): Seasonal courses of nutrients and haevy metals in water, sediment and above-and below-ground *Typha domingensis* biomass in Lake Burullus (Egypt): perspectives for phytoremediation. *Flora - Morphology, Distribution, Functional Ecology of Plants* **207**(11): 783-794. doi: 10.1016/j.flora.2012.09.003

[15] ESMAEILZADEH, M., KARBASSI, A., MOATTAR, F. (2016): Heavy metals in sediments and their bioaccumulation in *Phragmites australis* in the Anzali wetland of Iran. *China Journal Oceanology and Limnology* **34**(4): 810-820. doi: 10.1007/s00343-016-5128-8

[16] GHOSH, M., SINGH, S.P. (2005): A review on phytoremediation of heavy metals and utilization of its byproducts. *Applied Ecology and Environmental Research* **3**(1): 1-18.

[17] GRISEY, E., LAFFRAY, X., CONTOZ, O. CAVALLI, E., MUDRY, J., ALEYA, L. (2012): The Bioaccumulation Performance of Reeds and Cattails in a Constructed Treatment Wetland for Removal of Heavy Metals in Landfill Leachate Treatment (Etueffont, France). *Water Air and Soil Pollution* **223**(4): 1723-1741. doi: 10.1007/ s11270-011-0978-3

[18] GRUDNIK, Z.M. (2010): Seasonal changes in the concentration of some trace elements in macrophyte shoots. *Acta Biologica Slovenica* **53**(1): 55-61.

[19] KABATA-PENDIAS, A., PENDIAS, H. (2001): Trace Elements in Soils and Plants. 3rd Edition, CRC Press, Boca Raton, London.

[20] KANCLERZ, J., BOROWIAK, K., MLECZEK, M., STANISZEWSKI, R., LISIAK, M. (2016). *Phragmites australis* and *Typha angustifolia* as Potential Accumulators of Zinc and Copper in Water Ecosystem at City Area. *Annual Set the Environment Protection* **18**(1): 246-257

[21] KASTRATOVIĆ, V., KRIVOKAPIĆ, S., ĐUROVIĆ, D., BLAGOJEVIĆ, N. (2013): Seasonal changes in metal accumulation and distribution in the organs of *Phragmites australis* (common reed) from Lake Skadar, Montenegro. *Journal of the Serbian Chemical Society* **78**(8): 1241-1258. doi: 10.2298/JSC121026153K

[22] KLINK, A., WISLOCKA, M., MUSIAL, M., KRAWCZYK, J. (2013): Macro- and trace elements accumulation in *Typha angustifolia* L. and *Typha latifolia* L. organs and their use in bioindication. *Polish Journal Environmental Studies* **22**(1): 183-190.

[23] KUCAJ, E., ABAZI, U. (2015): Assessment of heavy metals in sediments and *Phragmites australis* in Tirana River, Albania. *European Journal of Physical and Agricultural Sciences* **3**(2): 54-61.

[24] LARSEN, V., SCHIERUP, H. (1981): Macrophyte cycling of zinc, bakar, lead, and cadmium in the littoral zone of a polluted and a non-polluted lake: II. Seasonal changes in heavy metal contents of above-ground biomass and decomposing leaves of *Phragmites australis* (Cav.) Trin. *Aquatic Botany* **11**: 211–30.

[25] LESAGE, E., ROUSSEAU, D.P.L., MEERS, E., TACK, F.M.G., DE PAUW, N. (2007): Accumulation of metals in a horizontal subsurface flow constructed wetland treating domestic wastewater in Flanders, Belgium. *Science of the Total Environment* **380**(1-3): 102-115. doi: 10.1016/j.scitotenv.2006.10.055

[26] LI, M.S., LUO, Y.P., SU, Z.Y. (2007): Heavy metals concentrations in soils and plant accumulation in a restored manganese mine land in Guangxi, South China. *Environmental Pollution* **147**(1): 168-175. doi: 10.1016/j.envpol.2006.08.006

[27] MAKSIMOVIĆ, T., ILIĆ, P. (2008): Bioakumulacija teških metala kao pokazatelj potencijala bioremedijacije vodenih biljaka na području ribnjaka Bardača. 37. Konferencija o aktuelnim problemima korišćenja i zaštite voda, "Voda 2008", Jugoslovensko društvo za zaštitu voda, Tara, 26-29 jun, pp. 131-136.

[28] MAKSIMOVIĆ, T., RONČEVIĆ, S., KUKAVICA, B. (2016a): Seasonal changes of Cu and Zn at *Phragmites communis* Trin., *Salvinia natans* L. and *Utricularia vulgaris* L. at area of fish pond Bardača. International Scientific Conference „*Contemporary Materials*“. Academy of Sciences and Arts of Republic of Srpska, pp. 579-589.

[29] MAKSIMOVIĆ, T., RONČEVIĆ, S., KUKAVICA, B. (2016b): Bioakumulacija željeza i mangana kod nekih vodenih makrofita na području ribnjaka Bardača. Skup Zbornik radova III СБЕРС 2015, Banja Luka, 12–14. novembar 2015. **7**(2): 87-96. doi: 10.7251/SKP1607087M

[30] MAKSIMOVIĆ, T., STANKOVIĆ, Ž., ILIĆ, P. (2007): Bioakumulacija Mn, Cd i Pb u vodenim makrofitama na području ribnjaka Bardača. 36. Konferencija o aktuelnim problemima korišćenja i zaštite voda, "Voda 2007", Jugoslovensko društvo za zaštitu voda, Tara, 26-29 jun, pp. 131-136.

[31] MAKSIMOVIĆ, T.R., BORIŠEV, M.K., STANKOVIĆ, Ž.S. (2014): Seasonal dynamics of copper and zinc accumulation in shoots of *Phragmites australis* (CAV.) Trin ex Steud., *Typha latifolia* L. and *Typha angustifolia* L. Novi Sad. *Matica Srpska Journal for Natural Sciences* **127**: 65-75. doi: 10.2298/ZMSPN1427065M

[32] MARCHAND, L., MENCH, M., JACOB, D.L., OTTE, M.L. (2010): Metal and metalloid removal in constructed wetlands, with emphasis on the importance of plants and standardized measurements: A review. *Environmental Pollution* **158**(12): 3447-3461. doi: 10.1016/j.envpol.2010.08.018.

[33] MAZEJ, Z., AL SAYEGH-PETKOVSEK, S., POKORNY, B. (2010): Heavy metal concentrations in food chain of Lake Valenjsko Jezero, Slovenia: an artificial lake from mining. *Archives of Environmental Contamination and Toxicology* **58**(4): 998–100. doi: 10.1007/s00244-009-9417-5

[34] MAZEJ, Z., GERM, M. (2009): Trace element accumulation and distribution in four aquatic macrophytes. *Chemosphere* **74**(5): 642-647. doi: 10.1016/j.chemosphere. 2008.10.019

[35] MILOŠKOVIĆ, A., BRANKOVIĆ, S., SIMIĆ, V., KOVAČEVIĆ, S., ĆIRKOVIĆ, M., MANOJLOVIĆ, D. (2013): The accumulation and distribution of metals in water, sediment, aquatic macrophytes and fishes of the Gruža Reservoir, Serbia. *Bulletin of Environmental Contamination and Toxicology* **90**(5): 563-569. doi: 10.1007/s00128-013-0969-8

[36] NIKOLIĆ, LJ., STOJANOVIĆ, S., STANKOVIĆ, Ž. (2003): Contents of macro - (N, P, K) and micronutrients (Fe, Mn, Zn) in four promising emergent macrophytic species. *Archiv für Hydrobiology* **14**(3-4): 297-306. doi: 10.1127/lr/14/2003/297

[37] RAI, P.K. (2009): Heavy metal phytoremediation from aquatic ecosystems with special reference to macrophytes. *Critical Reviews in Environmental Science and Technology* **39**(9): 697-753. doi: 10.1080/10643380801910058

[38] RAVERA, O. (2001): Monitoring of the aquatic enviorment by species accumulator of pollutants: a review. Scientific and legal aspects of biological monitoring in freshwater. *Journal of Limnology* **60**(1): 63-78. doi: 10.4081/jlimnol.2001.s1.63

[39] SAMECKA-CYMERMAN, A., KEMPERS, A.J. (2001): Concentrations of heavy metals and plants nutrients in water, sediments and acquatic macrophytes of anthropogenic lakes (former open cut brown coalmines) differing in stage of acidification. *Science of the Total Environment* **281**(1-3): 87–98.

[40] SASMAZ, A., OBEK, E., HASAR, H. (2008): The accumulation of heavy metals in *Typha latifolia* L. grown in a stream carrying secondary effluent. *Ecological Engineering* **33**(3-4): 278-284. doi:10.1016/j.ecoleng.2008.05.006

[41] ŠTRBAC, S., ŠAJNOVIĆ, A., GRUBIN, K.M., VASIĆ, N., DOJČINOVIĆ, B., SIMONOVIĆ, P., JOVANIČEVIĆ, B. (2014): Metals in sediment and *Phragmites australis* (coomon reed) from Tisza River, Serbia. *Applied Ecology and Environmental Research* **12**(1): 105-122.

[42] VERKLEIJ, J.A., SCHAT, H. (1990): Mechanisms of metal tolerance in higher plants. In: Shaw, AJ (ed): *Heavy Metal Tolerance in Plants: Evolutionary Aspects*. Boca Raton, FL. pp. 179-193.

[43] WEIS, J.S., GLOVER, T., WEIS, P. (2004): Interactions of metals affect their distribution in tissues of *Phragmites australis*. *Environmental Pollution* **131**(3): 409–415. doi: 10.1016/j.envpol.2004.03.006

[44] WEIS, J.S., WEIS, P. (2004): Metal uptake, transport and release by wetland plants:implications for phytoremediation and restoration. Environment International **30**(5): 685-700. doi: 10.1016/j.envint.2003.11.002

[45] WEIS, J.S., WINDHAM, L., WEIS, P. (2003): Patterns of metal accumulation in leaves of the tidal marsh plants *Spartina alterniflora* Loisel and *Phragmites australis* Cav. Trin ex Steud. over the growing season. *Wetlands* **23**(2): 459 – 465. doi: 10.1672/20-20

[46] YOON, J., CAO, X., ZHOU, Q., MA LQ. (2006): Accumulation of Pb, Cu and Zn in native plants growing on a contaminated Florida Site. *Science of the Total Environment* **368**(2-3): 456-464. doi: 10.1016/j.scitotenv.2006.01.016

[47] ZHAO, F.J., HAMON, R.E., LOMBI, E., MCLAUGHLIN, M.J., MCGRATH, S.P. (2002): Characteristics of cadmium uptake in two contrasting ecotypes of the hyperaccumulator *Thlaspi caerulescens*. *Journal of Experimental Botany* **53**: 535–543. doi: 10.1093/jexbot/53.368.535

[48] ZUBCOV, E., LUCIA, B., PHILIPENKO, E., LAURENTA, U. (2013): Study on metal accumulation in aquatic plants of Cuciurgan cooling reservoir. E3S Web of Conferences **1**: 41025.

[49] ZWOLSMAN, J.J.G., BERGER, G.W., VAN ECK, G.T.M. (1993): Sediment accumulation rates, historical input, post depositional mobility and retention of major elements and trace metals in salt marsh sediments of the Scheldt estuary, SW Netherlands. *Marine Chemistry* **44**: 73–94. doi: 10.1016/0304-4203(93)90007-B