International Journal of Agricultural Science, Research and Technology Available online on: www.ijasrt.com

Accumulation and distribution of metals in *Phragmites australis* (common reed) and *Scirpus maritimus* (alkali bulrush) in contaminated soils of Lia industrial area

M, Ebrahimi[1*]; M, Jafari[2]; Gh. R, Savaghebi[3]; H, Azarnivand[4]; A, Tavili[5]; F, Madrid[6]
[1]PhD student of range management, University of Tehran, *Corresponding author email: maebrahimi2007@yahoo.com, Ebrahimimds@ut.ac.ir
[2]Professor, Faculty of Natural Resources, University of Tehran
[3]Associate Professor, Faculty of Agriculture, University of Tehran
[4]Assistant Professor, Faculty of Natural Resources, University of Tehran
[5]Assistant Professor, Faculty of Natural Resources, University of Tehran
[6]Titled Superior Specialized, IRNAS-CSIC, Spain

The concentration of three metals, zinc, copper and chromium in roots, rhizomes, stems and leaves of *Phragmites australis* (common reed) and *Scirpus maritimus*, and in the corresponding sediment and water samples from Lia industrial area (Qazvin, Iran) were investigated to determine difference in distribution among plant organs. Data were collected at during 1-year period. Results showed that metals concentrations in plant organs decreased in the order of roots › rhizomes › leaves ›stems. Concentration of Zn, Cu and Cr were enriched in roots and rhizomes of both plants in summer and autumn. Stem concentrations of metals in *S. maritimus* however, had no significant difference throughout 1-year period. In contrast, the metal contents of leaves were elevated in spring and autumn. Patterns of leaves and stem concentration of Zn, Cu and Cr were similar to *S. maritimus* leaves. **[M. Ebrahimi et al. Accumulation and distribution of metals in *Phragmites australis* (common reed) and *Scirpus maritimus* (alkali bulrush) in contaminated soils of Lia industrial area. International Journal of Agricultural Science, Research and Technology, 2011; 1(2):73-81].**

Received: 14 June 2011, Reviewed: 29 June 2011, Revised: 8 July 2011, Accepted: 26 July 2011,

Key words: Phytoremediation, *Phragmites australis*; *Scirpus maritimus*; Zinc; Copper; Chromium.

1. Introduction

Some macrophytes have accumulator phenotypes for one or several metals (Kamal et al., 2004). These plants can accumulate metals in concentrations 100,000 times greater than in the associated water (Mishra and Tripathi, 2008), and therefore they have been used for metal removal from a variety of sources (Mishra and Tripathi, 2008). Macrophytes compared with other plant and animal species, have been reported to have a larger or comparable capacity for metal accumulation (Jana, 1988) and they can tolerate, take up and translocate high levels of certain metals that would be toxic to most organisms. They are described as plants that could complete their life cycle with foliar metal concentrations exceeding (mg kg^{-1} dry weight, DW) Cd > 100, Ni and Cu > 1000, and Zn and Mn > 10,000 (Zavoda et al., 2001).

The utilization of wetland areas as natural filters for the abatement of pollutants transported by water in rivers or lakes is considered to be an effective, low-cost, cleanup option to ameliorate the quality of surface waters. Indeed, wetlands have been extensively utilized in the last decades to remediate polluted water almost all over the world (Gopal, 2003).

The vegetation covering the wetland areas plays an important role in sequestering significant amounts of metals (Karpiscak et al., 2001; Mays and Edwards, 2001; Baldantoni et al., 2004) from the environment by storing them in the roots and/or shoots. Wetland plants also take up metals from the environment but tend mainly to accumulate these in the belowground tissues (Stoltz and Greger, 2002; Weis et al., 2004) and the capacity to accumulate heavy metals in the aboveground plant tissues represents a central point for the suitability of the plants for metals phytoextraction (Salt and Kramer, 2000). The amount of metals accumulated in the aerial part may vary during the growing season as a consequence of the inherent growth dynamics of the plant, as well as in response to variations in the metal levels and availability in the surrounding water and soil (Hardej and Ozimek, 2002). It is therefore important to evaluate the seasonal and spatial variations in plant accumulation in wetland systems in order to assess the potential for nutrient and metal removal by plant uptake and harvesting. The aim of

this study was to evaluate, the seasonal variation of concentrations of Zn, Cu and Cr in aerial and belowground parts of *Phragmites australis* and *Scirpus maritimus* and in the corresponding water and sediment samples, collected from the Lia industrial area of Qazvin city (Iran) in order to assess their potential for removal the metals.

2. Material and Methods

2.1. Study area

The site under examination is Lia area, an important industrial area of Qazvin (Northern Iran). It has a total area of 108 ha with 151 industrial factories. The main human activity is agriculture. The coldest and hottest months are February and July whose mean temperatures are, respectively, 7.2 °C and 21.7 °C with a yearly mean temperature of 13.9°C. The yearly mean rainfall is 321.5 mm and the soil is classified as aridisols. Industrialization in this area has exposed the soil to various effluent inputs including heavy metals. This has resulted in the region having wetland with contaminated soils which need to be improved. *Phragmites australis* and *Scirpus maritimus* are predominant macrophytes in the area.

2.2. Sampling collection

The sampling was carried out between May (2009) - February (2010). Sampling was done along transects in distances of 300 m in three locations. Samples considered were plant, industrial wastewater and sediment. In each sampling point, along 100m transects within 5m × 2m plots, the plant samples were collected and they were washed with tap water to remove sediments and quickly transported in plastic bags to the laboratory for analysis. Industrial wastewater r and sediment samples were collected at each sampling point. Industrial wastewater samples were collected in 0.5 L clean polyethylene bottles and kept at 3°C until analysis. Sediment samples were collected using a stainless steel collector at about 0 – 20cm and 20 - 40cm depths from each sampling point in spring (May), summer (August), autumn (November) and winter (February).

2.3. Sample analysis

Plant samples were preliminarily dissected in roots, rhizomes, stems and leaves to recognize the different bioaccumulation capability. Leaf and stem samples were prepared by considering the upper leaves and the whole stem. Plant organs were washed before analysis. As a second step, samples were dried at 70 °C to a constant weight for approximately 48 h and ground into fine powder in an agate mortar. Metals were analyzed after mineralization of 400 mg dry shoot material in a microwave oven with 5 ml of nitric acid (69% v/v), 5 ml deionized water and 2 ml H_2O_2 (30% v/v). The digest was made to 25 ml final volume with deionized water, filtered (0.45 mm, Millipore) and then analyzed for Zn, Cu and Cr using ICP/OES. Prior to analysis, industrial wastewater samples were passed through Whatman filters. Dried sediment samples were passed through a 2mm diameter sieve. About 100 mg dry sediment was digested with HNO_3 and HCl (3:1) in a microwave oven. After mineralization, the samples were diluted, filtered and analyzed. Metal concentrations (Zn, Cu, Cr) of industrial wastewater and sediment samples were measured as described for the plant samples. All the analyses were performed in five replicates.

2.4. Statistical analysis

All data were checked for their normality and homogeneity of variance, and where necessary, data were log-transformed before statistical analysis. The statistical processing was mainly conducted by analysis of variance (ANOVA). Measurements of each elemental concentration were compared taking into account three main factors: Time (months), plant species and plant organs. Regarding plants data, the statistical model was based on four groups (root, rhizome, stem, leaf), and aimed to show whether plant organs triggered a different accumulation pattern of a given trace element. Duncan test post hoc analysis was performed to define which specific mean pairs were significantly different. The ANOVA for industrial wastewater and sediment considered three groups (Zn, Cu, Cr) in order to detect significant different levels of concentration within the same kind of sample. All statistical calculations were performed using SPSS software.

3. Results and discussion

3.1. Metal concentration in plant tissues

Both species had root concentrations of metals that were greater than concentrations in leaves, stems, or rhizomes. In general, the metal levels decreased in the order of: roots › rhizomes › leaves ›stems for species, *P. australis* and *S. maritimus*.

Some seasonal variations in the metal contents of the different tissues of the plants were observed, although they were not always statistically significant. In *P. australis* concentration of metals in roots and rhizomes were generally greater in autumn (Table 1). Zn level in leaves and stems tissues were significantly higher in summer (Table 1).

In *S. maritimus* the levels of Zn in roots were significantly higher in summer and autumn whereas in the leaves, Zn concentration was higher in spring. Comparing the metal contents of leaves and roots, in all seasons, significant differences in Zn levels were not found in the rhizomes and stems (Table 1). In this study an increase in the Cu concentration occurred in *P. australis* leaves and

stems in spring, but roots and rhizomes showed the most elevated contents of Cu in autumn. Comparing both plant species Cu level was greater in the leaf tissues of *S. maritimus* than the leaf tissues of *P. australis* in most of seasons. The levels of Cu in *S. maritimus* leaves exhibited significant increase in summer while the level of Cu in roots and rhizomes were significantly higher in autumn. In contrast, the levels of Cu in stems were constant throughout a 1-year period. In many cases, a decrease in metal levels in leaves and stems of plants occurred simultaneously with an increase in the roots and rhizomes levels (summer – autumn), what could indicate that metals have been translocated between different organs of the plant. For instance, for *S. maritimus* a significant decrease of Cu level (summer – autumn) was observed in leaves and stems with a simultaneous increase in roots and rhizomes (Table 2).

Cr is an element regarded as toxic for plants. Cr concentration in the leaves and stems of *P. australis* were higher in spring, but the level of Cr in the roots and rhizomes reached their maximum values in autumn. The levels of Cr in *S. maritimus* roots displayed a seasonal pattern similar to that observed for Zn (Table 3). Level of Cr in roots and rhizomes were higher in summer but in contrast, level of Cr in *S. maritimus* leaves was higher in spring. Comparing the Cr contents of root and rhizomes, significant differences were not found in the Cr contents of stem and leaves (Table 3).

Table 1. Zn concentration (mg kg^{-1}) in the plant organs of *P. australis* and *S. maritimuss* collected at locations 1, 2 and 3 for whole sampling period.

Site	Species	Seasons	Root	Leaf	Stem	Rhizome
1	*P. australis*	Spring	55.3 ±2.33^{a}	64.2±2.35^{a}	50.9 ±3.56^{a}	211 ±5.51^{a}
		Summer	182 ±6.12^{b}	94.1 ±5.40^{b}	78.7 ±2.15^{b}	121 ±3.10^{b}
		Autumn	237 ±4.70^{b}	90.1 ±2.70^{b}	73.5 ±1.28^{b}	291 ±5.42^{c}
		Winter	284 ±5.50^{c}	60.0 ±1.39^{ac}	54.4 ±1.20^{a}	190 ±4.21^{a}
1	*S. maritimus*	Spring	124 ±5.20^{a}	78.2 ±2.60^{a}	57.0 ±2.54^{a}	145 ±3.22^{a}
		Summer	327 ±4.60^{b}	118 ±3.14^{b}	65.7 ±1.05^{a}	128 ±3.61^{a}
		Autumn	320 ±3.95^{b}	63.0 ±1.59^{a}	49.2 ±1.07^{a}	141 ±4.29^{a}
		Winter	143 ±2.96^{a}	80.0 ±2.54^{a}	53.3 ±2.71^{a}	135 ±3.42^{a}
2	*P. australis*	Spring	50.9 ±1.25^{a}	68.4 ±2.04^{a}	48.0 ±1.50^{a}	111 ±3.00^{a}
		Summer	180 ±4.50^{b}	141 ±5.03^{b}	93.1 ±3.71^{b}	154 ±4.52^{b}
		Autumn	201 ±4.73^{b}	71.2 ±3.41^{a}	36.2 ±2.00^{a}	172 ±3.71^{b}
		Winter	179 ±4.70^{bc}	52.0 ±1.04^{a}	27.3 ±0.94^{a}	181 ±4.50^{b}
2	*S. maritimus*	Spring	174 ±3.55^{a}	111 ±3.17^{a}	59.2 ±1.48^{a}	140 ±3.37^{a}
		Summer	386 ±4.56^{b}	74.4 ±3.41^{b}	66.2 ±1.52^{a}	145 ±2.66^{a}
		Autumn	371 ±5.00^{b}	72.3 ±2.03^{b}	71.0 ±2.52^{a}	150 ±2.94^{a}
		Winter	157 ±4.27^{a}	85.5 ±4.33^{b}	64.0 ±1.72^{a}	140 ±2.92^{a}
3	*P. australis*	Spring	77.0 ±2.25^{a}	63.8 ±1.05^{a}	50.6 ±1.10^{a}	120 ±3.50^{a}
		Summer	145 ±7.28^{b}	94.3 ±3.09^{b}	77.3 ±2.25^{b}	115 ±3.16^{a}
		Autumn	233 ±5.00^{c}	63.1 ±1.92^{a}	55.8 ±1.12^{a}	170 ±3.30^{b}
		Winter	102 ±2.52^{d}	70.6 ±2.17^{a}	41.7 ±1.05^{a}	165 ±3.39^{b}
3	*S. maritimus*	Spring	138 ±2.31^{a}	112 ±3.50^{a}	66.6 ±2.30^{a}	130 ±2.44^{a}
		Summer	278±4.02^{b}	87.6 ±4.00^{b}	71.2 ±3.07^{a}	128 ±2.53^{a}
		Autumn	302 ±4.82^{b}	60.1 ±2.30^{b}	61.3 ±1.50^{a}	132 ±1.62^{a}
		Winter	137 ±2.81^{a}	90.9 ±3.71^{b}	69.9 ±1.54^{a}	141 ±2.92^{a}

Note: Mean values are reported with SD in all parentheses and different letters indicate significant differences between the sampling time periods within a sampling location ($p<0.05$, post hoc Duncan test).

Table 2. Cu concentration (mg kg^{-1}) in the plant organs of *P. australis* and *S. maritimuss* collected at locations 1, 2 and 3 for whole sampling period.

Site	Species	Seasons	Root	Leaf	Stem	Rhizome
1	*P. australis*	Spring	63.5 ±4.00[a]	66.3 ±2.07[a]	51.5 ±2.76[a]	8.41 ±0.20[a]
		Summer	9.35 ±0.25[b]	6.69 ±0.21[b]	4.01 ±0.19[b]	7.20 ±0.04[a]
		Autumn	83.7 ±4.33[a]	6.43 ±1.35[b]	3.52 ±0.32[b]	13.6 ±0.55[a]
		Winter	55.3 ±3.51[a]	3.76 ±0.95[b]	2.60 ±0.11[b]	17.1 ±0.53[a]
1	*S. maritimus*	Spring	14.4 ±1.46[a]	11.7 ±1.04[a]	10.2 ±1.55[a]	10.7 ±1.09[a]
		Summer	18.5 ±1.32[a]	57.8 ±1.23[b]	11.2 ±1.32[a]	16.5 ±1.74[a]
		Autumn	70.3 ±2.43[b]	31.5 ±3.41[c]	13.6 ±1.42[a]	44.4 ±2.05[b]
		Winter	49.9 ±2.11[b]	25.7 ±2.06[c]	9.00 ±0.36[a]	40.3 ±2.11[b]
2	*P. australis*	Spring	73.8 ±2.55[a]	66.3 ±2.20[a]	49.5 ±2.77[a]	9.12 ±0.56[a]
		Summer	9.31 ±0.60[b]	6.37 ±0.28[b]	5.07 ±0.2[b]	6.96 ±0.60[a]
		Autumn	87.3 ±2.41[a]	4.52 ±0.20[b]	2.55 ±0.01[b]	18.5 ±1.62[b]
		Winter	50.8 ±1.95[b]	3.46 ±0.11[b]	2.41 ±0.17[b]	19.6 ±1.03[b]
2	*S. maritimus*	Spring	15.1 ±1.03[a]	11.3 ±1.12[a]	9.96 ±0.83[a]	14.1 ±0.53[a]
		Summer	20.9 ±1.54[a]	92.6 ±2.02[b]	11.9 ±1.02[a]	20.5 ±1.11[a]
		Autumn	59.0 ±2.61[b]	27.9 ±2.37[c]	13.7 ±1.23[a]	52.0 ±2.05[b]
		Winter	50.1 ±2.01[b]	13.2 ±1.22[a]	11.3 ±1.21[a]	33.1 ±1.50[b]
3	*P. australis*	Spring	84.6 ±2.43[a]	63.5 ±1.56[a]	53.6 ±1.77[a]	12.2 ±0.46[a]
		Summer	9.14 ±0.53[b]	5.86 ±0.26[b]	4.40 ±0.17[b]	6.72 ±0.26[a]
		Autumn	106 ±3.24[c]	5.39 ±0.20[b]	4.44 ±0.14[b]	35.7 ±1.15[b]
		Winter	93.5 ±3.02[a]	6.67 ±0.12[b]	8.03 ±0.19[b]	39.7 ±1.42[b]
3	*S. maritimus*	Spring	14.8 ±0.10[a]	11.4 ±0.23[a]	13.9 ±1.15[a]	13.3 ±0.65[a]
		Summer	47.6 ±1.34[b]	43.0 ±1.11[b]	17.2 ±1.22[a]	25.6 ±1.40[a]
		Autumn	63.3 ±2.09[b]	25.3 ±0.9[c]	18.2 ±1.09[a]	41.7 ±2.03[b]
		Winter	38.9 ±1.02[b]	17.3 ±0.44[a]	17.7 ±1.12[a]	38.0 ±1.33[b]

Note: Mean values are reported with SD in all parentheses and different letters indicate significant differences between the sampling time periods within a sampling location ($p<0.05$, post hoc Duncan test).

Table 3. Cr concentration (mg kg^{-1}) in the plant organs of *P. australis* and *S. maritimuss* collected at locations 1, 2 and 3 for whole sampling period.

Site	Species	Seasons	Root	Leaf	Stem	Rhizome
1	*P. australis*	Spring	56.6 ±2.39^{a}	63.4 ±1.22^{a}	36.8 ±1.06^{a}	4.33 ±0.02^{a}
		Summer	21.0 ±0.93^{b}	7.30 ±0.15^{b}	5.23 ±0.60^{b}	9.00 ±0.60^{b}
		Autumn	63.9 ±2.22^{a}	5.81 ±0.18^{b}	2.45 ±0.02^{b}	9.73 ±0.30^{b}
		Winter	45.4 ±1.96^{a}	4.03 ±0.12^{b}	4.30 ±0.11^{b}	15.5 ±0.82^{b}
1	*S. maritimus*	Spring	160 ±4.05^{a}	117 ±3.22^{a}	69.6 ±2.04^{a}	96.7 ±2.03^{a}
		Summer	317 ±6.86^{b}	103 ±2.10^{a}	55.3 ±2.13^{a}	202 ±4.65^{b}
		Autumn	180 ±3.21^{a}	106 ±0.90^{a}	72.0 ±1.92^{a}	151 ±1.50^{a}
		Winter	134 ±2.71^{a}	83.0 ±1.92^{a}	61.9 ±1.08^{a}	113 ±1.22^{a}
2	*P. australis*	Spring	55.8 ±1.22^{a}	77.2 ±2.13^{a}	41.9 ±1.62^{a}	10.1 ±0.41^{a}
		Summer	19.9 ±0.71^{b}	13.2 ±0.74^{b}	5.97 ±0.50^{b}	14.3 ±0.74^{a}
		Autumn	79.9 ±1.09^{a}	7.27 ±0.21^{b}	3.33 ±0.01^{b}	18.9 ±0.42^{b}
		Winter	52.4 ±1.27^{a}	6.23 ±0.20^{b}	3.00 ±0.02^{b}	14.2 ±0.34^{a}
2	*S. maritimus*	Spring	160 ±3.51^{a}	94.7 ±1.22^{a}	66.8 ±1.11^{a}	120 ±3.92^{a}
		Summer	339 ±4.25^{b}	92.0 ±1.30^{a}	70.7 ±1.03^{a}	171 ±2.27^{b}
		Autumn	180 ±2.71^{a}	75.0 ±1.21^{a}	60.1 ±1.00^{a}	103 ±2.08^{a}
		Winter	122 ±2.13^{a}	70.6 ±1.03^{a}	55.1 ±1.02^{a}	96.0 ±1.41^{a}
3	*P. australis*	Spring	59.6 ±1.22^{a}	77.6 ±1.18^{a}	41.7 ±1.14^{a}	9.44 ±0.03^{a}
		Summer	17.3 ±0.31^{b}	7.79 ±0.23^{b}	5.36 ±0.10^{b}	9.21 ±0.80^{a}
		Autumn	85.3 ±1.53^{c}	2.60 ±0.04^{b}	1.07 ±0.01^{b}	19.2 ±0.21^{b}
		Winter	70.1 ±1.51^{a}	1.93 ±0.01^{b}	2.27 ±0.01^{b}	18.8 ±0.24^{b}
3	*S. maritimus*	Spring	145 ±3.20^{a}	112 ±3.04^{a}	68.5 ±2.21^{a}	105 ±2.61^{a}
		Summer	405 ±6.27^{b}	96.1 ±2.20^{a}	77.8 ±2.33^{a}	231 ±4.25^{b}
		Autumn	208 ±2.41^{a}	104 ±2.22^{a}	66.7 ±2.06^{a}	99.6 ±1.72^{a}
		Winter	130 ±3.26^{a}	72.0 ±1.37^{b}	54.1 ±1.77^{a}	90.7 ±2.19^{a}

Note: Mean values are reported with SD in all parentheses and different letters indicate significant differences between the sampling time periods within a sampling location ($p<0.05$, post hoc Duncan test).

3.2. Metal concentration in sediments and wastewater

Soil sediment and industrial wastewater samples were also analyzed for metals Zn, Cu and Cr (Tables 4 and 5). In sediments, the concentration of metals decreased in the order Cu > Cr > Zn whereas in industrial wastewater samples the level of Zn was higher than the levels of Cr and Cu. Although concentrations of Cu, Cr and Zn exhibited a wide range of variation with time, no significant variation concentration levels were observed for the metals during the experimental period among locations (sites 1, 2 and 3).

Table 4. Mean concentrations of Zn, Cu and Cr (mg kg^{-1}) in soil sediments collected at locations 1, 2 and 3 throughout the experimental period.

Depth	Metal	Season	Site1	Site2	Site3
	Zn	Spring	38.0 ±0.24[a]	44.6 ±0.25[a]	44.4 ±0.37[a]
		Summer	30.2 ±0.02[a]	33.2 ±0.01[a]	29.8 ±0.02[a]
		Autumn	71.0 ±0.01[b]	61.0 ±0.01[b]	65.0 ±0.01[b]
		Winter	9.36 ±0.10[c]	8.00 ±0.10[c]	5.39 ±0.10[d]
0 – 20 cm	Cu	Spring	12.61 ±0.10[a]	13.9 ±0.20[a]	17.4 ±0.10[a]
		Summer	18.0 ±0.20[a]	27.7 ±0.23[a]	20.9 ±0.10[a]
		Autumn	13.2 ±0.20[a]	19.1 ±0.20[a]	17.5 ±0.10[a]
		Winter	16.3 ±0.25[a]	18.7 ±0.20[a]	17.6 ±0.10[a]
	Cr	Spring	12.0 ±0.20[a]	12.9 ±0.20[a]	16.9 ±0.23[a]
		Summer	64.6 ±0.10[b]	51.9 ±0.10[b]	53.1 ±0.28[b]
		Autumn	11.6 ±0.20[a]	15.3 ±0.20[a]	17.4 ±0.10[a]
		Winter	9.90 ±0.20[a]	11.0 ±0.20[a]	9.51 ±0.10[a]
	Zn	Spring	35.9 ±0.30[a]	45.2 ±0.35[a]	38.3 ±0.30[a]
		Summer	22.1 ±0.02[b]	19.1 ±0.01[b]	16.5 ±0.01[b]
		Autumn	18.7 ±0.10[b]	10.0 ±0.01[c]	20.0 ±0.10[b]
		Winter	23.1 ±0.01[b]	30.1 ±0.10[b]	20.1 ±0.01[b]
20 – 40 cm	Cu	Spring	16.1 ±0.37[a]	10.2 ±0.36[a]	9.88 ±0.22[a]
		Summer	11.6 ±0.22[a]	14.2 ±0.10[a]	9.64 ±0.10[a]
		Autumn	9.60 ±0.22[a]	10.3 ±0.20[a]	9.50 ±0.10[a]
		Winter	8.30 ±0.20[a]	8.00 ±0.36[a]	7.21 ±0.10[a]
	Cr	Spring	15.8 ±0.23[a]	14.2 ±0.42[a]	13.4 ±0.20[a]
		Summer	20.5 ±0.10[a]	35.9 ±0.10[b]	20.9 ±0.20[a]
		Autumn	4.67 ±0.10[b]	4.60 ±0.20[c]	6.29 ±0.10[c]
		Winter	3.79 ±0.10[b]	5.13 ±0.20[c]	6.11 ±0.10[c]

Note: Mean values are reported with SD in all parentheses and different letters indicate significant differences between the sampling time periods within a sampling location ($p<0.05$, post hoc Duncan test).

Table 5. Mean concentrations of Zn, Cu and Cr (mg li^{-1}) in industrial wastewater collected at locations 1, 2 and 3 throughout the experimental period.

Metal	Season	Site1	Site2	Site3
Zn	Spring	51.6 ±0.02[a]	51.2 ±0.02[a]	60.1 ±0.03[a]
	Summer	31.6 ±0.02[a]	34.4 ±0.01[a]	40.9 ±0.40[a]
	Autumn	33.7 ±0.02[a]	25.0 ±0.01[a]	39.9 ±0.02[a]
	Winter	16.2 ±0.01[a]	19.9 ±0.01[b]	19.7 ±0.01[b]
Cu	Spring	4.98 ±0.01[a]	5.37 ±0.01[b]	13.5 ±0.01[a]
	Summer	11.8 ±0.02[a]	15.0 ±0.01[a]	13.5 ±0.06[a]
	Autumn	14.1 ±0.01[a]	15.6 ±0.01[a]	14.7 ±0.01[a]
	Winter	21.6 ±0.02[a]	17.3 ±0.01[a]	9.34 ±0.01[a]
Cr	Spring	14.7 ±0.01[a]	15.1 ±0.01[a]	13.9 ±0.01[a]
	Summer	20.1 ±0.05[a]	24.4 ±0.05[a]	21.8 ±0.01[a]
	Autumn	19.7 ±0.01[a]	23.0 ±0.02[a]	12.1 ±0.01[a]
	Winter	16.3 ±0.01[a]	41.4 ±0.03[b]	16.1 ±0.01[a]

Note: Mean values are reported with SD in all parentheses and different letters indicate significant differences between the sampling time periods within a sampling location ($p<0.05$, post hoc Duncan test).

Seasonal and tissue allocation patterns of three metals (Zn, Cu, Cr) differed between *P.*

australis and *S. maritimus* under field condition. In this study, the fact that roots showed high accumulation of elements could imply relatively high availability in the sediments. Although higher root metals contents were expected, as the dominant uptake pathway of metals from the sediment is via the rhizosphere system. It is generally known that most metals tend to accumulate in the roots rather than in shoots (Fitzgerald et al., 2003), which suggests that the plants adopt either external or internal exclusion mechanisms to hinder translocation of metals to the aerial tissues (Hansel et al., 2001). On the other hand, stems (which consist mainly of vascular tissues) exhibit lower metabolic activity than leaves and, therefore, it is expected that they accumulate metals to a lesser extent than leaves (Sawidis et al., 1995).

The relatively low accumulation of heavy metals in above-ground tissues at most sampling times was probably due to the need of plants to prevent toxicity to the photosynthetic apparatus as suggested by other authors (Landberg and Greger, 1996; Stoltz and Greger, 2002; Bragato et al., 2006).

Zn plays an important role in plant nutrition and enzymatic activities. In both plants, level of Zn was higher in roots. Moreover, roots tend to be Zn accumulators (Weis et al., 2004). Several studies showed that Zn is variable during the growing season. Its concentration, indeed, declines during the vegetative period (Quan et al., 2007). In spring and summer there is normally higher plant activity (more hours of sun light and higher temperatures), with higher uptake of essential nutrients. The uptake of essential elements may also increase during the growth of the plant and their concentrations may be higher at the plant mature stage. Zn concentrations were not in the phytotoxic range (500–1500 mg kg^{-1}, (Chaney, 1989). Main sources of Zn in this area are industrial wastewater and fertilizers. Several authors showed that the amount of metals accumulated in the organs may vary during the growing season as a consequence of the inherent growth dynamics of the plant, as well as in response to variations in the metal levels and availability in the surrounding water and soil (Hardej and Ozimek, 2002). However, studies based on multiple year sampling campaigns (Vymazal et al., 2007) agreed with the main bioaccumulation trend in plant organs according to which metal concentrations decrease in the order of roots > rhizomes > leaves > stems.

Previous studies demonstrated that wetland plants tend to be root accumulators for several metals including copper and zinc (Stoltz and Greger, 2002; Weis et al., 2004). in a comprehensive review on metal accumulation by wetland plants, has been reported inconsistency among several works in which seasonal variations in metal levels were studied, and no clear trend can be inferred (Weis and Weis, 2004).

Cu is vital for plant nutrition and needed for various enzymatic activities of oxidation–reduction. Cu tends to accumulate in roots and is scarcely translocated to the above-ground organs (Siedlecka et al., 2001). Roots acted as a kind of filter what is the most effective strategy in protecting rhizomes and shoots from copper induced injuries (Furtig et al., 1999). Some studies found, as well as the present one, that most metals accumulated only within roots (Peverly et al., 1995; Bargato et al., 2006). It is common knowledge that metal concentrations in aquatic plants vary considerably according to the plant part as well as to the type of element (Larsen and Schierup, 1981; Schierup and Larsen, 1981; Stoltz and Greger, 2002).

Relatively low heavy metal concentrations in the aerial part are also reported in other works with *P. australis* (Peverly et al., 1995; Ye et al., 2003; Baldantoni et al., 2004).

The observed seasonal pattern demonstrated that in both plants metals in roots and rhizomes increased from summer to autumn whereas concentration of metals in leaves increased during their life span probably due to a higher uptake of nutrients in summer as discussed above for Zn. In contrast, Cu level in *S. maritimus* stems was constant through a one year period.

Cu concentration ratios in aerial parts tend to be constant during the growing season (Bonanno and Lo Giudice, 2010). In this study, Cu concentrations were above the phytotoxic range (25–40 mg kg^{-1}; Chaney, 1989). Because of the high urbanization of the area and agriculture as main business, Cu concentrations in plant tissues could be likely to be due to pesticides and industrial wastewater.

Regarding four organs plant in *P. australis* and *S. maritimus,* we observed a similar pattern for Cu and Cr. The concentration pattern of aerial parts and rhizomes are in agreement with other published data (Bragato et al., 2006; Vymazal et al., 2007). Metal concentrations in aerial parts depend largely on the vegetative season; in particular, accumulation may increase sharply at the end of the growing season (Bragato et al., 2006). Although Cr concentrations greater than 0.5 mg kg^{-1} are toxic to plants (Allen ,1989) in this study, the four organs plant showed Cr values above this phytotoxic threshold without visual negative effects for plant development.

Different patterns of accumulation of metals between plants, in relation with different metal contents in water and/or sediment were found in many studies (e.g., Markert, 1987). Interactions between elements can be originated by conflicting

and synergetic processes which may involve the metabolism of more than two elements. Thus, such interactions may affect the uptake and the translocation of a specific element, regardless of its availability in water and soil. Moreover, different factors besides water and soil pollution, such as atmospheric deposition onto leaf surfaces, seasonal physiology, the organs under study, species-specific capacities for uptake, translocation and compartmentalization of trace elements, may contribute to the different bioaccumulation (Bargagli, 1998).

4. Conclusion

Both the macrophytes *P. australis* and *S. maritimus* presented different patterns of metals in tissue types across the growing season. Metals can be removed from contaminated wetlands by many different processes, including plant uptake and accumulation in the aerial part of the plants. In order to maximize removal, harvesting should be done during the period of maximum content in plants. *P. australis* and *S. maritimus* displayed important and distinct seasonal variability in terms of metal concentrations. The present study has illustrated that the exchange of contaminants between plant organs, sediments and water, can significantly change between plant species and from one season to another. We suggest that further studies would be needed on investigating deeply the possible translocation of metals to tissues of plants. If this strategy is confirmed to be a good chance for decontaminating wetlands, it will be necessary to study the optimal conditions to remove of the highest amount of metals.

5. Acknowledgements

The authors thank Fahime Arab and Shole Baghbani for field assistance in collecting the sediment, plant and water samples, Ali Nazarzade for analysis of metals. This research was supported by a grant from the Natural Resources Faculty of Tehran University.

References

1. Allen, S. E. (1989). Chemical Analysis of Ecological Material, 2nd edition. Blackwell Scientific Publications, Oxford, 368 pp.
2. Baldantoni, D., Alfani, A., Di Tommasi, P., Bartoli, G., Virzo De Santo, A.(2004). Assessment of macro and microelement accumulation capability of two aquatic plants. Environmental Pollution 130, 149-156.
3. Bargagli, R. (1998). Trace Elements in Terrestrial Plants. An Ecophysiological Approach to Biomonitoring and Biorecovery. Springer, Berlin, 324 pp.
4. Bonanno, G., Lo Giudice, R. (2010). Heavy metal bioaccumulation by the organs of *Phragmites australis* (common reed) and their potential use as contamination indicators. J. Ecological Indicators. 10: 639–645.
5. Bragato, C., Brix, H., Malagoli, M. (2006). Accumulation of nutrients and heavy metals in *Phragmites australis* (Cav.) Trin. ex Steudel and *Bolboschoenus maritimuss* (L.) Palla in a constructed wetland of the Venice lagoon watershed. Environmental Pollution. 144, 967–975.
6. Chaney, R.L. (1989). Toxic element accumulation in soils and crops: protecting soil fertility and agricultural food chains. In: Bar-Yosef, B., Barrow, N.J., Goldshmid, J. (Eds.), Inorganic Contaminants in the Vadose Zone. Springer-Verlag, Berlin, pp. 140–158.
7. Fitzgerald, E.J., Caffrey, J.M., Nesaratnam, S.T., McLoughlin, P. (2003). Copper and lead concentrations in salt mash plants on the Suir Estuary, Ireland. Environmental Pollution 123, 67-74.
8. Furtig, K., Pavelic, D., Brunold, C., Brandle, R. (1999). Copper-and-iron induced injuries in roots and rhizomes of reed (*Phragmites australis*). Limnologica 29, 60–63.
9. Gopal, B. (2003). Perspectives on wetland science, application and policy. Hydrobiologia 490, 1-10.
10. Hansel, C., Fendorf, S., Sutton, S., Newville, M. (2001). Characterization of Fe plaque and associated metals on the roots of mine-waste impacted aquatic plants. Environmental Science and Technology 35, 3863-3868.
11. Hardej, M., Ozimek, T. (2002). The effect of sludge flooding on growth and morphometric parameters of *Phragmites australis* (Cav.) Trin. ex Steudel. Ecological Engineering 18, 343-350.
12. Jana, S. (1988). Accumulation of Hg and Cr by three aquatic species and subsequent changes in several physiological and biochemical plant parameters. Water Air Soil Pollution. 38, 105–109.
13. Kamal, M., Ghaly, A.E., Mahmoud, N., Cote, R. (2004). Phytoaccumulation of heavy metals by aquatic plants. Environment International 29, 1029-1039.
14. Karpiscak, M.M., Whiteaker, L.R., Artiola, J.F., Foster, K.E.(2001). Nutrient and heavy metal uptake and storage in constructed wetland systems in Arizona. Water Science and Technology 44, 455-462.
15. Landberg, T., Greger, M. (1996). Differences in uptake and tolerance to heavy metal in Salix from unpolluted and polluted areas, Appl. Geochem., 11, 175–180.
16. Larsen, V.J., Schierup, H.H. (1981). Macrophyte cycling of zinc, copper, lead and cadmium in the littoral zone of a polluted and a non-polluted lake. II.

Seasonal changes in heavy metal content of aboveground biomass and decomposing leaves of *Phragmites australis* (Cav.) Trin. Aquatic Botany 11, 211-230.
17. Markert, B. (1987). Interelement correlations in plants. Fresen. J. Anal. Chem. 329, 462–465.
18. Mays, P.A., Edwards, G.S.(2001). Comparison of heavy metal accumulation in a natural wetland and constructed wetlands receiving acid mine drainage. Ecological Engineering 16, 487-500.
19. Mishra, V.K., Tripathi, B.D. (2008). Concurrent removal and accumulation of heavy metals by the three aquatic macrophytes. Bioresource Technology 99, 7091-7097.
20. Peverly, J. H., Surface, J. M., & Wang, T. (1995). Growth and trace metal absorption by Phragmites australis in wetlands constructed for landfill leachate treatment. Ecological Engineering 5, 21–35.
21. Quan, W.M., Han, J.D., Shen, A.L., Ping, X.Y., Qian, P.L., Li, C.J., Shi, L.Y., Chen, Y.Q. (2007). Uptake and distribution of N, P and heavy metals in three dominant salt marsh macrophytes from Yangtze River estuary, China. Mar. Environ. Res. 64, 21–37.
22. Salt, D.E., Kramer, U. (2000). Mechanisms of metal hyperaccumulation in plants. In: Raskin, I., Ensley, B.D. (Eds.), Phytoremediation of Toxic Metals, Using Plants to Clean Up the Environment. Wiley and Sons, pp. 231-246.
23. Sawidis, T., Chettri, M., Zachariadis, G.A., Stratis, J.A. (1995). Heavy metals in aquatic plants and sediments from water systems in Macedonia, Greece. Ecotoxicology and Environmental Safety 32, 73-80.
24. Schierup, H.-H., Larsen, V.J. (1981). Macrophyte cycling of zinc, copper, lead and cadmium in the littoral zone of a polluted and a non-polluted lake. I. Availability, uptake and translocation of heavy metals in Phragmites australis (Cav.) Trin. Aquatic Botany 11, 197-210.
25. Siedlecka, A., Tukendorf, A., Skorzynska-Polit, E., Maksymiec, W., Wojcik, M., Baszynski, T., Krupa, Z. (2001). Angiosperms (Asteraceae, Convolvulaceae, Fabaceae and Poaceae; other than Brassicaceae). In: Prasad, M.N.V. (Ed.), Metals in the Environment. Analysis by Biodiversity. Marcel Dekker, Inc., New York, pp. 171–217.
26. Stoltz, E., Greger, M. (2002). Accumulation properties of As, Cd, Cu, Pb and Zn by four wetland plant species growing on submerged mine tailings. Environmental and Experimental Botany 47, 271-280.
27. Vymazal, J., Svehla, J., Kropfelova, L., Chrastny, V. (2007). Trace metals in Phragmites australis and *Phalaris arundinacea* growing in constructed and natural wetlands. Sci. Total Environ. 380, 154–162.
28. Weis, J.S., T. Glover, P. Weis. (2004). Interactions of metals affect their distribution in tissues of *Phragmites australis*. J. Environmental Pollution. 131: 409–415.
29. Weis, J.S., Weis, P. (2004). Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration Review. Environment International 30, 685-700.
30. Ye, Z.H., Baker, A.J.M., Wong, M.H., Willis, A.J. (2003). Copper tolerance, uptake and accumulation by *Phragmites australis*. Chemosphere 50, 795-800.
31. Zavoda, J., Cutright, T., Szpak, J., Fallon, E. (2001). Uptake, selectivity, and inhibition of hydroponic treatment of contaminants. Journal of Environmental Engineering 127, 502-508.