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ORIGINAL RESEARCH PAPER

Investigation on concentration of elements in wetland sediments and aquatic plants

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ABSTRACT: The major aim of the present study was to investigate elements (Fe, Ni, Pb, V, Zn) concentration in sediment and different tissues of *Phragmities australis* and *Typha latifolia* in Hor al-Azim Wetland southwest of Iran. Sampling of sediments and aquatic plants was carried out during spring and summer 2014. Results showed that the mean concentrations of chemical elements in *Phragmities australis* in root and stem-leaf were as follows: iron: 4448 mg/kg, nickel: 28 mg/kg, lead: 8 mg/kg, vanadium: 10 mg/kg and zinc: 15.5 mg/kg in root and Iron: 645 mg/kg, nickel: 15 mg/kg, lead: 4 mg/kg, vanadium: 4 mg/kg and zinc 16 mg/kg respectively. Also, the mean concentrations of iron, nickel, lead, vanadium and zinc in roots of *Typha latifolia* were 8696 mg/kg, 34 mg/kg, 5 mg/kg, 19 mg/kg and 27 mg/kg respectively. The mean concentrations of iron, nickel, vanadium, lead and zinc in stem-leaves of *Typha latifolia* were as follows: 321 mg/kg, 3 mg/kg, 7 mg/kg, 2 mg/kg and 14 mg/kg respectively. The mean concentrations of iron, nickel, vanadium, lead and zinc were as: 40991 mg/kg, 65 mg/kg, 60 mg/kg, 31 mg/kg and 60 mg/kg respectively in surface sediment of the study area. Concentration pattern of the elements in sediment were as: Fe>Ni>Zn>V>Pb. The highest concentration of the elements in the plant was seen in the roots. Also, *Typha latifolia* can uptake more concentration of elements than *Phragmities australis*. Based on the enrichment factor, nickel in summer had the highest enrichment *factor* values among the elements studied and it has a moderate enrichment.

KEYWORDS: Elements; Enrichment factor; Hor al-Azim Wetland; Phragmities australis; Typha latifolia.

INTRODUCTION

Chemical elements are ubiquitous, highly persistent, and non-biodegradable with long biological half-lives and they can accumulate in soils at environmentally hazardous levels (Burger *et al.*, 2007; Mensi *et al.*, 2008; Murugesan *et al.*, 2008; Uba *et al.*, 2009; Nouri *et al.*, 2009; Ahmad *et al.*, 2010; Sekhavatjou *et al.*, 2010). elements in essential and non-essential forms accumulate in nature especially in sediments (Fairbrother *et al.*, 2007; Karbassi *et al.*, 2007; Priju and

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 Narayana, 2007; Karbassi *et al.*, 2008; Muchaa *et al.*, 2008; Mazeja and Germb, 2009; Venugopal *et al.*, 2009). The toxicity of chemical elements is highly influenced by geochemical factors that influence element bioavailability (Fairbrother *et al.*, 2007). Wetlands represent some of the most productive habitat on earth. They are often referred to as "nature's kidneys" because of their ability to filter, metabolize, and sequester nutrients and metals. Wetlands have been applied for use as a flood control mechanism, as filters for removing toxic elements from aquatic ecosystems, treating urban storm water runoff, and purifying municipal wastewater (Kadlec and Knight, 1996). There are basically three reservoirs of elements in a wetland ecosystem: water, sediment, and biotic components.

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Among these reservoirs, the sediment could be recognized as the major repository for elements. As these sediments are an integral part of the pond system and may be influenced by pollution over long period of time and over a wide spread area, these are proved to be monitored easily and efficiently. As elements which are potentially harmful to human health persist in sediments for long time and may enter the food chain in significantly elevated amounts, it should be monitored properly in a regular interval. Several studies have looked at the possible contribution of submerged and emergent macrophytes on the overall budget of elements in rivers and lakes (Brix and Lyngby, 1983; Peverly, 1985; St-Cyr et al., 1994). For example, St-Cyr and Campbell (1996) showed that elements concentrations were higher in sediments than in the roots, which suggests that adjacent sediments are the main sink for metals. In addition, a mass-balance study showed that macrophyte beds were a total sink for particulate metals on a yearly basis and can be considered to retain metals (Jackson et al., 1994). According to Hosseini Alhashemi et al. (2011) reported that uptake trend of trace elements in plant decreases as root>stem>leaf. Accumulation levels of trace elements in different tissues of P. porphyrio and M. angustirostris are almost identical and considerable. Accumulation and toxicity of Cd in birds is more than plants in T. australis, Cu and Pb possesses the highest TF. Also Cr, Co, Mn, Ni, and Zn have higher TF from stem to leaf than root to stem in P. australis (Hosseini Alhashemi et al., 2011). Carranza-Álvarez et al. (2008) report that S. americanus and T. latifolia have the ability to extract Pb, Cd, Cr, Mn and Fe from their water surroundings; on the whole, the roots presented higher concentrations of elements than the stem and the leaves (Carranza-Álvarez et al., 2008). Macrophytes are believed to have significant effects on the biogeochemistry of sediments (Wigand et al., 1997). Macrophytes are essential components of wetlands by stabilizing and oxidizing the surface of sediments (Dunbabin et al., 1988; Brix, 1994). Aquatic organisms can bioaccumulate, biomagnificate or biotransfer certain elements to concentrations high enough to bring about harmful effects (Opuene et al., 2008). The presence of macrophyte beds also allows the deposition of particulate elements and organic matter by decreasing water flow (Kadlec, 1995; Caçador et al., 1996). Consequently, total metal concentrations should be higher in vegetated sediments However, there is no

general consensus: some studies show higher concentrations in vegetated sediments (Kostka and Luther III, 1995; Doyle and Otte, 1997) while others demonstrate the opposite situation (Otte et al., 1995; Caçador et al., 1996). The Hor al-Azim wetland is covered by different flora and fauna such as mangroves. hydrophyte vegetation, xerohalophytic vegetation, halophyte vegetation, fishes, and different types of birds. The climate in Hor al-Azim wetland and surrounding area is classified between semi-arid and arid, with a mean annual rainfall of 240 mm and a mean annual temperature of 24 °C. There is no evidence regarding natural sources of element in site, while most of element pollution is related to oil industry. Known sources of contamination in this area include oil fields activities and agricultural runoff from the use of fertilizers, herbicides, and pesticides. It should be pointed that there is not any investigation about elements in this important wetland, whereas numerous pollution sources discharge elements in the area of study. The results of present study can be useful to understand the effects of oil activities and other pollution sources on the environmental pollution in the area of study. The main goal of the present study is determination of elements (Fe, Ni, Pb, V, Zn) in sediments and different tissues of Phragmities australis and Typha latifolia in North Azadegan Zone, Hor al-Azim wetland. This Study has been performed in Hor al-Azim wetland North Azadegan Zone of Khuzestan Province, Iran in 2014.

MATERIALSAND METHODS

Elements analysis and sample collection

The present study is carried out in surface sediment of Hor al-Azim wetland North Azadegan Zone. The Hor al-Azim wetland is located southwest of Iran and lies to the east of the Tigris River, in the Iran-Iraq border, as well as is one of the Mesopotamian marshlands. This wetland is located north of Persian Gulf, ranging from 31° 002 N to 31° 472 N in latitude and 47° 202 E to 47° 572 E. The Hor al-Azim wetland is the main revenue of people in the west of Khuzestan province. The selected plants involving Phragmites australis and Typha australis are the most abundant plants. For determination of element concentrations in sediments 5 sampling stations were selected to measure Fe, Ni, Pb, V, and Zn in study area (Fig. 1). The sampling was carried out in spring and summer 2014 in the Hor al-Azim wetland. Preparations of sediments were done by

air drying and then passing samples through a $63-\mu m$ mesh. (Sieve No. 230, ASTM E-11). The sieved sediments were powdered by an agate mortar and pestle. About 0.5 g of the powdered sample was placed in a beaker containing 5 mL of 3:1 HNO3 to HCl and covered with a watch glass. Then, samples were heated until most of the liquid had evaporated, and allowed to cool before 3 mL of perchloric acid were added. Then the cover was replaced and heated again till evaporation of most of the liquid. Finally, samples were cooled to room temperature before being filtered. The filtrates were transferred to 50 mL volumetric flasks and brought to volume with 1 N HCl. Three samples of each two plant species including P. australis, T. latifolia, were randomly collected from sampling sites. The collected samples were thoroughly cleaned with distilled water for removal of soil and other extraneous particles. The plant samples were cut into two pieces involving root, stem-leaf and dried at 65°C for 24 h in an oven. To ensure uniform distribution of metals in the sample, the material was milled in a microhammer cutter and sieved through a 1.5-mm sieve (Hosseini Alhashemi et al., 2011).

Statistical analysis

Pearson correlation matrix was applied to identify the relationship between the six elements. Analysis of variance (ANOVA) was done to evaluate significant differences in element concentrations during sampling periods. All statistical analyses were carried out using SPSS software (version 17.0).

RESULTS AND DISCUSSION

The concentrations of elements in the sediments and different tissues of *Phragmites australis* and *Typha latifolia* in Hor al-Azim wetland is shown in Tables 1 and 2 respectively. The results of calculation of enrichment factors are shown in Table 3.

Iron

Iron is generally the most abundant metal in all of the reservoirs because it is one of the most common elements in the earth's crust (Usero *et al.*, 2003.). In the sediment Fe showed the highest concentrations in all stations. The highest concentration of Fe was 26603 mg/kg in station 2 in summer, whereas the lowest concentration of Fe was found as 2082 in station 3 in

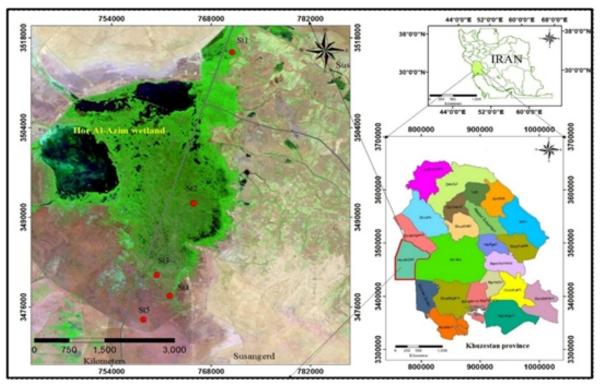


Fig. 1: Sediments sampling stations in Hor al-Azim wetland of Iran

summer. In comparison, Fe concentrations were the highest and Cu concentrations were the lowest of those recorded in the sediment Atatürk Dam Lake (Karadede and Ünlü, 2000) and Kovada Lake (Tekin-Özan and Kýr, 2005). Based on results from Table 2 the concentration of Fe in root of *T. latifolia* was the highest (10559 mg/kg) and in stem–leaf of *Phragmites australis* was the lowest (258 mg/kg).

Zinc

Although Zn is essential trace element, high levels can cause harmful health effects. Toxicity of high level Zn concentrations in man is well known (Clark et al., 1981). In the present investigation, in the sediment the lowest concentration of zinc was found 122 mg/kg in station 1 in spring while the highest concentration of zinc was found 42 mg/kg in station 4 in spring. As Table 2 indicates, mean concentrations of Zn is the highest in root (32 mg/kg) of T. latifolia in spring. The concentration of zinc was 12 mg/kg in stem-leaf of T. latifolia in spring. Rashed et al. (1995) reported that Zn concentration in the sediment of Nile Delta ranged between 18 to 104 µg/g dry water The upper toxic levels of Zn in various plants range from 100 to 500 μ g/g (Waganov and Nizharadze, 1981). The mean concentration of Zn in normal plants (above ground tissues) is $66 \,\mu g/g$ (Outridge and Noller, 1991), and the toxic level is up to 230 μ g/g (Borkert *et al.*, 1998; Long et al., 2003).

Vanadium

Vanadium complexes can reduce growth of cancer cells and improve human diabetes mellitus but can be toxic when present at higher concentrations (USEPA, 2011). Based on results from Table 1, the highest and lowest vanadium levels in the sediment were found as 103 mg/kg in station 3 and 34 mg/kg in station 1 in spring. The level of vanadium was the higher In root (23 mg/kg) of *T.latifolia* and the lower level of vanadium was found as 3 mg/kg in stem-leaf of *Phragmites australis* in spring. There is not much evidence for V toxicity to plants. Increased concentration of V (up to 3 mg/kg) in the nutrient solution under greenhouse conditions is reported to reduce the length of collard roots by 50% (Gettier *et al.*, 1987).

Lead

Pb continues to enter the environment primarily by anthropogenic means, retaining its status as a priority pollutant (EPA, 2006). Pb is believed to be the metal of least bioavailability and the most highly accumulated metal in root tissue while Pb shoot accumulation is much lower in most plant species (Kabata-Pendias and Pendias, 2001). The concentration of lead was the highest (122 mg/kg) in station 1 in spring and the lowest levels of lead were found as 1 mg/kg in station 5 in summer. Content of lead in stem-leaf (1 mg/kg) of *Phragmites australis* in spring was the lowest whereas

Elements	Summer					Spring					
Station No.	Zn	V	Pb	Ni	Fe	Zn	V	Pb	Ni	Fe	
1	45	48	2	72	16405	122	34	122	16	10997	
2	62	73	7	110	26603	65	67	26	27	259829	
3	59	66	28	92	2082	53	103	71	55	21068	
4	58	60	28	92	21073	42	43	10	108	16018	
5	45	49	1	64	17360	45	51	12	16	18467	
Min	45	48	1	64	2082	42	36	10	16	10997	
Max	62	73	28	110	26603	122	103	122	108	259829	
Average	54	59	13	86	16705	65	60	48	44	65276	

Table 1: Total concentration of elements in sediments Hor al-Azim wetland (mg/kg)

Table 2: Concentration of elements in different tissues of Phragmites australis and Typha latifolia in Hor al-Azim wetland (mg/kg)

		Summer				Spring						
Species	Tissue	Elements										
		Zn	V	Pb	Ni	Fe	Zn	V	Pb	Ni	Fe	
Phragmites	Root	15	10	2	16	4909	16	10	14	39	3987	
australis	stem-leaf	16	4	1	5	1032	16	3	6	25	258	
Typha latifolia	Root	21	14	2	26	6833	32	23	8	41	10559	
	stem-leaf	16	7	1	1	321	12	6	1	5	321	

Elements	Summer	Spring
Zn	1.6	0.5
V	1.3	0.3
Pb	2.3	1.8
Ni	3.6	0.4

Table 3: Enrichment factors (EF) in surface sediments of Hor al-Azim wetland

in root (14 mg/kg) of *Phragmites australis* in summer was highest. Al-Saadi *et al.* (2002) reported that the Pb concentration was the highest in spring in Habbaniya Lake's sediment.

Nickel

Nickel is the 24th most plentiful element of the earth crust (Younis *et al.*, 2015; Cempel and Nikel, 2006). Normal Ni concentration in plants ranges from 0.5–5 μ g/g and values above these values are poisonous (Allen, 1989). In the present investigation, in the sediment the lowest concentration of nickel was found in station 1 (16 mg/kg) in spring whereas the higher levels of nickel was found in station 2 in summer (110 mg/kg). The maximum nickel level observed Was 39 mg/kg in root of *Phragmites australis* in spring while the minimum nickel levels were found as 1 mg/kg in stem-leaf of *T. latifolia* in summer. Hosseini Alhashemi. (2011) reported that the mean Ni concentration was the 47 mg/kg in Shadegan wetland sediments.

Enrichment factor of the elements

In this study, the EF technique was used to assess the level of contamination in the sediments of Hor al-Azim wetland. According to this technique, metal concentrations were normalized to metal concentrations of average shale (Ghrefat and Yusuf, 2006). Widely used elements for normalization are Al (Chen *et al.*, 2007) and Fe (Ghrefat and Yusuf, 2006). In this study, iron has also been used as a conservative tracer to differentiate the metal contamination with respect to the average shale to quantify the extent and degree of metal pollution. To assess the level of metal enrichment in sediment samples of study area enrichment factor (EF) was computed using the following equation:

$$EF = (M_{sample}/Fe_{sample})/(M_{average shale}/Fe_{average shale})$$

Where:

 M_{sample} concentration of the examined metal in the examined sediment

 ${\rm Fe}_{\rm sample}$ concentration of the reference metal in the examined sediment

 $M_{average shale}$ concentration of the examined metal in the average shale

 $Fe_{average shale}$ concentration of the reference metal in the average shale

According to Chen et al. (2007), EF<1 indicates no enrichment, EF<3 is minor enrichment, EF=3-5 is moderate enrichment, EF=5-10 is moderately severe enrichment, EF=10-25 is severe enrichment, EF=25-50 is very severe enrichment, and EF>50 is extremely severe enrichment. The values of the average shale used in this work are from Turekian and Wedepohl (1961). These values are: Fe 47200, Zn 95, V 130, Pb 20 and Ni 68 mg/kg. In present study, the average of element concentrations in spring and summer were used to determination of enrichment factor. The calculation of enrichment factors showed that Ni in summer had the highest EF values among the elements studied and it has a moderate enrichment (average value 3.6). Zn, V and Pb in summer had minor enrichment (average value 1.6, 1.3 and 2.3 respectively). Zn, V, and Ni in spring exhibited the lowest EF values among metals studied (average value 0.5 and 0.3 and 0.4 respectively) and had no enrichment (Table. 3).

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interests regarding the publication of this manuscript.

CONCLUSION

Based on results of present study concentration of iron and lead were the highest and lowest respectively in sediment. In present study roots accumulate higher amounts of element. Also, comparison of studied metal concentration in sediments showed that levels of Fe, Zn, Pb and V in spring are more than summer. The results in present study showed that the concentration of elements in root is more than in stems leaf. Concentration of all elements with the exception of lead, in root of Typha latifolia is more than root of Phragmites australis. Generally high concentration of element in sediments in spring can be caused by more activities of oil companies around the wetland and increase salinity due to water shortage are the reasons to increased concentrations of elements in spring. Next to the station 2, revenue operation is more than other stations and because of that, concentration of the studied elements is high in this station. The results

of present study indicated of intra-relationship amongst transition of metals from sediments to plants.

The elevated EF value indicated that the sediment samples of study area may be enriched moderately with nickel.

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