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## Heavy elements accumulation in dominants aquatic plants at Al-Chibayish Marshes, South of Iraq

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**Abstract** - The present study concerned with the heavy elements (Cd, Cr, Ni and Pb) concentration that accumulated in dominant species of aquatic plants (submerged; *Ceratophyllum demersum*) and (merged; *Phragmites australis*, *Typha domingensis* and *Schoenoplectus littoralis*), in relation to the concentration of these elements in each of the dissolved phase of water and sediments samples which collected seasonally from four sites at Al-Chibayish marshes during August 2017 to April 2018. Also Bioaccumulation factor (BAF) was calculated. The results showed that the highest concentrations of heavy elements was in the sediments, then the aquatic plants and the lowest concentrations was recorded in dissolved phase, whereas the Bioaccumulation Factor (BAF) of heavy elements in aquatic plants, shows that *Ceratophyllum demersum* have the highest concentration than the other species.

راكم العناصر الثقيلة في النباتات المائية السائدة في أهوار الجبايش ، جنوب العراق  
رحاب سالم خزل<sup>1</sup> و مكية مهلهل الحجاج<sup>2</sup> و حامد طالب السعد<sup>3</sup>  
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**المستخلص** - تناولت الدراسة الحالية تراكيز العناصر الثقيلة (الكاديوم Ca والكروم Cr والنيكل Ni والرصاص Pb) المتركمة في الانواع السائدة من النباتات المائية الغاطسة (الشمبلان *Ceratophyllum demersum*) والبارزة (القصب *Phragmites australis* والبردي *Typha domingensis* والجولان *Schoenoplectus littoralis*)، ومقارنة تراكيز هذه العناصر في كل من عينات الماء (الطور الذائب) والرواسب والتي جمعت فصليا من أربعة مواقع في أهوار الجبايش للفترة من أب 2017 الى نيسان 2018. تم حساب دليل التراكم الحيوي للعناصر الثقيلة في النباتات المائية (BAF). أوضحت النتائج ان تراكيز العناصر الثقيلة في الرواسب أعلى مما هي عليه في النباتات المائية وأقل التراكيز سجلت في الطور الذائب من الماء. بينما أوضح دليل التراكم الحيوي للعناصر الثقيلة في النباتات المائية ان نبات الشمبلان *Ceratophyllum demersum* تمتلك أعلى التراكيز بالنسبة لأنواع الأخرى.

**الكلمات المفتاحية:** العناصر الثقيلة، النباتات المائية، دليل التراكم الحيوي، أهوار الجبايش

## Introduction

Southern marshes of Iraq play an important role in the conserving diversity of species in the Middle East, due to their large size, the abundance of their aquatic flora and their separation from the other systems (Bedair *et al.*, 2006).

Aquatic plants are one of the characteristics of the marshes which have been known by their multiple functions (Brix, 1997; Patel and Kanugo, 2010). They play an important role in cleaning the environment and protecting the health of water through utilizing plants in environmental sound technologies by their great vegetation cover and high productivity.

Thus many countries have resorted to using these low-cost plants to address many environmental problems by establishing artificial wetlands and cultivating them with different kinds of aquatic plants that are good in improving the ecosystem (UNEP, 2001).

According to the diversity of aquatic plants, it is widespread and good tolerance to the fluctuating environmental conditions, various kinds of plant families have been utilized as bio-indicator to study water contamination (Benabid *et al.*, 2008).

Considerable amounts of contaminants such as heavy elements are accumulated in Aquatic plants tissues. They are absorbing these elements across root and shoot structures due to their fast growth and great biomass (Bonanno and Lo Giudice, 2010; Matache *et al.*, 2013). Consequently, aquatic plants are so proposed as pollution-monitoring organisms (Shine *et al.*, 1998).

Plants that have the ability to take up elements that exceed the established background concentrations and greater than other species from the same water bodies are known as hyperaccumulators (McGeer *et al.*, 2003). There are many populations found in water rich in pollutants, this either due to geochemical factors or because of pollution (Prasad, 1997; Brooks and Herman, 1998; Benabid *et al.*, 2008). Plants are divided as accumulators, indicators or excluders depending on translocation and absorption of the elements by the plants above-ground level. Accumulator plants can continue to be accumulate concentration of pollutants in their tissues. Plants which have mechanisms to control translocation of contaminant from roots to shoots described as indicator plants, while excluders plants can control the pass of pollutants across plants root (Baker, 1981; Chaudhry *et al.*, 1998; Malik *et al.*, 2017).

Plants utilize various mechanisms to accumulate or exclude pollutants and in this manner keep up their growth. Accumulation and tolerance of elements by the plants is a complex phenomenon (Murtaza *et al.*, 2010). The movement of these elements through the root layer, translocation over xylem and sequestration and detoxification of them at the cell and entire plant levels are indispensable components received by aggregator plants (Lombi *et al.*, 2002). Understanding the mechanisms involved in phytoremediation is essential to effectively utilized this technique on environments. Plants have the normal ability to deal with pollutants by means of processes such as bioaccumulation and translocation. A technique which uses plants for the uptake of elements from water is mention to as phytoremediation (Greipsson, 2011). Phytoremediation is utilizing the momentous capacity of plants to accumulate metals and other compounds from the environment and to metabolizing different molecules in their tissues showing up promising for the elimination of contaminants from the ecosystem (Gurbisu and Alkorta, 2003).

The objective of this study is to determine the distribution of some heavy elements as dissolved, sediment and selected aquatic plants to study their ability to heavy metals accumulation in their tissues and examine the possibility of using them as bio-indicators.

## Materials and Methods

Water, sediments and aquatic plants samples were collected seasonally from four stations selected at Al-Chibayish marshes, southern Iraq, the first station (Abusubat), the second station (Al-Baghdadiya 1), the third station (Al-Baghdadiya 2), and the fourth station (Al-Hammara) (Fig. 1).

Water samples (5 L) was collected from each station, filtered as quickly as time permits through pre-washed (0.5 N HCl) and pre-weighted millipore filter papers (0.45  $\mu\text{m}$  pore size). The filtrate samples was pre-concentrated according to Riley and Taylor (1968), using chelating ion exchange resin (Purolite-C-100 resin in hydrogen form), heavy elements were eluted from column using 2 N  $\text{HNO}_3$ , collected in clean teflon beaker, heated at 70°C until the sample volume become less than 25 ml, then completed the sample to 25 ml with deionized water and placed in tightly stopper polyethylene vials, using Flame Atomic Absorption Spectrophotometer (FAAS) for analysis of the elements.

Plant samples were taken by hand then washed several time by marsh water to remove the adherence particulate as possible, then samples were kept in polyethylene bag, stored in ice-packed until return to the lab.

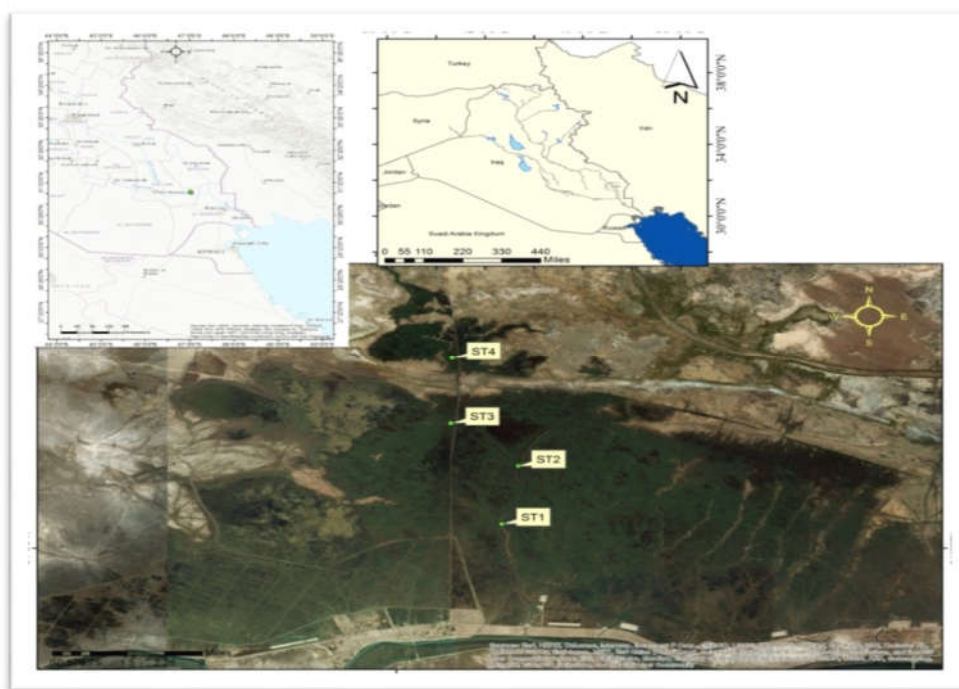


Figure 1. Study stations at Al-Chibayish marshes, south of Iraq.

In the laboratory samples of plants washed thoroughly by distilled water, dried, grounded and sieved utilizing a 63 $\mu\text{m}$  sieve and put (1g) into teflon beaker with 5 ml nitric acid then 2 ml Perchloric acid, heated at 70°C until all the materials were dissolved, add 10 ml of (0.5 N HCl) and the samples were diluted with deionized water to a volume of 25 ml and filtered. Samples were

stored in tight stopper polyethylene vials to be ready for analysis, using FAAS (Estefan *et al.*, 2013).

The samples of sediments were collected seasonally from each location utilizing Van Veen grab sampler, using polyethylene bags for preserving the samples, then placed in cold box until return to the lab. Sediment samples were dried in an oven at 50°C for roughly 3 days, grind finely utilizing an electrical mortar and sieved through a 63 µm mesh sieve, and put away in polyethylene sacks until analysis. Taken (1 gm) from the grinded and sieved sediments, and put it in 50 ml polyethylene tube.

The exchangeable part of heavy elements were extracted according to the method of Chester and Voutsinou (1981), and the residual heavy elements were extracted according to Sturgeon *et al.* (1982), samples were stored in tight stopper polyethylene vials to be ready for analysis. Total heavy elements concentration was calculated by adding exchangeable value to residual value.

Bioaccumulation Factor (BAF):

Bioaccumulation Factor of different elements rooted aquatic plants to sediment, and aquatic plants to water (dissolved phase) was calculated using the equation given by Wilson and Pyatt (2007).

$$\text{BAF}(\%) = \frac{C_{\text{plant tissue}}}{C_{\text{(sediment or water)}}} \times 100$$

Where:

$C_{\text{plant tissue}}$  the concentration of elements in plant tissue (µg/g dry weight).

$C_{\text{(sediment/water)}}$  the concentration of elements in sediment(µg/g dry weight) or water (mg/l).

## Results and Discussion

### Heavy Elements in Plants:

The concentration of environmental contamination could be reflected by organisms that have the capability to take up elements proportionally to their concentration in the surrounding environment, this is associated with organisms that accumulate the elements independently as their physiological needs, because they do not have the ability to discriminate between various elements (Brankovic *et al.*, 2011). The aquatic plants have the ability to absorb heavy elements from water column and sediments and accumulate them in their tissues, therefore, the aquatic plants are used as a good monitor and biological indicators for element pollution in the aquatic ecosystem (Cheng, 2003).

The mean concentration of elements (Cd, Cr, Ni and Pb) in *Phragmites australis* were (0.20, 5.27, 4.20 and 6.19) µg/g dry weight, respectively. In *Typha domingensis*, the mean concentration of elements were (0.20, 3.96, 3.05 and 5.61) µg/g dry weight, respectively. In *Schoenoplectus littoralis*, the mean concentration of elements were 0.20, 4.58, 3.49 and 4.31) µg/g dry weight, respectively. While the mean concentration of elements in *Ceratophyllum demersum* were (0.51, 9.73, 51.44 and 9.99) µg/g dry weight, respectively (Table 1).

The concentration of heavy elements in the tissues of the plants exhibited differences among seasons and stations (Table 1) due to many environmental factors such as the different ability of aquatic plant to possess and accumulate element in their tissue, and the uptake of the element which depended on plant species and the difference in the age state of plants, this finding was in agreement

with Cardwell *et al.* (2002) and Mahmood (2008) who found that there were specific seasonal differences in the concentration of element in the studied aquatic plants. Another reason for such concentration was the available element in water or sediment, different pollution source, growth form of plant (Saygideger *et al.*, 2004; Habeeb *et al.*, 2015).

Table 1. Concentration of some heavy elements ( $\mu\text{g/g}$  dry weight) in the studied aquatic plants for the period from August 2017 to April 2018 [first line (range) and second line (mean  $\pm$  S.D)].

	Aquatic Plants	Stations				
		St 1	St 2	St 3	St 4	Mean
Cd	<i>P. australis</i>	0.08-0.25	0.05-0.27	0.03-0.29	0.03-0.27	0.20
		0.20 $\pm$ 0.08	0.20 $\pm$ 0.10	0.21 $\pm$ 0.12	0.20 $\pm$ 0.11	
	<i>T. domengensis</i>	0.07-0.29	0-0.36	0.02-0.39	0.04-0.32	0.20
		0.18 $\pm$ 0.09	0.22 $\pm$ 0.15	0.21 $\pm$ 0.15	0.21 $\pm$ 0.13	
	<i>S. littoralis</i>	0.08-0.24	-	0.04-0.33	0.08-0.25	0.20
		0.18 $\pm$ 0.08	-	0.21 $\pm$ 0.12	0.19 $\pm$ 0.08	
<i>C. demersum</i>	0.39-0.55	-	0.37-0.57	0.34-0.87	0.51	
	0.45 $\pm$ 0.07	-	0.47 $\pm$ 0.09	0.6 $\pm$ 0.24		
Cr	<i>P. australis</i>	3.19-12.22	1.06-12.52	1.76-9.31	1.81-10.71	5.27
		6.37 $\pm$ 4.04	4.29 $\pm$ 5.51	5.61 $\pm$ 3.18	4.81 $\pm$ 4.09	
	<i>T. domengensis</i>	0.32-10.47	0.40-10.16	0.37-12.28	0-11.44	3.96
		4.70 $\pm$ 4.24	3.24 $\pm$ 4.63	4.64 $\pm$ 5.55	3.25 $\pm$ 5.47	
	<i>S. littoralis</i>	2.23-10.47	-	0.90-12.28	0.60-11.44	4.58
		4.91 $\pm$ 3.79	-	4.90 $\pm$ 5.22	3.94 $\pm$ 5.05	
<i>C. demersum</i>	2.18-21.30	-	2.28-9.98	2.74-23.35	9.73	
	11.38 $\pm$ 7.83	-	7.24 $\pm$ 3.46	10.57 $\pm$ 8.89		
Ni	<i>P. australis</i>	1.85-7.73	0.83-7.27	1.13-6.81	1.70-8.80	4.20
		4.75 $\pm$ 2.42	3.39 $\pm$ 2.79	4.28 $\pm$ 2.79	4.42 $\pm$ 3.20	
	<i>T. domengensis</i>	0.99-6.04	0.35-5.75	0.35-7.30	0.79-7.01	3.05
		3.12 $\pm$ 2.42	2.28 $\pm$ 2.42	3.75 $\pm$ 3.71	3.03 $\pm$ 2.79	
	<i>S. littoralis</i>	1.13-6.51	-	0.69-6.40	1.37-7.67	3.49
		3.43 $\pm$ 2.48	-	3.60 $\pm$ 3.12	3.43 $\pm$ 2.90	
<i>C. demersum</i>	37.79-74.20	-	35.14-51.26	48.52-61.63	51.44	
	56.43 $\pm$ 15.0	-	43.49 $\pm$ 7.6	54.38 $\pm$ 38		
Pb	<i>P. australis</i>	1.30-5.31	1.02-7.25	1.45-37.19	2.90-6.02	6.19
		4.09 $\pm$ 1.88	3.97 $\pm$ 2.60	11.92 $\pm$ 16.93	4.79 $\pm$ 1.42	
	<i>T. domengensis</i>	2.61-7.58	2.71-11.29	2.47-8.09	2.32-6.91	5.61
		5.62 $\pm$ 2.14	6.60 $\pm$ 3.67	4.86 $\pm$ 2.38	5.34 $\pm$ 2.05	
	<i>S. littoralis</i>	2.47-6.57	-	1.16-6.55	2.76-6.02	4.31
		4.65 $\pm$ 1.69	-	3.61 $\pm$ 2.24	4.67 $\pm$ 1.42	
<i>C. demersum</i>	5.58-13.99	-	5.56-12.57	5.80-13.46	9.99	
	10.69 $\pm$ 3.59	-	8.31 $\pm$ 3.11	10.95 $\pm$ 3.48		

Note: *S. littoralis* and *C. demersum* weren't found at station 2.

The variation of plant species contents may be due to the way of stored element, many plant species stored elements in their stems or at their roots. Also, the accumulation of elements in aquatic plants tissues are affected by the depth of the water column (Oudeh *et al.*, 2002).

The difference in accumulation may be due to the different accumulation mechanisms of heavy elements in the aquatic plants tissue which include: linked the toxic elements to the cells walls in the roots or stem which prevents transmission to the vegetable sap, or it is expels to non-sensitive place in the cells and storing in air vacuoles (Memon *et al.*, 2001). Cobbet (2000) pointed out that the tolerance of the plant to the high levels of elements may be due to binding these elements to peptides which containing the thiol group (-SH group) and this called phytochelatins, or through the elementlothioneins that are proteins found in the plant cell that plays an important role in the removal of toxicity by binding to the elements in the cell (Rauser, 1999).

According to Memon *et al.* (2001) phytochelatins and elementlothioneins in plants cell form complexes with heavy elements and translocate them into the air vascular. This is a mechanism of hyperaccumulation heavy elements in plants.

The studied plants were characterized by their accumulation of elements higher than their concentrations in water, but less than those in the sediments (Table 2). It is clear that the concentration of heavy elements is not necessarily related to those of the sediments. Stoltez and Greger (2002) pointed that it is not necessary to link the mineral concentration in the plants with their levels in the sediments. Thus the results disagree with these of Al-Saad *et al.* (1994) and Al-Taee (1999) who showed that the elements concentration in the tissues of the plant is higher than in the surrounding water or sediment. In the present results, the low concentration of elements within the plants tissues as compared to the sediments may be due to variation in accumulation mechanism (Marseille *et al.*, 2000).

The mean concentration of elements (Cd, Cr, Ni and Pb) in the dissolved phase were (0.06, 2.03, 0.56 and 2.97)  $\mu\text{g/l}$ , respectively (Table 2). Elements concentration in dissolved phase as follows  $\text{Pb} > \text{Cr} > \text{Ni} > \text{Cd}$ . The concentrations of the studied heavy elements as dissolved phase were below the permissible limits of drinking water according to the WHO (2011) limit, and this result was in agreement with most studies done on the marshes.

The decreasing of elements concentrations in the studied area may be due to many factors such as: the lowest level and flow rate of water in the marshes, quantities and qualitative of plankton and suspended material that load in the water, complexation with organic matter and precipitation to the sediments, accumulation of elements in aquatic plants (Harding and Whitton, 1978; Al-Khafaji *et al.*, 2012; Al-Awady *et al.*, 2015).

The last recipient of contaminants from natural and anthropogenic source in aquatic ecosystem are sediments (Hassan *et al.*, 2010). Therefore, they are good monitor for water contamination. Likewise, the elements concentration in the water as dissolved is mainly effect of recent pollution, while the accumulation of elements in the sediments that result of long term exposure (Brankovic *et al.*, 2011). The present results showed that the mean concentration of elements in the sediments were 0.65 (Cd), 99.62 (Cr), 120.81 (Ni) and 38.7 (Pb)  $\mu\text{g/g}$  dry weight, respectively (Table 2). Their concentration as the following order  $\text{Ni} > \text{Cr} > \text{Pb} > \text{Cd}$ . Finally a main portion of the heavy

elements, which enter the aquatic ecosystem settle down in the sediments, so the sediment act as archives for various contaminants such as heavy elements (Al-Khafaji, 2010). The low concentrations are in the dissolved phase than in the sediments because of the strong binding affinity of heavy elements to the sediments (Al-Hejuje, 2014).

Moreover, high level of heavy elements in sediments as compared with the concentrations in the dissolved phase because of the increasing abundance of plants at these sites, which played significant role in an increasing the heavy elements in the sediments, because plants can reduce the flow rate of water and the deposition of suspended matter, which having high level of heavy elements, to the sediments (Mashkhood, 2012).

Bioaccumulation Factor (BAF):

Bioaccumulation Factor was turned out to be important tools to identify hyperaccumulator species, because bioaccumulation factor is referred to the species efficiency to accumulate heavy elements into their tissues from the surrounding environment (Ladisalas *et al.*, 2012). Willson and Pyatt (2007) stated the plants with BAF greater than 100 have potential to act as hyperaccumulator and indicator of pollution.

Table 2. Bioaccumulation Factor (BAF) of heavy elements in the aquatic plants.

Plant Species	Metals	Metals Conc. in plant	Metals Conc. in Water and Sediment	BAF
<i>P. australis</i>	Cd	0.20	0.65 (S)	31.01
	Cr	5.27	99.62 (S)	5.29
	Ni	4.20	120.81 (S)	3.48
	Pb	6.19	38.70 (S)	15.99
<i>T. domingensis</i>	Cd	0.20	0.65 (S)	31.15
	Cr	3.96	99.62 (S)	3.97
	Ni	3.05	120.81 (S)	2.52
	Pb	5.61	38.73 (S)	14.47
<i>S. littoralis</i>	Cd	0.20	0.65 (S)	30
	Cr	4.58	99.62 (S)	4.60
	Ni	3.49	120.81 (S)	2.89
	Pb	4.31	38.73 (S)	11.13
<i>C. demersum</i>	Cd	0.51	0.06 (W)	895050
	Cr	9.73	2.03 (W)	479900
	Ni	51.44	0.56 (W)	9259230
	Pb	9.99	2.97 (W)	336850

S: elements concentration in sediments ( $\mu\text{g/g}$  dry weight ppm).

W: elements concentration in water ( $\mu\text{g/l}$  ppb).

In the present study the BAF in emergent species was calculated according to the concentration of heavy elements in the plants tissue to the sediments, while in submergent species it was calculated according to the concentration of heavy elements in plants tissues to water (Table 2).

The results of the present study showed that BAF values varied from one plant species to the other, and also from one element to the other, followed an order as mentioned below:

Cd: *C. demersum* > *T. domingensis*, *P. australis*, *S. littoralis*

Cr: *C. demersum* > *P. australis* > *S. littoralis* > *T. domingensis*

Ni: *C. demersum* > *P. australis* > *S. littoralis* > *T. domingensis*

Pb: *C. demersum* > *P. australis* > *T. domingensis* > *S. littoralis*

Generally, the BAF of *Ceratophyllum demersum* was the highest values (>100) for all the studied elements (Table 2). Therefore, *Ceratophyllum demersum* can be used as hyperaccumulator and bioindicator for heavy elements pollution, whereas the other studied species that showed low BAF values (<100) for the studied elements can't be classified as hyperaccumulators.

## Conclusions

In the present study, the concentrations of some heavy elements (Cd, Cr, Ni and Pb) in the sediments were greater than those in the water column, this indicated that the sediments acted as a sink and origin for these elements. Likewise aquatic plants under study have the ability to accumulate heavy elements higher than the concentration in the dissolved phase and that is due to the possibility of using these plants especially *Ceratophyllum demersum* as a monitor to the contamination of heavy elements in the aquatic environment.

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