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HEAVY ELEMENTS ACCUMULATION IN TOW SUBMERGED PLANTS (*NAJAS MARINA* LAND *CERATOPHYLLUM DEMARSUM*- SOUTHERN OF IRAQ)

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ABSTRACT

The content of heavy elements Copper (Cu), Zinc (Zn) and Iron (Fe) were studied in tow submerged plants species (*Najas marina* L and *Ceratophyllum demarsum*) collected seasonally for periods summer 2019 to spring 2020at two site selected along Al-Chibayish Marsh southern of Iraq to determine the ability of these species to accumulate elements from surrounding water and sediment. The result showed that the average concentration of elements in water for the Particulate phase higher than in the dissolved phase. Also, mean concentrations of particulate phase higher than their mean concentration in total sediments samples except for Fe concentration which was in sediments samples was higher than in particulate part of water. The uptake of total elements by two studied aquatic plants showed that the highest uptake of elements by the *C. demersum* spices excepted Fe which higher concentration in *N.marina*. Also, Bioconcentration factor (BCF) for different elements were calculated and according to these factor data, the order of heavy elements accumulation in two species were Fe > Zn> Cu.

KEY WORDS : Submerged plants, Heavy elements, *Najas marina*, *Ceratophyllum demarsum*, BCF, Al-Chibayish Marsh.

INTRODUCTION

Heavy elements are considered one of the significant harmful pollutants of the aquatic environment, and cause serious problems due to their high stability and unlimited periods of survival, as they can be transported to distant from their source (Das and Maiti, 2008). Also the presence of them such as Cu, Zn, Cd in water caused physical distress and be toxic for many life organisms in high concentrations (Li *et al*., 2015). These elements have accumulative effect, eventually reaching the food chain and their levels can increase through biological magnification (Jawad *et al*., 2018).

The wetland of Iraq as fresh water marshes have unique system. The biome mostly comprise many animals and plants, which inhabit this rich environment (Al-Saad *et al*., 2010; Al-Sabah and Aldhahi (2017). One of the most important central marshes in Iraq is Al-Chibayish marsh, in Nassiriya city.

Heavy elements in the mesopotamian marshlands, are introduced either in soluble or in particulate phases according to different sources including natural and anthropogenic sources (Al-Maarofi, 2013)

Upon physical conditions a limited number of heavy elements ions in water are soluble and thus bioavailable to living organisms, being either essential or non-essential. Indeed, many heavy elements (e.g. Fe, Ni, Cu, Zn, Mo and Co), are essential and play important roles in the functioning of critical enzyme systems for living organisms but become toxic when are present in excess concentrations (Broadley *et al*., 2012). Others like Pb, Cd, Ag, Cr and Hg have unknown biological function and show toxicity even at low concentrations (Al-Hejuje, 2014; Wani *et al*,. 2017).

Plants and sediments of marsh accumulate different pollutants that enter the aquatic environment through natural and anthropogenic activities (Singh *et al*. 2017). Therefor, most of the marshes have been used for their natural cleansing capacity for various contaminants such us heavy elements and pesticides (Joyce, 2012)

The accumulation issue of heavy elements in the plants tissues has received great attention by many researchers, because plants have the ability to remove heavy elements from the surrounding environment.

Various plant families have been utilized as bioindicator to study water pollution due to their diversity, wide spread and good tolerance to changing in the environmental conditions (Souza *et al*., 2013). Also, its ability to absorption and / or adsorption elements without causing toxicity or death the plant (Ashraf *et al*., 2011). Plants that can extract and accumulate heavy elements from polluted areas have several characteristics, including fast growth, dense and deep roots, easy harvesting, extraction, and accumulation a wide range of elements and their tolerance to high levels of them (Labonne *et al*., 2001). So aquatic plants play an important role in managing rivers, wetlands, marshes for protecting freshwater (UNEP, 2004).

Through active and passive absorption these plants can uptake large amounts of elements from water and/or sediments, with this elements absorption capacity, making these plants suitable for heavy elements alterations in the aquatic environment (Cai *et al*., 2018)

In addition, treatment systems with aquatic plants are low-cost technologies and can be adopted by developing countries for recycling/treatment of waste water especially that contaminated with heavy elements (Fawzy *et al*., 2012).

The tolerance and management of heavy elements with plants is based on various physiological mechanisms. The heavy elements disturbs the normal metabolism of plant, butmany factors determined the response of plant like : the tolerance level of pollutant, the inner pollutant concentration, stage development (ontogenetic), factors of climate (Al-Saadi *et al.,* 2013; Lu *et al*., 2018).

Aquatic plants play a significant role in eliminating nutrients and elements from wetlands. The most important role played by plants in the wetlands is to reduce the water flow speed, and therefore increase the deposition of contaminants and suspended materials in the sediments. So this process gives aquatic plants enough time to absorb these pollutants (Prasad, 2007).

The aim of the present study is to determine the heavy elements (Cu, Zn and Fe) concentration in water and sediments in order to detect the ability of the selected submerged aquatic plants species *Najasmarina L* and *Ceratophyllum demersum* to accumulate heavy elements and using these species as bio-indicator.

MATERIALS AND METHODS

The study area

The central marsh located between the Tigris and Euphrates rivers in Iraq, which is the heart of the ecosystem of the Mesopotamian marshes. The Al-Chibayish Marsh is one of the most famous of the Central Marshes in Thi-Qar province , especially Al-Baghdadia site, these marshes located north of the Euphrates and in the middle of the Central Marshes. Before drying these marshes in 1990, they were supplied with water from the Tigris River, and after re-immersion operations in 2003, they were provided by water from the Euphrates River (ROPME and UNEP, 2005; Hussain, 2014).

Plant species description

Najas marina L. is an annual, a spiny, submerged plants in fresh orbrackish water, it belonging to Naja daceae family, usually grows in lakes, ponds, streams and swamps. It have slender stem, much branched. Small leaves, whorls or opposite, filiform-linear, with very small flowers(Al –Mayah *et al*,. 2016).

Ceratophyllum demarsum A perennial submerged aquatic plants, rootless, it belonging to Ceratophyllaceae family, it is a green herbaceous plant with branches leaves, grows in marshes, still water, rivers and likes has the ability to spread and produce live mass even with moderate feeding conditions (Saup, 2003;Al –Mayah *et al*., 2016).

Sample collection

Water, sediments and plants samples were collected seasonally from summer 2019 to spring 2020, at two study stations (Abu Subat and Baghdadiya) at Al-Ghibayish marsh (Fig. 1), as follows: Water samples were collected from each sites under the water surface (30 cm) using polyethylene containers. Sediment samples were collected using Van veen Grap sampler and kept in plastic bags. At the same study stations, aquatic plant were collected by hand

and to remove the particulate matter, plant samples were washed several times by marsh water, after that samples were put in plastic bags until they reach the laboratory.

Heavy elements extraction

Water samples (5 l) were filtered using pre-washed (0.5N HCl) and pre-weighted Millipore filters paper (0.45 µm pore size), the filtrate was concentrated according to method of Riley and Taylor(1968), to determine the concentrations of heavy elements in the dissolved phase. While, the filter papers were digested as particulate phase.

Sediment samples were air dried for about 72 hrs. Then grounded finely by electrical mortar, passed through a sieve coarse mesh (63µm). Then taken (1g) of grounded samples, the heavy elements were extracted, as exchangeable part of the sediments.

Aquatic plant samples were air dried and grounded, then taken (1g) to extracted the heavy elements according to methods of Estefan *et al.*, (2013).

Heavy elements concentrations (Fe, Zn, Cu) in extracted water, sediment and aquatic plant samples were measured using flame atomic absorption spectrophotometer (FAAS), model A A-7000 (Shimadzu - Germany) for each element use hollow cathode lamps and stock standard solutions (1000 ppm) as needed.

The Bioconcentration factor (BCF) calculated according to the following equation.

$$B.C.F = \frac{Conc.of\ element\ in\ plant}{Conc.of\ element\ in\ water}$$

Statistical Analyses

Analysis of Variance (One –Way ANOVA) was applied by Minitab ver. 16.1 software to identify the existence of significant spatial and temporal differences.

RESULTS AND DISCUSSION

Heavy elements in water

The study showed a seasonal change in the concentrations of elements in the dissolved and particulate phases of water samples (Table 1). The results showed that the mean heavy element concentration in the dissolved phase were (24.63, 2.54, 0.63) µg/l for each of Fe, Zn and Cu, respectively. Statistical analysis showed the Cu concentrations have a significant differences ($p \leq 0.05$) among seasons, these differences due to different levels of contamination among seasons, while other elements showed no significant differences among seasons.Generally, the concentrations of studied heavy elements in the dissolved phase were below the drinking water limits according to the WHO (2011), these result was consistent with Awady *et al*.(2015) andAl-Atbee (2018) .The mean concentrations in the particulate phase were (5535.93, 836.23 and 85.35) µg/g dry

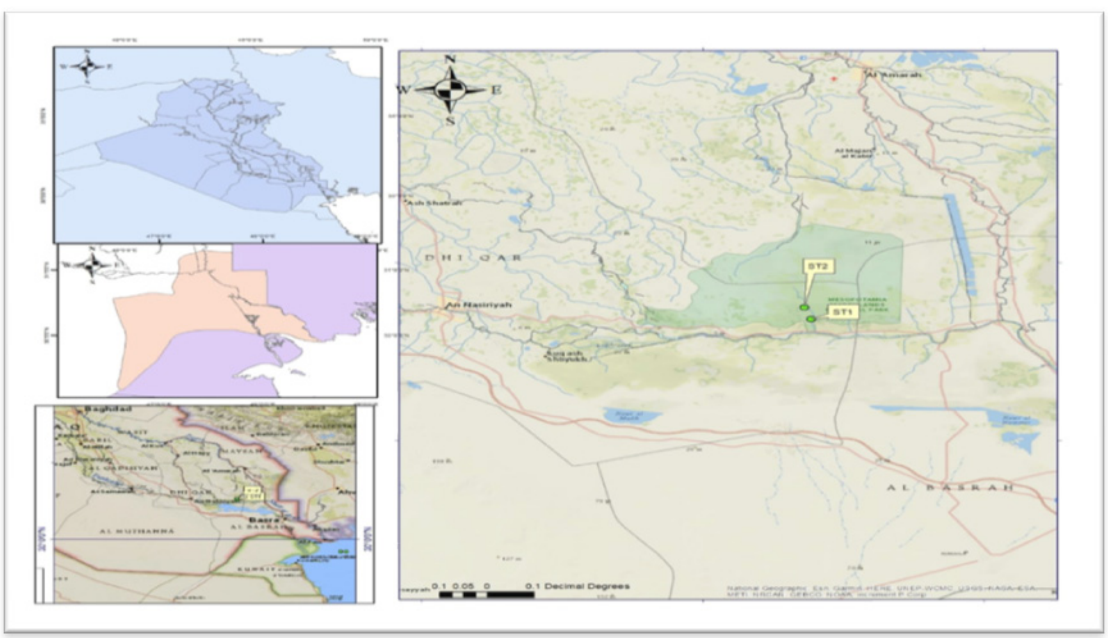

Fig. 1. Sample Locations

weight for Fe, Zn and Cuμ , respectively, their concentrations sequences as follows: Fe ˆ Zn ˆ Cu. Seasonally significant changes($p \leq 0.05$) were observed in Fe concentrations.

The resultfound that particulate phase concentration was higher than concentration of dissolved phase. It may be because the particulate substance were accumulated higher amount of heavy elements than dissolved water (Al-Hejuje, 2014), that lead to tendency of most elements to adsorption or bonding on the surfaces of suspended particulate matter which consist (living components) like microorganisms and other planktons which have the ability to concentrate elements in their tissues to higher levels than in water, or (non- living components) include organic matter, silts and clay in the water column(Habeeb *et al*.,2015).

The sediment of marshes are normally the final pathway of both natural and anthropogenic components derived to the environment(Al-Sabah and Aldhahi, 2017). In the present study the heavy elements in sediments samples were measured as exchangeable and residual phases. The mean concentrations of exchangeable phase were (2024.50, 25.59, 10.37) μg/g dry weight for each Fe, Zn and Cu, respectively, this values were found lower than residual phases concentrations, were (7762.19, 42.80, 26.41) μg/g dry weight for each Fe, Zn and Cu, respectively (Table 2). Statistical analysis showed significant differences ($p \leq 0.05$) among seasons and stations for Cu, Zn and Fe in the exchangeable phase. Also, there were significant differences among seasons ($p \leq 0.05$) for each Cu, Zn and Fe, also between stations for Cu and Fe in the residual phase of sediments. The content of heavy elements in sediments samples was seen as extensively greater than those obtained in dissolved water samples, that because of the heavy elements are not dissolved for a long time in the water, as they appear in the form of suspended colloids or are fixed by organic and mineral, and dissolved ketones for heavy elements are easy to attract and hold by clay minerals or organic compounds and then accumulate on sediments or aquatic plants (Hussain, 2014). Also, the studied stations of marshes characterized by density of aquatic plants which played an important role in increasing the heavy elements in the sediments. Aquatic plants causing decrease in the flow speed of marsh water and this leads to the remobilization of particulate matter that having heavy elements in the sediments (Al-Atbee ,2018).

Moreover, in the present study it was found the mean concentrations of particulate phase higher than their mean concentration in sediments samples except for Fe concentration which was in sediments samples higher than in particulate part of water. This mean that particulate part have a significant role to support sediment by heavy elements, also the heavy elements when enter the aquatic environment a major part of them that ultimately settle in the sediments (Grabowski *et al*. 2001).

The distribution of heavy elements in two submerged plants of Al-Chibayish marshes were showm in Table 3. The mean concentration of heavy elements in *Najas marina*were (10.07, 27.93, 1115.69) μg/g for each of Cu, Zn and Fe respectively. mIn *Ceratophyllum demersum* the mean concentration of heavy elements were (21.95, 50.06, 920.140)μg/g

Table 1. Heavy elements concentrations in dissolved (μg/l) and particulate (μg/g) phases of water at the two studied stations.

Stations	Season	Dissolved phase (μg/l)			Particulate phase (μg/g)		
		Heavy elements			Heavy elements		
		Cu	Zn	Fe	Cu	Zn	Fe
St.1	Summer	0.19	2.01	32.81	46.12	371.63	7962.16
	Autumn	1.50	1.94	4.48	119.24	167.5174	6228.25
	Winter	0.30	1.56	9.66	22.56	151.10	3695.33
	Spring	0.25	1.03	11.52	23.31	122.99	3586.70
St.2	Summer	0.34	2.62	21.71	236.13	4680.58	8620.39
	Autumn	1.77	3.95	39.56	166.34	687.227	7843.08
	Winter	0.36	5.63	58.56	25.05	161.68	2673.96
	Spring	0.29	1.60	18.72	44.01	347.15	3677.59
Mean	0.63	2.54	24.63	85.35	836.23	5535.93	
SD	0.59	1.43	16.91	75.10	1463.58	2237.03	

SD:Stander deviation

for each of Cu, Zn and Fe respectively. significant different of Cu among seasons ($p \leq .05$) were found in *Najas marina* species, Also, significant different ($p \leq 0.05$) of Zn and Fe elements among stations in *Ceratophyllum demersum.* Aquatic plants have the ability to absorb and circulate heavy elements in the food chains, although the process of interference in the transfer of elements between water, sediments and aquatic plants is not well understood. The uptake comparison of total elements by two studied aquatic plants showed that the highest uptake of elements for different concentrations was in the *C. demersum* species except Fe which has higher concentration in *N. marina*. The heavy elements concentration and accumulation in plant tissues varies depending on the different species of plant, growth form of plant (Habeeb *et al*., 2015) and between the various plant parts. Also the uptake elements by aquatic plants does not depend on the concentration of elements in the surrounding environment, but rather is regulated by physiological mechanisms of plant, which including: plant sequester and linked these elements in their cell walls and can store them in air vacuoles, to prevent them from transmission to the cytoplasm of sensitive cell where metabolic processes occur (Wani *et al*., 2017). Also Cobbet (2000) pointed out that some plants are tolerant to high elements levels because they bind to peptides and small proteins such as phytochelatins and element lothioneins which form complexes with elements and stored safely in air vacuoles.

The results showed that the heavy elements concentration in two studied plants were higher than in water for the dissolved phase and less than their concentration in the particulate phase and

Table 2. Heavy elements concentrations in exchangeable and residual phases of sediments (µg/g dry weight) at the two studied stations.

Stations	Seasons	Exchangeable phase (µg/g)			Residual phase (µg/g)			Total in sediments(µg/g)		
		Heavy elements			Heavy elements			Heavy elements		
		Cu	Zn	Fe	Cu	Zn	Fe	Cu	Zn	Fe
St.1	Summer	5.45	32.56	2309.43	22.50	31.35	7634.41	27.95	63.91	9943.84
	Autumn	11.61	21.93	1491.30	28.55	34.02	7097.50	44.50	40.53	15188.39
	Winter	6.40	16.65	769.151	22.47	53.35	5690.58	40.16	55.95	8588.79
	Spring	1.00	13.08	721.08	19.57	49.40	6425.06	53.37	74.06	13156.52
St.2	Summer	13.36	27.69	4360.88	31.14	12.84	10827.51	28.87	70.00	7041.59
	Autumn	18.88	33.89	3419.81	34.49	40.17	9736.71	48.35	103.33	7071.18
	Winter	19.60	34.85	1351.01	28.75	68.48	6302.03	20.57	62.48	7146.14
	Spring	6.62	24.03	1773.31	23.79	52.78	8383.70	30.42	76.81	10157.01
	Mean	10.37	25.59	2024.50	26.41	42.80	7762.19	36.77	68.38	9786.68
	SD	6.22	7.58	1202.21	4.77	15.92	1671.48	10.74	17.00	2828.71

SD : Stander deviation

Table 3. Heavy elements concentrations in plants tissue (µg/g dry weight) at the two studied stations.

Stations	Seasons	*Najas marina L*			*Ceratophyllum demerssum*		
		Heavy elements			Heavy elements		
		Cu	Zn	Fe	Cu	Zn	Fe
St.1	Summer	15.36	34.56	1447.15	25.84	47.84	639.91
	Autumn	10.73	22.32	1206.00	19.79	42.82	187.29
	Winter	3.24	15.52	330.45	15.12	45.94	612.39
	Spring	4.91	22.11	647.35	17.13	42.93	865.56
St.2	Summer	24.27	46.92	2540.26	32.76	60.03	1142.74
	Autumn	13.53	28.26	1433.21	23.48	52.02	1390.86
	Winter	3.49	27.83	427.89	20.08	58.69	1021.00
	Spring	5.05	25.91	893.19	21.4	50.22	1501.37
	Mean	10.07	27.93	1115.69	21.95	50.06	920.14
	SD	6.93	8.86	671.45	5.51	6.58	436.29

SD: Stander deviation

Table 4. Bioconcentration Factor (B.C.F) of heavy elements in the studied aquatic plants.

Plant species	Element	Element con. In dissolved water (μg/l ppb)	Element con. In plant (μg/g) *1000	B.C.F
Najas marina L.	Cu	0.63	10071.60	16102.19
	Zn	2.54	27928.82	10984.19
	Fe	24.63	1115687.16	45302.61
Ceratophyllumdemersum	Cu	0.63	21950.00	35093.03
	Zn	2.54	50061.25	19688.71
	Fe	24.63	920140.00	37362.39

sediments, this is consistent with the study of Hussain (2014) and Al-Atbee (2018). Most of the heavy elements are not available to the plant to absorb them freely, but rather in the form of dissolved complexes, and this depends on the surrounding environment (Stoltes and Greger, 2002).

The bioaccumulation factor was calculated for the studied elements in the tissues of plants compared to the elements in dissolved phase of water (Table 4), as this gave a clear indication of the accumulation of these elements in the tissues of aquatic plants which can be considered as biological filters to removal these elements from aquatic ecosystem.

All the studied elements took the same locations in the water in its dissolve, particulate, sediments and aquatic plants, which confirms the presence of an overlap between the system: water - sediments - aquatic plants. The higher concentrations of heavy elements of water, sediments and aquatic plants in the second station, Table (1, 2, 3) compared to the first station is due to the increase in human activities, waste of animals, oil spill from boats and fishing process by chemicals materials.

Generally, in all stages (water as dissolved or particulate , sediments as exchangeable or residual and aquatic plants) of the current study showed the highest concentration of elements were Fe. This is may be because of the pollution source (oil splits discharge from boats, sewage and the toxic chemicals that using for the process of fishing), also may be due to geology of study stations, which may contain naturally higher concentrations of this element (Al-Khafaji *et al*,. 2012; Al-Awady *et al*,. 2015)

CONCLUSION

The present work revealed the significant variation in elements contents of water, sediment and aquatic plants. High concentration of studied elements recorded in particulate phase than concentration in dissolved phase in all period of the study. The mean concentration of investigated elements in two submerged species had the following order : Fe > Zn >Cu. The result found can be used the aquatic plants under study as abioindicator to water contamination with heavy elements.

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