A comparison in accumulations of heavy metals in two species of aquatic plants in Al-Chibayish marsh south of Iraq

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Abstract:
The current study estimated the concentrations of heavy metals Zinc(Zn), Copper(Cu), Lead(Pb), Nickel(Ni) and Cadmium(Cd) in each of the dissolved and particulate phases water, sediments and in two species of plants (*Typha domingensis* and *Vallisneria spirallis*) in Al-Chibayish marsh in Thi-Qar province, southern Iraq. Samples were collected during the winter and spring of 2013 from two stations within the Al-Chibayish marshlands. Station one was exposed to various types of pollution, while the station two was not exposed to contaminated. Also the percentage of organic carbon in sediments as well as sediment texture were analyzed to identify their impact on the concentration of heavy metals. The results indicated that the mean concentration of heavy metals in all phases(water and sediment) and selected plants were highest at station one compared with station two , the results indicated that the accumulation patterns of heavy metals was greatest in the particulate phase followed by the sediment and plants respectively. Higher concentration of the studied heavy metals were observed in *Typha domingensis* more than their concentration in *Vallisneria spirallis* the range of concentration were Zn(87-131),(64-93); Cu(1.1-1.7), (0.9-1.4); Pb (0.7-4.6), (1.8-3.3); Ni (42-69), (32-66); Cd (0.7-1.8), (0.4-1.5) µg/g dry weight respectively, so it can be use this species in removing this type of pollutants from the aquatic environment. Metals accumulated by aquatic plants were mostly distributed in roots, suggesting that an exclusion strategy for metal tolerance widely exist in them. This technology involves efficient use of aquatic plants to remove detoxify or immobilize heavy metals. .

Key words: *Heavy metals, Metal accumulation, Phytoremdiation, Aquatic*

Introduction:

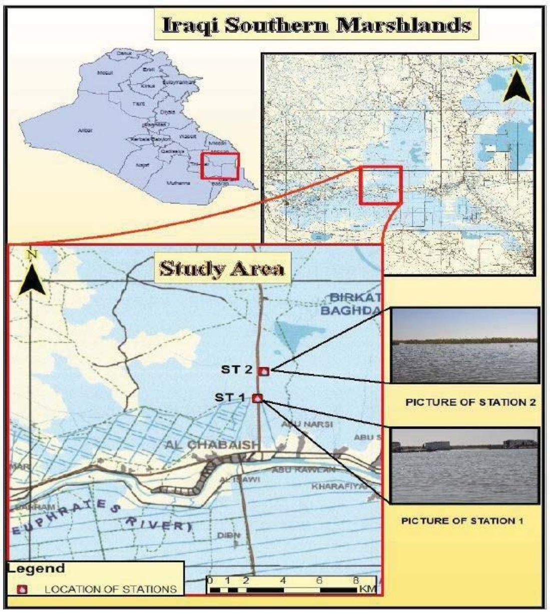
Heavy metals are the elements which have a specific gravity greater than 5 g/cm^3 (Järup 2003). Environmental pollution by heavy metals began with the use of fire. The process of releasing small amounts of metals into the air, as a result of burning wood, led to a change in the levels of metals in the environment (Nriagu 1990, 1996). A number of heavy metals and their toxic compounds are known as toxic substances, which can affect human health and living organisms. Some of these heavy metals accumulate in the water, soil and in the tissues of living organisms, and are able to persist in the environment, resulting in a range of harmful future effects (Ilyin *et al*. 2009 There are many global and local studies that have identified the close relationship between agriculture waste and an increase in heavy metals (Abychi and Doubul,1985; Singh *et al*.,1997). Many local studies have been done about the concentration and distribution of heavy metals in water, sediment and biota in inland water of Iraq among them marshs (Al-Khafaji,1996; Qzar,2009; Al-Haidary,2009; Al-Khafaji,2010). So, the aim of this study is to estimate the concentration of some heavy metals in water and sediments in the Al-Chibayish Marsh, and to determine the ability of the selected plants (*Typha domingensis* and *Vallisneria spirallis*) to accumulate this type of pollutants.

Materials and Methods:

Study area:

Al-Chibayish marsh is one of the largest marshes in the province of Thi-Qar. It is occupied the site 3100N, 47000E, which include large area, provid by water from Tigris and Euphrates rivers, this marsh comprises two sites, the first Al-Baghdadia which represented the second station (St.2). There is dense growth of aquatic plants specially *Phragmites austeralis* and *Typha domingensis* and water is available during all seasons. St.1 is exposed to contamination because many people living near by. The people are involved in many different livelihood including, buffalo breeding, fishing and boating industry.

Wastewater and animals waste are discharge into the marsh without treatment, in addition there are oil spills from fishing boats specially at St.1. Further more some people use chemical toxins in the process of fishing. St.2 is not exposed to pollution and it is far away from St.1 about 2Km, it was used as reference station for comparison of heavy metals pollution with the St.1.



Figure(1): study area within Iraqi marshlands.

Sample collection

Samples of water, sediment and a quatic plants were collected from two stations in the study area during the winter and spring of 2013. The Water was preserved in plastic bottles by the addition of few drops of nitric acid. Sediment samples were collected by using the samples collector (grab sampler) at the same stations of the study area, then preserved in plastic bags. Plant samples were collected manually then washed by marsh water for the purpose of disposal of suspended solids. After that, they were saved in plastic bags until reaching the laboratory.

Extraction of heavy metals from water

5L of water was collected from each station. Samples were filtered by using a filter glass and vacuum pump through filter papers (0.5 um pore size). The filtered water was considered as dissolved, while the retained matter was particulate. Extraction of heavy metals in the dissolved phase was performed according to the method of Riely and Taylor (1968). After filtration, the filters were dried in an oven at 60°C for 6 hours until dry, and then weighed to get the values of the total suspended matter. Sturgeon *et al*. (1982) method was used for the extraction of heavy metals from the particulate phase in water

Extraction of heavy metals from sediments

Sediments samples were digested after drying according to Yi, *et al*. (2007)

Extraction of heavy metals from plants

The a aquatic plant were drying then digested according to (Barman *et al.*,2000).

Determination of Total organic carbon (TOC%) and sediment grain size:

The TOC% content in sediment was measured according to ICARDA(1996). The sediment grain size was calculated according to a well tested method (Day, 1965).

Measuring of heavy metals

Concentrations of some heavy Metals (zinc, copper, lead, nickel and cadmium) were measured by using the flam atomic absorption spectrophotometer, model 210 VGP proved with hollow cathode lamps

Statistical analysis

This study was used to analyze the variance (ANOVA), F test, mean, standard deviation and correlation coefficient to find the significance among the stations by statistical system (SPSS-10).

Results and discussion:

Heavy metals take various chemical forms in the aquatic environment, including soluble free ions, organic or inorganic complexes, or they can be connected with solid suspended matter (clay, silt and sand, zoo and phytoplankton) (Hem 1985). These metals are affected by various factors such as temperature, pH and salinity (Al- Hjaj 1997; Mustafa 1985). In addition, heavy metals enter the aquatic environment through wastewater such as sewage (Chipasa 2003). Heavy metals in water can be distributed between the dissolved and particulate phases (Al-Khafaji, 1996).

The results of the present study found the mean heavy metal concentration in the particulate phase of the study area were Zn (550.5), Ni (110.8), Pb (13.1), Cu (11.57) and Cd (8.05) μg/g dry weight respectively. These values were higher than the mean concentrations in the dissolved phase, which were Zn (23.37), Ni (6.37), Pb (1.05), Cu (0.25) and Cd (1.37) μg/L respectively (Table 1). This was due to the particulate phase containing colloids, organic materials and metal hydroxides, which have a large surface area so it can adsorb heavy metals. Thus, the increased of concentrations for suspended matter in water due to the transfer of metals from the dissolved phase to the particulate phase (Warren & Zimmerman 1994). The results of this study agree with many previous studies (Al-Abadi 2011; Al- Awady 2012; AL-Tai 1999; Qzar 2009).

Table (1): concentration, (mean ±SD) for heavy metals in dissolved phase and particulate phase for station 1 and 2 in Al-Chibayish marsh, Iraq.

Dissolved phase (μg/l)							Particulate phase (μg/g) dry weight				
Season	stations	Heavy metals					Heavy metals				
		Zn	Cu	Pb	Ni	Cd	Zn	Cu	Pb	Ni	Cd
Winter	St.1	23.5	0.3	1.5	7.5	1	570	12	14.6	140	9.7
	St.2	15	0.1	1	4	0.5	450.9	9.7	6	58	3.5
Spring	St.1	34.8	0.4	2	8.5	2	680.9	14	22.5	173.5	12
	St.2	20.2	0.2	1	5.5	0.7	500.3	10.6	9.3	72	7
Mean		23.37	0.25	1.37	6.37	1.05	550.5	11.57	13.1	110.8	8.05
Standard deviation		7.25	0.11	0.41	1.74	0.57	86.34	1.622	6.23	47.63	3.16

he results also showed clear differences in heavy metal concentrations between stations and seasons (Table 1). Higher concentrations of these metals were found in Station 1compared with Station 2. This was due to the exposure of Station 1 to the various types of pollutants such as sewage, oil spill from boats, animal waste and chemicals used in fishing, because this station was located close to residential areas.

Statistical analysis showed significant differences between stations for Pb, Ni and Cd in the dissolved phase, and for Cu in the particulate phase. Also, there were significant differences between seasons at ($p<0.05$) for each of Cd, Zn, and Cu in the dissolved phase and Zn, Ni and Pb in the particulate phase. These differences are thus due to different levels of contamination between stations, as well as the impact of the different physical and chemical factors between the seasons. Generally, the heavy metal concentrations in the dissolved phase were below Iraqi WHO, EU and Australian standards (Table 2). Tables (3) show compare the results of current study with results of previous studies in relation to the dissolved phase.

Table (2): Comparison between heavy metals concentration in water (dissolve phase) µg/l) in Al-Chibayish marsh with some global and Iraqi standard.

Heavy metals	Present study	Iraqi standard µg/l (Barbooti *et al*.(2010)	WHO Standard µg/l (world Health Organization, 1993)	EU Standard µg/l (EU, 1998)	Australia Standard µg/l (NHMRC, 2011)
Zn	23.37	3000	3000	Not mentioned	Not mentioned
Cu	0.25	1000	2000	2000	2000
Pb	1.37	10	10	10	10
Ni	6.37	20	20	20	20
Cd	1.05	3	3	5	2

Table (3): Comparison between the mean heavy metals concentration µg/l in water in Al-Chibayish marsh with results of previous local studies.

Location	Heavy metals concentrations in dissolved phase µg/l					References
	Zn	Cu	Pb	Ni	Cd	
East Hammar marsh south of Iraq	4.57	1.52	6.04	-	0.22	(Qzar, 2009)
Al-Hammar marsh south of Iraq	2.29	0.7	0.17	2.13	0.45	(Al-Khafaji,2010)
Abu-Zariq Marsh South of Iraq	5.42	0.52	1.61	1.71	0.21	(Al-Abadi,2001)
Euphrates river in Nassyria city, south Iraq	10.03	-	22	7.21	2.22	(Farhood,2012)
Al-Chibayish marsh south of Iraq	23.37	0.25	1.37	6.37	1.05	Present study

Heavy metals in sediments

The concentration of heavy metals in sediments is affected by several factors, including human activities and some environmental factors such as temperature, salinity, the proportion of organic matter in sediments, and sediment grain size (Bentivegna *et al*. 2004), as well as plant density. In the present study sediment showed higher concentrations of heavy metals at Station 1 compared to station two (Table 4). This was due to the location of Station 1 near to residential areas, which discharged their waste directly into the marshes. These wastes increased the organic matter in the sediments, which absorbed the heavy metals. TOC% content at st.1 was more than its content at St.2 (Fig.2). This is also was proved through the results of this study where the mean concentrations of Zn (109.47) , Ni (81.25), Pb (5.1), Cd (2.32) and Cu (2.25)µg/g dry weight respectively in the sediment were more than the mean concentration of Zn (23.37), Ni (6.37), Pb (1.374), Cd (1.05) and Cu (0.25) µg/l respectively in the dissolved phase of water.
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In addition, increasing plant density in the marshes played an important role in increasing the heavy metals concentration in the sediments. Plants work to reduce the velocity of water flow and this leads to the deposition of suspended matter containing heavy metals in the sediments. This was confirmed by the result of the current study which found high concentrations of heavy metals in sediment compared with heavy metal concentrations in the dissolved phase (Table 1)

Sediment grain size also play an important role in the distribution and accumulation of heavy metals in the sediments. Small particle sizes, such as silt and clay tended to have higher concentrations of heavy metals because of the availability of a large surface area that allowed adsorption of metals on the particles surface of the (Bentivegna *et al.* 2004). This was confirmed by the results of the present study which found that the concentration of heavy metals in the sediment at Station 1 was higher than their concentrations at Station 2. This due to that Station 1contained a high level of silt (60.6%) and clay (21.2%) compared with Station 2, which contained a high amount of sand (38.2%) (Fig 3). This result was consistent with other studies findings (Al-Asadi 2009; Al-Khafaji 2010).

Table (4): Concentrations (means ±SD) of heavy metals µg/gm dry weight in the sediment in the study stations during the study period.

Heavy metals	Winter		Spring		Mean	Standard division
	Station 1	Station 2	Station 1	Station 2		
Zn	108.4	88	140	101.2	109.47	19.08
Cu	2.5	1.5	3	2	2.25	0.55
Pb	6.5	3.5	6.5	3.9	5.1	1.40
Ni	8.5	60	110	70	81.25	18.83
Cd	2.5	1	4	1.8	2.32	1.10

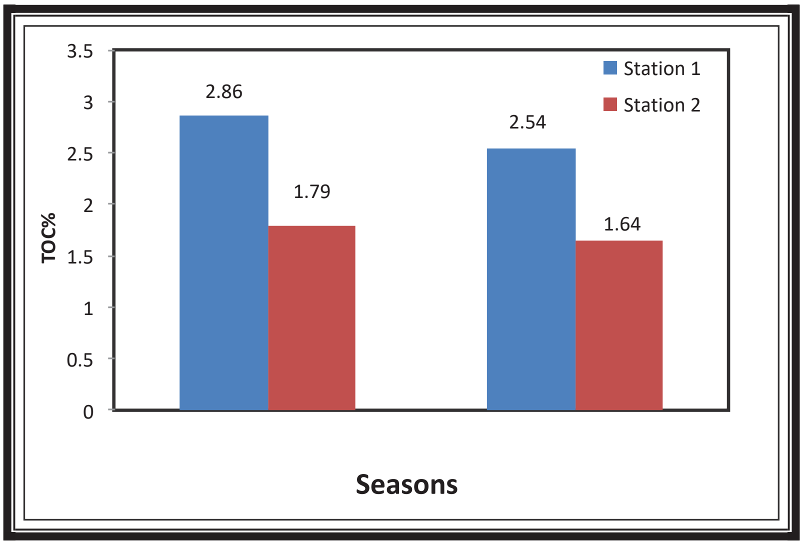
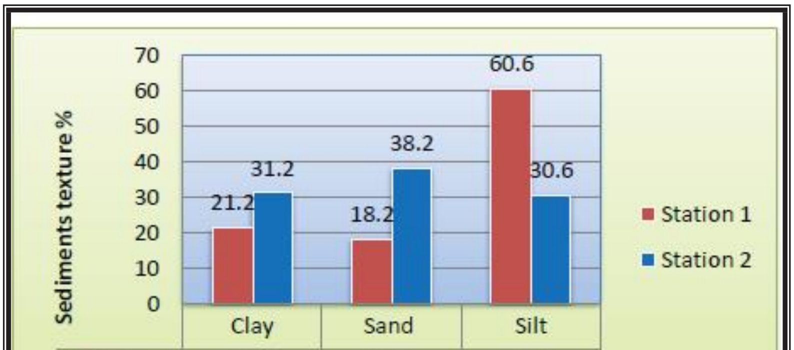


Fig.2: Total organic carbon (Toc%) content in the study stations during the study period.



	Clay	Sand	Silt
Station 1	21.2	18.2	60.6
Station 2	31.2	38.2	30.6

Fig. 3: Sediment texture% for the study.

Heavy metals in plants:

Plants have been used as a good indicator of heavy metal pollution, as they have the ability to absorb heavy metals from soils and sediments and accumulate them in their tissues (Cheng 2003). Absorption of heavy metals varies depending on the plant species (Ebrahimpour & Mushrifah 2008), and is affected by the bioavailability of the metals, the extent of their survival in the water (Fritioff & Greger 2003), the pH and the content of organic matter in the sediments (Jackson & Kalff 1993). The accumulation of heavy metals varied between the species plants and also between the plant parts (root, stem, leaves) (Bareen & Khilji 2008). The mean concentrations of heavy metals in *T. demersum* were Zn (99.75), Ni (54.5), Pb (3.72), Cd (1.35) and Cu (1.42) µg/g dry weight respectively, while the mean concentration of heavy metals in *Vallisneria spirallis* were Zn (83.5), Ni (44), Pb (2.77), Cd (0.95) and Cu (1.15) µg/g dry weight respectively . There were no clear variations in the concentrations of heavy metals between the plants studied (Table 5). This was due to the growth of these plants in the same area, making them similar in their exposure to different pollutants.

Seasonally, the concentration of heavy metals in tissues of plants during the spring was more than their concentration in the winter. This due to increased salinity and pH in spring, which works to increase deposition of suspended materials in sediments as well as increase organic carbon in sediments in spring which absorbed the heavy metals. In this case plants have a greater chance to absorb these metals from the sediments through their roots and store them in their parts. This is consistent with the research conducted by others (Farhood 2012; Salman 2006.

Table(6): Concentration (means ±SD) of heavy metals in plants μg/g dry weight in the plants at the study stations.

T. demersum (μg/g) dry wt.							*V. spirallis* (μg/g) dry wt.				
Season	stations	Heavy metals					Heavy metals				
		Zn	Cu	Pb	Ni	Cd	Zn	Cu	Pb	Ni	Cd
Winter	St.1	93	1.7	4.3	69	1.6	87	1.2	3.2	66	0.9
	St.2	88	1.1	0.7	42	0.7	93	0.9	1.8	38	1.5
Spring	St.1	131	1.5	4.6	45	1.8	90	1.4	3.3	40	1.00
	St.2	87	1.4	3.5	62	1.3	64	1.1	2.8	32	0.4
Mean±SD		99.75	1.42	3.72	54.5	1.35	83.5	1.15	2.77	44	0.95
Standard deviation		24.07	0.44	1.63	18.96	0.92	19.40	0.57	0.80	20.25	0.75

Conclusions:

The key findings for this study were that heavy metal concentrations were higher in Station 1 and these in turn were higher than at Station 2, and levels were higher in spring than in winter. In addition, the highest mean for heavy metal concentration was in the particulate phase, followed by the sediments, then the plants and was lowest in the dissolved phase.

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مقارنة تراكم المعادن الثقيلة في نوعين من النباتات المائية في هور الجبايش في جنوب العراق

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المستخلص

تقيسم الدراسة الحالية تراكيز المعادن الثقيلة (الخارصين والنحاس والرصاص والنيكل والكادميوم) في كل من الطورين الذائب والعالق للماء ، وكذلك في الرواسب ونوعين من النباتات المائية (*V. spirallis* and *T. domingensis*) في هور الجبايش خلال شتاء وربيع ٢٠١٣ جمعت من محطتين في الهور المذكور .والمحطة الاولى تتعرض الى انواع مختلفةمن التلوث في حين المحطة الثانية لاتتعرض الى ذلك كذلك تم قياس الكاربون العضوي ونسجة التربة كنسبة مئوية لمعرفة مدى تاثيرهما في تركيز المعادن قيد الدراسة .اشارة النتائج ان تركيز المعادن للماء والرواسب في جميع الاطوار وكذلك في النباتات في المحطة الاولى اعلى من تراكيزها في المحطة الثانية ، وقد كان تركيز المعادن في المادة العالقة اكثر من تركيزها في الرواسب والنباتات. ان التراكيز المرتفعة للمعادن ظهرت في نبات البردي اكثر من نبات ال *V. spirallis*

اذ كان مدى التركيز كالاتي: (٨٩-١٣١) ،(٦٤-٩٣) خارصين :
(١,١- ١,٧) ، (٠,٧- ١,٤) نحاس : (٠,٧-٤,٦) ،(١,٨- ٣,٣) رصاص: (٤٢-٦٢) ،(٣٢-٦٦) نيكل:
(٠,٧-١,٨) ، (٠,٤-١,٥) كادميوم ميكغم/غم وزن جاف على التوالي ، استنتج من الدراسه امكانية استخدام كلا النوعين من النباتات في ازالة هذ النوع من الملوثات من البيئة، و ، لذا ان استخدام هذه النباتات في الازالة تعد عملية كفوءة وواعدة.