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BIOACCUMALATION AND BIOMEGNEFICATION STUDY OF AL-CHIBAYISH MARSH PLANTS, SOUTHERN IRAQ

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Abstract

Water, sediment, and plant samples were collected from Al-Chibayish Marsh, which located in Dhi-Qar Governorate southern of Iraq to investigate the bioaccumulation and biomagnification in marsh plants (flora) and to assess the marsh plants pollution condition. The study was conducted by testing the macro elements (Mg, Ca, Na, P, N), organic compositions, microelements and heavy metals (Cd, Mo, As, Ni, Pb, Co, Li, Fe, Mn, Cu, Se, Cr, Zn) in water, sediments, and plants. Plant analyses revealed that the *Salvinia natans* plant species had the highest concentrations of macroelements Mg, Ca, Na, P, and N compared with other marsh plants and sediments. As a result, the cation binds itself to be more than one charged cationic site and this behaviour was observed in *Salvinia natans* sp. which has the highest organic composition (protein, fibre, oil, ash, carbohydrate) reaching 30% compared with marsh plants species. Due to the leaching effect, it appeared to be more involved in the dissolution of the minerals and in the binding process, since the percentage of the heavy metals (Fe, Cu, Zn, Mn, and Mo) concentrations was reached to 51%. In our results, we found that the microelements tend to be the highest percentage (68%) in the *Ceratophyllum* sp. compared to other plants Sp. and sediments. Accumulation of heavy metals was highest in *Vulgaris* (10%), and there was 5%, 9%, 4%, 4%, 5%, and 8% in *Salvinia natans*, *ceratophyllum*, *Schoenoplectus litoralis*, *Typha australis* leaves, Typha australis roots and sediments, respectively. The study also shows that the mean concentrations of microelements and heavy metals were in the order of Fe> Mn> As> Se> Pb> Cu> Zn> Mo> Ni> Cr> Cd> Li> Co. The concentrations of microelements and heavy metals in plant samples were much greater than the concentrations in water samples of Al-Chibayish Marsh (these water samples were taken from the same locations of plant samples). This is a clear indication of bioaccumulation and biomagnifications of microelements and heavy metals in plant tissues.

Keywords: Al-Chibayish Marsh, Bioaccumulation, Biomagnification, Heavy metals.

دراسة التراكم الاحيائي والتضخيم الاحيائي لنباتات هور الجبايش جنوب العراق

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الخلاصة

تم جمع عينات مختلفة من: رواسب ومياه و نبات هور الجبايش والذي يقع في محافظة ذي قار في جنوب العراق. ان الهدف هو لدراسة التراكم والتضخيم الاحيائي الحاصل في نباتات هور الجبايش وكذلك لتقييم مدى حالة تلوث النباتات. اجريت الدراسة عن طريق فحص العناصر الرئيسية **(Mg, Ca, Na, P, N)** والمكونات العضوية وكذلك العناصر الثقيلة **(Cd, Mo, As, Ni, Pb, Co, Li, Fe, Mn, Cu, Se, Cr, Zn)** في المياه والرواسب والنباتات.

نتائج التحاليل التي اجريت على النباتات كشفت ان نبات ***Salvinia natans*** كانت له اعلى قيمة بتركيز العناصر الرئيسية مقارنتا مع بقية انواع النباتات الماخوذة من الهور. وبالنتيجة الايونات الموجبة كانت تعمل على الترابط مع نفسها لتكوين ترابط ايوني موجبي الشحنة وهذا التصرف قد لوحظ بوضوح في النبات ***Salvinia natans*** والذي كان له تراكيز اعلى للمكونات العضوية من (بروتين والياف وزيوت ورماد وكاربوهيدرات) حيث وصل الى قيمة ٣٠ ٪ مقارنتا مع انواع النبات الاخرى. وبسبب تاثير الترشيح بدا ان بهذا النوع من النباتات اكثر مشاركة وتدخل في عملية التفكك والارتباط للمعادن. ايضا النتائج بينت ان النسبة المئوية لتراكيز العناصر الثقيلة من (حديد و نحاس و منغنيز و زنك و موليبيديوم) وصلت الى ٥١٪. في نتائج البحث وجدنا ان تركيز العناصر الثانوية حققت اعلى قيمة لها ٦٨٪ في نبات ***Cerataphylluim*** مقارنتا مع انواع النباتات الاخرى والرواسب. نسبة تراكم العناصر الثقيلة كانت باعلى قيمة لها وبقيمة ١٠٪ ومن ثم كانت بنسب ٥٪ و ٩٪ و ٤٪ و ٤٪ و ٥٪ و ٨٪ وعلى التوالي في عينات النباتات ***Salvinia natans*, *ceratophyllum*, *Schoenoplectus litoralis*, *Typha australis* leaves, Typha australis roots** ومن ثم الرواسب. والدراسة اوضحت ايضا ان معدل تراكيز العناصر الثانوية والثقيلة كانت بالترتيب التالي **Fe> Mn> As> Se> Pb> Cu> Zn> Mo> Ni> Cr> Cd> Li> Co** وتراكيز العناصر الثانوية والعناصر الثقيلة كانت في عينات النبات اكثر تركيزا من تراكيزها في عينات المياه لهور الجبايش(عينات المياه اخذت من نفس مواقع النمذجة للنبات). وهذا هو دليل واضح لحصول عملية التراكم والتضخيم الاحيائي للعناصر الثانوية والعناصر الثقيلة في انسجة النباتات.

Introduction

Marshes in Iraq are important for economic, social and biodiversity values characterized by frequency of water flows and quality, accumulation of nutrients and organic matter and the production of commercially important vegetation and fish. They support coastal fisheries, which endow them with a global dimension, they represent permanent habitats for many species, and they have an annual fly path followed by millions of birds follow during migration between Siberia and Africa [1]. Marshes are documented to improve water quality as they act as natural sinks for pollutants in water [2]. In the AL-Chibayish Marsh, the swamp biological system exhibits its social and environmental versatility. Subsequently, the Marsh Arab people here will have the capacity to hold conventional information frameworks and precede customary administration of the Marshes [3]. The three geographic zones of the Mesopotamian Plain incorporate Al-Hammar wetlands (AL-Chibayish Marsh is part of these wetlands); the Central Marshes; and Al-Hawizeh . Water input to this area derives from the Euphrates River originating in the Taurus Mountains of Turkey. It underpins a differing scope of widely varied vegetation and human populace of more than 5000 and 7000 people and is a noteworthy halting point for transitory winged animals. Reed (*Pharagmites communis*, *Typha augustata*) covers extensive regions of the marshes. The vegetation in the mud pads is generally *Carex* and *Juncus sp*., *Scripus brachyceras*. In the new water lakes, the sea-going vegetation commands hornwort (*Ceratophyllum demersum*), eelgrass (*Vallisneria sp*.) and pondweed (*Potamogeton lucens sp*.), and also base vegetation, for example, stonewart (*Chara sp*.). In the smaller lakes and back marshes, floating vegetation of waterlilies (*Nymphaea and Nuphar sp*.), water officer (*Pistia stratiotes*) and duckweed (*Lemna gibba*) are normal [4]. Iraq is a mainland with subtropical with sweltering dry summers and mellow wet winters [5]. The blustery season for the most part occurs from October to May followed by a dry season from June to September. The average yearly precipitation ranges from 42 to 185 mm. Within the marshland region, Al Amarah, Al Basrah and Al Nasiriyah stations demonstrate average yearly precipitation of 185.42, 152.4 and 109.22 mm individually [6].

While few previous studies have tended to the water quality and its effect on of AL-Chibayish Marsh plants one of them was Mashkhool, 2012, the study focused on some of heavy metals in water, sediments and plants of Al-Chibayish marsh. The results of this study suggested that the mean concentrations of heavy metals in water, sediments and plants were influenced by seasonal variations and by human activities. The study revealed that the concentration of metals in plants was higher than their concentration in the dissolved phase. This is a good indicator of the use of aquatic plants in the process of treatment of pollutants, and can also be used as evidence for the detection of contaminations [7]. few investigations have connected new devices to explore the exact levels and concentrations of macro elements, microelements and heavy metals in the marsh environment. Thus, the goal of the investigation is to address the levels and distributions of chemical and organic constituents in marsh environments and their effects as bioaccumulation and biomegnification processes in floras that live in AL-Chibayish Marsh. Consequently, we trust that the present investigation adds to the administration procedure, which not just meets the specialised prerequisites of the World Heritage Convention, but will likewise give new impetus to endeavor to protect nature in the Mesopotamian Marshes.

Material and Methods

Sediment, water, and plant samples were taken from three sampling stations from AL-Chibayish Marsh during the winter season (January 2017) (Figure-1). Sediment and plant samples were collected in labelled Plastic bages, while water samples collected in 2 liter polyethylene bottles then all these samples were transported to the laboratory. Plant samples were from 6 plant spacies: *Salvinia natans*, *Typha australis*, *Schoenoplectus litoralis*, *Tamarix Arabica*, *Ceratophyllum Sp*, and *Vulgaris* as shown in Figure-2 .

Plant and sediment samples were dried laboratory and prepared for chemical analysis. The concentrations of chemical constituents (Ca, Mg, K, Na, P, Ni, Pub, Cd, Mo, Se, As, Co, Cr, Li, N, Zn, Fe, MN, and Cu) and organic compositions (protein, carbohydrate), fiber, ash, oil, and humidity were determined and analysed by an Inductively Coupled Plasma Mass Spectrometry (ICP-MS) device. The chemical digestion of soil samples was completed according to Page et al.[8]. organic compositions (protein, carbohydrate), fiber, ash, oil, and humidity were determined by using IR spectrophotometry in the M-IR region (400-4000 cm^{-1}).

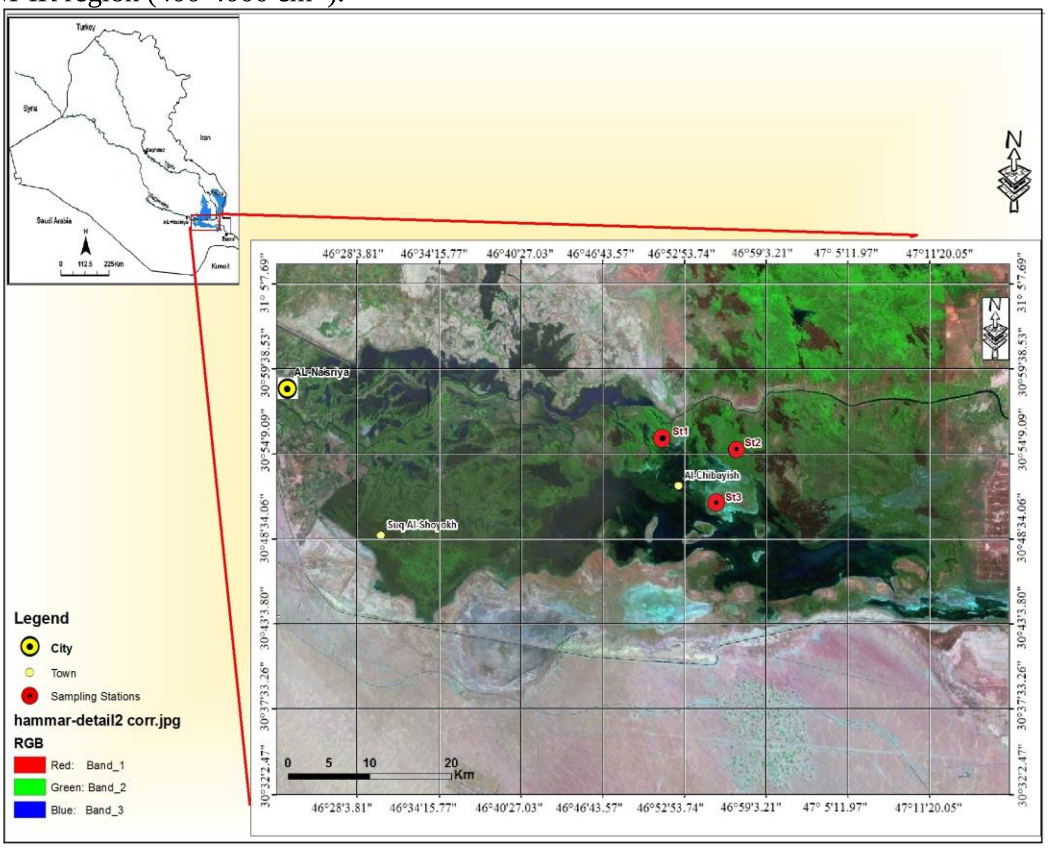


Figure 1-Map of study area with sampling stations in southern of Iraq

The recording of the Fourier-transform infrared spectroscopy (FTIR) absorption spectra were made directly by using Shimadzu IR Prestige-21 spectrophotometer with diamond horizontal ATR accessory (Horizontal Attenuated Total Reflectance) with a single reflection. The fingerprint region was identified in the range 400-1500 cm^{-1}. Micro elements and heavy metals concentrations in water sample were detected by using ICP-MS device The samples analyzed directly on the device without dilution and the result corrected for any spectral interferences.

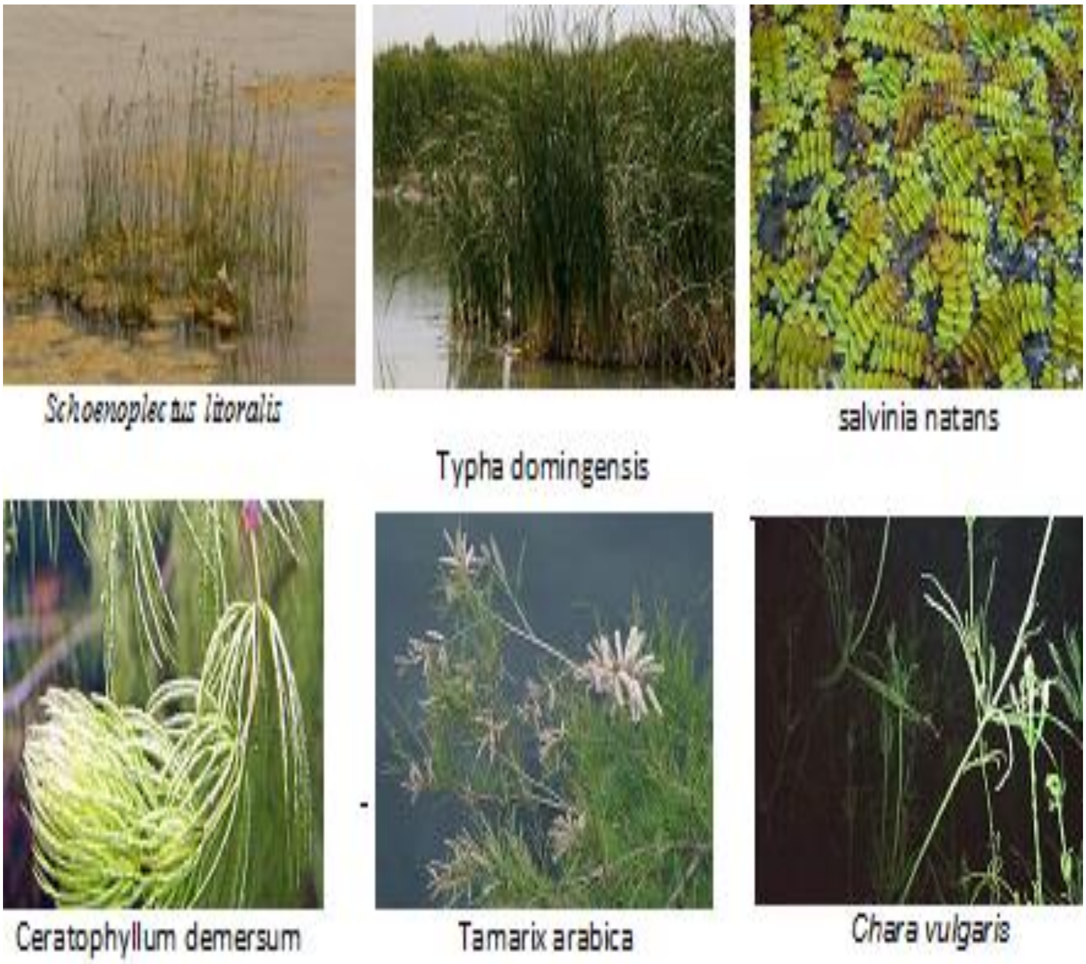


Figure 2-Digital photographs of some aquatic macrophytes collected from AL-Chibayish Marsh.

Results and Discussions

FTIR spectra analysis

The infrared and assignments for all samples are shown in Figure-3. the most intense peak was located at 3340-3392 cm^{-1} for plant and sediment spectra. These were assigned to N-H (aliphatic primary amine) and O-H (phenols, amide, amino acid). The wave number range from 2923-2983 cm^{-1} for all samples was assigned to C-H, alkane (Lipid). These two similar regions between plants and sediment may be illustrating the similarity of chemical composition of the main chains [9].

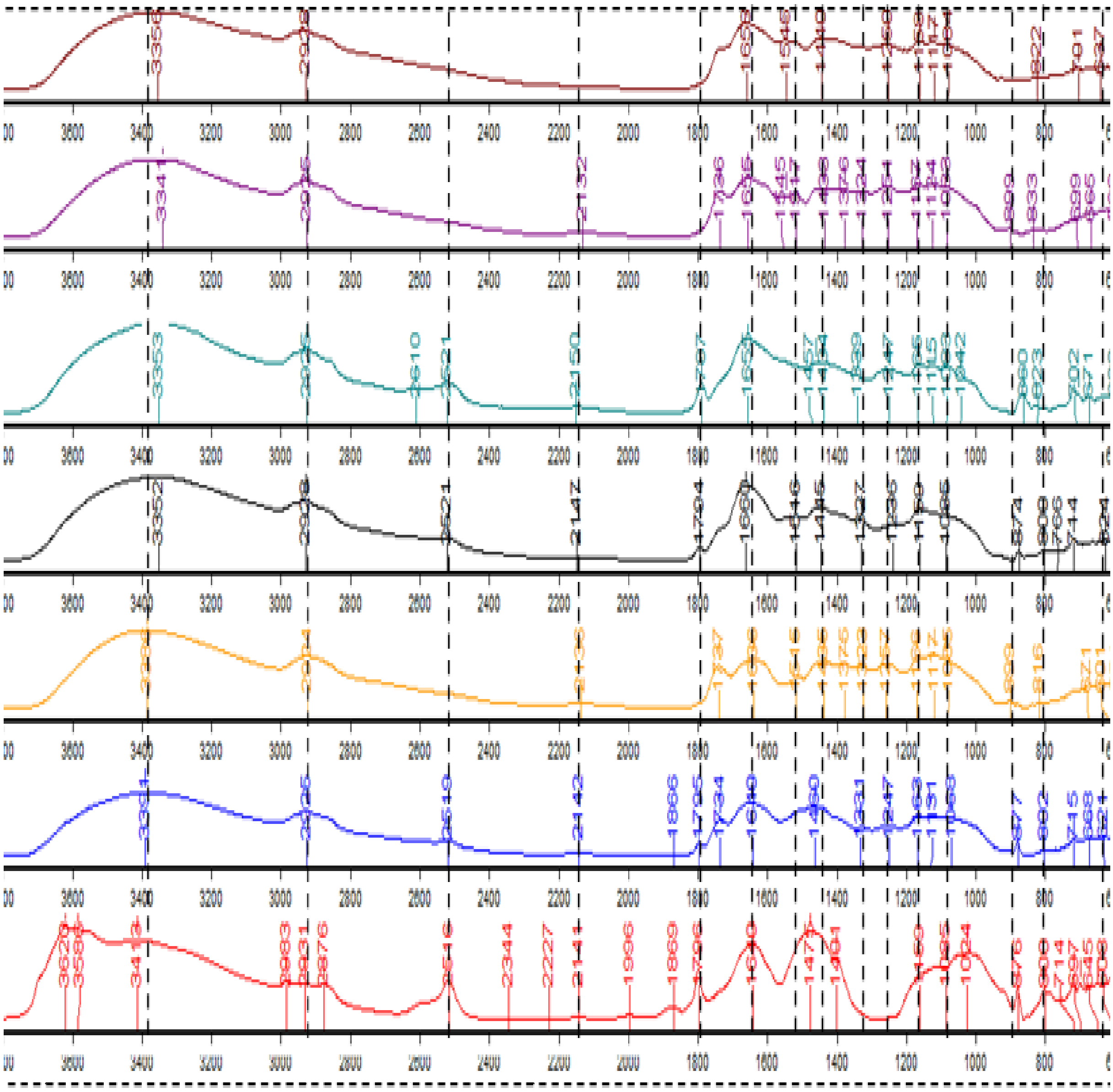
Plants and sediment have complicated absorbance peaks from 2619-2621 cm^{-1} and those assigned to C-H (aldehyde) were shown in *ceratophyllum sp.* (pink line), *Vulgaris* (sky line), *Typha australis* roots (blue line), and sediment (red line) compared with other samples like *Salvinia natans* (red wine line), *Schoenoplectus litoralis* (orange line), *Typha australis* leaves (black line). Absorbance peaks were located between 2132-2150 cm^{-1}, assigned azide (Azide, any of a class of chemical compounds containing three nitrogen atoms as a group, represented as ($-N_3$), and shown for all samples until *Salvinia natans* (red wine line).

However, absorbance peaks at 1704-1796 cm^{-1} were assigned to the functional groups of C=O and/or C=C, which because by the presence of impurities or smaller molecular weight molecules, for instance hemicelluloses [10]. Organic matter or lignin that have been shown only in the *ceratophyllum sp.* (pink line), *Vulgaris* (sky line), *Schoenoplectus litoralis* (orange line), *Typha australis* leaves (black line), *Typha australis* roots (blue line), sediment (red line), except *Salvinia natans* (red wine line). Wavenumber of 1610-1660 cm^{-1} was another obvious peak assigned by C=C (cyclic alkane). These similar regions in all samples may have behavior of protein and peptide [11]. Concerning the NO-region, the dominant signal was at around 1515-1545 cm^{-1} in all samples, which was caused by a nitro compound like amine salt. Plant and sediment have more complicated absorbance peaks from 1434-1475cm^{-1} and 1307-1339 cm^{-1}, which is caused by strong S=O and/or medium O-H bending indicating that these were intramuscular between the units and caused by sulfonyl chloride and alcohol, respectively [12].

The strong absorption band at 1247-1275 cm^{-1} show -N groups, which were attributed to aromatic amine and presence of inorganic elements (macro elements). However, the wavenumbers at the 1158-1166 cm^{-1}, 1115-1121 cm^{-1} and 1057-1085 cm^{-1} were assigned to C-O group due to high concentration of carbohydrate in all plants and sediments (*Salvinia natans* (red wine line), *ceratophyllum sp*. (pink line), *Vulgaris* (sky line), *Schoenoplectus litoralis* (orange line), *Typha australis* leaves (black line), *Typha australis* roots (blue line)). The strong bands at 860-899 cm^{-1}, 00-833 cm^{-1}, and 700-715 cm^{-1} were assigned to C=C groups, which were caused by alkene or silica, quartz mineral vibrations of kaolinite. The strong band at 624-670 cm^{-1} showed C-H groups like mono substituted benzene. Finally, the strong bonds of halo compound at 500-400 cm^{-1} were related to intramolecular bonding between halo (Cl, I, and Br).

Organic and inorganic composition

The electrical features of organic substances influence known chemical reactions. Both plants and sediment have complex organic compositions with chemical reactions (electrostatic columbic attraction, complex formation or chelating, and water bridging [6]. Figure-4 shows the cation is readily available in the sediment for transport into the plant roots or exchange with other cations on the sediment particles. The percentage of macro elements Mg, Ca, Na, P, N in *Salvinia natans* was 29%, the highest concentration of which compared with authored marsh plant (*Ceratophyllum* sp. (15%), *Vulgaris* (10%), *Schoenoplectus litoralis* (19%), *Typha australis* leaves (10%), *Typha australis* roots (9%) and sediment (8%). As a result, the cation binds itself to more than one charged cationic site. This behaviour was observed in Salvinia *natans* which have the highest organic composition (protein, fibre, oil, ash, carbohydrate) reaching 30% compared to marsh plants species 16% (*Ceratophyllum sp*.), 10% (*Vulgaris*), 20% (*Schoenoplectus litoralis*), 8% (*Typha australis* leaves), 8% (*Typha australis* roots)] and sediment (8%). Marshland plants have the easier dissolution of the cation from various mineral surfaces [13]. due to the leaching effect which appeared to be more involved in the dissolution of the minerals and in the binding process since the percentage of the heavy metal (Fe, Cu, Zn, Mn and Mo) concentrations were 51%. The leaching provides the carrier mechanism by which depleted nutrient elements are replenished at the root surface [14].



This study found that the microelements tend to be the highest percentage (68%) in the *Ceratophyllum Sp*. compared to *Vulgaris* (6%), *Schoenoplectus litoralis* (4%), *Typha australis* leaves (5%), *Typha australis* roots (9%) and sediment (12%). Accumulation of heavy metals i.e. Ni , Pb , Cd , Se , As , Co , Cr , Li was highest in *Vulgaris* (10%), and 5%, 9%, 4%, 4%, 5%, and 8% in *Salvinia natans*, *ceratophyllum sp*, *Schoenoplectus litoralis*, *Typha australis* leaves, *Typha australis* roots and sediment, respectively. The chelating of heavy toxic metallic elements present within the root marsh plant and sediment become less available for whole plant uptake [15]. The metal accumulation by aquatic plants such as *Salvinia natans*, *ceratophyllum sp.* and *Vulgaris* was more effective, which may be due to the direct uptakes of these metals via the leaves and/or roots plant from the marsh water [16].

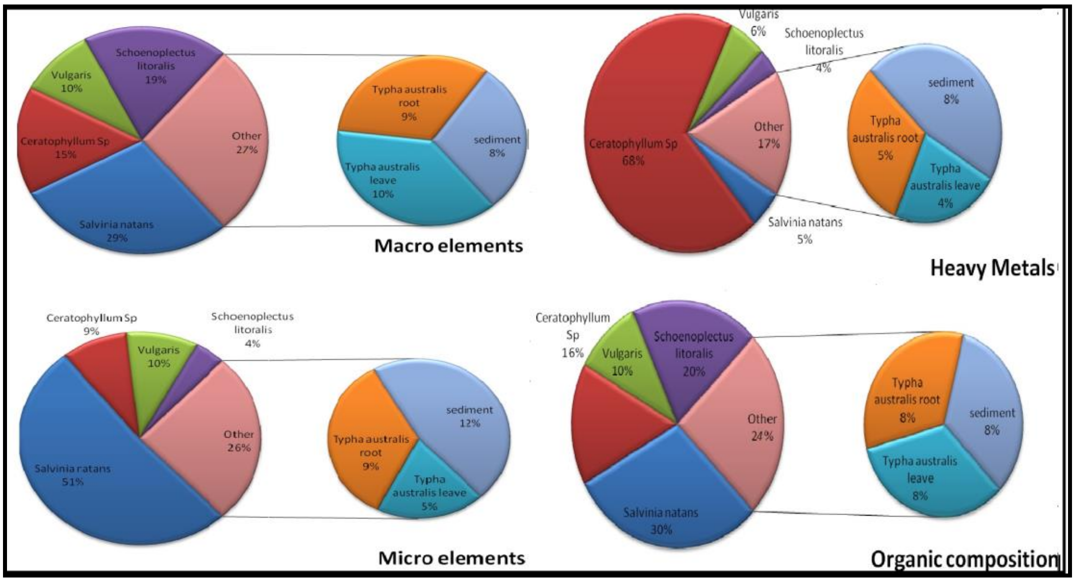


Figure 4-Comparisison of organic composition and inorganic of dried *Salvinia Natans, Ceratophyllum Sp., Vulgaris, Schoenoplectus litoralis, Tamarix Arabica, Typha australi leaves, Typha australis roots,* and sediments.

Pollution Assessment of Micro elements and Heavy metals in Plant Tissues

Investigating the content of Micro elements and Heavy metals in plant tissues can provide useful information on the status of the marsh environment. Micro elements and Heavy metals such as Cd, Mo, Se, As, Ni, Co, Cr, Li, Pb, Cu, Zn, Mn, and Fe were investigated in six plant species of *Typha australis, Salvinia Natans, Schoenoplectus litoralis, Tamarix Arabica, Ceratophyllum, Vulgaris*. Plant analyses for micro and heavy metals revealed that the mean concentration of these elements were in the order of Fe> Mn> As> Se> Pb> Cu> Zn> Mo> Ni> Cr> Cd> Li> Co (Table-1 and Figure-6). The concentrations of detected heavy metals in water sample were exceeded the Maximum contaminant level (MCL) [17,18] and WHO, Guidelines in drinking water [19] of these metals, this means the marsh water was polluted by these heavy metals. Human activities such as sewage discharge, chemicals from agricultural fertilizers and from fishing practices and oil spills from the oil industry and even from fishing boats were had a prominent role in increasing the concentration of heavy metals in marsh water and sediments. This led to the increase of heavy metals in plant tissues. Kabata-Pendias observed that there is a linear response of heavy metals absorption by several plant species in increasing their tissue concentrations from nutrient and soil solutions are illustrated in Figure-5. [20], these responses support the statement of the high accumulation of these elements in plants.

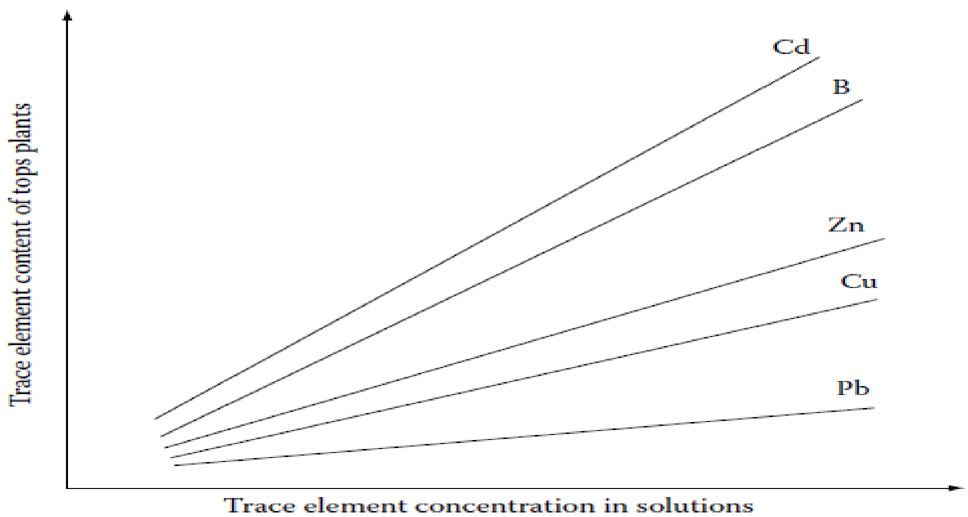


Figure 5-Trace element uptake by plants as a function of their concentrations in nutrient solutions.

The results also show that the most contaminated plant species with the trace elements was the *Ceratophyllum* species. However, we detected that this species has the highest levels of trace elements, while the most contaminated species after *Ceratophyllum* species was the *Typha Australis* species, then Vulgaris species, respectively (Fig. 5). The high concentration levels of heavy metals were found to be with As, Se, and Mo, moreover, we found in some species, that the concentration levels of these elements were greater than that of the toxic levels itself. The concentrations of microelements and heavy metals in plant samples were much higher than the concentrations of the same elements detected in water samples of AL-Chibayish Marsh (these water samples were taken from the same locations of plant samples) as shown in Table-1.

Table 1-Microelemente and heavy metal concentrations (mg/kg) in plant samples from AL-Chibayish Marsh with toxic level concentrations of these elements in plant tissues and mean concentrations in water samples of AL-Chibayish Marsh

Plant Type	Cd	Mo	Se	As	Ni	Co	Cr	Li	Pb	Zn	Cu	Fe	Mn
Salvinia natans	5.27	120.1	40.01	55	31.5	12.01	20.6	4.42	30.5	47.3	31.9	113	138
Typha australis root	8.13	28.2	85	11	48.7	8.21	43.9	14.9	63.8	44.6	41.7	778	211
Typha australis stem	4.01	11.9	29.2	39.9	9.6	5.08	17.9	2.89	23.3	19.7	22.2	86.2	64.1
Typha Australis leaves	5.48	20.8	48.5	65.5	20.6	11.5	25.2	5.67	36.9	27.9	33.9	277	240
Schoeno plectus litoralis	3.59	9.8	33.7	45.5	11.4	6.03	20.8	5.11	25.2	21.3	28.2	116	150
Tamarix Arabica	4.97	14.1	37.5	48.2	0 .16	7.66	22.4	5.29	28.1	47.2	34.5	99.2	47.9
Ceratop hyllum	70.6	21.1	73.1	105	73.6	15.4	35.2	61.8	50.1	31	48.1	281	409
Vulgaris	6.11	22.4	88.6	179	20.7	21.9	25.9	2.97	61.6	11.4	22	69.9	74.9
L.S.D 0.05	0.51	7.04	17.41	9.03	23.82	2.08	14.06	1.08	14.55	3.06	10.23	76.31	34.11
Toxic Levels	5–30	10-50	5-30	5–20	.0-100	15–50	5–30	5-50	30-300	)0-400	20-100	300-600	0–1000
Mean Conc. in Plant	13.52	31.05	54.451	3.637	30.871	0.973	26.487	2.881	39.937	31.3	32.812	227.537	166.862
Mean Conc. in Water (mg/L)	4.68	10.1	42.6	57.2	4.9	5.73	5.8	5.03	0.3	2.8	6.7	5.51	0.5
***MCL(mg/L)**	0.005	**0.07	0.05	0.01	**0.07	**0.05	0.1	0.7	0.015	5	1.3	0.3	0.05

* (MCL) Maximum contaminant level EPA, U.S. Environmental Protection Agency [17,18].
**WHO, Guidelines for drinking water quality [19].

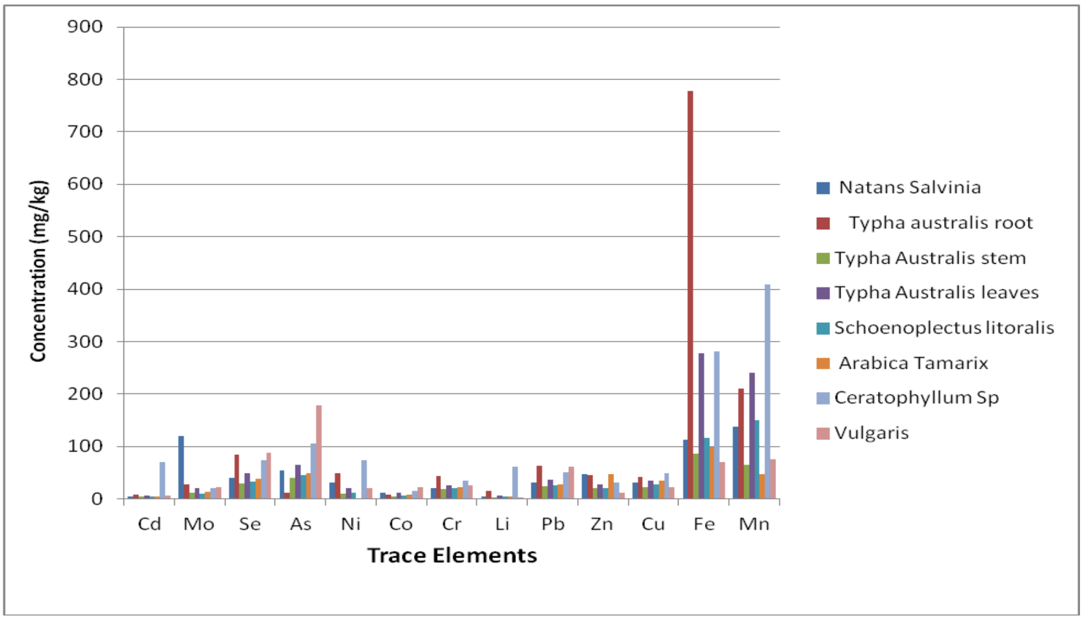


Figure 6-Microelements and heavy metals distributions in plant species of AL-Chibayish Marsh.

Conclusions

1 – AL-Chibayish Marsh plant analyses revealed that the *Salvinia natans* plant Sp. had the highest concentrations of macro elements Mg, Ca, Na, P, N compared with other marsh plants and sediments.
2 – *Salvinia natans Sp.* have the highest organic composition (protein, fibre, oil, ash, carbohydrate) reaching 30% compared to marsh plants species.
3 – Due to the leaching effect, which appeared to be more involved in the dissolution of the minerals and in the binding process, the percentage of the heavy metal (Fe, Cu, Zn, Mn and Mo) concentrations were 51%.
4 – The micro elements tend to be the highest percentage (68%) in the *Ceratophyllum Sp.* compared with other plants Sp. and sediments.
5 – Accumulation of heavy metals was highest in Vulgaris (10%), with 5%, 9%, 4%, 4%, 5%, and 8% in *Salvinia natans*, *ceratophyllum sp.*, *Schoenoplectus litoralis*, *Typha australis* leaves, *Typha australis* roots and sediments, respectively.
6 –The metals have the ability to accumulate in the tissues of aquatic organisms. In addition, the raising in metals uptake by plants was a direct response from it, because the marsh water had high concentrations of heavy metals and polluted by these metals.

All these conditions led to greater concentrations of microelements and heavy metals in plant tissues of AL-Chibayish Marsh than it concentrations that detected in water samples. That a clear indications of bioaccumulation and biomagnifications of microelements and heavy metals in plant tissues, and such an increase is a source of concern to human and animal health

Recommendations

Management regulations involving disposal, treatment, or reuse all sewerage, agricultural and oil industry wastes drainage is needed to reduce pollutants, as well as to reduce their impact as direct sources of marsh contamination. Also, long term monitoring programs can be executed through establishing water monitoring stations at selected points along Al-Hammar Marsh and its feeders. This research plays a significant role in highlighting the water pollution and the role of plants in the accumulation of heavy metals. However, further research is need. For example, future studies are required on fish in order to estimate heavy metal concentrations in their tissue, because fishes are the main food source for marshland residents. Complementary research is needed also to better understand the role of other aquatic plants in the absorption of heavy metals.

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