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ORIGINAL ARTICLE

Estimation of some Trace Metals in Water, Sediments and Two Species of Aquatic Plants in the Al-Garaf River at Al-Rafa District- Southern Iraq

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KEYWORDS

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ABSTRACT: The current study was conducted to determines the concentration of four trace metals (Cd, Pb, Cu and Fe) in water (dissolved and particulate) phase, sediment (exchangeable and residual) and two species of aquatic plants *Phragmites australis* and *Ceratophyllum demersium* in Al-Garaf river of Al-Rafa district in south of Iraq. The samples of the study were collected during the autumn and winter in 2018-2019 from three stations within Al-Rafa district. An Atomic absorption spectrophotometer was used to measure the trace metals. The results showed that the concentrations in dissolved phase were (0.20, 0.60, 0.12 and 158.11) µg/l, while their concentrations in particulate phase were (14.34, 46.73, 17.76 and 2200.74) µg g^{-1} dry weight respective. For sediment, the mean concentrations of these metals in the exchangeable and residual phase were as follows (5.08, 0.035) (17.29, 2.71) (11.87, 13.23) and (622.18, 2366.02) µg/g dry weight. Higher concentrations of the present study were observed in *Ceratophyllum demersum* more than their concentration in *Phragmites australis.* The current study concluded that the concentrations of studied metals in particulate phase were greater than their concentrations in sediment and also higher than their concentrations in the two plants.

INTRODUCTION

Water is the main source of the life it is essential for all living organism, but the most aquatic systems suffer serious ecological problems. To initiate from the increasing of population, growth of urban, industrial development and careless of the environment [1, 2]. Contamination of fresh water was a big problem in the recent decade [3]. Since, it made a harmful effect to aquatic organisms and human health [4 - 7]. The most affective causes for aquatic ecosystems contamination were the widespread use of fertilizers in agriculture and disposal of solid waste without treatment in to ecosystem [8]. Studying of heavy metals (HMs) and their effect has big attention on the last years. They introduce to the aquatic environment by naturally and human- made sources. Moreover, they have ability to accumulate to great toxic levels and influence on organisms [9, 10]. These metals release from agricultural, industrial releases, domestic remaining [11, 12], sewage sludge, burning of fossil fuels, chemical industries [13, 14]. Basically, heavy metals have the

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ability to accumulate in sediments and adsorb by plants then release into the food chain [15, 24]. The absorption can happen in low concentration in aquatic organism, plant and sediment [17].

Since, the aquatic plant accumulates HMs in their bodies, they improve the water quality so we can use it as bio-indictor for heavy metals [18, 19]. Plants exposed to high concentrations of heavy metals must respond in order to avoid the deleterious effects of heavy metal toxicity at the physiological, structural, and molecular levels [20]. Many factors can affect the process of accumulation including the degree of concentration in water and sediment, time of exposure and the type of tissue in the aquatic plant [21, 22]. *Phragmites australis well-known plant species that have great importance in aquatic systems* [23] and have a great ability to accumulate the heavy metals [24]. It has fast growth and appropriate biochemical structure, i.e. high amounts of cellulose. *Ceratophyllum demersum* is a permanent submerged, floating aquatic plant, rootless, which breeds in slow-moving waters. Firstly, it produces the bud in winter at the bottom of lake water and secondly it can make a new plant in spring. Interestingly, *C. demersum* are very useful for measuring the heavy metal pollution. Their tissue can absorb the toxic metals so they could be used to purification of aquatic ecosystems by eliminating the lower concentrations of heavy metals [25, 26].

Accordingly, the purposes of the current study were to measure the concentration status of four metals (Cd, Pb, Cu and Fe) in water, sediment and two species of aquatic plants *Phragmites austrails* and *Ceratophyllum demersium* in Al-Garaf river of Al-Rafa district, south of Iraq.

MATERIALS AND METHODS

Study areas

Al-Garaf is an old canal in Iraq that associates the Tigris river with the Euphrates river in east of Al-Nasiriya Governorate. It’s located in south east from Iraq. Basically, it extended from Tigris river and move into west south between Tigris and Euphrates rivers are located in the front of Kut city. Then, it could pass through Al-Hayy, Al-Qalea, Al-Garaf (where the current study area is a part of it) and Shatra it can be divided into two sectors, then both of them end up in wetland. Three stations were chosen in the third region of this river to implement the present study. These are station 1(St.1) the north of al raffia river (it has many fish aquarium) St.2 was at 7 km far from the first station in the center of al Raffe, while (St.3) was 5 Km at the end of al Raffe in the beginning of the new branch as shown in Figure 1.

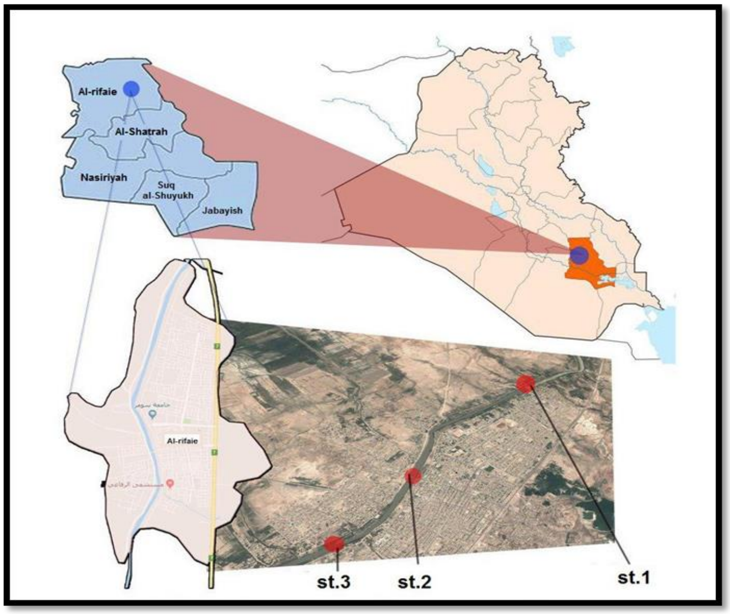

Figure 1. Map of the study area showed the study stations.

Sample's collection

Samples of water, sediments and plants were collected from Al-Garaf River during autumn and winter in 2019. Five liters of water were conserved in plastic bottles by adding few drops of nitric acid. Sediments were collected by Van Veen grab sampler then were preserved in plastic bags. The samples of plant were freeze, dried and ground with agate mortar (1g dry weight) then they were digested according to the procedure described by [27].

Trace elements measurement

Water samples were processed according to the method described by [28] while sediments were digested after drying according to [29] method. The samples of plant were freeze, dried and ground with agate mortar (1g dry weight) then digested according to the procedure described by [27], Triplicates with blanks solution were used for each sample (water, sediment and plants) in the present study.

The metal analyses of samples (Cd, Pb, Cu and Fe), were carried out by using a UNICAM-929 flame atomic absorption spectrophotometer (FAAS). The absorption wavelength and detection limits were 228.8 nm and 0.5–2.0 ppm for Cd; 217.0 nm and 5–20 ppm for Pb; 324.7 nm and 0.003 ppm for Cu, 248.3 nm and 0.005 ppm for Fe respectively, while elements concentration value was calculated from the calibration curve according to a specific method described by [28].

Statistical analysis

The data of this study was used for analyzing by using two-way ANOVA, mean, standard deviation and correlation coefficient to find out the significant differences among the stations and seasons of the study by using Duncan Test using SPSS (version.1.9).

RESULTS AND DISCUSSION

The main worry concern especially in many developed countries is the pollution of water, soils, sediments, and biotic organism due to their harmfulness, persistence and accumulative features [29].

The heavy metals content in water

The seasonal changes of heavy metal content were estimated for Al-Garaf River at Al-Rafa district-southern Iraq. Dissolved and suspended particulate phase for HMs in water were illustrated by using standard deviation. The results of the study presented that the highest concentration recorded for Fe while Cd has the lowest concentration. The concentration of HMs in water was arranged in the following order: Fe > Pb > Cu > Cd respectively. The highest value of Fe was (3197.12) µg l^{-1} in winter on (St.2). The reason for the higher concentration of iron than other elements may be due to the fact that the iron element is considered the most available element in the earth's crust.

Basically, all the concentration of heavy metal decreased in autumn more than winter. This could be happened because of increasing the ratio of water in the river beside the mount of industrial waste, and may be due to higher temperatures and increased evaporation processes, as well as an increase in organic matter in sediments as a result of an increase in the death rates of organisms in the aquatic environment due to high temperatures, lack of oxygen and increased salinity, as the increase in organic matter, which increases the concentration of heavy elements in sediments [30].

The results of the study showed that there was difference in heavy metals concentration between stations. The station 2 has more heavy metal than the other stations. This increasing happened because of high density of population, thrown the waste garbage without treatment and the effluents of municipal and industrial waste contain trace metals among their constituent [31] near this station. The value of heavy metal in particulate phase was highest comparing with dissolved phase for all metals (Table 1). The cause of this decrease resulting from adsorbing HMs on complexes compound with organic matter [32, 33] or increase the concentration of HMs in aquatic organism [34]. Plants can be playing a main role in reducing the HMs by reducing the speed of water flow and increase this leads to the deposition of suspended matter in the sediments.

Many factors that can affect the amount of pollution of heavy metal including the physical environmental factors and sediment grain size [35], the mount of organic matter and the plant. Furthermore, the main factor of heavy metal pollution is the mount of an industrial waste that thrown to the river especially in (St.2).

HMs concentration was high in the particulate phase resulting from the movement of water and the suspended solids loss the ability of deposition [36].

Table 1. Seasonal average values, ± standard deviation of four trace metals in the dissolved phase (µg/l) and particulate phase (µg/g) of water from Al-Garaf river.

Season	Station	Cd		Pb		Fe		Cu	
		Dis. ±SD	Part. ±SD	Dis. ±SD	Part. ±SD	Dis. ±SD	Part. ±SD	Dis. ±SD	Part. ±SD
Autumn	1	0.03± 0.01	14.34±2.50	0.48± 0.11	29.02±1.01	120.39±25.31	1004.00±39.10	0.08±0.005	17.76±3.65
	2	0.9± 0.02	27.06±3.04	0.70± 0.08	68.82±0.61	190.20±19.01	3195.12±499.72	0.14±0.04	27.07±.3.09
	3	0.06± 0.03	14. 09± 1.09	0.60± 0.07	39.20±4.90	160.61±30.01	2399.70±866.12	0.11±00.03	24.02±2.90
Winter	1	0.05± 0.01	12.66± 0.002	0.50± 0.13	31.02±1.01	122.40±24.7	1006.50±30.16	0.11±0.02	19.50± 4.01
	2	0.11± 0.05	29.31± 2.30	0.72± 0.10	70.94±0.65	192.98±25.00	3197.12±559.26	0.16±00.03	29.01±2.03
	3	0.07± 0.01	15.50± 3.01	0.62± 0.46	41.42±3.96	162.10±18.70	2401.98±997.40	0.12±00.02	26.24±1.69

Dis.:-dissolved phase; Part.:-particulate phase; St.:- station

The heavy metals content in sediment

Sediments play important role in the ecosystem by performing as tank or sink for pollutants and metals in the water. HMs entered into aquatic environment are commonly connected with particulate matter and joined with sediments [37].

The present study measured the concentration of HMs in sediment by using (µg g^{-1}) dry weight Table 2. The results revealed that the highest concentration of heavy metals was Fe while Cd has the lowest concentration. Our results shown that residual phase has more heavy metal than in exchangeable phase. Principally, increasing of organic matter content and particle size decreasing would increase the HMs concentration [38]. It's well-known, that the polluted sediment can affect the biodiversity of the ecosystem and hurt the aquatic environment's food chain. Therefore, the evaluating of contamination levels in sediments can be use as biomarkers for water pollution [36]. In the present study, (St.2). has highest value of heavy metals concentration because this station located near high population area and the river near this station has less mount of aquatic plants (the root and other tissue of plant could take the pollutants [40]. Moreover, physical factors including the pH, nutrients concentration and organic matter could affect the concentration of metals in these stations [41].

The result of this study revealed that the contamination level of heavy metals in sediment was higher than water concentrations of metals this happened due to anthropogenic activities in the river, and this result agree with study of [12] which certain That concentrations of heavy metals in sediments were found to be considerably higher than those obtained in reservoir water

Table 2. Seasonal average values, ± standard deviation of four trace metals in the exchangeable and residual phase (µg/g) of sediment from Al-Garaf River.

Season	st.	Cd		pb		Fe		Cu	
		Ex. ±SD	Res. ±SD	Ex. ±SD	Res. ±SD	Ex. ±SD	Res. ±SD	Ex. ±SD	Res. ±SD
Autumn	1	2.19±0.52	00.07±0.008	30.10±15.01	2.30±0.04	403.22±210.00	1394.02±205.03	5.00±1.40	9.22±4.03
	2	7.90±2.01	0.11±0.07	34.31±9.00	3.54±0.07	535.01±218.02	1743.03±81.80	17.17±2.33	10.99±2.90
	3	5.30±0.55	0.10±0.007	32.10±15.10	3.32±014	504.10±220.10	1615.10±120.05	13.01±2.00	7.90±3.01
Winter	1	3.92±0.21	0.08±0.003	05±0.08	0.07± 0.02	720.41±178.02	2543.11±167.30	10.40±0.83	12.15±2.30
	2	6.16±0.75	0.06±0.003	3.69±0.18	0.10± 0.03	811.10±89.2	3681.74±98.01	14.5±2.10	21.74±3.10
	3	4.98±0.39	0.07±0.0002	3.12±0.01	0.9± 0.03	759.23±209.13	3219.14±190.11	11.15±1.40	17.41±4.00

Ex.: - Exchangeable phase;Res.:- Residual phase; St.:-station

The heavy metals content in plants

Aquatic macrophytes represent a diverse group of plants with an immense potential for removal of variety of contaminants, including heavy metals, inorganic/organic pollutants, radioactive wastes, and explosives [42].

Aquatic plant recognized as bio-indicator for pollution especially for heavy metal pollution so they have an essential role in their environment. They have the capacity to change the concentration of heavy metal by absorbing and accumulating them in their tissues [43, 44]. Several causes that might influence the absorption of HMs such as the bioavailability of the metals [45], pH, plant species [46], and sediments with their organic matters amount [47].

The current study discovered that there were differences in the heavy element's concentrations between the both plants *P. austeralis*and *C. demerssum*in (St.2). than the other stations. This was due to (St.2). had exposure to pollutants such as sewage, oil spilt from boats and chemicals used for fishing, while (St.1).and (St.3). was less polluted. More ever, (St.2). has different type and diversity of aquatic plant in the river.

Interestingly, the results of this study exposed that there were differences in the concentrations of heavy metals in stations, seasons and selected plants.

The result (Table 3) indicated that *Phagmites* has lower concentration of heavy metals than *Ceratophyllum* the highest mean was 170.13µg/g for Fe in autumn while the lowest mean was 0.38 for pb in autumn. Interestingly, the (St.2). has higher concentration of heavy metals because it was exposed to many pollutants resulting from the increasing of population including, mining, use of agricultural pesticides and fertilizers, urban waste, traffic discharges, and industrial sewages [48]. The present study revealed that *Ceratophyllum ha*s more capacity to absorb heavy metal more than *Phagmite*s because it has large surface area and it is available through the year. Therefore, this plant is highly recommended for bio-monitoring studies. The previous study showed the ability of *C. demersum* to remove heavy metals compared with other aquatic plants and remove lead element [48]. The role of aquatic plant as a bio- indictor was taken of many studied [35]; they studied the accumulation efficiency of *Ceratophyllum* and *Phragmites australis.* While [49] indicated that the aquatic plant aquatic plants (*Ipomoea aquaticahave*) the ability to accumulate the HMs more than sediments. The ability of accumulation HMs in aquatic plant tissue related to the species and organs type [50] the aquatic macrophytes can alter the concentration of heavy metal from environments and reduce their influence [34].

While [51] were found that three emergent aquatic plants; *Veronica anagallis-aquatica*, *Cyperus iria*, and *Mentha longifolia* and one free-floating Nasturtium officinale All species were able to withstand unsuitable conditions, as shown by the 100% survival rate. The percentage Pb and Zn removal rate under the synergetic condition of the consortium attained 92% and 97%, respectively.

And this results agree with study of [19] which investigated the concentrations of some heavy metals in *Potamogeton malaianus*, *Nymphoides peltata*, *Eichhornia crassipes*, and *Hydrilla verticillata* to evaluate their potential to bioaccumulate heavy metals in Taihu Lake and These findings contribute to the application of submerged aquatic plants to heavy metal removal from moderately contaminated lakes ,also acceptable with study of [52] which certain that *P. australis* showed a direct response to the environmental conditions, and its application as a biomonitoring should be considered. The study of [53]; Showed that the plant *Plantago major* can be used as a bioindicator and biomonitor for traffic related heavy metals.

Table 3. Concentration of heavy metals in the plants µg/g dry weight at the studied stations.

		***C.demerssum*. Mean±SD**				***P.austeralis* Mean±SD**			
		Heavy metals				**Heavy metals**			
Season	**st.**	**Cd ±SD**	**Pb ±SD**	**Fe ±SD**	**Cu ±SD**	**Cd ±SD**	**Pb ±SD**	**Fe ±SD**	**Cu ±SD**
Autumn	1	0.94±0.12	0.95±0.09	86.02±8.01	0.98±0.07	0.82±0.05	0.83±0.09	80.92±5.01	0.90±0.03
	2	3.01±0.82	3.23±0.95	189.55±27.03	3.78±0.95	2.8±0.82	3.60±0.96	170.13±15.60	3.60±0.96
	3	2.55±0.75	2.79±0.65	131.03.05±17.05	2.99±0.10	2.29±0.36	2.78±0.66	170.01±17.17	2.86±0.85
Winter	1	0.59±0.08	0.43±0.4	70.02±3.10	0.53±0.04	0.51±0.03	0.19±0.02	61.04±1.19	0.31±0.09
	2	01.78±0.01	1.25±0.04	159.02±4.00	1.98±0.3	0.85±0.02	0.99±0.01	140.20±2.02	1.69±0.04
	3	0.99±0.02	1.00±0.05	145.01±3.90	1.01±0.3	0.79±0.03	0.97±0.05	132.02±6.06	0.99±0.05

CONCLUSIONS

The heavy metal is the important source of contamination for fresh water ecosystem .it released from many sources such as discharges of industrial and domestic sewage. Also, caused imbalance of the ecosystem. The study was conducted to measure the concentration of four heavy metal (Fe, Mn, Cd and Pb) in water, sediment and two species of aquatic plant (*Phragmites australis* and *Ceratophyllum demersium*). We can conclude that the concentrations of studied metals in particulate phase were higher than their concentration in dissolved phase, sediments and were higher than their concentrations in the two plants, also it exposed to different concentrations of heavy metals in stations, seasons and selected plants. The present study revealed that *Ceratophyllum* has more capacity to absorb heavy metal more than Phragmites. Therefore, this. supports the possibility of using this plant as bioindicator or a good evidence of contamination by this type of pollutant in the aquatic environment.

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Conflict of interests

No conflict.

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