

Concentration and accumulation of some trace elements in water, sediment and two species of aquatic plants collected from the Main outfall drain, near the center of Al-Nassiriyia city/ Iraq

تركيز وتراكم بعض العناصر النزرة في الماء والرواسب ونوعين من النباتات المائية المستجمعة من المصب العام قرب مركز مدينة الناصرية/ العراق

Basim Y. Al-khafaji

Afraha A. Maktoof Al-Awady

Science College/ Thi-Qar University

أفراح عبد مكطوف العوادي

باسم يوسف الخفاجي

كلية العلوم/ جامعة ذي قار

Abstract:

Concentration and accumulation of seven trace elements (Cd, Cu, Pb, Ni, Fe, Mn and Zn) were measured in water (dissolved and particulate) phase, sediment and two species of aquatic plants *phragmits australis* and *Ceratophyllum demerssum* collected during summer season, 2012 from the main outfall drain, some environmental parameter (Temperature, dissolved oxygen, salinity, pH) of water were measured, also total organic carbon TOC%, sediment texture were measured and expressed as percentage. Higher concentration of elements under study were observed in sediment more than their concentrations in water and plants, while particulate phase of water concentrated trace elements more than their concentration in dissolved phase, whereas the accumulation of trace elements in plants, showed that their concentration in *phragmits australis* was more than their concentration in *Ceratophyllum demerssum*. The study observed that it can use the two species of plants as bioindicator for accumulation of trace elements also the concentration of TE in the study samples were in acceptable range, when it compared with world wide range. The study showed that the possibility of using both plants to remove this type of pollutant from the aquatic environment and can be used in bioremediation for processes.

Key words: trace elements, aquatic plants, sediment

المستخلص

تم قياس تركيز وتراكم سبع من العناصر النزرة (الكاديوم ، النحاس ، الرصاص ، النيكل ، الحديد ، المنغنيز والخاصين) في الماء بجزئية الذائب والعالق والرواسب ونوعين من النباتات المائية القصب *pharagmits australis* والخويصة *Ceratophyllum demerssum* جمعت خلال فصل الصيف 2012 من المصب العام قرب مركز مدينة الناصرية ، تم قياس بعض الخصائص الفيزيائية والكيميائية درجة الحرارة (الماء والهواء) ، الأوكسجين المذاب ، الملوحة والذالة الحامضية للماء فضلا عن قياس كمية الكربون العضوي الكلي ونسبة الرواسب وعبر عنها كنسب مئوية . أظهرت الدراسة أن تركيز العناصر في الرواسب أعلى مما هو عليه في الماء (الجزء الذائب) ، أما تراكمها في الجزء العالق من الماء أعلى مما هو عليه في جزءه الذائب ، في حين سجل تراكمها في نبات الخويصة أعلى مما هو عليه في نبات البردي . لوحظ من الدراسة بالإمكان استخدام هذا النوعين من النباتات كدليل حيوي لتراكم العناصر النزرة ، وكذلك كانت تراكيز العناصر النزرة في عينات الدراسة ضمن الحدود المقبولة مقارنة بالحدود العالمية . بينت الدراسة إمكانية استخدام كلا النباتين في إزالة هذا النوع من الملوثات في البيئة المائية وبذلك يمكن استخدامها في المعالجة الحيوية لهذا الغرض .

الكلمات المفتاحية: العناصر النزرة، النباتات المائية، الرواسب

Introduction:

The pollution of water course with non biodegradation pollutants such as trace elements, chlorinated hydrocarbons and oil, is a serious problem [1]. Environmental pollution is a problem with high urgency in modern society out of the various kinds of pollution, the high contamination of aquatic system with toxic trace elements is one of a major concern since, these elements aren't biodegradable and their elevated uptake by crops may also affected food quality system mainly through nature input such as weathering and erosion of rocks and anthropogenic sources including urban, industrial and agricultural activities, terrestrial runoff and sewage disposal [2]. Trace elements discharge into aquatic system may be immobilized within the stream sediment by main processes such as adsorption and co-precipitation therefore, sediments in aquatic environmental serve as a pool that can retain metals or release metals to the water column by various processes of remobilization [3]. High levels of Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb and Zn were reported [4] in fish and submerging plants of the Ganges river and in water, sediment,

plant and fish of the Yamma river, India. studied trace elements in aquatic plant tissues [5], they found that *Potamogeton pectinatus* accumulated trace elements more than those of *G. densa* therefore, all plants can be used as biological indicators while determining environmental stress, however *Phragmites australis* has provide more appropriate [6] as well as [7] study the concentrations of trace elements in aquatic plants and sediment of the southern marsh. Despite the different matrices, sediments have been more analyzed because they present a clear indication of metal inputs and accumulation in aquatic environments [8]. Although the plants are considered an essential part of the food web in the region [9]. The development of the industry and expansion of the using of chemical compounds in different branches of industry leading to the environmental spread of trace elements and the increasing pollution with many trace elements in the southern river of Iraq has been the subject of considerable interest [10, 11, 12].

The aim of this study is to investigate trace elements (Cd, Cu, Ni, Pb, Mn, Fe and Zn) concentration and distribution in water, sediment and plants from main outfall Drain River and to assess the contamination status using various elements assessment indices, also to know the potential of using the plants under the study in phytoremediation in future.

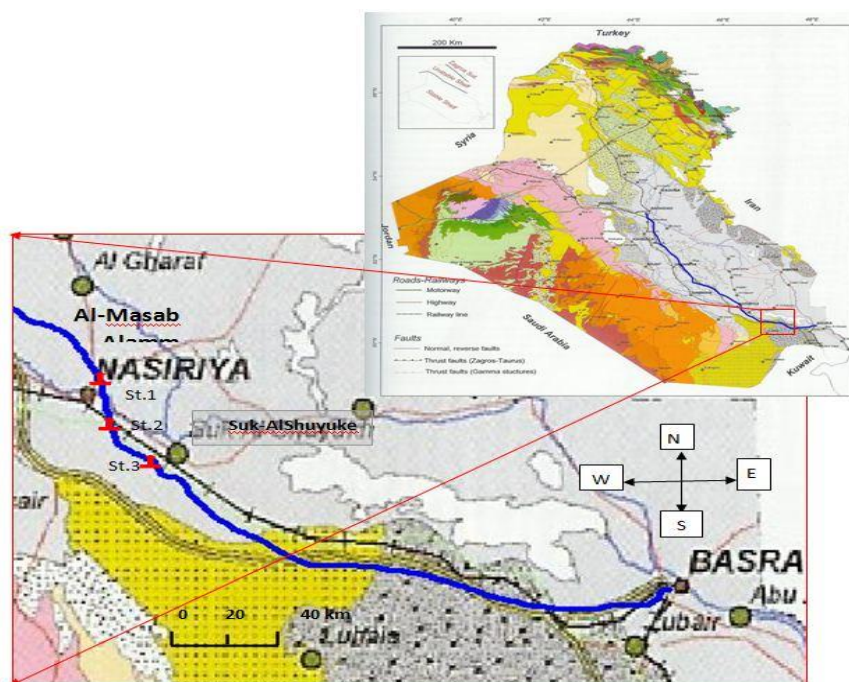
In this work the concentrations of Cd, Cu, Ni, Pb, Mn, Fe and Zn were determined in water, sediment and two of plants species *Ceratophyllum demersum* and *Phragmites australis* collected from main outfall Drain River.

Materials and methods

The Study area description

Main outfall drain is a river used to discharge the effluents of agriculture activities from its both sides. It is extended from Al-Shaklawiya near Baghdad from the north until Al-uttil Basrah at the south with length about 565 km [13]. It is dividing into three sectors (North, Middle and South), the south sector (which the present study area is a part of it) extended from the end of the mid sector until Shatt Al-Basrah in the south, with length about 165 km. The discharge of water is about 220m³/sec in its sector was used to sector [14]. New branch was opened in this sector with length 7 km, transform the water to southern marshes of Al-Nassiriya city.

Three stations were selected in the south sector of this river to implement, the present study, these are station 1 (St.1) was near Al-Holandee bridge and the general carriage in the center of Al-Nassiriya city, St.2 was 20 km far from the first station, while St.3 was in the beginning of the new branch as shown in Fig.(1).



Fig(1): Map of the study area showed the study stations.

Samples collection

Samples of water, sediment and plants were collected from MOD river during summer (May, June, July, August and September) 2012. 5 liters of water were taken from each station were collected by using polyethylene bottles with capacity 5L. The sediment samples were collected by using van veen grab sampler, and plants were collected from the same area, then placed in plastic bags and all samples (water, sediment and plants) preserved in a cooling box until reaching the laboratory. Also air and water temperature (°c), pH, dissolved oxygen (Do) mg/L and water electrical conductivity (EC $\mu\text{s}/\text{cm}$) were measured in the field by using Cyberscan 600 water proof portable meter, made in Singapore. The salinity was calculated according to the following equation.

$$\text{Salinity}\text{‰} = \text{EC } (\mu\text{s}/\text{cm}) * 0.64 / 1000.$$

Salinity values expressed as part per thousands (ppt).

Procedure

Trace elements measurement

Water samples were digested according to the method described by [15], while sediment was digested after drying according to [16] method. The samples of plant were freeze dried and ground with agate mortar (1g dry weight) then digested according to the procedure described by [17]. Triplicates with blanks solution were used for each sample (water, sediment and plants) in the present study. The levels of (Cd, Cu, Ni, Pb, Mn, Fe and Zn) in extractions were determined by air-acetylene flame atomic absorption spectrophotometers Shimadzu- 630-12 using different cathode lamps with air acetylene flame method, while elements concentration value were calculated from the calibration curve according to a specific method [18].

Total organic carbon TOC% content in the sediment was estimated by using a procedure described by [19], while sediment particles size analysis was analyzed mechanically by using a hydrometer and the percentage of different sediment particles (sand, silt and clay) were calculated according to the method of [20,21].

Results and Discussion

Table(1) shows the values of physical and chemical factors in the study area. The values of air temperature ranged from 31.32°C at st.1 in September to 39.6°C at st.3 in August, whilst water temperature values ranged from 21.86°C at st.1 in September to 32.00°C at st.3 in August. Temperature is an important factor, which regulates the biogeochemical activities in the aquatic environment [22].

The present study data showed that water temperature was affected by changes in air temperature that was due to the shallowness and small surface area in comparison with volume [23].

There are differences in the temperature among the station over the day and that come from the different time of sampling taking. These are agree with the [24, 25, 12]. The water salinity values for all stations varied between (4.01- 8.96) ‰.

The highest levels of salinity (8.95) ‰ were recorded in August at station 1, while the lowest level (4.01) ‰ was recorded in June at station 3. The higher values of salinity was observed in the study for the MOD because this river used as drainage water supply and this due to the levels of salinity were increased during the summer months, that was caused by increasing of the evaporation rate and low water level [26].

Hydrogen ion concentration (pH) showed slight fluctuations in water during the study period the pH was alkaline level, it has being know that Iraq water mainly tend to be alkaline, this agree with obtained by [27, 28]. The daily differences in pH values were because of removing carbon dioxide from bicarbonate by photosynthesis process during hours [29] or in water with high plant concentration. pH played an important role in solubility and hence trace elements mobilize in the water column. The low pH value lead to an increased concentration of metals in the dissolved phase [30]. Dissolved oxygen play an important role in aquatic environment. Some physical and biological factors affected the bioavailability of DO in water. These include temperature, salinity and amount of organic matter [31]. Oxidative consumption was confirmed by the result of this study when the lowest value of Do at st.1, the water here was affected by the input of easily biodegradable human and animal waste. Rising temperature lead to an increased metabolic activity for microorganisms and this lead to increase Do

consumption through the respiration [25], The values of Do in this study were consistent with the [1, 25, 32] studies.

Table(1): Mean values of some environment factors in the study area during the study period.

Months	Stations	Air Temp.°c	Water emp.°c	Salinity ‰	pH	Do (mg/l)
May	1	34.55	26.30	6.00	8.45	7.50
	2	35.24	27.20	4.99	7.65	7.65
	3	36.42	27.70	4.25	7.44	7.85
June	1	34.96	26.76	7.01	8.35	6.9
	2	35.60	27.55	5.00	7.55	6.85
	3	37.10	28.35	4.01	7.35	6.90
July	1	37.22	30.60	7.10	8.50	6.4
	2	38.30	31.22	5.13	7.84	6.6
	3	39.05	31.10	4.30	7.65	6.8
August	1	37.50	30.80	8.96	8.65	6.07
	2	38.23	31.86	8.03	7.92	6.20
	3	39.6	32.00	7.96	7.80	6.15
September	1	31.32	21.86	6.2	8.45	7.79
	2	32.00	22.88	5.30	7.85	7.82
	3	33.08	23.00	5.05	7.65	7.89

Trace elements in water

The result of analysis for Cd, Cu, Ni, Pb, Mn, Fe and Zn in water (dissolved and particulate) clarify in Table(2).

Table(2): Concentrations (Mean ±SD) of trace elements in water (dissolved µg/l and particulate µg/g dry weight) phases in the study station.

Metals	Station 1		Station 2		Station 3		Mean concentration in the region	
	Diss.±SD	Parti±SD	Diss.±SD	Parti±SD	Diss.±SD	Parti±SD	Diss.±SD	Parti±SD
Cd	0.09±0.03	16.14±1.98	0.06±0.01	13.58±1.20	0.03±0.001	10.87±1.16	0.06±0.011	13.53±1.44
Cu	0.14±0.016	27.06±2.93	0.11±0.009	24.01±3.95	0.08±0.009	20.03±2.76	0.11±0.01	23.7±2.54
Ni	3.12±0.86	68.85±0.66	1.99±0.16	64.82±0.50	0.95±0.08	45.06±0.44	2.02±0.64	59.57±0.53
Pb	0.70±0.08	43.63±8.13	0.60±0.20	39.29±5.91	0.48±0.15	35.28±3.31	0.59±0.14	39.4±3.11
Mn	3.59±0.40	270.63± 35.66	3.00±0.20	200.79± 20.40	1.95±0.12	180.79± 19.20	2.84±0.24	217.40± 25.08
Fe	190.62± 19.17	3193.21± 578.621	160.19± 30.25	2399.71± 896.59	120.37± 25.36	1999.69± 887.68	157.06± 24.92	2030.87± 787.62
Zn	21.16±2.92	98.01±4.03	18.13±4.00	89.35±10.0	14.10±2.50	63.06±8.01	17.79±2.14	83.47± 11.68

The partition of metals between dissolved and suspended particulate matter determines their ultimate fate in the aquatic environments. The mean concentrations µg/L of the mentioned metals in dissolved phase at the study station (1,2 and 3) were follows; Cd (0.09, 0.06, 0.03); Cu (0.14, 0.11, 0.08); Ni (3.12, 1.99, 0.95); Pb (0.70, 0.60, 0.48); Mn(3.59, 3.00, 1.95); Fe (190.62, 160.19, 120.37) and Zn (21.16, 18.13, 14.10) respectively. Metals concentration at St.1 were higher than their concentration in station 2, 3, this may be due to the close of the mentioned station from the region with high population density also it is situated close from the general garage of Al-Nassiriya city. So as a result of numerous processes happen in the garage for cars washing, therefore, the product of the mention process, directly discharge without any treatment to the canal of MOD near the mentioned station 1.

Trace elements in particulate matter were higher than their concentrations in dissolved phase for three stations Table(2). This may be due to the high amount of particulate matter in the study area during the study period. Decrease metals concentration in dissolved for river water may be due to adsorb TMs on sediment surfaces or complexes compound with organic matter [33, 34, 32] or accumulation TMs in plankton, aquatic plants and aquatic organism [35, 36]. Plankton organisms tend to concentrate TMs as high as 10^6 times their level in water [37], also the concentration of the trace elements in aquatic environment depends on many factors such as water discharge of the river, seasonal variations in quantities and qualitative of plankton and suspended material load of the river [38].

The concentration of dissolved trace elements is similar to those reported elsewhere, also its concentrations in the present study are in an acceptable range compared with the world wide Table (2,3) respectively.

Table (3): Comparison mean values of dissolved trace elements ($\mu\text{g/L}$) in the present study with the other studies elsewhere.

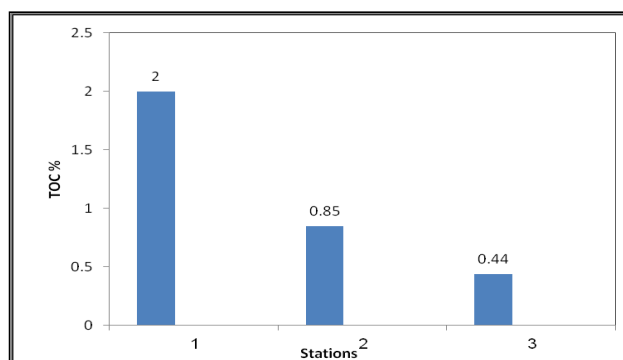
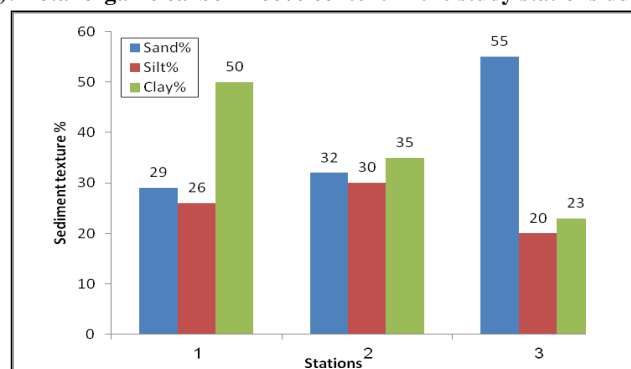
Location	Cd	Cu	Ni	Pb	Mn	Fe	Zn	References
Al-Hillia river-Iraq	1.09	1.81	0.27	4.21	0.96	6.74	8.73	39
Shatt Al-Arab river Basrah-Iraq	25.00	-	1209.00	95.00	-	-	1364.00	40
Euphrates river (between Al-Hindia dam, Kufa region)	2.14	2.48	0.07	0.10	6.12	105.69	10.50	41
Al-Hammar marsh south of Iraq	-	0.7	2.13	0.16	-	-	-	42
MOD river Iraq near Al-Nassiriyia city	0.05	0.03	1.73	0.35	2.42	154.05	12.12	25
World wid	0.22	7.0	-	3.0	-	-	20	43
MOD river Iraq near Al-Nassiriyia city	0.06	0.11	2.02	0.59	2.84	157.06	17.79	Present study

Trace elements in sediment

A major part of the heavy metals, that enter the aquatic environment eventually settle in the sediment [44]. So the sediment act as archives for many pollutants one of these are heavy metals [42]. Concentration of heavy metals in sediment showed in table (4). In the present study there were higher concentration of heavy metals observed at st.1 compared to st.2 and st.3 this was due to the location of st.1 near to residential areas , which discharged their waste directly into the MOD without treatment. These wastes increased the organic matter in the sediment Toc% content in the st.1 was more than its content in st.2 and st.3 during summer Figure (2). The mean concentrations of trace elements were Cd(4.87), Cu(16.5), Ni(45.86), Pb(23.4), Mn(259.69), Fe(2237.58) and Zn(22.65) $\mu\text{g/g}$ dry wt. concentration of TMs under study in sediment were higher than their concentrations in dissolved phase of water and lower than their concentrations in particulate phase of water. This mean that particulate phase play an important role to support sediment by heavy metals. In addition, the increasing of the plants density in the study area played an important role in increasing the concentration of trace elements in the sediment. Plants work to reduce the velocity of water flow and this led to the deposition of suspended matter containing trace elements in the sediments. Sediment particles size also plays an important role in the distribution and concentration of heavy metals. Description of the sediment texture at st.1. Small particle size, such as silt and clay tend to accumulate higher concentration of heavy metals because of the availability of large surface area that allowed adsorption of metals into the surface of particles [45,42]. This was confirmed by the high concentration of heavy metals in the sediment at st.1 comparing with st.2 and st.3, because st.1 contained a high content of silt 26% and clay 50% compared with st.2 which contained a high amount of sand 55% Figure(3), as well there was an increased concentration of trace elements in sediment in summer month Table (4) this is due to the high temperature which have a role in killing some phytoplankton and zooplankton and thereby increasing the deposit and accumulation of these materials, which increase the metal concentration in the sediment [46]. In addition high temperature lead to increase salinity through evaporation, when salinity increases the bond between the metals and suspended matter becomes stronger. This strong bond makes suspended material insoluble in water and then increases the deposition of these substances in the sediment.

Table (4): Mean concentrations ($\mu\text{g/g}$ dry weight) of trace elements in sediment for all study stations during study period.

Trace elements	Stations			Mean $\mu\text{g/g}$ dry wt.	Standard deviation
	Station 1	Station 2	Station 3		
Cd	7.16 \pm 0.10	5.09 \pm 0.07	2.38 \pm 0.04	4.87	0.07
Cu	24.39 \pm 1.89	16.40 \pm 1.64	9.47 \pm 2.23	16.5	1.92
Ni	50.01 \pm 20.70	45.69 \pm 11.86	40.10 \pm 4.05	45.86	12.20
Pb	33.25 \pm 11.65	27.69 \pm 3.35	9.26 \pm 2.04	23.4	5.68
Mn	296 \pm 105.01	250 \pm 96.03	203.08 \pm 50.60	459.69	83.88
Fe	2623.96 \pm 391.61	2280.5 \pm 280.97	1808.3 \pm 199.80	2237.58	290.79
Zn	30.17 \pm 1.32	20.89 \pm 4.36	16.90 \pm 2.08	22.65	2.58

**Fig (2): Total organic carbon Toc% content in the study stations during the study period****Fig (3): Sediment texture% for the station.**

Trace elements in plants

Aquatic plants have been shown to accumulate trace elements in their tissues and therefore have been used as biological indicators for metal pollution monitoring in the aquatic ecosystem. Table (5) shows the distribution of trace elements in aquatic plants of MOD river. The ability of plants to accumulation and elimination trace elements in relation to their concentration in ambient led to the observed variation in metal concentration in plants. The results showed higher concentration of trace elements in sediment than their concentration in plants these result were agreed with [7, 47, 48].

In this study there were differences in the trace elements concentrations between stations and a less clear difference between the selected plants. There were higher levels of trace elements in both species of plants *P. australis* and *C. demerssum* in station 1 than in station 2 and station 3. This was due to two reasons. Firstly, station 1 had exposure to different types of pollutants such as sewage, oil spilt from boats and chemicals used for fishing, while station 2 and 3 was less polluted. Secondly, the level of organic carbon in the sediment at station 1 was higher than its level at station 2 and 3 figure (2) as a result of sewage pollution. The metals remained in the sediments at station 1 for long periods of time and this provided greater opportunity for the plants to absorb, the range of cadmium concentration was 0.82- 2.01 $\mu\text{g/g}$ dry weight followed by lead 0.83- 2.23 $\mu\text{g/g}$ dry weight, while Iron have shown the

highest levels in the two species. The other elements are generally arranged in the following order of abundance Zn> Ni> Mn> Cu.

Generally, this study showed that the highest mean for trace elements concentration was in the particulate phase, followed by the sediments, then the plants and was lowest in the dissolved phase. The reason for the high concentrations in the particulate phase is due to continuous movement of water and the lack of time for deposition of the suspended solids [27,48]. The reason for the higher concentrations in sediment compared with plants and in dissolved phase is due to the plants density in the study area, which reduced water speed and thus provided an opportunity for the deposition of the maximum amount of suspended matter.

The higher concentration of elements in plants than in the dissolved phase is due to the concentration in sediments, which work to keep the trace elements as long as possible and thus provide the opportunity for plants to absorb these metals [7]. The cause of the low concentration in the dissolved phase compared to other phases is due to the effect of various physical and chemical factors such as salinity, temperature and pH, which leads to adhesion of metals with suspended materials, thereby reducing the concentrations of metals in the dissolved phase.

Finally, the results also showed the highest of metals in all stages (water, sediment and plants) were Fe, Ni and Zn. This is probably due to the source of pollution (sewage, oil splits from boats the use of toxic chemicals in the process of fishing) which have high levels of these metals. There may be some contribution from the geology of the region, which may contain naturally higher concentrations of these metals [28].

Table (5): Concentrations (Mean \pm SD) of trace elements in two plants (*C. demerssum* and *P. australis*) μ g/g in the study station.

Metals	Station 1		Station 2		Station 3		Mean concentration in the region	
	<i>C.demerssum</i> . Mean \pm SD	<i>P.australis</i> Mean \pm SD	<i>C.demerssum</i> . Mean \pm SD	<i>P.australis</i> Mean \pm SD	<i>C.demerssum</i> . Mean \pm SD	<i>P.australis</i> Mean \pm SD	<i>C.demerssum</i> . Mean \pm SD	<i>P.australis</i> Mean \pm SD
Cd	2.01 \pm 0.82	1.78 \pm 0.76	1.55 \pm 0.56	1.30 \pm 0.35	0.86 \pm 0.12	0.82 \pm 0.06	1.47 \pm 0.5	1.3 \pm 0.39
Cu	2.78 \pm 0.99	2.60 \pm 0.96	2.00 \pm 1.00	1.86 \pm 0.85	0.99 \pm 0.13	0.90 \pm 0.11	1.92 \pm 0.70	1.78 \pm 0.64
Ni	18.19 \pm 3.12	16.03 \pm 3.03	12.20 \pm 3.23	10.17 \pm 3.21	9.16 \pm 1.06	8.13 \pm 1.96	13.18 \pm 2.47	11.44 \pm 2.73
Pb	2.23 \pm 0.85	1.9 \pm 0.82	1.80 \pm 0.65	1.79 \pm 0.67	0.87 \pm 0.09	0.83 \pm 0.09	1.63 \pm 0.53	1.50 \pm 0.52
Mn	6.94 \pm 2.01	5.69 \pm 2.01	17.16 \pm 3.64	3.01 \pm 1.12	2.33 \pm 0.99	2.02 \pm 0.99	8.81 \pm 2.21	3.57 \pm 1.37
Fe	180.57 \pm 28.01	170.13 \pm 16.31	113.03 \pm 18.01	107.20 \pm 18.01	86.31 \pm 10.10	80.91 \pm 4.31	126.63 \pm 18.70	119.41 \pm 12.87
Zn	28.77 \pm 6.01	24.86 \pm 4.21	3.13 \pm 1.28	13.08 \pm 3.21	12.10 \pm 2.06	11.13 \pm 1.16	14.72 \pm 3.11	16.35 \pm 2.86

Conclusions

1. The variability in the levels of trace elements concentration in two species could be ascribed to biological variation between them rather than environmental factors.
2. The highest mean concentrations of trace elements were in the particulate phase, followed by the sediment, than the plants and was lowest in the dissolved phase. The trend of elements concentration was sediment> plants > water(dissolved phase)
3. Iron, Zinc and Nickel recorded higher concentration in all studied samples.
4. TEs in *P. australis* and *C. demerssum* come from the same source.
5. *C. demerssum* accumulated trace elements more than *P. australis*.
6. At the station 1 and station 2. The clay fraction was greater than sand fraction, this due to the associated of trace elements with fine particles size in clay.
7. Low concentrations of studied elements in the study area were not polluted by this type of pollutant according to WHO.

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