Concentration of some heavy metals in water, sediment and two species of aquatic plants collected from the Euphrates river, near the center of Al-Nassiriyia city, Iraq.

A frah A. Maktoof Al-Awady* Basim Y.Al-khafaji* Nabeel M. Abid**

*Biology Department –Science College-Thi-Qar University

**Analysis Pathological Department –Science College-Thi-Qar University

Abstract:

Concentration and accumulation of six trace elements (Cd, Cu, Pb, Ni, Fe 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, 2014 from the Euphrates river, some environmental parameter (Temperature, dissolved oxygen, salinity, pH) of water were measured, also total organic carbon (TOC%) and 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 *Ceratophyllum demerssum* was more than their concentration *Phragmits australis* in

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 its compared with world wide range. The study showed that the possibility of using both plants to remove these type of pollutant from the aquatic environment and can be used in bioremediation for processes.

Key words; *Trace elements, Aquatic plants, Water, Sediment, Euphrates river*

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 erosin 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 therefor, 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] .

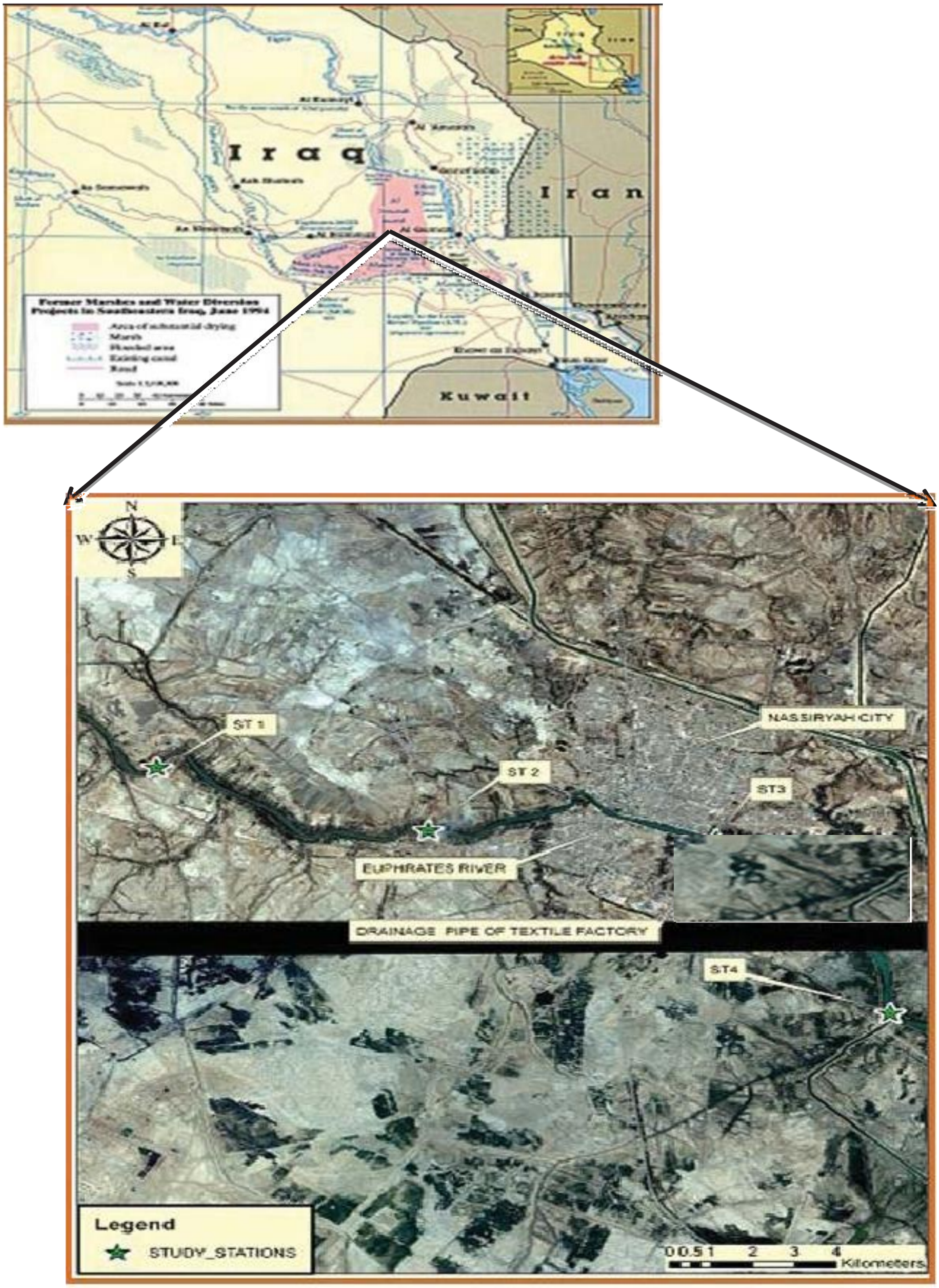

Fig.1: Map shown the study area.

Samples collection:

Samples of water, sediment and plants were collected from Euphrates river during summer (May, June, July, August and September) 2014. 5 litters 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 µs/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.

Salinity‰=EC(µs/cm*0.64/1000.

The 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 were digested after drying according to [16] method. The samples of plant were freez dried and ground with agate morter (1g dry weight) then digested according to the procedure described by [17]. Triplicates with blanks solution were used for each samples (water, sediment and plants) in the present study. The levels of (Cd, Cu, Ni, Pb, Fe and Zn) in extractions were determined by air- acetylene flame atomic absorption spectrophotometers (Shimadzu- 630-12) using different cathode lamps with air acetylene flam 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 31.00°c at st.1 in September to 44.01°c at st.2 in August, whilst water temperature values ranged from 23.12°c at st.1 in September to 36.00°c at st.2 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 (2.23- 3.16)‰.

The highest levels of salinity (3.16)‰ was recorded in september at station 3, while the lowest level (2.23)‰ was recorded in August at station 1. The higher values of salinity was observed in the study for the Euphrates river 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.2, 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 Temp.°c	Salinity ‰	pH	Do (mg/l)
May	1	34.01	26.03	2.60	8.35	10.75
	2	36.60	28.40	2.65	8.20	7.40
	3	35.30	27.98	3.00	8.10	7.43
June	1	37.80	29.23	2.20	8.11	8.01
	2	39.01	31.02	2.45	8.00	6.88
	3	38.23	30.00	2.65	7.35	6.95
July	1	37.99	29.21	2.30	8.00	7.75
	2	38.01	32.10	2.40	8.13	5.59
	3	39.23	31.22	2.82	7.15	6.00
August	1	41.02	33.15	2.23	7.99	6.65
	2	44.01	36.10	2.37	8.12	5.40
	3	42.20	34.31	2.79	7.20	5.39
September	1	31.00	23.12	2.75	8.30	8.89
	2	32.31	24.13	2.80	8.20	6.88
	3	32.03	24.00	3.16	8.18	7.00

Trace elements in water:

The result of analysis for Cd, Cu, Ni, Pb, 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	0.05±0.001	12.87±1.16	0.08±0.01	17.58±1.20	0.13±0.03	18.14±1.98	0.08±0.013	16.19±1.45
Cu	0.09±0.009	22.03±2.76	0.11±0.009	26.01±3.95	0.16±0.016	29.06±2.93	0.12±0.01	25.7±3.21
Ni	0.97±0.08	47.06±0.44	2.02±0.16	66.82±0.50	5.14±0.86	69.85±0.66	2.71±0.36	61.24±0.53
Pb	0.50±0.15	37.28±3.31	0.63±0.20	40.29±5.91	1.10±0.08	45.63±8.13	0.74±0.14	41.06±5.78
Fe	124.37±25.36	1000.69±887.68	160.19±30.25	2399.71±896.59	196.62±19.17	3197.21±578.621	160.39±24.92	2199.20±787.63
Zn	16.10±2.50	65.06±8.01	20.13±4.00	92.35±10.0	24.16±2.92	99.01±4.03	20.31±2.14	85.47±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 (0.05, 0.08, 0.13); Cu (0.09, 0.11, 0.16); Ni (0.97, 2.02, 5.14); Pb (0.50, 0.63, 1.10); Fe(124.37, 160.19, 196.62and Zn (16.10, 20.13, 24.16) respectively. Metals concentration at St.3 were higher than their concentration in station 1, 2, this may be due to the high metals content discharged from the waste- water treatment until which was located near station3. The effluents of municipal and industrial was contain considerable amount of heavy metals

Trace elements in particulate matter were higher than their concentrations in dissolved phase for three station (Table2). 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]. [37] has indicated that the plankton organisms tend to concentrate (TMs) as high also 10^6 times their level in water, 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 and 3) respectively.

Table (3):Comparison mean values of dissolved trace elements (µg/L) in the present study with the other studies elsewhere.

Location	Cd	Cu	Ni	Pb	Fe	Zn	References
Al-Hillia river- Iraq	1.09	1.81	0.27	4.21	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	105.69	10.50	41
Al-Hammar marsh south of Iraq	-	0.7	2.13	0.16	-	-	42
World wid	0.22	7.0	-	3.0	-	20	43
Euphrates river near Al-Nassiriyia city	0.08	0.12	2.71	0.74	160.39	20.31	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.3 compared to st.1 and st.2 this was due to the location of st.1 near to residential areas , which a high discharge of waste- water from the waste treatment unit near the former station. These wastes increased the organic matter in the sediment Toc% content in the st.3 was more than its content in st.1 and st.2 during summer (Fig.2). The mean concentrations of trace elements were Cd(5.87), Cu(17.75), Ni(46.26), Pb(24.4), Fe(2237.58) and Zn(23.65)µg/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 play 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.3 comparing with st.1 and st.2, because st.3 contained a high content of silt (28.06%) and clay (50.08%) compared with st.1 which contained a high amount of sand (38.01%) (Fig.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 increase 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 (µg/g dry weight) of trace elements in sediment for all study stations during study period.

Trace elements	Stations			Mean µg/gm dry wt.	Standard deviation
	Station 1	Station 2	Station 3		
Cd	3.38±0.04	6.09±0.07	8.16±0.10	5.87	0.07
Cu	10.47±2.23	17.40±1.64	25.39±1.89	17.75	1.92
Ni	41.10±4.05	46.69±11.86	51.01±20.70	46.26	12.20
Pb	10.26±2.04	28.69±3.35	34.25±11.65	24.4	5.68
Fe	1809.3±199.80	2281.5±280.97	2621.96±391.61	2237.58	290.79
Zn	17.90±2.08	21.89±4. 36	31.17±1.32	23.65	2.58

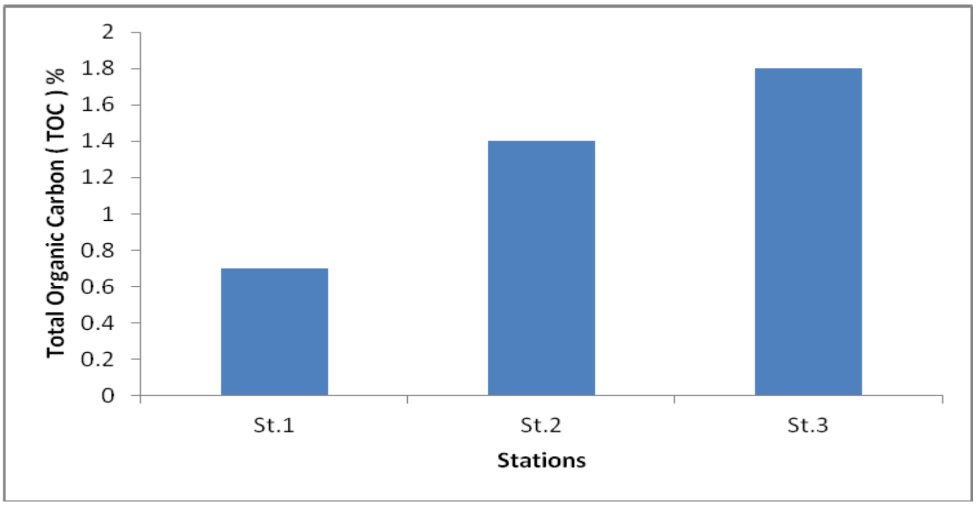

Fig.2: Total organic carbon (Toc%) content in the study stations during the study period.

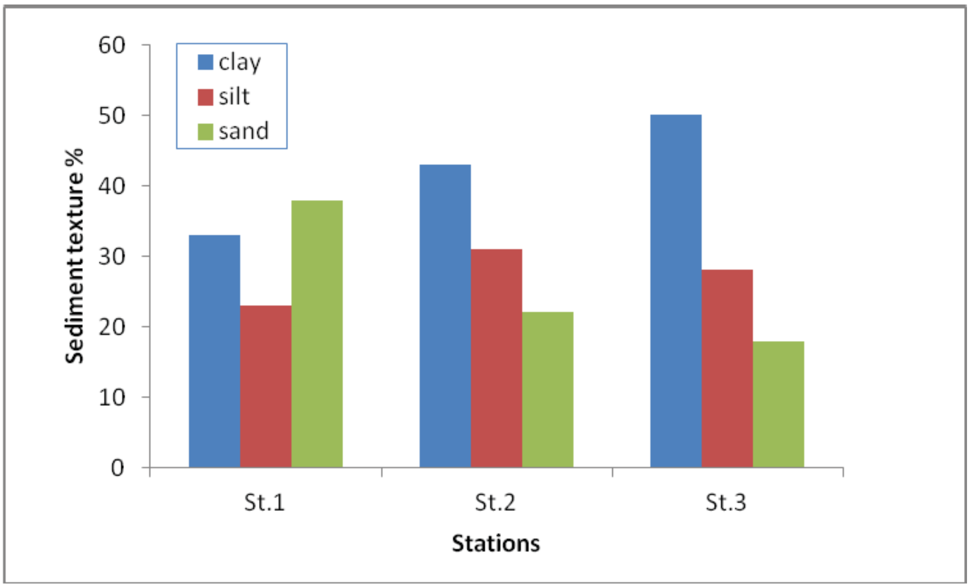

Fig.3: Sediment texture% for the station.

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)show the distribution of trace elements in aquatic plants of Euphrates 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 plant. There were higher levels of trace elements in both species of plants (*P. austeralis* and *C. demerssum)* in station 3 than in station 1and station 2. This was due to two reasons. Firstly, station 3 had exposure to different types of pollutants such as sewage, oil spilt from boats and chemicals used for fishing, while station 1and 2 was less polluted. Secondly, the level of organic carbon in the sediment at station 3 was higher than its level at station1 and 2(fig.2) as a result of sewage pollution. The metals remained in the sediments at station 3 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)µg/g dry weight followed by lead (0.83- 2.23) µg/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> 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 ±SD) of trace elements in two plants (*C. demerssum and P. austeralis)* µg/g in the study station.

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

Conclusions:

The variability in the levels of trace elements concentration in two species could be ascribed to biological variation between them rather than environmental factors. TEs in *P. austeralis* and *C. demerssum* come from the same source. Low concentrations of studied elements in the study area were that the study area was non polluted by this type of pollutant according to WHO.

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تركيز بعض العناصر النزرة في الماء والرواسب ونوعين من النباتات المائية المستجمعه من نهر الفرات قرب مركز مدينة الناصرية_ العراق.

أفراح عبد مكطوف العوادي* باسم يوسف الخفاجي* نبيل مهدي عبد**

*قسم علوم الحياة – كلية العلوم – جامعة ذي قار

**قسم التحليلات المرضيه – كلية العلوم – جامعة ذي قار

المستخلص

قيس تركيز وتراكم ست من العناصر النزرة (الكادميوم، النحاس، الرصاص، النيكل، الحديد والخارصين) في الماء بجزئية الذائب والعالق والرواسب ونوعين من النباتات المائية القصب *Pharagmits australis* والشمبلان *Ceratophyllum demerssum* جمعت خلال فصل الصيف ٢٠١٤ من نهر الفرات قرب مركز مدينة الناصرية، تم قياس بعض الخصائص الفيزيائية والكيميائية درجة الحرارة(الماء والهواء)، الأوكسجين المذاب، الملوحة والدالة الحامضيه) للماء فضلا عن قياس كمية الكاربون العضوي الكلي ونسجه الرواسب وعبر عنها كنسب مئوية.

أظهرت الدراسة أن تركيز العناصر في الرواسب أعلى مما هو عليه في الماء (الجزء الذائب) ، أما تراكيزها في الجزء العالق من الماء أعلى مما هو عليه في جزءه الذائب، في حين سجل تراكمها في نبات الشمبلان أعلى مما هو عليه في نبات القصب .

لوحظ من الدراسة بالإمكان استخدام هذا النوعين من النباتات كدليل حيوي لتراكم العناصر النزرة، وكذلك كانت تراكيز العناصر النزرة في عينات الدراسة ضمن الحدود المقبوله مقارنة بالحدود العالمية.

بينت الدراسة أمكانية استخدم كلا النباتين في إزالة هذا النوع من الملوثات في البيئة المائية وبذلك يمكن استخدامها في المعالجة الحيوية لهذا الغرض.

الكلمات المفتاحيه: العناصر النزرة، النباتات المائيه، الماء، الرواسب، نهر الفرات