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Phragmites australis and *Typha domingensis* as bioaccumulators and biomonitors of three trace metals along Shatt Al-Basra canal, south of Hammer marsh.

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Abstract

Three trace metals Cu, Pb and Zn at the region of Shatt Al-Basra canal in south of Hammer marsh, were determined monthly from Sep.2003 to Feb.2004 in water, surface sediments and two emerged aquatic plants (*Phragmites australis* and *Typha domingensis*) which were collected from four selected stations. Trace metal concentrations were high in the surface sediment with a clear local variation. While their values in the water samples were much lower than that found in the surface sediment, with clear local variations among the studied stations. *P. australis* showed its ability to accumulate higher concentrations of studied pollutants than *T. domingensis* and underground parts of both plants were accumulated higher concentrations than aboveground parts. The study of water samples and corresponding sediments from the canal near oil refinery discharging point showed that the area is polluted with different levels of Cu, Pb and Zn. Emergent aquatic plants *P. australis* and *T. domingensis* were good bioaccumulators and can be considered as an interesting candidate for potential use as biomonitors and phytoremediate for such pollutants.

1- Introduction

Trace metals, such as Zinc, Copper and Lead, introduce into water columns of riverers and streams from different sources, including; industrial, automobile exhaust, mines, and even natural soil. Trace metals become more concentrated as animals feed on plants and are consumed in turn by other animals. When they reach high levels in the body, heavy metals can be immediately poisonous, or can result in long-term health problems (Blaylock *et al.*, 1997; Ebbs and Kochian, 1997).

The fate of trace metals such as lead and zinc, in the aquatic environment is of extreme importance due to their impact on the ecosystem. The metals in such environment can be accommodated in three basic reservoirs: water, sediment, and biota. The importance of the biota reservoir is quite evident as organisms in any estuary can be adversely affected and human health hazards can arise through consumption of the affected organisms. The biota reservoir, however, is small compared to the water, which in turn is much smaller than the sediment reservoir.

Phragmites australis (Cav.) Trin. ex Steud. (common reed) and *Typhadomingensis* (cattails) are of the most widespread plant species in the world with a wide ecological amplitude. It has been long recognized that reed play a complex role from the point of view of water quality management because they are able to purify water by taking up nutrients and dissolved pollutants and provide habitat for many species. The investigations upon the role of the reed as a pollution treatment for some water categories in different ecological conditions, point out an interesting domain of scientific research from the varied gamut of environmental protection (Wolverton, 1982).

Distribution of trace metals accumulated by the *P. australis* (common reed) in estuarine areas of rivers of the northern Black Sea region were studied by Nebesnyi *et al.,* (1992). The territorial differentiation of trace metals accumulated by *P. australis* in the estuarine regions of the Danube (the Kiliian arm). Dniester, Dnieper, Kuban Rivers has been determined (Nebesnyi *et al.*,1992). High bulk composition of lead and molybdenum is typical of *P. australis* aggregations in the Danube, manganese-in the estuarine region of the Kuban, copper and nickel-in the estuarine region of the Dniester and zinc-in the estuarine region of the Dnieper in Russia.

Macrophytic plants are critical to high pollutant removal rates in treatment wetlands. Plants provide the necessary of environmental factors such as oxygen and nutrient transfer to the sediments and soils and through their fixation of reduced carbon to support a diverse microbial population (ITRC, 2003).

The aim of this study is to determine trace metals in water, sediment and two species of aquatic plants collected from Shatt Al-Basra canal and studying the possible role of *Phragmites_australis* and *Typha domengensis* to remove or bioremediate trace metals discharged from Basrah petroleum refinery.

2-Materials and methods

Shatt Al-Basrah is an artificial canal constructed for multi purposes; naturally, the sedimentation and erosion processes act together and finally they could change the initial geometry of the canal. The Khor Al-Zubair waterway is connected with Al Basrah canal, which is linked the south of Hammer marsh directly to the north of Basrah City(Al-Imarah et. Al., 2006). Four sampling stations were chosen to represent different sectors of Shatt Al-Basrah canal region (Fig.1) for the study of trace metals Cu, Pb and Zn.

Two plant species, from the study area *P. australis* and *T. domingensis* were selected for estimating the potential loading induced by three trace metals. The samples were collected from different sectors of the canal, and sorted in to aboveground and underground organs, dried at 40 ^{o} C for 24 h, then grounded and labeled for analysis.

Surficial soil samples were collected from the bottom sediments at the same site of plant samples, and then they were air-dried, sieved by 2mm sieves and kept for analysis.

Aboveground and underground parts of each plant and soil as well as water samples were chemically analyzed for detection of trace metals Cu, Pb and Zn, using the digestion technique for all samples by HCl and HNO_3 according to procedure of Sturgeon *et al.*, (1982). Atomic spectrophotometer model (Buck 210 VGP) was used for measurements.

Filtered water samples were run through 50x 2 cm ion exchange column filled with 50 – 100 mesh chelex-100 resin in a flow rate of 5 ml/min, then column is washed by 200 ml deionised water and the trace metals eluted by 30 ml 2 M nitric acid which was collected in 50 ml plastic beaker.

The elute was evaporated to near dryness, the residue was then dissolved in 1 ml 0.5 N hydrochloric acid and made up to 25 ml with deionised water and stored in 25 ml anlagen screw cap bottles and sealed for trace metals analysis.

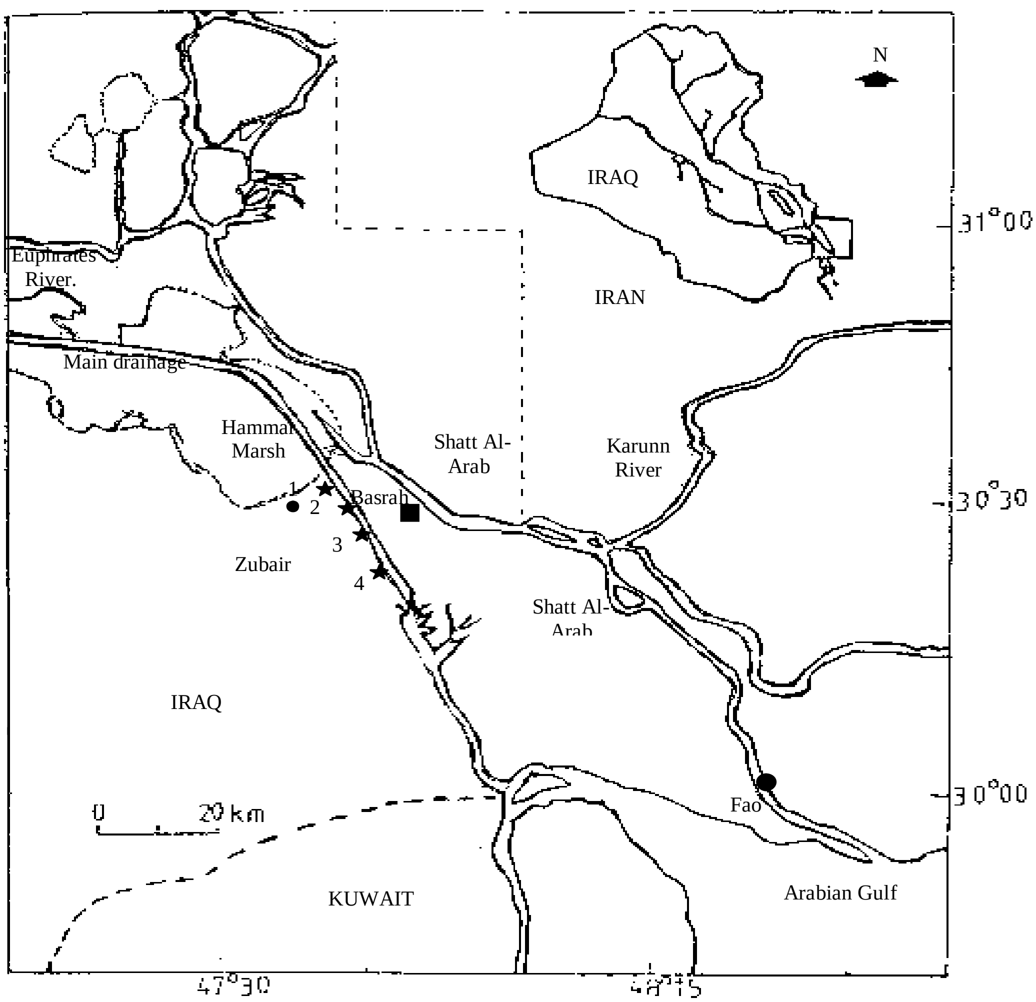

Fig.1. Map of Shatt Al-Basrah canal showing the locations of sampling sites

3- Results and discussion

Mean concentrations of Pb, Cu and Zn in the dissolved and particulate phases of water samples from different stations in Shatt Al-Basrah canal are shown in table 1. Percentages of TOC in different stations are shown in figure (2). Different concentrations of heavy metals in both exchangeable and residual phases of soil were recorded (Fig.3) explaining accumulation of these metals. The highest concentration was found in the underground organs of *P. australis* in comparable with aboveground organs of both plants(Figs.4&5).

Table 1: Mean Concentration of Pb, Cu and Zn in water samples(dissolved and particulate) during Sep.2003 to Feb.2004 in different stations.

Month	Station	Trace metal Conc.					
		Pb		Cu		Zn	
		Dissolved μg/l	Particulate μg/g(dry wt.)	Dissolved μg/l	Particulate μg/g(dry wt.)	Dissolved μg/l	Particulate μg/g(dry wt.)
Sep.2003	1	1.16±0.02	5.12 ±0.08	0.51±0.02	10.21±0.09	5.22±0.08	17.19±0.05
	2	3.6 ±0.11	8.81 ±0.15	0.72±0.02	16.22±0.11	6.93±0.08	20.15±0.09
	3	7.3 ±0.14	15.14±0.22	1.21±0.03	24.16±0.19	10.33±0.09	36.16±2.08
	4	7.06±0.14	11.91±0.18	1.93±0.03	18.17±0.08	9.31 ±0.05	28.76±1.00
Oct.2003	1	2.11±0.04	5.62 ±0.09	0.52±0.02	11.06±0.04	5.91 ±0.08	21.06 ±0.9
	2	4.54±0.07	9.17 ±0.11	0.82±0.02	17.91±0.05	7.25 ±0.03	20.36±0.59
	3	9.49±0.05	17.92±0.21	2.41±0.05	26.09±0.08	11.82±0.04	40.14±2.34
	4	8.61 ±0.08	13.81±0.18	1.14±0.03	19.71±0.04	10.29±0.09	32.66±2.21
Nov.2003	1	3.62±0.10	5.93 ±0.08	0.54±0.02	11.52±0.04	6.06 ±0.02	21.33±0.92
	2	5.18 ±0.03	9.72 ±0.14	0.91±0.02	18.36±0.05	7.81 ±0.04	20.89±1.09
	3	11.93±0.08	18.3 ±0.09	2.44±0.04	27.12±0.11	12.27±0.05	44.21±3.22
	4	9.22 ±0.07	14.26±0.02	1.23±0.03	20.18±0.09	10.78±0.05	36.03±2.68
Dec.2003	1	4.12±0.07	6.09 ±0.02	0.56±0.02	12.71±0.04	7.73 ±0.04	20.18±0.91
	2	6.26 ±0.04	10.12±0.10	1.04±0.02	19.36±0.06	8.12 ±0.02	30.18±1.55
	3	13.36±0.09	20.14±0.94	2.64±0.05	28.19±0.17	15.17±0.03	56.2 ±5.22
	4	11.34±0.08	15.25±0.11	1.34±0.03	22.18±0.12	12.97±0.05	40.18±3.05
Jan.2004	1	4.71±0.07	6.28 ±0.02	0.62±0.02	13.09±0.07	8.12 ±0.04	24.11±1.33
	2	8.77 ±0.07	12.26±0.10	1.12±0.03	21.06±0.12	8.97 ±0.05	33.11±2.31
	3	15.31±0.09	28.18±0.22	2.92±0.05	30.23±0.23	17.77±0.09	64.91±5.19
	4	13.39±0.08	17.18±0.21	1.53±0.03	24.41±0.18	13.77±0.08	44.28±4.28
Feb.2004	1	4.91±0.07	6.33 ±0.03	0.63±0.02	13.28±0.07	8.26 ±0.04	24.06±1.56
	2	7.86±0.12	12.96±0.08	1.17±0.03	22.26±0.14	9.14 ±0.05	36.39±2.33
	3	15.36±0.09	29.11±0.12	3.01±0.02	30.79±0.22	18.18±0.05	68.18±5.47
	4	13.81±0.12	17.78±0.22	1.60±0.02	24.75±0.14	14.13±0.04	46.49±3.27

(± S.D. : Standard deviation)

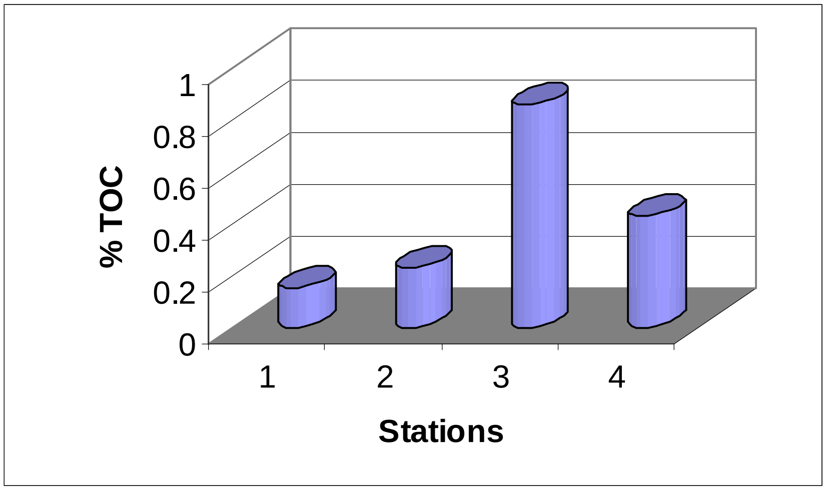

Fig.2: Mean of TOC (%) in different study stations during Sep.2003 to Feb.2004

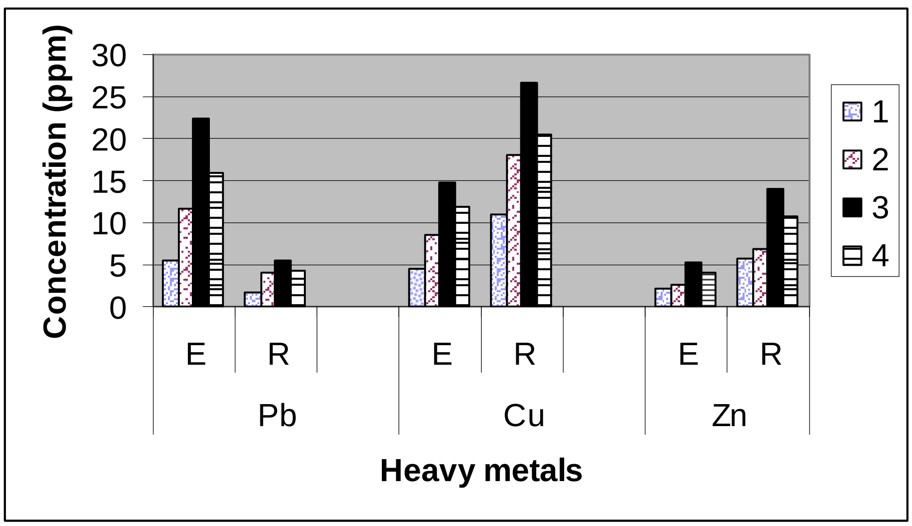

Fig.3 Mean values of three heavy metals in soil samples (E: Exchangeable; R: Residual) in different stations.

Pollution outputs associated with petroleum refining typically include metals and numerous toxic organic compounds. These pollutants may be discharged as air_emissions, wastewater or solid waste. Trace metals (Pb, Cu and Zn) showed monthly and regional variation during present study.

The relatively low concentrations of some dissolved trace metals in the study area throughout the months ascribed to removing of these metals by many ways such as adsorption on particulate matter, precipitation and removed by organisms. The distribution of trace metals between mobile phase and stationary phase of the sediment is the result of a number of

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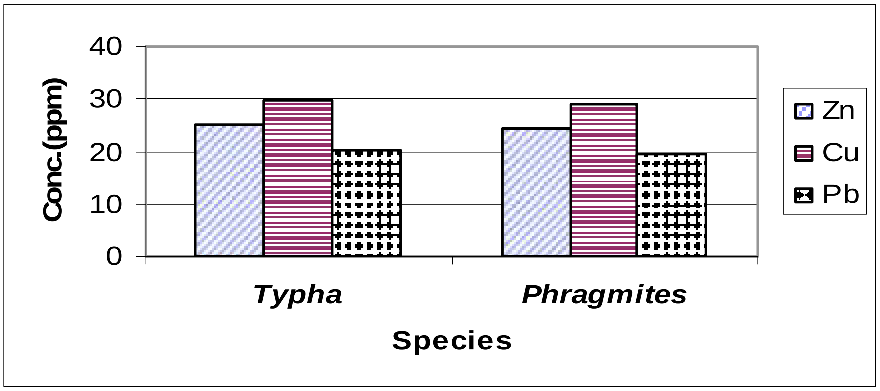

Fig.4: Mean concentration of three heavy metals in underground parts of two plants species.

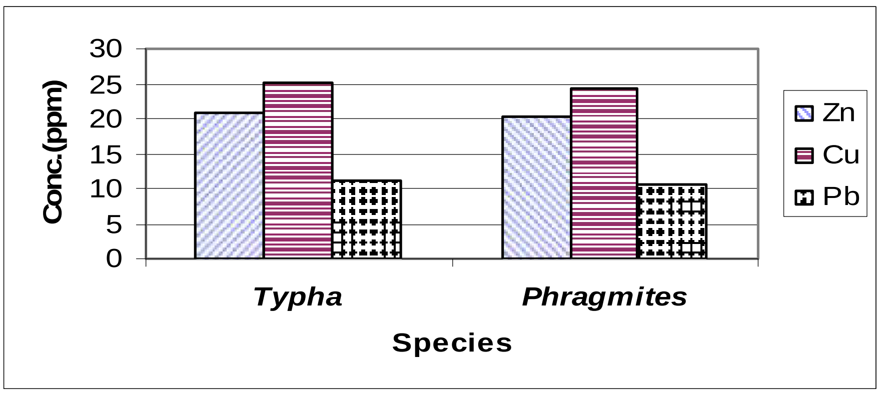

Fig.5: Mean concentration of three heavy metals in aboveground parts of two plants species

Particulate metals enter into a number of reactions, including complexation, precipitation and adsorption in the environment, these reactions affect their mobility and bioavailability, and however adsorption could be the first step in the final removal of metal from water (Allen, 1993).

All trace metals are expected to be associated with suspended particulate matter more than dissolved in solution that may due to its anthropogenic sources (Al-Khafaji, 1996).

processes like hydrochemical conditions

The values observed in the present study were higher compared with that of Shatt Al-Arab River (Al-Khafaji, 1996), whereas all values of trace metals in suspended particulate matter in this study were lower compared with that found in Shatt Al-Arab River (Abaychi and Doubul, 1985).

The high value of trace metals in suspended particulate matter measured at each station was due to anthropogenic and natural sources (Ansari *et al*, 1998). Lead levels were higher at all stations due to local discharge from Basrah oil refinery, in addition to dust fallout that may promote the region with great amounts of lead, as well as non point sources such as discharge coming from the northern sites to the study area in addition to agricultural activities.

Sediment is usually regarded as the ultimate sink for trace metals discharged in to the environment, therefore the analysis of trace metals in sediments offer more accurate means of detecting and assessing the degree of pollution (FAO, 1994; Lin *et al*., 1998).

The concentrations of Cu, Pb and Zn in sediments in the present study were less than those recorded by Abaychi and Doubul (1985), While Al-Hashimi and Salman (1985) found low concentrations of trace metals in the sediment from the same study area.

There are considerable differences in the partitioning of trace metals between exchangeable and residual fractions of the sediment. Trace metal concentrations in the residual fraction were greater than in the exchangeable fraction. This indicates that these metals enter the aquatic environment from anthropogenic sources. With the exception of Pb, trace metals concentrations were less than those reported for unpolluted sediments.

The amounts of adsorbed metals are related to the organic content of the sediment. Statically analysis promoted that some trace metals were accumulated in association with organic matter, there is a significant correlation ($p<0.05$) observed between TOC content and most of trace metal concentration for station 3. This indicates that TOC has a great effect upon metal concentrations in the sediments, which is agreed with Literathy *et al*., 1987 .

The high concentrations of trace metals in the sediment in some stations which could be arises from different sources; oil refinery discharges in the vicinity area, in addition to non point sources of metals.

High lead concentrations in the sediment from the study area may associate with traffic density from different sources. Lead is burned annually in internal combustion engines and introduced into atmosphere; therefore, lead accumulation in aquatic environment as a result of automotive emission (Al-Mudafer *et al*., 1992; FAO, 1994). Cu and Zn accumulation in sediment may be related to the oil and sewage wastes effluent that discharged to shatt Al-Basrah canal directly.

Plant samples showed different concentration of trace metals during present study. P. australis and *T. domengensis* were able to accumulate these metals from the surrounding environment.

The underground parts of both plants accumulated higher concentrations of metals than aboveground parts that may be due to direct contact with sediment which accumulated much concentrations of metal.

The different parts of *P. australis* accumulated Cu, Pb and Zn in concentrations more than different parts of *T. domengensis*.

The different concentrations in plant samples may come from diverse sources of metals input, beside irregular discharges of these pollutants into aquatic environment.

The relatively high concentrations of trace metals in plants may give indication of pollution by these metals by diverse sources from point and non point sources in the study location.

P. australis and *T. domengensis* may act as an important role on removal of pollutant and remediate its environment by different ways explained as below that discussed by many scientists worked on this line (Aprill and Sims, 1990; Ebbs and Kochian, 1997; Blaylock *et al*.. 1999; Zhu *et al*. 1999)

Phytoremediation takes advantage of the natural processes of plants. These processes include water and chemical uptake, metabolism within the plant, exudates release into the soil that leads to contaminant loss, and the physical and biochemical impacts of plant roots.

Plant material that is incorporated into the soil will increase the organic matter content of the soil, potentially leading to increased sorption of contaminants and humification (the incorporation of a compound into organic matter).

Contaminant loss may also increase as roots decay, due to release of substrates and the creation of air passages in the soil.

Cunningham *et al*. (1996) mentioned that higher plants were used to enhance the remediation of soils contaminated with recalcitrant organic compounds, but the mechanisms of dissipation have not been established. One possible step in the phytoremediation process is adsorption of the organic contaminant onto the surface of the roots and subsequent uptake and/or degradation.

The present study showed regional variations in heavy metals concentration between the different stations. The highest mean appeared in station 3 while the lowest mean was in station 1.

Station 3 was the most polluted than other stations because it is in touch with point source of oil refinery waste water discharges beside nonpoint sources came from other sites.

Regional variation of trace metals in dissolved phase from shatt Al -Basrah canal was observed. These values were generally lower than world wide average, this may be due to limited potential sources of trace metals pollution, whereas the relatively highest concentration of metals due to petroleum rich substrate of the area.

The results showed that Cu and Zn concentrations were higher in stations 3 and 4 than other stations.

High concentrations of TOC were recorded in sediment from station 3, because it is very close to the discharging point of Basrah oil refinery which receives direct irregular of waste water discharge comparing with other stations.

Concentrations of most trace metals in sediment from station 3 were greater than those from other stations .

It is concluded that the relatively high concentration of some trace metals in the canal indicated a possible accumulation of these pollutants, which have been due to wastewater discharges from Basra oil refinery, in addition to non point sources in this area.

P. australis accumulates trace metals more than *T. domengensis* and the underground parts of the both plants contain more concentrations than aboveground parts.

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دور نباتي القصب والبردي كمراكمات وادلة احيائية لثلاث معادن نزرة في قناة شط البصرة , جنوب هور الحمار.

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البصرة – العراق

الملخص

اجريت دراسة شهرية لتقدير ثلاث معادن نزرة وهي النحاس والرصاص والخارصين في قناة شط البصرة بجزئها الواقع جنوب هور الحمارخلال الفترة من ايلول 2003 لغاية شباط 2004 في عينات من المياه والرواسب واثنين من النباتات المائية ذات التواجد الدائمي وهما القصب والبردي ومن اربعة مواقع منتخبة ضمن القناة. كان تراكيز المعادن النزرة المدروسة مرتفعة في عينات رواسب سطح القاع مع وجوداختلاف موضعي واضح. بينما كانت تراكيزها منخفضة في عينات المياه بمقدار كبير مقارنة بتراكيزها في رواسب سطح القاع مع وجود اختلافات موضعية واضحة بين المحطات المدروسة.اظهر نبات القصب قابلية عالية لتراكم تراكيز اعلى من المعادن المدروسة بمقدار اعلى من نبات البردي, وكان التراكم بمقدار اكبر في الاجزاء السفلى المنغمسة في الرواسب لكلا النباتين مقارنة بالاجزاء العليا ضمن عمود الماء . ان دراسة عينات المياه والرواسب المرادفة لها من قناة شط البصرة قرب نقطة تصريف مصافي النفط في الشعيبة اوضحت ان المنطقة ملوثة بمستويات مختلفة من النحاس والرصاص والخارصين.وتؤكد الدراسة ان نباتي القصب والبردي ادلة احيائية جيدة ويمكن الاعتماد عليهما كادلة احيائية ومعالجات نباتية لهذا النوع من الملوثات.
