ENVIRONMENTAL ASSESSMENT OF TRACE METALS POLLUTION IN SEDIMENT OF KHOR AL-ZUBAIR, IRAQ

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Abstract

The purpose of this study was to determined and assess the concentrations of some trace metals in surface sediment from different locations of Khor Al-Zubair sediment during 2006. Samples of sediment were collected from seven stations, treated and analyzed for Cobalt, manganese, Nickel, Iron, Copper and Zinc by Atomic Absorption Spectrometric analysis. The Range and average concentrations measured in ug/g were 21.98-43.97 (30.14) for Co, 353.77-570.60 (507.01) for Mn, 34.56-69.13 (44.98) for Ni, 6676.023-7398.385 (7147.05) for Fe, 7.565-27.739 (14.04) for Cu and 27.41-58.48 (43.04) for Zn. Grain size analyses with total organic carbon have been also determined in those sediment. It is noted that the contamination factors in the investigated sediment were 1.69-3.38 for Co, 0.62-0.70 for Mn, 0.90-1.81 for Ni, 0.142-0.157 for Fe, 0.37-1.38 for Cu and less than one in Zn. In general, the contamination factors of trace metals in the present study could be arranged as following Co>Ni>Mn>Cu>Zn>Fe. Results were also compared with earlier studies carried out on trace metals content of fresh and coastal water in the region including the study area. Diversified natural and anthropogenic inputs may have provided the sources of this pollution. Further studies are needed to characterize the source, fate, biogeochemical processes and impacts of these trace metals on coastal habitats and marine life of the region.

Introduction

Heavy metals are widely spread in the aquatic environment, some trace metals are dissolved in water, absorbed by phytoplankton and particles suspended matter by some organism (e.g filter feeding). All of these steps can enter into the food chain, later find in the tissues of living organisms, after the death of these organism the heavy metals may deposit to bottom sediment (Al-Saad et al., 1997).

Marine sediments can be sensitive indicators for monitoring contamination in aquatic environments (Heba *et al.*, 2004). The bottom sediments serve as a reservoir for heavy metals and therefore deserve special consideration in the planning and design of aquatic pollution research studies. If a sufficiently large and stable sediment sink can be located and studies, it will allow the investigators to evaluate the geochemical change over time and possibly to established baseline levels against which current conditions can be compared and contrasted (Naser *et al.*, 2006). Heavy metals regarded as serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity and ability to be incorporated into food chains (Pekey *et al.*, 2004).

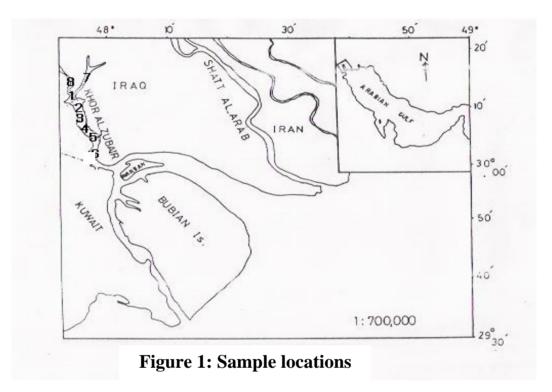
Khor AL-Zubair, due to its strategic position in southern Iraq ,link with the North-West Arabian Gulf from the south, and with Shatt Al-Basrah from north, the seawaters from the Arabian Gulf effects on the composition of the water of the Khor (Hussain and Ahmed,1999), the heavy metals entering the Khor are transported by prevailing currents. The main source of pollution in this area are power station, sewage effluent, industrial facilities, port facilities, agricultural activities, coastal construction and oil transportation activities (Al-Saadon, 2002).

The aim of the present study is to investigate the distribution of heavy metals(Co, Ni, Mn, ,Fe , Cu and Zn) and to evaluate their levels in the Khor Al-Zubair sediment.

Study area

Khor Al-Zubair is an extension of the Gulf waters in the lower reaches of Mesopotamia Fig (1). It has an approximate length of 42 km, a wide of 1 km at low tide, and an average depth of 10-20 m, During 1983 this water body was connected to an oligohaline marsh (Hor Al-Hammar,), changing the environment of the Khor from a hypersaline lagoon to an estuary one (Hussain and Ahmed, 1999). The topography of Khor Al-Zubair look like a spindle with tapering ends, at the northern and southern ends. The northern end receives fresh water influx of average 700 m3/sec throughout the tidal cycle. The current in the Khor is characterized by one direction through out the tidal cycle towards the southern end (Arabian Gulf), with velocity

exceeding 2m/sec during ebb tide and 0.66 m/sec in flood tide. At the Southern end, the water discharge reaches 10000 m3/sec with velocity range 0.8-5.78 m/sec. with big tidal range at Umm-Qasar reaching 4.3m. (Al-Badran *et al.*, 1996).



Materials and Methods

Sediment samples were collected from Khor AL-Zubair area during summer 2006 (Fig.1). Seven stations were selected in this area depending on their special features. Surficial sediment samples were obtained by mean of a Van Veen grab sampler. Trace metals analysis was performed on the <63 um fraction of the sediment which has been separated by sieving after drying and grinding. The determination of trace metals in sediment samples was done according to the following procedure described by Sturgeon *et al.*,(1982). Concentrated HCl and HNO3 (1:1) were added to each sample and evaporated to near dryness on the hotplate at 80°C, then mixture of concentrated HCLO4 and HF (1:1) were added. After heating to near dryness, 20ml of 0.5 HCL were added and cooled for 10 min. The extraction was decanted into 25 ml plastic volumetric flask. This step was repeated twice and all supernatant were combined. Finally samples were stored prior to trace metals analysis using a Pye-Unicam Atomic

Absorption type SP9 Pyeunicam.

Grain size analysis of the sediment was done according to Folk (1974), the Total Organic Carbon (TOC) of the investigated sediment was determined, using the wet oxidation method as mentioned by El-Wakeel and Riely (1957).

Results and Discussion

Sea bottom sediment accumulate metals and affect the near-bottom water layer due to resuspension or dissolution processes (Khan *et al.*,1998). Polluted sediment may act as a secondary pollution source for the aquatic environment. The study of metal concentrations in sediment is also useful for the estimation of polluted trends (Al-Saad, 1995).

The concentration of trace metals (Co, Mn, Ni, Fe, Cu, and Zn) in sediment of Khor Al-Zubair are given in Table (1). The Range and average concentrations measured in ug/g were 21.98-43.97(30.14) for Co, (507.01) for Mn, 34.56-69.13 (44.98)353.77-570.60 6676.023-7398.385 (7147.05) for Fe, 7.565-27.739 (14.04) for Cu and 27.41-58.48 (43.04) for Zn. The high values of Mn and Fe were found at station 1, The great amount of Co and Zn were recorded at station 2, while station 4 revealed high concentrations of Ni and Cu. The distribution of the metals in sediment of Khor Al-Zubair were irregular, there concentration were found low to moderate. Copper is an essential elements for all living organism. The irregular fluctuation might be due to regeneration of organic matter with which Cu forms soluble and insoluble metal chelates. The higher concentrations of some of these metals in this environment were due to the contamination of industrial and navigational discharge (Al-Saadon, 2002). The higher concentration might be harmful for the environmental quality as well as for the aquatic and benthic organisms. Zinc play an important role as a micronutrient required for plant growth and its variation in concentration depend on the generic characteristics of the sediment (Khan and Talukder, 1995), and its concentration has been related to the abundance of metal-reactive compound supposedly not significant affected by man's action (Luoma, 1990).

Mn is one of the more biochemical and active transition metals in aquatic environment, having considerable biological significance. The industrial discharge act as source of Mn. The source of metals in Khor Al-Zubair might be due to the combination of river in input (Shatt Al-Basra), shipping activities, discharge of untreated industrial effluent and domestic waste, city run-off and atmospheric fall-out.

The level of contamination expressed by the contamination factor (CF) Pekey *et al.*,(2004) and it was calculated as follows:

Cf= (metal content into the sediment) /(metal content in the natural reference sediment).

The contamination factors was classified into four groups (Pekey *et al.*2004). Cf < 1 refer to the low contamination factors 1< Cf<3 refers to the moderate contamination factors, 3 < Cf < 6 refers to the considerable contamination factors and Cf > 6 refers to the very high contamination factors. The values of contamination factors (Cf) are shown in Table (3). It is noted that the contamination factors in the investigated sediment were 1.69-3.38 for Co, 0.62-0.70 for Mn, 0.90-1.81 for Ni, 0.142-0.157 for Fe, 0.37-1.38 for Cu and less than one in Zn. In general, the contamination factors of trace metals in the present study could be arranged as following Co>Ni>Mn>Cu>Zn>Fe.

The statistical analysis between metals are shown in Table (4)which illustrated relationship between Co-Zn, Ni-Cu, and Mn-Fe.

There are few published reports available on the same area such as Samhan *et al.* (1979), Al-Hashimi and Salman (1985), Abaychi and DouAbul (1986), Abaychi and Al-Saad(1988), Al-Mussawy and Salman, (1989), Al-Edanee *et al.* (1991) and Al-Saadon, (2002), and the result were higher than the present finding (Table 5), while the comparison between the present concentrations with those reported in the literature concluded that the concentration observed in the Khor Al-Zubair were lower or higher than those recorded in other studies (Table 5).

Al-Saad *et al*, (1996) showed that the distribution of heavy metals in marine deposits was influenced by sediment texture, clay content and organic carbon. The result of grain size analysis shows that silt and clay are the main constituent followed by less percentage and sand (Table 2), However higher concentrations of Total Organic Carbon (TOC) were found at station 1,2 and 4. which are located very close to industrial discharge. Total Organic Carbon (TOC) in sediment gave good indicator for organic pollution (Al-Saad 1995). Nevertheless the concentration of heavy metals are not related to the organic carbon and /or grain size of the sediment. The same result were concluded by several workers such as Abaychi and DouAbul (1985) in the sediment from the North –West Arabian Gulf and also by Al-Taee (1999) in there samples from Al-Hilla River, and by Heba *et al.*, (2004) in the Red Sea.

As conclusion Khor al-Zubair has been polluted with heave metals came from different sources such as urban wastes, industrial effluents, land washout and shipping activities, and our recommendations (a): that all industries along Khor Al-Zubair should develop treatment facilities to neutralize the effluent (solid, liquid and gaseous) before discharging into the environment. (b): Sewage treatment plan should be installed in area for

proper treatment of the waste before discharging into the Khor. (c): The port authority should develop facilities to receive the waste material from ship and oil tanker. Appropriate legislation should be adopted to prevent dumping in the coastal and marine environment and (d): monitoring and evaluation in this area is very important.

Table (1): Concentration of trace metals in sediments samples (µg/g) from Khor Al-Zabair

Station No.	Со	Mn	Ni	Fe	Cu	Zn
1	21.98	553.48	34.56	7398.385	7.565	27.41
2	43.97	507.83	42.24	7107.110	12.609	58.48
3	35.17	570.60	57.60	7223.620	17.652	44.77
4	35.17	536.36	69.13	7177.016	27.739	45.68
5	26.38	496.42	38.40	7153.714	15.130	44.77
6	26.38	530.65	34.56	7293.526	7.565	42.94
7	21.98	353.77	38.40	6676.023	10.087	40.20
Means	30.14	507.01	44.98	7147.05	14.04	43.46

Table (2): Grain size analysis in sediment samples from Khor Al-Zabair With Total Organic Carbon (TOC%)

Stration No.	Sand %	Silt %	Clay %	Texture	TOC%
1	8	58	34	Silty clay loam	2.56
2	18	62	20	Silty loam	2.45
3	22	58	20	Silty loam	2.00
4	38	34	28	loam	2.60
5	42	24	34	Clay loam	2.62
6	44	32	24	loam	1.80
7	6	54	40	Silty clay	1.98

Table (3): Concentration factors (CF) of the sediments of Khor Al-Zabair

Station No.	Co	Mn	Ni	Fe	Cu	Zn
1	1.69	0.70	0.90	0.157	0.37	0.39
2	3.38	0.64	1.11	0.151	0.63	0.83
3	2.70	0.72	1.51	0.153	0.88	0.63
4	2.70	0.67	1.81	0.152	1.38	0.65
5	2.02	0.62	1.01	0.152	0.75	0.63
6	2.02	0.67	0.90	0.155	0.37	0.61
7	1.69	0.67	1.01	0.142	0.50	0.57

Table (4): Correlation coffection between different metals in Khor Al-Zubair

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	Zn	Cu	Fe	Ni	Mn	
Cu	0.346	•	-	-	-	
Fe	0.238	-	-	-	-	
Ni	0.294	0.944	0.038	-	-	
Mn	0.028	0.250	0.937	0.323	-	
Co	0.844	0.493	0.106	0.536	0.366	

Ni References Fe Location Cu Zn Mn 0.215-5.877-369.28-991.75 Mrghna estuary 0.595-20.695 2.578-25.515 Khan et al., 1998 4.258 25.005 **NE Bay of Bengal** 28.92 9.56 49.11 60.10 3499.40 Khan and Talukder, 1995 Bengladesh coast Ganges estuary, India **26** 71 32 553 31036 Subramanian et al., 1988 Veller River estuary, India 104 Mohanachandran, 1986 9 619 Cochin estuary, India 4.81 17.77 Nair et al., 1991 Estuarine, Jave Sea 6-54 33.122 Everaarts, 1989 ND **Gulf of Thailand** 2.6-12.1 15.38 Polprasert et al., 1979 Singapore estuary 10-80 100-500 Sin et al., 1991 North Sea 25-240 400-4000 ND **Everaarts and Fischer, 1992** River Tees, UK Davies et al., 1991 10-1100 40-2900 160-1800 Port Said, Egypt 14 **50** Saad et al., 1981 44.6 $1.5*10^5$ Kuwait 20.7 96.9 409.9 Samhan et al., 1979 Al-Hashimi and Salman, **North-West Arabian Gulf** 2.59 13.74 10.07 51.54 2400 1985 North-West Arabian Gulf 17.3-37.1 386-637 915-1643 4450-9371 Abaychi and Douabul, 1986 27-43 25.2 24.2 Abaychi and Al-Saad, 1988 **North-West Arabian Gulf** 39.9 751 5869 **North-West Arabian Gulf** 60 Al-Mussawy and Salman, 1989 94 389 31762 16 **72** 90 Al-Edanee et al., 1991 **Khor Al-Zubair** 28 541 9640

34.56-69.13

353.77-570.60

6676.023-7398.385

Present Study

27.41-

58.48

7.565-27.739

Khor Al-Zubair

Table (5): Comparison of trace metal concentrations ($\mu g/g$) in sediment of various estuaries, seas and oceans

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التقدير البيئى لملوثات العناصر النزرة في رواسب خور الزبير العراق

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المستخلص

تم في هذة الدراسة تقدير وتعين التراكيز لبعض العناصر النزرة في الرواسب السطحية لمناطق مختلفة من منطقة خور الزبير خلال العام 2006 جمعت عينات رسوبية من سبعة مناطق، ثم عوملت وحللت بها العناصر لكل من الكوبلت المنغنيز النيكل الحديد النحاس والخارصين باستخدام جهاز الامتصاص النزي. المنغنيز النيكل الحديد التراكيز بالميكروغرام لكل غرام وكما يلي 1.98 -21.98 تراوحت مدى ومعدل التراكيز بالميكروغرام لكل غرام وكما يلي 1.93 -21.98 تراوحت مدى ومعدل التراكيز بالميكروغرام لكل غرام وكما يلي 1.93 -34.56 وللنيك 1.57 -6676.023 وللنيك 1.57 -678 (7147.05) وللنيك الكوبلت وللمنغنيز 1.40 وللخارصين 1.57 -87 (84 (43.04)) وللخارصين 1.69 الحجم الحبيبي للرواسب ومحتواها من الكاربون العضوي الكلي، كما تم تحديد معامل التركيز لهذة العناصر في الرواسب المدروسة حيث تراوحت بين 1.69 معامل التركيز لهذة العناصر في الرواسب المنغنيز و 0.90 -1.81 الي النيك و على النحو التالي:الحديد حالخارصين حالنحاس حالمنغنيز حالنيكل حالكوبلت .

تم مقارنة النتائج التي توصلنا اليها مع الدراسات والنتائج الاخرى لمناطق مختلفة من العالم وتبين بان القيم التي توصلنا اليها تقع ضمن تلك الدراسات ، كما بينت الدراسة بان مصادر هذة الملوثات مختلفة المنشأ وأكدت الدراسة على وجوب إجراء دراسات مستقبلية لضمان حماية المنطقة من التلوث.

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