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Levels and Distribution of Trace Metals in the Southern Wetlands of Iraq

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Abstract

Trace metals Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn were determined in water and sediments from southern Iraqi wetlands represented by Marshes, (Al-Hawiezh, Central and Al-Hammar), Shatt Al-Arab, Garmat Ali and Northern Arabian Gulf. Subsurface water samples and bottom sediments were collected from each site of sampling on a seasonal basis during the period July/2004 to July/2005. Trace metals were extracted from each sample by means of standard methods and determined by adopting of Atomic Absorption Spectrophotometer. The highest mean concentrations for trace metals in water (in µg/l) were 85.97(Cd) in Beeshah, 407.98(Co) in Qurna, 57.83(Cu) in Mashab, 574.33(Fe) in Khite, 85.34(Mn) in Seebah, 181.0(Ni) in Mashab, , 90.25(Pb) in Beeshah, and 702.34(Zn) in Beeshah during different seasons of the study, while the highest mean concentrations of trace metals in sediments (in µg/g) were 35.92(Cd) in Central marsh, 836.46(Co) in Central marsh, 48.69(Cu) in Central marsh, 18435.50(Fe) in Al-Hawiezh marsh, 3648.28(Mn) in Qurna, 486.95(Ni) in Garmat Ali, 5435.5 (Pb) in Qurna and 539.8(Zn) in Qurna. Certain sites along Shatt Al-Arab river receive huge amounts of wastes from municipal, industrial and commercial which might increase the levels of pollutants in water and sediments, as it is found in Beesha at the top north of Arabian Gulf as pollutants in the particulate phase of water are precipitated.

Key Wards: Trace metals, Marshes, Sediments, Waters, N.W. Arabian Gulf

1-Introduction

There are numerous types of pollutants in the aquatic environments, such as organic materials, major ions and heavy metals. These pollutants could be introduce to the aquatic environment as a result of urbanization, industrialization and agricultural activities (Al-Kafaji 1996). Heavy metals are the major anthropogenic contaminant of estuarine and coastal waters. Humans have affected aquatic trace element cycling through direct discharges into streams and atmospheric emissions, which are deposited at varying distances from the source, and the human activities result in substantial inputs to the environment of Sb, As, Cd, Cr, Cu, Pb, Hg, Mn, Ni, Se, Sn, V, and Zn (Brigham 2000). Many heavy metals, even if present in minute quantities are toxic to plants and animals, thus their release to aquatic environments from either natural or anthropogenic sources has an adverse effect upon ecosystem health (Catherine and Gabriel 2000).

Trace metals in aqueous solution seldom frond as free ions but exist as ionic complex utilized by vary of organism in organic and hydrated legends which affected mobility, reactivity and solubility (Wood 1989). They are of environmental interest both as limiting nutrients and as toxicants. Cupper, Zinc and partly Nickel are essential to natural organisms in low concentrations, while they are toxic in higher concentrations. Cadmium and Lead are toxic even at low concentrations and not regarded as being micronutrient.

Trace metals appear in fresh water naturally and in trace concentrations and varied according to kind of sediment (Evans and Engel 1994). Speciation of metals in sediments is sometimes necessary to identify pollution sources, especially to distinguish between mineralized or lattice-hold metals and the more bio-available fraction (Kerstin and Forester 1989).

The aims of this study were firstly to quantify heavy metal concentrations in different classes of water categorized between brackish waters (Al Beesha, Northern Arabian Gulf) to fresh water (Al Hawiezh and central marshes and Iraqi inland waters) and to know if their are any temporal correlation among the sites, secondly to identify the environmental conditions associated with enhanced mobility, and to confirm whether those correlations were significant or not between sites, seasons, and metals.

2-Material and methods

Sites chosen for sampling in this study were two sites of Iraqi Marshlands [(1)Al-Hawiezh and (2)Central marshe], three sites along Shatt Al-Arab river [(3)Al-Qurnah, (4)Al-Seeba and (5)Ras Al-Beesha) and three sites at southern Al-Hammar Marsh [(6)Al-Mashab, (7)Al-Khiet and (8)Garmat Ali] as shown in fig.(1). Samples as subsurface water and surface bottom sediments were collected in a fine whether days on a seasonal basis during the period July/2004 to July/2005.

For water samples, polyethylene bottles prewashed by 0.5N HCl and distilled water were used. Each water sample is thoroughly mixed by shaking , and 100 ml of it is transferred into a glass beaker of 250 ml volume , to which 5 ml of conc. Nitric acid is added and heated to boil till the volume is reduced to about 15-20 ml, by adding conc. Nitric acid in increments of 5 ml till the residue is completely dissolved. The mixture is cooled , transferred and made up to 100 ml using metal free distilled water (limgis 2001).

Van veen grab sampler was used to collect bottom sediment from each site. In the lab, sediments were dried, grinded and extracted according to Sturgeon *et al*. (1982) procedure. The concentrations of trace metals, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn, were determined by flame Atomic Absorption Spectrophotometer (Pye Unicum Model SP9) in both water and sediments samples. SPSS program was used for statistical analysis.

Fig. 1: Sample locations during this study

3-Results and Discussion

The study allows comparing the trace metals concentrations in water and sediments samples from all different sites of Iraq aquatic environments. The distribution and concentrations of trace metals Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn are shown in figs. 2-9 for water and figs. 10-17 for sediment. The highest mean concentrations for trace metals in water (in µg/l) were 85.97(Cd), 407.98(Co), 57.83(Cu), 574.33

(Fe), 85.34(Mn), 181.0(Ni), 90.25(Pb), and 702.34(Zn) at the sites Beesha, Qurna, Mashab, Khiet, Seeba, Mashab, Beesha and Beesha respectively during different seasons of the study. In spite of the low different significantly there are clear variations among the studies sites for all metals, mainly due to different discharge of heavy waste, industrial and agricultural effluent as well as the nature of the bottom sediment compositions which assist that sediment do play a substantial effect in the dissolved metal contents(Anderson 1995), and also may be due to the release of metals from refolded soils that are contaminated with chemicals, mines and military ordinance. Metal concentrations can also vary significantly over short distances and as a function of tide (Batley 1995).

Most of high concentrations were during summer in which the high temperature lead to high evaporation rates, but all were still low in comparison with local standard levels (Iraqi Gazette, 1990) as shown in table (1) except Cadmium and Cobalt concentrations which are resulted from the influence of agriculture effluents and the damage effect of a pipe carrying crud oil to al-Hartha power station, Pb from leaded fuel and Zn from the erosion of ships skeleton.

Bottom sediment is the substrates which adsorbed and accumulated the metals in its natural conditions (Grot *et al* 1986). The highest mean concentrations for trace metals in sediment (in µg/g dry) were 35.92(Cd), 836.45(Co), 48.69(Cu), 18435.50(Fe), 3548.22 (Mn), 486.95(Ni), 543.75(Pb), and 539.80(Zn) at central marsh, central marsh, central marsh, Al-Hawieza, Al-Qurna, Garmat Ali, Al-Qurna and Al-Qurna respectively during different seasons of the study. Figs. 9-16 show low variations among the studied sites except Fe concentration which was high at the central and Al-Hawiezh marshes because these areas could be severely burned after drainage, some places with high surface organic covering sulfidic pyrite soils beneath altered chemically and then exposed to oxygen resulting in the formation of sulfuric acid (Fitzpatrick, 2004) , which in turn lead to the liberation of Fe, Ca, Mg and Cu . The overall conditions of certain areas of marshes will become hard like ceramic due to the conversion of FeS_2 to Fe_2O_3, on reflooding this soil will not rewet and cannot support plant life (Richardson and Hussain 2006).. In comparison with sediment quality standard, the trace metals concentrations were very low as shown in table (1).

The accumulation effects are greatly dependent on the sediment composition and structure, the same observation was reported by Hussain and Khan(2000).

When making comparison to present study water concentrations, it is important to note that the data are for total metals concentrations and so that be higher when comparison with other studies in Iraq(table 2), but lower than Hussain and Khan(2000) and Guien and Martin(2002) whom are detected total metal concentrations.

Table (1): Mean of trace metals concentrations in water and sediments from southern wetlands of Iraq with mean standard concentrations.

	Water							Sediment			
metal	**Present study 2004-2005**	EQS standards 2001	EU standards 1998	WHO standards 1993	Water quality Standards 1990	SPA Scope 1980	USEPA 1976+ 1992	**Present study 2004-2005**	NOAA 2000	CEQG 2002	USEPA 2004
Cd	**7.86**	10	5	3	5	10	5	**13.79**	1.2-9.6	0.6-3.5	
Co	**265.23**	-	-	-	50	500	-	**137.67**			
Cu	**23.02**	40	2000	2000	50	200	1000	**12.44**	3.4-270	35.7-197	390
Fe	**7621.14**	-	200	-	300	2000	100	**176.37**			
Mn		-	50	500	100	500	650	**28.47**			
Ni	**154.30**	10	20	20	100	200	-	**46.55**	20.9-51.6		
Pb	**67.62**	10	10	10	50	100	50	**32.60**	46.7-218	35-91.3	450
Zn	**118.51**	-	-	3000	500	2000	5000	**194.96**	-150 410	123	410

Table 2: Comparison the present water study trace metals concentration (μg/l) with the same in other area.

Site	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn	References
Shatt Al Arab river/Al Iraq	0.26	-	0.90	716	1.30	3.40	0.30	1.80	Abaychi and DouAbul (1985)
Shatt Al Arab river/Al Iraq	0.93	-	0.52	-	0.07	0.50	0.04	0.80	Abaychi and Mustafa (1988)
Shatt Al-Arab estuary	0.15	0.33	0.58	389.20	0.69	2.45	0.18	0.93	Al-Saad and Al Kafaji (1996)
Shatt Al-Arab estuary	0.19	0.37	0.47	173.00	1.52	2.85	0.23	0.82	Al-Khafaji (1996)
Shatt Al Hilla	1.11	3.27	1.81	6.74	0.96	0.27	4.21	8.73	Al-Taee (1999)
Karnafully estuary	8-168		125-482	4200-22230	282-931	101-572	33-540	206-985	Hussain and Khan(2000)
Danube delta	1.1-2.4	16-19	201-1092	3.78-4.04%	1286-2290	66-71	58-65	212-218	Guien and Martin (2002)
Shatt Al-Arab / Iraq	5.00	50.00	50.00	-	-	100.00	50.00	100.00	Analytical Report (2004)
Iraqi wetlands	7.86	265.23	23.02	7621.14	49.44	154.30	67.62	118.51	**Present study**

The comparison of sediments average concentrations(μg/g) with other studies inside and outside Iraq (table 3), reveal that Cu, Ni and Mn concentrations were rather low while concentrations of Cd, Co, Zn and Pb were higher, but still low in comparison with sediment quality standard(USEPA, 2004) and slightly higher than NOAA(2000) and CEQG (2002) for Zn and Cd metals concentrations.

According to tables 4, 5 and 6, statistical investigations revealed the presence of positive significant correlations between all studied trace metals except Co in water, while different correlations were found between trace metals concentrations in the sediment and the distribution of trace metals in sediments seems not to be related to the corresponding distribution in water.

Table 3: Comparison the present sediment study trace metals concentrations (μg/g dry) with the same in other area.

Site	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn	References
Shatt Al Arab river /Al Iraq	0.18	17.70	44.00	34.70	642.00	646.00	11.30	34.70	Abaychi&DouAbul(1985)
Al- Kuwait	1.50	0.91	20.5.	280.00	4099.00	96.90	22.70	280.00	Samhan *et al* (1986)
Shatt Al-Arab river	0.03	17.40	39.60	5.80	914.00	57.20	19.00	5.80	Abaychi&Al-Saad(1988)
Arab Gulf	0.03	18.60	24.20	25.20	751.00	39.80	6.60	25.20	Abaychi&Al-Saad(1988)
Kur Al-Zubier	0.26	-	28.00	72.00	541.00	90.00	29.00	72.00	Al-Edanee *et al* (1991)
Shatt Al-Arab river	0.05	-	30.00	135.00	917.00	421.00	22.50	135.00	Al-Mudafar *et al*(1992)
Al-Hammar lake	-	58.00	42.00	3149.00	700.00	197.00	-	88.00	Abaychi (1995)
Shatt Al-Arab estuary	0.27	16.98	29.24	31.99	404.10	104.20	17.74	31.99	Al-Kafaji (1996)
Shatt Al-Arab estuary	-	53.00	36.20	80.40	1063.30	398.60	63.10	80.40	Tarik & Thoraya (1997)
Shatt Al-Hilla	3.92	49.12	34.45	73.41	239.07	193.04	58.20	73.41	Al-Taee (1999)
Gurna	-	42.90	-	388.00	684.00	-	-	388.00	Itawi et al (2000)
Karnafully estuary	0.135-1.08		10118 -36.25	559.66-1117.78	11.6-29.56	16.99-35.11	11-36.21	0.16-7.47	Hussain & Khan (2000)
Unpolluted sediment	0.11	-	33.00	95.00	770.00	-	19.00	95.00	GESAMAP,1982
Iraqi wetlands	13.79	137.67	12.44	176.37	28.47	46.55	32.60	194.96	**Present study**

Tabel(4): Correlations between water trace metals concentrations

	Cd	Ni	Cu	Zn	Fe	Pb	Co	Mn
Cd Pearson Correlati	1							
Ni Pearson Correlati	.812**	1						
Cu Pearson Correlati	.727**	.568**	1					
Zn Pearson Correlati	.766**	.815**	.732**	1				
Fe Pearson Correlati	.612**	.668**	.287*	.378*	1			
Pb Pearson Correlati	.738**	.713**	.535**	.723**	.499**	1		
Co Pearson Correlati	-.155	-.124	-.029	-.199	.139	.266	1	
Mn Pearson Correlati	.497**	.752**	.258	.519**	.388*	.471**	-.073	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Tabel(5): Correlations between sediments trace metals concentrations

	CD.S	ZN.S	NI.S	CU. S	FE.S	PB.S	Co.S	MN.S	Cd,W	NI.W	Cu. W	ZN.W	FE.W	PB.W	Co. w	MN. W
CD.SEDIM Pearson Correlati	1															
ZN.SEDIM Pearson Correlati	-.010	1														
NI.SEDIM Pearson Correlati	.609**	-.064	1													
CU.SEDIM Pearson Correlati	.092	.030	.302	1												
FE.SEDIM Pearson Correlati	.526**	-.120	.638**	.357*	1											
PB.SEDIM Pearson Correlati	.012	.174	.235	.027	-.019	1										
CO.SEDIM Pearson Correlati	-.109	-.010	.117	.304	.035	-.117	1									
MN.SEDIM Pearson Correlati	.084	.560**	-.016	.150	.245	.045	-.004	1								
CD.WATER Pearson Correlati	.123	-.221	.146	-.138	.267	-.012	-.197	-.052	1							
NI.WATER Pearson Correlati	.235	-.163	.122	-.138	.337*	.019	-.337*	-.018	.812**							
CU.WATER Pearson Correlati	-.060	.232	-.029	-.148	.123	.102	-.168	.469**	.727**	.568**	1					
ZN.WATER Pearson Correlati	.249	.145	.068	-.029	.275	.000	-.239	.321	.766**	.815**	.732**	1				
FE.WATER Pearson Correlati	.167	-.322	.208	-.105	.297	.155	-.313	-.165	.612**	.668**	.287	.378*	1			
PB.WATER Pearson Correlati	.118	-.045	-.053	-.261	-.132	.256	-.323	-.183	.738**	.713**	.535**	.723**	.499**	1		
CO.WATER Pearson Correlati	-.233	.032	-.070	-.119	-.344*	.523**	-.172	-.133	-.155	-.124	-.029	-.199	.139	.266	1	
MN.WATER Pearson Correlati	.126	-.071	-.061	-.104	.160	.249	-.276	-.164	.497**	.752**	.258	.519**	.388*	.471**	-.073	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Tabel(6):Correlations between water and sediments trace metals concentrations

	Cd	Ni	Cu	Zn	Fe	Pb	Co	Mn
Cd Pearson Correlation	1							
Ni Pearson Correlation	.812**	1						
Cu Pearson Correlation	.727**	.568**	1					
Zn Pearson Correlation	.766**	.815**	.732**	1				
Fe Pearson Correlation	.612**	.668**	.287*	.378*	1			
Pb Pearson Correlation	.738**	.713**	.535**	.723**	.499**	1		
Co Pearson Correlation	-.155	-.124	-.029	-.199	.139	.266	1	
Mn Pearson Correlation	.497**	.752**	.258	.519**	.388*	.471**	-.073	1

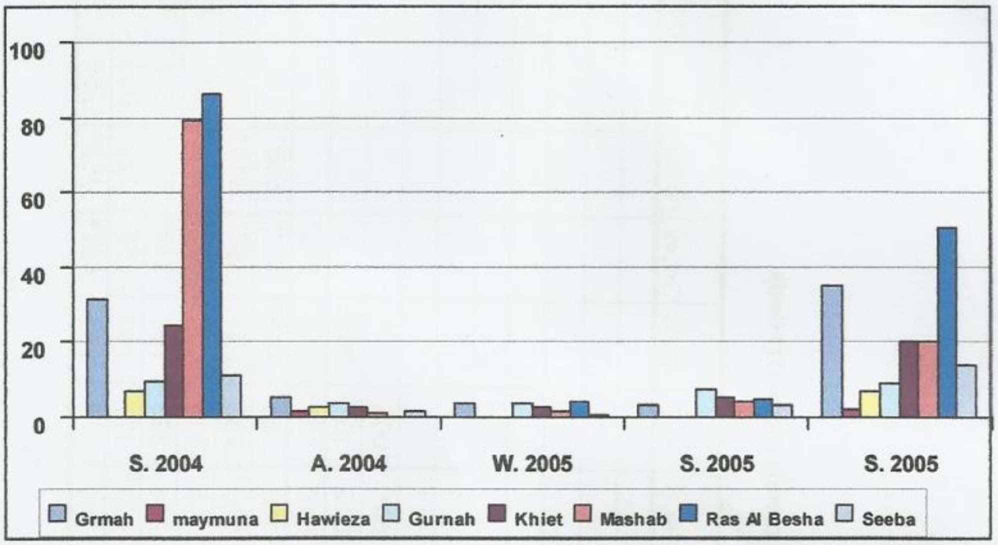

Fig. 2: Seasnal average conc. of Cadmium(Cd)in water (µg/L) from southern wetlands of Iraq

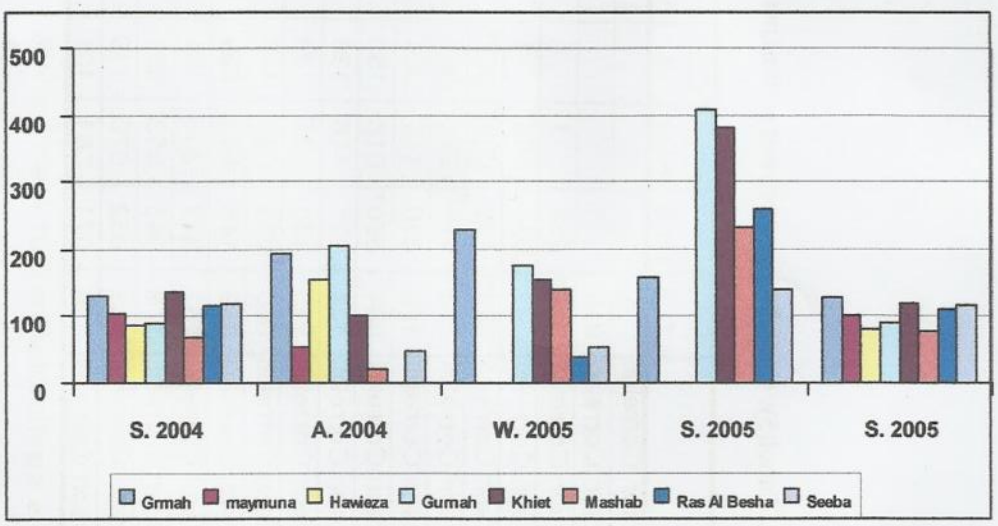

Fig. 3: Seasnal average conc. of Cobalt(Co) in water (µg/L) From southern wetlands of Iraq

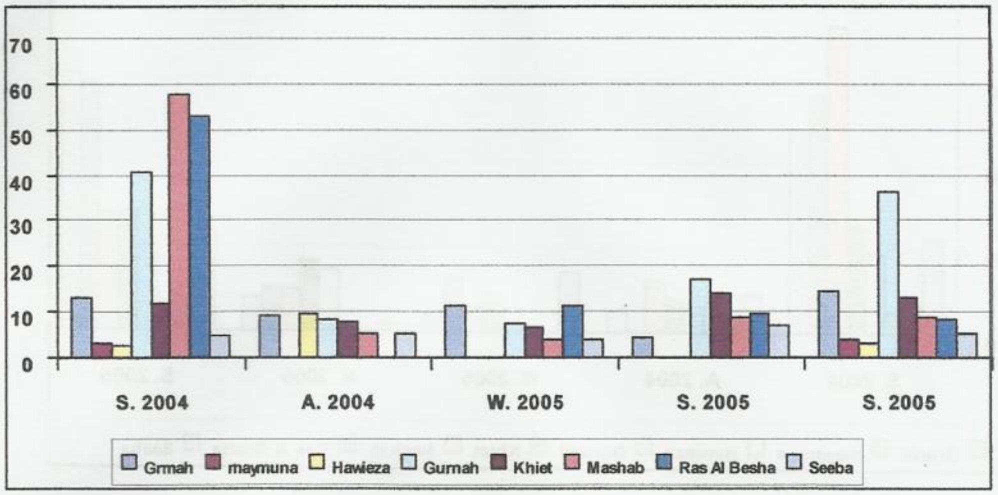

Fig.4: Seasnal average conc. of Copper (Cu)in water (µg/L)from southern wetlands of Iraq

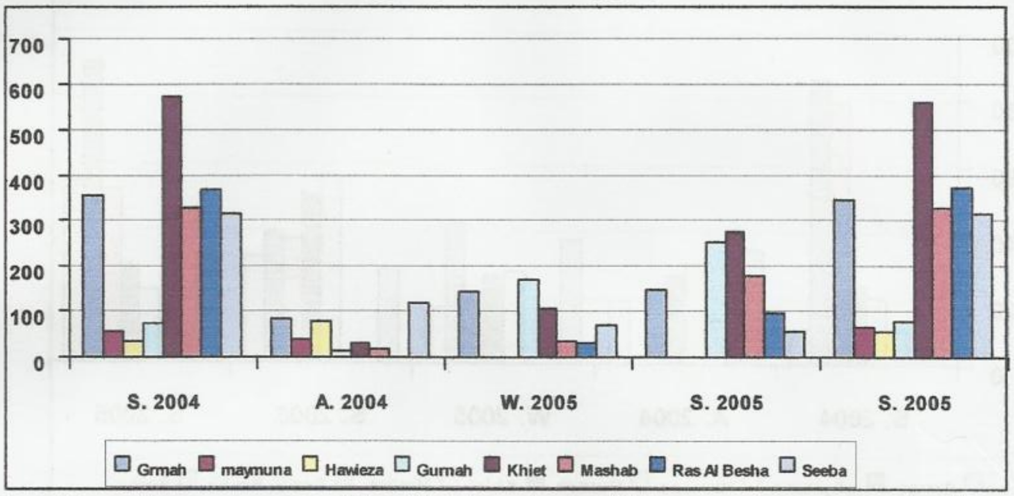

Fig.5: Seasnal average conc. of Iron(Fe) in water (µg/L)from southern wetlands of Iraq

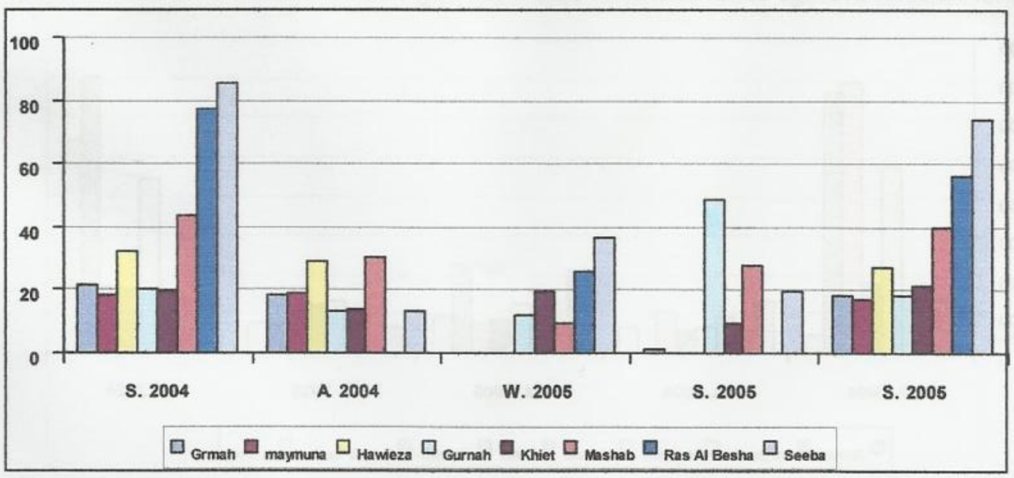

Fig.6 Seasnal average conc. of Manganes (Mn)in water (µg/L)from southern wetlands of Iraq

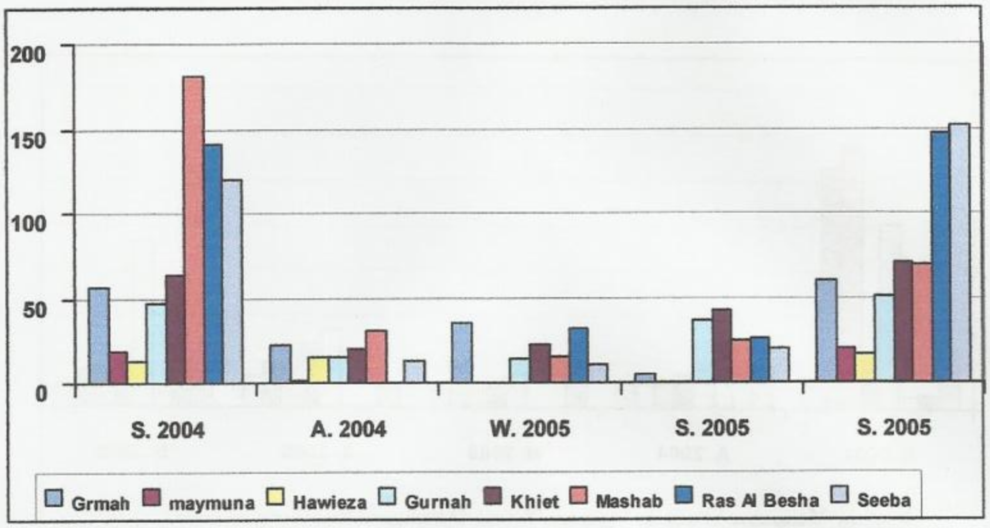

Fig.7: Seasnal average conc. of Nickel(Ni) in water (µg/L)from southern wetlands of Iraq

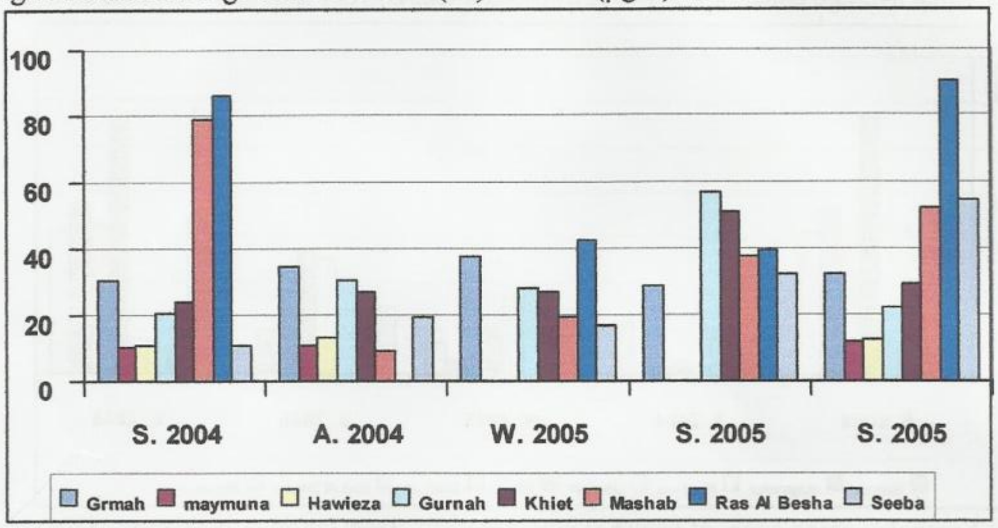

Fig.8: Seasnal average conc. of Lead(Pb)in water (µg/L)from southern wetlands of Iraq

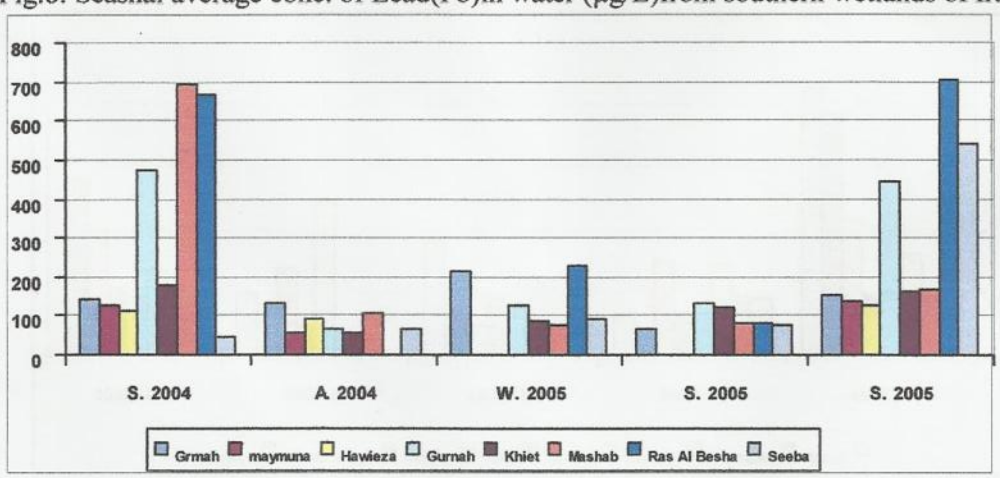

Fig.9: Seasnal average conc. of Zink(Zn) in water (µg/L)from southern wetlands of Iraq

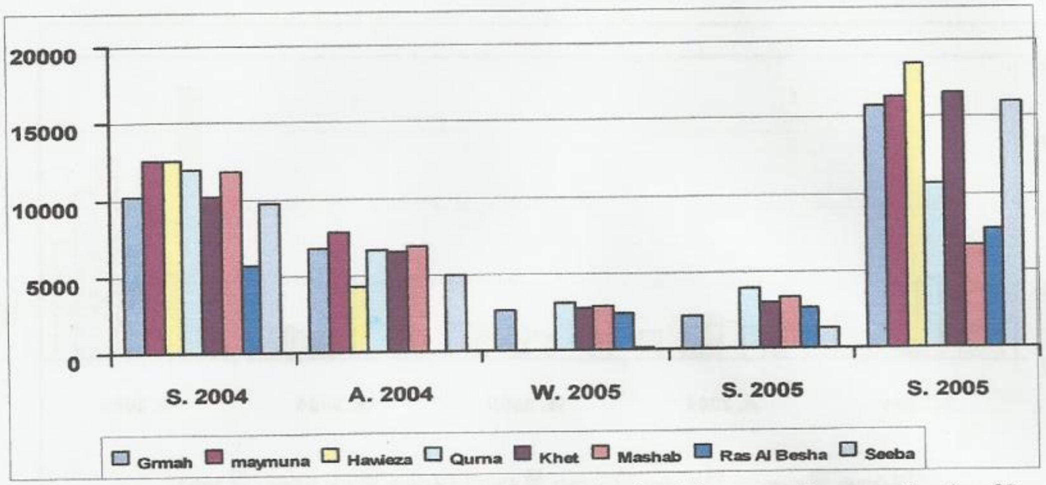

Fig.13: Seasnal average conc. of Iron (Fe)in sediment (μg/gm) from southern wetlands of Iraq

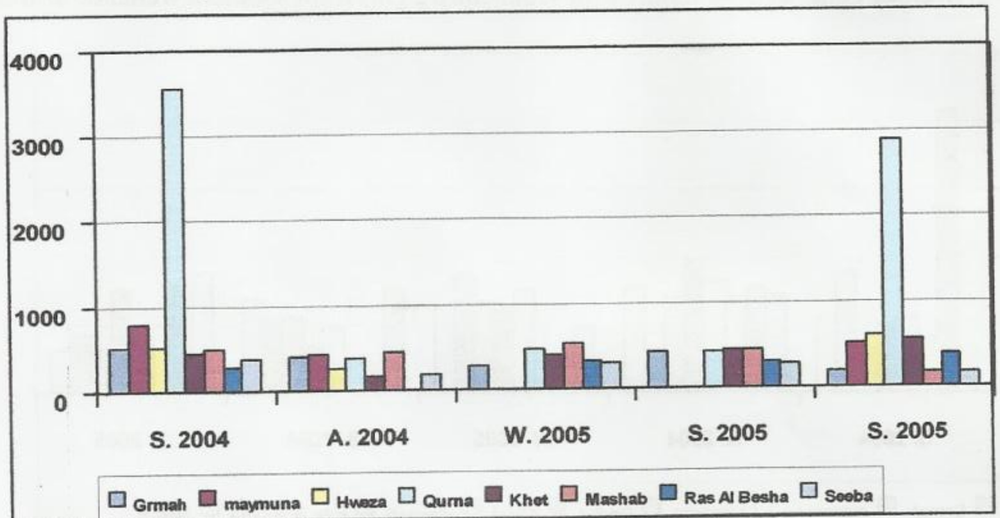

Fig.14 Seasnal average conc. of Manganes (Mn)in sediment (μg/gm) from southern wetlands of Iraq

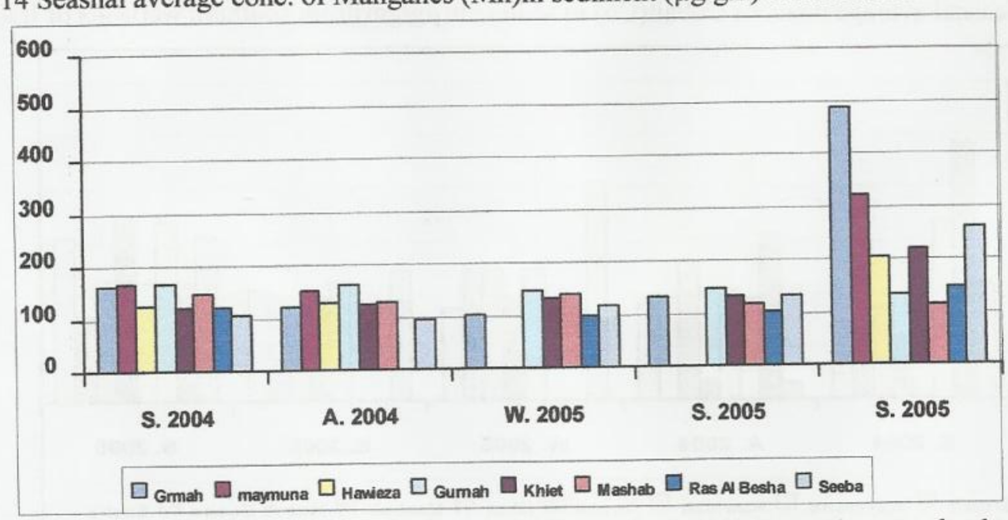

Fig.15: Seasnal average conc. of Nickel(Ni) in sediment (μg/gm)from southern wetlands of Iraq

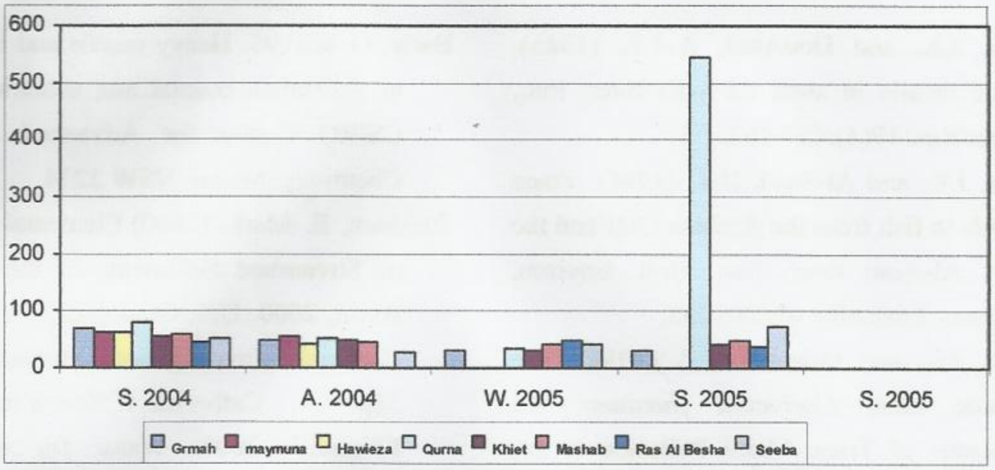

Fig.16: Seasnal average conc. of Lead(Pb)in sediment (μg/gm)from southern wetlands of Iraq

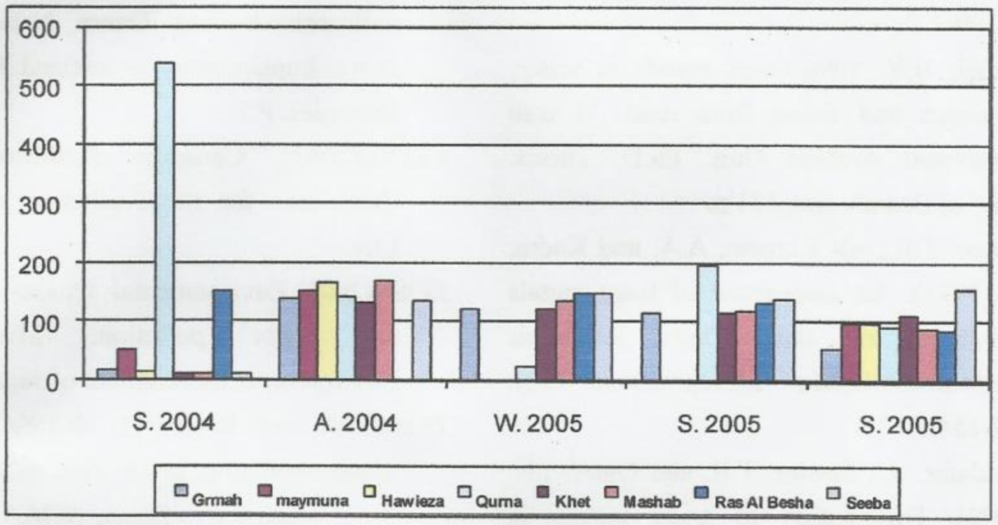

Fig.17: Seasnal average conc. of Zink(Zn) in sediment (μg/gm)from southern wetlands of Iraq

Conclusion

Data reported in this study show variable trends and unclear variations during seasons of study. This could be explain on the basis of alternative inflow of water into dried marshes as well as other sources of effluent, domestic, industrial and atmospheric fall out. Moreover, certain areas contain compounds ready for oxidation by oxygen; this will lead to incorporate the oxidation-reduction mechanisms.

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مستويات وتوزيع المعادن النزرة في مياه مسطحات العراق الجنوبية

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الملخص

أجريت دراسة لتقدير المعادن النزرة: الكادميوم والكوبلت والنحاس والحديد والمنغنيز والنيكل والرصاص والخارصين في مياه مسطحات العراق الجنوبية والمتمثلة باهوا ر الحويزة والوسطي والحمار وشط العرب وكرمة علي وراس البيشة عند شمال الخليج العربي. تم جمع عينات مياه تحت سطحية ورواسب قاعية لفترات موسمية خلال الفترة تموز\2004 إلى تموز\2005. استخلصت المعادن النزرة لكل عينة وتم تقدير تراكيزها بالطرق القياسية وباستخدام جهاز الامتصاص الذري اللهبي. كانت معدلات التركيز العليا للمعادن النزرة في المياه (بوحدات مايكرو غرام\لتر)بمقدار 85.95 (كادميوم) في البيشة، 407.9 (كوبلت) في القرنة، 57.83 (نحاس) في المسحب ، 574.33 (حديد) في الخيط ، 85.34 (منغنيز) في السيبة ، 181.0 (نيكل) في المسحب ، 90.25(رصاص) في البيشة و 702.34((كادميوم) في البيشة. وخلال فصول مختلفة، بينما كانت أعلى معدلات للتركيز في الرواسب (بوحدات مايكوغرام\غم وزن جاف)بمقدار 35.95 ((كوبلت) في الهور الوسطي و 836.46 (نحاس) في الهور الوسطي و 48.69 (نحاس) في الهور الوسطي و 18435.5 (حديد) في الحويزة و 3648.28 (نيكل) في القرنة و 486.95 (نيكل) في كرمة علي و 5435.5 (رصاص) في القرنة و 539.8 (خار صين) في القرنة. تميزت بعض المواقع على شط العرب وهور الحويزة بأنها تستقبل كميات كبيرة من مخلفات منزلية وصناعية وحركة نقل بالزوارق حيث سجلت مستويات عليا من الملوثات بالرواسب كما في راس البيشة عند أعلى شمال الخليج العربي.

كلمات دالة: معادن نزرة، اهوار، رواسب، مياه، شمال غرب الخليج العربي.