

## **ENVIRONMENTAL GEOCHEMISTRY OF HEAVY METALS IN A SEDIMENT CORE OFF BUSHEHR, PERSIAN GULF**

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### **ABSTRACT**

In present study, the geochemistry of a sediment core from the Persian Gulf is investigated. The sources of trace elements (Cu, Zn, Pb, Ni, Cr, Mn) have been investigated by the method of cluster analysis as well as chemical partitioning techniques. Cluster analysis shows that Pb, Cu, Cr and Zn are originated from oil pollution sources taking into account Zn as an oil pollution indicator. Higher concentrations of Mn at depth of 7cm clearly shows the movement of Mn from the lower layer of the sediment core. Considerable amount of Mn, Pb and Cu are found in lithogenous portion. The results of partition studies has revealed the percentile of anthropogenic portion of metals as: *Mn (46%) > pb (40%) > Cu (18%) > Zn (12.8%) > Fe (2.4%) > Cr & Ni (0.03)*. Finally, the concentration of studied metals are compared with those of mean crust and mean world sediments. Though concentrations of a few metals are higher than mean crust and mean world sediments but Cr in spite of its higher concentration is mainly derived from natural resources.

**Key words:** Persian Gulf, geochemistry, sediment, core, metal, pollution, oil

### **INTRODUCTION**

Trace element pollution in aquatic environment sediments caused by industrialization has been reported by many researchers around the world (Al-Masri et al., 2002 and Coker *et al.*, 1995). Human activities have lead to accumulation of toxic metals in the aquatic sediments (Heyvaert *et al.*, 2000 and Sadiq, 1992]. Geochemical studies of sediment are helpful in the assessment of pollution (Farmer, 1991 and Holm, 1988). Most trace metals tend to enrich in the modern organic sediments rather than inorganic sediments. Many researchers have used sediments to study the behavior of metals over time of sedimentation (Bellucci *et al.*, 2003 and Bertolotto *et al.*, 2003). Many sequential extraction and chemical partitioning methods have been developed and applied for determination of metal bonding and pollution detection in particulate phase (Chester and Hughes, 1967 and Karbassi, 1998). It is believed that metals in adsorbed carbonate, sulfide

and organic bonds are more related to pollution and have higher risk of bioavailability and contamination of the environment (Lee and Cundy, 2001 and Karbassi and Amirnezhad, 2004). The occurrence of elevated levels of trace metals especially in the sediments can be a good indication of maninduced pollution and high levels of heavy metals can often be attributed to anthropogenic influences, rather than natural enrichment of the sediment by geological weathering (9). There can be significant temporal and spatial variability in water column concentrations of heavy metal contaminants, which leads to problems in obtaining representative samples (Weis *et al.*, 1992). Sediments, on the other hand, integrate contaminants over time and are in constant flux with the overlying water column. The analysis of heavy metals in the sediments permits detection of pollutants that may be either absent or having low concentrations in the water column (Borretzen and Salbu, 2002 and Davis *et al.*, 1991), and their distribution in coastal sediments provides a record of the spatial and temporal history of pollution in a

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particular region or ecosystem. Heavy metal concentrations in the water column can be relatively low, but the concentrations in the sediment may be elevated. Low level discharges of a contaminant may meet the water quality criteria, but long-term partitioning to the sediments could result in the accumulation of high loads of pollutants (Martine and whitfield, 1983). Once heavy metals are discharged into coastal waters, they rapidly become associated with particulates and are incorporated in bottom sediments (Hanson *et al.*, 1983). The accumulation of metals from the overlying water to the sediment is dependent on a number of external environmental factors such as pH, Eh, ionic strength, anthropogenic input, the type and concentration of organic and inorganic ligands and the available surface area for adsorption caused by the variation in grain size distribution (Davis *et al.*, 1991). The objectives of this paper are to determine the origin, distribution and levels of sediment contamination by heavy metals in the Persian Gulf.

## MATERIALS AND METHODS

One 4 cm diameter gravity core was collected in the station located at 28° 50' latitude and 50° 43' longitude (off Bushehr coast) in the year 1996. The core was stored vertically at 4° C and sampled at 1cm intervals in the laboratory. The samples were freeze dried and 0.5 g of each sample, in triplicate, were placed in Teflon beakers containing 10 ml HNO<sub>3</sub>. The mixture was heated to near dryness and allowed to cool before 7 ml of HF was added. Then the mixture was heated to near dryness and allowed to cool. 10 ml of aquaregia was added to each sample and heated to near dryness. The samples were allowed to cool to room temperature and were then filtered. The filtrates were transferred to 50 ml volumetric flasks and made up to mark with 1N HCl. The metal determinations of the solutions were performed on a UNICAM atomic absorption spectrometer using the calibration curve method. The samples were analyzed for Ni, Cu, Cr, Pb, Mn, Fe, Zn, Al, Ca. Partition chemical analysis was done according to the of method described by Basaham and Al- Lihaibi (1993). One gram of each dry samples were taken in 250 ml Erlenmeyer flasks,

and 10 ml 0.53N HCl was added before they were shaken for 30 minutes. Duplicate samples were made for each batch. The accuracy and precision of the atomic absorption analyses and the possible loss of trace elements during the digestion steps was checked by the use of marine sediment standard MESS-1 (Table 1).

## RESULTS

The results of heavy metal analysis are shown in Table 2. The obtained data from Persian Gulf are compared with the means of metal concentrations from earth crust as well as world sediments in Table 3. Though concentration of a few metals are higher than mean crust and mean world sediment but Cr inspite of its higher concentration is mainly derived from natural resources. In order to know about the inter relationship among trace metals and also their origin, correlation coefficient were computed (Table 4). Finally correlation coefficient values were converted into a dendrogram using cluster analysis (Fig. 1). The cluster analysis is composed of four distinct clusters which provides visual means for easier interpretation of data. Chemical partitioning studies can be carried out in many ways (Foster and Wittman, 1981). A few of the methods (Chester and Hughes, 1967) provides various chemical bonds of metals with different sedimentary phases while other methods (Basaham and Al-Lihaibi, 1993) distinguishes between lithogenous and non-lithogenous sources. In the present study the later method (Basaham and Al-Lihaibi, 1993) was used and the results of chemical partitioning are tabulated in Table 5.

Table 1: Published and obtained analytical results of MESS-1

Element	MESS-1	This Study
Mn (ppm)	513 ± 25	488.7± 2.4
Ni (ppm)	29.5 ± 2.7	29.7± 0.359
Zn (ppm)	191± 17	183.3 ±1.011
Cu (ppm)	25.1± 3.8	26.0 ± 0.001
Pb (ppm)	34± 6.1	41.7 ± 1.76
Cr (ppm)	71 ± 11	70± 5.8
Fe (%)	3.1± 0.25	3.1± 0.37
Al (%)	5.84 ± 0.38	5.8± 0. 6
Ca (%)	0.481± 0.064	0.45± 0.02

Table 2: Metal concentrations and LOI in sediment core from Persian Gulf

Depth (cm)	Cu (ppm)	Pb (ppm)	Cr (ppm)	Zn (ppm)	Ni (ppm)	Mn (ppm)	Fe (%)	Al (%)	Ca (%)	LOI (%)
0-1	22.4	43.9	127.1	63.0	108.9	458.7	2.6	4.17	14.87	25.60
1-2	19.4	46.1	122.8	59.7	101.1	466.5	2.5	3.97	13.62	24.25
2-3	22.8	66.6	143.8	59.0	130.8	480.6	2.6	3.71	15.47	23.70
3-4	23.6	47.6	130.4	52.7	110.0	487.6	2.4	4.29	14.60	17.40
4-5	18.0	34.4	123.5	49.4	110.7	513.6	2.6	3.65	11.52	22.90
5-6	19.3	38.4	144.6	49.4	103.4	506.2	2.9	3.72	12.70	24.20
6-7	21.4	51.7	166.2	46.1	105.2	490.6	2.6	5.27	19.19	23.40
7-8	31.5	80.6	181.9	65.9	99.2	466.7	2.5	4.67	16.24	25.70
8-9	20.1	57.6	109.2	43.3	106.2	443.1	2.8	4.66	17.10	23.80
9-10	23.2	43.7	140.9	44.9	102.4	459.6	2.4	4.30	15.50	22.45
10-11	20.8	45.2	126.2	46.6	106.3	456.9	2.4	3.48	13.50	19.90
11-12	19.42	41.7	136.5	43.6	100.6	432.4	2.5	3.48	12.95	23.20
12-13	21.0	41.4	124.5	50.5	102.7	445.4	2.4	3.59	14.64	22.90
13-14	20.3	37.9	125.7	50.1	103.2	438.1	2.4	4.40	12.28	19.25
14-15	20.3	33.5	114.9	52.8	103.9	441.8	2.5	4.83	13.30	24.00
15-16	19.1	38.7	125.8	51.8	102.8	449.6	2.5	5.01	14.30	23.40
16-17	18.4	43.4	121.6	52.2	103.2	455.7	2.3	5.12	16.15	24.00
17-18	20.4	42.7	117.0	52.5	113.6	447.5	2.7	5.00	12.38	24.40
18-19	21.1	36.5	145.2	53.8	112.0	437.7	2.7	5.20	15.83	23.70
19-20	22.4	44.0	124.2	48.5	101.1	472.3	2.7	5.20	15.90	23.20
20-21	17.5	39.0	140.2	46.6	96.7	421.6	2.5	4.70	14.60	22.40
21-22	15.8	44.0	133.0	48.8	97.81	402.1	2.5	4.70	2.30	23.60
22-23	20.1	44.0	118.4	49.5	100.6	419.4	2.6	4.80	14.44	24.10
23-24	16.9	45.7	109.6	43.0	100.2	430.9	2.4	4.70	13.88	18.80
24-25	18.3	41.8	106.8	46.0	97.8	402.8	2.4	4.40	14.70	24.00
25-26	31.0	48.2	160.5	65.2	133.4	419.7	2.7	5.20	15.56	24.10
26-27	18.4	38.3	125.4	47.8	107.1	448.5	2.5	4.30	13.48	24.40
27-28	21.8	46.3	132.8	34.9	117.4	509.2	2.6	4.70	15.44	22.30
28-29	20.6	38.8	128.9	34.2	106.9	479.5	2.7	4.50	15.30	24.20
29-30	22.0	36.3	139.6	34.6	102.8	486.0	2.7	4.30	15.17	24.20
31-33	18.9	33.5	123.3	36.0	103.4	472.7	2.6	4.30	14.48	23.90
34-36	21.2	39.9	139.6	36.3	112.2	484.4	2.6	4.50	15.50	23.90
37-39	19.5	39.7	124.4	34.9	98.0	473.3	2.5	4.40	13.50	23.40
40-44	19.5	37.9	118.2	29.7	103.8	459.5	2.2	4.40	11.15	24.00
45-49	24.8	64.0	118.5	44.5	95.8	455.4	2.2	2.90	11.96	24.20
50-54	24.1	53.3	126.2	49.1	101.1	446.6	2.2	2.07	9.35	24.00
Min.	15.5	33.5	106.8	34.2	96.7	402.1	2.2	2.07	9.35	17.40
Max.	31.5	80.6	181.9	65.9	133.4	513.6	2.92	5.27	19.19	25.70
Mean	20.97	44.6	130.5	47.7	105.7	457.3	2.52	4.35	14.24	23.24
S.D.	3.22	9.72	15.69	8.74	8.16	27.73	0.16	0.68	1.84	1.76

Table 3: Metal concentrations of Mean Crust, Mean World Sediment and sediment core from Persian Gulf

Element	Mean Crust	Mean World Sediments	Mean Sediment Core(this study)
Cu(ppm)	50	33	28.50
Pb(ppm)	14	19	60.64
Cr(ppm)	100	-	177.28
Zn(ppm)	75	95	64.74
Ni(ppm)	80	52	143.55
Mn(ppm)	950	770	620.35
Fe(%)	4.10	4.10	3.44
Al(%)	8.20	7.20	5.93
Ca(%)	4.10	6.60	14.24

Table 4: Correlation coefficients amongst metal concentration and LOI in a sediment core from Persian Gulf

Element	Cu	Mn	Ni	Pb	Zn	Cr	Fe	Al	Ca	LOI
Cu	1.000									
Mn	0.128	1.000								
Ni	0.283	0.240	1.000							
Pb	0.634	0.027	0.120	1.000						
Zn	0.442	-0.232	0.320	0.411	1.000					
Cr	0.613	0.246	0.289	0.410	0.336	1.000				
Fe	0.244	0.331	0.322	0.044	0.122	0.595	1.000			
Al	-0.052	-0.145	0.150	-0.186	0.062	0.162	0.498	1.000		
Ca	0.233	0.148	0.226	0.234	0.101	0.419	0.812	0.616	1.000	
LOI	0.183	-0.015	0.027	0.140	0.130	0.191	0.084	0.080	0.080	1.000

Table 5: Partition chemical (anthropogenic portion of metals) analysis of sediment core from Persian Gulf

Depth (cm)	Cu (ppm)	Pb (ppm)	Cr (ppm)	Zn (ppm)	Ni (ppm)	Mn (ppm)	Fe (%)
0-1	4.29	18.47	0.035	17.24	0.031	224.6	0.08
1-2	3.44	18.49	0.035	7.13	0.031	212.1	0.08
2-3	3.33	17.92	0.035	5.12	0.031	210.9	0.07
3-4	4.88	18.56	0.035	8.15	0.031	206.6	0.08
4-5	3.27	17.59	0.035	3.03	0.031	194.8	0.05
6-7	4.97	17.84	0.035	5.09	0.031	219.1	0.08
8-9	2.70	16.64	0.035	4.08	0.031	203.1	0.06
10-11	3.47	18.69	0.035	5.84	0.031	213.5	0.06
13-14	3.12	16.81	0.035	4.46	0.031	187.6	0.05
16-17	4.22	18.18	0.035	6.28	0.031	208.2	0.06
20-21	3.85	17.45	0.035	5.102	0.031	210.1	0.07
24-25	3.42	18.43	0.035	4.405	0.031	217.8	0.08
29-30	4.27	18.38	0.035	16.90	0.031	211.3	0.07
34-35	3.97	17.99	0.035	3.46	0.031	209.9	0.06
39-40	3.58	17.15	0.035	3.29	0.031	208.9	0.05
44-45	3.35	18.04	0.035	2.38	0.031	215.4	0.04
49-50	3.60	17.25	0.035	3.77	0.031	208.8	0.06
53-54	4.19	18.08	0.035	4.19	0.031	216.3	0.05
Mean	3.72	17.88	0.035	6.10	0.031	209.9	0.06

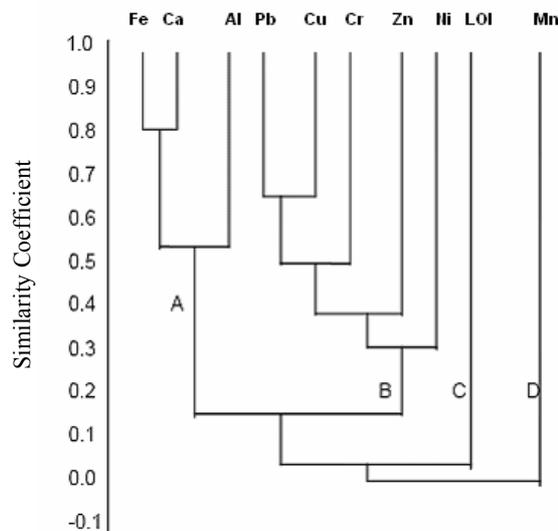


Fig. 1: Dendrogram of metals & LOI in sediment core off Bushehr

## DISCUSSION

High concentrations of Cu, Pb, Cr, Zn, Ni were found at depths of 8 cm and 26 cm. The highest concentrations of Ca, Fe and Al were measured at depth of 7 cm. Mn showed the highest value at depth of 5 cm. Many environmental geochemistry studies report higher concentration of trace metals in surface layers than deeper ones (Bellucci *et al.*, 2003 and Bertolotto *et al.*, 2003) due to development of industries and other man activities. It is well known that Mn is a mobile trace metal that has great affinity to mix up with Oxygen (Karbassi, 2004). Thus higher concentrations of Mn at depth of 7cm clearly shows the movement of Mn from the lower layer of the sediment core. However, due to anoxic conditions prevailing at the bottom of the Persian Gulf (Karbassi, 1998), some of Mn oxides are remobilized into the overlying waters. As shown in Table 3 concentrations of Pb, Cr and Ni are well above the mean concentrations of mean crust and mean world sediments. The lower concentrations of Fe and Al in comparison with mean crust and mean world sediments in indicative of significant geological differences in the Persian Gulf, in spite of oil pollution. Dendrogram in its "A" cluster shows that Fe and Ca are derived from lithogeneous source as they are linked to Al. In cluster "C" and "D" LOI and Mn respectively are linked with cluster "A" and "B" at a very insignificant similarity coefficient. Zinc as an indicator of oil pollution in linked with Pb, Cu, Cr and Ni in cluster "B" suggesting similar source for these elements. Further, lithogenous and anthropogenic portions of trace metals were assessed by chemical partitioning studies. As show in Table 5, considerable amount of Mn, Pb and Cu are found in lithogenous portion. Though Cr concentration is well above the mean crust and mean world sediments (Table 3) but a very small portion of Cr is found in anthropogenic fraction. This might be indicative of presence of Cr geological unit in the area of study. Such scattered findings has been reported by a few researchers (Bowen, 1979; Foster and Wittman, 1981 and Karbassi, 1998). The results of partition studies can be grouped as the percentile of anthropogenic

portion to total metal concentrations in the following pattern:

Mn (46%)> pb (40%)> Cu (18%)> Zn (12.8%)> Fe (2.4%)> Cr & Ni(0.03).

## REFERENCES

- Al-Masri, M.S., Aba, A., Khalil, H. and Al-Hares, Z. Sedimentation rates and pollution history of a dried lake: Al-Oteibeh Lake. *Science of the Total Env.* **293**(1-3), 177-189, 2002.
- Basaham, A. & Al-Lihaibi, S. S.. Trace elements in sediments of the western gulf. *Mar. Poll. Bull.* **27**, 103-107, 1993.
- Bellucci, L.G., El Moumni, B., Collavini, F., Frignani, M. and Albertazzi, S. Heavy metals in Morocco Lagoon and river sediments. *Journal de Phys.* **IV 107 (1)**, 139-142, 2003.
- Bertolotto, R.M., Tortarolo, B., Frignani, M., Bellucci, L.G., Albanese, S. and Cuneo, C. Heavy metals in coastal sediments of the Ligurian sea off Vado Ligure. *Journal de Phys.* **IV 107(1)**, 159-162, 2003
- Borretzen, P. and Salbu, B. Fixation of Cs to marine sediments estimated by a stochastic modeling approach. *Journal of Environmental Radioactivity.* **61**(1), 1-20, 2002.
- Bowen, H.J.M.. *Environmental chemistry of the elements.* Academic press, London, N.Y., Toronto, 333, 1979.
- Chester, R., and Hughes R. M. A chemical technique for the separation of ferromanganese minerals, carbonate minerals and adsorbed trace elements from Pelagic Sediments, *Chem. Geol.* **2**, 249-262, 1967.
- Coker, W.B., Kettles, I.M. and Shilts, W.W. Comparison of mercury concentrations in modern lake sediments and glacial drift in the Canadian Shield in the region of Ottawa/Kingston to Georgian Bay, Ontario, Canada: *Water, Air and Soil Poll.* **80**, 1025-1029, 1995.
- Davis, C.A. Tomlinson, K. & Stephenson, T. Heavy metals in River tees estuary sediments. *Environ. Technol.* **12**, 961-972, 1991.
- Farmer, J.G. The perturbation of historical pollution records in aquatic systems: *Environmental Geochemistry and Health.* **13**(2), 76-83, 1991.
- Forster, U. & Wittman, G. *Metal pollution in the aquatic environment.* 2nd revised Edn., Springer-verlag N.Y., 110-270, 1981
- Heyvaert, A. C., Reuter, J. E., Sloton, D. G., & Goldman, C. R. Paleo-limnological reconstruction of historical atmospheric lead and Hg deposition at lake Tahoe, California-Nevada. *Environ. Sci. Tech.* **34**, 3588-3597, 2000.
- Karbassi, A. R. (1998) Geochemistry of Ni, Zn, Cu, Pb, Co, Cd, V, Mn, Fe, Al & Ca in sediments of North Western part of the Persian Gulf. *Intl. J. Env. Studies,* **54**, 205-212.
- Karbassi, A. R. & Amirnezhad, R. (2004) Geochemistry of heavy metals and sedimentation rate in a bay adjacent to the Caspian Sea. *Intl. J. Env. Sci. Tech.,* **1** (3), 199-206.

- Lee, S.V. and Cundy, A.B. Heavy metal contamination and mixing processes in sediments from the Humber Estuary, Eastern England. *Estuarine Coastal and Shelf Sci.* **53** (5), 619-636, 2001.
- Martine, J.M. and Whitfield, M. The significance of river input of chemical elements to the ocean. In: Wong, C.S., Boyle, E., (1983). Bruland, K.W., Burton, J.D. and Goldberg, E.D. Ed. *Trace metals in sea water*. Plenum, New York. 265-296.
- Sadiq, M. Toxic metal chemistry in marine environments. 237-241, 1992.
- Weis, D.A., Callaway, A.B. and Gersberg, R.M. Vertical accretion rates and heavy metal chronologies in wetland sediments of the Tijuana Estuary. *Estuaries.* **24** (6A), 840-850, 2001.