

<http://www.pjbs.org>

**PJBS**

ISSN 1028-8880

**Pakistan  
Journal of Biological Sciences**

**ANSI***net*

Asian Network for Scientific Information  
308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

## Heavy Metals Pollution and Speciation in Sediments of Southern Part of the Caspian Sea

<sup>1</sup>M. Saeedi and <sup>2</sup>A.R. Karbassi

<sup>1</sup>Water and Environmental Research Laboratory, Department of Hydraulics and Environment, College of Civil Engineering, Iran University of Science and Technology, P.O. Box 16765-163, Narmak, Tehran, Iran

<sup>2</sup>Faculty of Energy and Environment, Science and Research Branch, Azad University, Tehran, Iran

**Abstract:** In the present investigation seven surficial sediment samples from southern part of the Caspian Sea were subjected to bulk and chemical partitioning studies. Though concentrations of metals (except for Mn and Cd) falls within the ranges of mean crust and mean sediments, but chemical partitioning data is indicative of pollution in the area of study. Proportions of metals that are presented in high risk fraction follows the pattern of Mn (88%)>Pb (71%)>Cd (61%)>Zn (55%)>Cu (53%)>Ni (35%)>Co (33%). Computed geochemical indices clearly reveal that sediments of coastal area of the Caspian Sea are contaminated with Cd, Mn and Pb to various degrees. Cluster analysis shows the affinity of Cu, Pb, Co and Zn with organics. Presence of considerable amount of Mn in reducible phase is suggestive of anoxic conditions that prevail over the sediments. High concentration of Ca (mean = 15.39%) is indicative of higher productivity in spite of presence of many pollutants in the area of study. Results of the present investigation showed that geochemical accumulation index (I<sub>geo</sub>) could not be effectively used to sediment pollution assessment in marine environment.

**Key words:** Sediment, contamination, metals, I<sub>geo</sub>, Caspian Sea

### INTRODUCTION

Studies on trace elements in sediments can provide useful information in detecting pollution in aquatic environments (Forstner and Wittmann, 1981; Baldi and Bargagli, 1982; Horowitz, 1985; Pagnanelli *et al.*, 2004). Human activities have lead to accumulation of toxic metals in the lake and Bay sediments (Williams 1991; Heyvaert *et al.*, 2000; Yang and Rose, 2003; Karbassi and Amirnezhad, 2004). However, heavy metals are not necessarily fixed permanently to the sediment but may be recycled via biological and chemical agents within sediments and water column (Helling *et al.*, 1990; Linnik, 2001). Therefore, research regarding bulk chemical composition of marine sediments will not yield information on the partitioning of heavy metals among the various components of the sediments (Chester and Hughes, 1967; Gupta and Chen, 1975; Ure and Davidson, 2001). Therefore, considering individual components is useful in interpretation of complex geochemistry of marine sediments. In the present investigation efforts have been made to determination and sequential chemical extraction of heavy metals in order to assess the association of metals with different phases of sediments from southern part of the Caspian Sea.

The Caspian Sea lies below sea level between the Caucasus Mountains and northern Iran. It covers an area of 371000 sq. km, being 1030 km long with the width ranging from 196 to 435 km. Its depth varies between about 25, 780 and 1035 m in the northern, central and southern parts of the lake, respectively. The salinity of water ranges from 4‰ in the northern parts to 13‰ in the southern parts.

There are many rivers flowing into the Caspian Sea via its southern coast through northern part of Iran that are ecologically of significant importance considering the Caspian Sea environment (e.g., SefidRud, Chaloos, Haraz, Babol, Talar, Tadjan and Gorganrud). Many of these rivers are used as transport agents for the disposal of industrial, agricultural and urban wastes. Therefore, it is essential to closely investigate the marine sediments contamination near coastline and river estuaries.

### MATERIALS AND METHODS

Surficial sediment samples were collected by Van Veen grab sampler on 10 March 2002 from near shore southern part of the Caspian Sea in the vicinity of Tadjan River estuary, in Mazandaran Province of Iran (Fig. 1). Through wet sieving, grain size <63 micron were

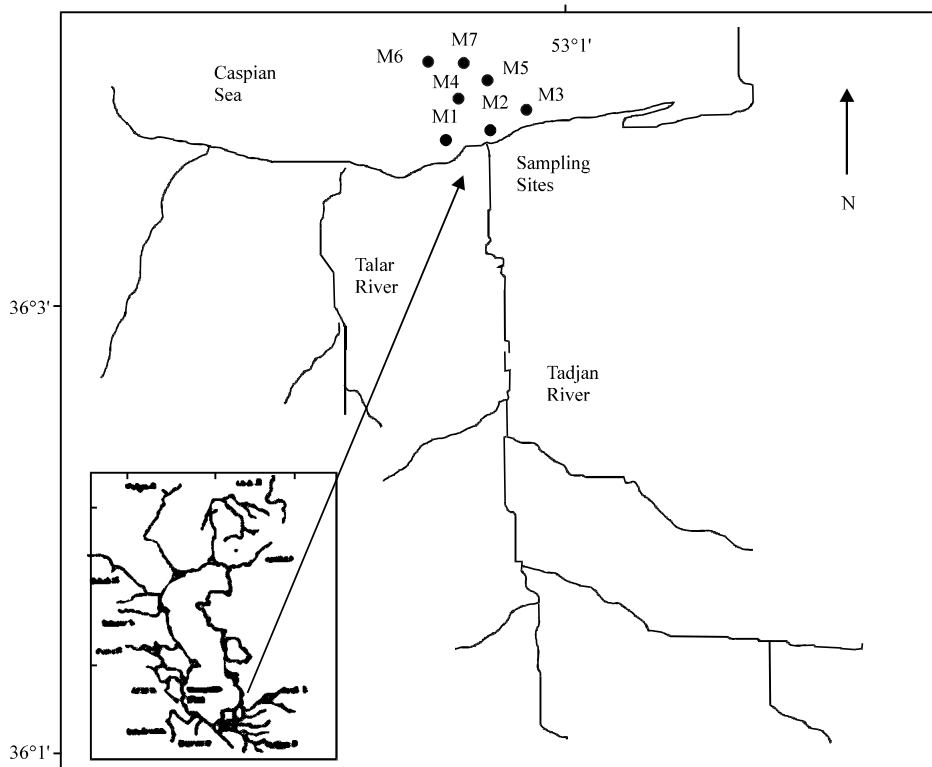


Fig.1: Schematic map showing location of sampling sites

Table 1: Published and obtained data for MESS-1

Element	Published data*	Obtained data
Co	10.8(1.9)	11.90
Cu	25.1(3.8)	26.40
Cd	0.59(0.1)	0.62
Pb	34.0(6.1)	36.70
Mn	513.0(25)	537.30
Ni	29.5(2.7)	31.10
Zn	191.0(17)	182.60
Fe <sub>2</sub> O <sub>3</sub>	4.36(0.025)	4.44
CaO	0.67(0.6)	0.70

\*Marine Analytical Chemistry Standard Program of National Research Council of Canada (April 1990), Values for trace metals are in ppm and for major elements are in%; Standard deviations are given within brackets

separated and used in bulk and sequential chemical partitioning analysis. Samples then were digested with HF-HNO<sub>3</sub>-HClO<sub>4</sub> and made up to volume with 1 N HCl. Chemical partitioning studies were carried out in five steps (Tessier *et al.*, 1979). Acids of AR grade and doubled distilled water were used throughout. Blank and duplicate sample solutions were prepared in a similar way. Elemental (Cd, Cu, Mn, Ni, Pb, Zn and Co) determinations were made on an AAS following EPA-7000s series (USPA., 1986). A standard sample (MESS-1) was used to check the precision of the analyses. Concentrations of the elements were in satisfactory agreement with the reported data (Table 1). Organic matter was estimated by recording

the Loss O Ignition (LOI) of samples for 4 h at 450°C in a muffle furnace (Glasby and Pzefer, 1998). Among the existing clustering techniques, the Weighted Pair Group Method was used (Davis, 1973). To assess trace metal pollution of sediments of the study area, geochemical accumulation index was calculated from the formulae (Forstner *et al.*, 1990):  $I_{geo} = \log_2 [C_n / (1.5 \times B_n)]$ .

Where  $I_{geo}$  is geochemical accumulation index,  $C_n$  is the concentration of metal in sediments and  $B_n$  is concentration of metal in the shale.

## RESULTS AND DISCUSSION

Concentration of heavy metals, Fe and Ca along with organic matter (LOI) is presented in Table 2. Concentrations of Pb, Cd and Zn are higher than mean crust. Copper, Pb, Co, Zn and LOI form cluster A at high similarity coefficients (Fig. 2). Cadmium and Ca form cluster C at a moderate positive similarity coefficient. Therefore, on the basis of similarity coefficients, Cd is originated from calcareous/biogenic sources in the region. High concentration of Ca (mean = 15.39%) is indicative of higher productivity in spite of presence of many pollutants in the area of study. Carbonate fraction which is the product of the environment, reflect the sedimentary

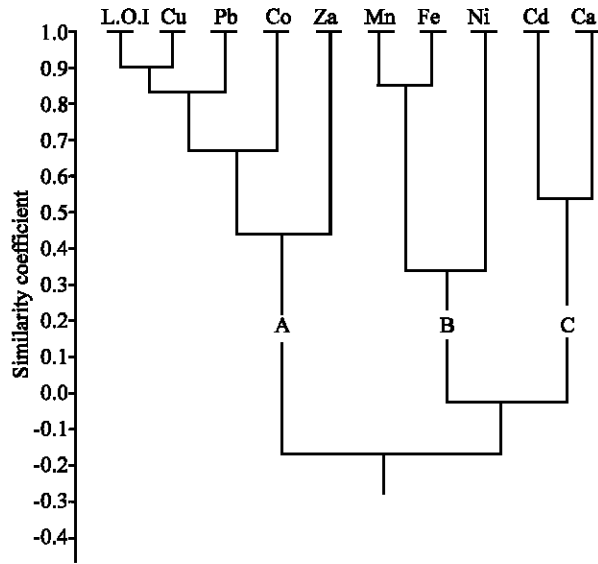


Fig. 2: Dendrogram of elemental concentrations and LOI of surficial sediments from southern part of the Caspian Sea

and depositional conditions prevailing in a basin (Milliman, 1974; Bathurst, 1979). Based on cluster analysis, it might be concluded that elements of cluster A have more tendency towards organic matter. Manganese and to a lower extent Ni are originated from lithogenous source.

As it was pointed out earlier, bulk chemical composition of sediments will not yield information on the partition of elements among various components of sediments and may not be sufficient for pollution detection studies (Chester and Hughes, 1967; Ure and Davidson, 2001). Thus, sequential chemical partition studies on samples M4, M5 and M7 were carried out to understand the association of metals with different bounds in sediments (Table 3). Figure 3 shows the average percentile of metals in different sedimentary phases. More than 50% of Cd, Pb, Mn, Cu and Zn are associated with different phases other than residual. The relative proportion of metals in MgCl<sub>2</sub>-soluble fraction (exchangeable) are: Cd (17%)>Zn (7%)>Mn (5%)>Pb (4%)>Ni (3%)>Cu and Co (0%). All metals (Mn (59%)>Pb

Table 2: Elemental concentrations and loss on ignition of surficial sediments from southern part of the Caspian Sea (mg kg<sup>-1</sup>)

Sample	Cd	Cu	Mn	Ni	Pb	Zn	Co	Fe(%)	Ca (%)	LOI (%)
M1	15.00	18.80	815.60	45.30	69.40	82.80	20.80	2.24	14.25	4.81
M2	9.20	21.50	842.00	42.70	88.00	99.30	23.00	2.23	18.16	5.58
M3	11.50	33.90	845.00	47.20	109.00	117.00	24.20	2.26	16.60	7.70
M4	8.90	15.70	784.90	75.00	60.20	108.00	21.10	2.26	14.16	5.18
M5	16.80	12.70	953.00	73.50	59.00	103.80	15.20	2.32	14.82	4.38
M6	16.80	13.70	865.00	67.30	59.60	80.40	15.40	2.28	14.62	4.76
M7	11.50	12.30	833.00	81.00	41.00	101.20	13.90	2.26	15.15	3.98
Min.	8.90	12.30	784.90	42.70	41.00	80.40	13.90	2.23	14.16	3.98
Max	16.80	33.90	953.00	81.00	109.00	117.00	24.20	2.32	18.16	7.70
Mean.	12.80	18.40	848.40	61.70	69.50	98.90	19.10	2.26	15.39	5.20
St. Dev.	3.37	7.62	52.62	16.13	22.40	13.17	4.16	0.03	1.21	1.21
Mean Crust*	0.10	50.00	850.00	80.00	14.00	75.00	20.00	4.10	4.10	N.A.
Mean sediment**	N.A.	33.00	770.00	52.00	19.00	95.00	14.00	4.60	6.60	N.A.

\*, \*\* Mean Crust and Mean sediment (Bowen, 1979), LOI: Loss on Ignition, NA: Not Announced

Table 3: Sequential chemical extraction of metals from surficial sediments of southern Caspian Sea (mg kg<sup>-1</sup>)

Sample	Extraction step	Cd	Cu	Mn	Ni	Pb	Zn	Co
M4	a	1.7	1.9	46.3	7.5	3.5	5.0	0.5
	b	2.3	2.9	446.0	10.0	21.0	24.5	1.5
	c	1.3	1.9	113.5	7.5	7.5	10.0	0.5
	d	0.5	3.3	71.0	7.6	9.0	15.0	1.2
	r	3.1	5.7	108.2	42.4	19.2	53.5	17.4
M5	a	2.3	1.9	32.5	2.5	2.0	6.7	0.2
	b	3.7	2.5	612.5	6.2	26.0	22.1	4.4
	c	2.4	1.4	140.5	8.5	5.3	11.3	1.6
	d	1.1	3.2	73.5	4.1	7.1	16.4	2.0
	r	7.3	3.7	94.0	52.2	18.6	47.3	7.0
M7	a	2.3	1.0	42.0	10.0	1.0	10.4	0.5
	b	2.6	1.6	475.0	13.4	20.0	22.3	2.9
	c	1.5	1.0	121.0	12.0	5.5	13.5	0.5
	d	0.6	2.9	94.0	10.5	6.2	14.7	1.1
	r	4.5	5.8	101.0	35.1	8.3	40.3	8.9
Mean	a	2.1	1.6	40.3	6.7	2.2	7.4	0.4
	b	2.9	2.3	511.2	9.9	22.3	23.0	2.9
	c	1.7	1.4	125.0	9.3	6.1	11.6	0.9
	d	0.7	3.1	79.5	7.4	7.4	15.4	1.4
	r	4.9	5.1	101.1	43.2	15.4	47.0	11.1

a,b,c and d are metal contents present in MgCl<sub>2</sub>, NaOH/HOAc, NH<sub>2</sub>OH/HCl in 25% HOAc and H<sub>2</sub>O<sub>2</sub>/HNO<sub>3</sub>+NH<sub>4</sub>OAc extractions, respectively and r [r = Bulk-(a+b+c+d)] is metal content in residual

Table 4: Geochemical accumulation indices (Igeo) of metals in sediments from southern part of the Caspian Sea using shale metal contents as background

	Cd	Cu	Mn	Ni	Pb	Zn	Co
Igeo	6	0	0	0	2	0	0
State of pollution	Very Extensive pollution	Clean	Clean	Clean	Moderate Pollution	Clean	Clean

Table 5: Geochemical accumulation indices (Igeo) of metals in sediments from southern part of the Caspian Sea using lithogenous fraction as background

	Cd	Cu	Mn	Ni	Pb	Zn	Co
Igeo	1	0	3	0	2	0	0
State of pollution	Clean-Moderate pollution	Clean	Moderate-extensive Pollution	Clean	Moderate pollution	Clean	Clean

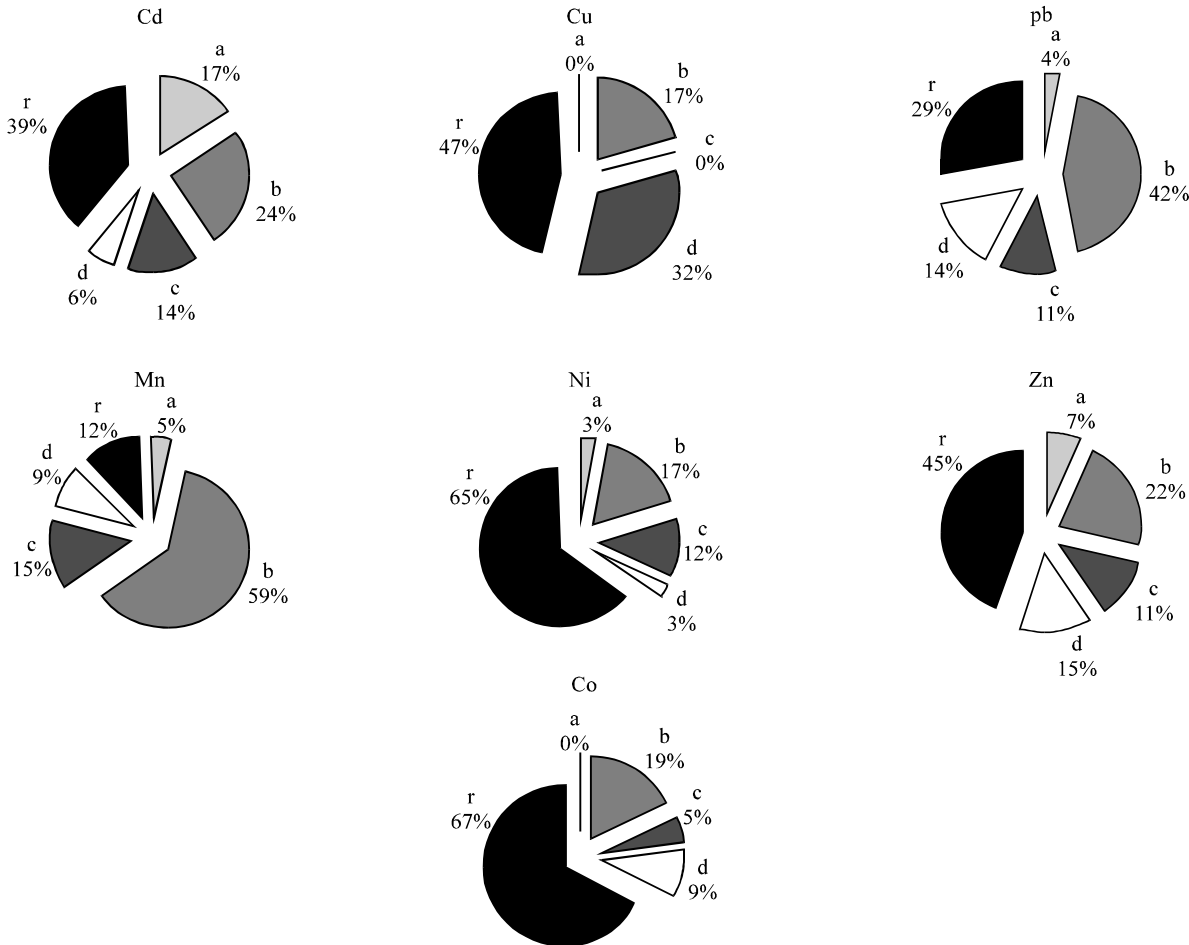


Fig. 3: Percentile of heavy metals in different fractions of surface sediments from southern part of the Caspian Sea (a,b,c and d are metal contents present in  $MgCl_2$ ,  $NaOH/HOAc$ ,  $NH_2OH\cdot HCl$  in 25%  $HOAc$  and  $H_2O_2/HNO_3+NH_4OAc$  extractions respectively and  $r [r = Bulk-(a+b+c+d)]$  is metal content in residual)

(42%)>Cd(24%)>Zn(22%)>Cu(21%)>Co(19%)>Ni(17%) are found at high concentrations in  $NaOH/HOAc$ -soluble fraction (Carbonate fraction bounds). While Cu is absent in  $NH_2OH\cdot HCl$  soluble phase other metals are found at moderate concentrations in this fraction. Presence of Mn sulfides in reducible phase may be indicative of gradual conversion of oxide environment into anoxic one (Karbassi, 1998). Though association between organic matter of sediments and transition elements has been

reported by many workers (De, 1987; Rosental *et al.*, 1986); such affinity is only seen for Cu and to lesser extent for Zn and Pb in the area of study. The results of sequential chemical partitioning studies have been grouped into high risk fraction (steps a, b, c and d) and low risk fraction (step r) in terms of the potential risk of metal bioavailability and probability of non lithogenous source of metals (Fig. 3). Results reveals that the proportions of metals present in High Risk Fraction

(HRF) in the sediments of the study area are: Mn(88%)>Pb(71%)>Cd(61%)>Zn(55%)>Cu(53%)>Ni(35%)>Co(33%). Since Mn is a very mobile element in the environment, therefore, high percentile of Mn in HRF fraction would be expected, but more than 50% of Cd, Pb, Zn and Cu in this fraction could be indicative of contamination. Geochemical accumulation indices (Igeo) were calculated for better assessment of metal pollution extent in sediments of the study area (Table 4). Using shale trace metal contents as the background concentration (Bn in Igeo formulae), sediments from the southern part of the Caspian Sea seems to be contaminated with Cd and Pb (Table 4). However, if an average metal content of sediments in lithogenous fraction is taken as the background concentration (Bn in Igeo formulae) sediments of the study area seems to be highly contaminated with Mn, Moderately contaminated with Pb and is rather contaminated with Cd. Since sediments of the study area contain more Cd than shale and Mn and Pb concentrations are more in shale when compared with contents of Pb and Mn in lithogenous fraction of sediments of the study area; interpretation of the results of trace metal analysis in terms of local background concentrations seems to be more meaningful (Table 5). As pointed out earlier, presence of Mn sulfides in reducible phase could be indicative of anoxic conditions. Under such conditions mobility of Mn increases (Karbassi *et al.*, 2001) and thus more Mn would be concentrated in surface sediments than underlying ones. Therefore accumulation of Mn at surface layers that has resulted in higher Igeo value does not necessarily reflect sediment pollution and may be related to coastal water quality in the study area.

### CONCLUSIONS

A significant part of Mn (88%)>Pb (71%)>Cd (61%)>Zn (55%)>Cu (53%)>Ni (35%)>Co(33%) in sediments of the southern part of the Caspian Sea is associated with high risk fraction. The relative proportion of metals in MgCl<sub>2</sub>-soluble fraction (exchangeable) are: Cd (17%)>Zn (7%)>Mn (5%)>Pb (4%)>Ni (3%)>Cu and Co (0%). All metals Mn (59%)>Pb (42%)>Cd (24%)>Zn (22%)>Cu (21%)>Co (19%)>Ni (17%) are found at high concentrations in NaOH/HOAc-soluble fraction (Carbonate fraction bounds). Results of geochemical accumulation indices revealed that using trace metal contents of shale as the background concentration (Bn in Igeo formulae), yields a different status of environmental pollution. Thus we propose to replace shale metal values with more realistic data such as lithogenous fraction of sediments of the study area in marine environments.

### REFERENCES

- Baldi, F. and R. Bargagli, 1982. Chemical leaching and specific surface area measurements of marine sediments in the evaluation of Hg near Cinnabar deposit. *Marine Environ. Res.*, 6: 69-82.
- Bathurst, R.G.C., 1979. *Carbonate Sediments and Their Diagnosis*, Elsevier Science Ltd., Saint Louis, Missouri, pp: 660.
- Bowen, H.J.M., 1979. *Environmental Chemistry of the Elements*. Academic Press, London, pp: 333.
- Chester, R. and R.M. Hughes, 1967. A chemical technique for the separation of ferromanganese minerals, carbonate minerals and adsorbed trace elements from Pelagic Sediments. *Chem. Geol.*, 2: 249-262.
- Davis, J.C., 1973. *Statistics and Data Analysis in Geology*. Wiley International.
- De, A.K., 1987. *Environmental Chemistry*, Wiley Eastern Ltd., New Delhi, pp: 265.
- Forstner, U. and G.T.W. Wittmann, 1981. *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Berlin.
- Forstner, U., W. Ahlf, W. Calmano and M. Kersten, 1990. *Sediment Criteria Development*, In: *Sediments and Environmental Geochemistry*, (Heling, D., P. Rothe, U. Forstner and P. Stoffers Eds.), Springer Verlag.
- Glasby, G.P. and P. Szefer, 1998. Marine pollution in Gdansk Bay, Puck Bay and the Vistula Lagoon, Poland: An overview. *Sci. Tot. Environ.*, 212: 49-57.
- Gupta, K.S. and K.Y. Chen, 1975. Partitioning of trace metals in selective chemical fractions of near shore sediments, *Environ. Lett.*, 10: 129-159.
- Helling, D., P. Roth, U. Forstner and P. Stoffers, 1990. *Sediments and Environmental Geochemistry*, Springer, New York.
- Heyvaert, A.C., J.E. Reuter, D.G. Sloton and C.R. Goldman, 2000. Paleolimnological reconstruction of historical atmospheric lead and Hg deposition at lake Tahoe, California-Nevada. *Environ. Sci. Technol.*, 34: 3588-3597.
- Horowitz, A., 1985. *A Premier on Sediment-trace Metal Chemistry*, H.S. Geological Survey Water Supply, Paper No. 2277.
- Karbassi, A.R., 1998. Geochemistry of Ni, Zn, Cu, Pb, Co, Cd, V, Mn, Fe, Al and Ca in sediments of north western part of the Persian Gulf. *Intl. J. Environ. Stud.*, 54: 205-212.
- Karbassi, A.R., R. Shankar and B.R. Marymatha, 2001. Geochemistry of shelf sediments off Mulki on the southwestern coast of India and their palaeoenvironmental significance. *J. Geol. Soc. Ind.*, 58: 37-44.

- Karbassi, A.R. and R. Amimezhad, 2004. Geochemistry of heavy metals and sedimentation rate in a bay adjacent to the Caspian Sea. *Int. J. Environ. Sci. Technol.*, 1: 199-206.
- Linnik, P.N., 2001. Bottom sediments of reservoirs as a potential source of secondary pollution of the aquatic environment by heavy metal compounds, *Hydrobiol. J.*, 37: 73-86.
- Milliman, J.D., 1974. *Marine Carbonates*. Springer-Vedrlag, Berlin.
- Pagnanelli, F., E. Moscardini, V. Giuliano and L. Toro, 2004. *Environ. Pol.*, 132: 189-201.
- Rosental, R., G.A. Eagle and M.Y. Orren, 1986. Trace metal distribution in different chemical fractions of near shore marine sediments. *Bison*, 1979. *Estuarine Coastal Shelf Sci.*, 22: 303-324.
- Tessier, A., P.G.C. Campbell and M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, 51: 844-851.
- Ure, A.M. and C.M. Davidson, 2001. *Chemical Speciation in the Environment*. Blackie, Glasgow.
- USPA., 1986. *Test Methods for Evaluating Solid Waste, SW-846*. 3rd Edn., US Environmental Protecting Agency, Washington, DC., USA.
- Williams, T.M., 1991. Sedimentary record of heavy metals in Loch Dee, Galloway since AD 1500, Holocene, 1: 59-68.
- Yang, H. and N.L. Rose, 2003. Distribution of Hg in the lake sediments across the UK, *Sci. Tot. Environ.*, 304: 391-404.