International Journal of Environmental Science & Technology
Vol. 1, No. 4, pp. 307-316, Winter 2005

Geochemistry of two sediment cores from the west coast of India

[1*] *A. R. Karbassi and* [2] *R. Shankar*

[1]*Iran Energy Efficiency Organization, Tehran, Iran*

[2]*Department of Marine Geology, Mangalore University, Mangalore 574199, India*

Abstract

Copper, Pb, Zn, Ni, Co, Mn, AI, Ca, magnetic susceptibility and loss on ignition of sediments from two cores near Mangalore along the western continental shelf of India have been studied. The sediments have high Al and organic matter contents due to the high sedimentation rate and their proximity to river mouths. Down-core variations of elements indicate a decrease of lithogenous component during probably the past few centuries. While abundance of calcareous shells in some zones has lead to the dilution of most of the metals, it appears that Pb and Mn are associated with this phase. Copper, Zn and Fe are associated with organic matter and detrital particles, whereas Ni and Co are predominantly associated with the insoluble fraction. Oxides/hydroxides of Fe and Mn are absent because of the reducing conditions and the high terrigenous influx. Geochemically, Mn and Fe are present in different phases of sediments (in the insoluble fraction and organic matter respectively). The Fe content of one of the cores is positively correlated with magnetic susceptibility.

Key words: *Geochemistry, metals, magnetic susceptibility, core sediments, India*

**Corresponding Author, E-mail: karbassi@iranenergy.org.ir*

Introduction

Geochemical studies of sediment cores are helpful in the assessment of pollution (Holm, 1988), changes in climatic conditions (Faganelli, *et al*., 1987 and Karbassi and Amirnezhad, 2004), rate of sedimentation (Karbassi, 1993), etc. While many geochemical studies have been carried out on the surficial sediments of the western continental shelf of India, not many workers have studied sediment cores (Borole, *et al*., 1982; Dilli, 1986; Borole, 1988; Karbassi, *et al*., 1988 and Manjunatha and Shankar, 1991). Heat and suspended and dissolved substances are factors that can effect the dispersion of trace elements in the waters, and accumulation or mobilization of trace elements in the sediments of aquatic environment (Al-Masri, 2002 and Butman and Bothner, 1998). Upward migration of trace metals may occur because of de-watering due to compaction and unidirectional ion migration, but, to a much greater extent, migration appears to be due to bacterial activity (Cline and Upchurch, 1973; Coker and shilts, 1979 and Karbassi, 1989 and 1996). Most trace metals tend to enrich in the modern organic sediment relative to inorganic sediment . In the present investigation, bulk and partition geochemistry and magnetic susceptibility (Xm) of two sediment cores near Mangalore along the western continental shelf of India (Figure 1) have been studied to understand the geological history of the area, the geochemical nature of sediments deposited at different times and association of base metals with the various constituent phases of sediments.

Materials and Methods

Sediment cores (C2-MJ20 and C3-SM20) were collected from water depths of 20 m off Manjeshwar and Someshwar in 1984 with a Phleger type corer using a polythene tube inside the perspex liner (Shankar, 1988). The sediments are brownish gray clayey silts deposited in the recent times. Shell fragments are present only from 14 to 50 cm. in core C2-MJ20 but absent in the other. Chemical partition studies were carried out in four sequential steps: 1) acetic acid 25% v/v; 2) acetic acid 25% v/v- 0.1M hydroxylamine hydrochloride; 3) 30% H_20_2 "extraction with 1M. ammonium acetate" and 4) hot 50% HCl (Chester and Hughes, 1967; Malo, 1977; Gibbs, 1973; Gupta and Chen, 1975). Bulk elemental concentrations, calcium, loss on ignition (LOI) and Xm were determined and cluster analysis carried out as given in Shankar and Karbassi (1991).

Results

The intra- and inter-core chemical composition is about the same, though Ni and Co contents are higher in core C3-SM20 (Tables 1 and 2). The organic matter content is high (11 to 21%) because of the high sedimentation rate at the core stations that are located close to the coast and to river mouths. From the core bottom upwards, Zn content (in C2-MJ20) and Ni and Ca contents (in C3-SM20) increase whereas Al content decreases (in C3-SM20).These variations reflect a decrease/ decreasing importance of detrital component in the sediments with time (i.e., probably during the past few centuries). The other parameters do not show much down-core variations except at 20-22 cm. in C2-MJ20 and at 1-2 cm in C3-SM20.

Table 1: Elemental concentrations, LOI and Xm of sediment core C2-MJ20

Depth (cm.)	Cu	Zn	Pb (ppm)	Ni	Co	Mn	Fe	Al (%)	LOI	Ca	Xm*
0-1	28	80	32	86	16	380	4.2	6.59	20	3.0	11
1-2	32	74	28	90	18	373	4.2	7.34	21	3.3	9.0
2-3	28	72	29	81	20	378	4.1	7.28	19	2.9	10
3-4	29	78	28	95	19	416	4.5	6.80	16	3.2	13
4-5	29	77	27	97	16	392	4.6	7.55	20	3.5	11
5-6	28	79	30	103	16	406	4.5	7.48	18	3.4	12
8-10	28	77	22	92	17	449	4.4	7.78	18	3.4	11
12-14	28	72	30	86	17	374	4.0	7.81	17	4.4	8.0
16-18	28	65	33	90	16	390	4.2	7.33	19	5.4	8.0
20-22	15	25	43	66	14	355	2.4	3.75	16	13	7.0
24-26	25	49	34	75	15	329	3.8	6.59	19	6.3	9.0
28-30	25	43	32	77	15	378	3.7	6.26	20	6.9	8.0
34-38	25	48	39	73	14	371	3.6	6.31	18	3.2	11
42-46	34	60	34	79	15	316	4.1	7.55	17	3.2	14
50-52	36	62	25	70	14	303	4.4	8.03	18	2.6	18
Min.	15	25	22	66	14	303	2.4	3.75	15	2.6	7.0
Max.	36	80	43	103	20	449	4.6	8.03	21	13	18
Mean	29	67	30	85	16	375	4.1	7.23	18	3.9	11

LOI: Loss on ignition, Xm: Magnetic susceptibility, Min.: Minimum, Max.: Maximum
*10^{-6} emu/g

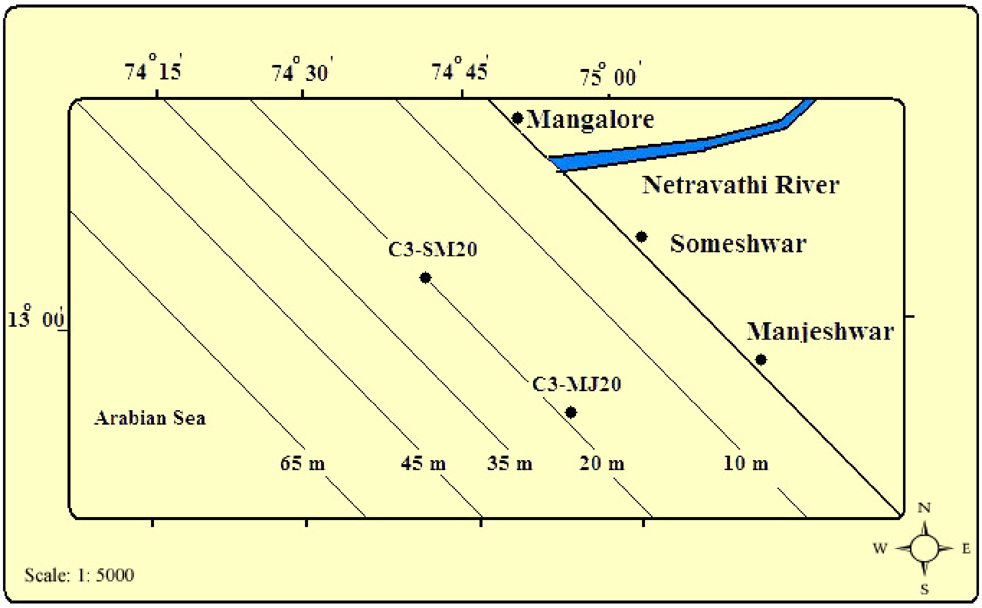

Figure 1: Map showing the locations of Sediment cores and bathymetry of study area

Table 2: Elemental concentrations, LOI and Xm of sediment core C3-SM20

Depth (cm.)	Cu (ppm)	Zn	Pb	Ni	Co	Mn	Fe (%)	Al	LOI	Ca	Xm*
0-1	30	76	32	119	17	341	4.1	6.57	12	3.4	14
1-2	76	107	34	139	22	306	5.0	7.05	15	3.0	14
2-3	33	64	31	133	17	308	4.6	6.72	13	2.8	15
3-4	31	51	33	104	17	376	4.4	6.19	17	3.2	12
4-5	29	55	31	110	22	449	4.2	6.94	16	3.6	13
5-6	36	66	32	128	20	309	4.2	7.42	16	3.2	15
8-10	40	75	27	142	21	308	4.9	7.37	14	2.8	12
12-14	43	78	34	147	23	275	4.9	8.25	19	2.4	11
16-18	38	73	32	133	25	318	4.5	7.75	20	3.0	13
20-22	37	69	29	130	25	326	4.8	7.48	17	2.8	13
24-26	36	66	21	119	25	350	4.5	7.54	14	2.4	13
28-30	39	69	28	122	27	340	5.4	8.17	16	2.6	15
34-38	37	64	26	110	27	331	4.4	7.24	11	2.6	15
42-46	36	62	29	110	27	333	4.1	7.09	17	2.5	19
Min.	29	51	21	104	17	275	4.1	6.19	11	2.4	11
Max.	76	107	34	147	27	449	5.4	8.25	20	3.6	19
Mean	39	68	30	125	23	334	4.6	7.27	16	2.9	14

LOI: Loss on ignition, Xm: Magnetic susceptibility, Min.: Minimum, Max.: Maximum
*10^{-6} emu/g

Table 3: Correlation coefficients for cores C2-MJ20 and C3-SM20

	Cu	Zn	Pb	Ni	Co	Mn	Fe	Al	LOI	Ca	Xm
Cu	1.00	0.96	0.25	0.51	0.15	-0.43	0.51	0.19	0.11	-0.17	0.06
Zn	0.64	1.00	0.21	0.72	0.19	-0.57	0.59	0.37	0.20	-0.25	0.11
Pb	-0.69	-0.77	1.00	0.26	-0.49	-0.14	-0.04	-0.21	0.33	0.51	0.42
Ni	0.31	0.83	-0.56	1.00	-0.07	-0.74	0.57	0.52	0.46	-0.25	0.24
Co	0.23	0.65	-0.51	0.55	1.00	-0.06	0.27	0.67	0.06	-0.60	0.22
Mn	-0.19	0.49	-0.36	0.71	0.52	1.00	-0.39	-0.43	-0.42	0.56	-0.07
Fe	0.81	0.89	-0.84	0.73	0.45	0.31	1.00	-0.13	-0.31	-0.44	0.16
Al	0.88	0.77	-0.80	0.52	0.35	0.10	0.89	1.00	0.49	-0.58	0.42
LOI	0.20	0.17	-0.22	0.05	0.09	-0.11	0.19	0.14	1.00	-0.39	0.39
Ca	-0.84	-0.80	0.67	-0.49	-0.40	-0.15	-0.87	-0.88	-0.28	1.00	-0.04
Xm	0.72	0.31	-0.41	0.00	-0.13	-0.33	0.51	0.49	-0.04	-0.59	1.00

Note: values on the upper and lower matrix correspond to sediment cores C3-SM20 & C2-MJ20, respectively.

Variations at these zones are due to the relative proportions of detrital and biogenic (calcareousshells) components as shown below: The 20-22 cm. zone (C2-MJ20) is characterized by high Ca content and therefore, by abundance of calcareous shells; because of dilution by calcareous shells, the metal contents are low. However, Pb content is high because it seems to be partially associated with calcareous shells. This is borne out by the high positive correlation between Ca and Pb (Table 3) and their clustering together (Figures 2 and 3). The 1-2 cm zone in C3-SM20, because of higher detrital input, has relatively low Ca and high metal contents except for Mn. The Mn content is low because it is partially associated with calcareous shells (Figures 2 and 3). For the same reason, Mn and Ca show positive correlation (0.56), cluster together, and Mn and Al are negatively correlated (-0.43). In core C2-MJ20, all the metals except Pb, are negatively correlated with Ca (Table 2). Lead and Ca, in turn, are negatively correlated with Al, whereas Mn is mildly correlated and the other metals positively correlated with Al, thus showing the association of Pb with calcareous shells and that of other metals with detrital particles. Inter-parametric correlations for C3-SM20, however, show some differences: Except Pb and Mn, all the other metals are negatively correlated with Ca, though Ca-base metal correlation coefficients are not high when compared to C2-MJ20. Because of their positive correlation with Ca, Pb and Mn are thought to be associated with calcareous shells. Positive correla-

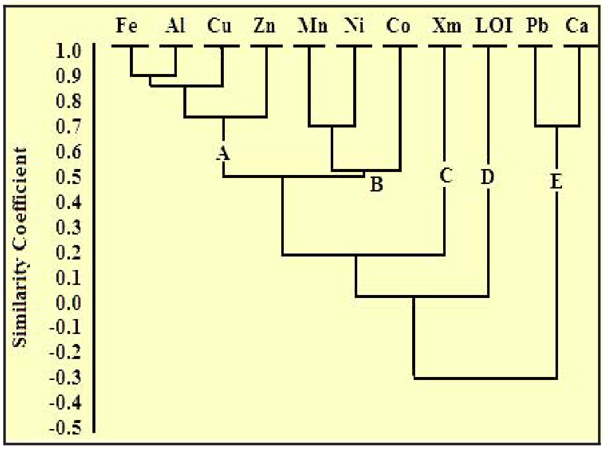

Figure 2: Dendrogram of geochemical and physical parameters of sediment core C2-MJ20

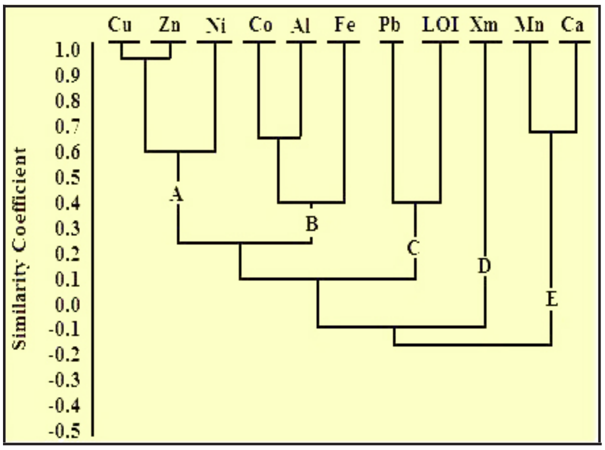

Figure 3: Dendrogram of geochemical and physical parameters of sediment core C3-SM20

tion of the other metals (except Pb, Mn and Ca) with Al (and negative correlation with Ca) indicates that they are associated with detrital particles. partition studies (Figure 4a-4n) show that Cu, Ni and Co are neither present as adsorbed species nor are associated with calcareous shells, as they are not leached out in step 1. Copper and Zn are associated with organic matter and detrital phases of sediments to various degrees, but more with organic matter in core C2-MJ20. Nickel and Co are predominantly associated with the insoluble fraction and only smaller proportions are found in the organic matter and resistant fractions. Because about 21% of the total Pb content is leached out in step 1, and because of its positive correlation with Ca, it appears that this proportion of Pb is associated with calcareous shells and is not present as adsorbed species. The rest is present predominantly in organic matter and insoluble fraction and to a lesser extent in the resistant fraction. Iron and Mn (besides other metals) are not leached out by hydroxylamine hydrochloride in core C3-SM20 indicating the absence of Fe-Mn oxides/hydroxides, which is related to the anoxic conditions and high terrigenous input from the Netravathi river (Figure 1). However, small proportions of Fe and Mn are present as oxides/hydroxides in core C2-MJ20. While Mn predominantly occurs in the insoluble fraction and to a smaller extent as adsorbed species and in organic matter and the resistant fraction, Fe is predominantly associated with organic matter and smaller proportions are present in the insoluble fraction and as adsorbed species. Geochemically, therefore, Fe and Mn are present in different phases of sediments. Although significant proportions of metals are removed in the H_20_2 leach, they are not significantly correlated with organic matter. Magnetic susceptibility was studied to know the correlation between Xm and Fe. Iron content correlates (0.51) with Xm in core C2-MJ20 but not in the other core. The lowest Xm value at 20-30 cm interval could be due to dilution by shells (Table1 and 2).

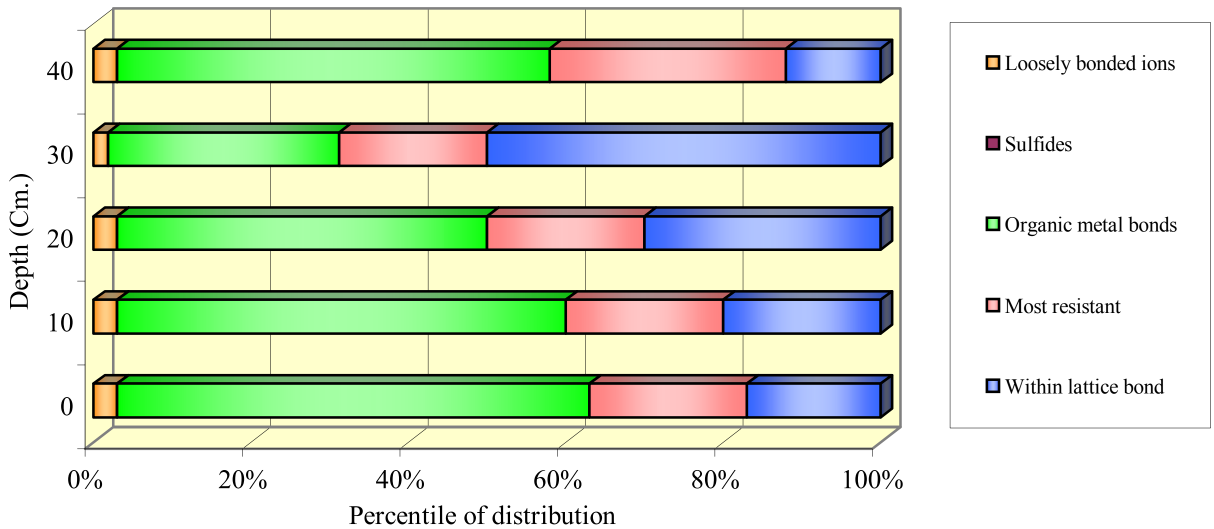

Figure 4a: Distribution of Cu in various sedimentary phases of sediment cores (Refers to sediment core C2-MJ20)

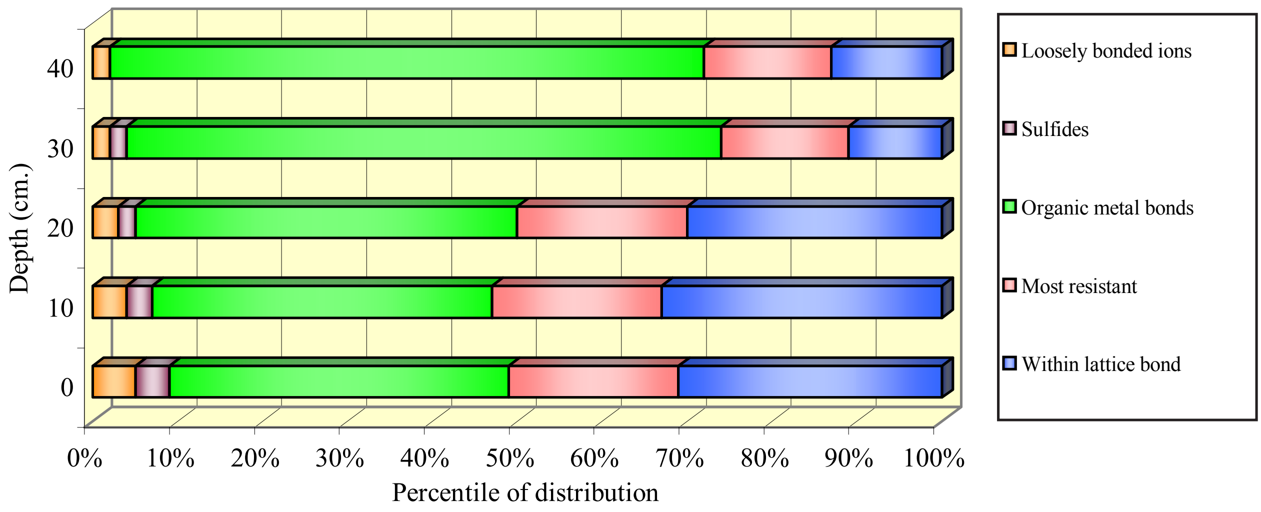

Figure 4b: Distribution of Zn in various sedimentary phases of sediment cores (Refers to sediment core C2-MJ20)

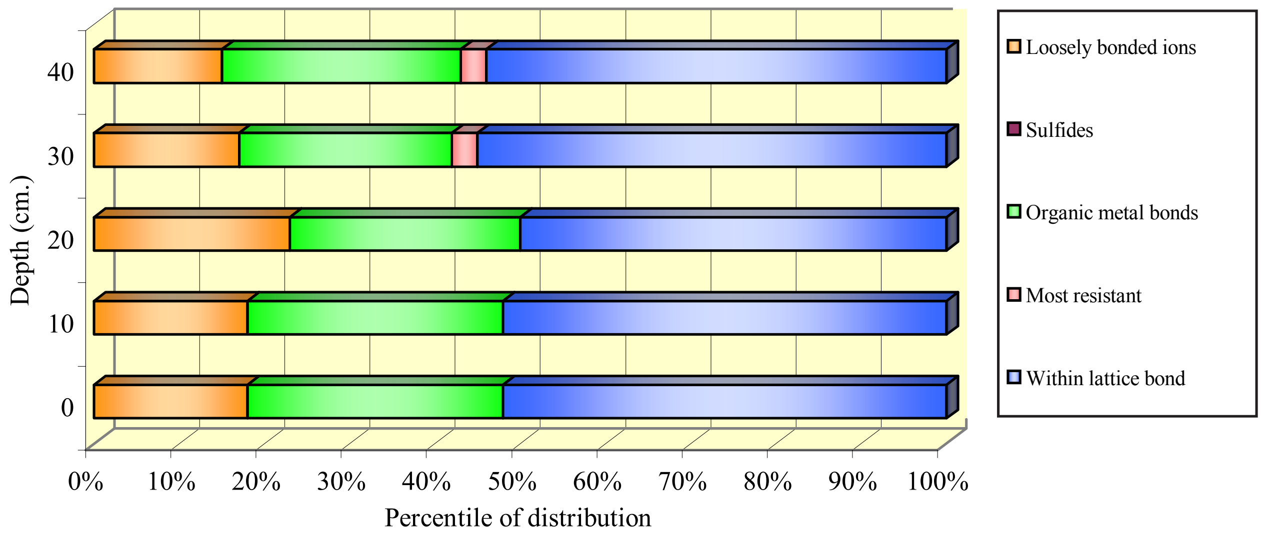

Figure 4c: Distribution of Pb in various sedimentary phases of sediment cores (Refers to sediment core C2-MJ20)

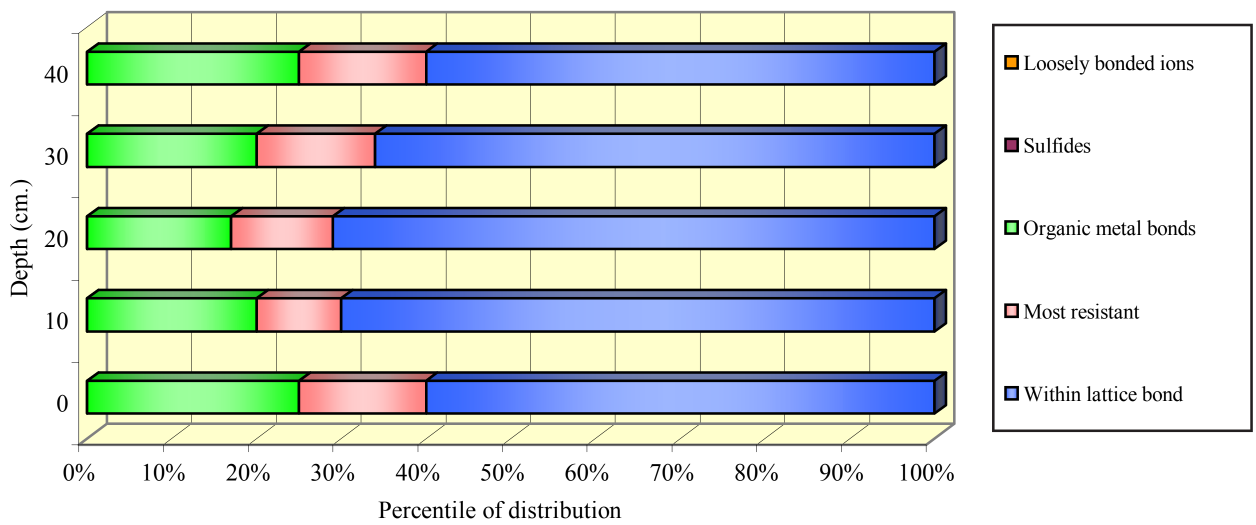

Figure 4d: Distribution of Ni in various sedimentary phases of sediment cores (Refers to sediment core C2-MJ20)

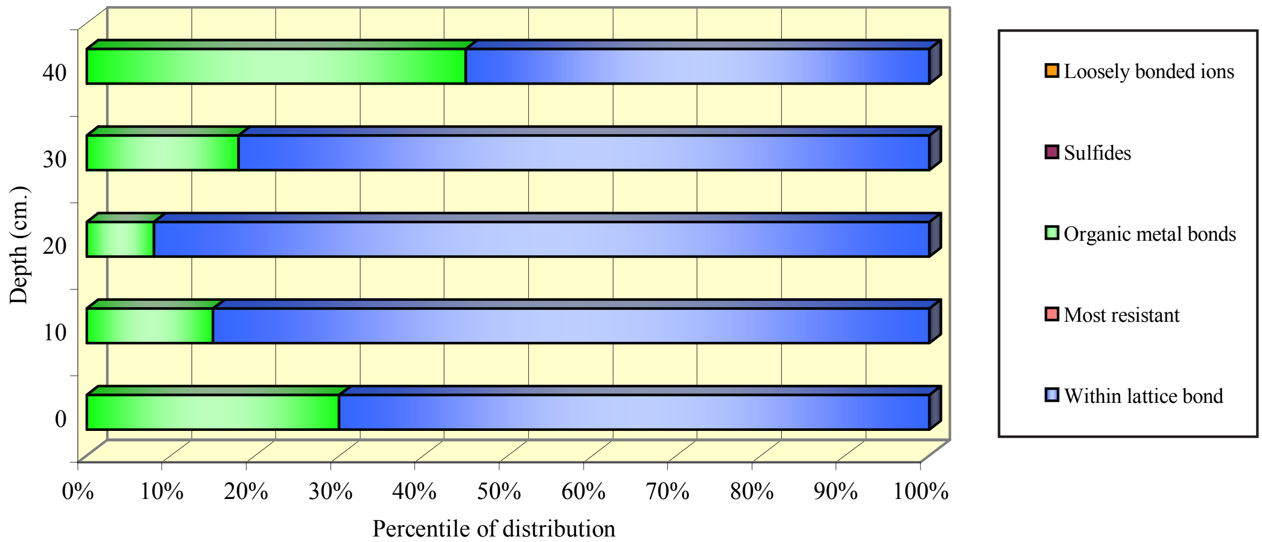

Figure 4e: Distribution of Co in various sedimentary phases of sediment cores (Refers to sediment core C2-MJ20)

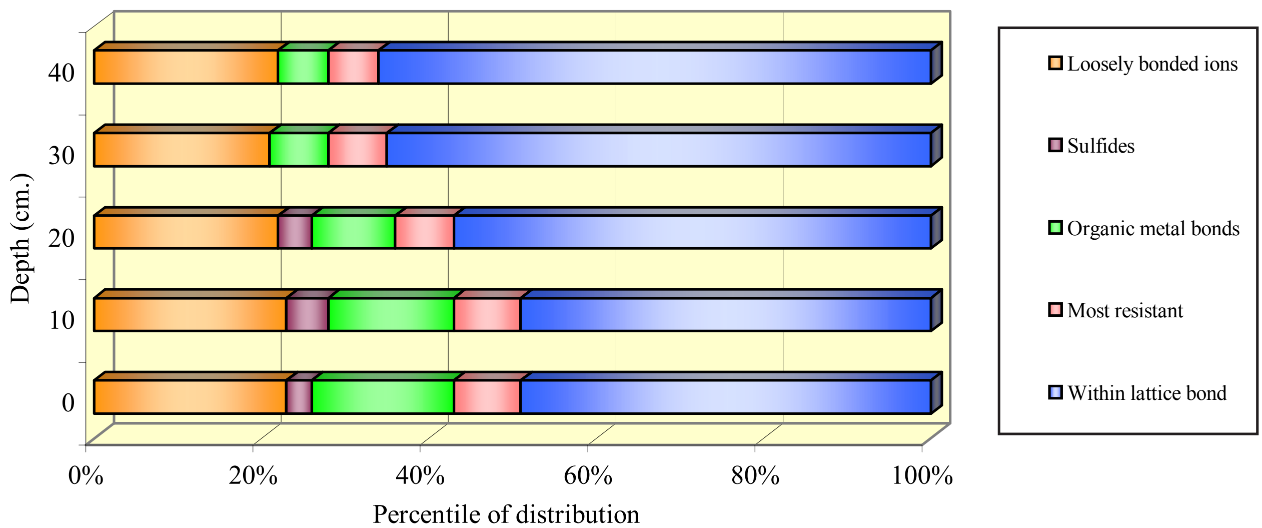

Figure 4f: Distribution of Mn in various sedimentary phases of sediment cores (Refers to sediment core C2-MJ20)

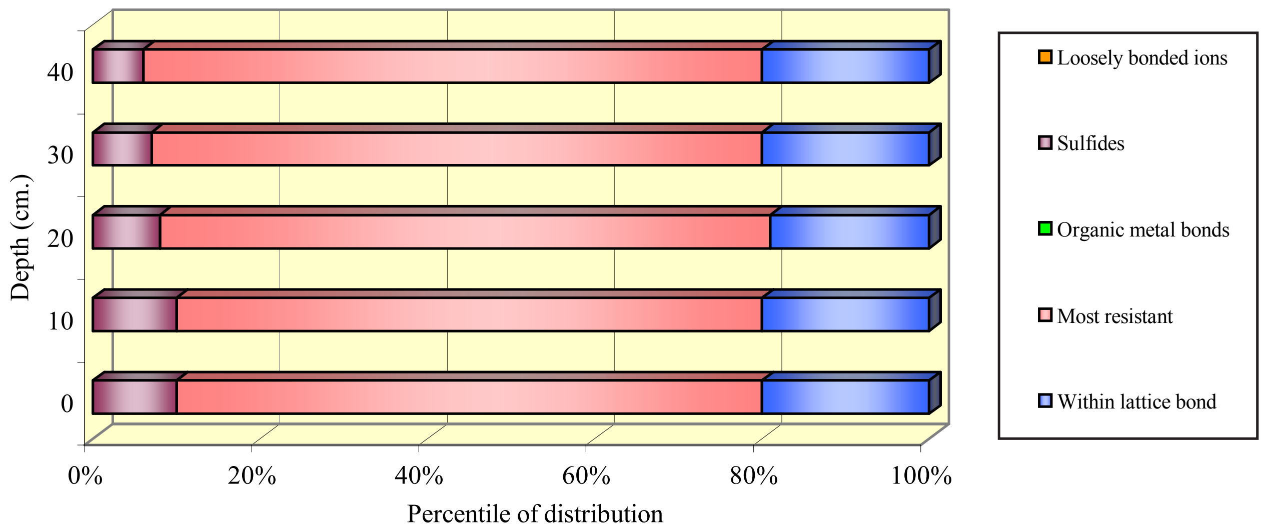

Figure 4g: Distribution of Fe in various sedimentary phases of sediment cores (Refers to sediment core C2-MJ20)

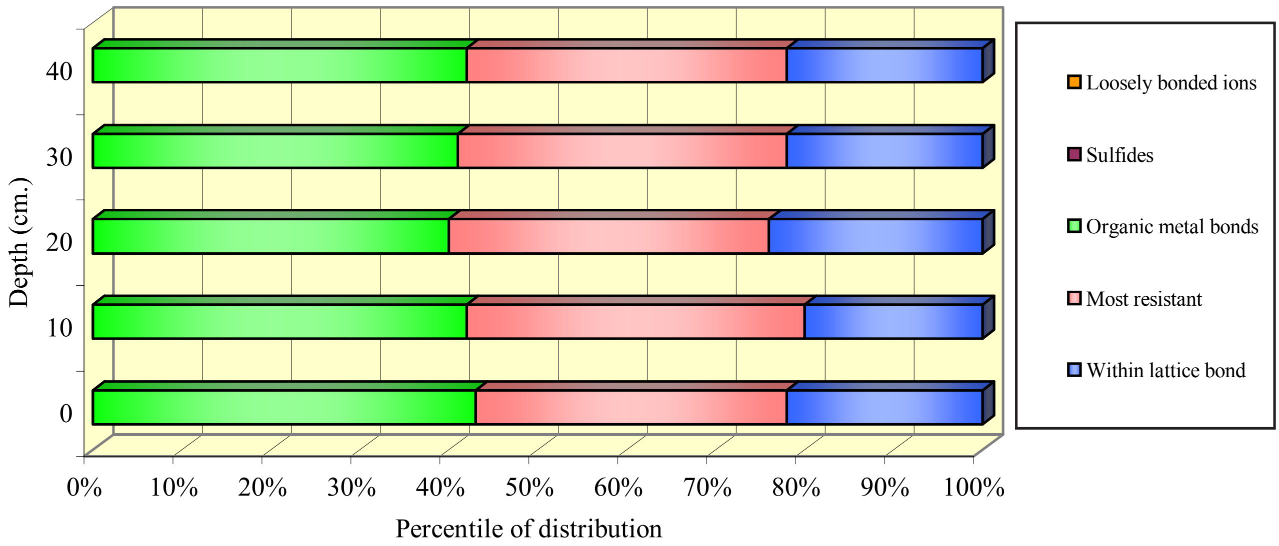

Figure 4h: Distribution of Cu in various sedimentary phases of sediment cores (Refers to sediment core C3-SM20)

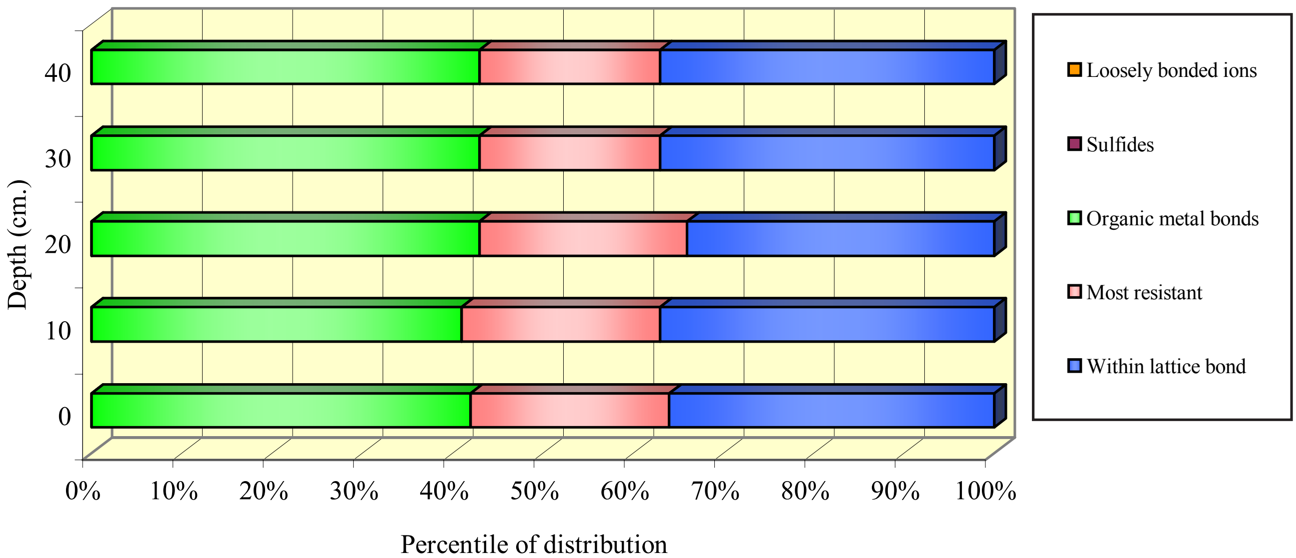

Figure 4i: Distribution of Zn in various sedimentary phases of sediment cores (Refers to sediment core C3-SM20)

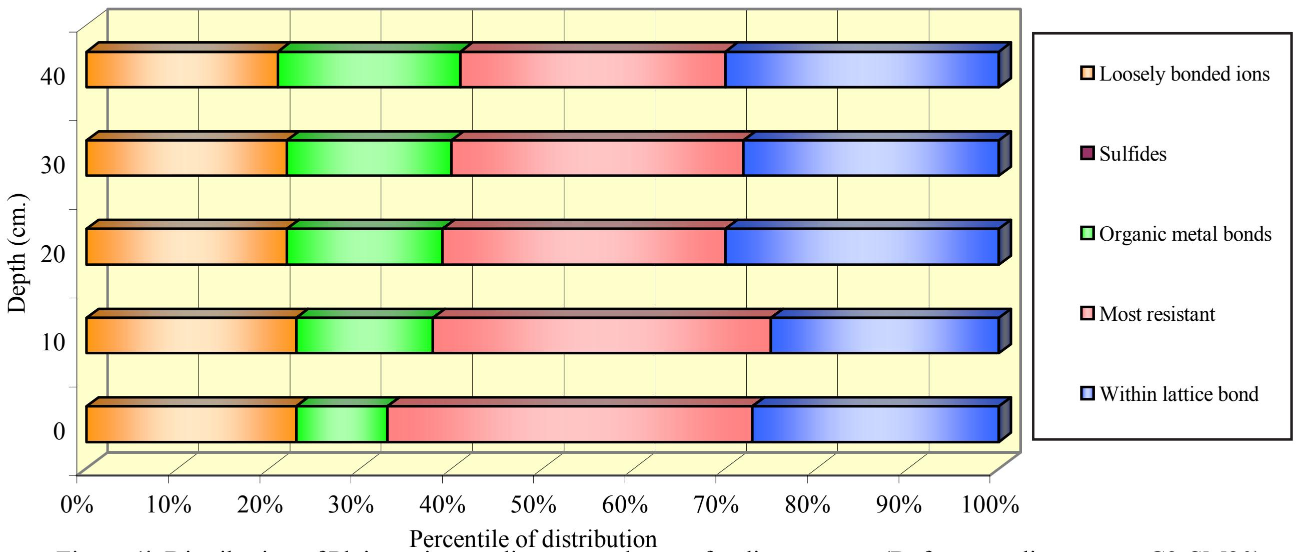

Figure 4j: Distribution of Pb in various sedimentary phases of sediment cores (Refers to sediment core C3-SM20)

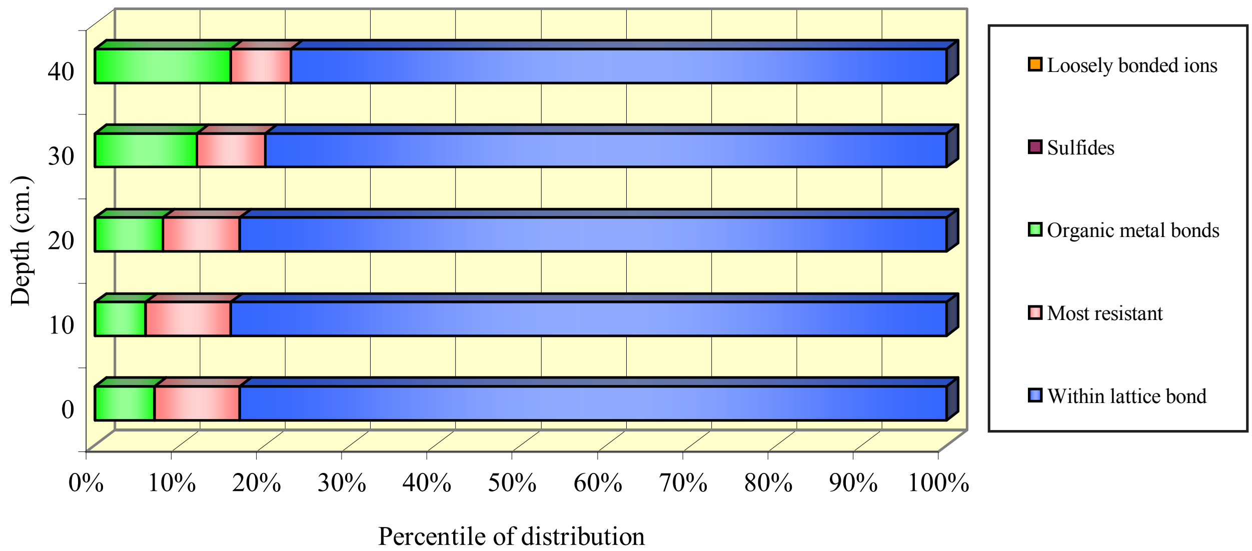

Figure 4k: Distribution of Ni in various sedimentary phases of sediment cores (Refers to sediment core C3-SM20)

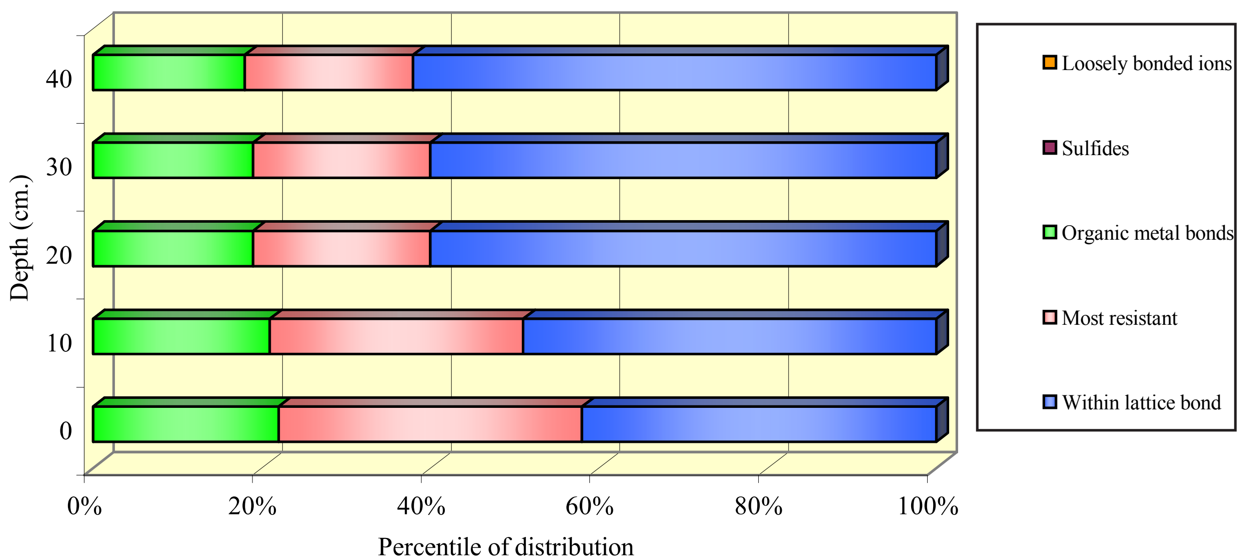

Figure 4l: Distribution of Co in various sedimentary phases of sediment cores (Refers to sediment core C3-SM20)

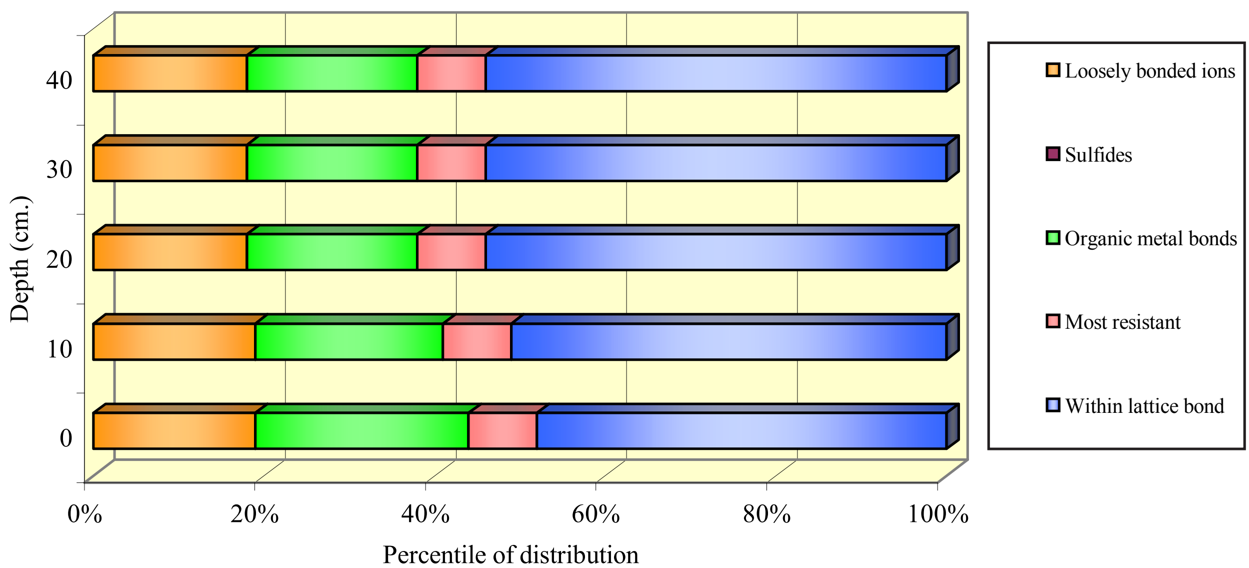

Figure 4m: Distribution of Mn in various sedimentary phases of sediment cores (Refers to sediment core C3-SM20)

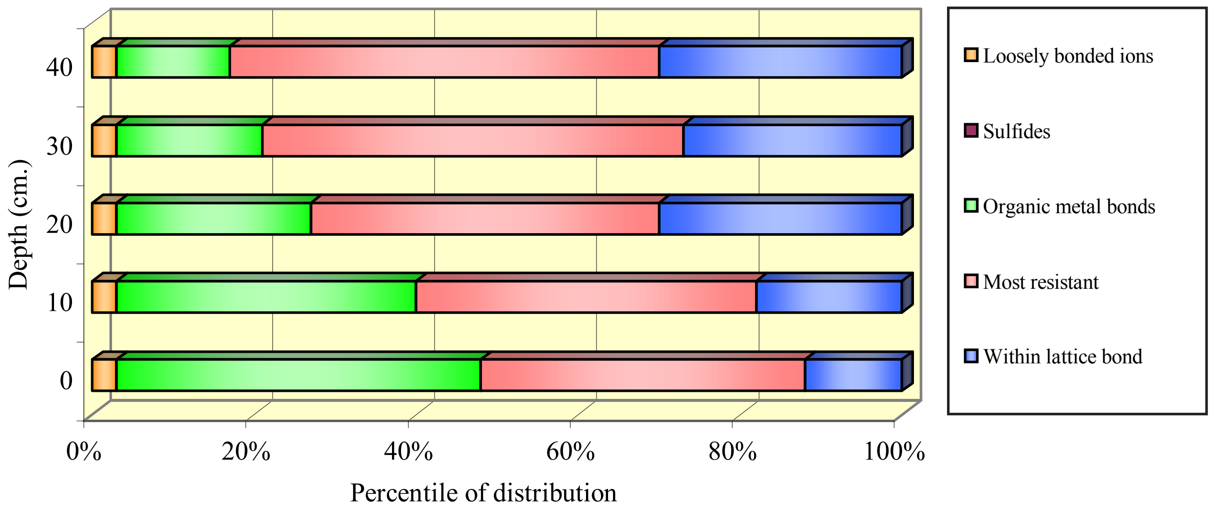

Figure 4n: Distribution of Fe in various sedimentary phases of sediment cores (Refers to sediment core C3-SM20)

Discussion and Conclusion

The geochemistry of cores studied reflects the high sedimentation rate in the near shore region. There appears to be a decrease in the detrital component in the past few centuries. The intra- and inter-core chemical composition is about the same, though Ni and Co contents are higher in core C3-SM20. The organic matter content is high (11 to 21%) because of the high sedimentation rate at the core stations that are located close to the coast and to river mouths. Calcareous shells act as diluents for most of the metals; however, Pb and Mn are associated with shells. Reducing conditions in the study area are reflected in the absence of Fe and Mn oxides /hydroxides. Iron and Mn are geochemically separated. The sediments have high Al and organic matter contents due to the high sedimentation rate and their proximity to river mouths. Down-core variations of elements indicate a decrease of lithogenous component during probably the past few centuries. While abundance of calcareous shells in some zones has lead to the dilution of most of the metals, it appears that Pb and Mn are associated with this phase. Copper, Zn and Fe are associated with organic matter and detrital particles, whereas Ni and Co are predominantly associated with the insoluble fraction. Oxides/ hydroxides of Fe and Mn are absent because of the reducing conditions and the high terrigenous influx. In core C2-MJ20, all the metals except Pb, are negatively correlated with Ca. Lead and Ca, in turn, are negatively correlated with Al, whereas Mn is mildly correlated and the other metals positively correlated with Al, thus showing the association of Pb with calcareous shells and that of other metals with detrital particles.

Acknowledgements

The authors would like to thank Drs. K. Venkaji and P.R. Naidu for the AAS facility; Drs. M.P.M. Reddy, H.P.C. Shetty, and T.R.C. Gupta for the boat facility; Dr. C. Raju for help in cluster analysis; Miss F. Salehi for text layout and drafting the Figures.

References

*Al-Masri, M. S., A. Aba, H. Khalil, and Z. Al-Hares, Sedimentation rates and pollution history of a dried lake. Science of the Total Environment, **293:** 177-189, 2002*

*Borole, D. V., Clay sediment accumulation on the monsoon-dominated western continental shelf and slope region of India. Mar. Geol., **45:** 33-51, 1988*

*Borole, D. V., M. M. Sarin and B. L. K. Somayajlulu, Composition of Narbada and Tapti estuarine particles and adjacent Arabian Sea sediments. Ind. J. Mar. Sci., **11:** 51-62, 1982*

Butman, B. and M. H. Bothner, Predicting the long term fate of sediments and contaminants in Massachusetts Bay. U.S. Geological Survey Fact Sheet, 172-197, 1998

*Chester, R. and M. J. Hughes, A chemical technique for the separation of ferromanganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. Chem. Geol., **2:** 249-262, 1967*

Cline, J. T. and S. B. Upchurch, Mode of heavy metal *migration in the upper strata of lake sediment. Proc. 16th Conference on Great Lakes Research. International Association on Great Lakes Research,* ***1:*** *349-356, 1973*

Coker, W. B. and W. W. Shilts, Lacustrine geochemistry around the north shore of Lake Superior. Geol. Sur. Canada., ***79:*** *1-15, 1979*

Dilli, K., Geochronology and geochemistry of a sediment core from Bombay coast. Mahasagar, ***19:*** *87-95, 1986*

Faganelli, J., B. Ogorolec, M. Misic, T. Dollenen and J. Pezdic, Organic geochemistry of two 40m sediment cores from the Gulf of Trieste Northern Adriatic). Coast. Shelf Sci., 25: *157-167, 1987*

Gibbs, R. J., Mechanisms of trace metal transport in rivers. Science, ***180:*** *71-72, 1973*

Gupta, S. K. and K. Y. Chen, partitioning of trace metals in selective chemical fractions of near shore sediments. Envi. Lett., ***10:*** *129-158, 1975*

Holm, N. G., Arsenic regeneration from estuarine sediments of the Bothnian Bay, Sweden. Chem. Geol., ***68:*** *89-98, 1988*

Karbassi, A. R., Geochemical and magnetic studies of riverine, estuarine and marine sediments. Ph.D. thesis, Mangalore University, India, 196, 1989

Karbassi, A. R., Geochemistry of a sediment core and applications of analysis in interpret ting data. The 16th Intl. Geo. Expl. Symp. Beijing, China, 1993

Karbassi, A. R., 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. Env. Studies, ***54:*** *205-212, 1996*

Karbassi, A. R. and R. Amirnezhad, Geochemistry of heavy metals and sedimentation rate in a bay adjacent to the Caspian Sea. Intl. J. Env. Sci. Tech., ***1 (3):*** *199-206, 2004*

Karbassi, A. R., B. R. Manjunatha and R. Shankar, Sedimentation rate and geochemistry of sediments off Mulki, West coast of India. Joint Oceanography Assembly (JOA), Acapulco, Mexico, p.54, 1988

Malo, B. A., Partial extraction of metals from aquatic sediments. Envi. Tech., ***11:*** *277-282, 1977*

Manjunatha, B. R. and R. Shankar, Pb-210 geochronology and geochemistry of two sediment cores off Mangalore, West coast of India. Joint Oceanography Assembly (JOA), Acapulco, Mexico, p.65, 1988

Shankar, R., Saving on the cost of perspex liner used in sediment coring operations. J. Geol. Ind., ***31:*** *591-593, 1988*

Shankar, R. and A. R. Karbassi, Geochemistry and magnetic susceptibility of surficial sediments of the New Mangalore Port. J. Geol. Soc. Ind., ***38:*** *412-417, 1991*