

ASSESSMENT OF HEAVY METAL CONCENTRATIONS IN SURFACE SEDIMENTS OF COLEROON ESTUARY OF TAMILNADU, EAST COAST OF INDIA

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Abstract: The abundance and distribution of the metals through the analyses of selected metals (iron (Fe), manganese (Mn), zinc (Zn), Lead (Pb), copper (Cu), cobalt (Co) and nickel (Ni)). Totally 20 surface sediments were collected in Coleroon river estuary (each season 10 samples) during monsoon and summer seasons of the year 2010, the samples were collected from mouth, estuary and freshwater zones of the river. The results of present study reveals that the study periods higher levels of metal concentration were observed in estuarine region were as lower levels were observed at mouth and freshwater zones. This study illustrates the usefulness of method for estimating pollution impact such as degree of contamination, enrichment factor and geo accumulation index for evaluation and interpretation of the heavy metal concentrations in surface sediments of Coleroon estuary. The Enrichment and contamination factor, geoaccumulation index shows that Zn, Pb and Cu unpolluted to moderately pollute the sediments. The present study indicates that other sources should be evaluated in the long-term monitoring program.

Keywords: Heavy metals, Coleroon estuary, Degree of contamination, Enrichment factor.

1. INTRODUCTION

Estuarine systems are among the most productive and dynamic ecosystems on earth. Coastal and estuarine watersheds currently support 75% of the world's population and are still rapidly being developed (Paerl, 2006). The growth in coastal areas has increased the anthropogenic effects on these systems, including the degradation of many water bodies due to increased amounts of land-based nutrients and other pollutants like heavy and trace metals, wastewater, herbicides, and pesticides (Hyland et al., 2000; Schropp et al., 1990; Dessai et al., 2009). Estuaries are a major repository of fine-grained sediment, as well as pollutants that are typically associated with them (Cook et al., 2007). Sediment samples can provide useful information on the history of trace metal input and may provide additional information on the variations of land use and local sediment dynamics (Conrad et al., 2007; Swarzenski et al., 2006; Dugar et al., 2011).

Trace elements, especially the so called

“heavy metals”, are among the most common environmental pollutants and their occurrence in waters and biota indicate the presence of natural or anthropogenic contamination. The main sources of metals in aquatic systems are the weathering of soils and rocks and anthropogenic activities (drainage of land and alterations in land use), whereby industrial and urban wastes are discharged into water bodies and so disturb the equilibrium between the metals in sediment/soils and ground water or surface water (Yu et al., 2001; Filgueiras et al., 2004; Anithamary et al., 2012). The objective of the present study:

1. Understand the nature of distribution of metals;
2. To estimate the pollution impact in Coleroon river estuary.

2. GENERAL SETUP OF STUDY AREA DETAILS

The Coleroon river (Fig.1) is bifurcation of river Cauvery at its deltaic form and ephemeral

which carry floods during monsoon. It generally flows from west towards east and the pattern is mainly sub parallel. The eastern coastal part near Pazhayar is characterized by back water. Coleroon river, a major waterway of the Trichy and Thanjavur district and finally joins the Bay of Bengal in eastern coastal part near Pazhayar. The influence of tide was noticed upto 15-17 km in the upstream direction. Since the area are underlined by sedimentary formation, the major land forms that occur are natural levees and Mailaduthurai coastal plain covering almost the entire study area with beaches beach ridges, mudflats, swamps, and backwater along the coastal stretch. The deltaic plains are found near the confluence of river Coleroon with sea in the east and also in the south. Flood plain deposits are observed along the river course.

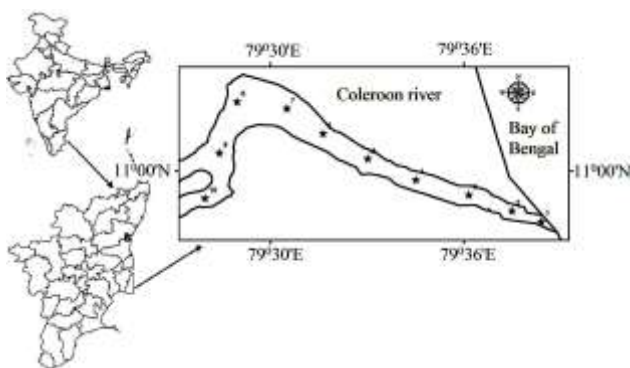


Figure.1. Map showing Location of the Study Area

2.1. GEOLOGY OF STUDY AREA

The study area mainly comprises of quaternary sediments and thickness increases south of Coleroon River. These sediments have been delineated as alluvial plain deposit of the Cauvery River and its distributaries. Narrow fluvio-marine deltaic plain deposits and marine coastal plain deposits and also observed Coleroon estuary (east coast formation). The fluvial deposits comprise flood plain, flood basin, point bar, channel bar and palaeo-channels with admixtures of sand, silt and clay. The Cretaceous formations of the coastal tract of the Cauvery basin consist of faunal rich marine sedimentary rocks, namely limestones, sandstones, clays and sandy beds etc. The mouth of the river comprises alluvium deposits which are composed of clays and silts and sediments derived from sea. The major mineral assemblages of Coleroon river sediments indicate major minerals are quartz, feldspar and pyroxenes, amphiboles. The finer sediments consists clay minerals.

3. METHOD OF THE STUDY

The study site is located on the east coast of

India, in the state of Tamilnadu (Table 1). The investigations have been carried out for period of (2010) and covering two seasons (monsoon and summer) ten stations were selected in the estuary, covering fresh water zone, estuarine and mouth zone. The sediment samples were collected by using a Van Veen grab sampler on board hired fishing boat. Sub-sampling of the sediments were done by taking upper 5cm of the sample from grab with help of plastic spatula. Locations were identified by global positioning system (GPS, GARMAN 76CSx). The collected sediment samples were air dried at 60°C for further analysis. Bulk metal extraction was carried out by adopting the procedure described by Tessier et al., (1979). As per the procedure 1 g of the sediment sample was ground to a fine powder and digested with 5:1 mixture of hydrofluoric and perchloric acid and the final residue was dissolved in 12 N HCl and diluted to 25 ml. The metal concentrations were determined by ICP-OES (Perkin Elmer optima 5300 DV).

Table.1. Concentration of Heavy metals

Metals/ Seasons (µg/g)	Monsoon		Summer	
	Min.	Max.	Min.	Max.
Fe	2005.7	2734.6	2107.5	3287.2
Mn	18.45	25.45	20.54	57.84
Zn	15.45	26.65	20.12	35.65
Pb	35.45	47.87	37.43	61.56
Cu	4.34	10.76	6.23	20.76
Co	1.098	3.76	1.567	5.03
Ni	0.876	3.07	1.32	3.98

4. RESULTS AND DISCUSSION

The surface sediment samples were collected and bulk metal extraction was carried out. The collected sediment samples should various metals extracted Fe, Mn, Zn, Pb, Cu, Co and Ni. The minimum and maximum concentration of metal during monsoon and summer seasons Fe 2005.7-3287.2 µg/g, Mn 18.45-57.84 µg/g, Zn 15.45-35.65 µg/g, Pb 35.45-61.56 µg/g, Cu 4.34-20.76 µg/g, Co 1.098-5.03 µg/g, Ni 0.88-3.98 µg/g. the values shown in Table 1. During summer season, higher metal concentration was observed when compared to monsoon season. The increasing order of metals in the study period Fe > Mn > Zn > Pb > Cu > Co > Ni. Generally, Fe toxicity is due to its rapid absorption by the body. Drinking water, iron pipes, cookware, and preparations are the main sources of iron and its target organs are the liver, cardiovascular system, and kidneys (Pais & Benton Jones 1997). The Fe and Mn are the dominant metal, normally the Fe and Mn oxides/hydroxides act as specific sink or source of heavy metals in the (Lacuraj & Maria 2006; Anithamary et al.,

2011). Fe and Mn are also removed from solution at low salinity during high discharge. However, at higher salinity, and increased concentration imply the release from surface sediments Evans et al., (1977) and suggests that Mn removed from estuarine sediments is reduced and subsequently remobilized at higher salinity. The Copper is an essential element to human life, however in high levels, it accumulates in blood, liver, and kidneys and causes anemia, renal and intestinal irritations, coma, death, and Wilson’s disease (Gratten et al., 2003; Pais & Benton Jones, 1997). This could be because location 2, 3, 4, 5 is located in an estuarine region, which releases waste or sewage to marine environment and fine sediments will adsorbed more metals. (Santamaria-Fernandez et al., 2005; Sullivan & Taylor, 2003; Venkatramanan et al., 2011). In comparison to these results, the concentrations of Cu in our samples are very low to moderate pollution should noted in study area. Zinc is a common metal in the human environment. Little is known about its toxic effects toward human beings Homady et al., (2002). High levels of Zn may cause Pancreatitis, anemia, muscle pain, acute renal failure, and death Pais & Benton Jones (1997). Lead is number two (after arsenic) on the top 20 list of the most poisoning heavy metals. Its target organs are the bones, brain, blood, kidneys, reproductive and cardiovascular systems, and thyroid gland (Homady et al., 2002; Massadeh et al., 2004). Were probably as consequence of the large use of yachts and boats. The values obtained in this study compared to these studies revealed the non pollution of our samples with respect to Pb. Nickel is a carcinogenic metal and overexposure to it can cause decreased body weight, heart and liver damage and skin irritation Homady et al., (2002). High nickel contents in soils and sediments are usually due to human activities Pais & Benton Jones (1997). In this study (Fig. 2a and b), sediment samples are thus considered as unpolluted with Ni.

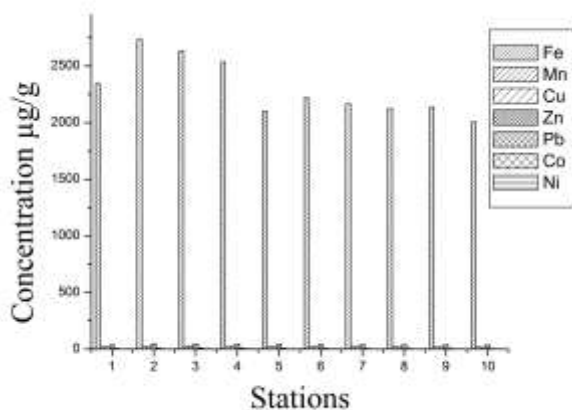


Figure.2a. Bar showing Heavy Metals Concentration during monsoon

The variations in total metal content are largely systematic along the estuarine with season. Most of the studied metals in two seasons show higher concentration were noted stations- 2, 3, 4, 5, compared to 1, 6, 7, and 8, 9, 10.

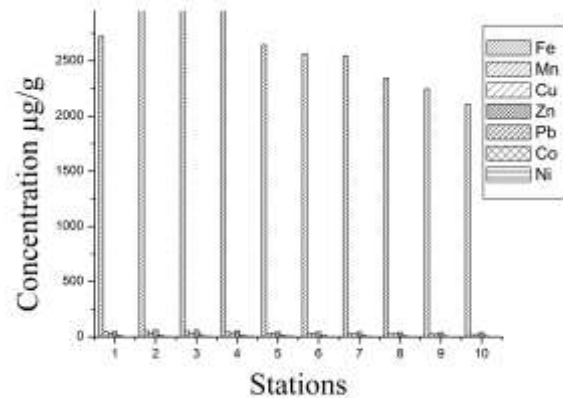


Figure.2b. Bar showing Heavy Metals Concentration during summer

4.1 Degree of contamination

Hakanson (1980) proposed an overall indicator of contamination based on integrating data for a series of seven specific heavy metals and the organic pollutant PCB. This method is based on the calculation for each pollutant of a contamination factor (C_f). However the C_f requires that at least five surficial sediment samples are averaged to produce a mean pollutant concentration which is then compared to a baseline pristine reference level, according to the following equation:

$$C_f = M_x / M_b$$

Where M_x (metal value) and M_b (background value) respectively refer to the mean concentration of a pollutant in the contaminated sediments and the pre-industrial “baseline” sediments.

Table.2a. Contamination factor values

Monsoon					
Cu	Zn	Pb	Co	Ni	Degree of Contamination
0.71	0.70	0.39	0.13	0.08	2.02
0.99	0.92	0.51	0.21	0.10	2.73
1.07	0.88	0.73	0.32	0.15	3.14
0.99	0.86	0.59	0.31	0.16	2.90
0.82	0.82	0.50	0.24	0.12	2.50
0.74	0.78	0.44	0.21	0.12	2.28
0.74	0.77	0.37	0.18	0.10	2.16
0.66	0.74	0.34	0.17	0.08	1.99
0.68	0.71	0.33	0.15	0.06	1.94
0.62	0.68	0.29	0.09	0.05	1.73

Table.2b. Contamination factor values

Summer					
Cu	Zn	Pb	Co	Ni	Degree of Contamination
0.94	0.85	0.74	0.15	0.10	2.77
1.17	1.12	0.88	0.24	0.11	3.51
1.23	1.07	1.10	0.29	0.13	3.83
1.14	0.98	0.94	0.30	0.17	3.53
1.02	0.79	0.79	0.27	0.16	3.02
0.96	0.75	0.66	0.20	0.10	2.67
0.87	0.71	0.45	0.16	0.09	2.28
0.74	0.66	0.36	0.12	0.08	1.97
0.65	0.60	0.26	0.10	0.06	1.66
0.56	0.61	0.24	0.07	0.04	1.53

The study by Hakanson (1980) analysed seven specific heavy metals (As, Cd, Cu, Cr, Hg, Pb, Zn) and the organic pollutant and thus considers eight possible measures of contamination. Hakanson's study also proposed that the numeric sum of the eight specific contamination factors expressed the overall degree (Hakanson 1980) of sediment contamination (C_d) using the following formula:

$$C_d = \sum_{i=1}^8 C_f^i$$

The calculated degree of contamination (C_d) is therefore defined as the sum of the C_f for the eight pollutant species specified by Hakanson (1980). The C_d is aimed at providing a measure of the degree of overall contamination in surface layers in a particular surface sediments or sampling site.

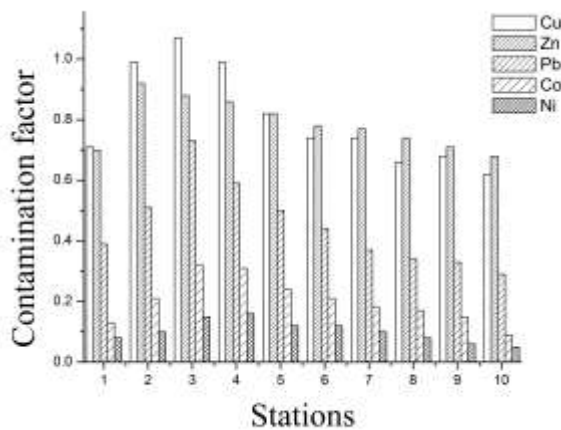


Figure.3a. Bar showing Contamination factor during monsoon

However the Hakanson (1980) classification terminologies and calculation formula is based on and is restricted to the seven specified in Hakanson's study. Furthermore all eight species must be analysed in order to calculate the correct C_d for the

range of classes defined by Hakanson (1980). In the present (Table 2 a and b) study with respect to degree of contamination factor, estuarine region samples fall in moderate to low degree of contamination (Stations- 2, 3, 4, 5). Whereas mouth and freshwater zone sediments fall in very low degree of contamination (Fig. 3a and b).

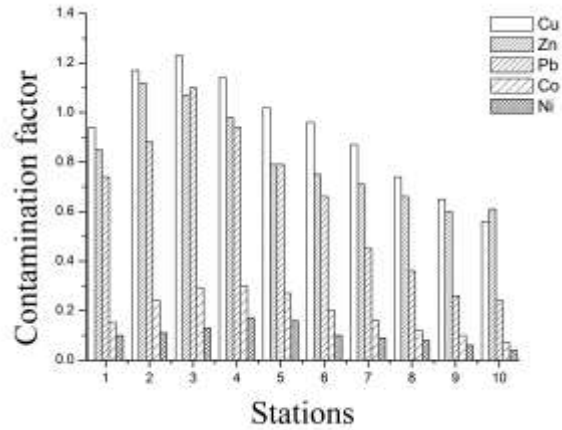


Figure.3b. Bar showing contamination factor summer

4.2. Enrichment Factor (EF)

The enrichment factor (EF) is an estimate of the anthropogenic influence on sediments. The enrichment factor (EF) reflecting the geochemical background of the contaminant element in estuarine and marine sediment. It utilizes a normalization element (Al or Fe) to moderate the deviations produced by heterogeneous sediments (Loring & Rantala, 1992). The reference should otherwise be present in such a large quantity in the studied environment that neither potential minute variations nor other synergistic or antagonistic effects towards the investigated elements are significant. For this purpose, Fe is often used as a normalize because anthropogenic inputs are commonly small compared to natural sources, and where Al concentration in the sediments were not analyzed (Wedepohl 1995).

The enrichment factor is calculated according to the following equation;

$$EF = M_x \times Fe_b / M_b \times Fe_x$$

Where M_x and F_{ex} are the sediment sample concentration of the heavy metals and Fe, while M_b and F_{eb} are their concentrations in a suitable background reference material Wedepohl, (1995). During postmonsoon and premonsoon seasons, based on the enrichment factor (EF) value, the emergence of an element can be distinguished, where it is from natural or anthropogenic origin Liu

et al., (2010). origin except Cu and Pb this two metals derived from anthropogenic origin (Fig 4a and b).

Table.3a.Enrichment factor value

Stations	Monsoon season				
	Zn	Pb	Cu	Co	Ni
1	-1.09	-1.94	-1.07	-3.48	-4.31
2	-0.70	-1.56	-0.61	-2.83	-3.91
3	-0.77	-1.04	-0.49	-2.21	-3.37
4	-0.80	-1.36	-0.61	-2.29	-3.21
5	-0.87	-1.58	-0.87	-2.66	-3.61
6	-0.95	-1.78	-1.02	-2.84	-3.70
7	-0.96	-2.03	-1.02	-3.09	-3.93
8	-1.02	-2.13	-1.18	-3.14	-4.21
9	-1.08	-2.18	-1.14	-3.30	-4.53
10	-1.14	-2.35	-1.28	-3.99	-5.02

Table.3b.Enrichment factor value

Stations	Monsoon season				
	Zn	Pb	Cu	Co	Ni
1	9.262	9.875	9.411	3.400	1.916
2	10.399	12.882	11.138	5.340	2.515
3	10.318	18.383	12.499	8.196	3.673
4	10.470	14.812	12.017	7.760	4.086
5	12.031	12.728	12.083	6.016	3.101
6	10.796	11.071	10.275	5.297	2.914
7	11.004	9.294	10.586	4.447	2.489
8	10.720	8.645	9.631	4.307	2.049
9	10.266	8.354	9.869	3.854	1.637
10	10.499	7.415	9.518	2.393	1.166

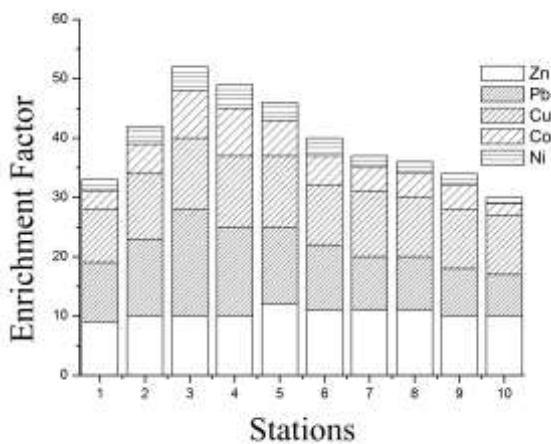


Figure. 4a. Bar showing enrichment factor monsoon

The metals having EF value < 1 reveal a natural origin (Table. 3 a and b), where as > 1 indicate enrichment due to natural or anthropogenic inputs. The EF for the metals Zn, Pb, Cu, Co and Ni were > 1 indicating natural and anthropogenic origin. With respect enrichment value mostly metals derived from natural.

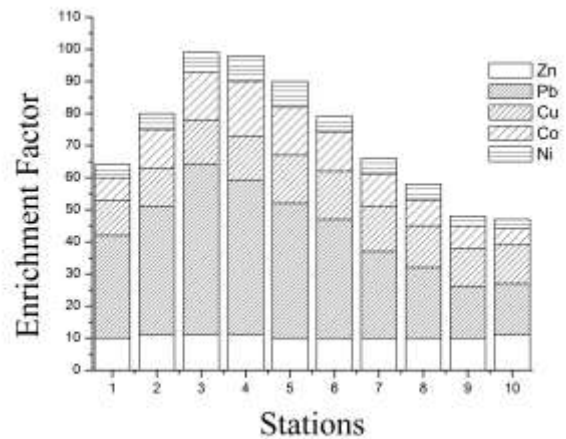


Figure. 4b. Bar showing enrichment factor summer

4.3. Geo-accumulation index (I_{geo})

The sediment quality guidelines provide values that allow for quantification of sediment contamination, further comparisons are required to make an overall assessment of the degree of metal contamination in estuarine sediments. This is largely a consequence of the presence of an unknown background metal concentration in the sediment. Expressing metal concentration as a geoaccumulation index (I_{geo}) relative to references sites or pre-industrial sediments from the study area represents an approach that can overcome this problem. The geoaccumulation index was originally defined by Muller (1969) as:

$$I_{geo} = \log_2 C_n / 1.5B_n$$

Where C_n is the concentration of the element in the enriched samples, and the B_n is the background or pristine value of the element. The factor 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments.

Table.4a.Geo-accumulation index value

Stations	Summer season				
	Zn	Pb	Cu	Co	Ni
1	9.985	32.012	11.495	6.725	4.066
2	11.125	40.240	12.273	11.613	4.667
3	11.136	53.379	13.813	14.959	6.209
4	11.010	47.722	14.054	16.501	7.971
5	10.288	42.271	14.751	15.320	7.791
6	10.270	36.871	14.776	12.007	5.348
7	9.934	26.561	13.962	10.202	4.867
8	10.164	21.958	13.286	8.398	4.667
9	9.910	16.302	12.474	6.823	3.345
10	10.869	16.019	11.796	5.141	2.644

Table.4b. Geoaccumulation index value

Stations	Summer season				
	Zn	Pb	Cu	Co	Ni
1	-0.77	-0.83	-0.57	-3.09	-3.81
2	-0.34	-0.50	-0.20	-2.30	-3.61
3	-0.38	-0.10	-0.07	-1.93	-3.20
4	-0.48	-0.26	-0.13	-1.79	-2.84
5	-0.77	-0.43	-0.25	-1.90	-2.87
6	-0.81	-0.63	-0.29	-2.25	-3.42
7	-0.87	-1.10	-0.38	-2.48	-3.55
8	-0.96	-1.38	-0.57	-2.76	-3.61
9	-1.06	-1.81	-0.73	-3.06	-4.09
10	-1.02	-1.83	-0.90	-3.47	-4.43

Where C_n (metal value) is the measured sedimentary concentration for metal B_n (background value) is the background value for the metal n ; the factor 1.5 is used because of possible variations in background values for a given metal in the environment, as well as very small anthropogenic influences (Ruiz, 2001). Although, I_{geo} was originally devised for use with the global standard shale values as background metal levels, Rubio et al., (2000) have shown that the use of regional background values yields more appropriate results. In this study, I_{geo} has been calculated using background values for world crustal average metal concentrations as presented by Wedephol (1995). The index of geoaccumulation consists of seven grades or classes, with I_{geo} as 6 indicating almost a 100-fold enrichment above background values. Muller (1969) proposed the descriptive classes for increasing I_{geo} values (Table 5).

Table.5. Sediment quality (Muller 1969)

I_{geo} Value	Class	Quality of sediment
<0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately polluted to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
>5-6	6	Extremely polluted

The I_{geo} method was used to calculate the metal contamination levels in the study area. The average I_{geo} is 1–6 indicating uncontaminated to extremely contaminated levels. The negative I_{geo} values found in the Table 4.a and b are the results of relatively low levels of contamination Zn, Pb, Cu, Co and Ni in study area (Fig. 5a and b).

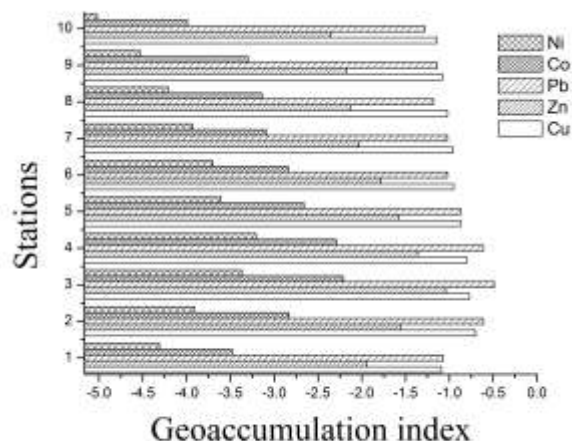


Figure. 5a. Bar showing geoaccumulation index monsoon

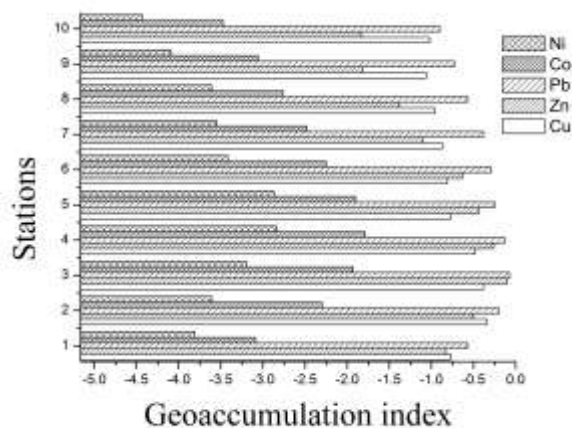


Figure. 5b. Bar showing geoaccumulation index summer

5. CONCLUSIONS

In the present study heavy metal concentration in the Coleroon estuarine sediments and its distribution in estuarine, mouth and fresh water region. The heavy metals like Fe, Mn, Zn, Pb, Cu, Co and Ni, the higher level of metals were observed in mid estuarine region whereas when compared to mouth and fresh water region. Method for estimating pollution impact such as contamination factor, enrichment factor and Geoaccumulation indexes have been put forward for quantifying the degree of metal enrichment in sediments. With respect to contamination factor Zn, Pb, Cu values indicates moderate level of contamination and Co and Ni values indicates low level of contamination. According to enrichment factor Co and Ni derived from natural or lithogenic origin, whereas Pb and Cu derived from agricultural activity. Based on geo-accumulation index all metals were recorded negative value indicates relatively low to moderate levels of contamination. In the

present study of Coleroon estuarine sediments were pollute moderate to low level.

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