GEOCHEMICAL SOURCES AND ENRICHMENT OF HEAVY METALS IN CORE SEDIMENTS FROM ESTUARIES OF CUDDALORE DISTRICT, TAMIL NADU, INDIA

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Abstract : ***The concentration of six trace factors, Fe, Cr, Co, Cu, Zn, Cd had been assessed in sediment samples of Ponnaiyar River, Gadilam River, Uppanar River, Vellar River, estuaries of Cuddalore District. Sediment samples collected from four locations of each estuary and elements were determined using Atomic Absorption Spectrophotometer (AAS). The parameter investigated were in the order of magnitude as by Fe>Cr>Co>Cu>Zn>Cd is existence range of trace metals in sediment samples. Among the studied heavy metals, Cd, Co, Cr, Cu, Fe, and Zn appear to reflect their background concentrations in sediments of Cuddalore estuaries. The most noteworthy groupings of Fe were found all through the sediments of estuaries by Fe>Cr>Co>Cu>Zn>Cd and the variation of metals in Gadilam River and Uppanar River is by modern wastage and un–characterized anthropogenic impacts. The consolidated waste materials, rapid urbanization and agriculture practices aggravate the genuine hazard to the estuarine environment.***

Index Terms - Estuarine Sediment. Heavy Metal Pollution. Enrichment factor. Geo–accumulation Index. Pollution Load Index.

I. INTRODUCTION

Contamination in an aquatic system, especially by heavy metals in sediments has become one of the maximum tough pollution problems owing to the toxicity, abundance, persistence, and subsequent bioaccumulation. Most of dissolved metal are discharged in aquatic environment and these are suspended as solids and strongly accumulate in sediments (Fu, et al 2014; Barlas, et.al 2005); Yi, et.al 2011); Gumgum, et.al 1994). Moreover, sediments also act as toxic through sinks element condemnation that may act as sources of heavy metals Hakanson, et.al (1980), Suresh, et.al (2012). The assessment of heavy metal contamination in estuarine sediments is a multifaceted procedure in which physical; chemical and biologic data are mandatory. Hence, in several areas the needed biologic data are not available. The environmental geochemistry evaluation of contamination is usually based on Sediment Quality Guidelines (SQGs). The other way of quantitative index is Geo–accumulation Index (Igeo), Enrichment Factor (EF), etc. with respect to reference asset value such as regional and local background values or average concentrations of shale, upper continental crust and continental crust etc. (Rubio et al., 2000; Woitke et al., 2003; Samir et al., 2006; Chen et al., 2007). The objectives of this paper are to explain the circulation pattern and pollution factor of heavy metals (i.e., Cd, Co, Cr, Cu, Pb and Zn) in estuarine sediments, and to assess the geochemical factors that control heavy metals. Furthermore, to measure the contamination status of the sediments to define how the metals enriched by anthropogenic input and or by natural background value is recognized.

II. GEOLOGY OF STUDY AREA

The study area (Fig 1) is Ponnaiyar estuary (N 11˚46’ 19” and 79˚ 47’ 42”E) the total drainage area of the river is 14,885sq.km. Gadilam estuary lies between (N 11˚44’ 11” and 79˚ 47’ 12”E). The total area of the basin is about 1,394sq. Km. Uppanar estuary falls in between (N 11˚43’ 15” and 79˚ 46’ 32”E) and Vellar estuary falls in (N 11˚20’ 19” and 79˚ 46’ 42”E). The total area of the river is 7,520.87 sq.km. The study is conducted in Ponnaiyar, Gadilam, Uppanar and Vellar River and estuaries of Cuddalore district from the survey of India toposheet 58M/14. These four rivers are perennial and flow from westward to eastward directions and drain at Bay of Bengal. The view geology of study region mainly occupied by sedimentary rock formations that contain clay, alluvium sandstone and minor patches of tertiary and quaternary aged Laterite soils. The district is noted for different geologic formations of Archaean rocks to recent sediments.

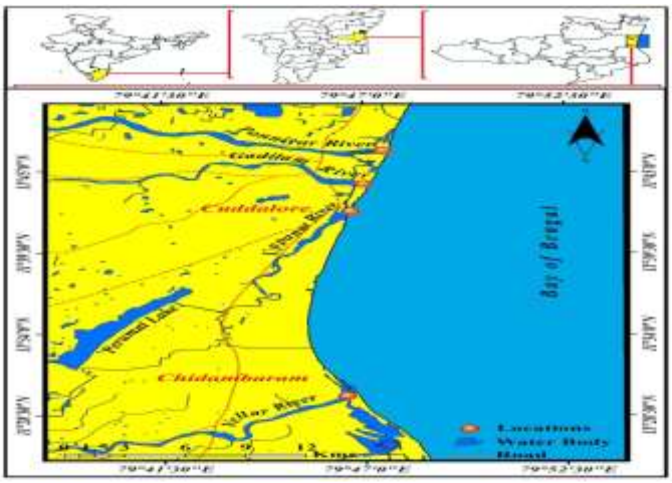

Fig 1. Study Area and Location Map

III. MATERIALS AND METHOD

Sediment sample analysis was done by collecting four core sediment samples each from Ponnaiyar, Gadilam, Uppanar and Vellar estuaries. Each sampling location was identified and recorded utilizing a handheld GPS Magellan). The collected samples were symbolised as S1, S2, S3, and S4 and stored for further analytical work. The samples were air dried at 50oC for 48h and analysed for Cr, Ni, Cu, Pb, and Zn in a range of 0.15 – 0.20g added with 2ml supra– pure HNO3 acids and 0.50 ml of H2O2 into Teflon bombs for digested the samples under the heat of microwave system (1200 mega Unit MLS of Milesstone High performance Microwave Digestion). These prepared samples are destabilized using deionized water (Elgastat Maxima). The preparation of four samples are prepared for assessment the heavy metals identify in Atomic Absorption Spectrophotometer (AAS).

IV. RESULTS AND DISCUSSION

HEAVY METAL IN SEDIMENTS

Metals found in the sediments are influenced by the factors like physical, hydrological characteristics within the region, atmospheric conditions, productivity, pH, soil texture, redox potential and cation exchange. The magnitude of heavy metals engaged in sediments is also affected in the individuality of the sediment due to which they are adsorbed. partition coefficient (Kd), Grain size, organic matter content, cation exchange, and mineral components which are main impact of dissolving of heavy metals in the aquatic environment like estuarine, sea ect. Gambrell (1994) recommended that prominent absorption of metals will not essentially create a threat, as they may never be released from the sediments and may not be reachable for excessive plant uptake. In the study area, heavy metal's analysis is conducted using AAS and the concentration of each metal like (Cu, Cd, Cr, Zn, Co, Fe) in Ponnaiyar, Gadilam, Uppanar, Vellar River is presented in the (Table 1)

Table1. Heavy metal concentration in sediments (mg/kg)

Location	Section	Cd	Cr	Cu	Zn	Co	Fe%
Ponnaiyar Estuary	**Top**	0.06	0.56	1.54	4.88	1.41	0.047
	Middle	0.09	0.96	3.18	6.68	2.03	0.048
	Bottom	0.18	1.78	7.99	13.52	5.05	0.049
Gadilam Estuary	**Top**	0.19	1.82	0.53	3.06	0.94	0.041
	Middle	0.16	1.78	0.42	3.29	0.89	0.032
	Bottom	0.12	1.56	0.39	3.56	0.76	0.038
Uppanar Estuary	**Top**	0.16	1.74	20.13	30.67	3.15	0.053
	Middle	0.14	1.27	14.19	20.68	2.49	0.052
	Bottom	0.05	0.63	1.64	5.81	1.9	0.051
Vellar Estuary	**Top**	0.08	1.97	5.17	9.16	4.15	0.042
	Middle	0.07	1.88	4.89	8.02	3.86	0.043
	Bottom	0.06	1.69	3.75	7.93	3.24	0.043

4.1 CADMIUM

Crystalline non–essential metal of cadmium is a stagnant condition of the natural environment. The concentration of cadmium ranges vary from the surface to bottom of the core sediments as 0.06–0.18mg/kg, 0.12–0.19mg/kg, 0.05–0.16mg/kg and 0.06–0.08mg/kg respectively in Ponnaiyar, Gadilam, Uppanar and Vellar River estuaries. The average absorption of cadmium in four locations ranges from 0.06–0.19 mg/kg. The higher concentration of cadmium is found in top sediment of Gadilam with 0.19mg/kg and Uppanar with 0.16 in top portion. But the lowest value is reported in the top of Ponnaiyar and bottom of Vellar river sediment. The high concentration of Cadmium is due to input of sewage discharge or though plastic pipes or industrial metal constituting a possible source of Cd in estuaries.

4.2 CHROMIUM

Trace element of Chromium is specifically essential element among the heavy metals because of toxic level is always highly elevated in aquatic environment, and it can also be bio–accumulated that enters the food chain. Aerial deposition and surface run off may be the principal processes by which chromium can enter aquatic systems, and its subsequent association with some particulate matter leads to its deposition in bed sediments. Therefore, sediments are leading route of exposure to chromium for aquatic organisms, since lots of varieties of organisms live in contact with bed sediments. Chromium VI is more toxic compared to Chromium III though the long–term exposure to chromium III can cause allergic skin reaction and cancer (Agency for Toxic substances and Diseases Registry, 2000). It is determined that in Ponnaiyar ranges vary in vertical section of the core from 0.56 –1.78, in Gadilam 1.56–1.82, Uppanar 0.63–1.74 and in Vellar 1.69–1.97. It is found that chromium concentration is more in all samples of Gadilam and Vellar. In general, it is found that on higher temperature area, chromium is more toxic and its compounds also cause cancer in humans (Lokhande, 2011).

4.3 COPPER

The maximum concentration of copper found from the mouth sediment sample is 14.11 mg/kg and minimum amount is 8.42 mg/kg. Presence of copper in the core sediments is 1.54–7.99 mg/kg in Ponnaiyar, 0.39–0.53 mg/kg in Gadilam, 1.64–20.13 mg/kg in Upper and Vellar is 3.75–5.17 mg/kg. The concentration of copper is high with 20.13mg/l in top layer of sediments from Uppanar and minimum concentration of 0.39mg/l found in bottom section of Gadilam estuary. In Uppanar, the trend of copper concentration is more and the mean copper concentration is by lowest river discharge (Usha Damodar and Vikram Reddy 2012). It is also said that extreme amount of copper in water may be due to the anthropogenic activities, agriculture, sludge and municipal and industrial solids wastes dumped into the river water and the occurrence of high percentage of Cu in Uppanar river is due to the natural weathering of soil. This higher accumulation rate may mainly be due to increased use of fertilizer and discharge into the river bed in the district.

4.4 Zinc

The concentration of zinc found in the core sediment's sample at Ponnaiyar, Gadilam, Uppanar and Vellar range between 4.88–13.52mg/kg, 3.06–3.56mg/kg, 5.81 to 30.67mg/kg and 7.93–9.16mg/kg. Here an elevated range of zinc is found in Uppanar samples from top to bottom. This metal can be naturally introduced into water by erosion of minerals from rocks and soil. However, zinc ores are slightly soluble in water. Zinc is generally found in nature, but in limited concentration. It is an important micronutrient in humans and only at very high concentration it may cause harmful effects. The zinc absorption in the study area may be emitted from different sources through discharges of many commercial productions of industries of metal processing and mining activities, urban runoff, and municipal sewages (Shah et al., 2005, Shrivastava et al., 2011).

4.5 Cobalt

Cobalt is present in sediments, since it is rapidly taken from solution by absorption and precipitated as secondary oxides where hydrous manganese oxides have a particularly strong absorption similarity for cobalt. There are different anthropogenetic sources of cobalt like fertilizers, special steels, coal combustion, and iron, silver and lead exploring and mineral processing (Reimann and de Caritat, 1998), in some cases are recorded from anthropogenic anomalies in drainage systems. The highest concentration of cobalt found in the estuary sediment sample is 4.15mg/kg and minimum amount is 0.76mg/kg. The concentration range of Co is 1.41–5.05mg/kg, 0.76–0.94mg/kg, 1.9–3.15mg/kg and 3.24–4.15mg/kg in Pannaiyar, Gadilam, Uppanar and Vellar River estuary respectively. Cobalt concentration is more in bottom sediment of Ponnaiyar and surfaces sample of Vellar estuary. This analysis result supposed that problems of environmental pollution due to cobalt generally less significant than among the associated other heavy metals (Cole and Carson, 1981).

4.6 Iron

Iron is the most abundant metal in earth crust. The concentration of iron found in four estuaries core sediment sample was quite high. The average concentration of iron depth wise from Ponnaiyar, Gadilam, Uppanar and Vellar estuaries ranges between 491–470mg/kg, 419–320mg/kg, 533–510mg/kg and 438–426mg/kg respectively. The iron concentration is little higher in Uppanar estuary sediment than other estuaries. Industrial waste disposed into this estuary and the urban, municipal wastage are the root cause. However, contamination of anthropogenic origin cannot be excluded, since the iron content is attributed by weathering of soil and rocks by various activities of mining and fertilizers for agricultural products.

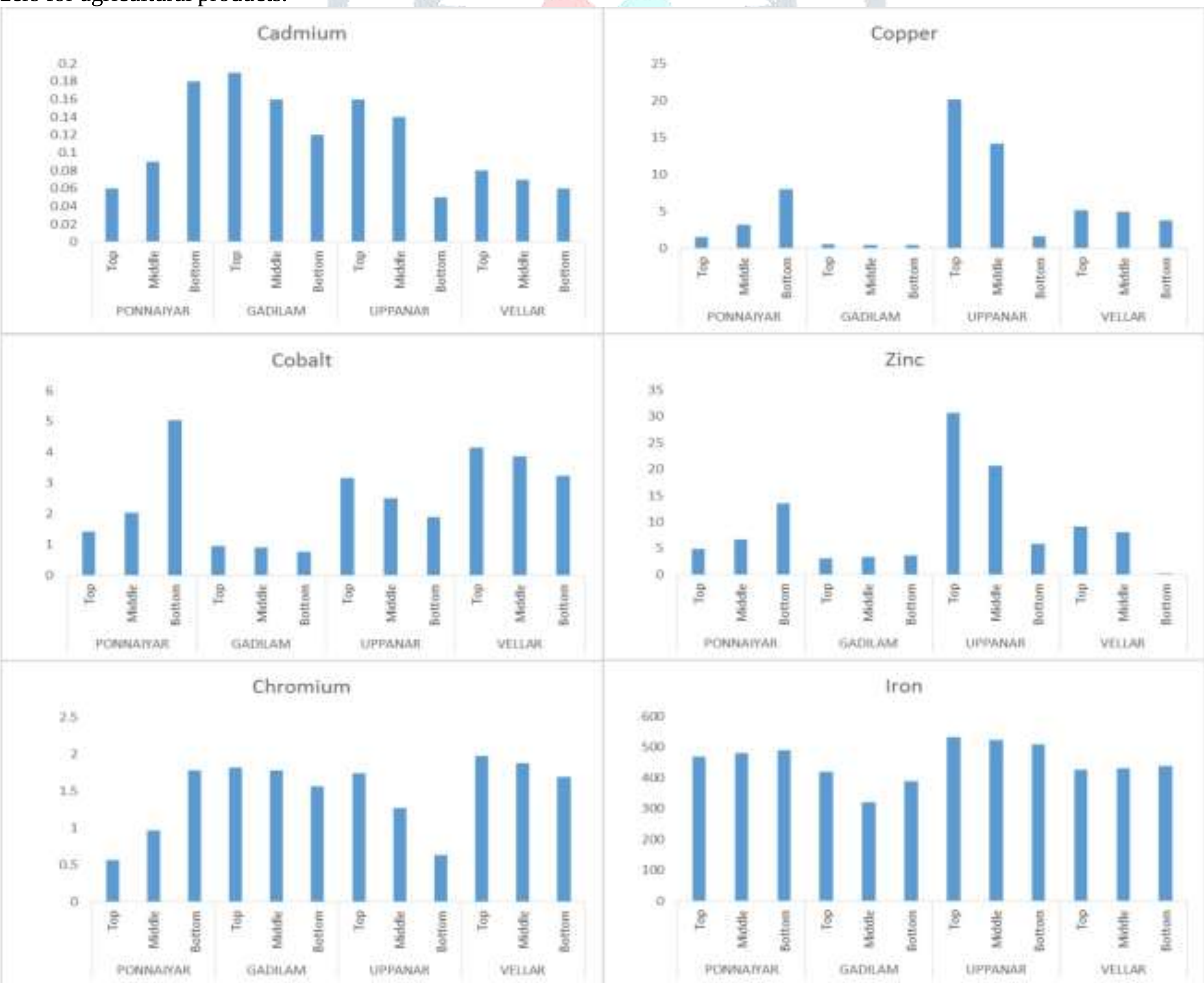

Fig 2. Heavy metal Concentration in the sediments (mg/kg)

V. ENRICHMENT FACTOR (EF)

The uses of Enrichment factor (EF) was differentiate between the metal derived from anthropogenic behaviour and those from natural process, and to review the quantity of anthropogenic influence Sutherland (2000). The definition of Enrichment factor equations are below,

$$EF(X) = \frac{(X/N)\ sample}{(X/N)\ control}$$

EF(X) represent as the enrichment factor for the metal X, (X/N) sample is ratio of the concentration of metal X to major metal N (Fe or Al) in the samples and (X/N) control pointed as concentration of ratio of metal. To reduce the effect of grain size, metal concentrations in sediments are considered in terms of enrichment factor. The use of enrichment factors permit for comparison of sediments, from diverse environments and the assessment of sediments is obtained to determine the metal content through diverse analytical technique (Cantillo, 1982).According to Orth and Wells (2009) the common move to estimate the extent to which the sediment has been impacted (naturally and anthropogenically) with heavy metal is to estimate the enrichment factor for the metal concentration above unpolluted background levels. Generally, the values of the enrichment factor to evaluate the level of the sediment with the metals. EF ≤ 1 No enrichment, EF < 2 Minimal enrichment, EF 2–5 Moderate enrichment, EF5–20 Significant enrichment, EF >40 extremely high enrichment. In the study area of the four estuaries the samples collected fall in <1 and classified as below background concentrations. The enrichment factor calculation result is shown in (Fig 3.)

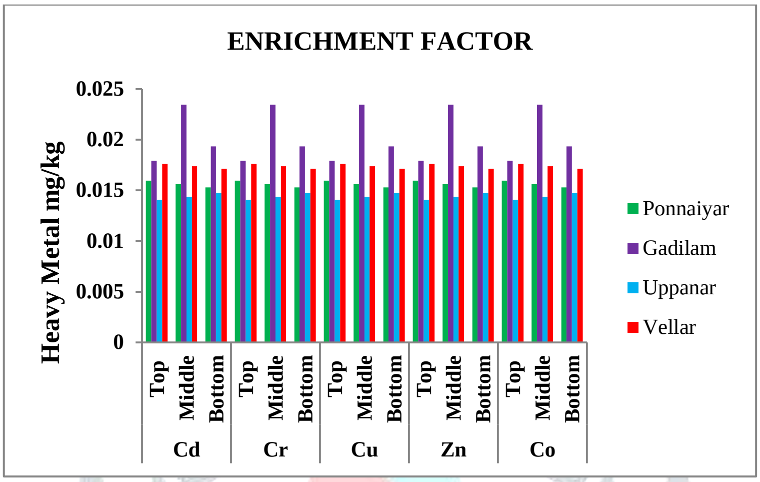

Fig 3. Enrichment Factor values for heavy metals in sediments (mg/kg)

VI. CONTAMINATION FACTOR (CF)

The levels of metals contamination in sediment are commonly derived in terms of a contamination factor (CF). Hakanson (1980) has recommended the CF formula for calculate the degree of contamination, that are followed

$$(CF) = \frac{Cm\ sample}{Cm\ \ Background}$$

Cm Sample = metal concentration in sample,

Cm Background= metal concentration in background or control sample,

Specific average value crustal elements are measured as background values in (CF) analysis (Turekian and Wedepohl 1961; Taylore and McLennan 1981). If (CF) <1 refers to low contamination; (CF) 1> to >3 refers to moderate contamination; (CF) 3> to >6 refers to considerable contamination; (CF) > 6 indicates very high contamination. The complete analysis of these contamination factor values of the metals in the study area evaluated with the background and toxicological indication values of sediments. It is clearly estimated that the sediment contamination in the study area are highlights lower contamination of all metals. The sediment samples of all location range between <1, that fall in the classification of Low polluted category (Fig 4).

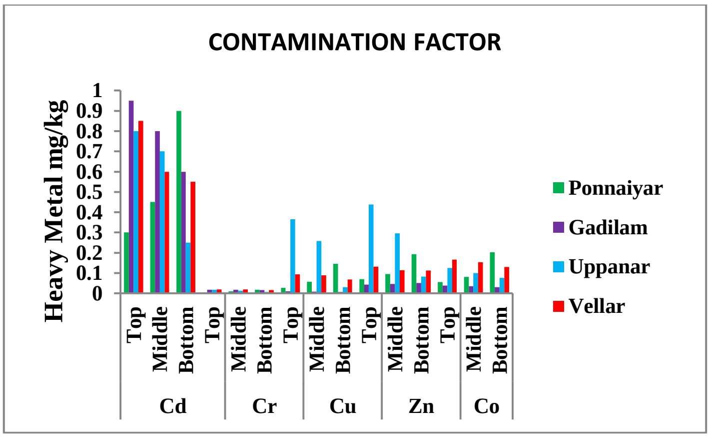

Fig 4. Contamination Factor values for heavy metals in sediments (mg/kg)

VII. GEO-ACCUMULATION INDEX (I-GEO)

Geo-accumulation index was determined by the following equation according to Muller (1969) which was described by Boszke et al (2004). I-geo = log 2 (Cn / 1.5 Bn) where, Cn = Measured concentration of heavy metal in the Tigris sediment. Bn = Geochemical background value in average shale of element n. The factor 1.5 is used for the possible variations of the background data due to lithological variations. I-geo was classified into seven grades: I-geo ≤ 0 (grade 0), unpolluted; 0< I-geo ≤1 (grade 1), slightly polluted; 1 < I-geo ≤ 2 (grade 2), moderately polluted; 2< I-geo ≤3 (grade 3), moderately severely polluted; 3< I-geo ≤4 (grade 4), severely polluted; 4< I-geo ≤5 (grade 5), severely extremely polluted; I-geo > 5 (grade 6), extremely polluted. It can be interpreted that all the sampling stations of Ponnaiyar estuary, Gadilam estuary, Uppanar estuary, Vellar estuary sediments are affected with severe trace metal contamination problem. The source of certain elements can be attributed to solid waste and effluent discharge from industries. All samples are classified as unpolluted to moderately polluted ranging between 0–1 (Fig 5).

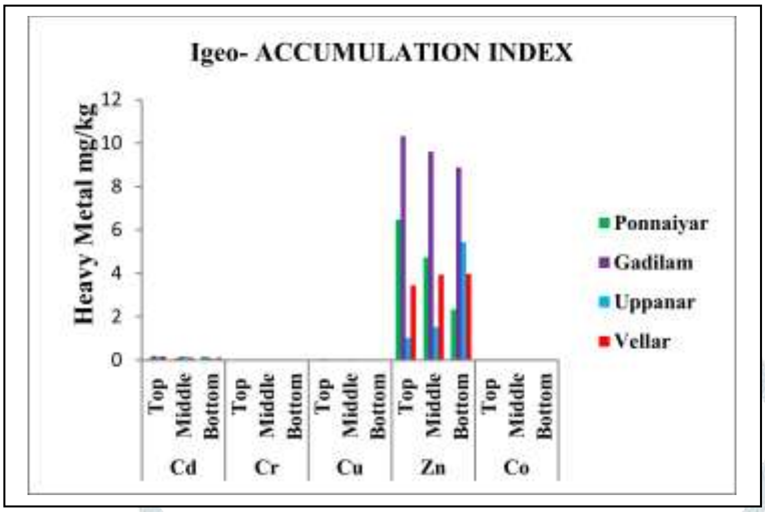

Fig. 5 Igeo Accumulation Index values for heavy metals in sediments (mg/kg)

VIII. POLLUTION LOAD INDEX (PLI)

Tomlinson (1980) had worked on a simple calculation method on Pollution Load Index (PLI) for measurement the extent of pollution due to the heavy metals in estuarine sediments. PLI range in sediments is calculated using the equation.

Pollution Load Index = $n\sqrt{CF_1 \times CF_2 \times CF_3 \times \ldots CF_n}$

Where,

Contamination factor - (CF), Concentration of pollutant in sediment - (C metal), Background value for the metal (C background), Number of metals (n), PLI - > 1 polluted and < 1 no pollution. In the entire sediment samples of the study area, the Pollution Load Index of Cu, Zn, and Co are high polluted but in the Ponnaiyar River, Gadilam River, Uppanar River, Vellar River sediments are highly influenced by Fe than the other metals (Fig 6).

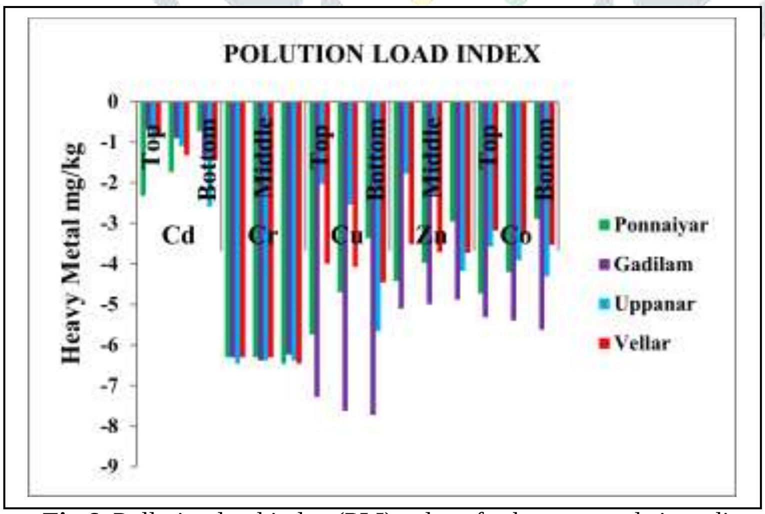

Fig 6. Pollution load index (PLI) values for heavy metals in sediments (mg/kg)

IX. CONCLUSION

The sediments collected from the estuaries of Cuddalore district encompass an elevated range of total metal content in Uppanar. The area with higher amount of cadmium is found in surface sediments of Gadilam and Uppanar. Chromium is abundant in all samples of Gadillam and Vellar estuary and an elevated metal range of copper, cobalt and zinc concentration is found in Uppanar estuary. Enrichment Factors directly suggested contribution of anthropogenic has significantly affected in the cases of Cr, Cu, Cd, Pb and Zn along estuaries. Contamination factor despite the fact that the five metals in the sediments of estuary is classified as low contaminated category. Enrichment factor detected below the background concentration is considerably lower than the crustal values. The Geo accumulation Index is in conformity with the other contamination indicators. Most of the sediment samples were classified under the “unpolluted to moderately polluted” categories. The controlling influence of the sediment samples can be “occasionally” or “frequently associated to toxic biological effects”. The pollution load index of Cu,Zn and Co of sediments in the river estuary is reported low compared with Fe in all river estuary. It is concluded that the analysis of the core sediments in estuaries demonstrates that under the present conditions, only small concentration of metals have accumulated in the sediments by dissolution. These metals require prolonged time periods in order to be removed through natural pathways. The spatial distribution of the metals in the sediments of the estuaries, show a drastic increase of metals in Gadilam and Uppanar contributed by hub of industries in SIPCOT complex when compared with Ponnaiyar and Vellar estuary of Cuddalore district.

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