**Abstract**

The heavy metals enrichment and contamination are deliberated from twenty-four sediment samples collected along the Tamirabarani river and estuary. The concentration and spatial distribution of heavy metals in Tamirabarani River and estuary are analyzed for Copper, Nickel, Chromium, Lead, Zinc, Cadmium and Iron. The extent of pollution in these sediments was assessed using enrichment factor (EF), contamination factor (CF), geo-accumulation index ($I_{geo}$), Pollution Load Index (PLI). The contamination factor specify low to moderately contaminated, except for Cd. $I_{geo}$ factors of all samples comprise strongly to extremely polluted index for Cd and moderately polluted index for Pb. The area PLI load for winter indicate higher variation than in summer, it is also noted that Pb and Cd are the major pollutants contributing high PLI values in the study area. This elevated value is mainly owing to the salinity intrusion and anthropogenic inputs. The constant variation of metals in sediment samples is due to the linking of industrial and anthropogenic influences. The combined and collective consequences go in front to a severe risk to the entire estuarine environment.

**Keywords:** Tamirabarani; River and estuary; Sediments; Heavy metals; Enrichment factors; Contamination factor; Geo-accumulation index; Pollution Load Index

**Introduction**

In recent past, there have been increasing interests regarding heavy metal contaminations in the environments, apparently due to their toxicity and perceived persistency within the aquatic systems [1]. There are basically three reservoirs of metals in the aquatic environment: water, sediment and biota [2]. The analysis of river sediment is a useful method of studying heavy metals to assess environmental pollution [3,4]. Heavy metals accumulate in the sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds [5]. Atmospheric particles generated by the natural sources are found to be accumulated as atmospheric metal load. In isolated areas, the amount of metal load by natural processes is higher, while the other side it may be due to anthropogenic sources. Aeolian process carries the soil particles on global scale to the atmosphere and end up in rivers that transport metal containing particles to lakes and to the ocean. Volcanoes eruption discharged materials is also a prime source for certain amount of cadmium in the air. As well as the metals that are part of vegetation can be released and extend through forest fires. Heavy metal pollution of an aquatic ecosystem has become a potential global problem today and these heavy metals are among the most common environmental pollutants, as well as their occurrence in waters and sediments is originated from natural or anthropogenic sources. A trace amount of heavy metals is always present in fresh waters from terrigenous sources, such as weathering of rocks, which may be recycled through chemical and biological contaminates in these ecosystems [6-10]. Heavy metal contamination in sediments could affect the quality and bio-assimilation and bioaccumulation of metals in an aquatic ecosystem. Further, these metals are immobilised within the sediments and thus might be involved in absorption, co-precipitation and complex creation [9-13].

**Materials and Methods**

**Study area**

Tamirabarani River originates from western Ghat hills flows all along the East coast and drains at Bay of Bengal. The present estuarine region falls in the part of Thoothukudi districts, east coast of Tamil Nadu state. It lies in the SOI toposheet Nos. 58 L/2 and located in between 8°25' N and 9°10' N latitudes and 77°10’ E and 78° 15’ E longitudes, with an area of (169.226  Sq. km) (Figure 1). The study area is blessed with deltaic system with different active and inactive distributaries. The southwestern part is dominated by river and the northern part by the sea [14].

**Sediments sampling and analysis**

In the study area, twenty-four sediment samples were collected at the river mouth estuary and distributary channels for two seasons (summer and winter) (Figure 2). The sampling locations were identified and recorded using a hand-held GPS (Magellan); surface sediment’s samples collected and packed in thick polyethylene bags. In the laboratory, the collected samples were frozen at -4°C to avoid soil contamination. The freezing of the samples below -4°C, avoid the growth of microbes or bacteria, which can result in the variation of metal in sediments. These samples were then dried in a hot-air oven and after homogenized using pestle and mortar. Dry sieving is done in 2 mm mesh sieve and stored for further analysis [10,15,16]. The sediment’s samples were digested and extracted based on the procedure of Manasrah et al. [17] and subjected for the assessment of trace metals using AAS with specific flame and wavelength (Atomic Absorption Spectrometer, Elico make) using a series of solution over the range 2–10 mg/l. The concentration of the metals was normalised and inferred for the following parameter.

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Result and Discussion

Enrichment factor

Enrichment factor (EF) is the proportional abundance of the chemical elements that helps to assess the degree of contamination. EF computed relative to the abundance of species in source material found in the Earth’s crust is considered as a better method for understanding the geochemical trends [8,9,18]. According to Harikuma et al., Sekabira et al., and Chandrasekaran et al. [8-10] has derived six categories as background concentration 1, depletion to minimal enrichment 1–2, moderate enrichment 2–5, significant enrichment 5–20, very high enrichment and 20–40 extremely high enrichment 40 (Table 1). It was found that the entire samples plunge below 1 and thus it is inferred that they represent the background concentration [19-21]. Moreover, the samples with higher Cd and Pb concentration are found in all locations of the study area comparatively higher than others due to the sea interface, which has high pH and salinity (Tables 1-3) and (Figures 3 and 4).

Contamination factor (CF)

The levels of contamination in sediment by metals are frequently expressed in terms of a contamination factor (CF). If CF, <1 denotes low contamination; 1> CF >3 means moderate contamination; 3>CF >6 indicates considerable contamination and CF >6 specifies very high contamination.
Geo-accumulation index ($I_{geo}$). This method provides the metal pollution in terms of seven (0 to 6) enrichment classes ranging from background concentration to very heavily polluted. (Table 6). Based on the classification system $I_{geo}$ factors for all samples displays strongly to extremely polluted index for contamination. The complete analysis of this contamination factor value of the metals in the study area is compared with the background and toxicological reference values of sediments. It appears that all the metals are low to moderately contaminated, except Cd, which shows very high contamination in all locations than summer. Especially locations from 5 to 18 in downstream has observed Cd contamination ranging from 78.35 to 106.25 and considerable absorption of Pb is found in downstream (Location 2 to 12) due to variation in salinity, which governs the formation of non-bio available Cd chloride complex, anthropogenic inputs and industrial wastage (Tables 4 and 5) and (Figures 5 and 6).

### Table 2: Enrichment factor-Summer.

| Location | Cu  | Ni  | Cr  | Pb  | Zn  | Cd  |
|----------|-----|-----|-----|-----|-----|-----|
| 1        | 0.534 | 0.534 | 0.534 | 0.534 | 0.534 | 0.534 |
| 2        | 0.46 | 0.46 | 0.46 | 0.46 | 0.46 | 0.46 |
| 3        | 0.421 | 0.421 | 0.421 | 0.421 | 0.421 | 0.421 |
| 4        | 0.524 | 0.524 | 0.524 | 0.524 | 0.524 | 0.524 |
| 5        | 0.468 | 0.468 | 0.468 | 0.468 | 0.468 | 0.468 |
| 6        | 0.488 | 0.488 | 0.488 | 0.488 | 0.488 | 0.488 |
| 7        | 0.46 | 0.46 | 0.46 | 0.46 | 0.46 | 0.46 |
| 8        | 0.455 | 0.455 | 0.455 | 0.455 | 0.455 | 0.455 |
| 9        | 0.436 | 0.437 | 0.436 | 0.437 | 0.437 | 0.437 |
| 10       | 0.453 | 0.453 | 0.453 | 0.453 | 0.453 | 0.453 |
| 11       | 0.517 | 0.516 | 0.517 | 0.517 | 0.517 | 0.517 |
| 12       | 0.605 | 0.605 | 0.605 | 0.605 | 0.605 | 0.605 |
| 13       | 0.688 | 0.688 | 0.688 | 0.688 | 0.688 | 0.688 |
| 14       | 0.674 | 0.669 | 0.674 | 0.674 | 0.674 | 0.674 |
| 15       | 0.603 | 0.603 | 0.603 | 0.603 | 0.603 | 0.603 |
| 16       | 0.517 | 0.516 | 0.516 | 0.516 | 0.516 | 0.516 |
| 17       | 0.601 | 0.601 | 0.601 | 0.601 | 0.601 | 0.601 |
| 18       | 0.64 | 0.639 | 0.637 | 0.639 | 0.639 | 0.64 |
| 19       | 0.563 | 0.562 | 0.563 | 0.562 | 0.562 | 0.562 |
| 20       | 0.775 | 0.774 | 0.775 | 0.775 | 0.775 | 0.775 |
| 21       | 0.854 | 0.854 | 0.854 | 0.854 | 0.854 | 0.854 |
| 22       | 0.812 | 0.811 | 0.811 | 0.812 | 0.812 | 0.812 |
| 23       | 0.873 | 0.872 | 0.872 | 0.872 | 0.872 | 0.871 |
| 24       | 0.91 | 0.911 | 0.912 | 0.91 | 0.91 | 0.954 |

### Table 3: Enrichment factor-Winter.

| Location | Cu  | Ni  | Cr  | Pb  | Zn  | Cd  |
|----------|-----|-----|-----|-----|-----|-----|
| 1        | 0.43 | 0.184 | 0.198 | 1.308 | 0.291 | 32.15 |
| 2        | 0.61 | 0.189 | 0.288 | 1.939 | 0.468 | 48.3 |
| 3        | 0.539 | 0.24 | 0.268 | 2.296 | 0.495 | 43.25 |
| 4        | 0.599 | 0.381 | 0.294 | 1.466 | 0.552 | 47.15 |
| 5        | 0.548 | 0.282 | 0.272 | 1.42 | 0.577 | 42.6 |
| 6        | 0.523 | 0.261 | 0.315 | 1.488 | 0.596 | 51.05 |
| 7        | 0.487 | 0.286 | 0.289 | 1.664 | 0.497 | 43.35 |
| 8        | 0.603 | 0.221 | 0.355 | 1.744 | 0.551 | 45.75 |
| 9        | 0.592 | 0.189 | 0.294 | 1.176 | 0.574 | 52.6 |
| 10       | 0.5 | 0.301 | 0.402 | 1.712 | 0.635 | 56.25 |
| 11       | 0.487 | 0.218 | 0.384 | 2.592 | 0.566 | 42.35 |
| 12       | 0.579 | 0.167 | 0.273 | 1.936 | 0.412 | 46.75 |
| 13       | 0.531 | 0.258 | 0.381 | 2.18 | 0.426 | 38.95 |
| 14       | 0.365 | 0.237 | 0.397 | 1.144 | 0.467 | 32.05 |
| 15       | 0.332 | 0.185 | 0.348 | 1.12 | 0.588 | 37.8 |
| 16       | 0.307 | 0.179 | 0.389 | 1.008 | 0.401 | 34.15 |
| 17       | 0.322 | 0.162 | 0.397 | 1.128 | 0.354 | 29.1 |
| 18       | 0.298 | 0.17 | 0.37 | 1.056 | 0.264 | 28.95 |
| 19       | 0.132 | 0.097 | 0.146 | 0.672 | 0.127 | 15.9 |
| 20       | 0.154 | 0.089 | 0.132 | 0.632 | 0.132 | 13.55 |
| 21       | 0.176 | 0.103 | 0.129 | 0.544 | 0.126 | 18.65 |
| 22       | 0.159 | 0.074 | 0.147 | 0.618 | 0.133 | 11.4 |
| 23       | 0.166 | 0.057 | 0.134 | 0.694 | 0.109 | 15.6 |

### Table 4: Contamination factor-Summer.

Figure 5: Contamination factor – Summer.
Cd and moderately polluted index for Pb. This higher value is chiefly owing to the salinity factor, comparatively higher than summer. The Igeo “uncontaminated” label is clearly appropriated for overall description of the heavy metals in sediments of estuary. The diagrammatic view of Igeo illustrate that higher values of Cd are distinguished in the estuarine part of the study area and it decreases in upstream area (Tables 7 and 8) and (Figures 7 and 8).

Pollution Load Index

Tomlinson et al. [23] has employed a simple method for Pollution Load Index (PLI) to assess the extent of pollution in metals of estuarine sediments. It is given as, if, PLI >1 as “polluted” and if < 1 as “no pollution”. In the study area, pollution load index values exhibited gives valuable information for the policy and decision makers on the pollution level of the area. The highest PLI values were observed in lower part of the river or estuary were water interchanges area of the river. The river with more water gives an idea about comparatively lower PLI values. The PLI values for summer and winter for Pb are (1.240 and 2.566) and Cd (2.615 and 69.963) describes higher PLI in winter than summer. It is noted that Pb and Cd are the major pollutants contributing elevated PLI values in the study area (Table 9).
Conclusion

It is estimated that EF of all samples in the study area go down below 1 and thus it is inferred that they represent the background concentration. Moreover, the samples with higher Cd and Pb concentration are found in all locations. This enrichment factors suggest minor to moderate enhancement of Cd and Pb is present in the sediments. Higher concentration of Cd and Pb are observed in winter season is due to high pH, salinity and anthropogenic activity in seaward and in downstream direction as a result of sea interface. The comprehensive analysis of the contamination factor for the average values of the metals in the study is compared with the background and toxicological reference values of sediments. It appears that all the metals are low to moderately contaminated, except Cd, which shows very high contamination. The element contribution and enrichment of metals compared with the toxicological levels shows that Tamirabarani River and estuary sediments are moderately polluted. The spatial distributions of contamination factor illustrate higher values for Cd is nearer the estuary region with varied salinity and tidal fluctuation, which is in agreement with the earlier interpretations. Based on the classification system proposed for Igeo factors, all samples have strongly below 1 and thus it is inferred that they represent the background concentration.

Table: 7 Geo-accumulation Index Summer.

| Location | Cu    | Ni    | Cr    | Pb    | Zn    | Cd  |
|----------|-------|-------|-------|-------|-------|-----|
| 1        | -1.797| -3.026| -2.916| 0.196 | -2.362| 4.421 |
| 2        | -1.295| -2.986| -2.375| 0.368 | -1.677| 5.006 |
| 3        | -1.471| -2.641| -2.481| 0.611 | -1.598| 4.847 |
| 4        | -1.322| -1.973| -2.348| 0.029 | -1.441| 4.973 |
| 5        | -1.451| -2.408| -2.461| 0.076 | -1.375| 4.827 |
| 6        | -1.518| -2.518| -2.249| 0.009 | -1.328| 5.086 |
| 7        | -1.621| -2.388| -2.375| 0.149 | -1.591| 4.856 |
| 8        | -1.312| -2.76 | -2.076| 0.215 | -1.441| 4.93  |
| 9        | -1.338| -2.98 | -2.348| 0.348 | -1.455| 5.129 |
| 10       | -1.581| -2.315| -1.897| 0.189 | 1.235 | 5.229 |
| 11       | -1.621| -2.78 | -1.963| 0.787 | -1.401| 4.817 |
| 12       | -1.368| -3.159| -2.455| 0.365 | -1.863| 4.96  |
| 13       | -1.495| -2.534| -1.973| 0.538 | -1.813| 4.697 |
| 14       | -2.036| -2.657| -1.916| -0.388| -1.681| 4.415 |
| 15       | -2.172| -3.016| -2.106| -0.428| -1.348| 4.654 |
| 16       | -2.285| -3.063| -1.946| -0.571| -1.19  | 4.508 |
| 17       | -2.215| -3.205| -1.913| -0.408| -2.079| 4.275 |
| 18       | -2.132| -2.85 | -1.95 | -0.571| -2.372| 4.488 |
| 19       | -2.328| -3.139| -2.435| -0.504| -2.504| 4.269 |
| 20       | -3.501| -3.943| -3.358| -1.156| -3.554| 3.405 |
| 21       | -3.279| -4.059| -3.504| -1.245| -3.495| 3.172 |
| 22       | -3.086| -3.853| -3.538| -1.458| -3.571| 3.634 |
| 23       | -3.229| -4.328| -3.348| -1.275| -3.495| 2.923 |
| 24       | -3.172| -4.694| -3.475| -1.109| -3.774| 3.378 |

Table: 8 Geo-accumulation Index Winter.

| Location | Cu    | Ni    | Cr    | Pb    | Zn    | Cd  |
|----------|-------|-------|-------|-------|-------|-----|
| 1        | -1.674| -2.578| -1.84 | 0.212 | -1.916| 5.119 |
| 2        | -1.139| -2.501| -0.794| 1.704 | -1.491| 5.501 |
| 3        | -1.335| -2.325| -0.524| 1.481 | -1.438| 5.568 |
| 4        | -1.116| -1.183| -0.627| 1.841 | -1.328| 5.358 |
| 5        | -1.202| -1.996| 0.79  | 1.561 | -1.176| 5.867 |
| 6        | -1.285| -2.069| -1.458| 1.521 | -1.118| 5.953 |
| 7        | -1.428| -2.033| -1.345| 1.481 | -1.398| 5.704 |
| 8        | -1.109| -2.192| -1.468| 1.451 | -1.265| 5.86 |
| 9        | -1.222| -2.275| -1.292| 1.541 | -1.365| 5.946 |
| 10       | -1.328| -1.877| -0.544| 1.704 | -1.112| 6.146 |
| 11       | -1.375| -2.196| -0.637| 1.534 | -1.265| 5.943 |
| 12       | -1.176| -2.342| -0.74 | 1.448 | -1.471| 6.016 |
| 13       | -1.289| -2.461| -1.887| 0.757 | -1.448| 5.89 |
| 14       | -1.601| -2.302| -1.222| 0.488 | -1.401| 5.797 |
| 15       | -1.766| -2.365| -1.966| 0.285 | -1.166| 5.87 |
| 16       | -1.803| -2.182| -1.847| 0.249 | -1.438| 5.67 |
| 17       | -1.857| -2.215| -1.474| 0.126 | -1.588| 5.674 |
| 18       | -1.674| -2.435| -1.89 | 0.269 | -1.744| 5.8 |
| 19       | -1.877| -2.335| -2.109| 0.305 | -2.099| 5.411 |
| 20       | -2.252| -2.973| -2.95 | -0.378| -2.508| 4.767 |
| 21       | -2.219| -3.033| -2.986| -0.146| -2.438| 4.72 |
| 22       | -2.219| -2.926| -2.986| -0.242| -2.641| 4.843 |
| 23       | -2.102| -3.159| -2.95 | -0.077| -2.518| 4.677 |
| 24       | -2.176| -3.073| -3.023| -0.192| -2.594| 4.81 |
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