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Metal Enrichment and Contamination in River and Estuary Sediments of Tamirabarani, South India

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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 sediments 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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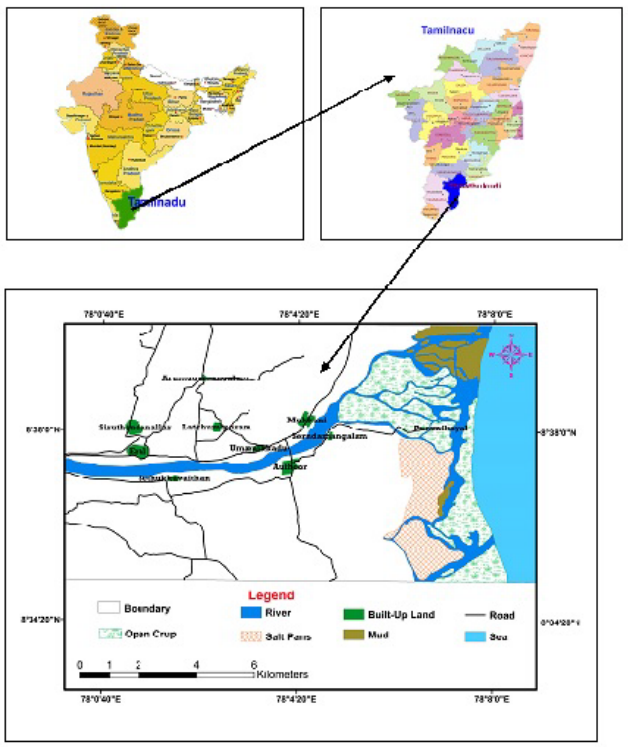

Figure 1: Study area base map.

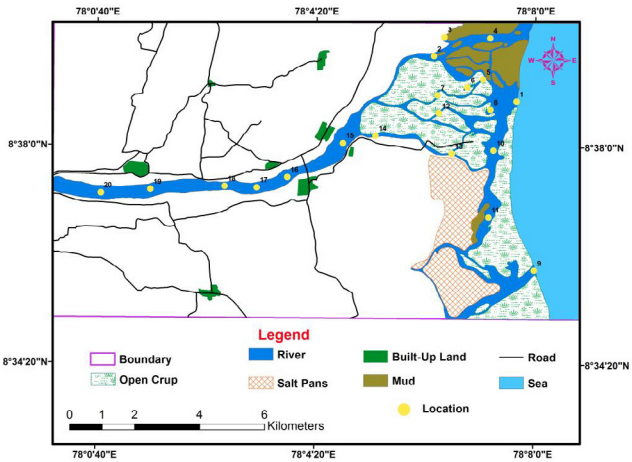

Figure 2: Study location map.

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

Enrichment Factor	Status
<1	No enrichment
1-2	Depletion to Minor enrichment
2-5	Moderate enrichment
5-20	Significant enrichment
20-40	Very high enrichment
>40	Extremely high enrichment

Table 1: Enrichment factor standard values.

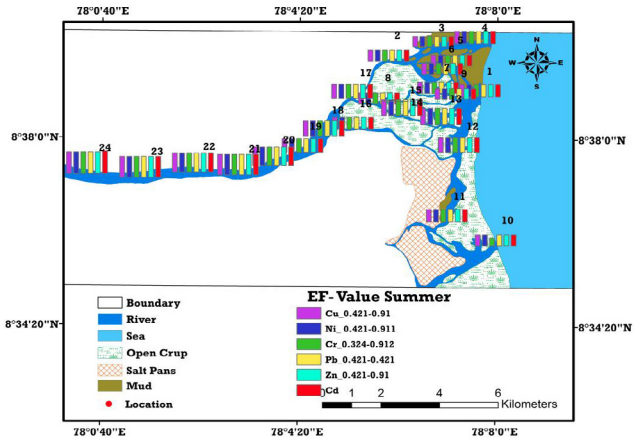

Figure 3: Enrichment factor – Summer.

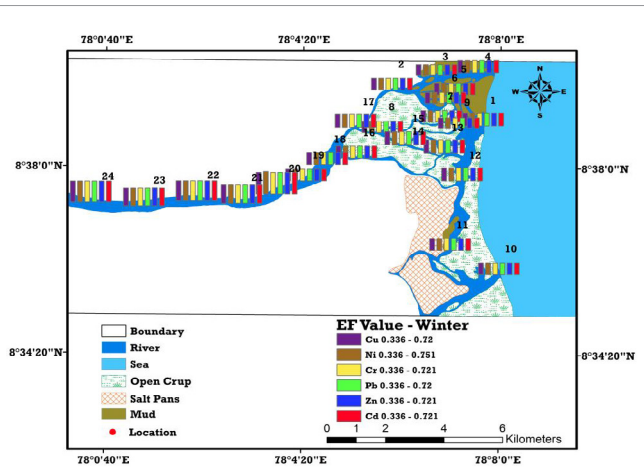

Figure 4: Enrichment factor – Winter.

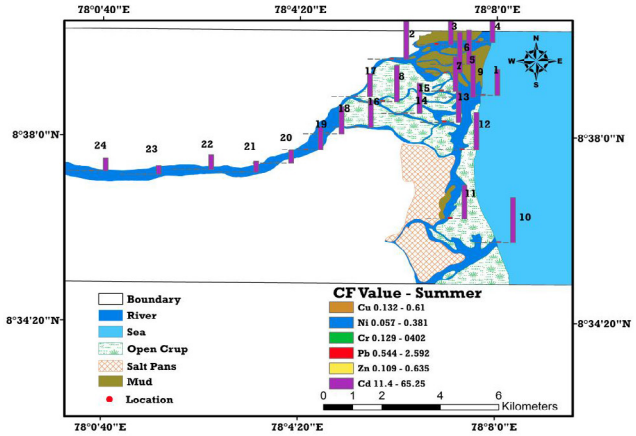

Figure 5: Contamination factor – Summer.

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	0.42
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	0.437	0.436	0.437	0.437
10	0.453	0.453	0.324	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	0.6	0.601	0.601	0.601	0.6
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	0.773
21	0.854	0.854	0.854	0.853	0.854	0.853
22	0.812	0.811	0.812	0.811	0.812	0.812
23	0.873	0.872	0.872	0.872	0.867	0.871
24	0.91	0.911	0.912	0.91	0.91	0.954

Table 2: Enrichment factor-Summer.

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 area 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).

Geo-accumulation index (I_{geo})

Enrichment of metal absorption was calculated by adopting geoaccumulation [22] methods, termed the 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

Location	Cu	Ni	Cr	Pb	Zn	Cd
1	0.432	0.432	0.432	0.432	0.433	0.433
2	0.388	0.388	0.388	0.388	0.388	0.388
3	0.36	0.36	0.36	0.36	0.36	0.36
4	0.403	0.403	0.403	0.403	0.403	0.402
5	0.378	0.378	0.378	0.378	0.378	0.378
6	0.362	0.369	0.369	0.369	0.369	0.369
7	0.38	0.38	0.38	0.38	0.38	0.38
8	0.371	0.371	0.371	0.371	0.371	0.371
9	0.336	0.336	0.336	0.336	0.336	0.336
10	0.369	0.369	0.369	0.369	0.369	0.369
11	0.396	0.396	0.396	0.396	0.396	0.396
12	0.431	0.431	0.431	0.431	0.431	0.431
13	0.443	0.443	0.443	0.443	0.444	0.443
14	0.413	0.413	0.413	0.413	0.413	0.411
15	0.428	0.428	0.428	0.428	0.428	0.428
16	0.402	0.402	0.402	0.402	0.402	0.403
17	0.429	0.429	0.429	0.429	0.429	0.428
18	0.409	0.409	0.409	0.409	0.409	0.409
19	0.388	0.388	0.388	0.387	0.388	0.388
20	0.72	0.751	0.721	0.72	0.721	0.721
21	0.609	0.609	0.609	0.609	0.609	0.61
22	0.663	0.663	0.663	0.663	0.663	0.663
23	0.59	0.59	0.59	0.59	0.597	0.589
24	0.694	0.694	0.694	0.694	0.694	0.694

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	1.112	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	0.341	0.208	0.387	1.008	0.289	33.7
19	0.298	0.17	0.277	1.056	0.264	28.95
20	0.132	0.097	0.146	0.672	0.127	15.9
21	0.154	0.089	0.132	0.632	0.132	13.55
22	0.176	0.103	0.129	0.544	0.126	18.65
23	0.159	0.074	0.147	0.618	0.133	11.4
24	0.166	0.057	0.134	0.694	0.109	15.6

Table 4: Contamination factor-Summer.

Location	Cu	Ni	Cr	Pb	Zn	Cd
1	0.469	0.25	0.418	1.74	0.397	52.15
2	0.68	0.264	0.864	4.896	0.532	68
3	0.594	0.298	1.042	4.193	0.552	71.25
4	0.69	0.421	0.97	4.192	0.596	61.65
5	0.651	0.375	0.866	4.432	0.662	87.6
6	0.614	0.357	0.545	4.296	0.69	93.05
7	0.556	0.366	0.589	4.192	0.568	78.35
8	0.694	0.328	0.542	4.112	0.623	87.25
9	0.687	0.309	0.612	4.368	0.581	92.6
10	0.596	0.408	1.026	4.896	0.692	106.25
11	0.578	0.327	0.964	4.384	0.623	92.35
12	0.663	0.295	0.897	4.096	0.54	97.25
13	0.613	0.272	0.405	2.536	0.549	88.95
14	0.493	0.304	0.642	2.107	0.567	83.55
15	0.441	0.29	0.383	1.832	0.667	87.8
16	0.428	0.33	0.416	1.785	0.552	81.7
17	0.413	0.322	0.446	1.64	0.498	76.6
18	0.469	0.277	0.404	1.808	0.446	83.7
19	0.407	0.296	0.347	1.856	0.35	63.95
20	0.314	0.19	0.194	1.152	0.263	40.9
21	0.336	0.183	0.189	1.354	0.276	39.55
22	0.321	0.197	0.189	1.266	0.24	43.15
23	0.349	0.167	0.194	1.418	0.261	38.4
24	0.331	0.177	0.184	1.31	0.248	42.1

Table 5: Contamination factor-Winter.

Igeo value	Sediment Quality	Location					
		Cu	Ni	Cr	Pb	Zn	Cd
< 0	Unpolluted	-	-	-	-	-	-
0-1	From unpolluted to moderately polluted	-	-	-	-	-	-
1-2	Moderately polluted	-	-	-	2 to 12	-	-
2-3	From moderately polluted to strongly polluted	-	-	-	-	-	-
3-4	Strongly polluted	-	-	-	-	-	-
4-5	From strongly to extremely polluted	-	-	-	-	-	20, 21, 22, 23, 24
>5	Extremely polluted	-	-	-	-	-	1 to 19

Table 6: Geo-accumulation index standard values.

Cd and moderately polluted index for Pb. This higher value is chiefly owing to the salinity factor, comparatively higher than summer. The I_{geo} "uncontaminated" label is clearly appropriated for overall description of the heavy metals in sediments of estuary. The diagrammatic view of I_{geo} 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).

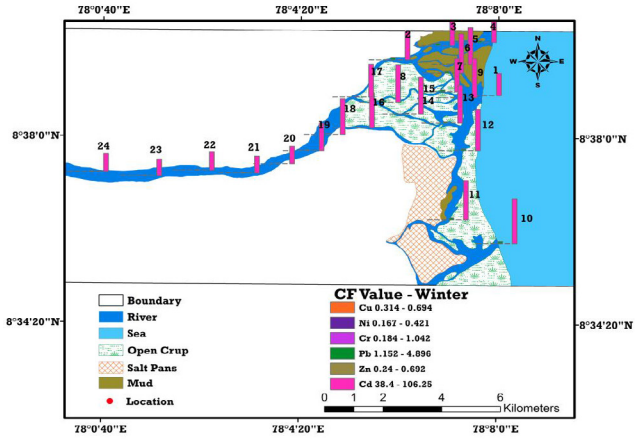

Figure 6: Contamination factor – Winter.

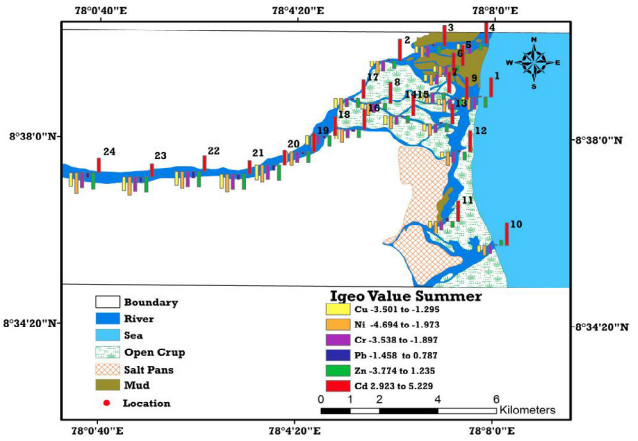

Figure 7: Geo-accumulation Index – Summer.

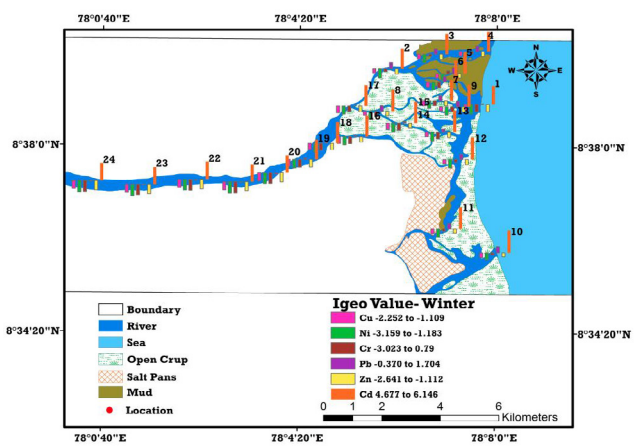

Figure 8: Geo-accumulation Index – Winter.

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	-1.9	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: 7 Geo-accumulation Index Summer.

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	1.481	-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	-1.122	-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	1.544	-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	-1.76	-2.365	-1.966	0.285	-1.166	5.87
16	-1.803	-2.182	-1.847	0.249	-1.438	5.767
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

Table: 8 Geo-accumulation Index Winter.

Metals	Seasons		Standard value	Remarks
	Summer	Winter		
Cu	0.367	0.498	>1	Unpolluted
Ni	0.179	0.282	>1	Unpolluted
Cr	0.269	0.476	>1	Unpolluted
Pb	1.240	2.566	<1	Polluted
Zn	0.349	0.472	>1	Unpolluted
Cd	2.615	69.963	<1	Polluted

Table: 9 Pollution Load Index.

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 I_{geo} factors, all samples have strongly to extremely polluted index for Cd and moderately polluted index for Pb. This upper value is mainly due to the salinity factor in summer. Spatial representation of I_{geo} shows that higher values of Cd are noted in estuarine part of the study area and decreases towards inland followed by Pb. Hence, it is inferred that the variation of this metal is mainly due to the variation in physico-chemical factors in the estuary. The highest PLI values were observed in lower part of the estuary, by outstanding massive mixing of sea and river water. The main streams with enormous water illustrate relatively lower PLI values. The PLI values for most of the sites confirm higher values in winter than in summer and Pb and Cd are the major pollutants contributing high PLI values. The results could be used as a baseline data for future prediction of anthropogenic effects, which can be utilized to assess and defined to establish a better management decision plan to reduce pollution.

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