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HEAVY METAL POLLUTION IN SURFACE WATER AND SEDIMENT: A PRELIMINARY ASSESSMENT OF THAMIRABARANI RIVER IN KANYAKUMARI DISTRICT

S. A. Anuja[1*] & P. Kavitha[2]

[1*]Research Scholar, Reg. No. 19233282032010, Women's Christian College, Nagercoil (Affiliated to ManonmaniamSundaranar University, Tirunelveli-627012, Tamil Nadu)
[2]Assistant Professor, Department of Chemistry, Women's Christian College, Nagercoil-629001, Tamil Nadu, India
[*]Corresponding Author: Email:saanuja@gmail.com

Abstract

The concentration and toxicity of five heavy metals (Cu, Zn, Cd, Ni and Pb) were measured in surface water and sediment of Thamirabarani river in Kanyakumari district, Tamilnadu, India. The present study was carried out the analysis of heavy metals in Thamirabarani river fromPechiparai Dam to Thengaipattinam estuary during the period from September 2020 to August 2021. The decreasing trend of metals were observed in water as Pb > Ni > Zn > Cd > Cu and in sediment as Zn > Cu > Pb > Ni > Cd. The value of studied metals exceeded the safe limits of drinking water, indicating that water from this river is not safe for domestic purposes. Total concentrations of Cd and Pb in the water samples were higher than WHO guidelines for drinking water quality for a maximum number of stations. Enrichment factor (EF), Contamination factor (CF) and Potential ecological risk index (Er^i) revealed high values of cadmium in the Thamrabarani river.

*Key words:*Heavy metal, Enrichment factor, Potential ecological risk.

1.Introduction

Contaminants containing high concentrations of heavy metals continue to be discharged into aquatic systems. These metals are often deposited on the bottom of such systems via precipitation and flocculation, thereby transforming the associated sediments into heavy metal repositories (Malvandi, 2017). Due to their non-degradability, toxicity, and resistance to metabolization (Fabio *et al*., 2021), heavy metals in sediments can harm aquatic organisms, as well as human health, through bioaccumulation and bio-amplification (Saiful *et al*., 2015).

Heavy metals in aquatic sediments originate from both natural sources (mainly erosion and rock weathering) and anthropogenic activities (e.g., industrial discharge, mining, agriculture, transportation, damming, sewage disposal, and wastewater runoff) (Xu *et al*., 2016).Accumulated heavy metals in surface sediments are released into the aquatic environment, causing secondary contamination of the hydrosphere, and increasing the risks to human health (Fanxi Li *et al*., 2022).Geochemical speciation and distribution of metals in the defined chemical fraction also been used in predicting the potential contamination, mobility and bioavailability (Caeiro *et al*., 2005). Thus, it is important to assess the concentrations and distribution of heavy metals in the riverine ecosystem

Large quantities of hazardous chemicals especially heavy metals have been released into rivers worldwide due to global rapid population growth and intensive domestic activities, as well as expanding industrial and agricultural production (Islam *et al*., 2014). Rivers in urban areas have also been associated with water quality problems because of the practice of discharging untreated domestic and industrial waste into the water bodies which leads to an increase in the level of metals in river water (Venugopal *et al*., 2009).

The behaviour of metals in natural water is a function of the substrate sediment composition, the suspended sediment composition, and the water chemistry (Mohiuddin *et al*., 2012). Sediment is an integral and dynamic part of the river basin, with a variety of habitats and environments. However, information on total metal concentrations is not sufficient for the assessment of an environmental impact of sediment contamination which leads to a particular interest in the chemical fractionation of sediment (Nwuche and Ugoji, 2010).

Heavy metals are classified among the most dangerous and toxic groups of anthropogenic environmental pollutants due to their toxicity, persistence and bioaccumulation in the environment (Nyarko *et al*., 2008). Heavy metals are elements that have free electrons. In sediment, the heavy metals present in different chemical forms and generally exhibit different physical and chemical behaviors in chemical interaction, mobility, biological availability, and potential toxicity (Sundaray *et al*., 2011).

Currently, heavy metal contamination has become an environmental problem in terrestrial areas throughout the world. Therefore, this study aims to examine the concentration of the Zn, Cr, Cu, Cd, Pb concentrations in the Thamirabarani river water and sediment and further calculate the pollution status using the Enrichment Factor (EF), Contamination Factor (CF), Pollution Load Index (PLI), Geo accumulation Index (Igeo),(Muller 1969).Potential Ecological Risk (Er^i) approach.

2.Materials and Methods

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The analysis for metal determination is normally carried out by flame atomic absorption spectrometry (FAAS). The main reasons for that are its low operational costs, when compared to other techniques, and its easy operation (Alvarado *et al*., 1988).

2.1 Study area and collection of samples

The Thamirabarani river basin is one of the 17 river basins of Tamil Nadu and is located in Tirunelveli, Thoothukudi and Kanyakumari districts. It is a perennial source of water supply for irrigation, drinking purposes and power generation. Thamirabarani river originates from Agastiyarmalai on the Western Ghats at an altitude of about 2000 m, with its number of tributaries (ie) servalar, Manimuthar, Gatanandhi, Pachaiyar and Chittar. This basin area has varied climatic conditions influenced by southwest and northeast monsoons.

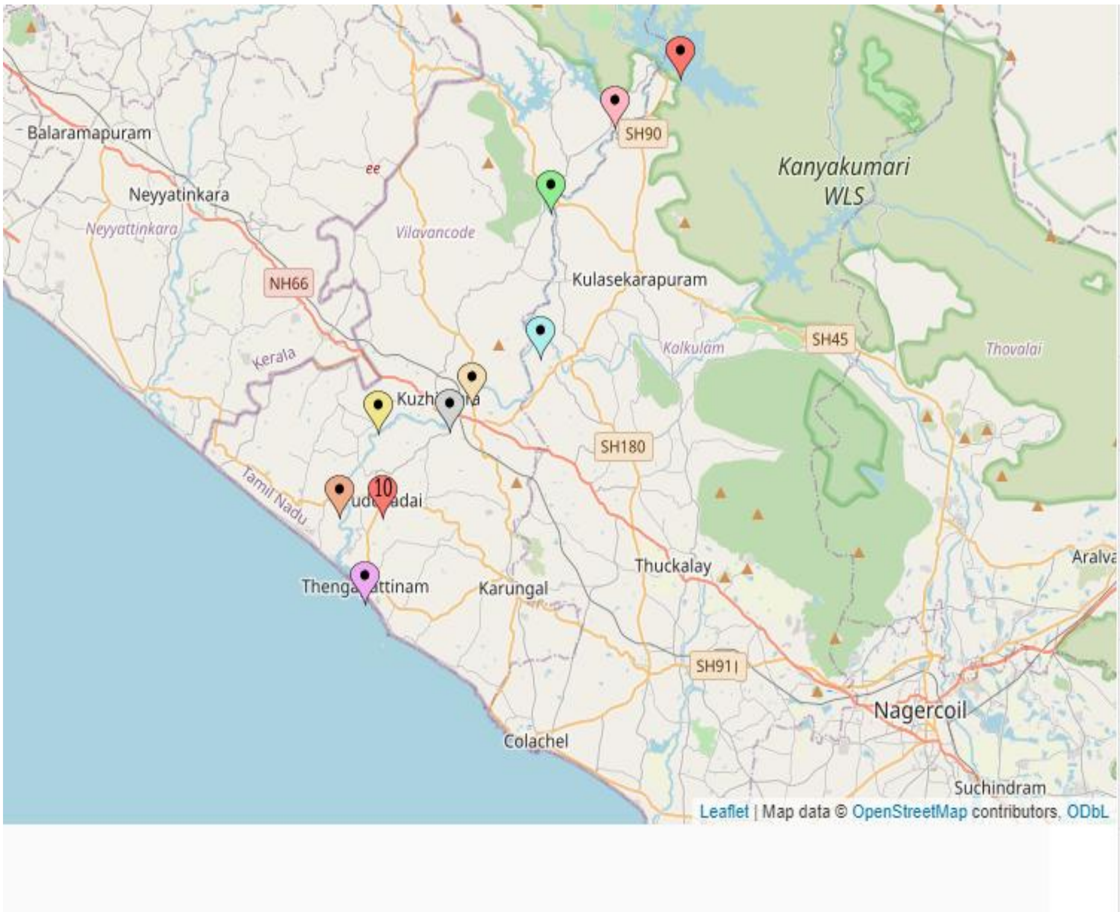


Fig. 1. Map of the study area of Thamirabrani River

Table. 1. Sampling Sites and their coordinates

Sampling sites	Location	Coordinates (DD)	
		Latitude	Longitude

S1	Pechiparai Dam	8.441760	77.234940
S2	Ambadi	8.434295	77.288075
S3	Kaliyal	8.383987	77.250812
S4	Moovatrumugham	8.336287	77.302378
S5	Gnaramvilai	8.321978	77.222254
S6	Vettuvenni	8.312045	77.207429
S7	Athencode	8.306023	77.178656
S8	GanapathiyanKadavu	8.274634	77.161428
S9	Painkulam	8.275101	77.172455
S10	Thengaipattinam	8.238387	77.167776

2.2 Analysis of heavy metals in water

Samples from ten selected sampling stations were collected in pre-cleaned plastic bottles every month. Sampling bottles were preconditioned with 5% nitric acid and then rinsed thoroughly with distilled water and rinsed with sample water at the sampling site. Samples were acidified with 1-2 ml of concentrated nitric acid (per liter) at the point of collection and transported to a laboratory for analysis. From the collected water samples 5 heavy metals such as copper, zinc, cadmium, nickel and lead were estimated using Atomic absorption spectroscopy.

2.3 Analysis of heavy metals in sediments

The sediments were collected from ten stations from Thamirabarani river (S1-S10). The collected samples were transported to the lab.The samples were dried in an oven at 80^0C over night,sieved mechanically using a 0.5mm sieve.25g of each sediment sample was digested with 20ml aqua regia (HCl/HNO_3 3:1) in a beaker (open-beaker digestion) on a thermostatically controlled hot plate.The resulting digest was diluted upto 50 ml with deionized water. The concentration of heavy metals (Cd, Cr, Cu, Pb and Zn) were analyzed by using a flame atomic absorption spectrometry (AA-6300, Version-1.03) with air acetylene (C_2H_2) flame.

2.4Assessment of sediment contamination

The sediment quality guidelines (SQGs) offer a simple, comparative mean for evaluating the risk of contamination in aquatic ecosystem The enrichment factor (EF), contamination factor (CF), geoaccumulation index (Igeo) and Potential ecological risk index (PERI or Eri) were used to determine metal contamination in the sediments of Thamirabarani river. The enrichment factor (EF) is used to determine the anthropogenic contribution in heavy metal concentrations (Zhang *et al*., 2013).

Table. 2.Classification of sediments based on pollution indices

Parameter	Formula	Range	Degree of contamination
EF	$\frac{(C_x/Fe)\ sample}{(C_x/Fe)\ background}$	$EF < 2$ $2 \leq EF < 5$ $5 \leq EF < 20$ $20 \leq EF < 40$ $EF > 40$	Deficiency to minimal enrichment Moderate enrichment Significant enrichment Very high enrichment Extremely high
CF (Hakanson, 1980)	C heavy metal / C background	$C_f^i < 1$ $1 \leq C_f^i < 3$ $3 \leq C_f^i < 6$ $6 \leq C_f^i$	Low contamination Moderate contamination Considerable contamination Very high contamination
PLI	$(CF_1 \times CF_2 \times CF_3 \ldots CFn)^{1/n}$	$PLI < 1$ $PLI > 1$	Low contamination high contamination
Igeo (Muller, 1969)	$\log_2 (C_n / 1.5 B_n)$	$Igeo < 0$ $0 \leq Igeo < 1$ $1 \leq Igeo < 2$ $2 \leq Igeo < 3$ $3 \leq Igeo < 4$ $4 \leq Igeo < 5$ $Igeo > 5$	Uncontaminated Uncontaminated to moderately contaminated Moderately contaminated Moderately to strongly contaminated strongly contaminated strongly to extremely contaminated Extremely contaminated
Er^i	$Tr^i \times (C_n / C_{ref})$	$Er^i < 40$ $40 \leq Er^i < 80$ $80 \leq Er^i < 160$ $160 \leq Er^i < 320$ $320 \geq Er^i$	Low Moderate Considerable High Very high

3.Results and Discussion

3.1 Heavy metals in water

The mean values of heavy metals Cu, Zn, Cd, Ni and Pb in water sample are presented in Table 3 and Fig 2.

The overall behaviour of heavy metals in the aquatic environment is strongly influenced by the association of metals with various geochemical phases in sediments (Morillo *et al*., 2004). In the present study theconcentration of Cu and Zn in water were ranged from 0.00093 (S5) to 0.02107 (S10) and from 0.0055 (S1) to 0.2350 (S9). These are within the permissible limits.In aquatic ecosystems, the proportion of heavy metals present as dissolved ions is low because most metals are deposited in the associated sediments (Awadh and Kong, 2021).

Among the heavy metals analyzed, the total concentration of Pb in water was highest. The highest Pb (0.2270 mg/L) concentration was obtained at S10, which was higher than the WHO recommended guidelines at all stations.

Table. 3. Heavy metal concentrations in surface water

Station	Cu	Zn	Cd	Ni	Pb
S1	0.00207	0.0055	0.0021	0.03377	0.04703
S2	0.00197	0.0528	0.0171	0.00737	0.05393
S3	0.00460	0.0157	0.0264	0.01743	0.04830
S4	0.00387	0.0230	0.0080	0.03397	0.08463
S5	0.00093	0.0160	0.0027	0.02980	0.07353
S6	0.00387	0.0374	0.0222	0.02807	0.09453
S7	0.00260	0.0089	0.0163	0.04767	0.09137
S8	0.00550	0.0073	0.0166	0.06630	0.11620
S9	0.00693	0.2350	0.0174	0.10540	0.15813
S10	0.02107	0.1180	0.0234	0.19977	0.22700
Mean±SD	0.0053±0.006	0.0520±0.073	0.0152±0.008	0.0570±0.057	0.0995±0.056
Guideline value	1.5	3	0.003	0.07	0.01

3.2 Heavy metals in sediment

The mean values of heavy metals Cu, Zn, Cd, Ni and Pb in sediment sample are presented in Table 4 and Fig 3.

Among heavy metals Zn was the highest in concentration. The highestconcentration of Zn (62.220μgg^{-1}) at S9 (Painkulam). The main agricultural form (coconut field) surrounded by station 9. The cadmium enrichment of Thamirabarani river sediment could have been caused by atmospheric emission, leachates from defused Ni-Cd batteries and Cd plated items (Mohiuddin *et al*., 2011). The result indicate that this level of heavy metals found in the sediment of the

Thamirabarani river might create an adverse effect on the aquatic ecosystem associated with the rivers especially since it receives agricultural runoff water.

Table 4.Heavy metal concentrations in surface sediments

Station	Cu	Zn	Cd	Ni	Pb	PLI
S1	32.203	23.523	0.0889	7.1080	9.7280	0.3448
S2	15.493	20.853	0.0262	4.6227	6.2147	0.1910
S3	45.847	54.873	0.3402	6.9243	9.0423	0.5620
S4	36.597	36.920	0.1663	2.0107	9.0323	0.3357
S5	35.017	36.580	0.2307	2.1210	9.6763	0.3635
S6	21.453	53.807	0.7114	3.4637	3.0073	0.3894
S7	26.103	52.987	0.6322	3.4123	4.9327	0.4339
S8	33.467	48.337	2.5067	5.6588	4.1907	0.6317
S9	29.173	62.220	1.4417	6.7683	7.3080	0.6704
S10	22.677	41.480	0.5890	3.1823	2.8103	0.3490

3.3 Pollution Indicators

The highest EF values obtained for Cd (15.1702) and Cu (7.0692) indicated significant enrichment (5≤EF<20). This might have happened due to higher concentration in sediment and lower geochemical background values resulting to higher EF values of Cd. The EF values of Zn (2.5849) and Pb (3.2161) indicated moderate enrichment.The highest CF values were noted for Cd (2.2444) were represented moderate contamination (1≤ CF< 3) in the study area. The remaining metals (Cu, Zn, Ni and Pb) show low contamination factor value (<1).The Igeo values showed the following decreasing order Zn>Cu>Ni>Pb>Cd for the studied river (Fig. 4). The highest Igeo values obtained for Zn (11.7559). The Igeo value of metals like Zn, Cu, Ni and Pb were >5 indicated extreme contamination of the sediment in the Thamirabarani river.The maximum value of potential ecological risk index (Er^i) was recorded for Cd (67.333) indicating moderate potential ecological risk. The PLI value of Thamirabarani river during the study period was ranging from 0.1910 (S2) to 0.6704 (S9) suggest that low contamination of the sediment in the study stations (Table. 4).

Table.5 .The mean and index values of metals in sediment of Thamirabarani river

	Cu	Zn	Cd	Ni	Pb
Mean	29.80	43.16	0.67	4.53	6.59
EF	7.0692	2.5849	15.1702	0.6926	3.2161
CF	0.9314	0.3398	2.2444	0.0924	0.4121

Igeo	9.252	11.7559	-3.8287	7.071	6.0013
Er^i	4.6567	0.3398	67.333	0.462	2.0607

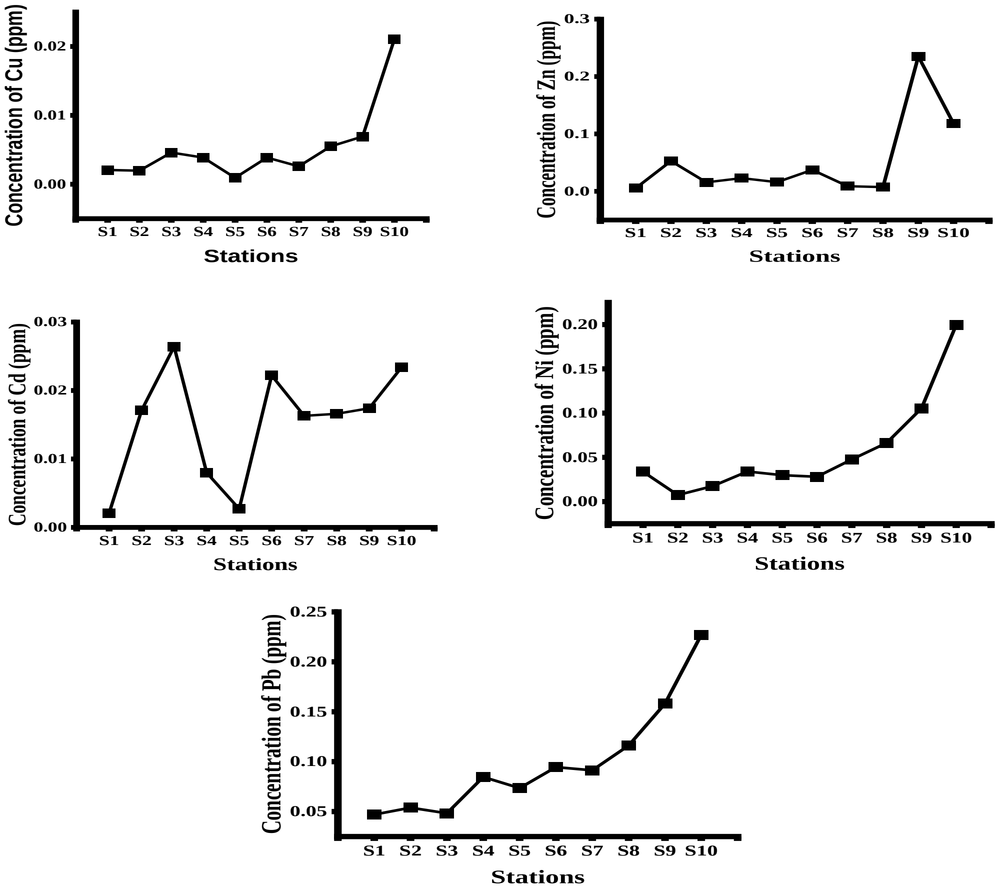
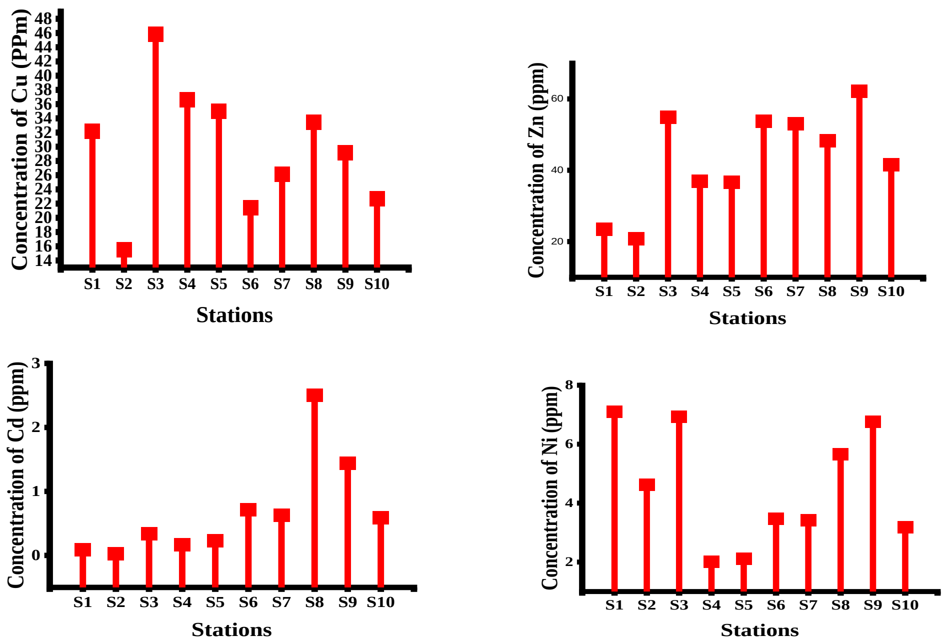


Fig. 2.Relative distribution of heavy metal concentrations in surface water



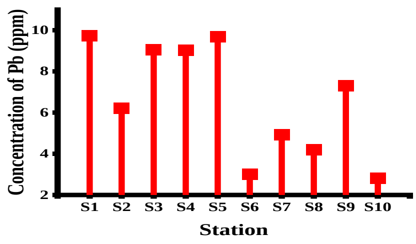


Fig. 3.Relative distribution of heavy metal concentrations in surface sediments

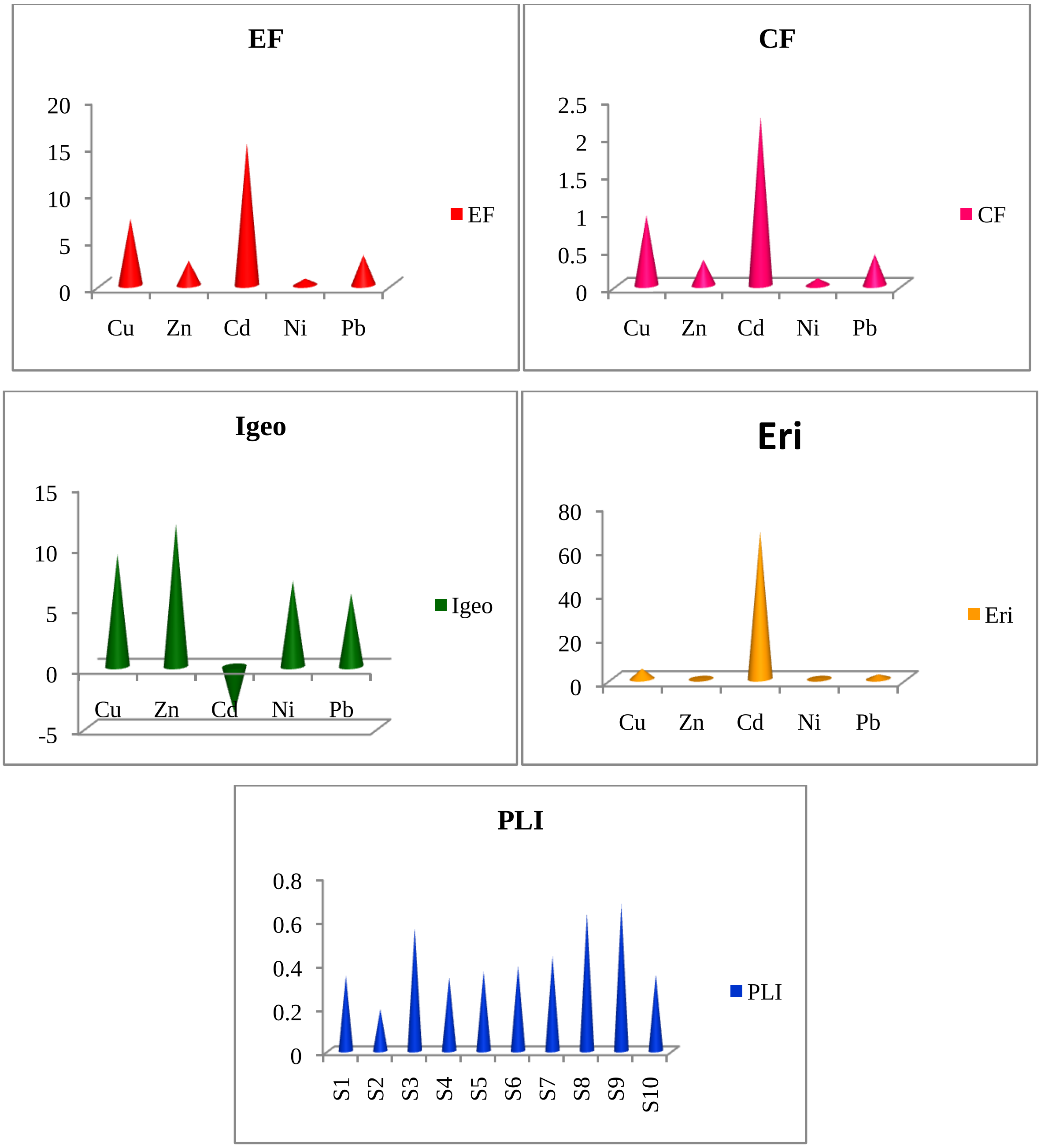


Fig. 4.Pollution Indicators values of heavy metals in sediment

5. Conclusion

This study has shown that the sediment of the Thamirabarani river was heavily polluted with heavy metals. Significantly higher levels of metals were observed in sediments compared to water. As some of the selected metals like Cd and Pb were exceeded the safe levels, the water from contaminated sites should not be used without treatment. Finally, it is concluded that further detailed assessment of these two vital metals are highly recommended for the study stations.

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