
**ASSESSMENT OF THAMIRABARANI RIVER SEDIMENT CONTAMINATION
USING POLLUTION INDICATORS AND MULTIVARIATE STATISTICAL
METHODS****S. A. Anuja***

*Research Scholar, Reg. No. 19233282032010, Women's Christian College, Nagercoil
(Affiliated to Manonmaniam Sundaranar University, Tirunelveli-627012, Tamil Nadu)

P. Kavitha

Assistant Professor, Department of Chemistry, Women's Christian College,
Nagercoil-629001, Tamil Nadu, India

C. Hemlet Jothi

Research Scholar, Women's Christian College, Nagercoil (Affiliated to Manonmaniam
Sundaranar University, Tirunelveli-627012, Tamil Nadu)

Corresponding Author: S. A. Anuja**Email:saanujaa@gmail.com****Abstract**

The current research was designed to assess the degree of sediment contamination by heavy metal in Thamirabarani river by using pollution indicators and multivariate statistical methods. Between September 2020 and August 2021, seasonal basis sediment samples are collected from five distinct location and subjected to standardised analysis. These statistical techniques, including Two-way ANOVA, Pearson Correlation Index, PCA and CA, were demonstrated the research. The quality of sediment needs to be better understanding about the statistical methods. Three factors that account for 95.4% of the data's total variation were found using PCA. The sediment's heavy metal contamination were distributed Fe > Mn > Cu > Zn > Al > Cd > Ni. the contamination was evaluated pollution indicators method such EF, CF, Igeo and PLI. Estimated EF values show that there is a noticeable enrichment of pollutants in copper (Cu). Therefore, river water can be used for irrigation securely, but it need to go through a lot of processing is necessary before for home uses in order to avoid negative public health effects.

Keywords: Cluster analysis, Heavy metal, Pollution Indicators, Principal component analysis, Sediment contamination, Thamirabarani river.

Introduction

Rivers and streams are active environments that support a variety of physical and chemical processes, Sediments are a crucial natural sink where a lot of contaminant are removed from river water (Bai and Reji, 2012). The quality of water dumped in surface water framework has increased as a result of massive industrial waste and sewage entering the rivers. River contamination is a pressing and emerging problem in most developing nations today,(Ibrahim *et*

al., 2020). The biggest source of the heavy metals in aquatic habitats is sediment, The heavy metal pollution in the aquatic environment more than 90% sediment were affixed to particulate matters.(Zheng Na *et al.*, 2008).

Inorganic and organic materials have contaminate the sediment of many regions waterways, lakes, and estuaries. Metals are a common and major pollutant among inorganic elements in aquatic sediment (Guvén and Akinci, 2011). Pollution of heavy metals in the river water environment is an worry since risks associated with food and their agglomeration in aquatic habitats. Contrary to most of thre pollutants, trace metals have no biological decay and follow a worldwide biological cycle with natural water acting as the main transport medium (Shaha and Hossain, 2011).

By introducing dissolved heavy metals in to the water section in response to shifting physical and chemical conditions, sediment and suspended particulate matter perform an important part in the adsorption of those metals, Heavy metals are naturally present in different concentrations.(Kabassi *et al.*, 2008; Hahladaki *et al.*, 2013). Sediments heavy metals are successfully trapped because these are poorly soluble in water, the presence of numerous trace elements in the sediments may indicate that there has been human contamination (Sojka and Jaskula, 2022; Goher *et al.*, 2014).

Finding correlations between sediments heavy metal content was the goal of the current research. More specifically, this study's objectives were to apply a variety of widely used and accurate environmental qualitative metrics like EF, Igeo, PLI, multivariate statistical analysis is also judge the ecological risk associated with sediment purity.

The results of current research will aid in location of heavy metals found in sediment as well as their contamination and spread along the Thamirabarani river. Understanding the amount and location of heavy metals, the degree of pollution, and the detrimental effects on biological components will help in developing future environmental planning strategies for the river, It will also play a significant role in providing this benchmark data.

Materials and Methods

study area and sample collection

Thamirabarani river Basin is one of the 17 river Basin in Tamil Nadu, India and is located in Tirunelveli, Thoothukudi and Kanyakumari districts.It is a reliable source of water for electricity production, drinking and irrigation. Thamirabarani river originates from Agastiyarmalai on the Western Ghats at an altitude of about 2000m, 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.

The study stations 1 to 5 fall along the Thamirabarani river from Pechiparai Dam to Gnaramvilai. The geographic sample Table. 1.and Fig.1 display sample sites and their coordinates.

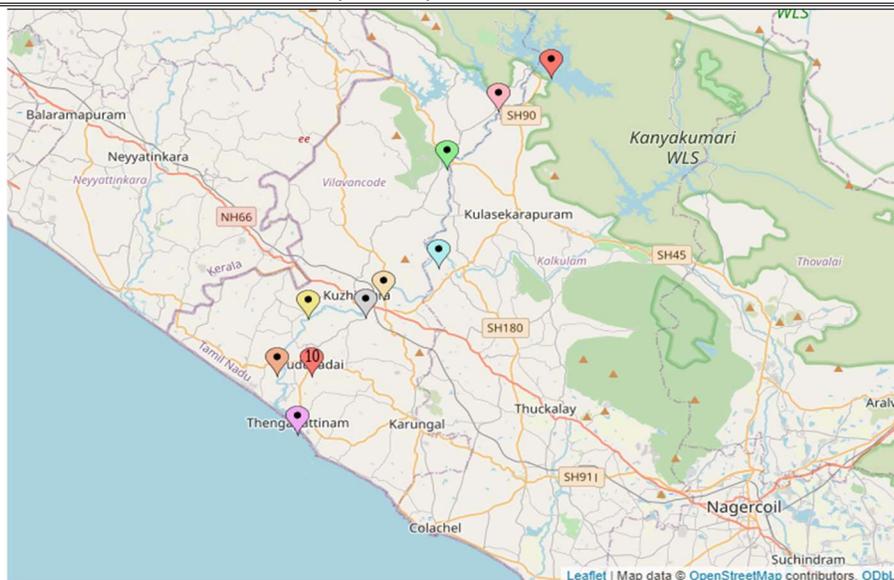


Fig. 1 Map of River Thamirabarani in Kanyakumari district, Tamil Nadu, India with study station

Table. 1 Details of the study sites with sampling location

Sampling sites	Location	Coordinates (DD)		Observations
		Latitude	Longitude	
S1	Pechiparai Dam	8.441760	77.234940	Largest Dam in Kanyakumari.
S2	Ambadi	8.434295	77.288075	Rubber estates.
S3	Kaliyal	8.383987	77.250812	Sewage out fall.
S4	Moovattumugham	8.336287	77.302378	Kothai and Pahralsi unify to flow.
S5	Gnaramvilai	8.321978	77.222254	Brick Kiln, Sand Mining.

Heavy metal analysis in sediments

The samples were taken from five stations from riverine region (S1-S5) by upholding the Environmental protection Agency normal operating procedures (USEPA 2001). After being collected, the sediment was separated, sealed, labeled, packaged, and taken to the environmental science lab in an airtight polythene bag (Kubra *et al.*, 2022). The samples were split in to sub samples for further analysis after being exposure to air dry, and passed through 2 mm sieve (Anwar *et al.*, 2021). 25 g of sediment were disintegrate by means of chemical action in an hot plate by add 20 cc of (HCl/HNO₃ 3:1).The resulting digest was reduced with distilled water up to 50 ml.

Flame atomic absorption spectrometry was used to find the level of heavy metals concentration (Cd, Cr, Cu, Pb and Zn) (AA-6300, Version-1.03) with air acetylene (C₂H₂) flame.

Methods for assessing pollution indicators

A straightforward, comparable method for determining the impact of pollution in aquatic environments were Enrichment factor (EF), Contamination factor (CF), geo accumulation index (Igeo) and pollution load index (PLI). These metrics which are Frequently calculate the amount of pollutions present in sediments (Fikret Ustaoglu and Yalcin Tepe, 2018 ; Tian *et al.*, 2017).

Calculation of EF

Enrichment factor is a powerful indicator to assess human activity on the abundance of a given metal. For testing the extent of anthropogenic impact on the sediment (Sojka *et al.*, 2019; Pandey *et al.*, 2019).

According to Brady *et al.* (2015) assessing the enrichment factor.

$$\text{Enrichment ratio} = \frac{(C_x / \text{Fe})_{\text{sample}}}{(C_x / \text{Fe})_{\text{background}}}$$

Where, C - Concentration of the metal 'x'

Calculation of CF

To evaluate, contamination factor is employed to metal contamination and investigate heavy metal pollution carried status of the sediment. (Duodu *et al.*, 2016; Kabir *et al.*, 2020). The data is derived for relationship among the determined metal content and background metal concentration in river sediments (Hakanson, 1980).

Contamination factor = (C heavy metal / C background.)

Calculation of Igeo

Geo accumulation Index is the measurement and degree of pollutants heavy metals contamination. The list of Igeo has been used extensively to evaluate sediment pollution (Ali *et al.*, 2016; Islam *et al.*, 2014). Igeo is a strategy laid out by Muller (1969) metal pollution of sediment to be identified and defined sediments by contrasting present concentration levels with standard levels and determined by the subsequent formula.

$$\text{Geo- accumulation Index} = \log_2 (C_n / 1.5 B_n)$$

Where,

C_n - calculated metal concentration,

B_n - reference value of the measured metal,

1.5 - natural fluctuation coefficient.

Calculation of PLI

Pollution load index is an important methods for estimating the capability of causing toxicity level of sediment. The following algorithm was used to determine pollution load index (Islam *et al.*, 2015).

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$$

Where,

CF- Indicates the contamination factor of metals.

n - Indicates number of metals thought about for the derivation of final product.

Pollution load index values much higher than 1 denote the presence of heavy metal pollution, while Pollution load index values below 1 denote the absence of any pollution (Reymond and Sudalaimuthu, 2022).

Statistical analysis

Concentration of heavy metals and their maximum, minimum quantity were investigated with Two-way ANOVA and also determined the amount of correlation between metals were analyze by using the way of PCI (Pearson Correlation Index). The similarity level among stations was found by CA and PCA they are used to reduce the number of factors and to find new components. The software such as Minitab and Orgin Pro 22 to carry out these statistical calculation and diagrams.

Results and Discussion

Spatial distribution of Pollution Indicators

The outcomes of three various pollution evaluation techniques were used to establish the Thamirabarani river sediment quality was demonstrated in Tables 3, 4 and 5. Enrichment factor was classified into five categories as follows;

EF is < 2, deficiency to minimal enrichment;

EF = (2 – 5), moderate enrichment;

EF = (5 – 20), significant enrichment;

EF = (20 – 40), very high enrichment;

EF is > 40, extremely high enrichment;

According to the EF; the sediment pollution level of the river was found as a inadequate to basic enrichment (EF<2) for Fe, Mn and Al in all stations. Zn, Pb and Cd were detect as slight increase in the enrichment of (EF = 2 - 5) and Cu is in significant enrichment of (EF = 5 – 20) respectively. Previous studies have shown that when the metal's enrichment factor (EF) is ranged between 0.05 and 1.50, that also represent the crustal origin in nature and when it is greater than 1.5, it indicates the human influences. (Siddiqui and Pandey 2019).

The amount of heavy metals contamination in the sediment of the Thamirabarani river was assessed according to the CF value. Contamination factor was categorized into four different divisions;

CF < 1 less contamination;

1 ≤ CF < 3 medium contamination;

3 ≥ CF < 6, considerably contaminated and

CF > 6 very high contamination.

The metals like Iron, manganese, zinc, aluminium, cadmium, nickel and lead were found to be less contamination level the (CF<1) and Cu in medium contamination level (1< CF< 3) respectively. In contrast station 1 (Pechiparai dam) to 5 (Gnaramvilai) are situated in the apex of the Thamirabarani river just where no huge human endeavor, particularly at pechiparai dam. So it appears to be these stations are contaminated and connected with geologically natural processes. Similar patterns of outcomes were found by Alahabadi and Malvandi, (2018).

The geo accumulation index was evaluated in seven different groups and categorised by

Igeo ≤ 0 Practically uncontaminated;

0 < Igeo < 1 uncontaminated to moderately contaminated;

1 < Igeo < 2 moderately contaminated;

2 < Igeo < 3 moderately to strongly contaminated;

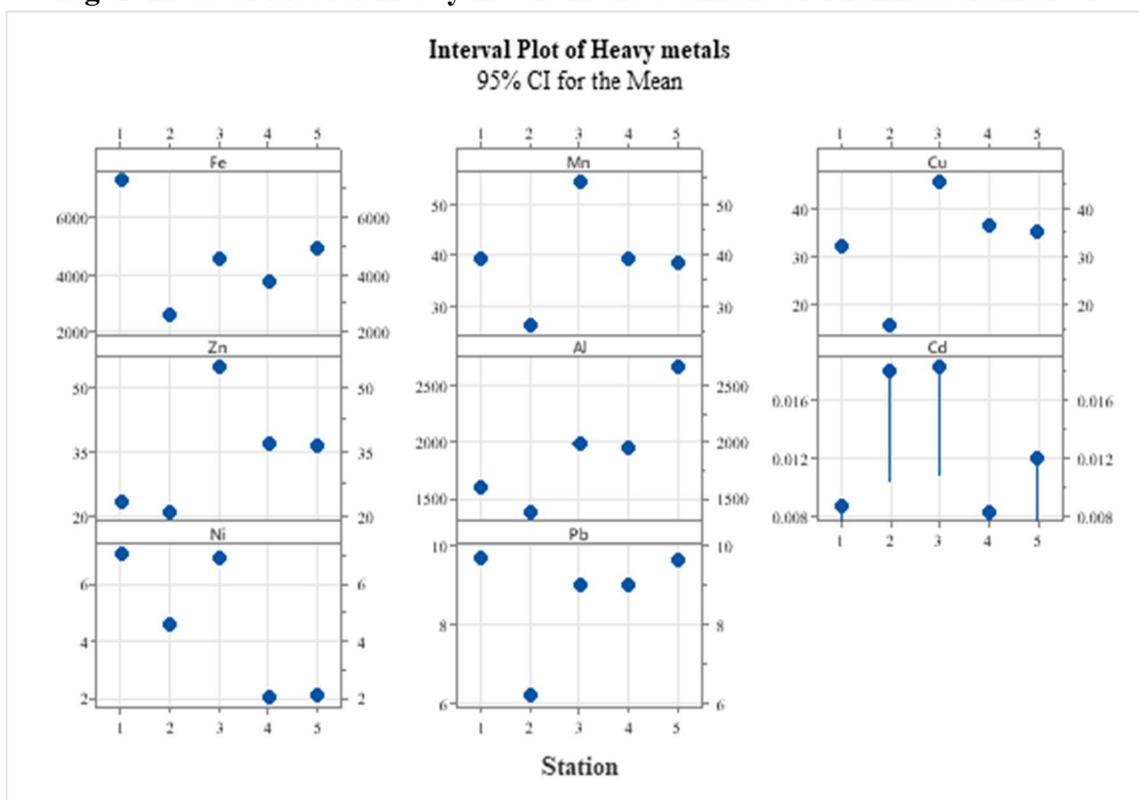
3 < Igeo < 4 strongly contaminated;

4 < Igeo < 5 strong to extremely contaminated;

Igeo ≥ 5 extremely contaminated;

To assess the geo accumulation index levels, and the sediment pollution levels of the River Thamirabarani was discovered as practically uncontaminated. As a result, the level of trace metals was higher than the practically uncontaminated class in all river sediment in every season's (Ustaoglu and Islam, 2020).

The Pollution Load Index the Table.3. Provides the derived values for each of the stations. The PLI analysis samples of sediment were shown in Fig. 3. The PLI value of > 1 denotes the sediment was polluted whereas < 1 denotes the sediment has zero pollution. The PLI measurement revealed a significant amount of pollution at stations 3 mixing point of domestic sewage and station 5 mixing point of agricultural sewage outfall and Brick kiln. Same investigation were carry out by (Shiji *et al.*, 2015).

Fig. 2 Interval Plot for Heavy metals in the sediment of Thamirabarani river**Table. 2 Enrichment Factor of metal in the surface sediments of Thamirabarani river Basin, India**

Station	Fe	Mn	Cu	Zn	Al	Cd	Ni	Pb
1	1	0.25873 3	4.96356 1	0.91356 1	0.11397	0.21775	0.71547 4	2.99879 1
2	1	0.48708 5	6.79321 7	2.30384	0.27994	1.26276	1.32366 2	5.44977 5
3	1	0.57197 8	11.2490 1	3.39245 6	0.22531 3	0.71959 7	1.10952 8	4.43728 3
4	1	0.50628 7	11.0190 3	2.80097 7	0.27137 9	0.41298	0.39536 3	5.43915 7
5	1	0.37316 5	7.98516	2.10183 5	0.28099 1	0.43892 9	0.31586 6	4.41315 9
WSR*	3590 0	750	32	127	69300	0.2	49	16

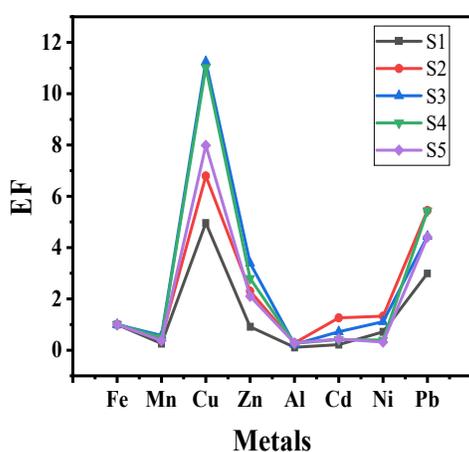
WSR*- Background values of metals

Table. 3 Contamination Factor and Pollution Load Index of metals in the surface sediments of Thamirabarani river Basin, India

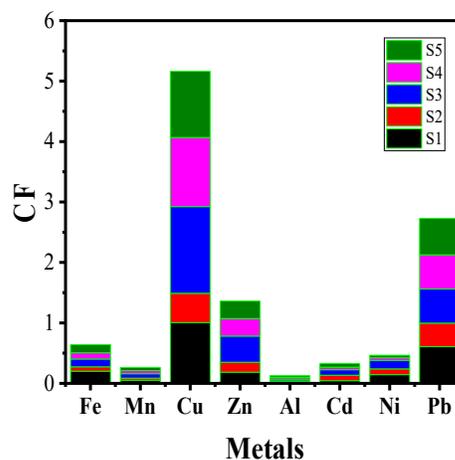
Statio	Fe	Mn	Cu	Zn	Al	Cd	Ni	Pb	PLI
1	0.2027	0.0524	1.0063	0.1852	0.0231	0.0441	0.1450	0.608	0.1913
2	0.0712	0.0347	0.4841	0.1641	0.0199	0.09	0.0943	0.3884	0.1082
3	0.1273	0.0728	1.4327	0.4320	0.0286	0.0916	0.1413	0.5651	0.2622
4	0.1037	0.0525	1.1436	0.2907	0.0281	0.0416	0.0410	0.5645	0.1774
5	0.1370	0.0511	1.0942	0.2880	0.0281	0.0601	0.0432	0.6047	0.2000

Table. 4 Geo accumulation indices of metals in the surface sediments of Thamirabarani river Basin, India

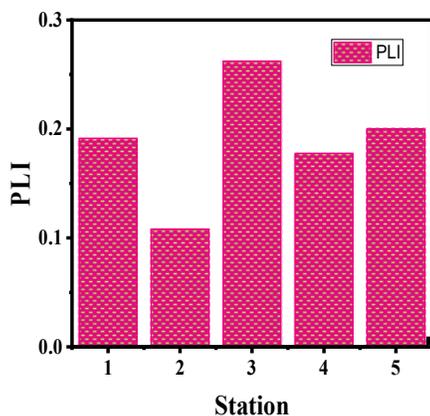
Station	Fe	Mn	Cu	Zn	Al	Cd	Ni	Pb
1	-	-	-0.5758	-3.0176	-	-5.0859	-3.3702	-1.3028
2	-	-	-1.6313	-3.1914	-	-4.0588	-3.9909	-1.9492
3	-	-	-0.0662	-1.7956	-	-4.0326	-3.408	-1.4082
4	-	-	-0.3913	-2.3673	-	-5.1705	-5.192	-1.4098
5	-	-	-0.4549	-2.3806	-	-4.6402	-5.1149	-1.310



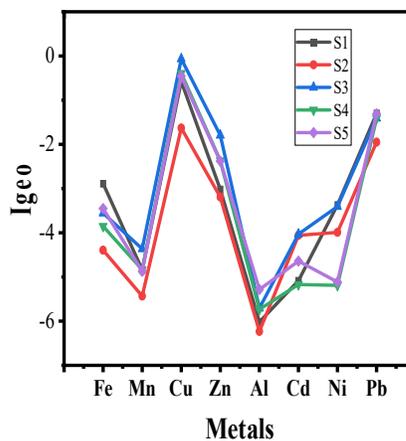
(a) Enrichment Factor



(b) Contamination Factor



(c) Pollution Load Index



(d) Geo accumulation Index

Fig. 3 Pollution Indicators Plot for a) EF, b) CF, c) PLI , d) Igeo**Multivariate Statistical Analysis**

The measured average metal concentrations were depicted in Fig.2. The Two-way ANOVA were conducted to assess the dissimilarity among metals in between seasons and stations along the Thamirabarani river sediment. The metals like Mn and Ni were not significantly varied in between stations and seasons of the river sediment ($p > 0.05$). As opposed to that, Cu was significantly varied between stations and seasons ($p < 0.05$), is given in Table. 5).

Table. 5 The two-way ANOVA for Heavy metals in the sediment between stations and Seasons of Thamirabarani river Basin , India

Source of Variation	SS	df	MS	F	P-value	F crit	
Fe							
Stations	36625538	4	9156385	4.27403	0.038463	3.837853	S
Seasons	7240753	2	3620376	1.689924	0.244238	4.45897	NS
Error	17138642	8	2142330				
Total	61004933	14					
Mn							
Stations	1235.135	4	308.7839	1.532106	0.281159	3.837853	NS
Seasons	1014.719	2	507.3596	2.517387	0.141888	4.45897	NS
Error	1612.337	8	201.5422				
Total	3862.192	14					
Cu							
Stations	1467.459	4	366.8647	15.51455	0.000772	3.837853	S
Seasons	380.8802	2	190.4401	8.053629	0.012127	4.45897	S
Error	189.172	8	23.6465				
Total	2037.511	14					
Zn							
Stations	2195.885	4	548.9713	46.70592	1.37E-05	3.837853	S
Seasons	61.43092	2	30.71546	2.61324	0.133839	4.45897	NS
Error	94.03028	8	11.75379				
Total	2351.346	14					
Al							
Stations	2155622	4	538905.6	0.548616	0.703704	3.259167	NS
Seasons	18636546	3	6212182	6.324122	0.008102	3.490295	S
Error	11787595	12	982299.5				
Total	32579763	19					
Cd							

Stations	2.49531	4	0.623828	0.99722	0.446247	3.259167	NS
Seasons	33.45588	3	11.15196	17.82698	0.000102	3.490295	S
Error	7.506798	12	0.625566				
Total	43.45798	19					
Ni							
Stations	38.8227	4	9.705675	0.589702	0.676521	3.259167	NS
Seasons	27.8474	3	9.282468	0.563989	0.649036	3.490295	NS
Error	197.5032	12	16.4586				
Total	264.1733	19					
Pb							
Stations	25.48731	4	6.371829	2.570931	0.091914	3.259167	NS
Seasons	133.3257	3	44.4419	17.9316	9.91E-05	3.490295	S
Error	29.74096	12	2.478413				
Total	188.554	19					

The relationships between two different parameters were described by an invariant method of correlation analysis. The Pearson correlation index of heavy metals calculated the source and migration of heavy metals (Alghobar and Suresha, 2015; Pingping *et al.*, 2021).

In the current study, Pearson Correlation Index explain how heavy metals in sediment are related to one another was given in Table. 6. Based on the percentage the relationship consists of the following order; extremely high value (0.9-1), high value (0.7-0.89), moderate value (0.5-0.69), weak value (0.26-0.49) and very weak value (0-0.25) respectively. These adverse value indicates the negative relationship between two metals and denotes a lower of one metal concentration by a higher of another metal concentration. In Thamirabarani river sediment, A weak negative association has been found between lead and cadmium ($r = -0.621$). As opposed to that, Fe demonstrated strong positive relation with Pb ($r = 0.774$); Mn showed a high positive relation with Cu ($r = 0.953$) and Zn ($r = 0.859$). In the previous studies for river, sediments analyzed high correlation between Mn, Cu, and Zn is caused by geogenic processes and parent rock composition (Kumar *et al.*, 2018).

Table. 6 Pearson correlation coefficient matrix for the heavy metals in the Thamirabarani river sediments

	Fe	Mn	Cu	Zn	Al	Cd	Ni	Pb
Fe	1							
Mn	0.372	1						
Cu	0.398	0.953**	1					
Zn	-0.038	0.895**	0.873**	1				
Al	0.133	0.376	0.563*	0.524*	1			
Cd	-0.526	0.079	-0.161	0.278	-0.197	1		
Ni	0.467	0.374	0.120	0.060	-0.535*	0.346	1	

Pb	0.774**	0.634*	0.784**	0.413	0.625*	-0.621*	0.003	1
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* Correlation is significant at (0.05) level.

**Correlation is significant at (0.01) level.

The PCA were carried out the objective of present relations between metals and to demonstrate the correlation between the factors (Moldovan *et al.*, 2022) The component matrix shows that, the first PCA stands for Mn, Cu and Pb; the second PCA stands for Zn and Cd; the third PCA stands for Fe, Al and Ni. Three Principal components were identified using eigenvalues > 1 ; These Principal components are described 95.4% of the overall variance in the dataset. The scree plot is used to identify the numerous constituents that explain most of the variation in the data. The biplot is also appropriate for these results and demonstrate that the general opinion is concentrated in a component. Each component is believed to be of a common origin. Distinct components are regarded as of different origins. In general it can be said that Cd, Cu, and Pb were primarily of the anthropogenic origin at most of the studied sites (Pratat *et al.*, 2020).

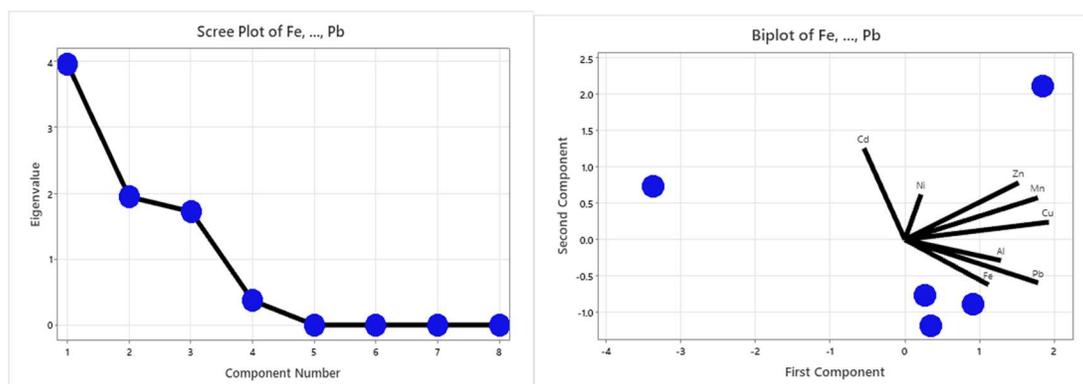


Fig. 4 Scree and Biplot for Heavy metals in Thamirabarani river sediment

Dendrogram is useful for the research and comprehension of the sampling location and concerning the analysed concentrations of trace element and their origins (Shirani *et al.*, 2020). The dendrogram is used to display a tree diagram that shows how clusters were performed at each step in the amalgamation procedure and is also used to view the similarity or distance values for the clusters at each step.

Based on the results of cluster analysis, two groups were created from the sampling stations at level of resemblance 18%. The first group includes the metals like Fe, Mn, Cu, Zn, Al and Pb; similarly the second group consists of the metals like Cd and Ni as depicted in Fig. 5. On the basis of cluster analysis (CA), Multifactor were confirmed to exist influencing the high potential of rapid increase algae blooms and excess growth regions are distinct in each of the water body's. (Jaskula and Sojka, 2019).

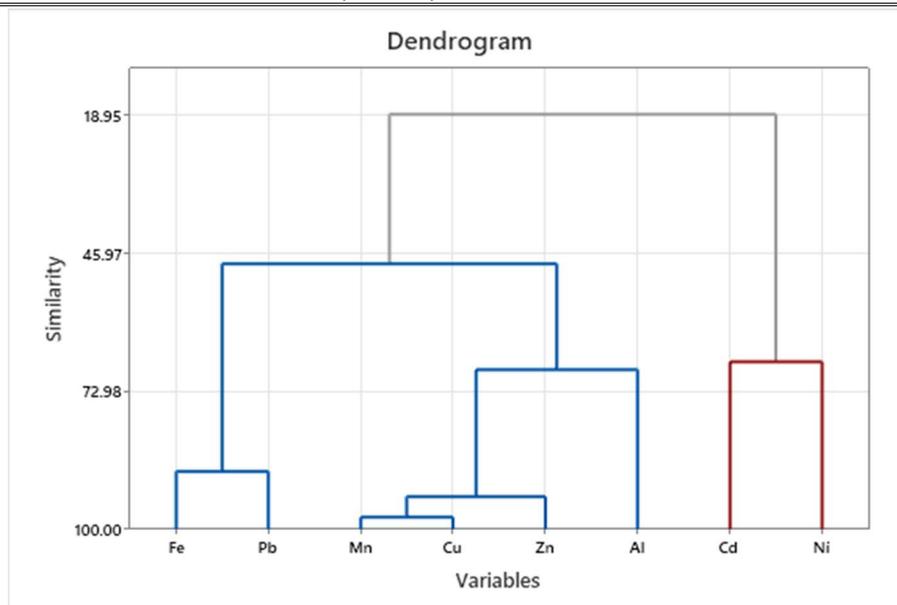


Fig. 5 Cluster analysis Dendrogram for the heavy metals in Thamirabarani river sediment

Conclusion

The current study implies the geographic and distribution variation of heavy metals in the Thamirabarani river sediment were identified and the aquatic environment is safe on a scientific basis. A complete thought of the heavy metal variables, such as EF, CF and .PLI. According to the value of EF, the amount of cadmium (Cd) in the sediment samples was considerable maximum enrichment of contamination. Better information about the quality of surface sediments was found out from the results of multivariate statistical assessment methods. PCA was used to identify three components accounting for 95.4% of the overall variation between the dataset. Therefore, the water from the Thamirabarani river can be utilized for use in irrigation with suitable care taken in advance, But substantial analysis methods is needed before household use and to avoid adverse health problems.

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