INTERNATIONAL JOURNAL OF MULTIDISCIPLINARY EDUCATIONAL RESEARCH
ISSN:2277-7881; IMPACT FACTOR :6.514(2021); IC VALUE:5.16; ISI VALUE:2.286
Peer Reviewed and Refereed Journal: VOLUME:10, ISSUE:4(2), April :2021
Online Copy Available: www.ijmer.in
Digital certificate of publication:http://ijmer.in/pdf/e-Certificate%20of%20Publication-IJMER.pdf

ACCUMULATION AND CONTAMINATION ASSESSMENT OF TRACE ELEMENTS IN SEDIMENT OF THE RIVER PERUMBA, KERALA, INDIA

[1]Anagha Raghunath, [1]Udayasuriyan Rajendran and [2]Sapna Jacob
[1&2]Department of Zoology
[1]Bharathiar University, Coimbatore and [2]Payyanur College, Edat, Kannur
[1]Tamil Nadu and [2]Kerala, India

Abstract

In this study, accumulation of trace elements (Mn, Zn, Cu, Fe, Cr and, Ni) on bed sediments of Perumba River, Kannur, Kerala, India were determined. The concentration of Mn was higher than other elements followed by Zn, Cu, Fe. However, the concentration of Cr and Ni were found to be very low. A significant correlation was observed within the trace elements and physico-chemical parameters. The contamination assessment revealed that Cr and Ni were partially uncontaminated, Cu and Fe moderately uncontaminated and Mn and Zn heavily polluted in the few sites of the sediment. Owing to environmental management, these results could be used as a contribution to the information and rational management of the riverine system.

Keywords: Sediments, Trace Elements, Physico-Chemical Parameters, Igeo Index

Introduction

Our environment is polluted due to increased industrialization, use of fertilizers, and man-made activities on the ecosystem. Hence, assurance of the quality of air, water, and the soil is the need of the hour. To understand the dispersion, transport, and biological impact of trace elements in the environment, knowledge about their speciation, distribution and the effect of physicochemical parameters are also essential (Govil et al., 2011). The variation in the concentration of trace elements may attribute to the considerable variations in the physicochemical parameters (Shiji et al., 2015).

Many activities like land use/land cover change (Narsimlu et al. 2015), sewage, mine waste and industrial waste (Gautam et al., 2013), atmospheric pollutants, pesticides, and fertilizer are the main contributors of heavy metals discharged into the various aquatic environment (Adaikpoh et al., 2005; Lepane and Heonsalu, 2007; Amin et al., 2014; Singh et al., 2016, 2017).

The effects of trace metals contaminations in the rivers, lakes, and seas have been well-documented in the different organisms (Triebskorn et al., 2008; Manahan, 2009; Zubcov et al., 2012; Burada et al., 2017). Therefore, it is of great importance to assess and monitor trace metals in the aquatic system. Moreover, the level of trace elements in the sediments can provide useful information regarding mid-and long-term pollution of the aquatic bodies, since they are able to seal and occasionally release important amounts of heavy metals depending on the river regime and extreme situations, such as flooding or severe drought or changes in redox potential (van Gestel, 2008; Verhoeven, 2009) and the assessment of sediment quality plays an important role in the good ecological and chemical status of water (Borja and Heinrich, 2005).

Perumba River is a major freshwater river - originates from Pekunnu of Kannur district, Kerala, and flows 51 km westward. It bifurcates into two distributaries at Ezhimala, one of which joins Kavvayikayal and the other drains to the Arabian Sea. It has a drainage area of 300 sq. km and navigable up to 16 km. Macharuthode, Mathamangalam, Challachal, Nitaringapuzha, and Mukkuttenkarachal are the important tributaries (Ishaque, 2018). A major portion of the river has a lining of mangrove patches along its length. About 3 sq km of the River is covered by mangrove forest. Mangroves represent a critical ecological habitat to a diverse range of fauna. Mangroves are at risk from environmental pollutants, especially trace elements that are associated with a diverse range of anthropogenic activities including wastewater discharge. In the view of this scenario, studies on important trace elements in sediments of Perumba river- a major freshwater river in Kannur district, Kerala, India need to be assessing to establish baseline data on trace elements of that region. The untreated drainage, industrial effluents, pesticide-contaminated surface running water, etc. from different outlets influences the concentration of the trace elements in the Perumba River.

Materials and Methods

Sample collection

The sediment samples were collected from the bank of Peruvamba River (**Fig. 1**). The sampling spots are within 4 panchayats – Ramanthali, Kunhimangalam, Kadannapalli-Panapuzha, Cheruthazham, Eramam- Kuttur- and 1 municipality- Payyannur- of Kannur district. A systematic sediment-sampling was conducted, and the samples weighing about 1-2 kg of sample (**Table 1**). To avoid influence from various arbitrary surface conditions, sampling was taken from the depth of10 to 20 cm below the surface to 30 cm. The sampling was carried out using a plastic spatula. Plant materials, Grass, root mat, stones, pebbles, and other wastes were removed from the samples. The samples were collected in self-locking polythene bags and brought to the laboratory for further analysis.

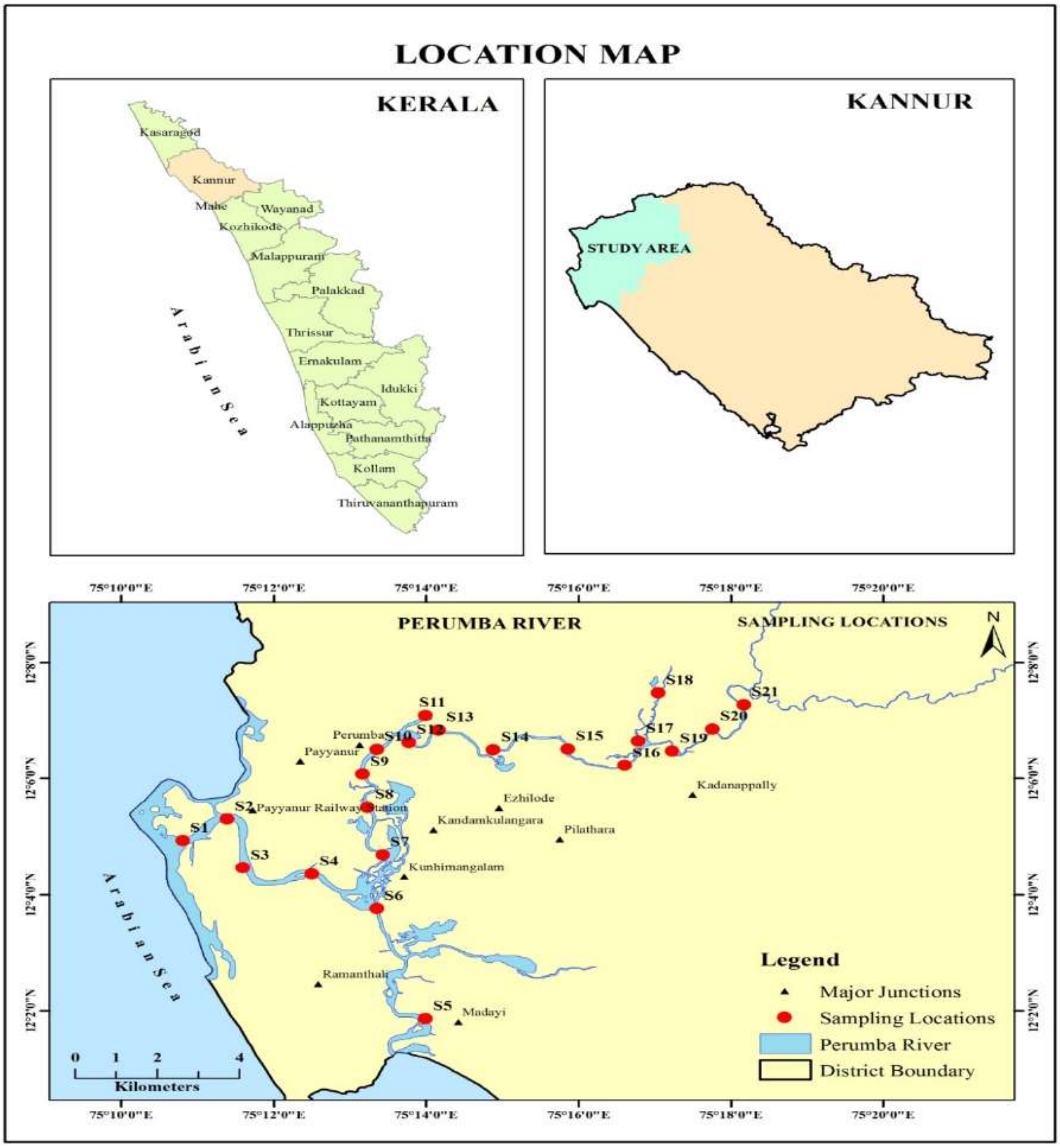

Fig. 1 Location map of the study area

Table 1Location of the sampling points

Sl No.	Sample ID	Longitude	Latitude
1	S1	75.18017	12.08225
2	S2	75.18987	12.08841
3	S3	75.19324	12.07447

4	S4	75.20835	12.07268
5	S5	75.22237	12.06301
6	S6	75.22462	12.07877
7	S7	75.22108	12.09227
8	S8	75.23057	12.09634
9	S9	75.21941	12.10128
10	S10	75.22254	12.10847
11	S11	75.23322	12.11815
12	S12	75.2296	12.11047
13	S13	75.23606	12.11398
14	S14	75.24807	12.10829
15	S15	75.26435	12.10856
16	S16	75.27677	12.10384
17	S17	75.27969	12.11077
18	S18	75.28407	12.1246
19	S19	75.28719	12.10794
20	S20	75.29597	12.11424
21	S21	75.30282	12.12118

The physico-chemical parameters of the samples viz. pH and electrical conductivity were also determined (APHA, 1995). For measuring the Organic Matter content0.1-0.2 g of 2mm sieved sediment sample is prepared by adding K_2Cr_2O7 and H_2SO_4 and titrated against Ferrous Ammonium Sulphate (FAS). Organic matter is calculated by substituting the titre value of each sample in the standard equation.

Analysis of Sediments

The samples were processed following standard procedures. Samples were air-dried and sieved through a 250 mm sieve and then taken to the laboratory for analysis. In the laboratory, 20g of sediment sample was weighed and mixed with 40 ml of DTPA (Diethylene Triamine Penta Acetic acid is a chelating agent which extracts the available forms of Iron, Manganese, Zinc, and Copper when buffered at pH 7.3). It is then kept for 2 hours, shaken, and filtered using No. 42 Whatman filter paper. This filtrate is then taken for analysis of heavy metal using Flame Atomic Absorption Spectrometer (FAAS).

Statistical Analysis

The data were statistically analyzed using the Statistical Package for Social Science (IBM SPSS Statistics 20.0). A Pearsons bivariate correlation was used to evaluate the inter element relationship in sediment.

Geo-accumulation index (Igeo)

According to Muller (1981) the geo-accumulation index (Igeo) was calculated to know the contamination level of the trace elements in the sediments of the river.

$I_{geo} = Log_2 \{ (Cm)/ (1:5 \times Bm) \}$

Where Cm is the concentration of metals in the study area, Bm is the concentration of the same metal at the control site, and 1.5 is a factor for possible variation in the background concentration due to litho logical variation.

Result and Discussion

The least concentration of the metal is found in sample S5 and the highest concentration is found in sample S8. The least concentration of the Mn is found in sample S5 and the highest concentration is found in sample S8. The lowest concentration of Zn was found in S2 and the highest concentration was found in S7. The minimum concentration of Cu in the study area was found in S8 and the maximum concentration of Cu was found in S18 respectively. Among the 21 samples, the least concentration was observed in the sample from S1 and the highest concentration was in sample S14. The concentration of trace element from various sampling points

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indicates that the iron (Fe) was found in higher quantity and the least was Copper (Cu). As per the results, it can also be seen that the concentrations of trace elements are within the permissible level given by BIS (2012). Even though, few sites showed higher concentration than the permissible limit at mangrove abundant sites due to the anthropogenic inputs coupled with erosion and physical mixing of the sediments (**Table 2 and Fig. 2**). Similarly, consistent with a weak flow, moderate levels of trace metals in sediments were found in the south estuary, since it receives considerable quantity of both domestic and agricultural effluents from the Kuttanad backwaters (Martin et al., 2012)

Mn was only the element to potentially present an ecological risk due to its high bioavailability (ratio in concentrations of trace element in the bioavailable fractions (exchangeable/carbonate bound) to the total concentrations of trace element) (Thanh-Nho et al., 2019). Zinc is one of the 14 essential trace elements required by living organisms. But once the metal is present beyond the threshold level, it can lead to life-threatening conditions (Khan, 2010). Cu is a natural mineral that is abundant in nature and its anthropogenic sources are pesticides, fertilizers, corrosion-resistant materials, and domestic wastewater (Nanzeen et al., 2019). Apart from this, copper sulphate is the most widely used algicide for preventing diseases in fish breeding (Authman et al., 2015). We suggest that the lower concentrations of Cu measured may be related to Cu association with sulphide, which limit its bioavailability.

The concentration of Fe and Mn in river sediments is many times higher in the mud fraction when compared with bulk sediment in the Vamanapuram river (Veena et al., 2019). The increase in the concentration of Fe and Mn in finer silt and clay is primarily related to the greater surface of these particulates. In this study overall the Fe concentration were higher in mangrove abundant area, where the mangrove sediments are rich in iron because these ecosystems develop downstream lateritic soils. Higher values of Fe compared to mangroves all over the world may be attributed to the possibility of Fe precipitation as iron sulphide, which is a common phenomenon in mangrove sediments (Nobi et al., 2010).

During the study period, the concentration of chromium in water remained below the WHO maximum allowable concentration of 50 µg/l. Chromium naturally occurs in rocks, animals, plants, soil, and volcanic dust and gases. The abnormal state of Cr in wastewater effluent indicates the contamination from textile and tanneries (Pachpande and Ingle, 2004). When these effluents enter the river contaminate both the water and sediment of the river.

Ni in the aquatic system forms complexes with varying organic and inorganic soluble materials. It adsorbs directly on clay particles and has the capability to co-precipitate with hydroxides of iron and manganese. It is bio-accumulated through aquatic organisms such as phytoplankton, seaweeds, and algae (Singh et al., 2017). The moderate Ni and Cr concentrations in the Can Gio mangrove plants may result from their association to the refractory fraction (i.e., more than 80 %, Table SD2). For plants, Ni is a micronutrient that is required at very low concentrations, and which can inhibit plant growth at high concentrations.

The behavior of trace elements in sediments depends not only on the contamination level which is expressed by total content but it is also on the form and origin of metal and the properties of the samples themselves. It is a fact that the heavy metal concentration in an ecosystem depends on various factors including the trace elements itself, the location of study, climatic condition, and physico-chemical parameters. Soil pH, electrical conductivity, and organic matter content can be particularly important to the form of heavy metal and its bioavailability.

Table 2 Concentrations on trace elements (ppm) in the sediments

Site No.	Mn	Zn	Cu	Fe	Cr	Ni
S1	1.736±0.072	0.694±0.045	0.017±0.006	3.203±1.087	0.0012±0.0009	0.0002±0.0001
S2	1.844±0.032	0.224±0.078	0.067±0.012	5.957±2.138	0.0015±0.0006	0.0015±0.0006
S3	10.244±3.053	0.674±0.083	0.003±0.001	23.012±4.312	0.0035±0.0008	0
S4	2.357±0.213	0.361±0.076	0.385±0.109	23.138±4.876	0.0019±0.0007	0.0019±0.0007
S5	0.565±0.065	0.513±0.069	0.125±0.098	10.209±3.254	0.0018±0.0006	0.0016±0.0008
S6	1.494±0.0.54	0.378±0.056	0.004±0.001	7.823±1.243	0.0042±0.0012	0.0011±0.0006
S7	2.646±0.174	3.820±1.080	0.002±0.001	24.216±5.322	0.0033±0.0008	0
S8	21.057±4.214	1.608±0.487	0.004±0.002	24.365±4.987	0.0021±0.0009	0.0021±0.0009
S9	5.950±1.398	0.691±0.076	0.306±0.032	18.720±2.678	0.0049±0.0006	0
S10	0.841±0.096	1.100±0.123	0.353±0.087	17.552±3.276	0.0024±0.0008	0
S11	8.272±2.130	3.546±1.087	0.009±0.003	24.879±5.389	0.0050±0.0009	**0.003**±0.001
S12	3.869±1.087	1.152±0.325	0.006±0.002	21.873±4.276	0.0019±0.0007	0.0015±0.0007

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S13	10.371±2.453	1.886±0.411	0.008±0.003	22.502±6.322	0.0015±0.0005	0.0011±0.0006
S14	7.189±2.132	3.188±0.646	0.002±0.001	25.049±5.340	0.0022±0.0009	0.002±0.001
S15	5.424±1.059	1.524±0.298	0.003±0.001	23.371±4.978	0.0030±0.0006	**0.003**±0.001
S16	12.424±3.243	0.874±0.046	0.005±0.002	18.073±3.695	0.0022±0.0009	0.0013±0.0005
S17	9.976±1.854	1.152±0.212	0.007±0.003	18.689±3.123	0.0012±0.0005	0
S18	15.401±3.215	1.495±0.421	0.936±0.198	19.252±3.965	0.0033±0.0009	0
S19	12.424±3.077	0.802±0.065	0.009±0.002	21.166±4.222	0.0026±0.0006	0
S20	10.971±2.140	0.561±0.084	0.004±0.001	16.370±3.124	0.0018±0.0009	0
S21	13.310±2.143	1.699±0.312	0.006±0.002	18.385±2.676	0.0034±0.0007	0.0011±0.0006

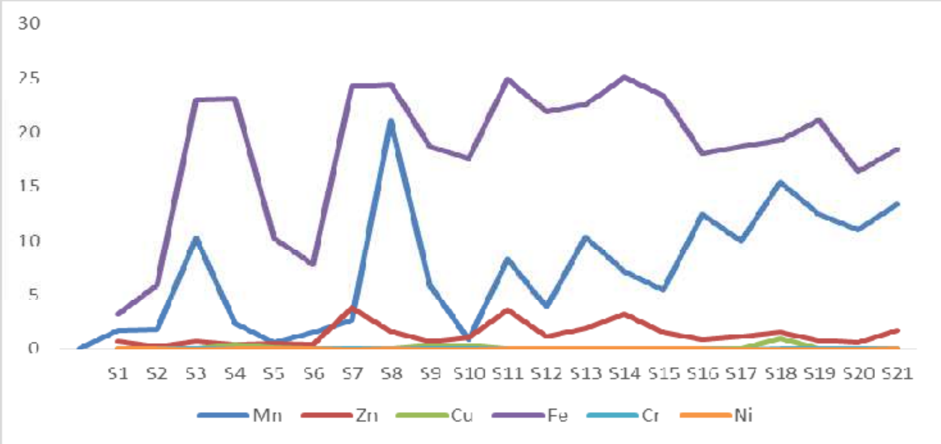

Fig. 2 Variation in concentration of trace elements Fe, Cu, Zn, Mn, Cr, Ni

Table 3 Permissible limit of the trace elements (BIS (Bureau of Indian Standard) 10500; 2012)

Trace elements	Permissible limit (ppm)
Mn	0.5
Zn	5
Cu	0.05
Fe	0.3
Cr	0.05
Ni	0.02

The pH value of the sediment samples collected from the Perumba River shows a wide range of values. The sediments samples from S21 and S4 can be said to be strong to extremely acidic. The highest value of alkalinity in the study area is found in sample S9. The least value of EC was found in sample S20 and the highest value was in sample S14. The least value of organic content was found in sample S1 and the highest value was in sample S4 **(**Table 4**)**.

Determination of mutual relationships and the strength of association between the trace element concentration and physico-chemical parameters have been carried out by Pearson correlation (Adam and Eltayeb 2012). A significant correlation is found between the trace element concentration and Electrical conductivity. Correlation between the Zn and Ec was higher than the other metals at a significant level of 0.01 and Fe and Ni were significantly correlated at the level of 0.05. Between the trace elements, Fe and Zn were highly correlated at the significant level of 0.01 (**Table 5**).

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Table 4 Physico-chemical parameters

Sample ID	pH	Electrical Conductivity (mS)	Organic Matter (%)
S1	6.46	4.75	0.15
S2	6.1	5.951	0.3
S3	7.12	9.648	0.45
S4	5.1	38.5	6.15
S5	6	6.66	0.65
S6	6.38	10.06	0.75
S7	6.04	52.09	1.65
S8	6.41	38.81	2.85
S9	7.38	10.4	4.35
S10	6.3	4.78	2.55
S11	6.15	32.37	2.4
S12	6.3	11.83	0.3
S13	6.03	11.84	1.5
S14	6.1	70.04	1.95
S15	6.59	14.59	1.35
S16	7.07	0.702	0.9
S17	6.17	0.65	1.05
S18	6.13	0.79	0.75
S19	6.15	0.058	0.6
S20	6.83	0.05	0.45
S21	4.73	0.097	0.22

Table 5 Pearson bivariant Correlation

	Ph	**Ec**	**Oc**	**Mn**	**Zn**	**Cu**	**Fe**	**Cr**	**Ni**
Ph	1	-.189	-.111	.060	-.098	-.098	-.059	.179	-.363
Ec	-.189	1	.482*	-.069	-.140	-.140	.507*	.110	.451*
Oc	-.111	.482*	1	-.094	.310	.310	.409	.211	.223
Mn	.060	-.069	-.094	1	.050	.050	.455*	.050	-.009
Zn	-.098	-.140	.310	.050	1	1.000**	.011	.157	-.223
Cu	-.098	-.140	.310	.050	1.000**	1	.011	.157	-.223
Fe	-.059	.507*	.409	.455*	.011	.011	1	.256	.080
Cr	.179	.110	.211	.050	.157	.157	.256	1	-.228
Ni	-.363	.451*	.223	-.009	-.223	-.223	.080	-.228	1

**Correlation is significant at the 0.01 level (2-tailed)
*Correlation is significant at the 0.05 level (2-tailed)

Geo accumulation index (I_{geo}) of trace elements in the sediments

Interpretation with references to the seven-grade classification (**Table 6**) according to Muller (1969, 1981) shows that the sediments are unpolluted for Cu, Cr and Ni with moderate enrichment (**Table 7**, **Fig. 3**). Fe has values that fall to moderately contaminated in all sites except S1, S2 and S20. Zn shows heavy contamination at the first sampling point 1l and 14 and uncontaminated to moderately polluted in the remaining sites. Mn shows moderately to heavily contaminate at the sampling point S8 and uncontaminated to moderately polluted in other sites. However, Zn and Mn show uncontaminated to moderate contamination in most of the sites (**Fig. 3**).

Table 6 Geo-accumulation index ranges (Muller (1981)

Ranges	**Sediment Quality**
Igeo<0	Practically Uncontaminated
0<Igeo<1	Uncontaminated to moderately contaminated
1<Igeo<2	Moderately contaminated
2<Igeo<3	Moderately to heavy contaminated
3<Igeo<4	Heavily contaminated
4<Igeo<5	Heavily to extremely contaminated
5<Igeo	Extremely contaminated

Table 7 Geo accumulation index (I_{geo}) of trace elements in the sediments

Site No.	**Mn**	**Zn**	**Cu**	**Fe**	**Cr**	**Ni**
S1	0.1743	0.696	0.001	0.192	0	0
S2	0.185	0.2249	0	0.358	0	0
S3	1.027	0.676	0	1.392	0	0
S4	0.236	0.3622	0.004	1.283	0	0
S5	0.0566	0.515	0.001	0.614	0	0
S6	0.1498	0.379	0.004	0.478	0	0
S7	0.2646	3.83	0	1.457	0	0
S8	**2.1057**	1.613	0	1.576	0	0
S9	0.61	0.6932	0.003	1.126	0	0
S10	0.084	1.102	0.003	1.056	0	0
S11	0.828	3.557	0	1.687	0	0
S12	0.387	1.155	0	1.324	0	0
S13	1.041	1.892	0	1.399	0	0
S14	0.719	3.198	0	1.879	0	0
S15	0.542	1.529	0	1.498	0	0
S16	1.242	0.8766	0	1.123	0	0
S17	1.001	1.1559	0	1.1222	0	0
S18	1.540	1.5	0.009	1.272	0	0
S19	1.242	0.8048	0	1.322	0	0
S20	1.130	0.562	0	0.989	0	0
S21	1.331	1.704	0	1.101	0	0

Igeovalue for Cr was found between 0 and 1 and comes under class 1, this demonstrates the sediment is uncontaminated to moderately contaminate (Singh et al. 2013a, b, c). The main sources of Zn were smelting, fertilizers, and pesticides used in agriculture, soil erosion due to rainfall, fossil fuel, and land construction activities (Higgins et al. 2007; Xiang et al. 2002; Chen et al. 2004). Fe is an essential metal for most living organisms and humans. It is a constituent of proteins, many enzymes, including hemoglobin and myoglobin (Yip et al. 1996; Brody 1999).

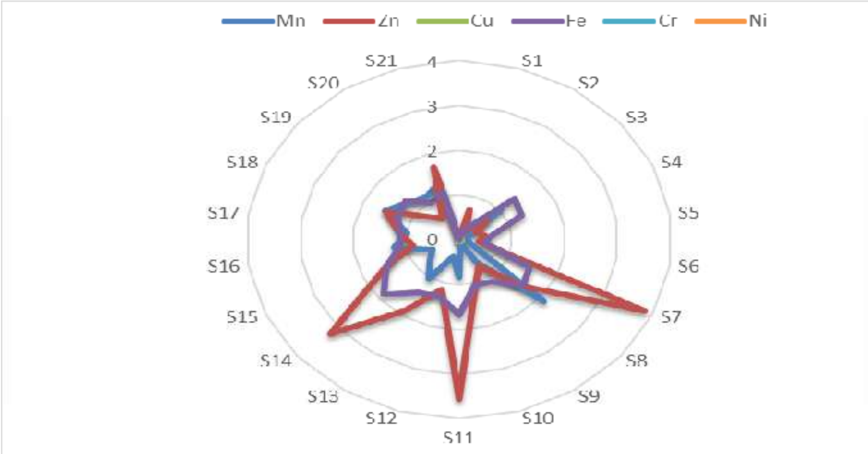

Fig. 3 Geo accumulation index (I_{geo}) of trace elements in the sediments

Several negative Igeo values were noted for all considering metals at many sites and showed that the Ghaghara river bed sediment is uncontaminated for most of the trace metals in the study area. A previous study carried out by Singh et al. (2013a) on the Ganga River noted several negative Igeo values for Co, Ni, Cu, and Pb at various sites. Geo-accumulation index permits the assessment of the level of sediment contamination to global standards. The geo-accumulation index was introduced by Muller (1979). The calculated Igeo class value was found between 0 or 1, Igeo class values showed uncontaminated to moderately contaminated river sediments (Singh et al. 2017).

Conclusion

The concentration of trace elements higher than the safe recommended values might create an adverse effect on the riverine ecosystem. But here, all these elements viz. Mn, Zn, Cu Fe, Ni and Cr are well within the corresponding permissible levels. The correlation between the heavy mineral concentrations and the physico-chemical parameters are significant. Perumba River is out of risk in case of these trace elements since it has not crossed the safe limits. However, in a few sites have been heavily contaminated, which indicates the accumulation of trace elements due to their activities like agricultural wastes/pesticides/soil erosion etc. Unfortunately,most of the time, the rivers are monitored without paying any attention to the sediments which are in constant interaction with the river. In the day-by-day activities, it may increase the concentration of trace elements in the river system, hence it is necessary to monitor the riverine system to maintaining as safe for both aquatic animals and humans.

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INTERNATIONAL JOURNAL OF MULTIDISCIPLINARY EDUCATIONAL RESEARCH
ISSN:2277-7881; IMPACT FACTOR :6.514(2021); IC VALUE:5.16; ISI VALUE:2.286
Peer Reviewed and Refereed Journal: VOLUME:10, ISSUE:4(2), April :2021
Online Copy Available: www.ijmer.in
Digital certificate of publication:http://ijmer.in/pdf/e-Certificate%20of%20Publication-IJMER.pdf

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Number of Words: 4,142 (approx.)

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