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Ecotoxicity and Ecosystem Health of a Ramsar Wetland System of India

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ABSTRACT

In this study one economically important Ramsar wetland system of India, Vembanad wetland system, is studied to determine the environmental pollution. Six surface sediment samples collected from two extreme zones of the wetland system were analyzed for heavy metals such as Copper, Zinc, Manganese, Cadmium, Lead, Nickel and Mercury. Highest metal concentration was found at industrial zone and lowest concentration was detected at southern upstream of the wetland system. The results showed that the pollution level is significant in the industrial zone. Comparison of the results with different sediment quality guidelines indicated ultra high degree of contamination in the industrial zone. The numerical value of degree of contamination, pollution load index, sum of toxic units, enrichment factor and geo-accumulation index confirmed the above fact. Based on National Oceanic and Atmospheric Administration Guidelines, the health of the ecosystem was seriously impaired with frequent occurring of biological effects in the industrial zone. The percentage of heavy metal calculated with respect to the industrial zone as the base line and the correlation analysis with organic matter indicated that, mobility of the specific metal has higher impact on its concentration at the fresh water region of the wetland.

Keywords: *Heavy Metal, Sediment Quality Guidelines, Degree of Contamination, Pollution Load Index, Index of Geo-Accumulation*

1. Introduction

Sediments are the layers of relatively finely divided matter covering the bottom of rivers, streams, lakes, reservoirs, bays, estuaries and ocean. Unlike water quality which is susceptible to seasonal variation, dependent on in and out flow and weather, sediment quality is more constant and will have more farfetched implications. Assessment of sediments in a complex aquatic system resulted in a better understanding of the adverse impacts that contaminants in sediments pose to fish, wild life and humans who depend this impacted waterways. Therefore apart from polluted water, fate of contaminated sediment has been chosen as one of the aspects responsible for ecological decline. Lake sediments provide a useful archive of information on changing lacustrine and watershed ecology [1]. The composition of the sediment sequences provides the best natural achieves of recent environmental changes [2].

Sediment is a habitat and major nutrient source for aquatic organisms. Sediment analysis is important in evaluating qualities of total ecosystems of a water body in addition to water sample analysis practiced for many years because it reflects the long term quality situations independent of the current inputs [3] and it is the ultimate sink of contaminants in the aquatic system [4]. Accumulation of heavy metals occur in upper sediment of the aquatic environment by biological and geochemical mechanisms and becomes toxic to sediment dwelling organisms and fish, resulting in death, reduced growth, or in impaired reproduction and lower species diversity [5]. Trace elements also occur naturally in rock forming minerals; hence they can reach the environment from natural processes [6]. The occurrence of metals in aquatic ecosystems in excess of natural background loads has become a problem of increasing concern. Heavy metals in environment may accumulate to toxic levels without visible signs. This may occur naturally from normal geological phenomenon such as ore formation, weathering of rocks and leaching or due to increased population, urbanization, industrial activities, agricultural practices, exploration and exploitation of natural resources [7].

One of the major problems that heavy metals cause with respect to their effects on aquatic organisms is their long biological half-life. Therefore, they are among the most frequently monitored micropollutants, and reliable techniques have been established for their extraction and quantification [8-10], since sediment contamination by heavy metals in rivers and estuaries has become an issue of increasing environmental concern. Such contamination is often caused by human activities, including mining, smelting, electroplating and other industrial processes that have metal residues in their wastes, and by non-point source surface runoff.

It is accepted that without defensible sediment quality guidelines it would be difficult to assess the extend of sediment contamination [11]. Sediments were classified as non-polluted, moderately polluted and heavily polluted, based on Sediment Quality Guidelines of United State Environmental Protection Agency [12]. Hakanson *et al.* [13] had suggested a contamination factor (Cif) and the degree of contamination (Cd) to describe the contamination of given toxic substance. Tomlinson *et al.* [14] had employed a simple method based on pollution load index (PLI) to assess the extent of pollution by metals in estuarine sediments. The need for chemical guidelines that could be used to predict adverse biological effects in contaminated sediments lead to the development of sediment quality guidelines [15-18]. The ecotoxicological sense of heavy metal contamination in sediments was determined using sediment quality guidelines developed for marine and estuarine ecosystem [19]. The potential acute toxicity of contaminants in sediment sample can be estimated as the sum of the toxic units (∑TU) defined as the ratio of the determined concentration to PEL value [20]. Pollution will be measured as enrichment factor (EF), which is the amount or ratio of the sample metal enrichment above the concentration present in the reference station or material [21,22]. Sediment geo accumulation index (GeoI) is the quantitative check of metal pollution in aquatic sediments [23]. These impacts were assessed by means of the geo-accumulation index (Igeo) [24] and Igeo classification is reported based on the chemical analysis of the bulk sediments. The Igeo has been widely utilized as a measure of pollution in freshwater [25-27] and marine sediments [28-30].

The over all objective of this research work was to evaluate the degree and extend to which the heavy metal contamination has affected the Vembanad wetland system, one of the Ramsar site in the south west coast of India. In this study heavy metals such as copper, zinc, manganese, cadmium, lead, nickel and mercury in surface sediments were analysed using different sediment quality guidelines. The numerical value of different sediment quality indices such as degree of contamination, pollution load index, sum of toxic units, enrichment factor and geo-accumulation index were also calculated for the data interpretation. Hence the present study aimed to understand the pollution load at industrial region of the wetland system and its impact towards the fresh water region of the Vembanad Lake.

The Vembanad wetland system (Latitude 9˚30' and 10˚12'; Longitude 76˚10' and 76˚29') is a complex aquatic system of coastal backwaters, lagoons, marshes, mangroves and reclaimed lands with an intricate network of natural and man made channels and its associated drainage basins are situated in the humid tropical region on the south west coast of the Indian peninsula. The total area of the wetland system is 2195 km^2. This system includes the Vembanad backwaters and the lower reaches of the five rivers draining in to it. The five rivers which drain in to the Vembanad Lake are Muvattupuzha, Meenachil, Manimala, Pamba and Achenkoil. All these rivers originate from the Western Ghats, flow westwards through the wetland system and join the Lakshadweep/ Arabian Sea. The wetland is typically divided into two distinct segments, the freshwater dominant southern zone and the salt-water dominant northern zone both separated by a bund at Thanneermukkom. The estuarine zone and organically rich sedimentary substratum of the inshore region makes it a highly preferred and desirable habitat for shrimps breeding. Vembanad is renowned for its live clam resources and sub-fossil deposits. Vembanad wetland has been designated as a Ramsar Site in November 2002.

The wetland system is facing many problems, which include; pollution due to industrial, agricultural and domestic effluents. It is estimated that nearly 260 million liters of effluents reach the estuaries daily form the industries located in the northern part of the wetland system [31]. The Cochin estuarine system receives effluents containing a large dose of heavy metals [32]. The distribution and toxicity of heavy metals in core sediments also indicated severe pollution in the wetlands [33,34]. The increasing loads of sewage and industrial waste have created conditions that are extremely destructive to flora and fauna. During the tidal activity pollutants from the northern side moves towards the southern side making the fresh water system also threatened. In addition agricultural inputs from the lands located around the lake also pollute the freshwater region of the lake.

Sampling Stations

Six sampling stations were selected in the wetland system starting from the northern industrial region to the southern fresh water region. Six surface sediment samples were collected from each site, using a gravity corer with PVC core-liner. Four centimeters of the surface sediments were extracted from the core-liner and placed in labeled polythene bags. In the laboratory the sediments were air-dried [23] to a constant weight and homogenized with a pestle and mortar, in order to normalize for variation in grain size distribution. The sampling sites are marked in the area map (**Figure 1**).

2. Analytical Methods

For the digestion of the sediment sample one gram of dried and homogenized sediment sample was weighed into 250 ml beaker. An empty beaker was included in the analysis as a reagent empty blank. 50 ml of distilled water was added to the sample. The digestion was performed with a mixture HNO_3 and $HClO_4$. Digestion was continued until the volume was reduced to about 15 ml. The beakers were allowed to cool to room temperature. The digests were then filtered into a 50ml volumetric flask and made up to the volume with distilled water [35]. The digested samples were analyzed for heavy metal following Atomic Absorption Spectrophotometer [15] by Thermo M5 series. The concentration of manganese, cadmium, copper, lead, nickel, zinc and mercury were determined in sediment samples and the values are reported in units of mg/Kg.

The contamination factor for the sediment samples were calculated by the equation;

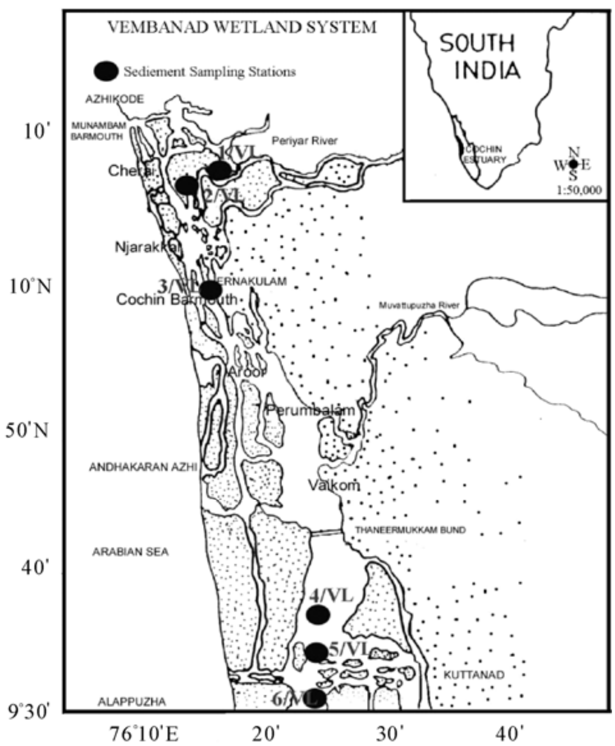

Figure 1. Area map of Vembanad wetland system showing the sediment sampling sites.

Contamination Factor (CF) = Metal content in sediment/Background level of metal (1)

The method proposed by Tomlinson *et al.* [14] had employed in the present study to find the sediment pollution load index (PLI) which is given by the equation;

$$PLI = (\text{Product of n number of CF values})^{1/n} \quad (2)$$

Enrichment factors (EF) for metal concentration in sediments at all the stations was calculated and used for comparison. The following equation was used to calculate the EFc values.

$$EFc = X/Fe\ (\text{sediment})/X/Fe\ (\text{Earth's crust}) \quad (3)$$

where X is the metal studied and X/Fe is the ratio of the concentration of element X to iron. Iron was chosen as the element of normalization because natural sources (98%) vastly dominate its input. The crustal abundance data of Bowen [36] were used for all EF values.

The geoaccumulation index Igeo values were calculated for different metals as introduced by Muller [37] is as follows:

$$Igeo = Log_2(C_n/1.5{*}B_n) \quad (4)$$

where C_n is the measured concentration of element n in the sediment simple and B_n is the geochemical background for the element n which is Esther directly measured in pre civilization sediments of the area or taken from the literature (average shale values). The factor 1.5 was introduced to include the possible variation of the background values that are due to lithological variations.

3. Results

One of the simple ways of assessing the level of pollution in an aquatic ecosystem is the comparison with different sediment quality guidelines. The range and the mean concentration of heavy metals determined in the sediment samples and their comparative assessment with different international sediment quality guidelines are tabulated in **Table 1**. The concentration of copper varied from 38.7 mg/Kg to 1723.75 mg/Kg. Zinc has a variation from 70.7 mg/Kg to 1963.67 mg/Kg. Manganese concentration in the surface sediments according to the present investigation varied from 320.51 mg/Kg to 15586.88 mg/Kg. Cadmium in the sediment ranges from 0.27 mg/Kg to 6.35 mg/Kg. The concentration of lead ranged from 21.70 mg/Kg to 162.59 mg/Kg. Nickel has a variation from 49.59 mg/Kg to 75.70 mg/Kg.

The level of contamination in aquatic system can be assessed by determining a factor called the degree of contamination (mCd). Elemental background concentration reported for continental crust was used as the reference value. The calculated value for the degree of contamination ranges from 1.47 to 35.39. The extend of pollution in an aquatic environment can be evaluated by a

Table 1. Concentration range of different heavy metals and its comparison with different SQGs.

Element mg/Kg	Mean	Range	Ontario MOE		NOAA SQG		FDEP SQG		CCME		CSCR	USEPA		
			Low	Severe	ERL	ERM	TEL	PEL	IGM	PEL		SQG NP	SQG MP	SQG HP
Cu	799.15	38.87 - 1723.75	16	110	34	270	18.7	110	35.7	197	60 - 125	<25	25 - 50	>50
Zn	528.21	70.07 - 1963.67	120	820	150	410	124.0	270			70 - 400	<90	90 - 200	>200
Mn	4928.9	320.51 - 15586.88	460	1110							1500 - 3000	-	-	-
Cd	6.63	0.27 - 26.35	0.6	10	1.2	9.6	0.68	4.20	0.6	3.5	3 - 8	-	-	-
Pb	66.40	21.70 - 162.59	31	250	46.7	218	30.2	110	35	91.3	100 - 400	<40	40 - 60	>60
Ni	64.35	49.59 - 75.70	16	75	20.9	51.6	15.9	43	123	315	100	<20	20 - 50	>50

ERL-Effect Range Low, ERM- Effect Range Median, TEL-Threshold Effect Level, PEL-Probable Effect Level, IGM-Interim sediment quality Goals, NP-Non Polluted, MP-Moderately Polluted, HM-Heavily Polluted.

simple method based on pollution load index (PLI). The world average concentration of elements reported for Shale was taken as the reference for PLI. Station 6/VL reported lower PLI value (1.02) and the highest (12.92) was reported for station 2/VL. The potential acute toxicity of contaminants in sediment samples can be estimated as the sum of toxic units ($\sum TU$) defined as the ratio of determined concentration to PEL values. The TU values also show the same trend as like mCd and PLI. The different values observed for degree of contamination, pollution load index and sum of toxic units are summarized in **Table 2**. All the values indicated metal contamination in the Vembanad Lake.

A common approach to estimate how much the sediment is impacted (naturally and anthropogenically) with heavy metal is to calculate the enrichment factor (EF) for metal concentrations above uncontaminated background levels. The average standard reported for Shale was used as the reference value in the present study. The enrichment factors for different metals in different stations are tabulated in **Table 3**. Index of geochemical accumulation (Igeo) has been used widely to evaluate the degree of metal contamination or pollution in terrestrial, aquatic and marine environment. World average reported for Shale was used as the control in the present study. Geo-accumulation index for different stations is summarized in **Table 4**.

Correlation matrix provides clues about the carrier substances and the chemical association of these metals in the ecosystem. In the present study Pearson's correlation has employed for different metals with organic matter. The correlation matrix is given in **Table 5**.

4. Discussion

4.1. Spatial Variation of Heavy Metals

Figure 2 represents the spatial variation of different heavy metals in the surface sediments of Vembanad wetland system. The mean concentration of different heavy metals follows the order manganese > copper > zinc > lead > nickel > cadmium > mercury. The average concentration of copper is 799.15 mg/Kg, which was above the all compared sediment quality guidelines. The highest deposition was found in the Cochin bar mouth and lowest was reported in the station 6/VL, which is in the southern end. High level of copper indicates a higher input of organic matter deposition, which might be from urban and industrial waste water sediment deposition. The average concentration of zinc is 528.21 mg/Kg, which was also above the all sediment quality guidelines. Manganese in earth crust is 1060 mg/Kg; in soils it is 61 - 1060 mg/Kg. The station 2/VL has reported 15586.88 which is far away from the guideline values. A uniform decreasing trend was observed for manganese except for the station 1/VL. The average abundance of cadmium in the earth crust is 0.16 ppm; in soils it is 0.1 - 0.5 mg/Kg. Increased cadmium concentration might be related to industrial activity, atmospheric emission and deposition of organic and fine grain sediments. Lead is considered as a good indicator of pollution by urban run-off water. The use of gasoline is mainly responsible for the lead pollution especially in urban area. The average concentration of lead in the present study is 66.40 mg/Kg, which is in the category of highly polluted sediments according to United State Environmental Protection Agency Guidelines. The background value of nickel in the earth crust is 1.2 mg/Kg; in soil it is 2.5 mg/Kg. Nickel is used principally in its metallic form combined with other metals and nonmetals as alloys. The mean value of nickel is 64.35 mg/Kg, which is above the United State Environmental Protection Agency Guidelines for highly polluted sediments. The mercury pollution is severe in the sediments of the Cochin bar mouth with a concentration of 4.91 mg/Kg.

Table 2. Spatial variation of heavy metals and different index values.

Element/Stations	1/VL	2/VL	3/VL	4/VL	5/VL	6/VL	Continental Crust	Average shale
Cu mg/Kg	1346.25	1588.13	1723.75	47.60	50.30	38.87	55.00	45.00
Zn mg/Kg	578.11	1963.67	70.07	223.00	156.68	177.75	70.00	95.00
Mn mg/Kg	4040.00	15586.88	8714.38	501.67	320.51	410.00	950.00	900.00
Cd mg/Kg	7.03	26.35	5.23	0.27	0.35	0.55	0.20	0.30
Pb mg/Kg	27.18	78.27	162.59	28.65	80.03	21.70	12.50	20.00
Ni mg/Kg	70.56	72.82	49.59	64.73	75.70	52.67	75.00	68.00
Hg, mg/Kg	0.56	0.23	4.91	0.136	0.345	0.270		
mCd	12.54	35.39	13.55	1.51	2.11	1.47		
PLI	5.48	12.92	5.52	1.09	1.23	1.02		
SUM TU	17.94	30.39	19.81	3.09	3.61	2.56		

mCd: Degree of Contamination, PLI- Pollution Load Index, SUM TU- Sum of Toxic Units.

Table 3. Enrichment factor calculated for the sediment samples of Vembanad wetland system.

Element/Stations	Enrichment Factor					
	1/VL	2/VL	3/VL	4/VL	5/VL	6/VL
Cu	19.94	23.53	25.54	0.71	0.75	0.58
Zn	4.06	13.78	0.49	1.56	1.10	1.25
Mn	2.99	11.55	6.46	0.37	0.24	0.30
Cd	15.61	58.56	11.61	0.59	0.79	1.21
Pb	0.91	2.61	5.42	0.95	2.67	0.72
Ni	0.63	0.71	0.49	0.63	0.74	0.52

Table 4. Sediment geo-accumulation index (Igeo) calculated for sediments of Vembanad wetland system.

Element/Stations	Index of Geo-accumulation					
	1/VL	2/VL	3/VL	4/VL	5/VL	6/VL
Cu	4.32	4.56	4.67	−0.50	−0.42	−0.80
Zn	2.02	3.78	−1.02	0.65	0.14	0.32
Mn	1.58	3.53	2.69	−1.43	−2.07	−1.72
Cd,	3.96	5.87	3.54	−0.75	−0.35	0.28
Pb,	−0.14	1.38	2.44	−0.07	1.42	−0.47
Ni	−0.67	−0.49	−1.04	−0.66	−0.43	−0.95

Table 5. Pearson Correlation Matrix for different heavy metals with organic matter.

	Cu	Zn	Mn	Cd	Pb	Ni	Hg	O.M
Cu	1.00	0.50	0.84	0.68	0.57	−0.08	0.57	−0.27
Zn		1.00	0.81	0.97	−0.04	0.48	−0.32	0.53
Mn			1	0.93	0.50	0.08	0.29	0.11
Cd				1.00	0.19	0.34	−0.07	0.37
Pb					1.00	−0.31	0.87	−0.31
Ni						1.00	−0.65	0.86
Hg							1.00	−0.70
O.M								1.00

O.M: Organic Matter.

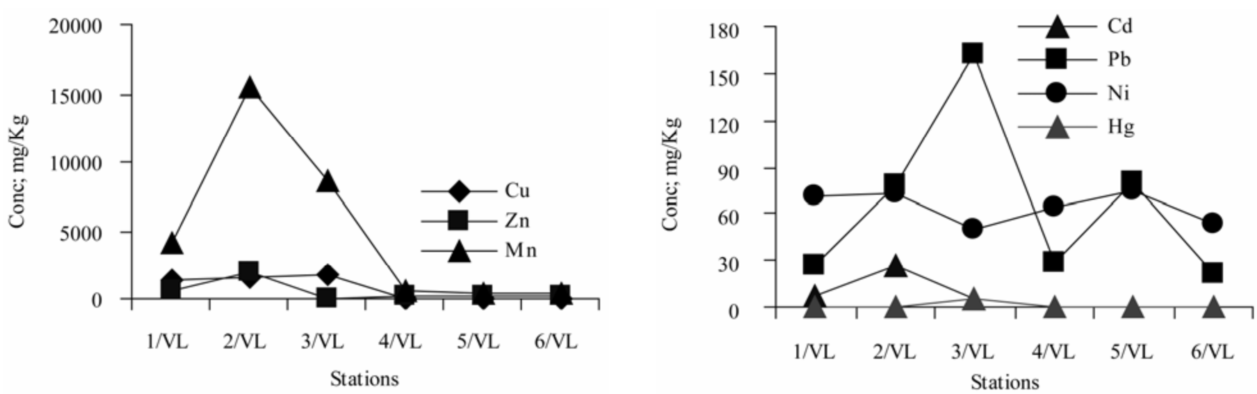

Figure 2. Spatial variation of different heavy metals in the surface sediments.

4.2. Sediment Quality Indices

The index value of various sediment quality indices such as degree of contamination, pollution load index and sum of toxic units are depicted in **Figure 3**. The degree of contamination (mCd) in an ecosystem is usually expressed by the following terminologies.

mCd ≤ 1.5 nil to very low degree of contamination
1.5 ≤ mCd < 2 low degree of contamination
2 ≤ mCd <4 moderate degree of contamination
4 ≤ mCd <8 high degree of contamination
8 ≤ mCd < 16 very high degree of contamination
16 ≤ mCd <32 extremely high degree of contamination
mCd ≥ 32 ultra high degree of contamination

Comparison of the results with the above terminologies indicated that ultra degree of contamination is observed at the station 2/VL which is located near the outlets of many industries. The other two stations 1/VL and 2/VL, near by the industrial units indicated very high degree of contamination. Moving towards the south a comparative decrease in the contamination was observed. The two stations, 4/VL and 5/VL experienced low degree of contamination. Sediment in the southern end indicated very low degree of contamination. The spatial variation of degree of contamination indicated that the movement of contaminated water and sediments from estuarine region to southern half of Vembanad wetland system at the time of high tide contaminated the fresh water region to some extend.

The pollution load index of the wetland follows the same order as the degree of contamination. If the PLI value is greater than one it indicates pollution and if it is less than one it shows no pollution. The PLI can provide information about the quality of the environment, which provides valuable information to the decision makers on the pollution level of the area. Hence according to PLI values all the stations in the wetland system is polluted.

The sediment quality guidelines of the National Oceanographic and Atmospheric Administration (NOAA) of the Unite States shows Effect Range Low (ERL) and Effect Range Median (ERM) values, which represents the percentile ranges of toxicity tolerance in bioassay

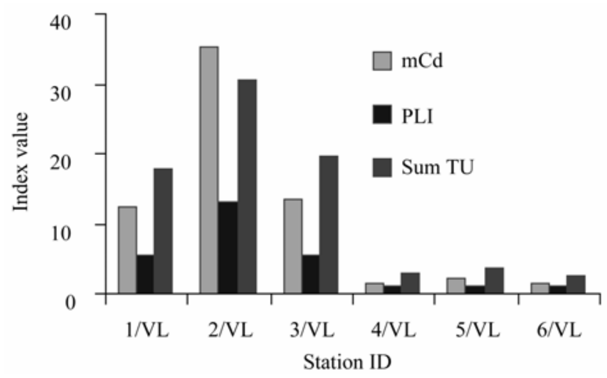

Figure 3. Variation of different sediment quality index values for Vembanad wetland system.

tests for aquatic and benthic biota. These effects are given by

Metal < ERL minimal effect range biological effects are rarely observed

ERL < Metal < ERM moderate effect range biological effects occur occasionally

Metal > ERM probable effect range biological effects occur frequently

The mean concentration of copper and zinc exceeded the ERM limits, which represents a probable effect range with in which adverse biological effects frequently occur. Spatial variation of trace elements indicated that biological effects are rare in southern half and frequent in estuarine side. The potential acute toxicity for the sediments were determined by calculating the sum of toxic units and showed similar trend like mCd and PLI.

The enrichment factor method normalizes the measured heavy metal content with respect to a sample reference such as iron. It can be used to differentiate between the metal originating from anthropogenic activities and those from natural procedure, and to assess the degree of anthropogenic influence. Five contamination categories are recognized on the basis of the enrichment factor, which are

EF < 2 deficiency to minimal enrichment

EF 2 - 5 moderate enrichment

EF 5 - 20 significant enrichment

EF 20 - 40 very high enrichment

EF > 40 extremely high enrichment

A value of $0.5 \leq EF \leq 1.5$ suggests that traces of metal may be due to crystal materials or natural weathering processes. Samples having EF value greater than 5 are considered to be contaminated with that particular element. **Figure 4** represents all the EF values of the heavy metals. The station 2/VL showed very high enrichment for the metal cadmium. It is presumed that high EF values indicate an anthropogenic source of heavy metals, mainly from activities such as industrialization and urbanization. Comparatively less enrichment was observed in samples of southern region. But according to Khan *et al.* [38] EF value less than one are considered significant. Areas with EF values <1 should be viewed with caution as they imply preferential release of these metals, making them bioavailabe.

The Index of geo-accumulation calculated for the degree of metal pollution is assessed in terms of seven contamination classes based on the increasing numerical value of the index as follows:

Igeo

Igeo < 0 unpolluted

0 <= Igeo < 1 unpolluted to moderately polluted

1 <= Igeo < 2 moderately polluted

2 <= Igeo < 3 moderately polluted to strongly polluted

3 <= Igeo < 4 strongly polluted

4 <= Igeo < 5 strongly polluted to very strongly polluted

Igeo >= 5 very strongly polluted

Figure 5 represents the geo-accumulation index for different heavy metals in the wetland. It indicates strong pollution in the industrial zone and unpolluted to moderate pollution in the freshwater region. Elements copper

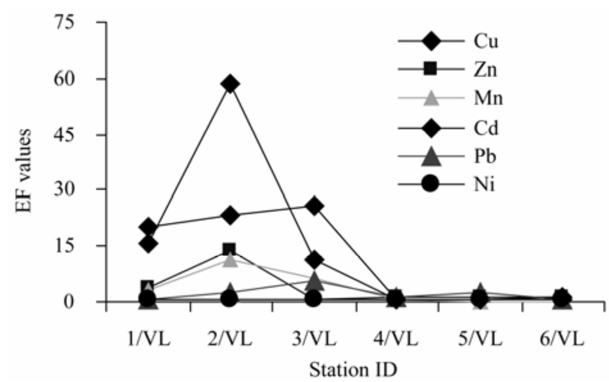

Figure 4. Variation of enrichment factor along different stations.

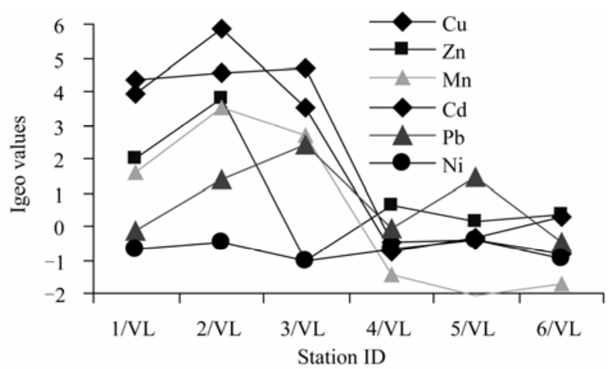

Figure 5. Variation of geo-accumulation index for different stations.

and cadmium have higher values in northern half where as it is very low in southern side.

4.3. Pearson's Correlation Matrix

Correlation analysis of heavy metals with organic matter present in the sediment was carried out. Zinc and nickel have good correlation with organic matter where as mercury have a strong negative correlation. The element cadmium has good correlation with all other elements except mercury. Copper also has good correlation with other metals except nickel and organic matter. The percentage of different metals in the sediments of fresh water region with reference to industrial zone was calculated. The concentration of nickel in both the regions was same, which indicated the higher mobility of the metal nickel. The lowest percentage was reported for copper, which indicated its lower mobility. The above facts were conformed from the correlation matrix, where nickel has good correlation with organic matter and copper have no correlation. Hence the concentration of the heavy metals in fresh water is a proportionate of the mobility of metal and contamination load at industrial side.

5. Conclusions

The study of "Ecotoxicity and ecosystem health of a Ramsar wetland system of India" showed a clear pattern of anthropogenic impact on Vembanad wetland system. From the observation it is clear that manganese and copper showed more pronounced level followed by zinc, lead, nickel, cadmium and mercury. Comparison of heavy metal concentration with different international sediment quality guidelines indicated that most of the heavy metal concentration in the northern side of the wetland system has crossed the extreme limits where as southern half is with in the range of guideline values. The assessment of level of contamination by calculating the degree of contamination for different stations confirmed ultra degree of contamination at station near by industrial area. Enrichment factor determined for the deferent heavy metals indicated anthropogenic origin of heavy metal in estuarine side. Index of geo-accumulation was also showed the same trend like enrichment factor. According to NOAA guidelines the health of the ecosystem was seriously impaired with frequent biological effects were occurring in estuarine side. The extend of pollution at the fresh water region also depends on the mobility of the specific metal. Nickel has higher mobility which has hundred percentage contribution, where as copper is less mobile which indicated its lowest contribution from the industrial zone. Anthropogenic source from the industrial activities at the upstream of the wetland contributed huge load of heavy metals to the estuarine region which is seriously attacking the fresh water region of the Vembanad wetland system.

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