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Distribution and Fractionation of Heavy Metals in Surface Sediments of Chilika Lagoon, East Coast of India

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Abstract: *Heavy metal contamination was assessed in the sediments of Asia's largest lagoon, Chilika lake lying on the east coast of India. Sediments were collected from 11 locations, from four different sectors and were analysed for Pb, Cu, Zn, Co, Cd, Ni, Mn and Fe. Based on the $I_{geo}$and CF values the results obtained reveal that sediments are highly polluted with Cu, Zn and Ni at some location, whereas a moderate pollution for Pb is observed at most of the sites.Slight pollution of Cr was also observedat few sites.According to PLI, sites near the sea mouth and river confluence are highly polluted due to agricultural, municipal and domestic wastes. Large boat traffic is another major cause of metal pollution. Metal speciation analysis reveals residual fraction is the most dominant fraction for most of the metals, followed by reducible fraction. The carbonate bound fraction for Mn (11.96-34.46), Pb (3.43 – 27.46%), Zn (0.2 – 26.29%) fall in medium risk category according to the Risk Assessment Code (RAC). The results expose that heavy metal contamination is prominent in Chilika lake sediments due to increased agriculture in the basin, discharge of untreated waste and boat traffic.*

I. Introduction

The estuaries and lagoon are major repositories of land based pollutants. Sediments in these systems act both as source and sink of heavy metals.Once metals reach the water column, they associate with particulate phases, binding to the fine-grained sediment components, such as hydrous iron and/or manganese oxides, sulphides, organic compounds and clay minerals **[1].**Heavy metals can be adsorbed on the particle surfaces of clays, iron, and manganese oxyhydroxides or organic matter present in the lattice of secondary minerals, such as, carbonates or sulphides; occluded in amorphous iron and manganese oxyhydroxides, sulfides or remains of biological organisms; and present in the lattice of primary minerals **[2].**The different chemical species of metal rather than its total concentration is crucial to understand its effects on biota, as well as its biogeochemical transformation and fate under varying environmental conditions. The exchangeable, acid soluble and oxidisable are known as extractable species. In unpolluted sediments, the metals exist in residual fraction mostly. With the increase in heavy metal pollution, the species of metals in the extractable fraction increases **[3].** Anthropogenic impacts alter the predominant environmental conditions (e.g. pH, redox potential, organic matter) which in turn remobilize the sediment-bound metal ions and make them bioavailable to the environment. Therefore metal fractionation was performed on sediments to infer the different associations of metals present in the sediments. The metals were extracted by BCR sequential extraction method into acid soluble, reducible and oxidisable fractions.Chilika is the largest lagoon in Asia, designated Wetland of International importance under Ramsar convention in 1981. Chilika is a dynamic ecosystem partly due to its connection with the Bay of Bengal on the eastern side and freshwater inflow from 52 rivers and rivulets joining it in the north and west. Historically the lagoon has undergone a considerable reduction in surface area, in part, due to input from natural processes but mostly due to human activities. The anthropogenic activities in its catchment basin have increased substantially in the past decade. Intensification in agriculture has lead to the increase in soils and sediments reaching the lagoon. The western catchment contributes nearly 536 m^3 S^{-1}, and the distributaries of the Mahanadi River (Daya, Bhargavi, and Nuna rivers) contribute an average of 850 m^3 S^{-1}**[4].**Lack of catchment basin management has led to the influx of a huge amount of suspended sediment into the lagoon, which has altered the ecology of the lagoon significantly. The purpose of this investigation is to document the heavy metal concentration and metals' affinity for specific geochemical phases in the recently deposited sediments in the lagoon.

II. Study Area

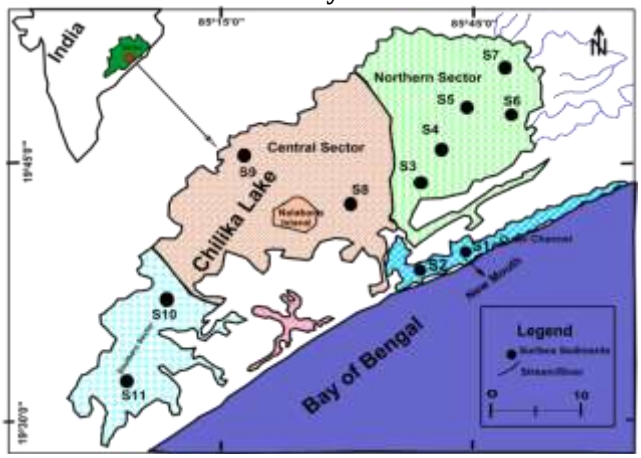


Fig 1: Study area with sampling locations

Chilika lagoon, the second largest coastal lagoon of Asia on the east coast of India in the state of Odisha, is a designated Wetland of International Importance (Ramsar Site under the Convention on Wetlands) since 1981. Chilika lies between latitude $19^0$28' -$19^0$54'N; and longitude $85^0$05'–$85^0$28' E and long. Chilika has a length of 64.5 kms and a variable breadth of 20 kms. It is a shallow water body with an average depth of 1.5m. Chilika went through a phase of rapid degradation during 1950-2000 owing to increasing sediment loads from catchments and reduced connectivity with the sea. Its fisheries underwent a major decline, invasive weeds proliferated and the wetland shrank in area and volume. Agricultural activities in the Chilika basin have intensified in the past decade increasing the chemical fertilizer use.

III. Materials and methods

III.I Sampling and total metal analysis

A total of 11 surface sediments were collected from four sectors of the lagoon **(Fig 1).**The sediments samples were collected with grab sampler, stored in polythene bags and brought to the laboratory in ice boxes. They were air dried first and then oven dried at 80^0C for two days. When the sediments achieved constant weight, they were then ground with mortar and pestle and passed through 125µm sieve. Heavy metals in sediments were analyzed as per the method of **[5].**0.1 g of finely ground sample (< 125µm) was digested using three acids HNO_3, HCl and HF (2 ml of aqua regia, HNO_3/HCl in 1:3 ratio and 5 ml of HF) at 100^0C for 1.5 h. After the digestion is complete, 5.6 g of boric acid crystal (H_3BO_3) was added and the final sample volume was made 100 ml by adding double distilled water. The gelatinous precipitate of borosilicate was separated by centrifugation followed by filtration with Whatman 0.45µm cellulose nitrate filter paper. The filtered samples were analysed on Atomic Absorption Spectrophotometer. The single element standards for heavy metals were obtained from Merck. All reagents and standards were prepared in double distilled water. Quality assurance and quality control were assessed using duplicates, method blanks, and standard reference materials. A standard was run after every 10 samples to check the validity of results. The recovery percentage of heavy metals in standard reference material ranged between 88- 105 %.

III.II Metal fractionation

Sequential extraction of metals in the surface sediments was performed by BCR sequential extraction method. The BCR three-step sequential extraction procedure modified by **[6]**was followed. After the sequential extraction steps, the residual metal content in the sediment was determined by digestion with mixture of aqua regia (3:1, HCl:HNO_3) and HF in accordance with the method of digestion for total metals mentioned in **section 3.1**. The sequential extraction in the cores was performed at 10cms depth. The recovery percentage of metals ranged from 85-110%.

IV. Results and Discussion

The concentrations of heavy metals in sediments has been shown in **(Table 1).** In general the metal concentration in the sediments was in the following order Fe >Mn> Cu > Zn > Cr > Ni >Pb> Co > Cd. The concentration of heavy metals in Chilika sediments have been compared with the natural background values. Metal concentrations in the surface sediments have been compared with the corresponding values of these metals in the average shale **[7].**Average shale values have been taken as background value in many other studies **[8, 9, 10, 11].**Except for Fe, Mn and Cd all the other heavy metals have average values greater than the shale values.

Table 1: Comparison of heavy metal concentration in Chilika sedimentswith Average Shale Values (AVS)

S. No	Avg Value ± Stddev	Min-max	Average Shale Values
Zn	549.97± 630.58	65.7- 1893.3	95
Co	18.44± 9.54	4.2- 34.2	19
Pb	59.05± 35.19	0-112.5	20
Cr	152.47± 109.67	0-342.7	90
Cd	0.31 ± 0.04	0.25-0.37	0.3
Cu	546.32 ± 586.28	50.2-1817.7	45
Ni	220.8 ± 331.63	0- 987	68
Mn	339.18 ± 251.28	83 - 876	850
Fe	30884.38± 10111.28	18041 -50957	47200

IV.IGeoaccumulation Index

Enrichment in the sediments in relation to the background values was evaluated in terms of geoaccumulation index (I_{geo}). Geoaccumulation index (I_{geo}) was used to assess heavy metal accumulation in sediments as introduced to measure the degree of metal pollution in aquatic sediment studies **[12].**

$I_{geo} = Log_2 (Cn/1.5Bn)$

Where, Cn is the measured concentration of a heavy metal in sediments, Bn refers to geochemical background value in average shale of element n, and 1.5 is the background matrix correction due to lithological and terrigenous effects.

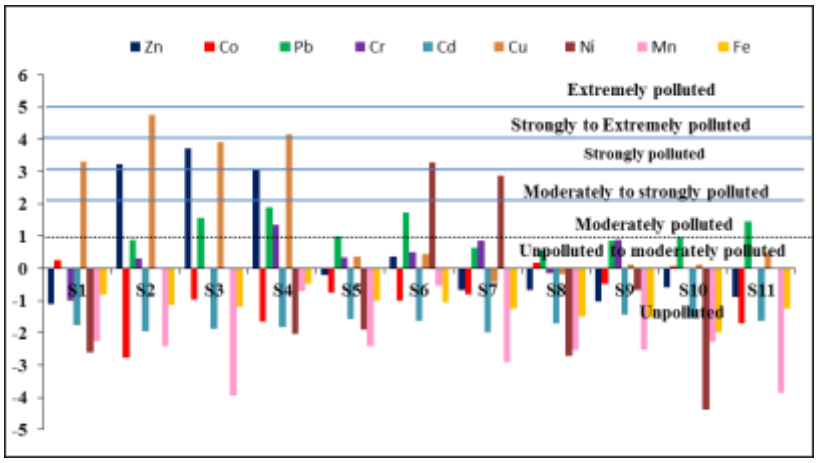


Fig 2: Geoaccumulation Index for heavy metals in Chilika sediments

According to I_{geo}classification, Cu has I_{geo}values lying between 0 - 5 at sampling sites S1, S2, S3 and S4 and for Zn the I_{geo} values were between 0 - 4 at sites S1, S2 and S3. These sites are moderately to strongly polluted by Cu and Zn. These sites have boat movement in large numbers for tourism and fishing. The major source of Cu and Zn are antifouling paints used in the bottom of the boat in order to prevent the growth of encrusting organisms **[13, 14, 15].**The other sources of these metals are surface runoff from agricultural land enriched in metals originating from fertilizers (Urea, Diammonium Phosphate, NPK complexes) and pesticides (Copper oxychloride). Phosphate fertilizers like Diammomiun phosphate (DAP), and to a lesser extent nitrogen fertilizers, are important sources of Zn, Cr, Cu**,** Ni and Pb**[1, 16].** I_{geo}values for Ni at sites S6 and S7 indicate moderate to strong pollution. Anthropogenic influx of Ni in the lake system may be due to silt brought by distributaries of Mahanadi river carrying untreated municipal and industrial waste from upstream**[17].**Moderate pollution for Pb is observed in the entire lagoon based on the I_{geo} values. Except at site S1 sediments at all other locations show moderate to moderately severe enrichment and I_{geo}values greater than one for Pb, indicating anthropogenic input of Pb in Chilika sediments **(Fig 2).** Pb may have reached the water body through motor boats which are powered by gasoline containing Pb**[18, 19,20]**. Though leaded gasoline has been banned in India, its use in the past and low degradability as well as persistence could be the reasons for high Pb concentrations. The other sources of Pb can also be atmospheric fallout of vehicular exhaust **[21, 22,23,24]**. In similar study **Satpath and Panda et al.(2015)**[**25]**have reported paint effluents and industrial discharge brought by rivers in Dhamra estuary to be the cause Pb pollution. Low to moderate geoaccumulation is observed for Cr at sites S4, S7 and S9. Cr is concentrated in the northern and southern sectors and possibly comes from municipal waste and industrial effluents. Sediments at S8 and S10 show moderate enrichments for cobalt**.** High Co could be an indicator of corrosion-resistant paints used for fishing boats in the nearby fishing jetty **[25].**

IV.IIContamination Factor (CF) and Pollution Load Index (PLI)

A contamination factor is the ratio between the sediment metal concentration and concentration of metal in the background. Metal enrichment is reflected in the sediments if the CF > 1 for a particular metal. CF < 1 means that there is no metal enrichment by anthropogenic inputs. To calculate the CF, world average shale value (AVS) has been used as the background value.

Contamination Factor was proposed by Hakanson**(1980)[26]** to express the level of contamination by each metal in sediment.

$$\text{Contamination Factor} = \frac{\text{Metal Concentration in the sediments}}{\text{Background Value of Metal}}$$

According to **Hakanson, 1980[26]**the CF values were classified into four groups.

1≤ CF low contamination factor

1≤ CF < 3 moderate contamination

3≤ CF < 6 considerable contamination

6 ≥ CF Very high contamination factor

Contamination factor values reveal extremely high contamination for Cu and Zn probably due to large number of boats plying in Chilika for tourism and fishing **(Fig 3).** Another important source of these metals are fertilizers used in agriculture. At sites S6 and S7 Ni also has CF > 6 as a consequence of large pollutant load brought by the rivers (Daya, Bhargavi, Nuna), joining at the northern end of the lagoon (**Fig 3).**

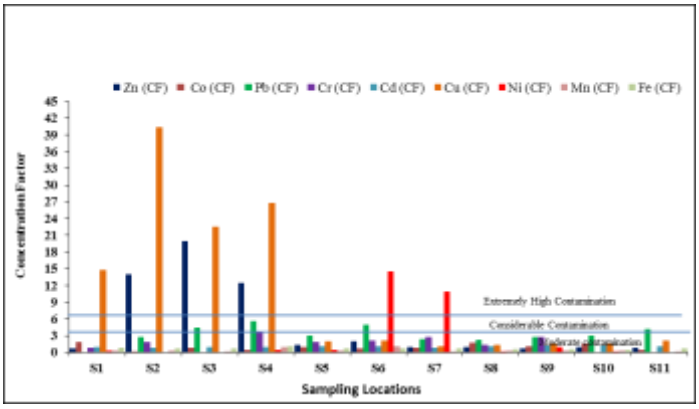


Fig 3: Contamination factor of metals in Chilika sediments

To assess the sediment environmental quality, an integrated pollution load index of metals was calculated according to **Tomilson, 1980 [27]**

$$PLI = (CF1 * CF2 * CF3 * CFn)^{1/n}$$

where CF metals is the ratio between the content of each metal to the background value.

A site with PLI value >1 is polluted whereas PLI value < 1 indicates no contamination. In Chilika

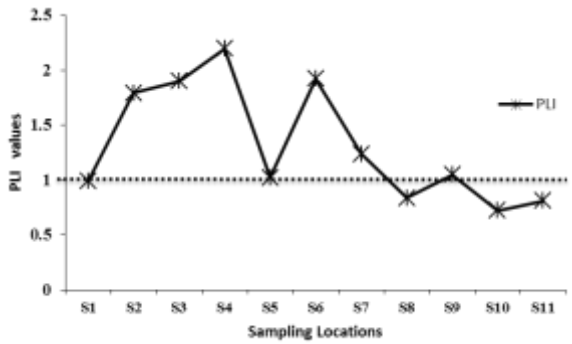


Fig 4: Pollution Load Index of sampling locations in Chilika

In Chilika most of the sites have a PLI values equal to or greater than 1 **(Fig 4).** Sampling sites S2, S3, S4, S6 and S7 have high pollution loads as indicated by the PLI values. The high values of PLI in the locations

near to the sea mouth (S2, S3, S4) indicate that the accumulation of metals in these regions were from agricultural and domestic discharges, which build up due to the less tidal flushing. Another pollution source is the pollution caused by large number of boats moving in this region **[20].** Locations in the northern sector (S6 and S7) also show PLI values >1. This region receives large amount of silt brought by the distributaries of Mahanadi river which bring along with them domestic and municipal waste from the capital city of Bhubaneswar [**28,29].**

IV.IIICorrelation between heavy metals and OC and TN in the sediments

A correlation analysis was performed among metals and OC and TN in sediments. A good relation exists between some metals, and positive correlation between metals and OC and TN has also been observed **(Table 2).** In sediments a good correlation exits between some metals and TN: Co (r = 0.70), Ni (r = 0.71), Mn= 0.78 (P < 0.01). The contribution of nitrogen in aquatic environment is mainly from death and decay of organisms, from industrial and domestic wastewater as well as loss from nitrogenous fertilizer which in the process of discharge bring about co-release of the heavy metals **[19]**Strong positive correlation between Cu and Zn is due similar sources like fertilizers and pesticides used in agriculture and leaching from antifouling paints used in the boats **[10, 13].**A positive correlation between Co and Ni (r = 0.58), Co and Mn (r = 0.51) and Co and Cd (r = 0.49) is observed. These metals are well correlated probably due to their common source from paints used in the boats and other purposes **[25].** Mn is positively correlated to Cu (r = 0.54) and Cr**(**r =0.53)probablybecause of Fe-Mn oxides being the important metal carriers in aquatic sediments, thus binding these metals to the sediments **[30,31].**A positive correlation is observed between Pb and Fe (r = 0.58) probably due to their common source from road dust, paints and automobile exhausts [**22, 23, 24].**Also Fe-Mn hydroxide acts as host phase for this metal **[32;33].**

Table 2: Correlation among Heavy Metals and Organic carbon (OC) and Total Nitrogen (TN)

	Zn	**Co**	**Pb**	**Cr**	**Cd**	**Cu**	**Ni**	**Mn**	**Fe**	**OC**	**TN**
Zn	1										
Co	0.06	1.00									
Pb	0.38	-0.16	1.00								
Cr	0.05	0.02	0.08	1.00							
Cd	-0.35	**0.49**	0.00	-0.10	1.00						
Cu	**0.86**	0.09	0.23	0.16	-0.39	1.00					
Ni	0.18	**0.58**	0.17	0.20	-0.02	0.17	1.00				
Mn	0.42	**0.51**	0.29	**0.53**	0.18	**0.54**	0.47	1.00			
Fe	0.36	-0.15	0.18	0.18	**-0.53**	**0.49**	0.05	0.46	1.00		
OC	0.47	0.27	**0.58**	-0.11	0.46	0.21	0.31	0.45	-0.12	1.00	
TN	0.42	**0.70**	0.42	0.15	0.42	0.35	**0.71**	**0.78**	0.05	**0.76**	1.00

IV.IVMetal Fractionation in Surface Sediments

The metal fractionation studies were performed on selected metals viz., Pb, Cr, Zn, Cu, Ni, Mn and Fe. The metal fractionation profile in sediments has been shown in **Fig 5**. The metal fractionation revealed dominance of different fractions for different metals, however residual fraction was the most dominant fraction for all the metals at 11 sites in the lagoon. The result shows that the residual fraction dominates for all the metals in surface sediments, however Mn, Zn and Pb are associated with acid soluble fraction in significant amount. Mn, Pb and Znhavesomedegree of affinity for carbonates, this is the reason why we find an appreciable portion of these metals associated with carbonate fraction. Higher content of Mn in carbonate bound fraction is most likely due to their similarity in ionic radii to that of calcium, which allows them to substitute Ca in carbonate phase **[34, 35].**The heavy metals associated with different fractions in Chilika sediments are in the following the order:

Pb: Residual > Reducible > Acid Soluble > Oxidisable
Cr: Residual > Reducible > Oxidisable > Acid Soluble
Cu: Residual > Reducible > Oxidisable > Acid Soluble
Zn: Residual > Reducible > Acid Soluble > Oxidisable
Fe: Residual > Reducible > Oxidisable > Acid Soluble
Mn: Residual > Acid Soluble > Reducible > Oxidisable
Ni: Residual > Reducible> Oxidisable > Acid Soluble

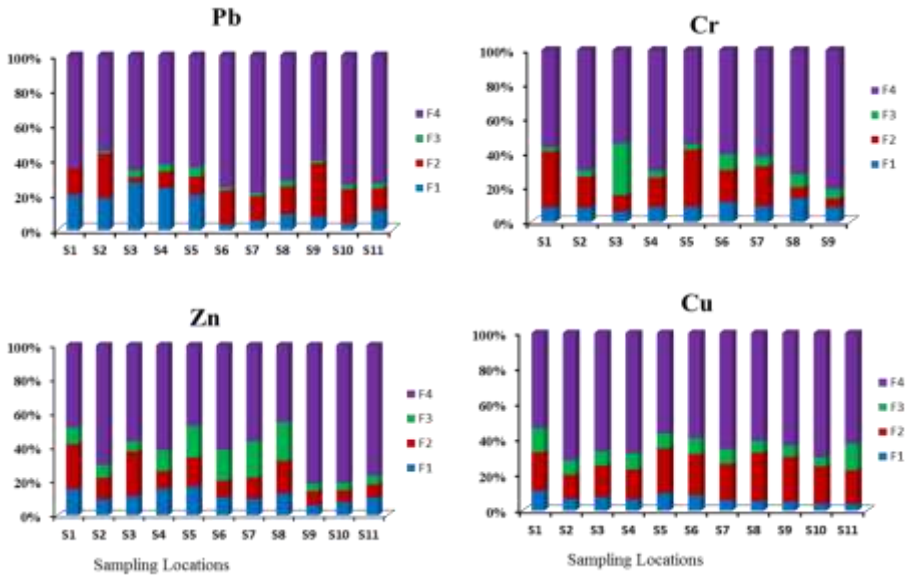
Fraction I (Acid soluble fraction-bound to carbonates) - This fraction contains metals bound to the carbonates. These metals are loosely bound and are the most bioavailable fraction. They can easily dissolve in the water column with the changing environmental conditions. The percentage fraction of different metals in all the 11 surface sediments is as follows. Pb (3.43 – 27.46 %), Zn (0.2 -26.29%), Ni (0.1-12%), Cr (6.29 – 13.18%), Cu (3.84 –11.15%), Mn (11.96 - 34.46), Fe (0.36 – 4.87%). Considerable amount of Pb, Zn and Mn

found in the acid soluble or carbonate bound fraction is most likely due to the similarity of their iionic radii with that of the calcium and therefore they get co-precipitated with $CaCO_3$ **[36, 37].**Presence of Mn, Pb and Zn in higher concentration indicates their ability to replace Ca in carbonate minerals due to their similar ionic radii and charge **[35].** Pb shows abehaviour similar to the Zn in co-precipitation with carbonate minerals. The flocculation of its colloids can also be attributed to the higher Mn concentration in reducible phase **[38].**The metals present in the exchangeable and carbonate fractions are considered to be weakly bound and may equilibrate with the aqueous phase, thus becoming more bioavailable. Metals in this fraction are the most mobile and readily available for biological uptake in the environment. Cr and Cu are also associated to a very small extent with phase.

Fraction II (reducible fraction – bound to Fe and Mn oxides) - The Fe–Mn oxides have a scavenging effect and provide a significant sink for heavy metals in the aquatic system. The release of the metals from the matrix is most likely to be affected by the redox potential and pH**[39].**This phase accumulates metals from the aqueous system by the mechanism of adsorption and co-precipitation.Metal bound to Fe–Mn oxide fraction are unstable under reducing conditions. Under reducing conditions the metal ions are dissolved into the water column**.** The metals bound to Fe-Mn phase are sensitive to anthropogenic inputs**.** Different metals in this fraction are as follows: Pb (2.75 – 30.52%), Zn (6.7-30.9), Ni (9.03 – 77.83%), Fe (5.28 – 29.50%), Mn (3.45 – 40.58%), Cr (4.73 – 31.75%), Cu (13.60 -27.32%). The relatively higher concentrations of elements such as Cu, Zn, Cr, Ni, etc., associated with this fraction are caused by the adsorption of these metals by the Fe–Mn colloids **[34, 40].**These metals readily get adsorbed to this fraction. Ni shows a very large fraction associated with Fe-Mn oxide which may due to its strong affinity with Fe-Mn oxides. Upto 40% of Mn is found adsorbed to this fraction in some of the surface sediments.

Fraction III (Bound to organic matter and sulphides) – Organic matter, with high molecular weight acids, plays an important role in the distribution and dispersion of heavy metals, by mechanisms of chelation and cation exchange processes**[40].** Degradation of organic matter under oxidizing conditions can lead to the release of metals bound to these materials **[39].** The percentage of different metals bound to this fraction are as follows**:** Pb (1.55 -5.24%), Zn (5.6- 33%), Ni (23.25 -79.87%), Fe (0.22 -9.82%), Mn (1.73 – 30.82%), Cr (2.40 - 31.32%), Cu (5.02 -14.79%). Generally, Ni is present predominantly in oxidisable and residual fractions in aquatic sediments **[41].**

Fraction IV (Residual Fraction – strongly associated to the crystalline structure of minerals) – Residual species refer to heavy metals which are enveloped in the lattices of primary mineral and secondary silicate mineral; their properties are very stable. Thus they do not make great contribution on the transportation and bioavailability of heavy metals in the sediments. As a result, they are generally considered safe to the environment. More than 50 % of most of the metals fall into this category. Fe has the highest percentage falling into this fraction, while Mn has the least amount in the residual phase.



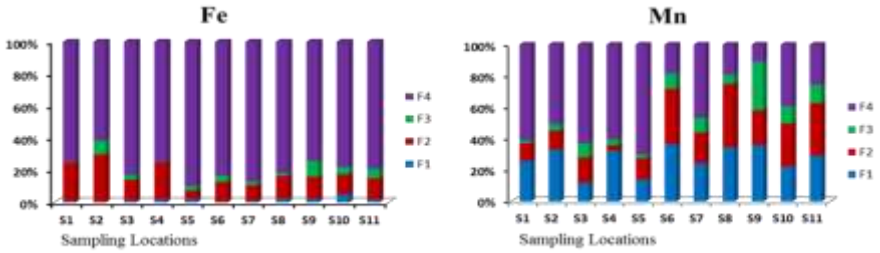


Fig 5: Percentage of different metal fractions in surface sediments of Chilika Lagoon

IV.V Risk Assessment Code (RAC)

RAC assesses the availability of metals in sediments by applying a scale to the percentage of metals in the acid soluble fraction (exchangeable and carbonate bound metals). This is important because the fractions introduced by anthropogenic activities are characterised by the exchangeable and bound to carbonate fractions, which are weakly bonded metals that can equilibrate with the aqueous phase and thus become more rapidly bioavailable. According to RAC guideline, for any metal, sediment which can release in acid soluble fraction, less than 1% of the total metal will be considered safe for the environment and sediments with 11–30% carbonate and exchangeable fractions are at medium risk to the environment. On the contrary, sediment releasing more than 50% of the total metal in the above acid soluble fraction isconsidered being highly dangerous, which can easily enter, the food chain **[42]**Theclassification index for RAC has been presented in **Table 3 and Fig 6.**

Table 3: Risk assessment code category

Category	Risk	Metals in Carbonate and Exchangeable Fractions %
1	No risk	< 1
2	Low risk	1-10
3	Medium risk	11-30
4	High risk	31-50
5	Very high risk	>50

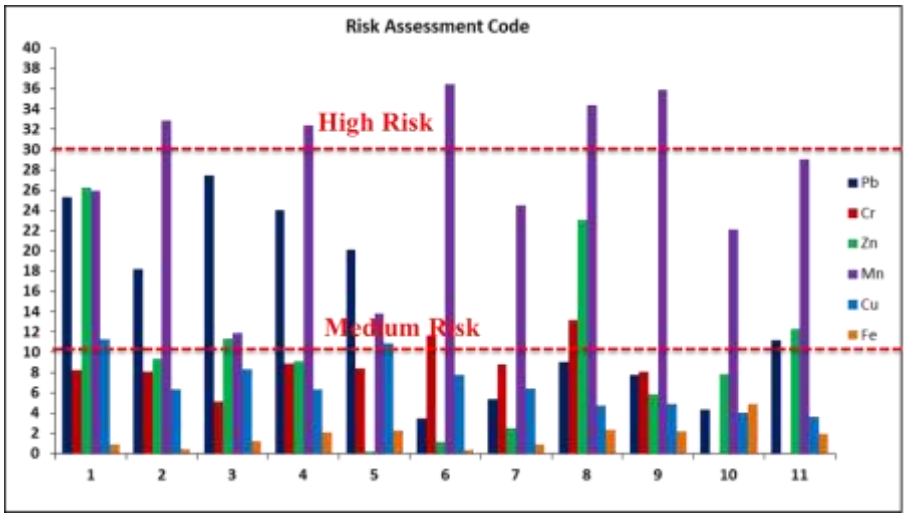


Fig 6: Risk assessment code for heavy metals in surface sediments

Mn is the metal found in medium to high risk category at all the sampling locations. In surface sediments at S2, S4, S6, S8, S9 more than 30% of the Mn can be released into acid soluble fraction, thus falling into high risk category. Pb, Zn and to a little extent Cr also falls into medium risk category at some sampling locations. Though Mn and Zn are essential nutrients, their higher availability may cause risk to the sediment dwelling organisms. Pb and Cr are non-essential metals and their their bioavailable fraction may cause considerable risk.

V. Conclusion

The present study on heavy metal analysis in Chilika lagoon surface sediments reveals considerable contamination of the sediments with Cu, Zn, Pb, Ni and Cr.$I_{geo}$and CF values suggested sediments are extremely polluted with some metals. PLIvalues also suggests high degree of contamination in outer channel and northern sector regions. Industries are absent around Chilika, therefore the major source of pollution are agricultural runoff, domestic sewage and urban waste brought by the distributaries of Mahanadi river. Boat movement and tourism are another major factors contributing to the pollution load in the lagoon. Fractionation profiles reveal medium risk of pollution by metals like Mn, Pb, Zn and Cr. Management at the basin level is recommended to curb large sediment inflow into the Chilika lagoon. Care must be taken to stop release of untreated domestic sewage into the lagoon.

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