

STUDY OF GEOCHEMICAL ASSOCIATION OF SOME TRACE METALS IN THE SEDIMENTS OF CHILIKA LAKE: A MULTIVARIATE STATISTICAL APPROACH

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Abstract. In order to establish the natural processes and geochemical factors responsible for enrichment of trace metal ions (Cu, Co, Ni, Zn and Cr) with respect to textural parameters (sand, silt and clay weight percentages) along with depth, multivariate statistical approach has been carried out for sediments in different water zones of Chilika lake, the largest brackish water lagoon in Asia. The rotated varimax factor results reveal that Cobalt enrichment is controlled by both textural parameters as well as adsorption mechanism. In fresh and saline water region, textural parameters and in mixed water, adsorption phenomenon predominates. Zn in fresh water is related to clay, whereas it is in adsorbed state in mixed water. Cu in fresh water sediments is in adsorbed state and in mixed water it is related to depth and Co concentration. Cr does not show any specific association in fresh water, but in both mixed and saline water it is associated with clay minerals. Although both textural parameters and adsorption mechanism play an important role for the enrichment of trace metal ions in these lagoonal sediments, their relative importance varies with specific metal ions as well as the water quality. Sequential extraction technique was used to characterize the various forms of metals in the $<63\mu$ size sediments of Chilika lake. The concentrations determined indicated selective accumulation of the various metals in the different phases with spatial variability in different water zones. Slightly higher availability of Co and Zn near Balugaon township in exchangeable phase may be related to anthropogenic activities. Among the non-lithogenous (NL) phases, reducible phase associated with higher concentration of Ni, Cu and Cr. Organic bound Zn and Co contributed highest percentages among NL fractions. Residual fraction contributed more than 50% in most of the cases, reflected the predominance of physical weathering, high erosion rate along the drainage basin.

Keywords: Chilika lake, factor analysis, sediment, geochemical speciation of heavy metals

1. Introduction

The chemical composition of sediments gives an useful indication of the past situation of metabolic and depositional process in the coastal lagoons. Lake sediments represent one of the ultimate sinks for trace elements discharged into aquatic environment. Yet relatively little is known about the potential pathways in which

trace elements are entering into the environment. There are common basic biogeochemical processes, difference in time scale of mixing and transport, biological productivity in sedimentary regions lead to major differences in pollutant routes. Determination of total metal content in sediments provides important information about pollution level if the background concentration is known. However, to understand the mobilization of heavy metals and assess the bioavailability, the total concentration is not enough (Salmons and Forstner, 1984). Therefore, it is vital to perform chemical partitioning studies of heavy metals in the sediments to accurately assess the toxic potential.

In recent years, various statistical procedures based on multivariate data have been used to formulate environmental classification of sediment and sedimentary rocks. Classification of this type also has contributed in part for better understanding of sedimentary processes. The current approach to quantitative classification of environment involves the use of either the Q-mode technique of factor analysis (Cattel, 1965) or one of the several different grouping techniques (Sokal and Sneath, 1963; Lance and Williams, 1966). Factor analysis is a useful explanatory tool in multivariate statistical analysis, which can be applied to discover and interpret relations among variables or to test hypothesis. The general purpose of the factor analysis technique is to find out a way of condensing the information contained in a number of original variables into a smaller set of new composite dimension with a minimum loss of information. Depending on the objective of the problem one can perform R-mode factor analysis, which extracts relations between variables or Q-mode factor analysis, which extracts information from cluster of samples. An important concept in factor analysis is the rotation of the factors. The main aim of rotation is to find new directions so that loading on few variables tend to 1 and others tend to 0. This reduction of ambiguities that accompany the initial unrotated factor loading improves the interpretation. The varimax rotation (Kaiser, 1958) has been proved very successful as an analytic approach. Finally, factor scores can be computed from the original raw data measurement and the rotated factor loading so as to create an entirely new set of smaller number of composite variables to replace the original set of variables. A factor analysis creates a minimum number of new variables, which are the linear combination of original one. Such new sets of variables retain the same amount of information regarding the existence of structure in a large array of numbers.

2. Study Area

2.1. GEOGRAPHICAL POSITION

Chilika lake the largest brackish water lagoon in the Indian subcontinent and a Ramsar site is located along the east coast of India ($19^{\circ}28' - 19^{\circ}54' N$; latitude and $85^{\circ}05' - 85^{\circ}28' E$ longitude).

2.2. GEOLOGY OF THE BASIN

Geologically, Chilika and its surroundings can be classified into four geomorphic units viz. (1) Fluvial (2) Denudational (3) Coastal, and (4) Aeolian.

Fluvial landform is the deltaic plain in the northern side of the lagoon extending between the Mahanadi River systems such as Daya, Bhargavi and Nuna. A gentle slope is marked from the alluvial plain towards southwest. Denudational landform is present in the western and southern boundary of the lagoon, which are denudational hills of easternghats. These hills are composed of hard metamorphic precambrian rocks like gneisses, quartzites and charnockites. The southeastern part of the lagoon comprises of coastal plain in form of coastal sand bar and islands. The position of the mouth and its width changes due to influence of wave action and long shore-current in form of littoral drift. The sand spit is morphologically divided into beach and sand dune belt. The coastal sand dunes are discontinuous linear features parallel to the coast all along the northeastern part with width ranging between 1.0 to 1.8 Km. Sand dunes along with Nalabana Island, which is situated in the center of the lagoon are included in aeolian landforms.

2.3. CLIMATE

The climate of Chilika is similar to that of coastal Orissa. Three principal seasons like summer, monsoon and winter are experienced in this area. The summer season is from March to June, monsoon from July to October and winter from November to February.

2.4. DRAINAGE PATTERN

The drainage area of Chilika Lagoon is 3560 km². Fifty-two numbers of rivers and rivulets drain into the lagoon. Important rivers such as Daya, Bhargavi, Nuna, Makara, Mandakini, Kansari, Salia and small streams from the hills located on the western side of the lagoon (part of easternghats) bring fresh water in to the lagoon mostly during monsoon period. The Mahanadi river system drain into the lagoon in the northern side and the deltaic region is submerged during the rainy season.

2.5. ANTHROPOGENIC ACTIVITIES OF THE LAGOON

Chilika lake is presently under threat from both natural and anthropogenic pressure. The problems are siltation, extensive growth of invasive weed species, eutrophication, salinity gradients, changes in water quality, depletion of fishery resources, chocking of river mouth and inlets, extensive aquaculture, operation of excess number of mechanized boats, obstruction of migratory routes of economic species in the creeks and overall loss of biodiversity which resulted in degradation of the lake ecosystem (Nayak *et al.*, 2004).

2.6. LITERATURE REVIEW

A number of researchers have worked on Chilika lake relating to hydrography, geology, sedimentology, flora and fauna, productivity, fishery and economic activities. Annadale and Kemp, 1915 initiated the investigation in Chilika particularly impact on flora and fauna. The water quality studies were carried out by Banerjee and Roychoudhury (1966), Venkataratnam (1970), Sarkar (1977), Subba Rao *et al.* (1981), Panda *et al.* (1989) and Nayak *et al.* (2004) studied the distribution of nutrients along with other physico-chemical characteristics of Chilika lake water. Venkataratnam (1965), Panda (1993), Pattnaik (1993), Panda *et al.* (1995) and Panda (1996) studied the geochemistry of heavy metals in Chilika lake sediments.

3. Objective of the Present Study

3.1. THOUGHT PROCESS

It is the normal practice to analyze the whole lagoonal samples taking them as single population. But considering the diversity of the mechanisms played in lagoonal sediment-water geochemical balancing, it was felt that we should treat them separately on the basis of influence of salinity so as to reveal the information regarding the influence of salinity on the trace metal adsorption or removal from water by sediments and vice versa. Fresh water zone, mixed water zone and saline water zone were separated, taking the salinity range <10 ppt, 10–25 ppt, >25 ppt respectively.

As the estuarine system has a coupling interaction of both fresh and saline water, and the water quality affects the geochemistry of its associated sediments, we have undertaken the study of Chilika, where the influence of both the system can be visualized. Further geo-statistical approaches have been followed to characterize and understand the trace metal association with the bottom sediments with respect to the influence of different water qualities such as continental, fresh, mixed and saline.

4. Material and Methods

4.1. FIELD ANALYSIS

Bottom sediments of 40 stations in Chilika lake (Figure 1) during post monsoon period were collected using a Peterson type grab sampler.

4.2. TEXTURAL PARAMETERS

Sediments were air dried at room temperature. A portion of the sample (≈ 50 grams) was taken for grain size (sand, silt and clay %) analyses. For grain size analysis,

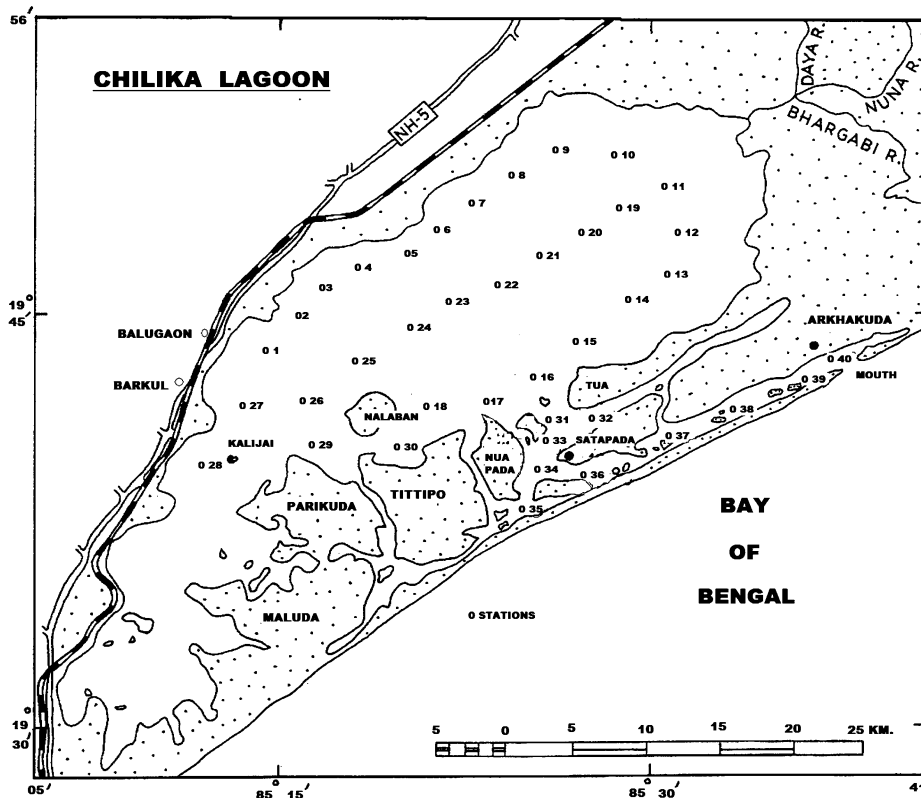


Figure 1. Map of Chilika Lake showing sampling stations.

samples were treated with 35% H_2O_2 and 1N HCl to remove organic matter and carbonate respectively (Van Andel and Postma, 1954). After treatment, sediment samples were wet sieved through 230 mesh (0.0625mm) ASTM sieve for separation of sand samples. Size analysis of very fine particles (silt and clay) was carried out by pipette analysis method (Krumbein and Pettijohn, 1938).

4.3. METAL ANALYSIS IN BULK SEDIMENTS

Trace metal concentrations were determined for Cu, Cr, Zn, Co and Ni. About 1 g dried and powdered samples were taken in 100 ml teflon beakers followed by addition of 2 ml of $HClO_4$, 12 ml of HF and 8 ml of HNO_3 . The samples were tightly closed and kept in hot plate at about 150 °C for 6 h (Li and Thornton, 1992). The contents were transferred completely and finally 10 ml of 10% HNO_3 was used to rinse thoroughly for complete transfer of the contents. Finally, the volume was made up in a 50 ml volumetric flask. The determination of Cu, Ni, Co, Cr and Zn were done by atomic absorption spectrophotometer (AAS), SHIMADZU, model

No- AA-670/GV4. The standard solutions of the above metals used to calibrate the instrument were prepared from reagents brought from Bureau of analytical samples Ltd., Newham Hall, Middle Borough, Cleveland, England. All the samples were analysed in triplicate with blanks similarly treated for metal analysis. The precision and accuracy of the methods were systematically and routinely checked analyzing USGS reference sample no. GXR (soil), where it has been found the precision (coefficient of variation of five replicate analysis) were 3% for Cu & Cr and 4% for Co, Ni and Zn.

4.4. CHEMICAL PARTITIONING OF TRACE METALS

Trace metals (Cu, Co, Ni, Zn and Cr) were sequentially extracted following the method proposed by Tessier *et al.* (1979) into five phases operationally defined as exchangeable (F₁), Carbonate (F₂), Fe-Mn hydroxide (F₃), Organic (F₄) and residual (F₅). The detailed scheme is as follows:

1. Exchangeable fraction (1M MgCl₂, pH 7.0)
2. Carbonate bound fraction (1M NaOAc adjusted to pH 5.0 with acetic acid)
3. Fe-Mn oxide bound fraction (reducible phase) (0.04M NH₂OH.HCl in 25% (v/v) HOAc at 96 °C)
4. Organic bound (oxidized phase) (5 ml of 30% H₂O₂ and 0.02M HNO₃ 3 ml of 30% H₂O₂ at 85° C),
5. Residual fraction (total digestion with a concentrated mixture of HNO₃/HClO₄/HF).

Metal concentrations such as Cu, Co, Ni, Zn and Cr in each leachets were analysed by using AAS. The precision and accuracy of the methods were systematically and routinely checked as per the procedure followed in metal analysis of bulk samples.

4.5. STATISTICAL ANALYSIS

The factor analysis was carried out for bulk and partitioning data using SPSS 10.0 statistical packages. During collection of bottom sediment, two different types of sediments were encountered. The top few millimeters were carefully separated out from the bottom sediments (Sharma *et al.*, 1993), which might be the recent sediment of the last monsoon. During multivariate analysis, we have treated separately the top and bottom sediments and one with combination of both to retrieve the best possible information contained in them regarding the geochemical controls for the enrichment of trace metals in different zones.

In order to establish the natural processes and the geochemical factors responsible for enrichment of trace metal ions such as Cu, Co, Ni, Zn, and Cr with respect to textural parameters (sand, silt and clay) and depth, the R-mode factor analysis with

rotation was applied (Sahu, 1973). The sorted rotated factor loading for all stations, fresh water (station no. 10, 11, 12, 13, 14, 19, 20, 21 and 22), continental fresh water (station no. 1, 2, 3, 4, 5, 6, 7, 8, 9 and 27), mixed water (station no. 15, 16, 17, 18, 23, 24, 25, 26, 28, 29, 30, 31, 32 and 33) and saline water (station no. 34, 35, 36, 37, 38, 39 and 40) have been considered for discussion. Factor loadings were calculated using eigen value greater than 1 and sorted by the results having values greater than 0.4 considering the significant influence towards the geo-chemical processes (Sahu *et al.*, 1998; Rath *et al.*, 2000).

5. Results and Discussion

5.1. SPATIAL DISTRIBUTION OF TRACE METALS IN LAKE SEDIMENT

The results of depth, textural characteristics and trace metal concentrations of 40 sediment samples covering whole lagoon with their range and average in four different water zones are shown in Table I.

Trace metal concentrations and their distribution in Chilika lake sediments for different water zones show varying and different behavior. The metal concentrations are found in following ranges (in $\mu\text{g/g}$): Cu (trace-89.8), Ni (66–365), Co (12–92), Zn (trace-72) and Cr (trace-158). The depth is varying from 0.6 to 3.33 m, where freshwater zone showing lower depths due to high siltation through river sediments. Sediment texture is mostly sandy in saline water zone, sandy silt and silt-sandy in fresh water zone, whereas other parts of the lagoon is varying from sandy to clayey in nature. The metal concentration in the stations of continental water zone show slightly higher level compared to other zones, which is due to mixing of pollutants from urban solid wastes (Balugaon township), fishing Jetties as well as catchment areas. These anthropogenic sources of metals are easily available to the lagoon's ecological cycle and possibly enter in to the food chain of aquatic organisms under suitable physico-chemical conditions. Thus, chemical speciation of heavy metals is carried out for evaluation of metal bioavailability in the present lake system.

These results of trace metal concentrations will be further examined in the following paragraphs by multivariate statistical analysis.

5.2. CORRELATION BETWEEN VARIABLES

Correlation coefficient is indices that measure the strength of a relationship between variables. The emphasis is on the degree to which two sets of values vary together around their respective means and on the direction of covariation of the variables. Correlation coefficient matrices are calculated among all 9 variables for different water zones and a comprehensive chart is given in Table II. The relationships among the variables showed significant variations for top and bottom sediments as well as different water zones. The different mode of occurrences of trace metals (Cu,

TABLE I
Range and average of depth, trace metal concentrations along with sand, silt, clay percentages in the sediments of Chilika lake for different water zones

Parameters (unit)	Fresh water			Continental fresh water			Mixed water			Saline water		
	Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.
Depth (m)	0.73	1.70	1.24	1.45	2.64	1.97	0.62	2.82	1.67	0.83	3.33	1.88
Sand (%)	0.5	92.1	27.0	0.5	78.0	22.2	3.1	86.2	53.9	24.6	84.7	57.8
Silt (%)	1.3	61.2	19.3	10.8	48.3	23.1	2.3	29.2	13.6	2.2	15.4	9.1
Clay (%)	4.6	93.1	53.6	11.3	79.9	54.8	8.4	85.3	32.5	0.3	68.8	33.1
Cu (ppm)	3.2	89.8	40.9	29.0	62.8	46.7	Trace	66.1	35.6	23.0	44.2	31.4
Ni (ppm)	94.0	365.0	190.4	117.0	203.0	158.0	66.0	260.0	165.3	92.0	294.0	220.4
Co (ppm)	21.0	92.0	53.9	45.0	82.0	62.5	12.0	82.0	41.9	20.0	50.0	37.2
Zn (ppm)	Trace	72.0	17.1	6.0	24.0	18.0	Trace	36.0	8.7	1.4	35.0	15.3
Cr (ppm)	9.0	158.0	70.6	65.0	154.0	108.5	Trace	108.0	46.0	21.0	75.0	50.6

TABLE II

Comprehensive result of correlation analysis of sedimentological parameters for different zones of Chilika lake

Water zone	Parameters	Positive	Negative		
All water	Depth				
	Sand		Zn (0.496), Cr (0.393)		
	Silt	Co (0.454)			
	Clay	Cr (0.524), Zn (0.457), Ni (0.328)			
Fresh water	Total	Depth	Co (0.728)	Cr (0.601)	
		Sand	Cr (0.667)		
		Silt	Co (0.735)	Cr (0.583)	
		Clay	Zn (0.593), Cr (0.379)		
	Top	Depth	Co (0.814), Ni (0.319)	Cr (0.407)	
		Sand	Cr (0.432)	Co (0.336), Ni (0.316), Zn (0.309)	
		Silt	Co (0.749)	Zn (0.685), Cu (0.575), Ni (0.468), Cr (0.401)	
		Clay	Zn (0.589), Cu (0.515), Ni (0.467), Cr (0.433)		
		Bottom	Depth	Zn (0.825), Co (0.786)	
			Sand		Cu (0.573), Ni (0.526), Cr (0.497)
Continental fresh water	Total	Silt	Zn (0.783), Co (0.659)		
		Clay	Cu (0.865), Ni (0.827), Cr (0.798)	Co (0.427)	
		Depth	Co (0.414)	Zn (0.617), Cr (0.430)	
		Sand	Co (0.647)	Zn (0.889), Cr (0.607), Cu (0.385)	
	Top	Silt	Cr (0.740), Zn (0.631), Cu (0.462)		
		Clay	Zn (0.965), Cr (0.798), Cu (0.513), Ni (0.359)	Co (0.405)	
		Depth	Cu (0.817), Zn (0.532)	Co (0.567), Ni(0.505), Cr (0.358)	
		Sand		Zn (0.882), Ni (0.777), Cr (0.323)	
		Silt	Ni (0.916), Co (0.851), Cr (0.802), Zn (0.595)	Cu (0.696)	
		Clay	Zn (0.780), Cr (0.660), Ni (0.614)		

(Continued on next page)

TABLE II
(Continued)

Water Zone		Parameters	Positive	Negative
Mixed	Total	Depth	Co (0.657)	
		Sand		Zn (0.520), Cr (0.470)
		Silt	Zn (0.502)	Cr (0.531), Co (0.512)
		Clay	Cr (0.637), Zn (0.398)	
	Top	Depth	Cr (0.625), Zn (0.313), Ni (0.305)	
		Sand		Cr (0.874)
		Silt		Cr (0.986)
		Clay	Cr (0.989), Co (0.426), Zn (0.417), Ni (0.336)	
	Bottom	Depth	Cr (0.853), Zn (0.686), Co (0.637)	
		Sand		Cr (0.752), Zn (0.432)
		Silt	Zn (0.705)	Cr (0.897), Ni (0.338)
		Clay	Cr (0.896), Co (0.725), Zn (0.463), Ni (0.312)	
Saline	Total	Depth		Cr (0.803)
		Sand	Zn (0.481)	Cr (0.898)
		Silt	Zn (0.682), Co (0.496)	Cr (0.653)
		Clay	Cr (0.970), Cu (0.413), Ni (0.376)	Zn (0.342)

Co, Ni, Zn and Cr) is mainly controlled by the physical parameters like depth and textural characteristics (Sand, Silt and Clay) of the sediments. Some of the major findings related to enrichment of metal ions in the lake sediments are discussed below.

Depth is not showing any strong relationships with the metals in whole lake sediments taking as one entity (combination of all water zones). Co in fresh water top sediments, Zn and Co in bottom sediments are strong positively correlated with depth. Also Cu and Zn in continental fresh water top sediments, Co in mixed top sediments and Cr, Zn and Co in mixed bottom sediments are positively correlated with depth. A weak negative relationship of Cr in fresh water sediments, a moderate to weak negative relationships of Zn and Cr in continental total, Co and Ni in continental top and a strong negative correlation of Cr in saline water zone with depth is observed. These different modes of association of trace metals with respect to depth are reflecting the spatial variations of metals in the lagoon.

The negative relationships of most of the metals with sand percentages of the sediments are found. However, weak positive relationships of Cr in fresh water total and the top sediment, a moderate positive relationship of Co in continental fresh total sediment and a weak positive relationship of Zn in saline zone are associated with sand percentage. Different mode of association of trace metals are observed

for the top and bottom sediment, as top sediments are recent deposited suspended sediments.

The interrelationship among the trace metals with silt content of the sediment is observed in many estuarine environments (Panda *et al.*, 1999; Sahu *et al.*, 1998; Panda 1993). Co, Cr, Zn in all water zone and fresh water top along with Ni in bottom sediments, all the metals except Cu in continental fresh water zone, Cr and Co in mixed top and Zn, Cr and Co in mixed water bottom sediment and all metals except Cr in saline water zone are covariate with silt content. However, negative relationship between Ni, Cr in fresh water top sediments, Cu in continental top and Cr in saline water zone with silt content is observed.

Clay minerals have relatively high metal content due to greater active surface area on which metals may adsorb. Therefore, association of most of trace metals with clay and silt could be attributed to increase adsorption area of fine-grained sediments. Thus association of most of metals with clay could be expected. These metals may in under go sorption (flocculation, precipitation, etc.) and adsorption onto fine particles such as clay minerals (Forstner and Wittmann, 1983). But weak negative relationships of Co in continental fresh water sediment and Zn in saline water zone sediment are found.

Due to complexity of the relationship, it is difficult to draw more clear conclusions directly. However, the use of factor analysis is to explain the structure of the correlations in more detail.

5.3. FACTOR ANALYSIS

The results of sorted rotated factor loading scores along with eigen values, percentage of variances are shown in Tables III–VII. For the sake of simplicity and better understanding we have compiled all the results and finally a comprehensive chart is given in Table VIII for discussion purpose.

5.3.1. Factor Analysis with Respect to All Stations

The sorted rotated factor loading pattern of all stations are shown in Table III. From the table, it is observed that the five factors derived are showing a total cumulative variance of 80.7% only. Out of which factor-1 is responsible for 29.3%, which indicate poor response of individual factor towards defining the geochemical responses. However, factor 1 is found to constitute clay and sand as major components, which show strong negative correlation towards each other. This is a common phenomena in fluvial deposits. The lower correlation value of Cr and Zn with clay minerals in factor 1 suggests poor enrichment of these two elements. The scavenging action of clay minerals of Zn and Cr has already been reported (Sahu *et al.*, 1998; Panda *et al.*, 1999). Considering the above observations, factor 1 may be termed as “**Clay Factor**”.

Factor 2 shows a variance of about 16.9%, where silt and cobalt are positively correlated to each other. It is difficult to predict association of silt and cobalt with

TABLE III
Sorted rotated factor loadings for all water zones

Parameter	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Clay	0.949				
Sand	-0.931				
Co		0.897			
Silt	0.318	0.763		-0.301	
Ni			0.854		
Zn	0.334		0.702	-0.376	
Depth				0.956	
Cu			0.381		0.726
Cr	0.553				-0.687
Eigen Values	2.933	1.691	1.315	0.986	0.746
Variance Explained	29.30%	16.90%	13.20%	12.00%	9.30%
Cummulative variance explained	29.30%	46.20%	59.40%	71.40%	80.70%

the limited analytical result in the present work, where other information such as organic carbon content, Fe, Mn etc. are lacking. However, association of Co may be related to granulometry (Loring, 1984). So, this factor can be termed as “**Silt Factor**”.

Factor 3, which explains 13.2% of total variance, has strong positive loading on heavy metals like Ni and Zn. This shows a common source, may be related with adsorption on clay mineral. The occurrence of Ni (0.85) and Zn (0.70) show their association with clay materials (Krauskopf, 1956). Zinc (Zn^{2+}) being a chalcophile element, can substitute for Fe^{2+} and Mg^{2+} . Therefore, the association of Zn with iron coatings and Mg bearing aluminium silicates may be the possible sites to carry Zinc although organic source of Zn cannot be ruled out (Bostrom *et al.*, 1974; Loring, 1976; Paropokari, 1990).

Factor 4 shows a variance of 12.0% with major influence from depth. In this factor depth is having weak negative relationships with Zn and silt.

Factor 5, accounting for only 9.3% of the total variance, reflects distinctly negative correlation of Cu (0.726) with Cr (-0.687). This indicates two different sources for Cr and Cu.

From the above discussion it is found that clay and silt are responsible for the enrichment of trace metal ions like Cu, Ni, Co, Zn and Cr in the Chilika lake. Considering very low values of factor loading (29.9%), it is decided to analyze the samples as fresh water, mixed water and saline water borne deposits separately. The samples collected near the central margin areas are taken as continental fresh water deposits. This consideration will give us the information in better way to understand the geological response at a microscopic scale.

TABLE IV
Sorted rotated factor loadings of fresh water zone

Parameter	Factor 1	Factor 2	Factor 3	Factor 4
(a) Top and bottom sediments				
Depth	0.873	0.421		
Silt	0.846			0.653
Co	0.746			0.328
Cr	-0.731		0.248	
Clay		0.945		
Sand	-0.397	-0.849		
Cu			0.882	
Ni	-0.379	0.372	0.658	0.584
Zn		0.563	0.684	
Eigen values	3.194	2.657	1.936	0.989
Variance explained	32.0%	26.6%	19.4%	7.80%
Cummulative variance explained	32.0%	58.6%	78.0%	85.80%
(b) Top sediments				
Zn	0.939		0.329	
Cu	0.932			
Ni	0.898		0.333	
Cr	0.875	-0.456		
Depth		0.928	0.345	
Co		0.921		
Silt	-0.600	0.714		
Sand		-0.347	-0.935	
Clay	0.344		0.924	
Eigen values	3.817	2.588	2.162	
Variance explained	38.1%	26.4%	23.7%	
Cummulative variance explained	38.1%	62.5%	86.2%	
(c) Bottom sediment				
Cu	0.983			
Ni	0.937			
Clay	0.924	0.324		
Cr	0.915	-0.379		
Depth		0.968		
Silt		0.959		
Zn	0.293	0.956		
Co	-0.567	0.819		
Sand	-0.641	-0.768		
Eigen values	4.403	4.326		
Variance explained	43.2%	44.1%		
Total cummulative variance explained	43.2%	87.3%		

TABLE V
Sorted rotated factor loadings for continental fresh water zone

Parameter	Factor 1	Factor 2	Factor 3
(a) Top and bottom sediments			
Sand	-0.954		
Zn	0.943		
Clay	0.891		0.366
Cr	0.785	0.339	
Silt	0.720	0.398	-0.378
Ni	0.261	0.912	
Co	-0.261	0.898	-0.301
Depth	-0.354		0.889
Cu	0.444		0.726
Eigen values	4.185	2.000	1.800
Variance explained	42.7%	21.6%	15.8
Total cumulative variance explained	42.7%	64.3%	80.10%
(b) Top sediments			
Sand	-0.986		
Zn	0.840	-0.347	
Clay	0.813		0.548
Ni	0.715	0.652	
Depth		-0.876	
Co		0.764	0.452
Silt	0.573	0.721	
Cu	0.383	-0.629	0.458
Cr	0.538	0.627	0.403
Eigen values	4.095	3.610	1.454
Variance explained	40.80%	35.30%	13.6
Total cumulative variance explained	40.80%	76.10%	89.70%

5.3.2. Factor Analysis for Fresh Water Sediments

Table IV(a) shows the sorted rotated factor loading for combined top and bottom sediments of fresh water origin. The four factors derived constitute about 85.8% of the total variance out of which factor 1 is responsible for 32%, factor 2 for 26.6%, factor 3 for 19.4% and factor 4 for 7.8%. Factor 1 shows high correlation among silt, Co and depth. Both Cr and Ni show negative correlation with the above three. Therefore, the mode of enrichment of Co is altogether different from Ni and Cr. The source of Co as revealed from literature is two types, lithogenic and organic. Although it is difficult to predict the association of Co with silt but their mutual association with depth and negative correlation with Ni and Cr indicates both the sources might be equal responsible for the enrichment of Co. The factor may be termed as “**depth-silt factor**”.

TABLE VI
Sorted rotated factor loadings of mixed water zone

Parameter	Factor 1	Factor 2	Factor 3	Factor 4
(a) Top and bottom sediments				
Clay	0.978			
Sand	-0.927	-0.360		
Cr	0.754	0.400		
Depth	0.825			
Co	0.628	0.348	0.369	
Silt		-0.794		
Ni		0.745		
Zn	0.336	0.540		
Cu			0.883	0.960
Eigen values	3.328	2.372	1.625	0.823
Variance explained	34.20%	25.50%	15.70%	9.20%
Total cumulative variance explained	34.20%	59.70%	75.40%	84.60%
(b) Top sediments				
Clay	0.990			
Sand	-0.985			
Cr	0.982			
Silt	-0.979			
Depth	0.715		0.457	
Zn		0.984		
Ni		0.937		
Co	0.237	0.719	0.615	
Cu			0.976	
Eigen values	4.516	2.437	1.636	
Variance explained	46.10%	26.80%	0.162	
Total cumulative variance explained	46.10%	72.90%	0.891	
(c) Bottom sediments				
Clay	0.986	0.000		
Sand	-0.854			
Cr	0.892			
Silt	-0.952			
Depth	0.840		0.518	
Zn		0.963		
Ni		0.896		
Co	0.437	0.748	0.643	
Cu			0.917	
Eigen values	4.672	2.631	1.257	
Variance explained	48.10%	27.60%	12.80%	
Total cumulative variance explained	48.10%	75.70%	88.50%	

TABLE VII
Sorted rotated factor loadings for saline water zone (top and bottom sediments)

Parameter	Factor 1	Factor 2	Factor 3
Sand	0.990		
Clay	-0.992		
Co			0.998
Ni		-0.971	
Cr	-0.943	0.332	
Silt	0.842		0.518
Cu	-0.393		-0.919
Depth	0.713	0.662	
Zn		0.997	
Eigen values	4.282	2.523	2.194
Variance explained	41.50%	26.00%	21.90%
Total cumulative variance explained	41.50%	67.50%	89.40%

Factor 2 shows association of clay with Ni and Zn. As discussed earlier both Ni and Zn are associated on the clay minerals. The negative correlation of sand indicates the importance of textural parameters for controlling the scavenging action of clay minerals for Ni and Zn. This factor is accounting 26.6% of the total variance.

Factor 3 shows the association of Cu, Ni, Zn and Cr thereby indicating their occurrence as adsorbed species.

Factor 4 explains 7.8% of the total variance. On the fresh water region, a major role is played by silt relating to the fixation of Ni and Co.

From the Table IV(b) the fresh water top sediments show three factors constituting a cumulative factor loading of about 86.2%. Factor 1, which is responsible for 38.1% of total variance shows inter correlation of Cu, Ni, Zn and Cr. Silt is negative correlated (-0.6) with the above trace metals. The associations of these trace metal ions and their co-variation indicates a common process of enrichment in the sediments. Adsorption mechanism seems to play the major role in removal of these trace metal ions. So, this factor may be termed as “**adsorption factor**”.

Factor 2 shows a variance of about 26.4%. Here depth and silt are found to play a major role for the adsorption of Co. Rao and Setty (1976) has reported high Co value and correlation of Cr with depth as its association with coarse fraction, which is supported by the negative correlation of sand with depth. This factor may be termed as “**depth factor**”.

Factor 3 is a textural factor indicating negative correlation of clay and sand, which explained 23.7% of total variance.

The fresh water top sediments involving adsorption mechanism, plays the major role in fixation of trace metals like Cu, Ni, Zn and Cr. Association of cobalt shows a different mechanism related to depth, which may be related to organic or terrigenous source.

The two factors for the fresh water bottom sediments calculated are shown in Table IV(c) found to have a loading of about 87%. Factor 1 shows association of clay with Cu, Ni and Cr indicating the enrichment of these trace elements in finer fraction of the sediments. The negative correlation of sand and clay confirms the control of textural parameters. Cobalt is negatively correlated with clay as well as other two elements indicating different sources. As sand and cobalt found to covary, the source of Co may be terrigenous input. Factor 1 is found to have controls from clay fraction as well as sand fraction for the enrichment of Cu, Ni, Cr and Co. This factor may be termed as “**Textural factor**”.

The importance of factor 2 is also very high, considering its factor-loading equivalent to factor 1 (43%). Depth is positively correlated with Co and Zn and negatively with sand indicating different source for Co and Zn. In factor 1, Co was found to be in association with coarse fractions but for factor 2, the antipathy relation with coarse fraction shows a bimodal mechanism of enrichment in fresh water bottom sediment. From the literatures it is found that organic carbon play a major role in the fixation of both Co and Zn. As our data is lacking that information, it may be organic carbon responsible for the fixation of Co and Zn.

In the case of fresh water top sediments, adsorption mechanism is found to play a major role for enrichment of Cu, Ni, Zn and Cr. Co show a different mode of association. Bottom sediments indicate dominant role of clay minerals for the enrichment of Cu, Ni and Cr. Co shows two types of sources. Zn is related to depth, but when we consider all (top and bottom), it gives a different picture as discussed earlier. Thus the fresh water top sediments, which are considered to be very recent sediment, the enrichment of trace metals are mainly caused by **adsorption** mechanism

5.3.3. Factor Analysis for Continental Fresh Water Sediment

The sediments collected near the continental zone on the southwestern margin of central Chilika lake has been treated separately from the fresh water sediment discussed earlier. Considering the direct influence of any continental sediment not coming through the major rivers i.e. Daya and Bhargavi. As the sediments are found to contain mostly clay fraction and considering few stations, we can find top and bottom stratification as it was observed in the most of the stations in the fresh water origin, here we perform factor analysis putting them in two groups. Group-1 is combination of top and bottom and group-2 top sediments only (Table V(a) and V(b)).

The results of the factor analysis for the combined top bottom sediment of the continental fresh water of Chilika lake are shown in Table V(a). About 80% of the total variance is covered by three factors. Factor-1, which is about 42.7 % of the total variance indicating the control of clay for enrichment of Zn, Cr and Cu, showing their strong negative correlation with sand.

Factor 2 shows covariance of Ni and Co indicating a separate mechanism of their occurrence. Factor 3 shows correlation of Cu with depth.

From the above observations, the continental fresh water sediment shows associations of Zn, Cr and Co in together with clay minerals whereas Ni and Cu show a different mode of formation, which may be associated with the organic mode. The occurrence of Cu in relation to depth indicates its relation with pH of the bottom water for its stabilization in sediments. The role of organisms at the deeper parts of the continental fresh water region cannot be ruled out also for the fixation of Cu.

5.3.4. *Factor Analysis for Mixed Water Sediment*

The results of the factor analysis of the sediments from top, bottom and combined sediments of mixed water zone are shown in the Table VI(a), VI(b) and VI(c). It is interesting to note that there is no significant difference observed among the three groups. As the name suggests the zone is mixed up. In the mixed zone clay and depth are found to have significant role for the fixation of Cr and at times Co. Sand and silt are negatively correlated with Cr, Ni, Zn and Co in Factor 2. The interrelationship among these metals may be due to the mechanism of adsorption. Cu and Co in factor 3 has got strong relation with depth indicating separate mechanism.

In the mixed water zone, the role of clay is found to be very limited as it only adsorbs Cr. As Cu and Co relates to depth, this may be related to the organic substance. Therefore, the dual source of Co is significant in mixed water zone.

5.3.5. *Factor Analysis for Saline Water Sediments*

In the saline water zone, the number of observations is very few. Therefore, we did not separate them into different groups rather treat them as single population. The results of the factor analysis for three factors are shown in Table VII.

Factor 1 comprises clay showing covariance with Ni and Cr and negative variance with Co. Silt is found to be enrich with Co and Cr and depth is related to Ni (factor 3). Cr is found to be associated with both fine and medium fraction of sediments. Ni is related to fine sediment enrichment as well as depth, indicating two different sources. Although clay content is related to depth but as clay and depth are found in two different factors, the clay content seems to be independent of depth factor. Cu and Zn do not have any trend with the physical or textural parameters.

6. Chemical Speciation of Trace Metals

The concentrations of trace metals (Cu, Co, Ni, Zn and Cr) in the $<63\mu\text{m}$ fraction (Silt + Clay) of the Chilika lake sediments are given in Table IX. Sediments from 7 selected stations are considered for the sequential leaching of heavy metals, out of which station no. 1 and 5 (continental fresh water zone), station no. 10 and 11 (fresh water zone), station no 23 and 31 (mixed water zone) and station no. 40

TABLE IX
Metal concentrations ($\mu\text{g/g}$) in different geochemical phases of Chilika lagoon sediments

Metal	Station	Exchangeable	Carbonate	Reducible	Organic	Residual	Total
		F1	F2	F3	F4	F5	
Cu	1	2.4	3.7	20.9	13.1	48.0	90.3
	5	0.9	6.0	19.0	15.0	65.0	109.5
	10	0.5	4.2	12.5	15.3	66.4	104.7
	11	0.4	2.2	21.0	19.5	50.2	100.1
	23	0.5	4.3	25.5	16.1	55.4	104.2
	31	0.4	6.1	22.0	15.0	68.0	116.5
	40	0.3	8.9	1.5	2.3	57.2	72.8
	Avg.	0.8	5.1	17.5	13.7	58.6	99.7
Co	1	9.3	7.2	15.7	30.2	26.1	97.5
	5	7.5	8.2	23.6	38.7	21.5	103.8
	10	1.3	2.1	2.7	4.1	47.8	59.4
	11	1.0	1.8	3.2	6.8	51.4	67.5
	23	6.3	4.2	29.5	40.7	15.3	102.0
	31	5.8	6.9	43.6	37.3	18.7	115.1
	40	4.5	10.5	12.5	47.4	33.7	110.0
	Avg.	5.1	5.8	18.7	29.3	30.6	93.6
Ni	1	1.5	0.5	19.5	13.3	71.3	109.5
	5	1.0	7.2	17.9	14.7	56.1	100.9
	10	0.3	6.8	17.7	16.2	49.7	99.9
	11	0.2	0.5	16.1	13.2	48.0	83.0
	23	0.8	8.3	28.6	18.2	62.4	127.5
	31	0.7	5.0	26.1	20.2	58.2	120.4
	40	0.2	3.9	17.3	15.3	53.9	90.8
	Avg.	0.7	4.6	20.5	15.9	57.1	104.6
Zn	1	7.1	14.6	12.2	44.5	27.5	106.2
	5	4.9	10.6	18.3	41.6	31.8	108.5
	10	2.1	13.3	9.3	22.1	44.5	92.4
	11	1.8	8.9	12.5	22.9	41.8	89.0
	23	2.5	5.1	15.0	27.2	48.0	100.2
	31	3.2	12.7	17.4	32.6	39.7	110.1
	40	2.9	7.6	10.6	20.7	21.5	66.6
	Avg.	3.5	10.4	13.6	30.2	36.4	96.1
Cr	1	1.0	2.2	13.2	2.2	55.1	82.3
	5	0.9	8.0	7.5	9.1	31.1	59.7
	10	0.3	1.9	6.2	1.6	26.8	39.0
	11	0.3	6.1	6.1	5.2	19.1	38.4
	23	0.2	0.9	4.6	1.2	20.4	27.5
	31	0.3	5.2	3.5	4.2	19.3	33.3
	40	0.2	0.6	2.5	0.5	17.6	21.9
	Avg.	0.4	3.6	6.2	3.4	27.1	40.7

(saline water zone). The affinity of metal concentrations in five different geochemical fractions and their relation with different water zones (Figure 2) is discussed below.

6.1. EXCHANGEABLE FRACTION

Metals in this phase are readily available and relatively mobile for biological uptake. Thus, a high environmental risk factor is associated with higher availability of metals in this fraction. The sequence of leaching of heavy metals by IM $MgCl_2$ i.e. exchangeable phase follow the order $Cr > Ni > Cu > Zn > Co$ with respect to their absolute concentration. In comparison with other non-lithogenous fraction, this phase contributes poor elemental availability to the bottom dwelling organisms, which is partially related to high pH (Panda *et al.*, 1995). The stations 1 and 5 are having comparatively higher elemental concentration especially Co and Zn, which may be originates from the pollution sources like sewage of Balugaon township and anthropogenic activities near fishing jetties respectively. Comparatively poor availability of metals is observed in fresh water zone sediments as well as saline water zone sediments, which are mostly sandy texture sediments. Forstner and Wittmann (1983) reported that heavy metals adsorb onto solid particles carried by river and other fresh water systems, which are desorbed when mixing with high pH saline water. Thus, it may be considered to be very low metal concentration and geochemically insignificant.

6.2. CARBONATE PHASE

The sequence of leaching of heavy metals by NaOAc (pH 5.0) i.e. carbonate phase in the lake sediments follow the order $Zn > Co > Cu > Ni > Cr$. This phase seem to be little geochemical significance as the elements bound to this fraction are less than 16%. Relatively higher percentage of Zn in carbonate fraction is most likely the result of similarity in their ionic radii to that of calcium, which allows it to substitute Ca (Pederson and Price, 1982; Zhang *et al.*, 1988; Sahu *et al.*, 1998; Panda *et al.*, 1999). The results of Paropokari *et al.*, 1980 show that even sediments having 75–90% of $CaCO_3$, the carbonate phase is not a significant contributing factor to the trace metal content of the sediments. Thus, the low carbonate content of the sediments precludes the possibility of this phase making any significant contribution to the amount associated with carbonate phase of sediments. The Co and Cu concentration in this phase is recorded higher in saline water zone (station 40). Therefore, this fraction reflects heavy metal distribution of detrital origin as well as biogenic decomposition in the lagoon.

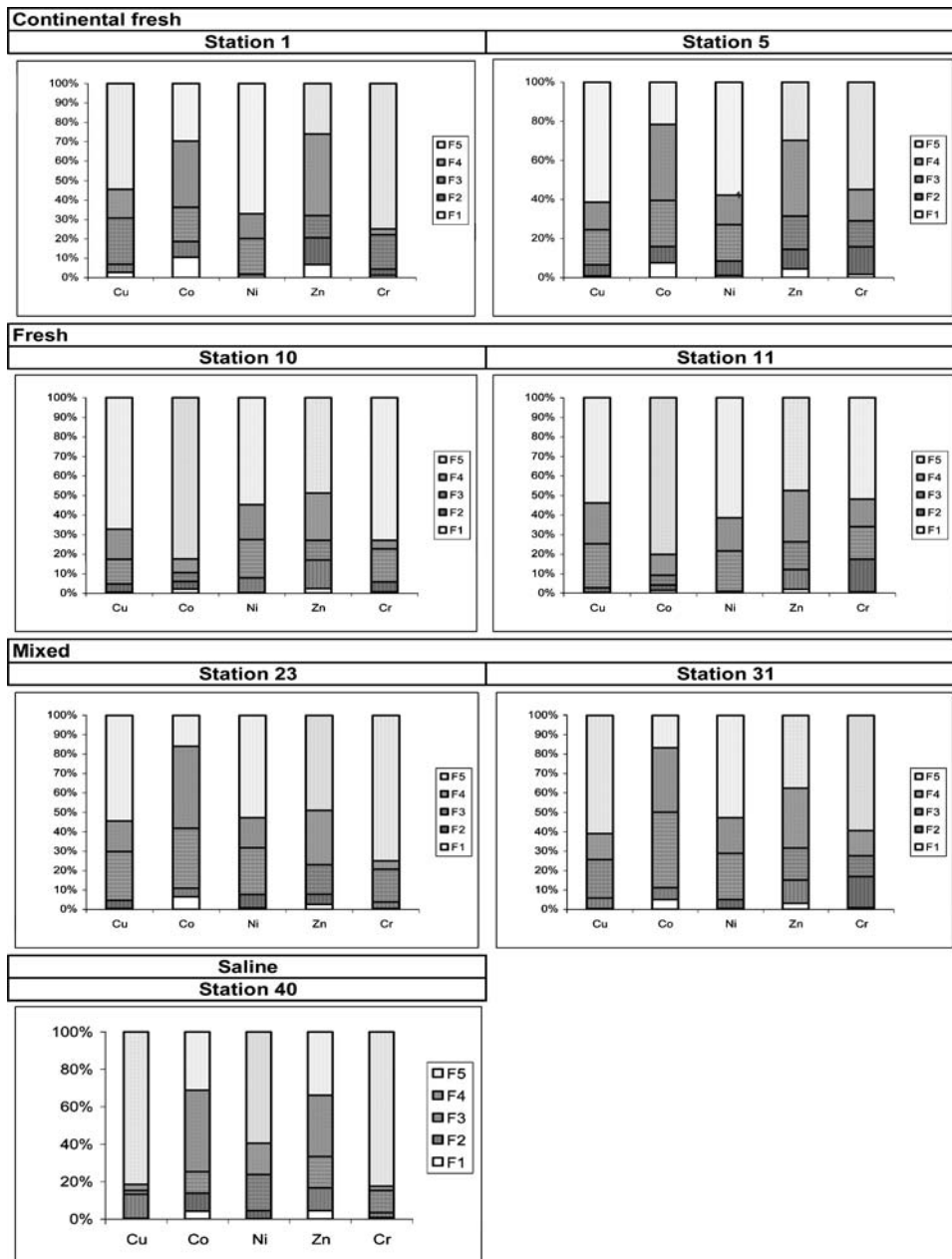


Figure 2. Percentage of metals in different geochemical forms of the lake sediments.

6.3. REDUCIBLE PHASE

The sequence of leaching of 0.4M $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 25% HOAc i.e. Fe,-Mn hydroxide phase follows the order: $\text{Ni} > \text{Co} > \text{Cu} > \text{Zn} > \text{Cr}$. Among non-lithogenous fraction, this fraction contributes appreciable percentage of metals like Ni, Cu, Cr and Zn. Relatively higher concentrations of the above elements associated with this fraction are caused by the adsorption by the colloids of Fe and Mn (Jenne, 1968). The higher concentrations of Ni, Co and Cu are associated with mixed water zone sediments (station no. 23 and 31), whereas Cr and Zn are associated with fresh water continental zone sediments (station no. 5 and 1).

6.4. ORGANIC PHASE

The metals bound to organic fraction contribute relatively significant amount among non-lithogenous fractions i.e. 3.1–19.5% Cu, 6.8–43.1% Co, 12.1–16.8% Ni, 23.9–41.9% Zn and 2.2–15.2% Cr. The absolute concentrations in organically bound fraction follow the order: $\text{Zn} > \text{Co} > \text{Ni} > \text{Cu} > \text{Cr}$. The average concentrations of Zn and Co show highest among non-lithogenous fractions. However, other metals are contributing second highest into non-lithogenous fractions. Heavy metals are associated with organic matter through biological uptake and adsorption with subsequent incorporation into resistant organic degradation products, such as humic substances.

6.5. RESIDUAL PHASE

Trace metals concentration in residual fraction are higher than those observed in any of the proceeding extractions, representing more than 50% except Zn and Co. Zn and Co in most of the cases are associated with organic and reducible phases. This fraction reflects the predominance of physical weathering, high erosion rate along the drainage basin and high sediment rates in the lagoon.

Based on the mean content of heavy metals, the metals appear to concentrate in the geochemical phases of the sediments in the following order.

Cu : Residual > Reducible > Organic > Carbonate > Exchangeable
Co : Residual > Organic > Reducible > Carbonate > Exchangeable
Ni : Residual > Reducible > Organic > Carbonate > Exchangeable
Zn : Residual > Organic > Reducible > Carbonate > Exchangeable
Cr : Residual > Reducible > Carbonate > Organic > Exchangeable

7. Conclusion

This study presents necessity and usefulness of factor analysis techniques for evaluation and interpretation of complex data sets in a brackish water lake system with a view to get better information about the sediment quality with respect to heavy metal enrichment.

The study concluded that both **textural parameters** and **adsorption phenomenon** play important role for enrichment of trace metal ions in brackish water lagoonal sediment but their relative importance varies with specific metal ions as well as the different water quality zones.

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