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Environmental Quantification of Heavy Metals in the Subarnarekha, Estuary and Near-shore Environment, East Coast of India

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Abstract: Concentration of heavy metals (Pb, Cd, Hg, Cu, Ni, Co, Cr, Mn and Fe) in the sediments was measured from the river, estuarine and coastal environment off Subarnarekha River, Bay of Bengal. The degree of contamination of the sediments was evaluated through enrichment factor (EF), geo-accumulation index (Igeo) and pollution load index (PLI). The high ER's and Igeo values for Cu and Cr were due to the chromite and copper mines, and Cu ore processing plants situated on the upstream catchments of the river. PLI for Subarnarekha estuary and coastal environments were calculated with respect to world surface rock average, where the site indices are greater than unity. Multivariate statistical analysis like factor and cluster analysis were performed in order to assess the geochemical processes responsible for heavy metal distributions and relationship between stations respectively.

Key words: Subarnarekha river, estuary, offshore, PLI, Igeo, ER, multivariate statistics, India.

Introduction

Heavy metals contamination in terrestrial and aquatic environments has significantly increased since the on set of the industrial revolution. Estuaries, rivers, lakes as well as mining and industrial areas are particularly contaminated due to effluents and solid wastes. Heavy metals concentration in such sediments is usually much higher than the normally expected from natural sources (Salomons and Forstner, 1984).

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Continental materials that are transported by rivers to the ocean may be natural or anthropogenic. The former are derived from weathering and erosion process, whereas industrial processing of metals and ores, use of metals and metal compounds, industrial wastes etc contribute for the latter. Heavy metals in naturally weathered products are mainly present in the crystalline/silicate structure of clay minerals, whereas anthropogenic materials are relatively unstable chemical forms such as absorbed species and easily reducible phases (Salmons and Forstner, 1984). Partitioning of heavy metals into the various accumulative phases or sediments (exchangeable, carbonate, easily reducible phase, organic matter including sulphides, and crystal lattice of detrital minerals) through sequential leaching provides information on heavy metal contamination (Forstner and Wittmann, 1981). However, the above process is time consuming and expensive chemical leaching techniques. To reduce the above difficulties, simple indices such as the enrichment factor (EF), geo-accumulation index (Igeo) and pollution load index (PLI) are very much useful (Muller, 1979; Manjunatha et al., 2001; Singh, 1999; Rath et al., 2005).

The multivariate statistical techniques are the appropriate tool for a meaningful data reduction and interpretation of multi-constituent chemical and physical measurements (Massart et al., 1988). The techniques such as cluster analysis (CA) and factor analysis (FA) have widely been used as unbiased methods in analysis of sediment and water quality data for drawing meaningful conclusions (Vega et al., 1998; Helena et al., 2000; Voncina et al., 2002, Simeonov et al., 2003; Singh et al., 2004). Cluster analysis helps in grouping objects (cases) into classes (clusters) on the basis of similarities within a class and dissimilarities between different classes. The results of CA help in interpreting the data and indicate patterns (Vega et al., 1998).

In this present study, concentration of some heavy metals (Pb, Cd, Hg, Cu, Ni, Co, Cr, Fe and Mn) were measured in three different periods in the sediments of Subarnarekha river, estuary and their near-shore stations. The data were compared with some Indian estuarine and coastal sediment as well as with Indian, world river and world surface rock average. In order to better understand the geochemical processes responsible for enrichment of heavy metals, multivariate statistical analysis such as FA and CA were carried out. The data obtained in this study provide an assessment of the anthropogenic impact and may be useful for future environmental monitoring.

The Study Area

The area under study is bounded by 22° 30' N and 86° 29' E to 21° 20' N and 87^0 35'E (Figure 1). The river Subarnarekha forms the major drainage in the study area. The basin extends over an area of approximately 19,296 km^2, has a total length of 395 km and has a peak discharge of 16,990 $m^3 s^{-1}$ into Bay of Bengal.

Geology of the Basin

The major part of Subarnarekha basin lies in an Indian shield, which contributes precambrian and metamorphic

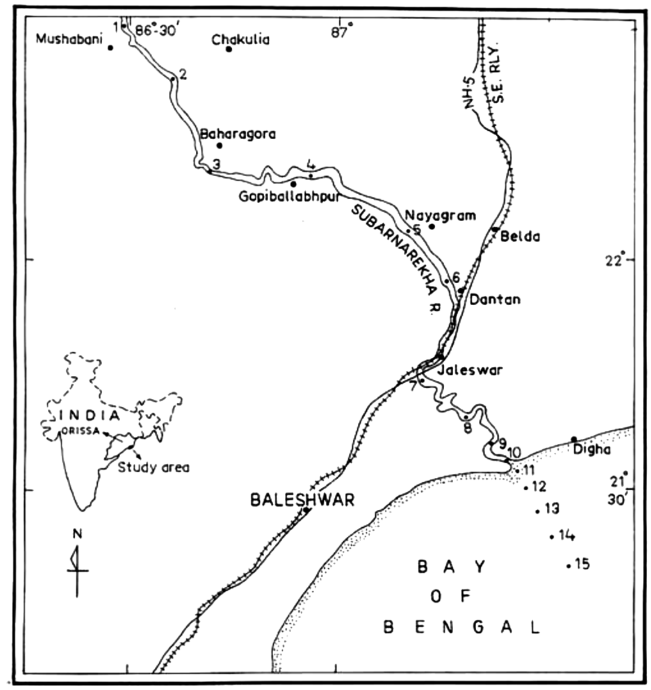

Figure 1: Map of study area showing sampling stations.

rocks. The major rock types in the basin include granites, dolomites, sedimentaries and their metamorphic counter parts (Saha, 1994). The basin is rich in varied mineral resources comprising ores of the copper, iron, uranium, chromium, gold, vanadium etc. along with the minerals including limestone, dolomite, kyanite, asbestos, baryte, apatite, china clay, building stones etc.

Anthropogenic Set up

Location of major industries, largely unplanned exploitation of the mineral resources, municipal township, and mining activities on the upstream catchments areas enhanced the anthropogenic load of heavy metals to the basin. The major industries and mines present in its catchment areas are Jamsedpur steel plant, UCIL (Uranium Corporation of India Limited), Moubhandar and Rakha copper tailing dump etc.

Materials and Methods

Sediment samples were collected from 15 locations covering the estuarine and coastal environment of Subarnarekha river during three different periods (March'01, Aug.'01 and Dec.'01). The sediment samples were homogenized and air-dried at room temperature. Powdered samples were digested in triplicate in Teflon beakers with $HClO_4$-HF-HNO_3. The concentration of metals (Fe, Mn, Cu, Ni, Co, Cr, Pb and Cd) was determined by AAS (Perkin-Elmer-3400) in flame mode and that of Hg was determined in flameless mode with background correction. For Hg, sediments were digested for two hours with aquaregia to which 5% $KMnO_4$ and potassium persulphate solution were added (Donazzalo et al., 1984). All the samples were analyzed in triplicate with blank similarly treated for metal analysis. The precision and accuracy of the methods were systematically and routinely checked by USGS reference sample No. GXR, where it has been found that the precision (coefficient of variation of five replicate analysis) were 3% for Cu, Cr and Fe and 4% for Pb, Cd, Co, Ni, Mn and Zn.

Results and Discussion

The metal concentrations (Pb, Cd, Hg, Cu, Ni, Co, Cr, Mn and Fe) in the sediments of Subarnarekha river and coastal environment are presented in Table 1. The metal concentration in the sediments of some major rivers, estuaries and coastal sea of India are compared with our present status and presented in Table 2.

Enrichment Ratio (ER)

In heavy metal studies, different authors have compared their data pertaining to a particular environment with that of similar environment in other places of the country/world (Borole et al., 1977; Subramanian et al., 1987). Enrichment factor analysis (Simex and Helz, 1981) has been used for this study.

$$\text{Enrichment Ratio (ER)} = \frac{(C_x / \text{Fe})\ \text{sample}}{(C_x / \text{Fe})\ \text{background}}$$

where C_x is the concentration of metal x.

Anthropogenic sources of 'Fe' are small compared to 'Al' in our study area, so Fe is chosen as the element for normalization. Al has been used for normalization of the metal values in sediments as a chemical trace for alumino-silicates especially for the clay minerals (Salmons and Forstner, 1984; Bhosale, 1989). But in general, the textural characteristic of the sediments in our present investigation was sandy, silty-sand type nature. So the use of Al as a normalisation element is not of much significance for the universal comparison of the sediments (Rath et al., 2000). As stated by Forstner and Wittmann (1981) and Jenne (1976), in the case of Fe, particularly the redox sensitive iron-hydroxide and oxide under oxidation constitute significant sink of heavy metals in aquatic systems. Even a low percentage of $Fe(OH)_3$ has controlling influence on the heavy metal distribution in an aquatic system. Because of importance, Fe could be used as normalisation element for the sedimentary geochemistry, which would provide better result and also help universal composition.

The average metal concentration of three different periods had been taken for consideration to quantify metal contamination with respect to Indian river average (Table

Table 1: Distribution of Trace Metals in the Sediments of Subarnarekha River, Estuary and Coastal Environments

Station	*Trace metal concentrations (µg/g) except Fe (%)*								
	Pb	*Cd*	*Hg*	*Cu*	*Ni*	*Co*	*Cr*	*Mn*	*Fe*
1	21.4	2.8	0.046	57.0	27.0	10.2	267	550	2.50
2	26.8	3.2	0.052	77.6	33.7	11.9	318	830	3.23
3	18.6	3.9	0.048	78.5	34.1	12.3	286	620	2.08
4	21.2	3.9	0.050	78.1	36.8	13.1	310	643	2.85
5	23.0	4.4	0.047	83.8	48.4	16.8	355	710	3.22
6	20.1	3.2	0.044	79.6	39.4	12.6	336	482	2.18
7	19.0	2.8	0.039	76.1	33.8	11.6	407	410	1.82
8	24.3	2.4	0.038	87.5	53.7	21.1	316	777	3.76
9	23.8	2.2	0.038	63.3	45.7	13.3	302	425	2.79
10	19.5	2.0	0.022	65.2	34.6	15.0	210	327	2.08
Avg.	**21.8**	**3.1**	**0.042**	**74.7**	**38.7**	**13.8**	**310**	**577**	**2.65**
11	18.2	1.8	0.022	47.1	30.3	14.2	235	410	2.50
12	17.6	1.8	0.016	50.5	34.4	14.1	175	445	2.84
13	16.5	1.0	0.015	52.5	26.2	16.2	128	391	2.65
14	13.8	0.7	0.010	47.8	22.1	13.0	94	366	2.55
15	10.2	1.0	0.008	22.4	20.8	15.2	105	324	3.02
Avg.	**15.3**	**1.3**	**0.014**	**44.1**	**26.8**	**14.5**	**147**	**387**	**2.71**
Avg. (total)	**19.6**	**2.5**	**0.033**	**64.5**	**34.7**	**14.0**	**256**	**514**	**2.67**

Table 2: Comparison of Heavy Metal Concentration in the Sediments of Subarnarekha to that of other Estuaries

River/Estuary	*Trace metal concentrations (μg/g) except Fe (%)*								
	Pb	*Cd*	*Hg*	*Cu*	*Ni*	*Co*	*Cr*	*Mn*	*Fe*
Godavari estuary (Biksham & Subramanian, 1988)				56	45	53	121	1260	4.25
Rushikulya estuary (Pradhan et al., 1998)	44				23	20			2.06
Vellar estuary (Mohan, 1995)		7		45	190	48	222	4854	3.93
Brahamani River (Subramanian et al., 1985)	11			14	29		78	221	1.74
Brahmaputra River (Subramanian et al., 1985)	13			17	47			644	2.90
Godavari River (Subramanian et al., 1987)	13			73	52			1040	4.23
Krishna River (Subramanian et al., 1987)	9			49	30			319	1.76
Mahanadi River (Chakrapani & Subramanian, 1990)	60			57	9			2020	5.61
Narmada River (Subramanian et al., 1985)	5			46	23			514	3.14
Bay of Bengal (Subramanian et al., 1985)	5			26	64		84	529	3.90
Indian River average (Subramanian et al., 1985)	11			28	37	31	87	605	2.90
World River average (Martin & Meybeck, 1979)	150			100	90	20	100	1050	4.80
Present study	19.6	2.5	0.033	64.5	34.7	14	256.3	514	2.67

3). Cr, Zn, Cu, Pb and to some extent Mn and Ni are highly enriched in almost all estuarine and riverine stations of our study area. Co showed depletion trend (<1) in all the stations. Mn and Ni showed depletion trend in coastal stations (St 11-15). In general the coastal stations showed lower values of EF in comparison to estuarine and riverine stations, which might be due to mixing of contaminated river sediments with uncontaminated coastal sediments. The enrichment factor of Cd and Hg with respect to Indian river average is not determined due to lack of data. High enrichment factor values of metals like Cr and Cd in all the stations and Cu in riverine and estuarine stations were found with respect to world river average. Also Mn and Co is enriched (>1) in some of the riverine stations of our study area. The depletion ratios (<1) were observed in most of the metal ions (except Cr and Cd) for coastal stations. High enrichment of these above metals with respect to Indian and world river average is mainly due to upstream industrialisation and mining activities on the riverbank. The high ER's for Cu and Cr might be attributed from upstream tailing and effluents of Cu and resistant chromite grains from chromite mines in the upstream of the river respectively.

Geo-accumulation Index (Igeo)

The geoaccumulation index (Igeo) has been used successfully in the quantification of metal accumulation, which compare the present status with the pre-civilized background values (Muller, 1979).

$$\text{Igeo} = \log_2 \{Cx/1.5Bn\}$$

where Cx = concentration of element 'n' and Bn = geochemical background value (The world surface rock average, Martin & Meybeck, 1979).

Based on world surface rock average, the Igeo values are calculated and presented in Figure 2. Igeo may be classified in seven grades. An Igeo of '6' indicates a 100-fold enrichment of an element above the background (Muller, 1979). Igeo value for 0-1 indicates slight pollution and less than 0 meaning no pollution. Classes 1-2 and 2-3 indicate moderate to strong pollution (Manjunatha et al., 2001).

The Subarnarekha estuarine and near-shore sediments are classified as unpolluted with respect to Pb, Ni, Zn,

Table 3: Enrichment Ratios of Trace Metals in the Sediments of Subarnarekha with Respect to Indian/World Average

Station	*Pb*	*Cd (world)*	*Hg (world)*	*Cu*	*Ni*	*Co*	*Cr*	*Mn*	*Fe*
1	2.26/0.27	5.42	0.49	2.38/1.10	0.8.5/0.58	0.38/0.98	3.56/5.13	1.05/1.01	0.86/0.52
2	2.19/0.27	4.72	0.43	2.51/1.16	0.82/0.56	0.34/0.88	3.28/4.73	1.23/1.18	1.11/0.67
3	2.36/0.29	8.92	0.62	3.95/1.81	1.28/0.87	0.55/1.42	4.58/6.61	1.43/1.37	0.72/0.43
4	1.96/0.24	6.51	0.47	2.87/1.32	1.01/0.69	0.43/1.10	3.63/5.23	1.08/1.03	0.98/0.59
5	1.88/0.23	6.57	0.39	2.72/1.25	1.18/0.80	0.49/1.25	3.67/5.30	1.06/1.01	1.11/0.67
6	2.43/0.30	7.06	0.54	3.82/1.76	1.42/0.96	0.54/1.39	5.14/7.41	1.06/1.01	0.75/0.45
7	2.75/0.33	7.48	0.57	4.37/2.01	1.46/0.99	0.60/1.53	7.45/1075	1.08/1.03	0.63/0.38
8	1.71/0.21	3.08	0.27	2.43/1.12	1.12/0.76	0.53/1.35	2.80/4.04	0.99/0.95	1.30/0.78
9	2.25/0.27	3.81	0.36	2.37/1.09	1.28/0.87	0.45/1.14	3.61/5.20	0.73/0.70	0.96/0.58
10	2.47/0.30	4.51	0.28	3.28/1.51	1.30/0.89	0.68/1.73	3.37/4.85	0.75/0.72	0.72/0.43
11	1.92/0.23	3.54	0.23	197/0.91	0.95/0.65	0.53/1.36	3.13/4.52	0.78/0.75	0.86/0.52
12	1.64/0.20	2.96	0.15	1.86/0.85	0.95/0.65	0.46/1.19	2.05/2.96	0.75/0.72	0.98/0.59
13	1.64/0.20	1.81	0.15	2.07/0.95	0.77/0.53	0.57/1.47	1.61/2.32	0.71/0.68	0.91/0.55
14	1.43/0.17	1.23	0.10	1.96/0.90	0.68/0.46	0.48/1.22	1.23/1.77	0.69/0.66	0.88/0.53
15	0.89/0.11	1.62	0.07	0.78/0.36	0.54/0.37	0.47/121	1.16/1.67	0.51/0.49	1.04/0.63

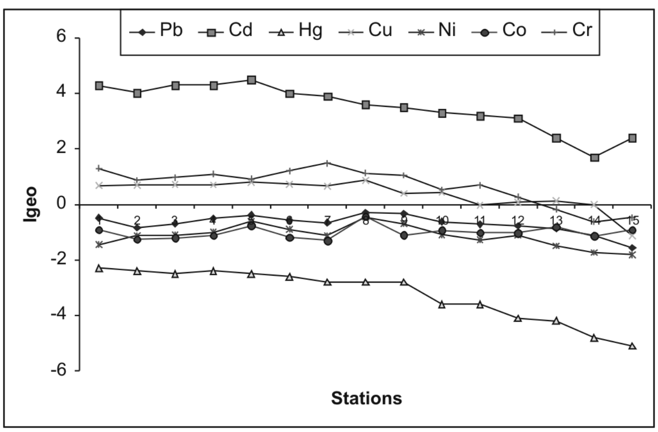

Figure 2: Geo-accumulation indices of metals at different sampling stations.

Co and Hg, whereas moderately to highly polluted with respect to Cr, Cu and Cd. The upstream chromite and copper mines and some Cu ore processing plants situated on back of Subarnarekha river are mainly responsible for the enrichment of these metals into the marine and coastal environments. The Igeo values for Co, Cu and Cd are very low in case of near-shore sediments in comparison to estuarine sediment. The high value Igeo in case of Cd might be related to higher availability of Cd in our shale.

Pollution Load Index (PLI)

Pollution load index is used in order to find out the mutual effect of different studied metals. PLI for a particular station (site index) has been calculated (Tomlinson et al., 1980) by taking the *n*th root of the *n* highest contamination factors multiplied together:

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

where '*n*' is the number of metals in this study.

$$CF_j \text{ (contamination factor)} = \frac{\text{Concentration of metal } j}{\text{Background of metal } j}$$

Background value is used here as base level for world surface rock average (Martin and Meybeck, 1979). Similarly PLI for the study area (site index) had been calculated taking *n*th root of *n* site indices multiplied together.

PLI for Subarnarekha estuary and near-shore coastal environment are given in Table 4, which are calculated by taking average metal concentrations for three different periods. The site indices for Subarnarekha estuarine sediments (St. 1 to 10) were greater than unity as compared to near-shore stations (St. 11-15). The Subarnarekha estuary and coastal index were 1.17 and 0.74 respectively.

Factor Analysis

In order to understand the association of metal ions in the sediments, factor analysis with rotation has been carried out for 15 cases. The result of factor analysis for three factors are given in Table 5, where factor values >0.60 are taken considering their significant influence towards the geochemical process (Sahu et al., 1998). Three principal components (PC) or factors (eigen value greater than unity) explaining 90.7% of the variance or information contained in the original data set were retained, which is sufficient to give a good idea of the data structure.

A varimax rotation of PCs was used to clarify the above picture as it achieves a simpler and more

Table 4: Pollution Load Index (PLI) in the Stations of Subarnarekha River, Estuary and Coastal Enviroments

Station	*Contamination factor*										
	Pb	*Cd*	*Hg*	*Cu*	*Ni*	*Co*	*Cr*	*Mn*	*Fe*	*Station PLI*	*Average estuarine*
1	1.1	21.7	0.26	1.8	0.6	0.5	2.75	0.76	0.70	1.04	PLI
2	1.3	24.4	0.29	2.4	0.7	0.6	3.28	1.15	0.90	1.29	1.17
3	0.9	29.7	0.27	2.5	0.7	0.7	2.95	0.86	0.58	1.14	
4	1.1	29.7	0.28	2.4	0.8	0.7	3.20	0.89	0.79	1.24	
5	1.2	33.9	0.26	2.6	1.0	0.9	3.66	0.99	0.90	1.40	
6	1.0	24.6	0.24	2.5	0.8	0.7	3.46	0.67	0.61	1.15	
7	1.0	21.8	0.22	2.4	0.7	0.6	4.20	0.57	0.51	1.07	
8	1.2	18.5	0.21	2.7	1.1	1.1	3.26	1.08	1.05	1.39	
9	1.2	17.0	0.21	2.0	0.9	0.7	3.11	0.59	0.78	1.13	
10	1.0	15.0	0.12	2.0	0.7	0.8	2.16	0.45	0.06	0.90	
11	0.9	14.2	0.12	1.5	0.6	0.8	2.42	0.57	0.70	0.90	Average
12	0.9	13.5	0.09	1.6	0.7	0.7	1.80	0.62	0.08	0.87	Coastal
13	0.8	7.7	0.08	1.6	0.5	0.9	1.32	0.54	0.74	0.77	PLI
14	0.7	5.0	0.06	1.5	0.5	0.7	0.97	0.51	0.71	0.63	0.74
15	0.5	7.9	0.40	0.7	0.4	0.8	1.08	0.45	0.84	0.85	

Table 5: Rotated Factor Matrix

Variables	*Factor 1*	*Factor 2*	*Factor 3*
Hg	0.980		
Cd	0.930		
Cr	0.921		
Cu	0.880		
Pb	0.815		
Mn	0.720		0.650
Co		0.820	
Zn		0.750	
Ni	0.600	0.750	
Fe			0.895
Eigen values	6.053	2.241	0.772
% of variance	60.5	22.4	7.7
Cumulative % of variance	60.5	82.9	90.7

meaningful representation of the underlying factors by decreasing the contribution to factors of variables with minor significance and increasing the more significant one (Massart et al., 1988; Jackson, 1991).

The first factor representing 60.5% of the total variance was found to be strongly associated with Hg, Cd, Cr, Pb, Mn and Ni. This factor may be related to the solid effluents discharge into the river by the mining and industrial activities. The second factor contributes 22.4% of the total variance and was strongly loaded with Co, Zn and Ni. This metal ion may be related to the adsorption by the fine grain particulates in the estuarine environments. The third factor associated with Fe and Mn, indicates the iron group of rocks to be the input source in the basin. This factor showed 7.7% of the total variance.

Cluster Analysis

The relationship among stations obtained through cluster analysis using average linkage between groups and synthesized by the dendogram plots are shown in Figure 3. Ward's method was selected because of small space distorting effect (Helena et al., 1999) and has been proved to be an extremely powerful grouping mechanism (Willet, 1987). The dendograms indicate the status of pollution as well as the effect of contamination into the stations, which are categorized into different groups. From a look at the dendogram plot, the following three distinct groups were observed:

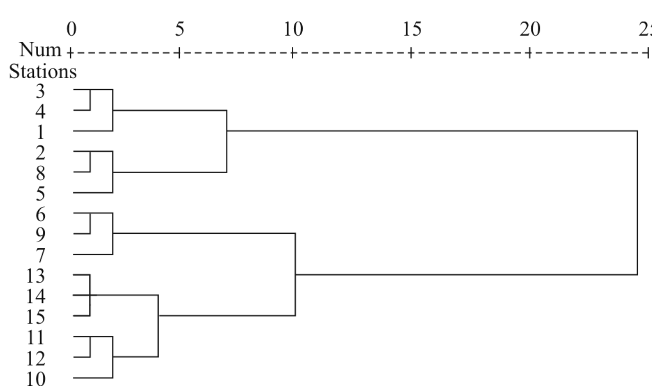

Figure 3: Rescaled distance cluster combine.

Group	Station No.
1	(3-4-1) - (2-8-5)
2	6-9-7
3	(13-14-15) – (11-12-10)

The first and second groups consist of river stations, whereas the third group relates to coastal stations. The grouping among the groups 1 and 2 may be related to the local anthropogenic activities. Stations like 6, 7 and 9 are very much responsible for contributing metal concentrations to the coastal stations (group 3). The group 3 stations are sub-divided into two i.e. near-shore stations (10-11-12) and offshore stations (13-14-15).

It is evident that CA technique is useful in offering reliable classification of fresh, estuarine and saline systems in the whole region and make possible to design a future spatial sampling strategy in an optimal manner for getting good conclusive result. For rapid assessment of sediment quality, only one or two sites in each cluster may serve as good in spatial assessment of the sediment quality as the whole network.

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