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Biogeochemical quality assessment of the sediments in Kerala coast

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ABSTRACT

Sediments are the reserve of environmental variation and analysis gives the diverse nature of the environmental chemical pattern. Present attempt provides an insight on the biogeochemistry (*BGC*) of sediment in selected stations of Kerala coast, India. Sampling along the Kerala coast was done during May – June 2009 in cruise no: 267 of Fishery and Oceanographic Research Vessel, Sagar Sampada. Eleven samples were collected from four stations - Cape, Trivandrum, Kollam and Cochin. Study of organic matter (*OM*) is significant as it exerts a strong control on the diagenic alterations in the sediment. Samples were analyzed for their Texture; *OM*- Protein, Carbohydrate, Tannin and lignin, Lipid; Trace metal; Total phosphorus and CHN. Among the eleven analyzed sediment, sample from Cochin station has high clay (>30%) and silt (>40%) content. The rest of the stations showed elevated amount of sand content. Generally the investigation reveals an inverse relation between lipid with other *OM*- Protein, Carbohydrate, Tannin and lignin. The order of relative distribution of *OM* were Protein > Carbohydrate > Tannin and Lignin > Lipid. High concentration of trace metal, Fe was found at Kollam and Cochin. Trace metal concentration was directly related to *OM* distribution. But C/N and Fe/P ratios were inversely related to *OM* and trace metal.

Keywords: Biogeochemistry, sediment, organic matter, texture, trace metal, Kerala coast.

1. Introduction

Coastal zone is the most rich and productive ecosystem. Enhanced productivity leads to the abundance of marine species in the coast. India has a coastline of 6,000 km in which Kerala is highly significant for the physiographic setting which is responsible for the environmental variability and dynamism. These highly sensitive ecosystems serve as reservoirs for dredged spoils, sewage, industrial and municipal effluents and other type of pollutants. The coastal waters are not only rich in biodiversity but also support the livelihood, nearly three quarters of the world population dependent on the coastal ecosystem particularly the fishing communities. The coastal ecosystems are now highly disturbed and very much threatened, encountering problems like pollution, siltation and erosion, flooding saltwater intrusion, storm surges and other activities due to ever expanding human settlements. The west coast of India is environmentally more susceptible than the east coast primarily as the Arabian Sea-the unique ecosystems in the world manifests in rich biological production throughout the year in the course of different processes (Mathupratap *et al*. 1996). Sediment is naturally occurring material that is broken down by processes of weathering and erosion, and is subsequently transported by the action of fluids such as wind, water, or ice, and/or by the force of gravity acting on the particle itself. According to the origin of their particles, the grain sizes, and

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where they are deposited, these sediments are of four types - lithogenous, biogenous, hydrogenous and cosmogenous. The *OM* plays a major role in the *BGC* of oceans not only because the sediment provides a significant reservoir in the global carbon cycle, but also they drive early diagenesis. The production and destruction of *OM* in any ecosystem are primarily a biologically mediated process and cause significant changes to the oxygen and carbon dioxide concentrations and allows the quality of the aquatic environment. The *OM* in the sediment is a complex mixture of dead and living material which originates from water column transport of particulate organic carbon and in situ synthesis. *OM* includes both labile compounds (amino acids and sugars) as well as more refractory compounds (humic acid, tannin and lignin, lipids etc).

For the present study geographically important four prominent zones –Cape, Trivandrum, Kollam and Cochin were selected along the Kerala coast. Cape is at the tail tip end of India. Three seas –Arabian Sea, Indian Ocean and Bay of Bengal meet over here. Trivandrum is the capital of Kerala, is the only one part of the southern Kerala, where cliffs are found. Kollam is the most scenic cities in the State. It is the southern gateway to backwaters of Kerala. Cochin (Queen of Arabian Sea) is the commercially and industrially important city which lies on the west coast of India. To find out the *BGC* of the coastal environment, *OM* and Trace metal distribution was spatially quantified and compared with Texture and CHN in the above referred sites.

2. **Materials and methods**

Eleven sediment samples were collected in cruise no. 267 in FORV Sagar Sampada on 29thMay 2009 to 4th June 2009 from Tuticorin to Cochin. Sediments were collected from four identified stations [Cape (1), Trivandrum (4), Kollam (4) and Cochin (2)] of Kerala coast, India (Figure. 1). The Description of location sites were given in Table1. Surficial sediment samples were collected using a Van veen grab, sealed, transported to the lab and stored in deep freezer. Sediments were air dried, finely powdered and used for chemical analyses. Textural characteristics, quantification of *OM* (Protein, Carbohydrate, Tannin & Lignin and Lipid) Metal analysis, Total phosphorus and CHN analysis were carried out.

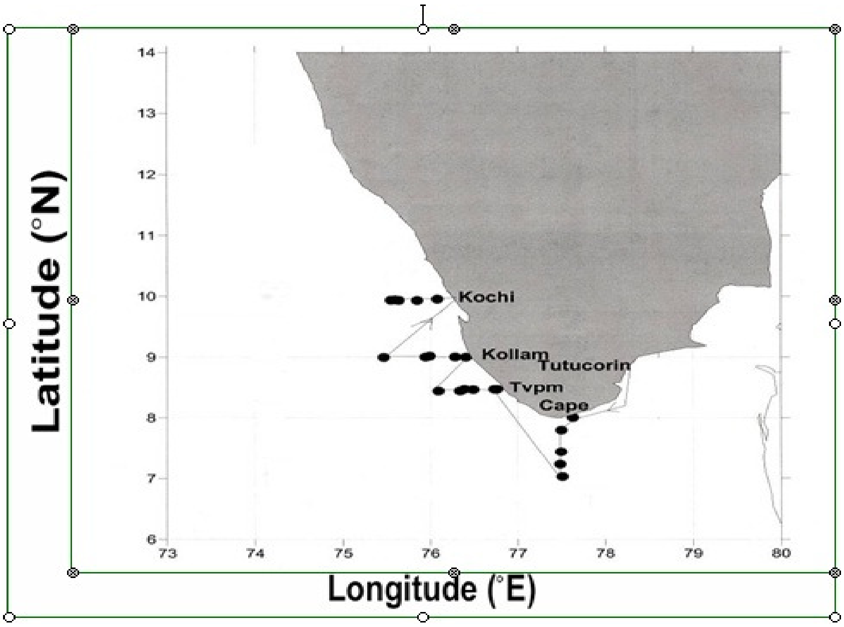


Figure 1: Showing the cruise track and sampling sites

Table 1: Location of sampling sites

Transect	Depth (m)	Location
Cape1(M1)	50	0747.64^0N,7730.177^0E
Trivandrum1(M2)	30	0830.048^0N,7650.874^0E
Trivandrum2(M3)	50	0830.040^0N,7643.831^0E
Trivandrum3(M4)	100	0828.117^0N,7629.712^0E
Trivandrum4(M5)	200	0827.902^0N,7624.012^0E
Kollam1(M6)	50	099.010^0N,0756.851^0E
Kollam2(M7)	90	0859.353^0N,0756.043^0E
Kollam3(M8)	100	0900.034^0N, 7617.013^0E
Kollam4(M9)	200	0900.084^0N,07623.524^0E
Cochin1(M10)	<200	957.77^0N,7616.919^0E
Cochin2(M11)	<100	959.213^0N,7616.084^0E

Textural characteristics (sand, silt, and clay) were determined using pipette analysis by Lewis 1984. Inorganic carbonates and *OM* were removed using 2N HCl and 30% H_2O_2 respectively. Protein was measured using Copper reagent and Folin –Ciocalteu phenol reagent (Lowry *et al* 1951). Carbohydrate estimation was done by Phenol- Sulphuric acid method (Dubois *et al.* 1956). The estimation of Tannin and lignin was performed by Sodium tungstate phosphomolybdate acid method (APHA 1995). Total lipid was determined by the Sulphophosphovanillin method (Barnes and Black stock1973). For metal analysis samples were digested with 5:1 mixture of HNO_3 & $HClO_4$, filtered and analysed using ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy). Elemental compositions, CHN of the samples were determined by using VarioEL 111 CHN Analyser. Total phosphorus was estimated by using the standard method by Kopacek and Hejzlar (1993) Pearson correlation was carried out to test correlation of *OM* with Textural characteristics and Metal concentration.

3. Results and discussion

Textural characteristics of the four stations were shown in Table 2. Sand content was high in Cape, Trivandrum and Kollam (> 87%). Both clay (>30%) and silt (>40%) content were greater at Cochin. Among the eleven stations the percentage of sand fraction is highest at Kollam (99.3%) and lowest at Cochin (11.9%). Clay was highest at Cochin (33.171%) and lowest at Trivandrum (0.203%). Silt was maximum at Cochin (42.748%) and minimum at Kollam (0.132%).Grain size is one of the basic attributes of sediments and its distribution is essential to delineate the sedimentary environments. Its delivery reveals the physical effects of environment on deposition and hydrodynamic conditions existing at the time of deposition. The settling of terrestrial and marine particles delivers *OM* along with toxic pollutants to the surface sediments that induce high changes in the biological activity. Most of the *OM* enters the biological food web in the surface waters and is used for new heterotrophic biomass production. Because of this intense recycling, it is difficult to determine the *OM* flux at different levels of the photic zone. Although the fraction of *OM* buried in sediment is small relative to the amount produced by photosynthesis in oceanic surface waters, empirical relationships were derived from the analysis of Sedimentary *OM* to estimate oceanic paleo-productivity. The lithogenic materials introduced by the rivers accelerate the removal of newly fixed *OM* from the water column to the sediments. Textural character difference, inputs from other water bodies and land runoff are the contributing factors for *OM* distribution. Protein, Carbohydrate, Tannin and lignin and Lipid were the main analyzed constituents of *OM*. Spatial distribution of organic matter is given in figure 2. The essential organic nitrogen compounds- proteins are widely distributed in sediments and the present study showed maximum concentration (68.65 mg/g) at Cochin and minimum (0.204 mg/g) at Trivandrum.

Table 2: Textural characteristics of sediment

Samples	Sand (%)	Clay (%)	Silt (%)
M1	87.72	6.85	5.43
M2	94.91	2.34	2.75
M3	98.51	0.746	0.744
M4	99.05	0.203	0.747
M5	94.89	4.72	0.39
M6	97.87	1.998	0.132
M7	99.3	0.4996	0.2004
M8	97.74	0.227	0.473
M9	97.97	1.663	0.367
M10	11.9	31.88	56.22
M11	24.351	33.171	42.748

In the investigated samples concentration of carbohydrate was maximum (111.2 mg/g) at Cochin and minimum (14.42 mg/g) at Trivandrum .Carbohydrates are some of the major biochemical compound produced by living organisms and constitute an important fraction of dissolved and particulate *OM* (Skoog and Benner 1997; Borsheim *et al*. 1999; Burdige *et al*. 2000). These are consumed by microheterotops in both fresh water and marine ecosystems and contribute essentially to the bacterial production (Rich *et al*. 1996). Tannin and Lignin, a high molecular weight polycyclic aromatic compound are widely distributed throughout the plant kingdom. It was found maximum (29.78 mg/g) at Cochin and minimum (2.188 mg/g) at Trivandrum. The increased concentration at Cochin may result from the retting of coconut husk. Lipid one of the contributing component of *OM* are produced biologically. The result pointed out a reversal trend in the concentration. It was maximum (7.223 mg/g) at Trivandrum and minimum (0.204 mg/g) at Cochin. The distribution of lipid is inverse to other organic matter (protein, carbohydrate and tannin and lignin) under investigation. Similar trend was found in the coastal sediment of NW Adriatic Sea (Dell'anno *et al*. 2008). This may be due to the low hydrophilic nature and high survival rates during sedimentation compared to other biogenic compounds.

Among the eleven stations the lipid concentration was less compared to other *OM* under study. The order of relative distribution of *OM* were Protein > Carbohydrate > Tannin and Lignin > Lipid. Generally the distribution of *OM* was directly related to texture. Low concentration of *OM* in Trivandrum was found due to the sandy nature of sediment. The Cochin sites showed an increase of *OM* with clay content. The study of Renjith and ChandramohanaKumar, 2007 corroborate this trend and established the muddy nature of sediment. The protective effect of *OM* by adsorption on mineral particularly on the clay surfaces also contribute to a great extent. Previous studies by Keil *et al*. 1994 Mayer 1994 also support the result. Earlier research in Western continental shelf of India (Josia Jacob *et al*.2008) revealed that spatial variation of sediment texture influence the *BGC* of the surficial sediment. Protein to carbohydrate ratio and lipid to carbohydrate ratio were embodied to understand the age of the sample and the bouncy of the sediment (Fabiano *et al.* 1998; Gremare *et al*. 2002). Protein to Carbohydrate ratio is an index used to determine the origin of particle present in the sediment and to distinguish the presence of recently formed fresh materials (Cauwet 1978; Danovaro *et al*. 1993; Cividances *et al.* 2002).

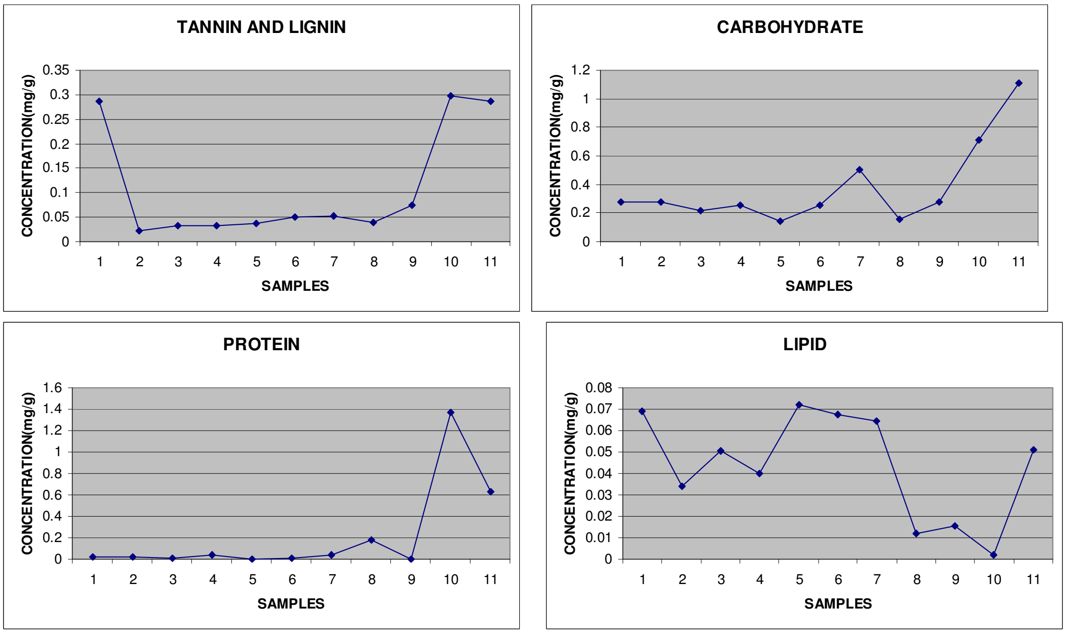


Figure 2: Spatial distribution of organic matter in Kerala coast

The study reveals the *OM* at Cape and Trivandrum were aged as having low (<1) protein to carbohydrate ratio, but at Kollam and Cochin were comparatively fewer aged as the ratio was greater than one (Figure.3). Allothonous inputs from the neighboring water bodies enhance the above factor. Protein to carbohydrate ratio is maximum at Cochin and minimum at Trivandrum. Proteins tend to be mineralized faster than carbohydrate and causing higher amounts of fresh particles (Newell and Field 1983; Lee and Fuhrman1987). This would increase the protein content of these minerals and reflex the high index value. Earlier studies by Pusceddu *et al*. 2000 showed that protein to carbohydrate ratio were high in productive areas, such as estuaries and coastal regions. The nutritional value of the analyzed sediment samples was also low because the lipid to carbohydrate ratio (Figure .4) was less than one. The river inputs to the coastal zone, together with the intense physical and biological activity in coastal waters, make the marine realm the most dynamic of dissolved organic matter which was modified by the physicochemical processes occurring in the mixing zone, particularly flocculation and photo oxidation. These processes affect the structure and the biodegradability of *OM*, which in turn reflects the energetic of the coastal zone. Lipid to carbohydrate ratio was maximum at Trivandrum and minimum at Cochin. The riverine inputs, seasonal autochthonous production contributes to a great extent in the coastal zone. C/N ratio and Fe/P were inversely related to *OM*. This was maximum at Cape (438) and minimum at Cochin (12.304). The concentration of elemental Nitrogen and phosphorous were prominent at Cochin; this is due to the muddy and productive nature of these sediments.

Correlation analysis of *OM* with textural behavior and trace metal were carried out and are depicted in Table 3 and 4 respectively. Except lipid other *OM* had significant positive correlation with clay content, and negative correlation with sand content. Correlation of metals- with clay gave strong positive relation; this is because of the high adsorption capacity of clay. The liberation of elements during the early diagenic decomposition of *OM* trapped in muddy sediment also accounts the inference (Kuma *et al.* 2000; Wells *et al.* 2000).

Biopolymeric carbon exhibits a significant correlation with protein and carbohydrate which supports their major contribution to *OM*.

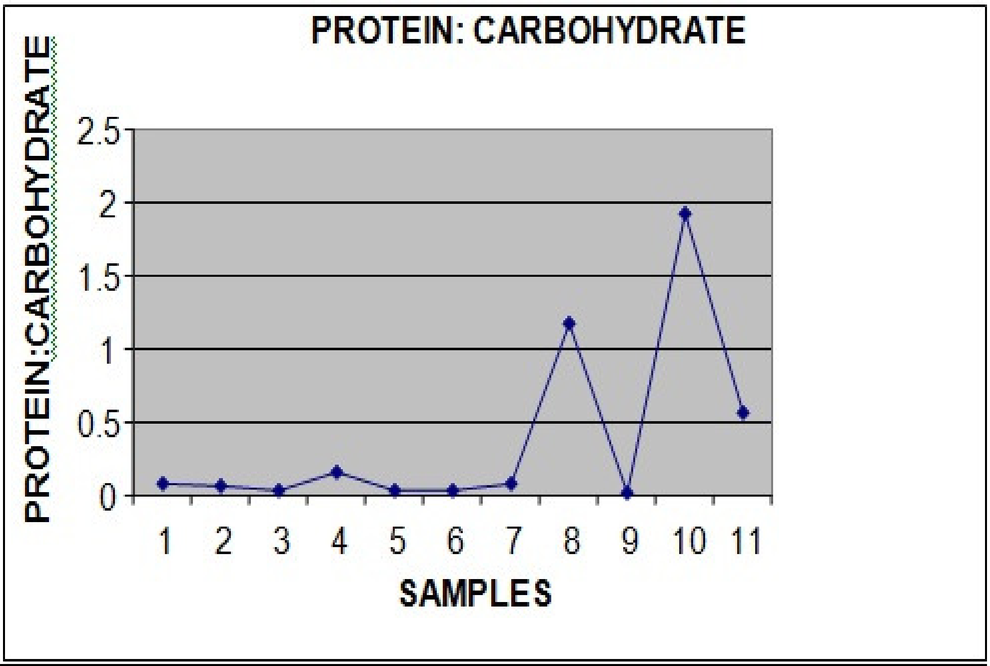


Figure 3: Spatial distribution of protein to carbohydrate ratio in Kerala coast

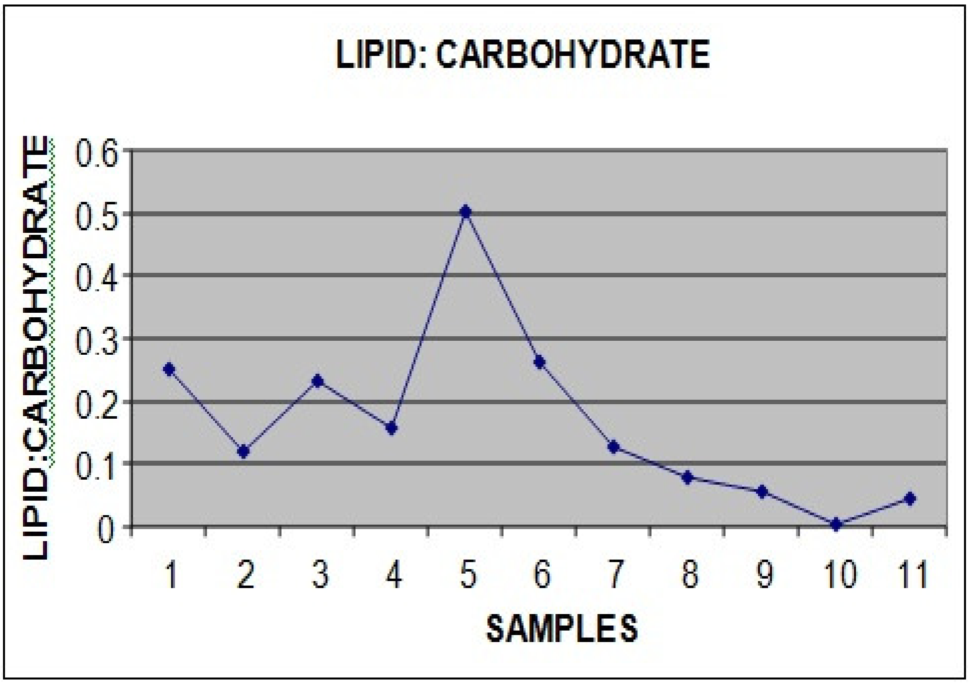


Figure 4: Spatial distribution of lipid to carbohydrate ratio in Kerala coast

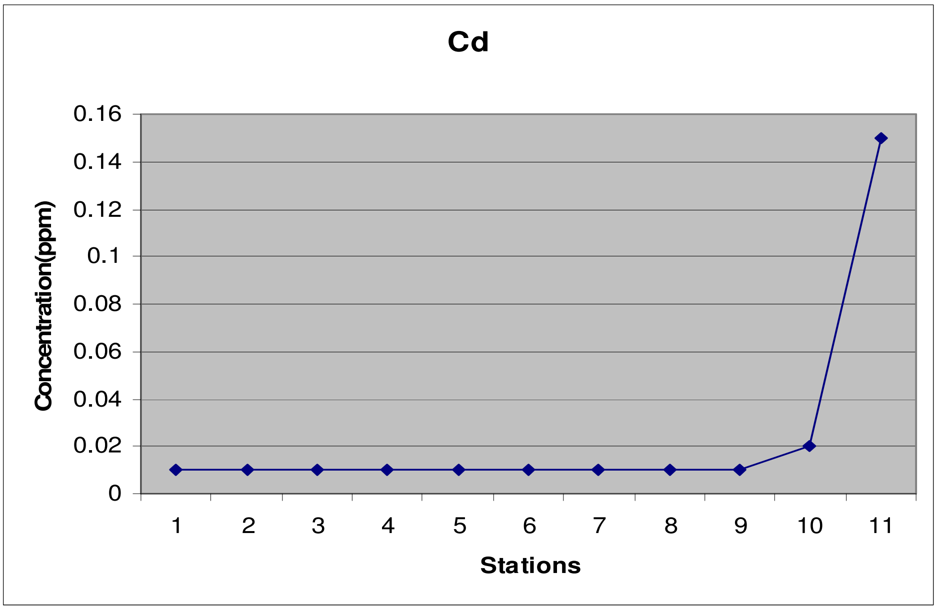
The marine ecosystem is the reservoir of various toxic pollutants including a wide range of metals and earlier studies (Sujatha *et al*.2000, 2008, 2009; Lalu Raj *et al* 2002; Ranjitha Raveendran & Sujatha C H 2011) supports. Sediments are important carriers of trace metals in the coastal environment and the current learning reflect the metal distribution in these sedimentary phases. The metal concentration follows in the order: Fe > Zn > Mn > Cu > Co > Cd (Figure 5). In general the maximum metal concentration was at Kollam and Cochin. This may be due to the better adsorption capacity of metal and also the increased terrestrial inputs and industrial effluents. The CHN distribution is given in Table 5.Carbon had high concentration at Kollam. Nitrogen and Hydrogen were prominent at Cochin.

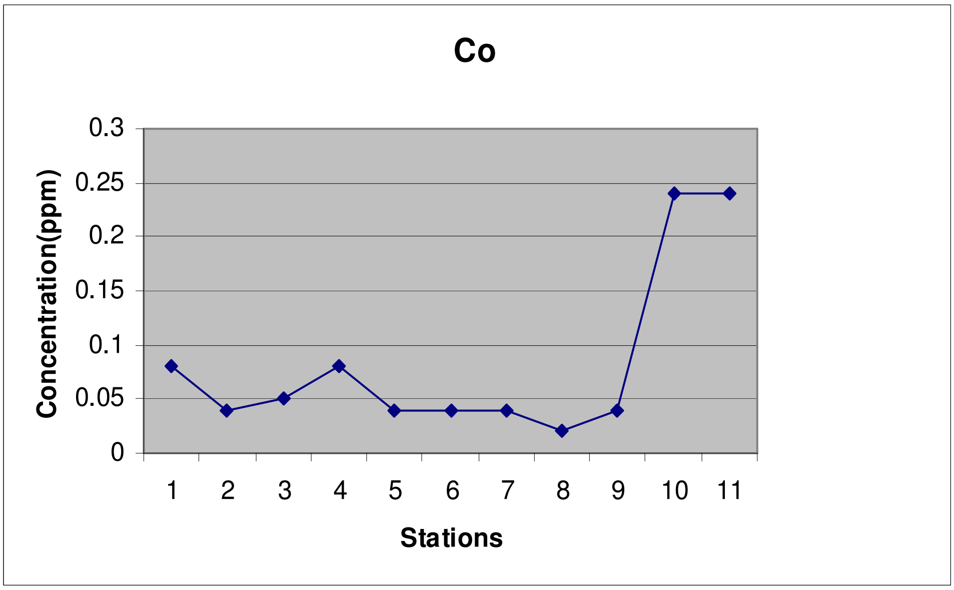
Table 3: Correlation Texture with Organic matter Distribution

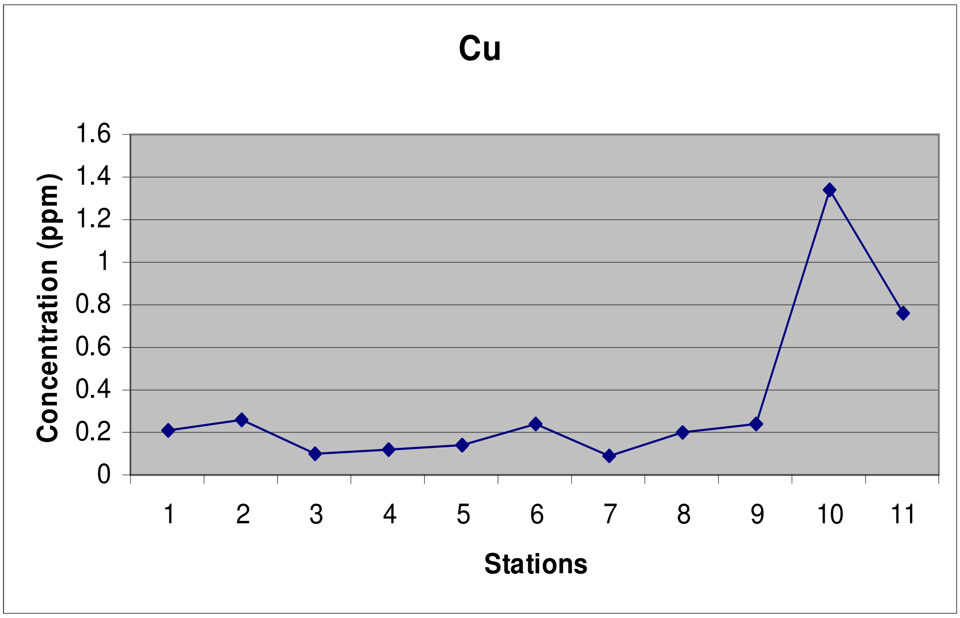
	SAND(%)	CLAY(%)	SILT(%)	CARBOHYDRATE	LIPID	PROTEIN	TANNIN AND LIGNIN
SAND(%)	1	-0.99	-1	-0.858	0.3424	-0.94	- 0.990881766
CLAY(%)	-0.99088	1	0.978	0.883	-0.2495	0.885	0.839564601
SILT(%)	-0.99691	0.978	1	0.839	-0.3853	0.958	0.805159406
CARBOHYDRATE	-0.85849	0.883	0.839	1	-0.1097	0.695	0.707681699
LIPID	0.342354	-0.25	-0.39	-0.11	1	-0.53	- 0.097399985
PROTEIN	-0.9375	0.885	0.958	0.695	-0.5315	1	0.703873002
TANNIN AND LIGNIN	-0.82186	0.84	0.805	0.708	-0.0974	0.704	1

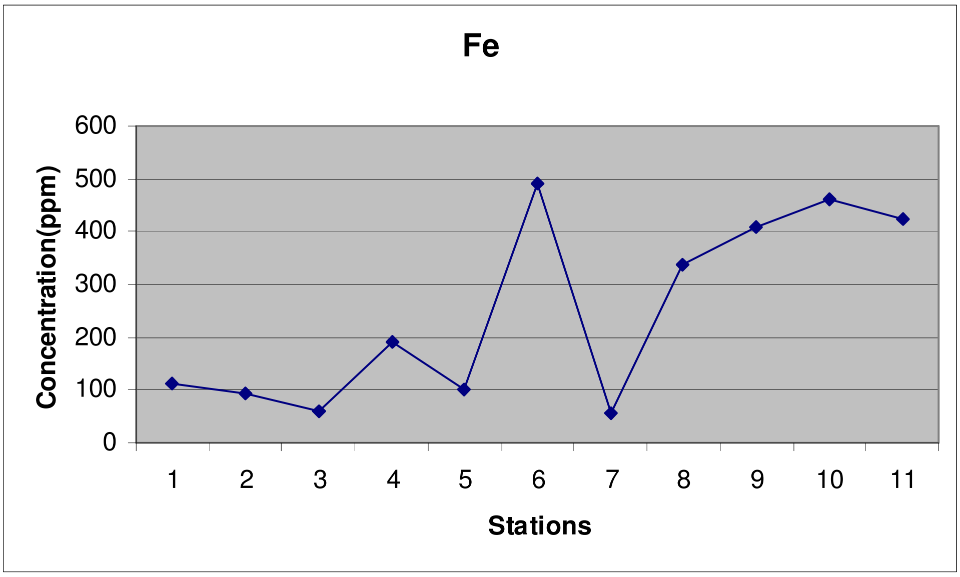
Table 4: Correlation clay with metal distribution

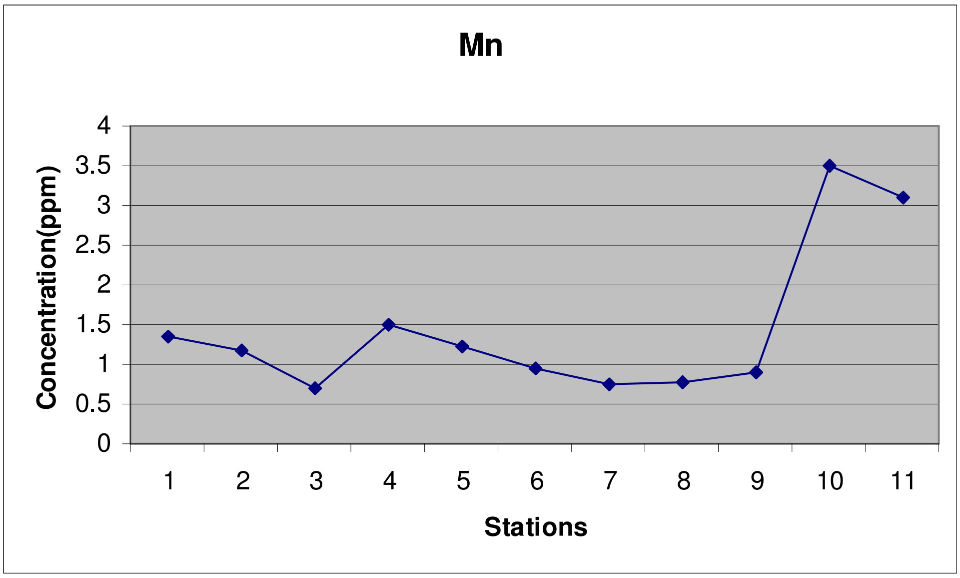
	CLAY(%)	Cd	Co	Cu	Fe	Mn	Pb	Zn
CLAY(%)	1	0.728	0.975	0.914	0.5066	0.965	0.9812	0.8221
Cd	0.728253	1	0.704	0.434	0.3622	0.627	0.7051	0.9852
Co	0.975225	0.704	1	0.897	0.4713	0.978	0.9828	0.798
Cu	0.914274	0.434	0.897	1	0.5956	0.925	0.9283	0.5763
Fe	0.506566	0.362	0.596	0.596	1	0.485	0.5979	0.453
Mn	0.964721	0.627	0.978	0.925	0.4846	1	0.9697	0.7319
Pb	0.981214	0.705	0.983	0.928	0.5979	0.97	1	0.8086
Zn	0.82208	0.985	0.798	0.576	0.453	0.732	0.8086	1

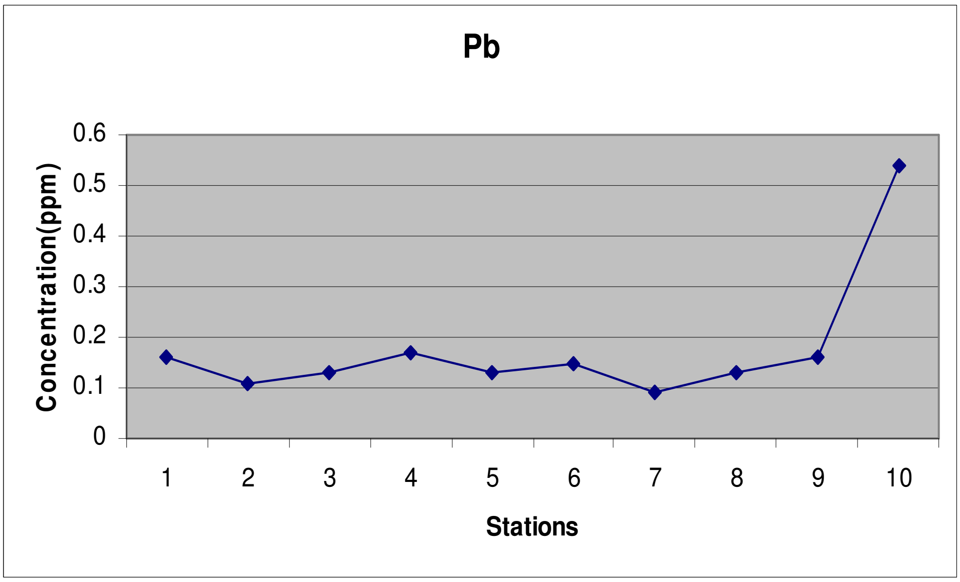

Cd
Concentration(ppm)
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
1
2
3
4
5
6
7
8
9
10
11
Stations


Co
Concentration(ppm)
0.3
0.25
0.2
0.15
0.1
0.05
0
1
2
3
4
5
6
7
8
9
10
11
Stations


Cu
Concentration (ppm)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
7
8
9
10
11
Stations


Fe
Concentration(ppm)
600
500
400
300
200
100
0
1 2 3 4 5 6 7 8 9 10 11
Stations


Mn
Concentration(ppm)
4
3.5
3
2.5
2
1.5
1
0.5
0
1 2 3 4 5 6 7 8 9 10 11
Stations


Pb
Concentration(ppm)
0.6
0.5
0.4
0.3
0.2
0.1
0
1 2 3 4 5 6 7 8 9 10
Stations

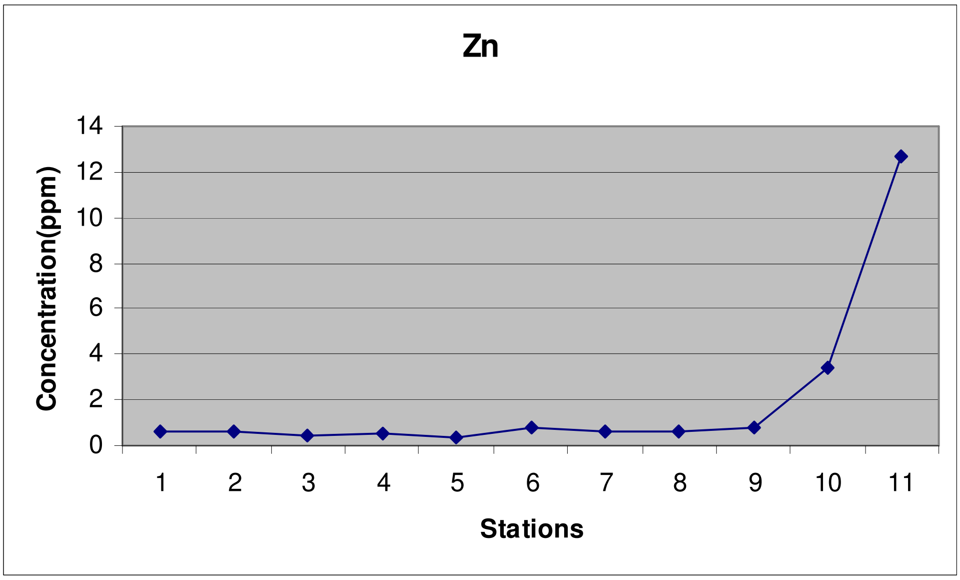


Figure 5: Spatial distribution of metal in Kerala coast

4. Conclusion

This study highlights the quantification and spatial distribution of sediment *OM* and trace metal in selected stations of Kerala coast and focuses on the spatial variation correlation pattern of *OM* with Textural behavior, CHN and Trace metal distribution. The *OM* and trace metal composition were directly related to the muddy nature of the sediment. The concentration of metals and *OM* were maximum at Cochin, due to the better adsorption capacity of clay content in the sediment. Increased input of industrial effluents, discharge from rivers, and the intense physical and biological activity in coastal waters are other factors responsible. The C/N and Fe/P ratios were inversely related to *OM*. The muddy nature of Cochin site showed maximum nitrogen and phosphorous concentration similar to that of Fe content. This study could strengthen as a baseline biogeochemical data and would amplify future research on these lacunas for coastal zone execution measures.

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