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Study on Environmental Geochemistry of Cu & Zn in Karaikal Coast

G.Ramesh*, T.Ramkumar, M.V.Mukesh and T.Immanuvel David

Department of Earth Sciences, Annamalai University, Annamalainagar, Tamil Nadu-608002, India.

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ABSTRACT

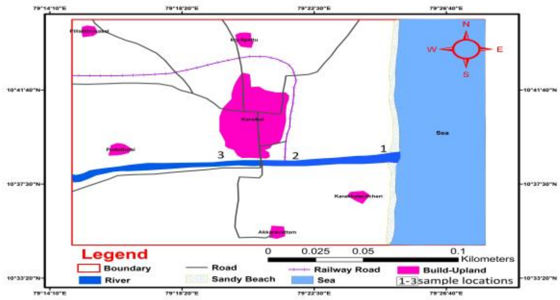
The present study was carried out in order to study about the textural characteristics of sediments, trace metal concentration (Cu, Zn), and their seasonal changes along with the influence of organic matter and physico-chemical parameter like pH, temperature, salinity and rainfall. Samplings were done at 3 different stations during 4 seasons starting from premonsoon-2009 to summer-2010. The changes in the phi mean grain size are due to selective winnowing of the finer grain size population by waves and currents acting in that environment. The sediments were well sorted to moderately well sorted in nature, skewness of the sediment samples were nearly symmetrical to coarse skewed and kurtosis ranged from mesokurtic to extremely leptokurtic in nature. The organic matter concentration range from 3.2% to 9.7% as minimum and maximum respectively. Concentration of reactive copper ranged from12.8ppm to 34.16ppm and the zinc concentration ranged from 39.3ppm to 228.2ppm.Thus in the present study the concentration of trace metals (copper & zinc), organic matter, grain size distribution and the interaction of Physico chemical parameters during different seasons were discussed.

Introduction

The coasts separate continents from seas and may develop in various geomorphic and sedimentological variants. There are many excellent works dealing with the classification and types of coast. Widely accepted classifications are those of Valentine (1952) and Shepard (1963, 1976). The coastal zone of India is important in view of its productive eco systems, concentration of population and for exploitation of renewable and non-renewable natural resources (Nayak et al., 1996). The coastal vegetation plays an important role in the deltaic environment by enhancing the sedimentation and stabilization of the seashore and sea bottom. It provides habitat and nursery areas for many commercially important fish and crustaceans (Robertson and Duke, 1987) and plays an important roll in chemical buffering, water quality maintenance and storage of genetic materials (Saenger et al., 1983) besides contributing considerable amount of organic matter (Odum and Heatel, 1972; Day *et al.*, 1973; Prakash *et al.*, 1973; Boto 1982; Untawale and Jagtap, 1991) thereby increasing the productivity of the coastal waters.

Description of the Study Area

The Arasalar estuary is situated at Karaikal (Lat.79° 52' E Long.10° 55'N) of Bay of Bengal. The Arasalar is a tributary of the river Cauvery, having a total run of 24 km. It enters Karaikal region, a little east of Akalanganni. It forms the natural boundary line separating Niravi Commune from Tirunallar on the north-west and Karaikal on the north east. The Nattar, branching off from Arasalar at Sakkotai in Thanjavur District, runs a distance of 11.2km in a south-easterly direction across Nedungadu and Kottucheri Communes before emptying itself into the sea. The Vanjiar fed by the Arasalar, takes its course along the northern boundary of Tirunallar Commune, drops on a south-easterly curve towards Karaikal Commune and merges with the Arasalar, south-east of Karaikal town after covering a distance of about 9 km. The Nular, also fed by the Arasalar, runs a distance of 13.77 km. before it joins Vanjiar northeast of Karaikal town. The study area comprises of estuarine and coastal environment. The estuarine environment from the mouth of the river in downstream to fresh water in upstream direction which extends about 9 km. The coastal environment comprises of beach and near shore from the mouth of river. Totally 3 samples were collected. Station 1 is situated nearby mouth of the estuary (marine zone), station 2 and 3 in a mixed environment.



Materials and Methods

Sediments were collected using a grab sampler. The samples were collected from Karaikal coasts during the period of pre-monsoon-2009, monsoon-2009, postmonsoon-2010 and summer-2010. About 2 Kg. of sediment samples are collected using grab sampler. These samples were transferred to clean polybags, numbered and transported to the laboratory. Some samples were air-dried and some were kept as wet samples. The sampling stations were represented as 1, 2, and 3 respectively. Sediment samples are first desalinized and dispersed with sodium hexa Meta phosphate. They are then air dried, thoroughly mixed and utilized for granular metric analysis. The sediment samples that have less than 5% silt and clay are sieved at quarter φ interval using ASTM Standard test sieves in a Ro-Tap sieve shaker for 20 minutes. . From the weighted sample, the statistical parameters such as mean size (Mz), standard deviation (□), skew ness (SK_I), and kurtosis (K_G) were calculated using the formula of Folk and Ward (1957).

Tele:
E-mail addresses: georames@gmail.com

Extraction of Copper and Zinc

The amount of copper and zinc present in the sediment sample was determined by mild acid extraction (Rantala and Loring, 1977) CH_3COOH is used to remove elements. In this method, exactly 5 grams of sediments was transferred in a 100 ml evaporating dish and 50ml of 25 % acetic acid was added followed by stirring. The evaporating dish was covered and kept stand alone 24 hours. After 24 hours acetic acid was decanted in a 100 ml centrifuge tube, it is centrifuged until clear. The supernatant poured in a 200 ml volumetric flask. The sediment in the dish is washed up to 3 times with 10 ml of distilled water each time pouring the washings in the centrifuge tube, it is recentrifuged and again the supernatant collected in the volumetric flask. Finally, the supernatant was made up to 200 ml with water and stored in a polypropylene bottle for analysis. The supernatant water was analyzed for copper and zinc concentration using the inductively coupled plasma emission spectrophotometer (ICPES). The concentration was expressed in ppm. The accuracy of the present measurement was ± 0.5 ppm.

Discussion

Mean size

The cumulative frequency graph drawn was used to determine the mean size of the sediments (Mz). The variations in the mean size in all the three station during various seasons were distinguishable (Table-2). During the study period an increase and decrease of the phi mean grain size was observed. In the second station, the mean grain size was maximum (2.5 φ) during post-monsoon and minimum (2.2 φ) was during monsoon, whereas in the station-3, the mean grain size was maximum (2.6 φ) during summer and minimum (2.2 φ) during monsoon (Table-2). It is noticed that the phi mean size decreases the sediment becomes coarser and if the phi mean size increases the sediment becomes finer. The decrease and increase of mean size may depend upon the location of the sampling station, and action of currents in the environment. The mean grain size also depends upon the transport mechanism of the sediments. During monsoon season there existed a decrease in phi mean size in all the three stations. This may be due to the addition of finer particles by the rainfall during the season. An increase phi-mean size (2.5φ & 2.6φ) was noticed during post-monsoon and summer at station-1. The increase of phi-mean of the sediments during these seasons could be attributed to low fluvial discharge and relatively better mixing of saline and freshwater that might have facilitated flocculation and coagulation resulting in settling of suspended fine particles which in turn increased the phi mean size to increase

Standard Deviation

Sorting effect of the grains was determined by using standard deviation data. The values ranged from (0.49-0.67) in the station-1. In the station-2 these values ranged from (0.46-0.59) and (0.49-0.63) in the station-3 respectively (Table-3). Throughout the study period the sediments were moderately well sorted. The standard deviation was maximum (0.67 φ**)** during pre-monsoon in station-1. The minimum standard deviation (0.46 φ**)** was noticed in station-2 during summer season. In station-1 the maximum standard deviation (0.67 φ) was noticed during pre-monsoon and minimum was noticed (0.49 φ) during post monsoon. In station-2, it was maximum (0.59 φ**)** during monsoon and minimum (0.46 φ**)** during summer.

In station-3 the maximum standard deviation value (0.63 φ**)** was noticed during post monsoon and the minimum value (0.49φ) was noticed during summer season. The difference in sorting may be due to the difference in energy conditions, winds, waves, tides might be the possible agencies for the distribution of energy. Tidal currents might have formed the alternating high and low energy zones, these lead to better sorting of sediments during monsoon. Once the sediments attain the maximum sorting value, and further they fall in the competency of water flow result in the increase of fine particles and leads to poor sorting. Similar observations were recorded by Ramkumar (1995) in Vellar estuary. Almost all the station during most of the season indicates moderately well sorted nature except station-1 during post-monsoon and in station-2 during summer. The moderately well sorted character of the sediments indicates the influence of stronger energy condition of the depositing agents .The higher sorting values indicate that the tidal force may not be strong enough to suspend the fines. The higher sorting value indicates that the mixing of sediments may be due to the early rainfall during study period.

Skewness

Standard deviation

It is expressed by inclusive graphic standarddeviation of Folk & Ward (1957) as it covers both the tails of the distribution. Standard deviation is apoorly understood measure that depends on the sizerange of the available sediments, rate of depositing agent and the time available for sorting. The sortingvariation observed attributes to the difference in water turbulence and variability in the velocity of depositing current. The skewness values ranged from (-0.25 to 0.074 φ) in the first station. In the second stations it ranged from (-0.29 to 0.07 φ), where as in the third station it ranged from (–0.3 to 0.07 φ) (Table-4). In the first station skewness is maximum (0.074 φ) during post monsoon and minimum (-0.25φ) during monsoon. At the second station the skewness was maximum (0.07 φ) during summer and the minimum skewness was noticed (-0.29 φ) during the monsoon season. In the third station the skewness was maximum (0.07 φ) during pre-monsoon and minimum (-0.3φ) during post monsoon. The skewness is a measure of the degree of symmetry, describing the tendency of the data to spread preferentially of one side of the average. It is an important parameter in grain size studies since it is a sensitive indicator of sub population mixing. The skewness value revealed that the sediments during the study period ranged from nearly symmetrical to coarse skewed. The variation in the skewness could be explained by the material in sample.

In the present study, during pre-monsoon season the stations-2 and 3 showed that the samples were nearly symmetrically skewed and this may be due to the mixing of two populations mixed in equal amounts and attained the skewness symmetrical in nature. During pre-monsoon in station-1 and monsoon period in all the three stations, samples were coarse skewed which indicates the influence of water movement along with movement of finer particles. In station 2 and 3 during summer and pre-monsoon the sediments were nearly symmetrically skewed. During the study the skewness are mostly coarse skewed and nearly symmetrical. The losses of finer sediment during post monsoon and pre monsoon in all the stations are due to the reworking of sediments associated with a high energy environments leading to removal of fine grained fractions which made the skewness negative.

Kurtosis

Kurtosis is measure of peakedness. The kurtosis values ranged from (0.95 to 4.04 φ**)** in the first station, (1.03 to 1.98 φ**)** in the second station and (1.06 to 1.65 φ**)** in the third station (Table-5). The kurtosis value ranged from Masochistic to Extremely Leptokurtic. In first station the kurtosis was maximum (4.04 φ**)** during post-monsoon and minimum (0.95 φ**)** during pre monsoon.

Table 1. Textural classification of sediment samples

Sources	Station-1	Station-2	Station-3
Premonsoon (2009)	Fine Sand	Fine Sand	Fine Sand
Monsoon (2009)	Fine Sand	Fine Sand	Fine Sand
Postmonsoon (2010)	Fine Sand	Fine Sand	Fine Sand
Summer (2010)	Fine Sand	Fine Sand	Fine Sand

Table 2. Phi-mean size of sediment samples

Season	Station-1	Station-2	Station-3
Premonsoon (2009)	2.5	2.49	2.61
Monsoon (2009)	2.28	2.21	2.21
Postmonsoon (2010)	2.57	2.58	2.21
Summer (2010)	2.40	2.54	2.63

Table 3. Sortng characteristics of sediment and their classification

Season	Station-1	Station-2	Station-3
Premonsoon (2009)	0.67(M.W.S)	0.48(M.W.S)	0.58(M.W.S)
Monsoon (2009)	0.54(M.W.S)	0.59(M.W.S)	0.59(M.W.S)
Postmonsoon (2010)	0.49(W.S)	0.55(M.W.S)	0.63(M.W.S)
Summer (2010)	0.57(M.W.S)	0.46(W.S)	0.49(W.S)

M.W.S=> Moderately well sorted, W.S => well sorted

Table 4. Skewness values of sediment and their classification

Season	Station-1	Station-2	Station-3
Premonsoon (2009)	-0.16(C.S)	0.05(N.S)	0.07(N.S)
Monsoon (2009)	-0.25(C.S)	-0.29(C.S)	-0.13(C.S)
Postmonsoon (2010)	0.074(N.S)	0.068(N.S)	-0.3(C.S)
Summer (2010)	-0.12(C.S)	0.07(N.S)	0.03(N.S)

N.S=> Near symmetrical C.S=> Coarse skewed

Table 5. Kurtosis values of sediments and their classification

Season	Station-1	Station-2	Station-3
Premonsoon (2009)	0.95(M.K)	1.5(L.K)	1.2(M.K)
Monsoon (2009)	1.70(V.L.K)	1.03(M.K)	1.24(L.K)
Postmonsoon (2010)	4.04(E.L.K)	1.98(V.L.K)	1.06(M.K)
Summer (2010)	2.13(V.L.K)	1.57(V.L.K)	1.65(V.L.K)

M.K=> Mesokurtic V.L.K=> Very leptokurtic
E.L.K=> Extremely leptokurtic L.K=> Leptokurtic

At the second station the kurtosis is maximum (1.98 φ**)** during post monsoon and minimum (1.03 φ**)** during monsoon season. At the third station the maximum kurtosis was noticed (1.65 φ**)** during summer and minimum (1.06φ) during post monsoon. According to cadigan (1961), Kurtosis is measure of peakedness, it is also a function of internal sorting or distribution. The present study showed that the kurtosis ranged from Measokurtic to Extremely Leptokurtic. Kurtosis is a ratio of sorting in the tails than the sorting at the center of distribution. The Mesokurtic character of the sediments indicates moderate winnowing action of the depositing agent. The Leptokurtic nature of the sediments indicates the mixing of a predominant population with very minor amount of coarser and finer materials. In station 1 and 3 during pre monsoon, in station-2 during monsoon, in station-3 during post monsoon seasons shows Mesokurtic. This may be due to the presence of very fine sand. Apart from Measokurtic most of other stations shows Leptokurtic. The Leptokurtic behaviour of the sediments also indicates the variations of the energy conditions of the environmental setup of depositions of the sediments.

Geochemical studies

Copper

According to several historians, copper was the first metal harnessed by man. In igneous rocks the average concentration of copper has been estimated at 55 ppm. The average concentration in sedimentary rock is lower: 45ppm in shale's, 5 ppm in sandstone and 4ppm in limestone. Thorton (1979) quoted concentration of copper up to 175ppm in the soils present in India. It occurs naturally in many minerals such as cuprite (Cu_2O), Malachite [$CuCO_3$.Cu (OH) $_2$] Azurite [2$CuCO_3$. Cu (OH) $_2$], Chalcopyrite ($CuFeS_2$), chalcosite (Cu_2S) and Bornite (Cu_5FeS_2). Nriagu (1989) estimated mean worldwide emissions of copper from natural source and are as follows, wind blooms dust, 0.9-15 X 103 tonnes; forest fires 0.1-7.5 X 103 tonnes volcanic particles 0.9-18X103 tonnes; biogenic processes 0.1-6.4X103 tonnes; , sea salt spray 0.2-6.9X103 tonnes. The concentrations of trace metal (Copper and Zinc) were recorded for four seasons. The trace metal Copper concentration ranges from 12.8 ppm to 34.16 ppm. The minimum concentration of copper was recorded during the pre-monsoon-04 at station-1, whereas the maximum concentration was recorded during the post-monsoon at station-2.

The concentration by organic matter with reference to the copper concentration showed greater of correlation (Fig-2-4), which indicates the specific adsorption of copper on the surfaces of organic matter. Regarding the station wise variations of copper, a relatively low level of concentration was observed at station-1 and 3, when compared with the station-2. This could be due to the competitive replacement of trace metals by the alkaline earth metals (calcium and magnesium), which are abundant in the seawater. Boury (1983) stated that the increase in pH in saline water enhance the absorptive of sediments for trace metals. In the present study the organic matter and copper concentration had good amount of correlation between the distribution patterns. Precipitates which has the affinity to scavenge metals, as they pass through the water reroute to the sediments (Ramkumar, 1995).

Zinc

The distribution and transportation of zinc in sediment depends upon the species of zinc present and the characteristic of the environment. pH primarily determines the solubility of zinc. At acidic pH values, zinc may be present in the aqueous phase in its ionic form. It may also form stable organic complexes. The formation of such complexes can increase the mobility and solubility of zinc.

Zinc is unlikely to be leached from soil owing to its adsorption on clay and organic matter. Acidic soils and sandy soils with a low organic content have a reduced capacity for zinc absorption. The occurrence of maximum concentration of 228.2 ppm at station-2 indicates the zinc concentration was higher in the relatively higher organic matter rich environment. The overall variations in the concentration of zinc in the sediment are visible. The zinc concentration shows some degree of correlation (Fig.5-7).

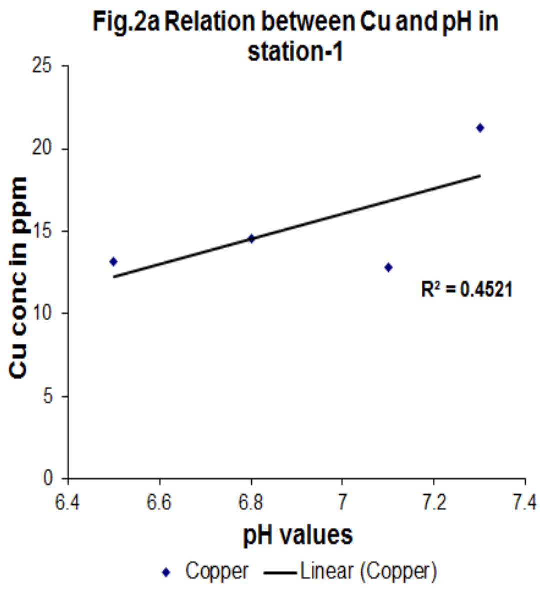
The sharp increase in salinity as the fresh water mixes with seawater would result in the precipitation and coagulation of colloidal clay particles and co precipitation of metals or adsorption on to the particles and remove considerable amount of metals from the solution. The lower concentration of zinc 39.3 ppm was recorded from station-1. . The lower concentration of zinc in the sediments possible indicating the non-detrital source is not significant in the sediments. The concentration of zinc in the reducible.

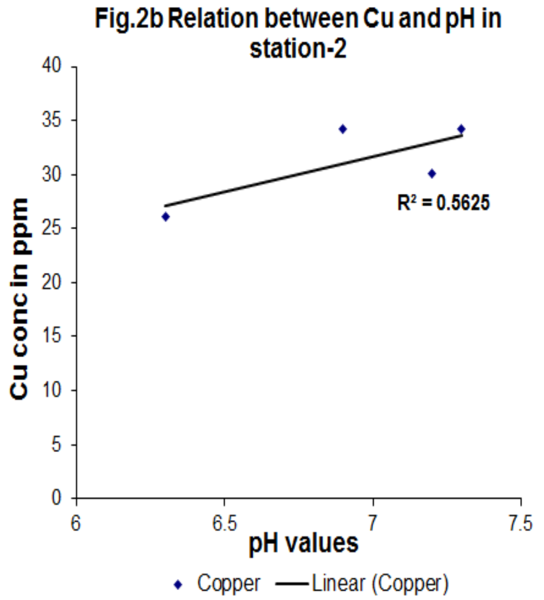
Summary and Conclusion

An attempt has been made in order to study the textural characteristic of sediments, trace metal concentration (copper & zinc), organic matter and their influence in physico-chemical parameters in three stations during different seasons. Samples were collected from 3 stations during 12 months in all the four seasons from (premonsoon-09 to summer-10). The nature of work along was divided into 2 aspects. The first part of the work was carried out in order to study the variation in textural characters of the sediments at different seasons and the second part of the work is to determine the distribution of trace metal (copper & zinc) concentration in Karaikal coast sediments.

The phi mean size of the sediment samples was in the range between 2.2φ to 2.5φ in station-1, 2.2φ to 2.58 φ in station-2, and 2.2 φ to 2.6 φ in station-3. The phi mean size was maximum (2.5 φ) in station-1 during post monsoon and minimum (2.2 φ) was during monsoon season.

The standard deviation of the data dealt the sorting characteristic of the sediment grains. Sorting nature of the sediments in Karaikal coast varied from well sorted to moderately well sorted and this may be due to the seasonal changes and the location of the sampling station.





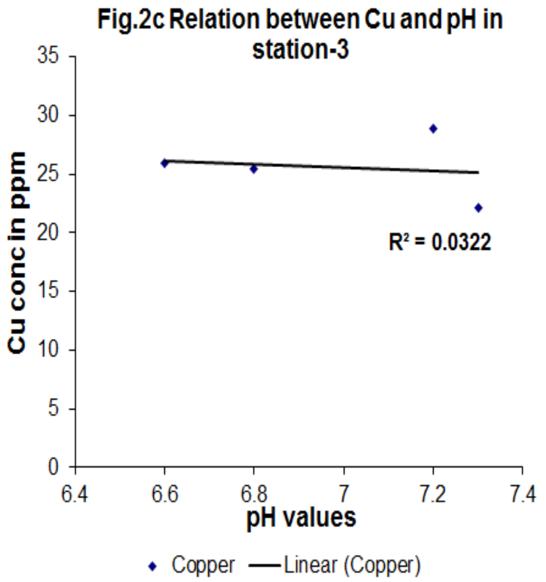


Fig.3a Relation between Cu and S % in station-1

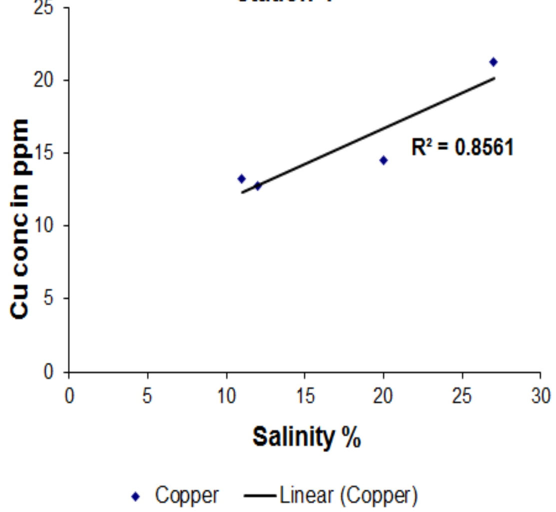


Fig.4a Relation between Cu and Om in station-1

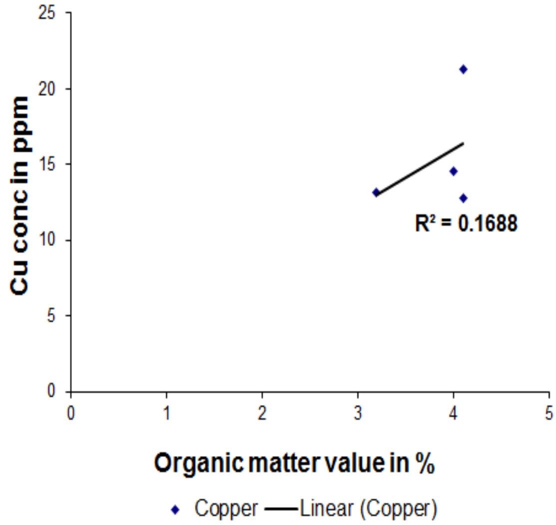


Fig.3b Relation between Cu and S% in station-2

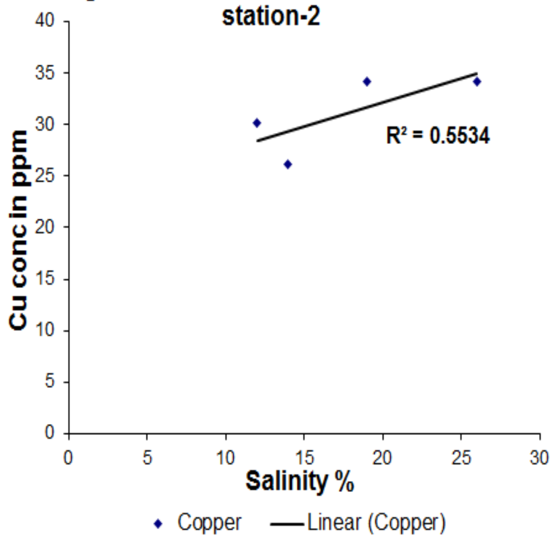


Fig.4b Relation between Cu and Om in station-2

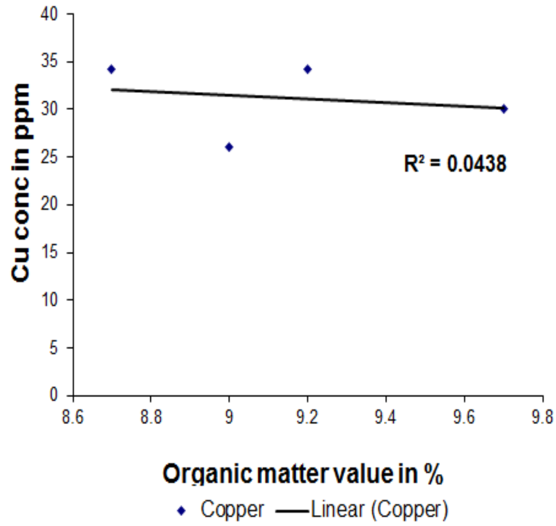


Fig.3c Relation between Cu and S% in station-3

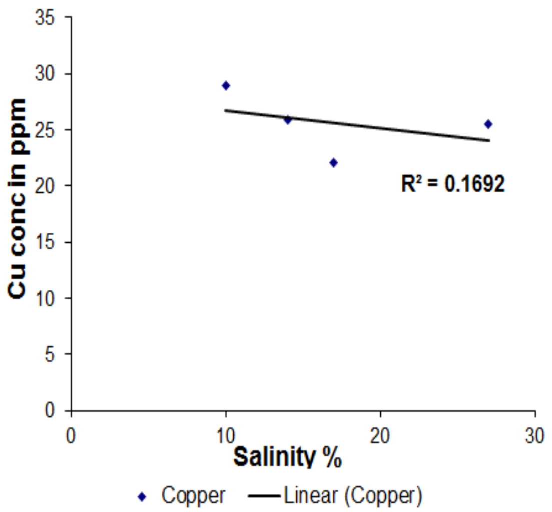


Fig.4c Relation between Cu and Om in station-3

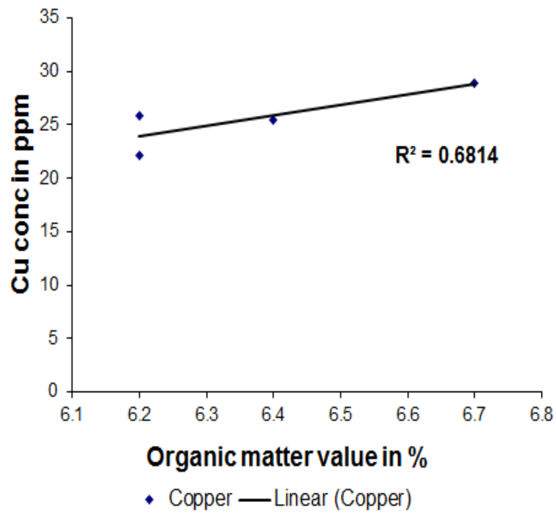


Fig.5a Relation between Zn and pH in station-1

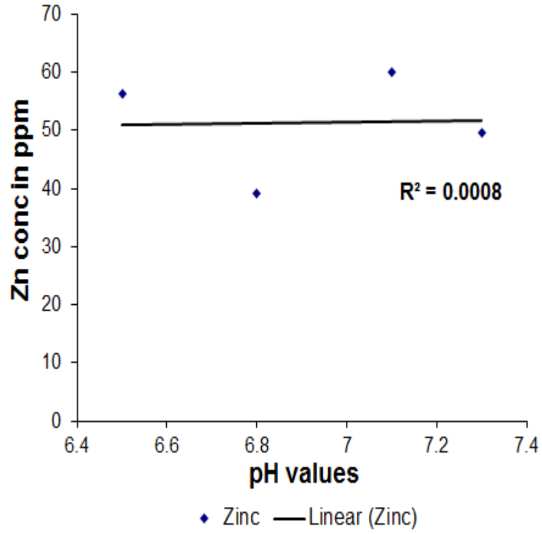


Fig.6a Relation between Zn and S% in station-1

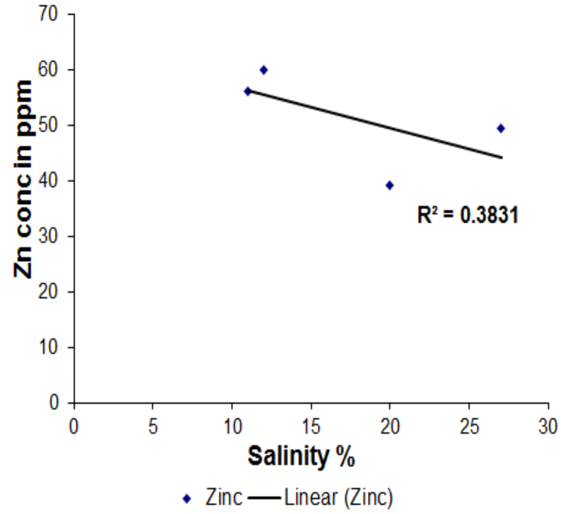


Fig.5b Relation between Zn and pH in station-2

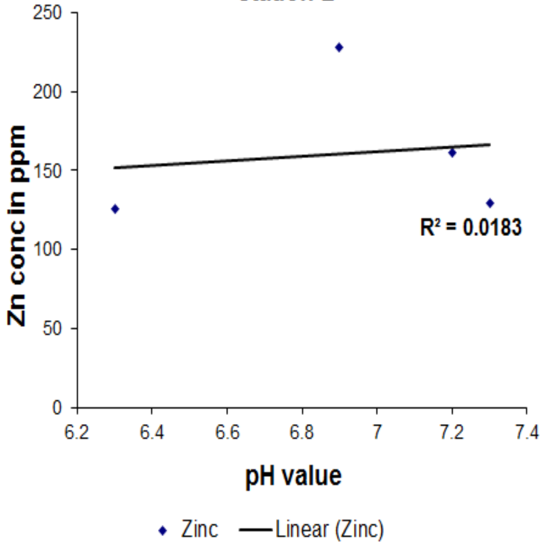


Fig.6b Relation between Zn and S% in station-2

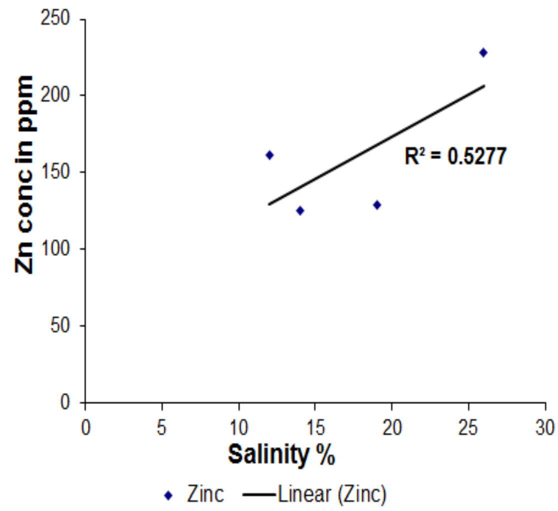


Fig.5c Relation between Zn and pH in station-3

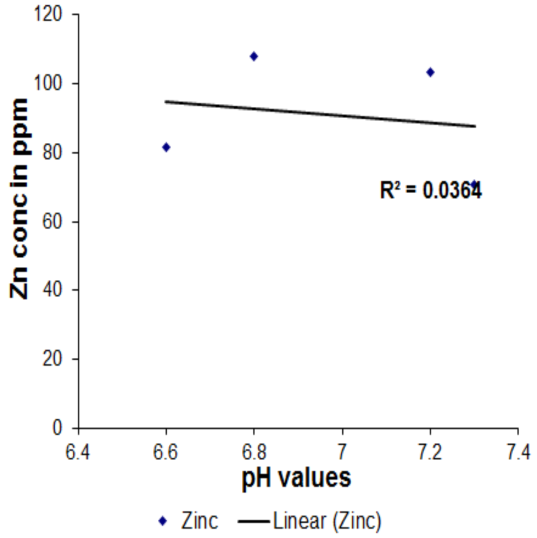


Fig.6c Relation between Zn and S% in station-3

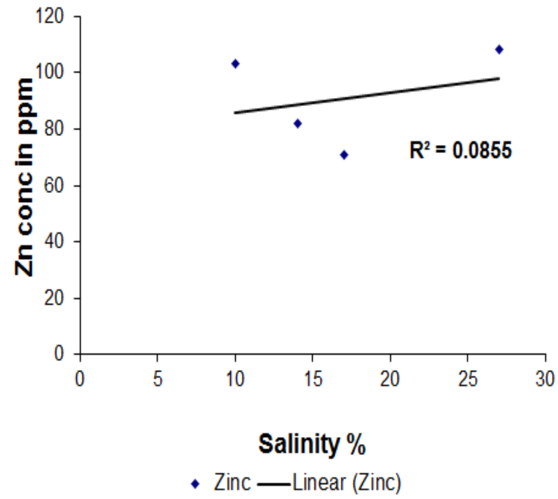


Fig.7a Relation between Zn and Om in station-1

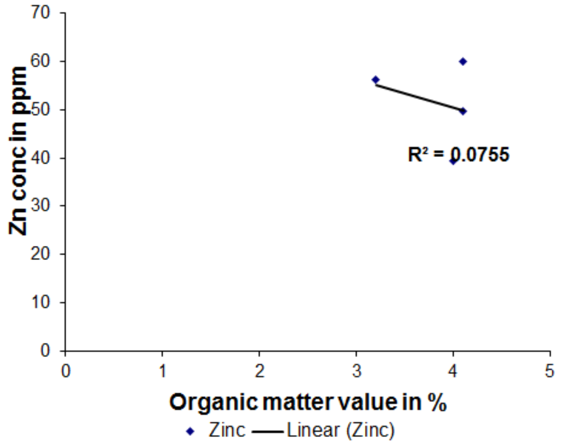


Fig.7b Relation between Zn and Om in station-2

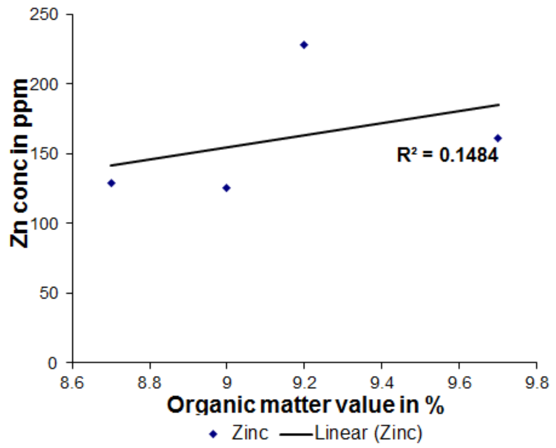
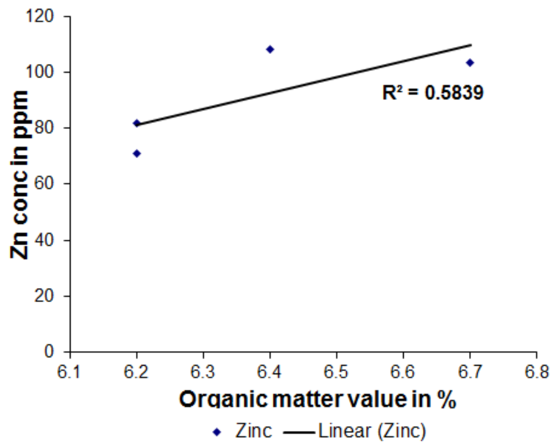


Fig.7c Relation between Zn and Om in station-3



The skewness value reflects the measure of the degree of symmetry. The skewness values ranges from nearly symmetrical to coarse skewed.

The present study shows the kurtosis ranging from mesokurtic to leptokurtic, which are used to determined peaked ness and also the function of internal sorting or distribution. The second part of the investigation was done in order to determine the concentration of trace metals (copper & zinc). Initially the distribution of organic matter was done and the concentration ranges from 3.2 % to 9.7 %. This organic matter content was maximum 9.7% was found during the pre-monsoon-03 in station-2. The minimum 3.2% was found during the monsoon-03 season in station-1.The concentration of copper was recorded maximum during post-monsoon at station-2 (34.16ppm). The higher concentration of copper in the station was mainly due to the organic matter, anthropogenic sources mainly depend upon the location of sampling station, and Zinc concentration was maximum at station-2 during summer-04 seasons. The Relatively higher concentration of zinc in this station was due to the anthropogenic activities and the location of sampling station particularly where the fine sediments get accumulated and relatively the depth was greater when compared with station-1 where the concentration of copper and zinc was low. It is also observed that the concentration of organic matter and the level of pH and salinity influence the concentration of the element to notable extent. Thus the nature of distribution of sediments during different season in different station clearly indicates the interaction and influences of Physico chemical parameter with the sediment bound trace metal concentration of copper and zinc.

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