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Trace Metal Concentration in Sediments of Tamirabarani River in Relationships with Physico Chemical Characteristics - A Study Using Gis Application

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Abstract* – A study is carried out to investigate the concentrations and distribution of trace metals to the sediments of Tamirabarani River, south east coast of India. Nearly sixteen soil samples collected from river mouth and tributaries and analyzed for traces elements show high-rate concentration of Hg (3.52-24.69µg g^{-1}) Cu(2.2-17.82µg g^{-1}), Ni(7.83-15.2µg g^{-1}), Cr(58.3-145.5µg g^{-1}), Pb(3.48-12.93µg g^{-1}), Zn(9.3-74µg g^{-1}) and Cd(1.41-4.92µg g^{-1}). The pH, EC, and TDS values reported as (8.1-9.5) (384-16250) (303-33050) .The abundances of such metals caused by the river contribution of sediments from areas with unplanned agricultural development and from the industrial, activity carried out on the riverbanks. It is concluded that in and around Mukkani area, the concentration of heavy metals is higher due to anthropogenic and industrial effluent in Tamirabarani River.

Keywords: Sediments, Trace elements, Tributaries, spatial distribution, Tamirabarani River

I. INTRODUCTION

It has long been known that, in the right concentrations, many metals are essential to life and ecosystems (Morgan, J.J. and Stumm, W.1964, Butt, E.M et. al 1964, Yunice, A.A., Perry, E.F., and Perry, H.M 1968). Chronic low exposures to metals can lead to severe environmental and health effects. Similarly, in excess, these same metals can be poisonous (Handovsky, H, 1926, Lamb, R1964, Wahlberg, J.E 1965, Hecker, L.H et. al 1974, Nriagu, J.O 1988). The main metal threats are associated with heavy metals such as lead, arsenic, cadmium, and mercury. Unlike many organic pollutants, which eventually degrade to carbon dioxide and water, heavy metals will tend to accumulate in the environment, especially in lake, estuarine, or marine sediments (Long E.R et. al 1995). Heavy metals are closely connected with environmental deterioration and the quality of human life, and thus have stimulated concern all over the world. More and more countries have signed treaties to monitor and reduce heavy-metal pollution (OECD, 1996). Moreover, this field of research has been receiving increasing scientific attention due to its negative effects on life (Nriagu, J.O, 1988, Long, E.R, 1995, Abernathy, C.O 1999, Boening, D.W 2000).The trace element in water and biota indicates the presences of natural or anthropogenic contamination. In a coastal ecosystem, the environmental quality is an issue of growing international attention (Forstner, 1983). The main sources of metals in an oceanic system are the weathering of soil, rock and anthropogenic activities. In an aquatic ecosystem, the nearly 99% of pollutants are biodegradable and are settled in sediments. To estimate the pollution index of the preservation of organic matter in fine grained, which can lead to trace metal enrichment by increasing absorptive capacity of sediments (Alberic et al, 2000, Bryan and Lang stone1992, Bubb and Lester 1994). However, trace elements need not necessarily to stick to the sediments as recycling and can occur by biological, chemical, and physical process (Adams et al., 1992; Rees et al., 1996; Das et al., 1995; Lee et al., 2003).

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II. MATERIALS AND METHODS STUDY AREA

The study area is along the coastal region associated with Tamirabarani river discharge area, which falls in the part of Thirunelveli and Thoothukudi districts, east coast of Tamilnadu state, India (Fig.1). It lies in the top sheet Nos.58/G, H and 58 L/2 (scale1,250,000) published by survey of India and located in between 8˚25N & 9˚10N latitudes &77˚ 10 E &78˚ 15'E longitudes (Fig.2). Tamirabarani River originates from western ghat hills in the western part within the study area and confluences in the East coast of Bay of Bengal. The study area is blessed with deltaic system with different functioning and inactive distributaries (Fig.3). Western part is dominated by active river and tide dominated distributaries are along the coast (Magesh et. al 2011).

The geology of the study area is occupied by three districts geological formations namely i) Archean, ii) Tertiary, iii) Recent to sub recent, which gives the details of the geological formations and the distribution of the rock types present in the basin.

The Archean formations comprised 90% of the aerial distribution of rock's type in the catchment, which consists of Aeolian, Gneiss, Pyroxene-Granulite, Fluvial, Fluvial marine, Garnet-Biotite-Gneiss, Hornblende, Biotite-Gneiss charnockites, calc gneisses, calc granulites, crystalline limestones and quartzite. The coastal belt is occupied by tertiary formations and recent sediments, which occur in the form of a narrow zone parallel to the coastline with the thickness increasing towards the shore (Kumarasamy 2010, Balasubramanian et al 1985). (Fig.4).

III. SEDIMENTS SAMPLING AND ANALYSIS

Nearly sixteen sediment samples collected at the river mouth and tributaries. Each sampling location identified and recorded using a hand-held GPS (Magellan). Physical parameters were determined in the field using a portable multi parameter kit PC Tester 35(Multi parameter). Sub-surface sediment's sample collected for geochemical analysis packed in thick polyethylene bags. In the laboratory, the collected samples were deep frozen at -4^{o} to avoid soil contamination and dried in a hot-air oven at 40^{o}C before crushed to powder using agate mortar (Shetye et al., 2009). The samples subjected to analyze trace metals using the AAS (Elico) method by using a series of solution over the range 2-10mg/l.

GIS- Analysis

The geospatial distribution of trace element was accomplished by a spatial analysis component in Arc GIS. Analysis sample is attributed to Arc GIS 9.1 by input data to make a spatial distribution graph from the low and higher values from the analytical results of the sediment's samples. µg

IV. RESULTS AND DISCUSSION

The physical parameter's pH, EC, and TDS values of the study area range from (8.1-9.5) (384-16250) (303-33050) (Table.1).The calculated values of trace elements like (Hg, Cu, Ni, Cr, Pb, Zn, and Cd) in the sediments samples are shown in (Table 2). The high value and low value are presented by elements such as Mercury (3.52-24.69µg g^{-1}), Copper (2.2-17.82µg g^{-1}), Nickel (7.83-15.2µg g^{-1}), Chromium (58.3-145.5µg g^{-1}), Lead (3.48-12.93µg g^{-1}), Zinc (9.3-74µg g^{-1}) and Cadmium (1.41-4.92µg g^{-1}). The fluctuation in values is movement of sea water in shore sediments and abundance of metals in the sediments is expected to reflect the long-term exposure of the sediments, due to various anthropogenic detection, including the nearby chemical plant and industries.

Physical parameters of sediment samples

pH

pH is the degree the intensity of acidity or alkalinity and measures the concentration of hydrogen ions. The pH of the water samples varied from 8.1- 9.5 at different times and the result disclose that the pH value was not within the desirable limit of BIS and WHO standards (Palanichamy S. and A.Rajendran, 2000). A spatial distribution model is prepared based on the maximum and minimum pH values; it shows that nearly seven samples fall in minimum category, and nine samples goes with maximum values (Fig.5). River waters with a pH of 5.5 and below are particularly a risk (Sulochana, B., and K. Muniyandi, 2005). Basically, the pH was determined by the amount of dissolved carbon dioxide, which forms carbonic acid in water (Sudaramanickam et. al, 2008, Soundarapandian, et. al. 2009). The pH of ground water can also be lowered by organic acids from decaying vegetation and the dissolution of sulfide minerals (Horvath, D.J. 1976). Usually alkaline pH is considered to be good for promoting high primary productivity. However, the present value shows more congenial conditions for earliest production. Natural waters with slight seasonal variations and sudden change would indicate industrial pollution. Further, considerably acidic or greatly alkaline waters are undesirable because of corrosion hazards and possible difficulties in treatment. The pH was considerably slightly higher in Tamirabarani river water, which may be due to greater input of effluents from different types of industries located in and around the study area.

EC

Conductivity is the measure of capacity of a substance or solution to conduct electric current. Conductivity is reciprocal of the resistance and in this study, electrical conductivity values ranged from 468-16250 at different times over the study area. EC values indicate the presence of more salts in river water as suggested by (Dhembare, A.J., B.S.Gungal and Pondhe, G.M. 2002). Spatial distribution map is constructed and classified as low, medium and high. Based on the values remarking is done, which show low values in location of 1,6,11,15,16, medium value is found in 4,7,10,17, and high value is recorded in 3,7,8,9,13,14 (Fig.7). EC values are good indicators of the relative difference in water quality between distinct aquifers (Rashid, A.K. 1982). It was related to TDS content, and its value becomes higher than the increase to the degree of pollution.

TDS

TDS indicates the total amount of inorganic chemicals dissolved in water samples. It suggested that water with a hardness of 50 ppm was considered to be soft; however, a hardness of 300 ppm was admissible for domestic use, whereas it should be 2 to 80 ppm for boiler feeders, and an upper limit of 150 ppm was usually recommended for agriculture. WHO and ISI permitted limit for total hardness of water is 150 mg L^{-1} (Trivedy, R.K. and P.K. Goel, 1984). Desirable limit of 300 mg L^{-1} suggested by (Abdullah and Musta. 1999). Spatial distribution map is constructed and classified as low, medium and high. Based on the classification low value is found at 1,5,6,11,15,16, medium value at 4,7,10, and high value noted at 3,8,9,12,13,14,17 (Fig.7). According to Mahesh Kumar and Prabhahar 2012 the values between 150 and 300 mg L^{-1} of TH in water was hard, and if TH greater than 300 mg L^{-1} it is very hard. In this study area observed TDS ranges between (303-33050) it’s too high due to saline water intrusion.

Trace metal concentration of sediment samples:

Mercury

Mercury is a metal which is liquid at normal temperatures and pressures. Mercury also forms organo metallic compounds, some of which have found industrial and agricultural use. This organo metallic compounds are stable, although some are readily broken down by living organisms, while others are not readily biodegraded.

The burning of fossil fuels is a source of mercury. The chloralkali industry, the wood pulping industry release significant amounts of mercury. Although the use of mercury is decreasing, high concentrations of the metal are still present in sediments associated with the industrial applications of mercury. Mercury concentration in sediments of study area shows a maximum value of 25.69 μ g-1 and minimum of 3.52μg g^{-1}. This is more than the permissible limits as prescribed by Trivedy, 1990 & TNCPCB Report 1997. The higher amount of mercury in sediments may be due to the treated and untreated effluents discharges directly into the river from heavy chemical industries located on the bank of the river and sewages discharged into the river. The meager amount mercury in water and sediments is said to be toxic and harmful to the society, which can affect the total environment directly or indirectly. The spatial distribution map for mercury is constructed based on low, medium and high values location.(1,2,6,7,11,12,13,14,16), (8,9), (3,4,10,15) These shows that (Fig.8a). This higher concentration of mercury which is also been reported to affect the fragile coral reef ecosystem of Gulf Mannar.

However, local variations from these values are considerable, especially in coastal sea water and in lakes and rivers, where mercury associated with suspended material may also contribute to the total load or were near to anthropogenic sources, e.g. close to mining sites and chloralkali plants for the industrial extraction of mercury. Even though, the majority of mercury in the environment can be considered to be natural rather than the result of human activities.

Mercury exists in the environment in a variety of forms and has a complex biogeochemical cycle. The most hazardous form, methyl mercury, is produced at a relatively high rate in wetlands and newly flooded aquatic habitats. It is likely that distinct spatial variation on multiple spatial scales exists in net mercury concentration in Tamirabarani, including variation within each tidal wetland, among tidal wetlands in the same region, and among tidal wetlands in different regions.

Copper

The average concentration for Cu in sediment was computed ranging from 2.2-17.82ppm, and reported to be more than the tolerance limits for the trace metals (Trivedy, 1990 & TNCPCB Report). In general, increase Cu from the marine to the river zone is reported Sankaranarayanan and Reddy (1973). During the monsoon period, when freshwater discharge is maximum, the copper level was high and dissolved labile copper concentrations were also high both at the surface and in bottom waters (George et al. 1984). During summer, the variation in concentration may be mentioned that there is no significant relation between salinity and the copper concentration for inshore and estuarine waters (Sankaranarayanan and Reddy, 1973). Spatial distribution map is built and classified as low, medium and high. The low-value sector is marked in 1, 2,3,4,9,11,15,16, medium value one in station 10 and high value is noted in 5,6,7,8,12,13,14 (Fig.8b). In the study are the stronger concentration of copper is due to lithogenic sources, dumping of industrial wastages and also due to un-classified anthropogenic actions. Occurrence of higher concentration of Cu in the water can also be attributed to the resulting of natural weathering of soil and discharges from industries and sewage-treatment plants (Hutchinson 1988; Romo-Kröger et al. 1994; Wu et al., 2001).

Nickel

Nickel concentration reported as 7.83-15.2ppm, and found to be more than tolerance limits. In the study area, the higher amount nickel concentration is due to lithogenic sources, industrial wastages and sometimes-anthropogenic activities. Spatial distribution map nickel in the study area is constructed and classified as low, medium and high. Based on these values, the values identified in 1,3,5,4,9,10,14,15,16, medium value in 12, and high value is noted in 2, 7, 8,11,12,13 respectively (Fig.8c). It occurs as both sulphide and oxide minerals. Nickel is a fairly toxic element, the volatile compound like nickel tetra carbonyl Ni (CO)4, which is used for the extraction of the element by the Mond process is poisonous.

V. CHROMIUM

Chromium ranges from 58.3-145.5ppm, and observed chromium concentration is very high due to lithogenic sources, industrial wastages and anthropogenic activities. Chromium is found naturally in rocks, soil, plants, and animals, including people. Spatial distribution map for chromium is constructed based on low, medium and high values. The down value marking is done in locations like 2, 4, 5, 6, 12, 13, 14, 16; medium value is identified and marked in 1, 9 and upward value is noted in 3,10,11,15, (Fig.8d). It occurs in combination of other elements as chromium salts, some of which are soluble in water. The pure metallic form rarely occurs naturally. Chromium does not evaporate, but it can be present in air as particles. Because it is an element, chromium does not degrade nor can it be destroyed. Chromium is an important element in metallurgy, and used as a constituent of stainless and in "Chrome plating" and as pigments.

Lead

Lead occurs in nature at an average crustal abundance of 16 μ g-1. Like soils in the terrestrial system, sediments are the primary sinks for lead in the aquatic environment. For deep ocean sediments, the natural average value is about 47 μ g-1 but with wide fluctuations (Craig, 1980). Lead values in bay, estuarine and other coastal sediments (marsh environments) have been much altered by man's activities. In the study area, spatial distribution map for lead is constructed and classified based on the value as low, medium and high. Low value of Pb is identified and marked in 3,5,6,7,8,9,10,14; medium value is found in location 4,11,13,16 and high value noted in 1,2,12,15 (Fig.8e). The average Pb levels in Indian River sediment is about 14 μ g-1 (Dekov et al., 1999), which is lower than the world average. The average Pb in Indian river particulates are ~51 μg g-1 (Dekov et al., 1999), which are also lower than the World River particulates of 150 μ g-1 (Martin and Meybeck, 1979). Nolting et al., (1996) observed that the low and constant Pb concentrations indicating the minor importance of anthropogenesis input from the Laptev Sea in contrast to other areas of the world as anthropogenesis inputs are considered to be the major source of elevated Pb concentrations in marine sediments (Nolting et al., 1999).

Lead concentration ranges in the study area from 3.48-12.93 µ g-1, more than the standards. It is also said that the higher concentration observed lead due to lithogenic sources, industrial wastages and sometimes anthropogenic activities. Natural sources of lead into the surface environment arise from the weathering of geological materials and emissions from the atmosphere from volcanoes, windblown dust, sea spray, biogenic material and forest fires. Lead occurs naturally in small concentrations in all rocks and soils, and lead metal is used in ammunition, as oxides in glass and ceramics and in metal casting.

Zinc

As similar to Cu, there is a general trend observed that for zinc, decreasing its concentration based on monsoon variations. Zinc can enter the aquatic environment from a number of sources, including industrial discharges, sewage effluent and runoff (Boxall et al., 2000). Zingde et al. (1976) reported that the average concentration for Zn (18.7 µg l-1) in estuarine waters around Goa. A gradual decrease of dissolved metals towards the Arabian Sea is observed (Zingde et al., 1976). This is particularly recognizable for Zn, which decreases from 20.3 µ g-1 from 6 to 7.2 µ g-1 (Zingde et al., 1976). Input of organic wastes into the estuary, which comes from municipal sewage, contributes to the Zn increase in sediments. This source also contributes to the high organic carbon content, where a maximum value of 3% was observed in the mouth region (Alagarsamy, 1991).

Zinc concentration ranges in the study area from 9.3-74 µ g-1, which is more than the tolerance limits. In the study area, the observed zinc concentration may be from industrial wastages and anthropogenic activities. Based on the analytical values a spatial distribution map for Zn is constructed and classified based on low, medium and high values. In low value marking is found in the majority of the locations in 1,2,3,4,7,12,13,16, medium value is found in 6,10,15,and high value found in11,14,(Fig.8F). Zinc is present not only in rock and soil, but also in air, water and the biosphere. Plants, animals and humans contain zinc, and this metal is used for anti corrosion coatings, roof cladding, batteries and some specialized alloys.

VI. CADMIUM

It is one of the most dangerous pollutants due to its high-potential toxic effects, and is extremely toxic, and the primary use of water high in Cd could cause adverse health effect to consumers such as renal disease and cancer (Fatoki et al. 2002 and Passos et al. 2010). The Average mean concentrations of Cd ranged from 1.41-4.92ppm in the study. Based on the observed cadmium concentration in the sediment samples of the study area, spatial distribution map for Cd is constructed based on the values and classified as low, medium and high. Low value concentration is found in locations in 3, 15, 16, medium value found in 5,6,9,10,14 and high value is noted in 1, 2, 4, 7, 8, 12, 13(Fig.8g).

The zinc concentration and accumulation in the sediments of an estuary may be due to lithogenic sources, industrial wastages or anthropogenic activities. Higher Cd concentration in the downstream is attributed to the reasons of human activities such as discharge of industrial effluents of fertilizers industries and chemical industries along the river. The probable sources of Cd in the river water are from the catchment soils and runoffs from agricultural soils. Cadmium was found as an imparity of zinc carbonate, and it does not have a definite taste or order.

VII. CONCLUSION

The identified trace metals in sediments of Tamirabarani surface sediments are moderately or strongly contaminated, to some extent, probably as a result of anthropogenetic activities provide a useful means of distinguishing between the natural and anthropogenetic sources of metals entering the river zone. It is observed that, in general, lowest metal concentrations are found during the monsoon, compared to the pre- and post-monsoon. The comparison of the metal levels in the sediments from different areas of the estuary indicated that there is a detectable anthropogenic input to the Tamirabarani estuary. The trace metals Hg, Cu, Ni, Cr, Pb, and Zn showed the influence of organic wastes from municipal sewage entering an industrial waste to the estuary. It is proposed that continuous monitoring and further studies in the area should be carried out soon to ascertain long-term effects of anthropogenic impact and to assess the effectiveness of minimizing the human activity to upgrade the marine environment in the Tamirabarani estuary on the east coast of India as the industrial and sewage activities influence the geochemical process in the estuarine systems. It is concluded that by establishing the recognized collection of bio monitors can identify the relative importance of different metal sources (e.g. water column, new sediment, old sediment) in an aquatic habitat. Global bio monitors are particularly useful for putting local metal bio availabilities into an international context.

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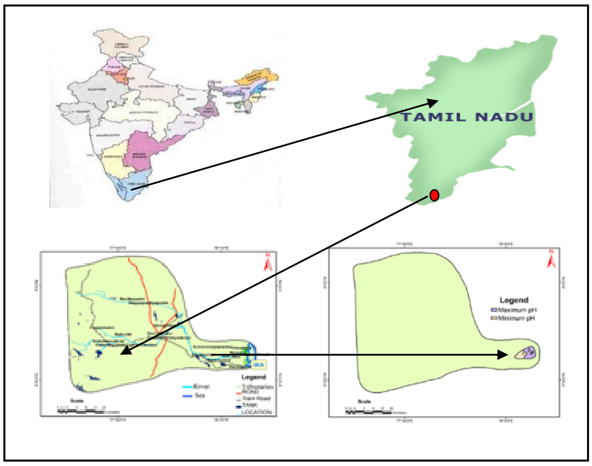

Figure1. State & District Boundary

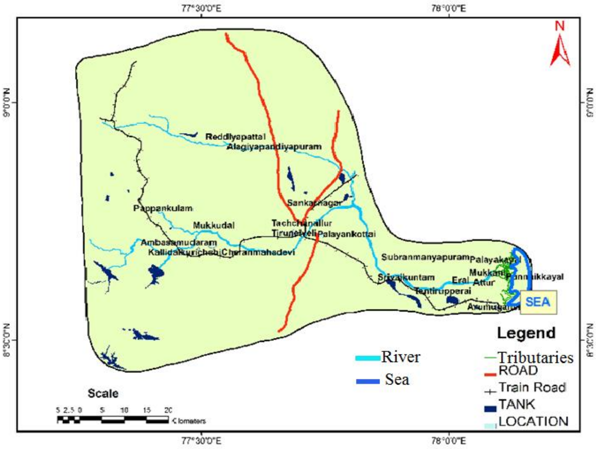

Figure2. Study area Map

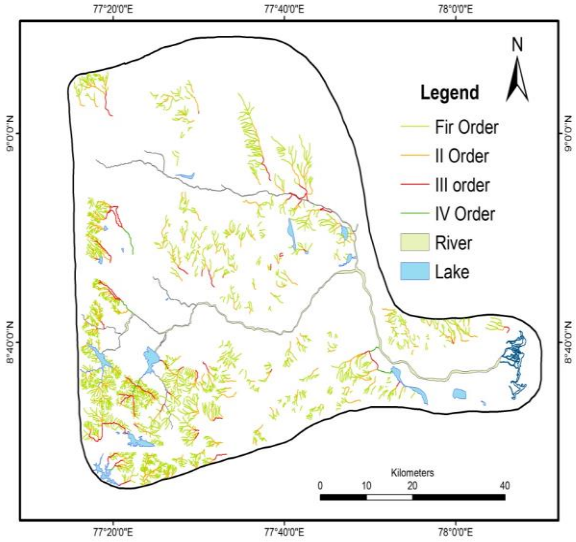

Figure3. Drainage map of study area

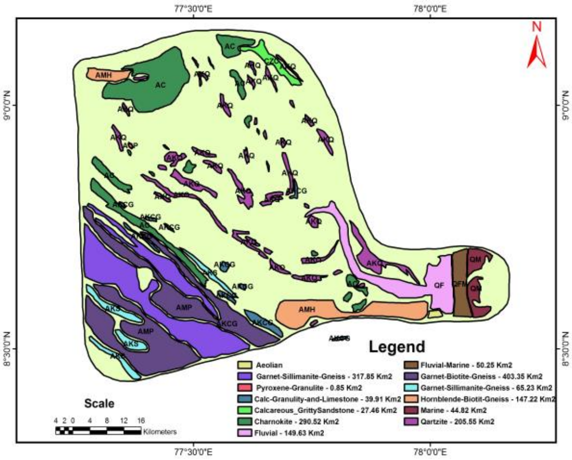

Figure4. Geology map of study area

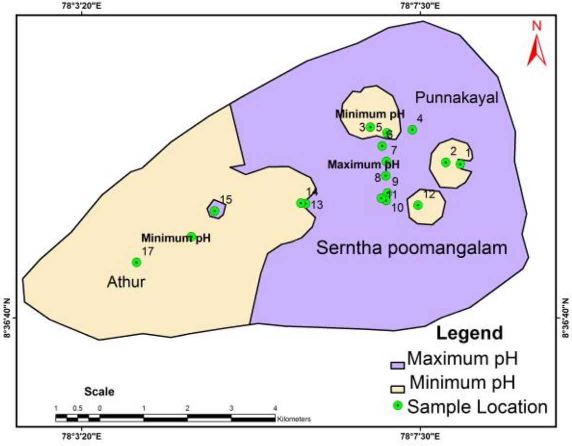

Fig.5 Spatial distribution map for pH

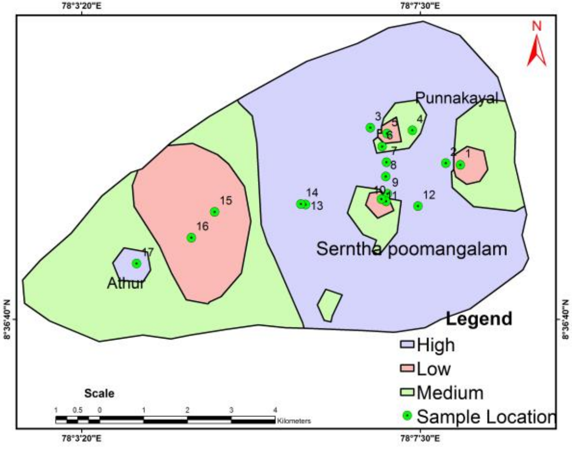

Fig.6 Spatial distribution for Ec

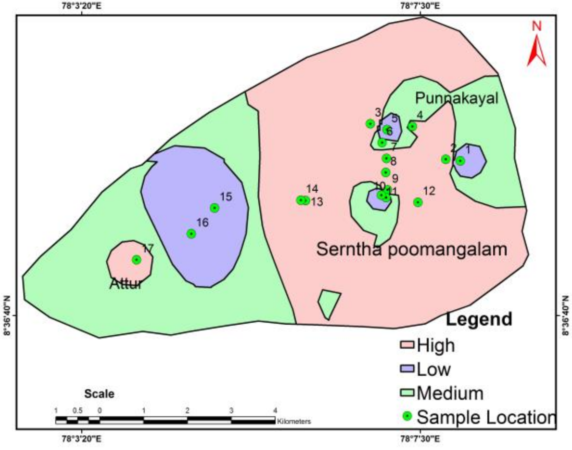

Fig.7 Spatial distribution for TDS

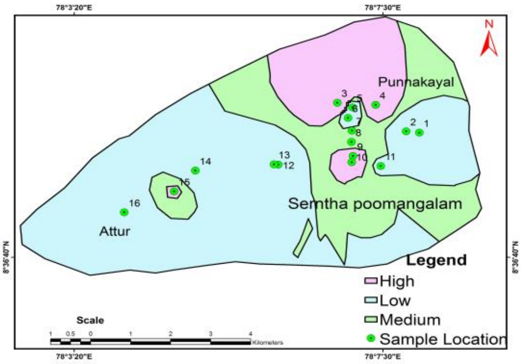

Fig.8a Spatial distribution for Mercury

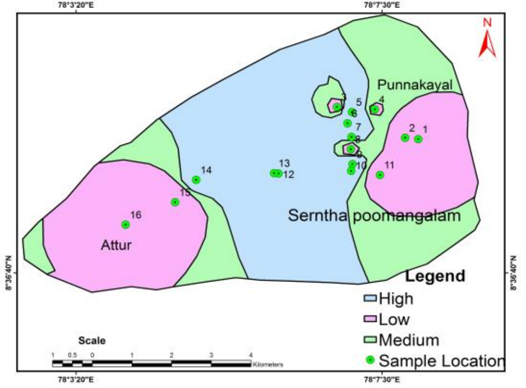

Fig.8b Spatial distribution for Copper

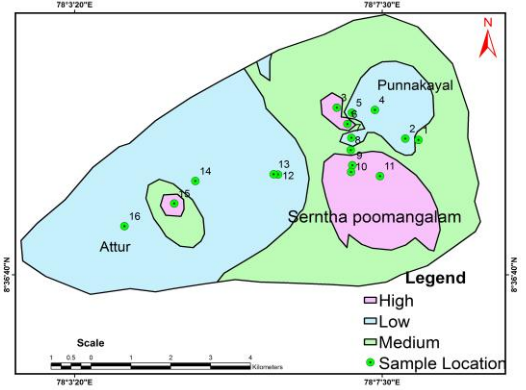

Fig.8d Spatial distribution for Chromium

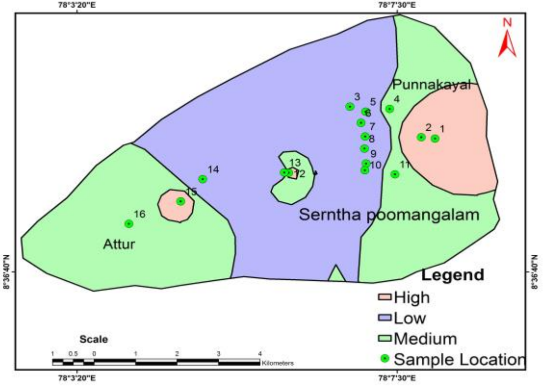

Fig.8e Spatial distribution for Lead

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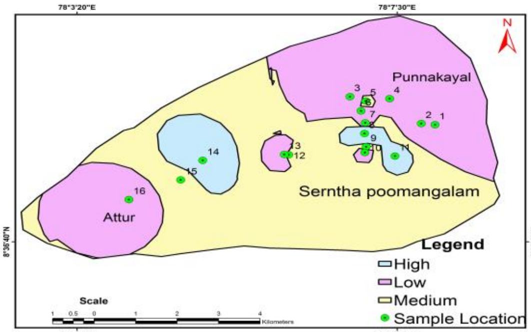

Fig.8f Spatial distribution for Zinc

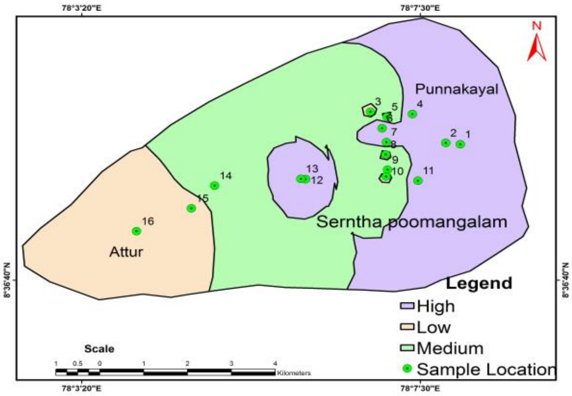

Fig.8g Spatial distribution for Cadmium

Table: 1 showing the physical parameters of sediment samples

S.No	PH	EC	TDS
1.	8.6	468	370
2.	8.4	2470	1950
3.	8.2	3120	2300
4.	8.75	1560	1230
5.	8.1	16250	33050
6.	9.5	1300	1026
7.	8.7	2275	1500
8.	9.3	2210	1745
9.	8.5	2275	1800
10.	9.4	1040	821
11.	8.8	385	303
12.	8.3	2340	1847
13.	8.85	1820	1438
14.	8.1	2210	1750
15.	8.6	559	440
16.	8.4	845	667

Table 2 Trace metal concentration in sediments Samples of study area in µg g^{-1}

S.No	Hg	Cu	Ni	Cr	Pb	Zn	Cd
1	BDL	2.2	BDL	58.6	10.43	18.6	4.21
2	BDL	3.92	7.83	BDL	12.93	9.3	4.92
3	24.69	3.74	BDL	94.5	BDL	BDL	1.42
4	15.28	5.44	BDL	BDL	5.26	20.27	2.81
5	BDL	15.85	BDL	BDL	BDL	29.17	1.45
6	BDL	13.86	15.2	112.3	BDL	24.1	4.22
7	4.85	9.78	11.8	BDL	BDL	12.66	2.88
8	4.75	2.18	BDL	58.3	BDL	74	1.41
9	9.75	15.84	BDL	120.4	3.48	30	2.11
10	9.75	7.92	BDL	103.3	BDL	16.07	1.46
11	3.52	BDL	11.93	145.5	5.36	39.74	2.88
12	BDL	17.82	12.5	BDL	8.57	30.86	2.78
13	BDL	10.85	BDL	BDL	BDL	16.1	2.9
14	BDL	10.78	BDL	BDL	BDL	47.77	2.22
15	7.67	BDL	BDL	84.4	6.96	26.63	1.48
16	BDL	3.96	BDL	BDL	5.42	17.75	BDL

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