



Environmental Geochemistry of Core Sediment in the Cochin Estuary (CE), India

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Abstract

Distribution of toxic metal in the sediment core is an important area of research for environmental impact studies. Sediment cores were collected from two prominent region (C₁ and C₂) of CE and subjected to geochemical analysis to determine distribution of toxic metals (Cd, Co, Cr, Cu and Pb), texture characteristics, total organic carbon (TOC) and CHNS. Statistical analysis was done to understand the interrelationship between the components. In the studied cores, metal contamination level was identified for Pb, Cu; Cr, in C₁ and C₂ respectively. The metal distribution depends on the granulometric factor, geogenic mineral components and anthropogenic input. Correlation analysis (CA) and Principal component (PCA) analysis also support these results.

Keywords: Toxic metal, sediment core, texture, CE.

Introduction

Environmental geochemistry deals with the chemistry of solid earth, aqueous and gaseous components and life forms to assess heavy metal contamination impact on the planet's ecosystem. It predicts areas that could be at threat from natural and anthropogenic chemical intrusion and extends in to the realm of assessing physical, chemical and biological remediation technologies. Recent works on the relationship between toxic metal and marine system have highlighted the importance of chemical behavior of metals. Heavy metals are behaved to be toxic and carcinogenic to living organisms^{1,2}. Due to their toxicity and non biodegradable nature lead to great concern in aquatic environment. Some metal ions are severe poisons, assimilated and stored in the tissues of organisms, create noticeable bad physiological effects^{3,4}. Increased industrialization in many regions generated heavy discharge of heavy metals, into water bodies or on land. Discharges from mining, electroplating, painting and printing processes, automobile battery, and petrochemical industries contains high levels of such heavy metals as copper, zinc, cadmium and lead^{5,6}.

The pollutants have low residence time in the water, so the measurements are not decisive owed to water discharge fluctuations. The same holds true for the sediments and their study plays an important role for assessing contamination. The enrichment of chemical elements in sediment by anthropogenic pollution must account for a number of geologic, minerologic, hydrologic and biological processes controlled both by internal and external factors. Geochemical investigation of sediments have recently been practice in quality exploration^{7,8} and provide a valuable documentation of information on altering natural balance⁹.

The contamination history of an area can be revealed from sediment history. Currently, a major anxiety on environmental pollution because of urbanization and industrial development emerged¹⁰. Estuarine sediment concentration of trace metals can be elevated due to high inputs from natural, as well as anthropogenic sources. Hence, the goal of environmental chemists to understand the transport and distribution of trace metals in estuaries¹¹. Sediments can incorporate and accumulate many metals added to a body of natural water. Sediment cores are a pricey and exclusive resource of immense scientific value and are extremely useful tool used in conjunction with geochemical studies. The sediment core analysis is interesting because the bottoms sediment are the records of materials which have fallen into the water body over time.

Numerous problems faced by CE include pollution due to industrial, agricultural and domestic effluents. The industries liberate nearly 260 t d⁻¹ of effluents to the system. Discharges of waste nearly containing 0.104M m³/d organic load was poured into the nearby backwaters from sixteen major industries around CE¹². The CE receives a large dose of heavy metal effluents containing heavily toxic ones. Geochemical fractions of surface sediment trace metal distribution around CE in recent years was carried out by several researcher¹³⁻¹⁸. The review of geochemical research carried out on core sediment so far on and off the west coast reveals that considerable amount of work still remains to be done with regard to geochemistry and metal pollution in these sediments. This study presents the environmental quality assessment of two sediment cores from the prominent region of CE.

Material and Methods

Two sediment cores (C₁ (N 09° 55.489', E 076° 18.370') and C₂ (N 09° 59.822', E 076° 16.030')) were manually collected in

November 2009 at different parts of the CE. The first site is well regulated by a bund (namely Thannirmukham) in order to prevent the intrusion of salt water into the paddy fields. During the monsoon season the bund remains opened. Second site (C₂) was Vallarpadam. With the advent of International Container Transshipment Terminal (ICTT) project, this area has become the backbone of the economy of the State of Kerala. It focuses on the enhancement of containerization in India, resulting in the improvement of trade and economic growth. Widespread activities like dredging and piling, along with anthropogenic inputs are carried out frequently. This zone has a perennial connection with the Arabian Sea and experiences an irregular encroachment of saline water intrusion there by making cradle grounds for diverse types of flora and fauna.

Sediment cores were sliced into segments according to the lithology and the pH (Thermo Orion 420A+ model) of the sub samples was immediately measured and then they were frozen at 4°C for further analysis. These subsamples were air dried, finely powdered and used for further chemical analysis. Texture was determined using pipette analysis by Lewis¹⁹. TOC was determined by total organic carbon (TOC) analyzer (Elementar Vario Select, Germany). In order to correct the carbon associated with tin cups samples were run with blank. Sediment standard supplied by Elementar Vario Select, Germany, were used to calibrate the TOC analyzer. The detection limit for OC is 0.06%. For metal analysis, 0.5g samples were treated with 5:1 mixture of concentrated HNO₃ and HClO₄²⁰ and concentration was analyzed by AAS (Perkin Elmer 3110) method. The analytical procedure precisions were checked using a triplicate analysis of a certified reference material (BCSS-1) from the National Research Council of Canada.

Results and Discussion

Trace metal distribution in the study area was evaluated by pH, Texture, TOC and elemental composition.

Colour and pH: C₁: Whole core exhibited blackish brown in nature. Values of pH ranged from 7 to 8.

C₂: Mixed black and grey colour from 0-36cm and uniform black colour from 36-63cm. Values of pH ranges from 7.87 at 63cm depth to 8.68 at 9cm depth and it was found to exhibited a decreasing trend with minor fluctuations from surface to bottom.

Textural Characteristics: C₁- Sand was increased to 18 c.m., decreased till 36 c.m. decreased to 42 c.m then increased to the bottom. Clay and silt increased to 24c.m, decreased to 36 c.m and intensified to the bottom. Sand content is dominated in the core. Relative textural distribution was in the order sand > clay > silt.

C₂- Sand percentage was decreased to 30c.m then increased to the bottom. Clay and silt content was increased along the core as

depth increased. Sand content was intensified in the core, the textural variation was in the order sand > clay > silt.

TOC: The amount of organic matter preserved within sediment refers to TOC. It served in sediment as a function of the amount of various sources reaching the sediment surface and the rates at which they are degraded by microbial processes during burial. The variation of TOC is given in figure 1.

C₁ -TOC values ranges from 0.566% to 0.718%. Highest at crown portion and lowest at bottom. Percentage of TOC decreased from top to bottom of the core.

C₂-Percentage of TOC ranges from 0.687% to 1.220%. Maximum was noted in middle portions and minimum in top portions of the core. TOC values increased towards bottom of the core.

CHNS: The autochthonous (produced in an estuary) and allochthonous (supplied from the sea and rivers) sources generate sediments of estuaries. To differentiate marine from terrestrial C:N ratios are often used²¹ i.e. the ratio indicates the origin of the source. If they are from a terrestrial source, the ratio would generally be >20. Since estuarine sediments incorporate a mixture of these two sources, relative changes in the C/N ratio can indicate changes in the proportions of organic carbon sources to the estuary. Information on the distribution of these elements is therefore important for the evaluation and reconstruction of past environments. In the present study C/N ratio varies from 11.88 to 14.20, averaging 12.9 for core C₁ and from 20 to 22, averaging 21 for C₂. Thus both core revealed terrestrial origin.

The ratio of total organic carbon (TOC) percentages to total sulfur (TS) percentages in sediments as an environmental indicator arised from the process of biological sulphate reduction. Under anoxic conditions dissolved sulfate is reduced to hydrogen sulfide gas, which reacts with iron minerals to form iron sulfides. These ratios reflect the importance of sulfide reduction in the decomposition and thus give a qualitative indication of the redox status of the environment of deposition. Aerobic marine sediments typically have ratios greater than 5. Marine sediments undergoing sulfate reduction under euxinic/inhospitable bottom conditions typically have this values lower than 1.5. Marine sediments undergoing sulfate reduction below an oxygenated water column typically have ratios in the range from 1.5 to 5²². On the basis of this ratio, C₁ core has the ratio in the range 0.698 to 2.981, C₂ core has the ratio in the range 0.465 to 1.226 indicates sediments in the stations was predominantly anoxic stipulation.

Percentage of elemental distributions (CHNS) in all the two sediment cores were in the order as follows; C> S>H>N.

Environmental Geochemistry of Toxic Metals: Earth's crust naturally contains metals; and as a result of erosion and

weathering of parent rocks are present in all environments. From other toxic pollutants metals are biodegradable which gave it a distinguishing face in aquatic ecosystem contamination. They accumulate and biomagnified in the food web as a major group of compounds involved in environmental pollution. The accumulation of metal contaminants in sediments can pose serious environmental problems to the surrounding areas. Trace metal contamination in sediment could affect the water quality and the bioassimilation and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implications on human health and ecosystem. Present work includes the environmental geochemistry of toxic metals – cadmium, cobalt, copper and lead in the core sediments of CE.

Worth of Cd, Co, Cr, Cu and Pb: Earth's crust contain about 0.1 ppm of Cadmium. A very large amount of cadmium is released into the environment naturally, about half of this cadmium is released into water bodies through weathering of rocks and some cadmium is released into air through forest fires and volcanoes. The rest of the cadmium is released through human activities, such as mining, extraction, and processing of copper, lead, and zinc, solid waste incineration, reprocessing of galvanized metal, and sewage sludge. Cadmium can also be found in some batteries, fertilizers, tires, and many industrial processes.

Cobalt is of relatively low abundance in the Earth's crust and in natural waters. It is essential to all animals. Most of the Earth's cobalt is in its core. Blue-green algae (cyanobacteria) and other nitrogen fixing organisms needed cobalt in the marine environment. It is not found as a free metal and is generally found in the form of ores. Cobalt is usually not mined alone, and tends to be produced as a by-product of nickel and copper mining activities.

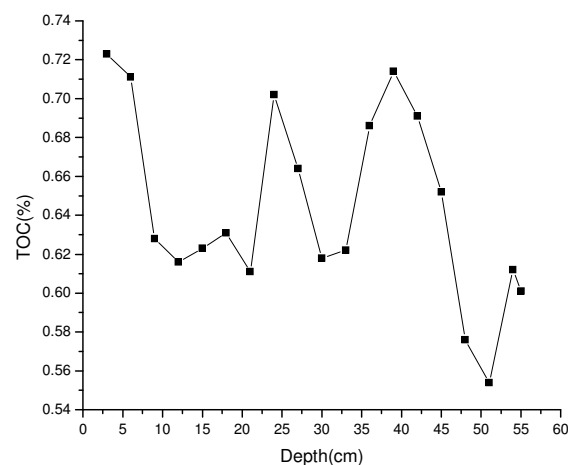
Chromium compounds are found in the environment, due to erosion of chromium-containing rocks and can be distributed by volcanic eruptions. It is the 24th most abundant element in Earth's crust with an average concentration of 100 ppm. Though widely distributed in soils and plants, chromium is rare in natural waters. The two largest sources of chromium are chemical manufacturing industries and natural gas, oil, and coal combustion. Chromium may also reach waterways via: road dust; cement-producing plants; the wearing down of asbestos brake linings from automobiles or similar asbestos sources; municipal refuse and sewage sludge incineration; automotive catalytic converter exhaust; emissions from cooling towers that use chromium compounds as rust inhibitors; waste waters from electroplating, leather tanning, and textile industries.

Copper is an essential nutrient, required by the body in very small amounts. The U.S. Environmental Protection Agency has found copper to potentially cause stomach and intestinal distress, liver and kidney damage, and anemia, depending on the level and term of exposure. Persons with certain diseases

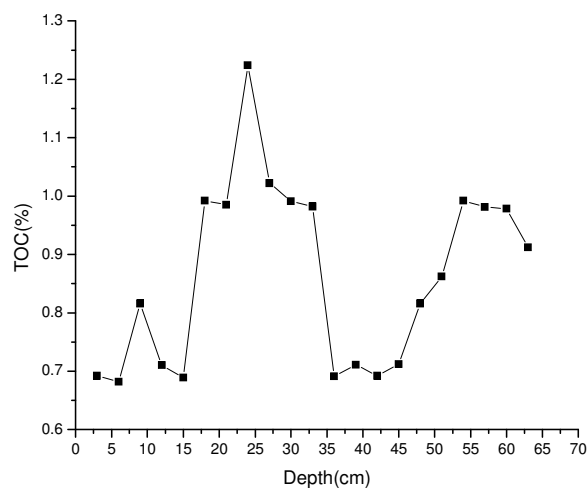
may be more sensitive than others to the effects of copper contamination. Copper releases to land and water are primarily from smelting industries. Municipal incineration may also produce copper. Copper is also widely used in household plumbing materials.

Metallic lead occurs in nature, and is rare. Lead is usually found in ore with zinc, silver and copper, and is extracted together with these metals. Seawater contains trace amounts of lead (2-30 ppt). Lead is used by ton in products such as batteries, ammunition, solder, pipes, and in building construction.

Toxic metal Distribution in CE: Distribution of toxic metal in cores C₁ and C₂ were given in figure 2 and figure 3 respectively.



(a) C₁



(b) C₂

Figure-1
Variation of TOC in C₁ and C₂ cores

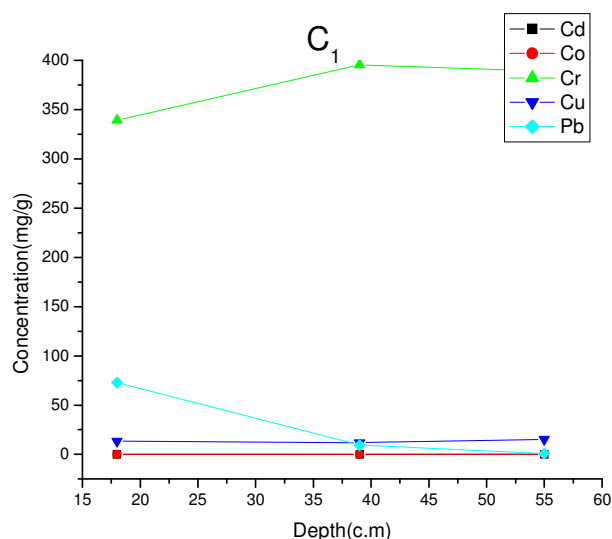


Figure-2
Variation of Toxic Metals in C₁ Core

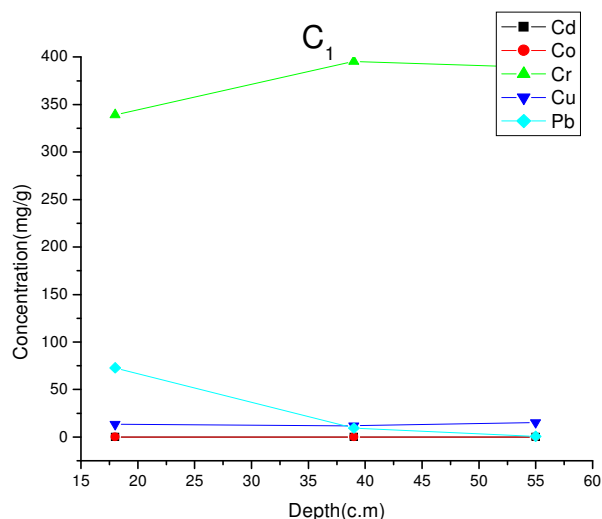


Figure-3
Variation of Toxic Metals in C₂ Core

Cd and Co were below detectable level. Cr, Cu had high concentration at bottom section and low concentration at top section of the core. Pb had diminished at the top and intensified toward the middle.

Concentration of Cd was detected only at the 21-24 section of the core. Co and Pb were below detectable level. Cr, Cu were intensified at the bottom section of 57-60 of the core. Minimum value of both occur at middle section of the core.

Both stations are situated in the high flow persistence and saline region. The total metal content is intensified in C₂ than in C₁. This reflects the heavy anthropogenic inputs in the site C₂. Some

metals show decreased trend may due to strong rectilinear current. Which maintain an effective flushing²³. On the other hand certain others show moderate level due to dynamic strong flow and anthropogenic sources.

Enrichment factor were interpreted as suggested by Birth²⁴ for metal studied with respect to natural background concentration. $EF < 1$ indicates no enrichment, $EF < 3$ is minor enrichment, $EF = 3-5$ is moderate enrichment, $EF = 5-10$ moderately severe enrichment, $EF = 10-25$ severe enrichment, $EF = 25-50$ is very severe enrichment and $EF > 50$ is extremely severe enrichment. Cores behaved as a Cd free zone. Co and Pb had no enrichment in the analysed area. Cr had severe enrichment in core C₁, moderate enrichment at C₂. Cu showed minor enrichment both cores. The enrichment was normalized relative to depth in the sediment core was expressed using anthropogenic factor. In the studied cores metal contamination level was identified for Pb, Cu; Cr, in C₁ and C₂ respectively.

Statistical Analysis: Principal Component Analysis (PCA) and correlation analysis (CA) were done to understand the interrelationship between the parameters. In core C₁, the first factor shows the strong loading of Cr, Cu along with fine fractions of the sediment shows metals are associated with fine fractions. This revealed the granulometric dependence of the metals. In the second factor metal load showed the geogenic mineral association in these sediments. Third factor again revealed the granulometric dependence with clay. The fourth factor (Pb) exposed metal purely from anthropogenic source. In C₂ core revealed only the anthropogenic input of the metals. Thus the metal distribution depend on the granulometric factor, geogenic mineral components and anthropogenic input. CA revealed no significant positive relation of clay and metal content. This indicate the anthropogenic enrichment of these metals.

Conclusion

This study reveals the distribution of Cd, Cr, Cu and Pb in the core sediment of CE. The variation of metal content in this study found as $Cr > Cu > Pb > Co = Cd$; $Cr > Cu > Cd > Co = Pb$ for C₁ and C₂ respectively. Metal contamination level was identified for Pb, Cu (C₁) and Cr (C₂). PCA and CA gave granulometric, geogenic and anthropogenic input in the study area.

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