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RESEARCH ARTICLE

BIENNIAL METAL DISCREPANCY IN THE SURFACE SEDIMENT OF COCHIN ESTUARINE SYSTEM

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ABSTRACT

This study gave the first report on the biennial metal divergence in the sediments of Cochin Estuarine system (CES). Surface sediments from 6 prominent regions of CES were sampled in 2009 and 2011 for the geochemical and environmental assessment of trace metals (Cd, Co, Cr, Cu, Pb Fe, Mg, Mn, Ni and Zn).Besides texture, total organic carbon (TOC) and CHNS were also done. The contamination and risk assessment were performed by determining geochemical indices. Comparison with sediment quality guidelines were done to assess the probability for ecotoxicological threat to the estuary. Results showed that the measured heavy metals had varied spatial distribution patterns, indicating that they had complex origins and controlling factors.

INTRODUCTION

Cochin Estuarine System (CES), one of the largest tropical estuaries of India is facing gross pollution problems including the untreated effluents from industries and domestic sectors. A number of investigations in recent years on surface sediment trace metal were carried out in CES (Shajan 2001; Balachandran et al. 2005, 2006; Renjith & Chandramohanakumar 2009; Ratheesh Kumar et al. 2010; Paneer Selvam et al.2012). The review of geochemical research has been carried out on sediment so far on and off the west coast and reveals that considerable amount of work still remains to entangle with regard to geochemistry and metal pollution in sediments. Most of the studies are based on one time or seasonal sampling during a year sample collection from areas known for environmental pollution. Though in any area in which distribution of inorganic pollutant in sediments collected with a considerable time period can provide a clue for change in the environment and such studies are limited. For a long period there were no pollution control regulations and the untreated effluents including those from heavily polluting industries were being discharged into the CES. In this context, present work attempted to provide the first detailed monograph on biennial distribution of metals in the surface sediments from the prominent regions of CES.

MATERIALS AND METHODS

Sampling

Surface sediments (top 0-5 cm) were collected from six locations of CES during November 2009 and 2011 (dry season). This was performed using a stainless steel grab sampler used repeatedly (three to five times) at each station, followed by thorough mixing of collected sediment on an aluminum tray in order to obtain a more representative sediment sample. All samples were kept in ice chest boxes on board and during transportation.

Study Area

Study area is divided into three zones viz South, Middle, and North (Fig.1)

South Zone

The zone situated in the fresh water region, originated from southern bough of Moovattupuzha. Major source of pollution is from agriculture runoff and it is far from Industrial effluents (Stations S1 and S2).

Middle Zone

This zone is well regulated by a bund (namely Thannirmukham), which was constructed in order to prevent the salt water intrusion into the paddy fields. The bund remains open during monsoon season. With the advent of ICTT project, this area has become a backbone for the economy of State of Kerala. It focuses to enhance containerization in India, resulting in improving trade and economic growth. Widespread activities like dredging, piling, along with anthropogenic inputs are intriguing 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 (Stations M1 and M2).

North Zone

This zone originates from the industrial locale of Periyar - the life line of Kerala. Large scale industries on the river bank discharge effluents directly into these waterways resulting the accumulation of varying amounts of nutrients in the Periyar River (Stations N1 and N2).

METHODS OF ANALYSIS

Texture was determined using pipette analysis by Lewis 1984. Total organic carbon (TOC) was determined using TOC analyzer.

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Metal analysis was done according to Loring and Rantala 1992, and concentration was analyzed by AAS (Perkin Elmer 3110).

RESULTS AND DISCUSSION

Grain Size, Toc and Chns

Grain size distribution was given in Fig. 2. The samples in the 2009 collection revealed mud content was found to be greater in the south and north zone of the estuary but in the next set (2011) it showed a fluctuated pathway. This may resulted due to the association of strong hydrodynamic conditions of the rivers by antropogenic activities. TOC< 5% (Alagarsamy 1991) indicate un polluted estuary. TOC values were greater than 5 in sediments of 2011 sampling revealed the polluting nature of these sediments.C/N ratios are often used to differentiate marine from terrestrial input (Redfield et al. 1963; Atkinson and Smith. 1983, Perdue and Koprivnjak. 2007), although selective degradation of the different minerals in sediments can affect the C/N ratios (Muller. 1997). Ratio lowers than 17 in order to be of nutritional use to invertebrates (Russel. 1970). In this research findings C/N ratio showed to be greater than 17 revealed allochthonous input.These sediments also undergo sulfate reduction below an oxygenated water column exhibiting TOC: TS ratios were in the range 1.5 to 5 and well corroborated by Berner and Raiswell (1983).Except middle region all others had TOC: TS values greater than 1.5 for both years of study. These results exposed the oxic nature for north - south zones and anoxic nature for middle zone.

Metal Distribution

Metal biennial distribution is given in Fig.3**.**Fe is a minor element in sea water and a major element in particulate matter and sediment. Northern and southern zone of the estuary was showing higher amount of Fe compared to the middle zone in both the year studied. This result showed the antropogenic origin of this metal through agricultuaral and industrial activities. Mg is the second most abundant cation in the aquatic system. Several physical, chemical and biological processes control the distribution of Mg. Average concentration of Mg was enriched in all zones of the estuary in the year 2009 but the concentration was diminished in 2011. Mn is a minor element in sea water and present in appreciable amount in estuarine and marine sediment. Mn react with trace metals which exist as oxyanions and forms insoluble phase. Therefore an understanding of marine chemistry of Mn will help to explain the chemical behavior of many trace elements in marine environment. Mn was greater in the southern and middle portion of the estuary than the northern region of the estuary in both years analysed. The sourcs generators are agricultural, domestic waste and antropogenic activities in this region.Ni rank the 23rd in crustal abundance. Both year investigation revealed Ni concentration is higher in the northern region of the estuary. This strongly support the industrial input of the metal. Zn is fourth among the metals in the world in annual consumption. Major sources of Zn was manufacturing, industrial and agricultural runoff. In the study area Zn was intensified in the northern part of the estuary during both years of investigation. Cd is a oxyphilic and sulphophilic element.It is obtained as a byproduct in industrial activities. In both years of study Cd concentration was abundant in the northern region of the estuary. Co is an essential element plays an important role in the biochemical reactions of life. Majour source is from industrial input justified the higher concentration at north zone of the estuary in both years. Cr serves as an important effluent in manufactuaring and industrial activities. It was found to be enriched in the middle zone of the estuary in both years. Cu in its free state widely distributed in nature and has a dominant role in biological system. In both years Cu had an intensification in northern zone of the estuary. Pb is a non essential element and is toxic in nature. In both year of study Pb concentration was intensified in all zones. All the major and minor metals identified had found to be of greater content compared to different SQGs (Table-1).

Geochemical Normalisation Methods

Enrichment Factor (EF)

Sediment collected in 2009 showed that Mg has minimal enrichment in all zones of the study area. Mn gave extremely high enrichment in the south zone and minimal enrichment in the middle and north zone. Ni revealed to be extremely high enrichment in south zone. Middle region had moderate to significant enrichment. North zone showed very high enrichment. Zn had significant enrichment in the south zone and in the remaining zones revealed to be minimal enrichment. But the sediment in 2011 Mg, Mn and Zn were revealed to be of minimal enrichment and Ni had significant enrichment. Cd, Co, Cr, Cu and Pb had extremely high enrichment in the south zone. Middle and northern zone had significant enrichment for Co, Cr and Cu. Northern zone Cd and Pb showed extremely high enrichment, Co and Cu had moderate enrichment and Cr had significant enrichment for the sediments in the year 2009.In the next set Cd showed extremely high enrichment in the southern-northern region and very high enrichment in the middle zone. Co had moderate enrichment in the southern zone , significant enrichment in middle and north zone. All the zones Cr revealed to be of minimal enrichment. Cu had extremely high enrichment in south zone and significant in middle – north region.Pb showed to be significant enrichment for south - middle region and extreme enrichment at north zone.

Contamination Factor (CF)

Metals in the study area revealed moderate contamination for Ni and low contamination for other metals. Contamination factor was high for Cd, moderate for Co and Cu, low for Cr and considerable for Pb in the study area during 2009 samplling. But for the sediment collected in 2011 showed low contamination for Cr but all the other metals had very high contamination.

Geoaccumulation Index (IGEO)

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IGEO studies in sediments collected in 2010 reveled uncontamination for Fe, Mg, Mn in all the zones of the estuary. But Ni and Zn showed moderately to heavily polluted in north and middle zone of the estuary. South zone is uncontaminated for Ni and Zn. Southern zone was moderately to heavily contaminated with Cd, moderately with Pb, and uncontaminated to moderately contaminated for Cr, Co and Cu. Middle zone revealed heavily to extremely contaminated with Cd,moderately to heavily contaminated with Pb and moderate contamination for Co, Cr and Cu. North zone showed extreme contamination for Cd. Co, Cr and Cu showed moderate contamination. Pb revealed as moderately to heavily contamination. In the sediments in 2011 Cd showed extreme contamination and all the other metals showed moderate contamination in the entire zones.

Table1 Sediment Quality Guidelines (SQGs)

SQG	LEVELS	Cd ppm	Co ppm	Cr ppm	Cu ppm	Fe %	Mg %	Mn ppm	Ni ppm	Zn ppm	Pb ppm
ELEMENTAL BACKGROUND		0.2	20	100	55	4.72	1.5%	950.0	75.0	70.0	12.5
	NP	-----	-----	<25	<25	-----	-----	-----	<20	<90	<40
USEPA	MP	-----	-----	25-75	25-50	-----	-----	-----	20 - 50	90 - 200	40-60
	HP	-----	-----	>75	>50	-----	-----	-----	>50	>200	
ONTARIO MOE	LEL	0.6	-----	-----	16	-----	-----	460	16	120	31
	SEL	10	-----	-----	110	-----	-----	1110	50	820	250
NOAA SQG	ERL	1.2	-----	-----	34	-----	-----	-----	20.9	150	46.7
	ERM	9.6	-----	-----	270	-----	-----	-----	51.6	410	218
FDEP SQG	TEL	0.68	-----	-----	18.7	-----	-----	-----	15.9	124.0	30.2
	PEL	4.20	-----	-----	110	-----	-----	-----	43	271	110
CCME	IGM	0.6	-----	-----	35.7	-----	-----	-----	123	-----	35
	PEL	3.5	-----	-----	197	-----	-----	-----	315	-----	91.3
CSCR		3 - 8	-----	-----	60 - 125	-----	-----	1500-3000	100	70 - 400	100 - 400
ANZECC	ISQG	0.7	-----	52.3	18.7	-----	-----	-----	-----	124	-----
WHO			2.0	25	25	-----	-----	30	20	123	-----
CBSQG		0.99	-----	43	32	-----	-----	460	23	120	36

NP:Non Polluted ,MP: Moderately Polluted, HP: Heavily Polluted, LEL:Lowest effect level, SEL:Severe effect level, ERL:Effect range low,ERM:Effect range median,TEL:Threshold effect level,PEL:Probable effect Level,IGM:Interiem sediment Quality goals

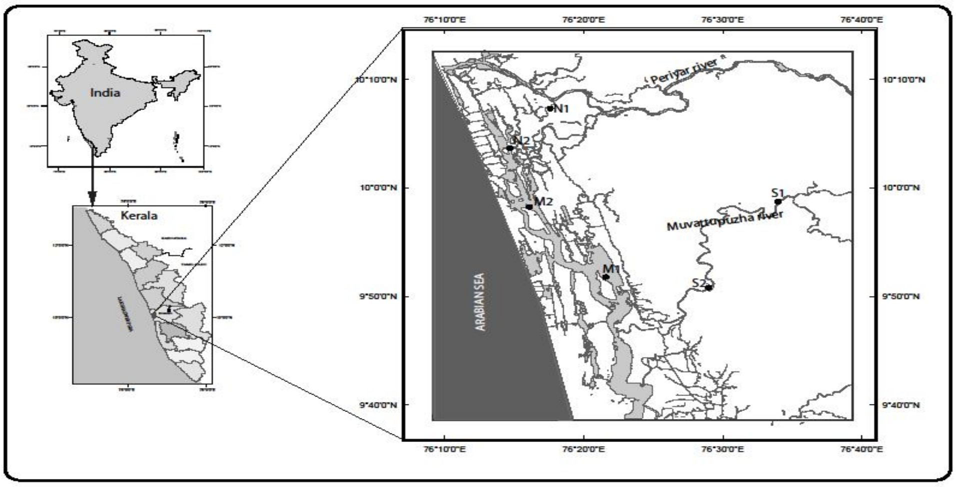
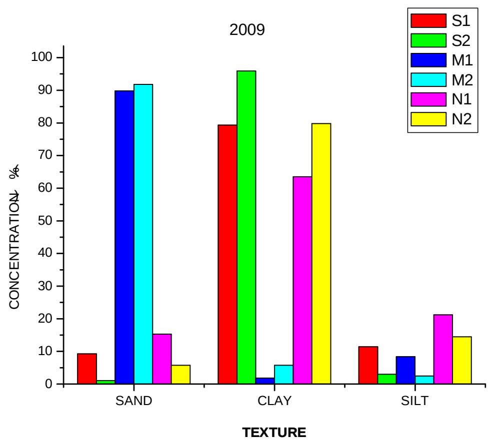


Fig 1 Map showing Study Area



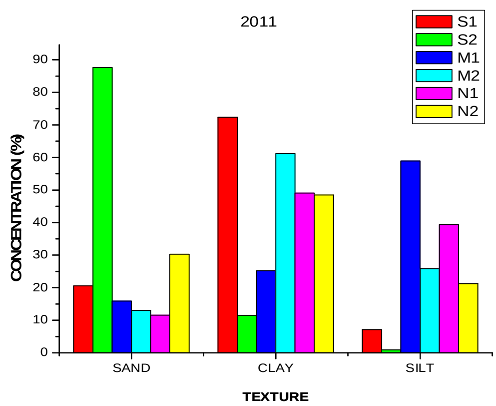


Fig 2 Binneal Grain size distribution

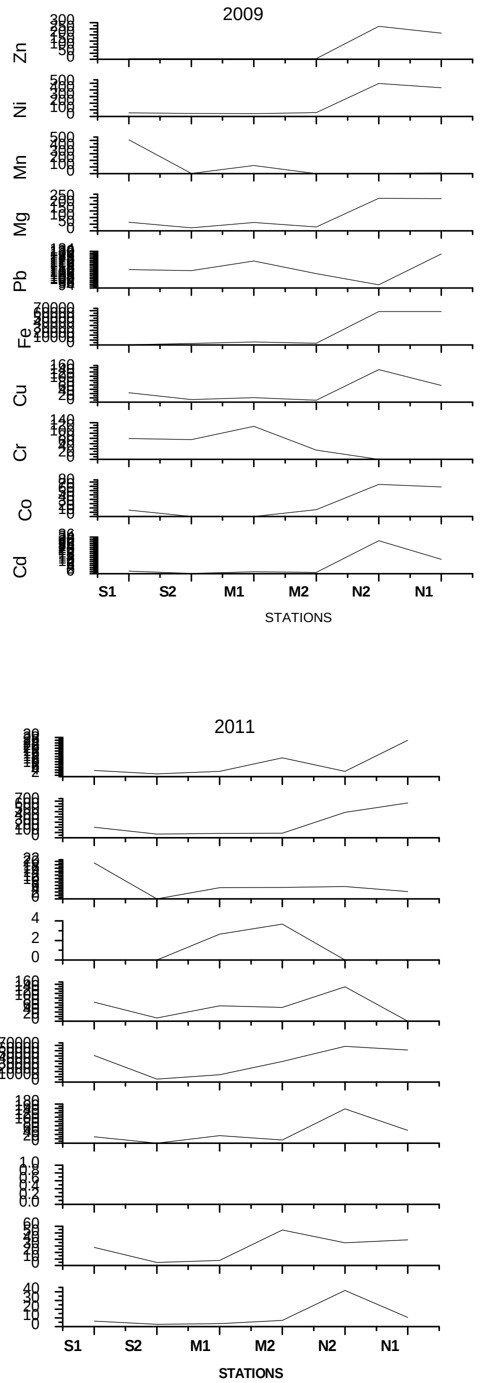


Fig 3 Binneal Metal distribution

Pollution Load Index (PLI)

In 2009 year sediment PLI revealed low contamination in the study area for major metal and severe for minor metal. But for the next set PLI was high revealing greater pollution load. On comparing the metal distribution and associated risk in biennial (2009 and 2011) revealed greater metal content was for the formal samples. Metal showed fluctuated behavior due to strong hydrodynamic and textural variation. The Principal component analysis (PCA) and Correlation Analysis (CA) also support these results.

CONCLUSION

The study showed a clear biennial metal pattern of the surface sediment in the CES. All the metals showed varying concentration and the comparison with SQG revealed heavy rate of pollution in the estuary. The factor analysis and geochemical index effectively differentiate the natural anthropogenic sources of metals. Yearly assessment exposed severe pollution in the northern region of the estuary. These give an additional data set on the past reviews on metal pollution studies. The possible sources of metal contamination in the transect was anthropogenic origin, such as agriculture runoff, discharge of industrial wastewater and municipal sewage through the estuary and adjoining coastal area. The present cram emphasizes the researchers for further analysis on metal fractions and to develop clear cut on the current pollution status. Also this suggests the need for suitable sediment quality guideline appropriate to the conditions of Kerala with support from different branches of science.

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