Toxic Metal Distribution in the Core Sediment of Cochin Estuarine System (CES)

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ABSTRACT: This article present the result from a study of two sediment cores collected from the environmentally distinct zones of CES. Accumulation status of five toxic metals: Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu) and Lead (Pb) were analyzed. Besides texture and CHNS were determined to understand the composition of the sediment. Enrichment Factor (EF) and Anthropogenic Factor (AF) were used to differentiate the typical metal sources. Metal enrichment in the cores revealed heavy load at the northern (NS_1) region compared with the southern zone (SS_1). Elevation of metal content in core NS_1 showed the industrial input. Statistical analyses were employed to understand the origin of metals in the sediment samples. Principal Component Analysis (PCA) distinguishes the two zones with different metal accumulation capacity: highest at NS_1 and lowest at SS_1. Correlation analysis revealed positive significant relation only in core NS_1, adhering to the exposition of   the intensified industrial pollution.

Key words: Toxic metal, Core sediment, CES, Enrichment Factor, Anthropogenic Factor

INTRODUCTION

Cochin Estuarine System (CES) situated at the tip of the northern Vembanad lake is a tropical positive estuarine system with its northern boundary at Azheekode and southern boundary at Thannirmukham bund. The lake has 80 km length and the width varies between 500 and 4000 m. The depth of the estuary often varies considerably, the major portion of the estuary has a depth range of 2–7 m. Water from two major rivers - Periyar and Muvattupuzha drains into this estuary. The nutrients and pollutants introduced into the estuary control to a great extent in the distribution and abundance of less tolerant species in ecologically sensitive areas in the backwaters. CES, widely regarded as one of the polluted estuaries in India (CPCB, 1996), entails contaminated freshwater inputs and discharges of effluents and partially treated sewage from many points throughout its tidally mixed zone. Recently, changes brought about in the estuary like reclamation and consequent shrinkage of the backwaters (Harikumar *et al.,*2009). Furthermore, the discharge of pollutants has made an adverse impact on the potential of aquatic ecosystems that used to support high levels of bio productivity and biodiversity.

Heavy metal concentration in the estuarine and coastal sediments is usually quiet high due to significant anthropogenic metal loading carried by tributary rivers (Muniz *et al.,* 2004; Guerra Gracia Jose & Gracia Gomez 2005). Thus sediments may serve as a metal pool that can release metals to the aquatic system and ultimately create toxic effect on the ecosystem due to bioaccumulation and persistent nature (Graham-Evans *et al.,* 2003; Mc Cready *et al.,* 2006). In recent years, increasing attention was given in the level of heavy metals in the sediment band (Carral *et al.,* 1992, 1995; Carballeira *et al.,* 1997; Harikumar *et al.,* 2009; Ratheesh Kumar *et al.,* 2010; Paneer Selvam *et al.,* 2012).

Geochemical study of core sediment is a helpful tool in the assessment of pollution settled in the aquatic systems. For a long period there were no pollution control regulation in the Cochin estuary, consequently partially or untreated effluents from the industries were discharged in to the water body and getting accumulated in the bottom sediment phase. Therefore the present study is to understand the characteristics of toxic metals in the core sediments of CES. Two sediment cores were collected from two prominent fresh water areas of the system. One has the industrial origin and other has domestic effluent. Toxic metal (Cd, Co, Cr, Cu, Pb) distribution, grain size

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parameters and CHNS were determined to pinpoint a clear cut idea on the quality of the CES. This is the first detailed baseline dataset on toxic metal description of the core sediment in the CES.

MATERIALS & METHODS

The study area includes the CES (Fig. 1) and systematically described into two zones the South and the North in view of the environmental variability. SS_1 comprises the sampling station situated in the fresh water region and originate from the southern bough of Muvattupuzha. Many people living aside to it consider the aquatic body as their water source for various aesthetic and domestic purposes other than drinking uses. The NS_1 station situated near the vicinity of the industrial region and originates from the locality of River Periyar, which is known as the life line of Kerala. The cores were collected during low tide by pushing a hand held PVC pipe (150-300 cm long and 6.3 cm

diameter) in November 2009 by a diver at the above mentioned zones of the CES. Water depth in the area was found to be 1.5m for both NS_1 and SS_1. The different length of the core obtained were 45 cm (SS_1) and 23 cm (NS_1). Sediment cores were sliced into 3 cm segments, transferred to plastic vessels and frozen at 4^oC till further analysis. These sub samples were air dried, finely powdered (< 63 micro meter) separated using 230 ASTM sieve and used for further chemical analysis. Texture was determined using pipette analysis by Lewis 1984. For metal analysis, 0.5g samples were treated with 5:1 mixture of concentrated HNO_3 and $HClO_4$ (Loring & Rantala 1992) and concentration was analyzed by AAS (Perkin Elmer 3110) method. Accuracy of the analytical procedure was checked using a triplicate analysis of a certified reference material (BCSS-1) from the National Research Council of Canada (Table 1).
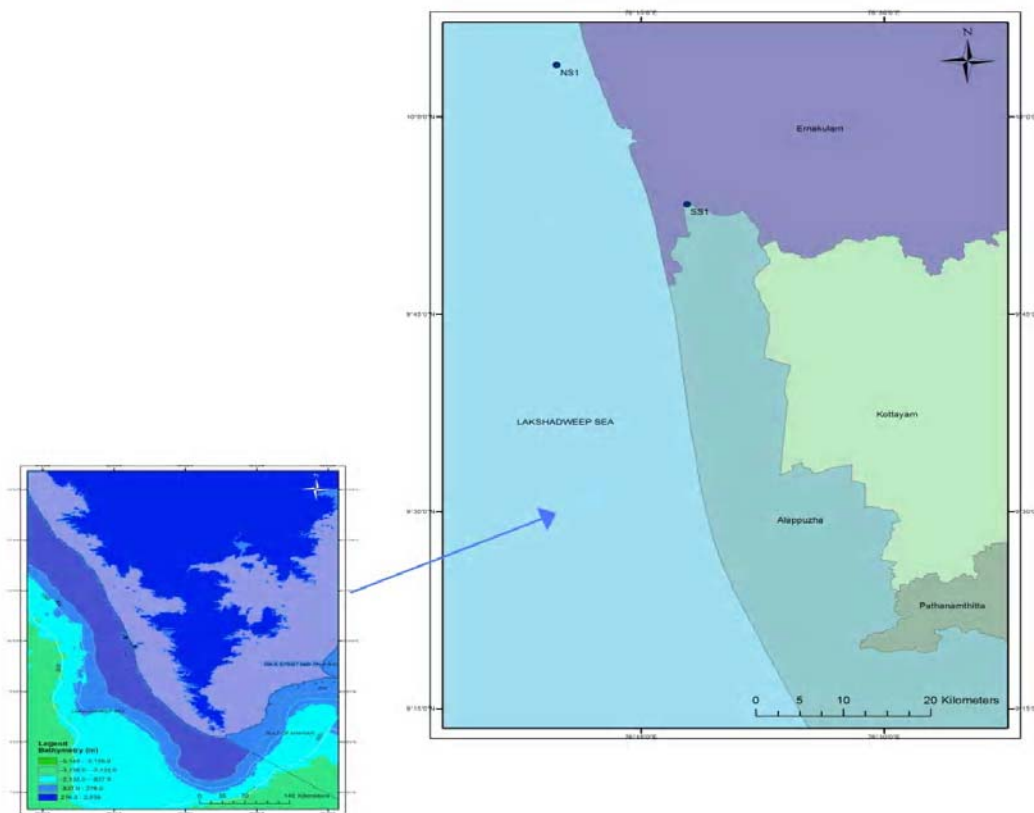
Fig. 1. Location map of sampling stations
Table 1. Comparitive values of BCSS-1 in the present study

Concentration (ppm)	Cd	Cr	Co	Cu	Pb
Metal extracted[a]	0.3	123	11.4	18.5	22.7
Metal extracted[b]	0.291	133	9.2	18.2	19.6
Accuracy (± %)	3	9	10	2	20

[a]Certified values corresponding to the total extraction of trace metals from the standard reference material BCSS-1.
[b]Values of the metals extracted from the standard reference material BCSS-1 in the present study.

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RESULTS & DISCUSSION

Increased human activities such as industrialization, coupled with over-population and raise in ambient temperature amongst other factors, have become major environmental issues in recent years. Despite, intensive agriculture and other anthropogenic activities have led to land degradation, environmental pollution and decline in crop productivity and sustainability. These adverse effects have been of great concern to human and animal health. Toxic heavy metal analyses is an important part of environmental pollution impact assessment (Narin *et al.,*1998; Loska *et al.,* 2000; Chiboski 2000; Solecki & Chibowski 2000, Ratheesh Kumar *et al.,* 2010; Paneer Selvam *et al.,* 2012 Manju P Nair & Sujatha C.H 2012; Manju P Nair *et al.,* 2012). Determination of the heavy metal contents in various environmental segments such as soil, natural waters, plants, dusts, etc (Ranjbar 1998; Macias Zamora *et al.,*1999; Soylak *et al.,* 2000) have been continuously performed by earlier researchers.

Much concern has been focused on the investigation of the total metal concentration levels in sediments of different estuarine waters. Sediments contribute a complex mixture of inorganic and organic components and are in built indicator of pollutants in the aquatic system, (Sujatha & Jacob Chacko1991; 1992; Sujatha & Jacob Chacko 1994; Soylak *et al.,*1996; Loska *et al.,* 2000; Kut *et al.,* 2000; Paneer Selvam *et al.,* 2012) , especially trace heavy metal levels of the sediment samples have been widely determined by various researchers. (Narin *et al.,* 1998; Balram *et al.,* 1999; Perezcid *et al.,*1999). Trace metals are undergoing various physico chemical processes and recycled randomly via both biological and chemical constituents within the sedimentary compartment and water column.

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; Harikumar *et al.,* 2009; Ratheesh Kumar *et al.,* 2010; Paneer Selvam *et al.,* 2012). The present research attempt was carried out to compile a systematic data set to the toxic metal distribution (Cd, Co, Cr,Cu and Pb) in the core sediments of two diverse zones in the CES (Fig. 2).

Concentration of toxic metal in core SS_1 given in Table 2. Cadmium concentration was below detectable level in this core .Cobalt concentration ranges between 0-1.49mg/g. Highest level was found at the bottom of the core. Chromium content was intensified as depth increased. It was varied from 32.98 to 94.55 mg/g. Highest concentration Cu was observed in the top layers of the core and assorted between 29.01 to 55.57 mg/g. Lead showed an increased trend towards the surface of the core. Table 3 represent concentration of toxic metal in core NS_1 .Cadmium content ranged from 2.47 to 5.29 mg/g and was decreased with increase in depth. The load of Cd is comparatively high in this core reveals that the loading of Cd is mainly through industries. Human exposures to environmental cadmium are primarily the result of fossil fuel combustion, phosphate fertilizers, natural sources, iron and steel production, cement production, nonferrous metals production and municipal solid waste incineration. Cobalt concentration was intensified towards the middle part and then diminished.It showed a variation between 0 to 12.04 mg/g. The greater Co content is due to sewage or industrial runoff. Chromium was increased to the middle then lowered. Sources of Cr in the study area were from industrial or sewage effluents. Copper was varied between 33.10 to 72.51 mg/g and
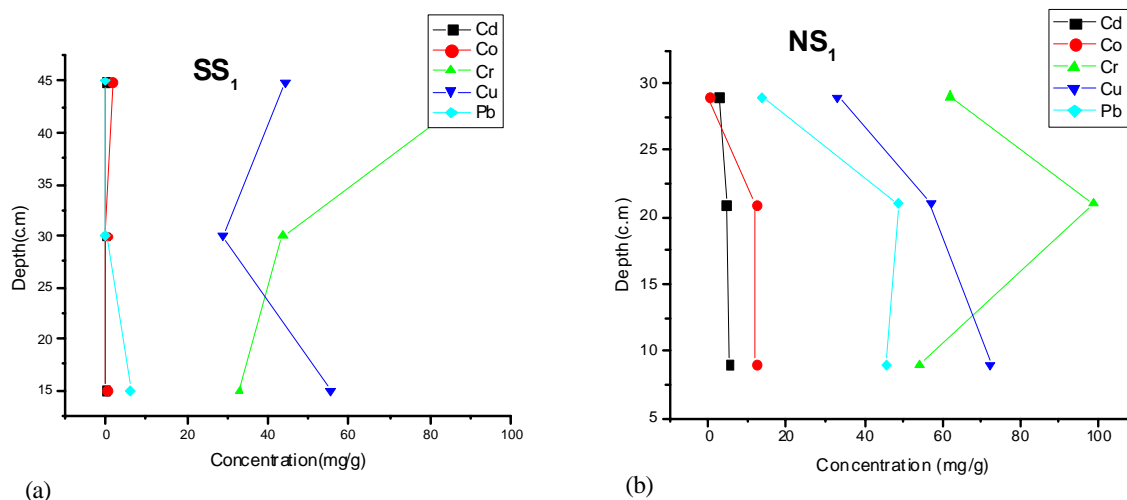

(a)   (b)

Fig. 2. Distribution of Toxic metal

showed an intensification to the top. Lead concentration was increased at the middle then lowered toward the bottom of the core NS_1. Lead content greater at NS_1 core originates mainly from industrial activity. In cores SS_1 and NS_1 the sediments were enriched with clay, so the adsorption is greater and metal content is high. SS_1 core is from the fresh water region the metal content intensified due to inputs from domestic and agricultural activities. Core NS_1 is also a fresh water area but it is situated in the industrial field .All the metals analyzed were present here; this may be from the industrial effluent.

Enrichment factor (EF) was interpreted 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. The metal analysed showed a speckled enrichment . EF distributions for cores SS_1 and NS_1 were given in Table 4 and Table 5 respectively. Cadmium showed severe enrichment in core NS_1 but the SS_1 core behaved as a "Cd free zone". Cobalt had no enrichment in the studied area. Chromium had minor enrichment, in SS_1 bottom , at NS_1 middle and bottom portion of the core

. Copper showed minor enrichment in the two cores. Lead had minor enrichment at the top and bottom and moderate enrichment in the middle,for NS_1 . In all the sites showed metal enrichment because of the antropogenic inputs and heavier load at NS_1 core due to industrial activities. 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 Cu (SS_1) and; Cd, Cu, Pb (NS_1). C/N ratio also indicated the same allothonous input in the core. Elemental distributions (CHNS) in all the four sediment cores were in the order as follows C> S>H>N.

Principal Component Analysis (PCA) and correlation analysis was done to understand the interrelationship between the parameters. The factor loading matrixes generated by using sediment variables. The first factor shows the strong loading of Cr,Cu along with fine fractions of the sediment reveals the association of metals with fine fractions. This revealed the granulametric dependence of the metals.In the second factor metal load showed the geogenic mineral association in these sediments. Second factor gave good load of Cu again revealed the geogenic source. Third factor again revealed the granulametric dependence with clay.The fourth factor (Pb) exposed

Table 2. Concentration of toxic metal in core SS_1

Sections	Cd(mg/g)	Co(mg/g)	Cr(mg/g)	Cu(mg/g)	Pb(mg/g)
Top	0	0	32.98	55.57	6.21
Middle	0	0	43.63	29.01	0
Bottom	0	1.49	94.55	44.25	0

Table 3. Concentration of toxic metal in core NS_1

Sections	Cd(mg/g)	Co(mg/g)	Cr(mg/g)	Cu(mg/g)	Pb(mg/g)
Top	5.29	11.99	54.152	72.51	45.68
Middle	4.46	12.04	98.77	56.97	48.79
Bottom	2.47	0	61.99	33.10	13.89

Table 4. Enrichment factor of toxic metal in core SS_1

Sections	Cd	Co	Cr	Cu	Pb
Top	0	0	0.61	2.08	0.53
Middle	0	0	0.85	1.13	0
Bottom	0	0.092	1.23	1.16	0

Table 5. Enrichment factor of toxic metal in core NS_1

Sections	Cd	Co	Cr	Cu	Pb
Top	21.58	0.77	0.74	1.98	2.82
Middle	19.71	0.84	1.45	1.69	3.265
Bottom	18.07	0	1.51	1.62	1.54

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Int. J. Environ. Res., 8(1):133-138,Winter 2014

metal purely from antropogenic source Third (Pb) and fourth (Co,Cr) factor showed these metals are purely from anthropogenic source. In NS_1 Core in first factor metals and clay were loaded positively revealed the grain size dependence. Second and third factor exposed anthropogenic input.Thus the metal distribution depend on the granulometric factor, geogenic mineral components and anthropogenic input. Correlation analysis revealed positive significant relation only in core NS_1, revealed the intensified pollution in the industrial area.

CONCLUSION

Sediment core collected from CES revealed variation in different geochemical components. In the studied cores metal contamination level was identified for Pb (NS_1) ; Cu (NS_1,SS_1). Greater metal content was detected in core NS_1 collected from the industrial area. PCA revealed metal load depends on granulometric factor, geogenic mineral components and anthropogenic input also conforms the domestic and industrial orgin of these components.

ACKNOWLEDGEMENTS

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