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Spatial and Temporal Variability of Trace Element Concentrations in a Tropical Lagoon, Southwest Coast of India: Environmental Implications

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ABSTRACT

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The study of space-time distribution and variations of heavy metals in the coastal environments has been extensively used in understanding the pollution levels and in the management of coastal zone. In the present study, trace metal concentrations viz. Cu, Ni, Co, Zn and Cd in sediment cores recovered from the Vembanad lake, the largest estuarine-lagoonal system on the west coast of India, were analysed to understand the pollution levels and the impact on the coastal environment. Based on the statistical analysis of the data, it is understood that the natural processes and anthropogenic activities in the Vembanad watershed region contribute to the spatial and temporal variations of trace metal concentrations. The data further reveal good correlation between Zn and Cd, Ni and Cd, Ni and Zn and Cu and mean size of the sediment. Pollution Load Index values suggest that the pollutants are enriched 2-4 times higher than the background values. The metal enrichment in sediments is due to industrial and sewage effluents.

ADDITIONAL INDEX WORDS: *Coastal sediments, heavy metals, pollution.*

INTRODUCTION

Geochemical studies of aquatic sediments have acquired great significance in the last few decades due to the growing awareness of environmental pollution and its impact on the ecosystem. Since the early 1970s, sediment-associated trace metal contaminants, their carrier phases and the natural regulating mechanisms have received wide public attention; and the research has been focused on major fluvial and coastal regimes to monitor the trace metal discharges and their behaviour.

Recent population growth and economic development are extending the problems associated with land degradation, pollution, urbanization and the effects of climate change over large areas of earth's surface giving increasing cause for concern about the state of the environment (PLANT *et al*., 2000). The monitoring of materials from anthropogenic activities is particularly important for the assessment of environmental quality and protection. Among such materials, heavy metals are a subject of major concern for their inherent toxicity (LEONARDO *et al*., 1991).

Enrichment of heavy metals, radionuclides and radioactive pollutants is noticed in sediments of coastal areas like Bombay, Goa and Cochin because of industrialization. There are proposals to set up new industries in and around of these cities. In view of this, the present study is taken up to estimate the metal concentrations in the coastal area of Cochin. Studies on the trace element distribution patterns in the sediments of Vembanad lagoon are a few (MURTY and VEERAYYA, 1981; BORAKKAR et al., 1984; MALLIK and SUCHINDHAN, 1984; PAUL and PILLAI, 1986; NAIR et al., 1990; SHIBU et al., 1990; PADMALAL et al., 1997; MANJUNATHA et al., 1998). These studies mostly confined to the spatial distribution of trace metal concentrations of surficial sediments. The present study is focused on the spatial as well as temporal variation of trace metal concentration, its controlling factors and an assessment of the pollution levels of the Vembanad lagoon sediments during the recent past.

STUDY AREA

Vembanad lagoon (popularly called Vembanad Lake) is the largest backwater system on the southwest coast of India. It runs parallel to the coast and extends from Alleppy in the south to Munambam in the north. The length of the lagoon is about 80 km and the breadth varies from a few hundred meters to about 14.5 km. The lagoon floods an area of about 244 km^2 over recent to sub-recent sediments. The Vembanad lagoon opens to the Arabian sea at two places; one at Fort Cochin (Figure 1A) and the other at Munambam (north of the study area). Seven major rivers debouch into this backwater system, five in the south and the remaining two in the north. On the southern side, a barrage/bund has been constructed near Thannermukham to prevent salt-water intrusion into the southern part of the lake during extreme droughts. The present study area is confined to the central part of the lagoon, where it receives run-off from both the sides. The study area is conspicuous with a number of industries situated in the region and receives a large amount of industrial and municipal effluents before being discharged into the sea.

HYDROGRAPHY

During the southwest monsoon season (June-September), the meteorological and oceanographic conditions along the coast differ drastically, and heavy influx of the rivers into the lake because of the intense monsoon. These conditions lead to the formation of a salt wedge near the Cochin inlet, whereas in the non-monsoon season, the river influx reduces and an increase in salinity longitudinally leading to the mixed conditions of the Vembanad lagoon (RASHEED *et al*., 1995). The distribution of temperature in the Vembanad lagoon is a function of the input of freshwater from rivers and the intrusion of saltwater from Arabian sea. The temperature of water varies between 25ºC and 31ºC. Low salinity values (0-10 x 10^{-3}) were recorded during the monsoon months. The estuarine water is diluted considerably near the Muvattupuzha river confluence in the southern part and at Periyar river mouth in the northern part during the monsoon. The salinity values range between 10 x 10^{-3} and 24 x 10^{-3} during the non-monsoon periods. The pH values of the surface and bottom waters range from 6.6 to 7.4 and a slight increase is observed seasonally up to the post-monsoon period (ANIRUDHAN, 1988).

GEOMORPHIC AND GEOLOGIC SETTING

Vembanad lagoon occupies a major portion of the central Kerala coast. The central Kerala region can be divided into three geomorphic units viz., (1) the uplifted prograding shoreline of

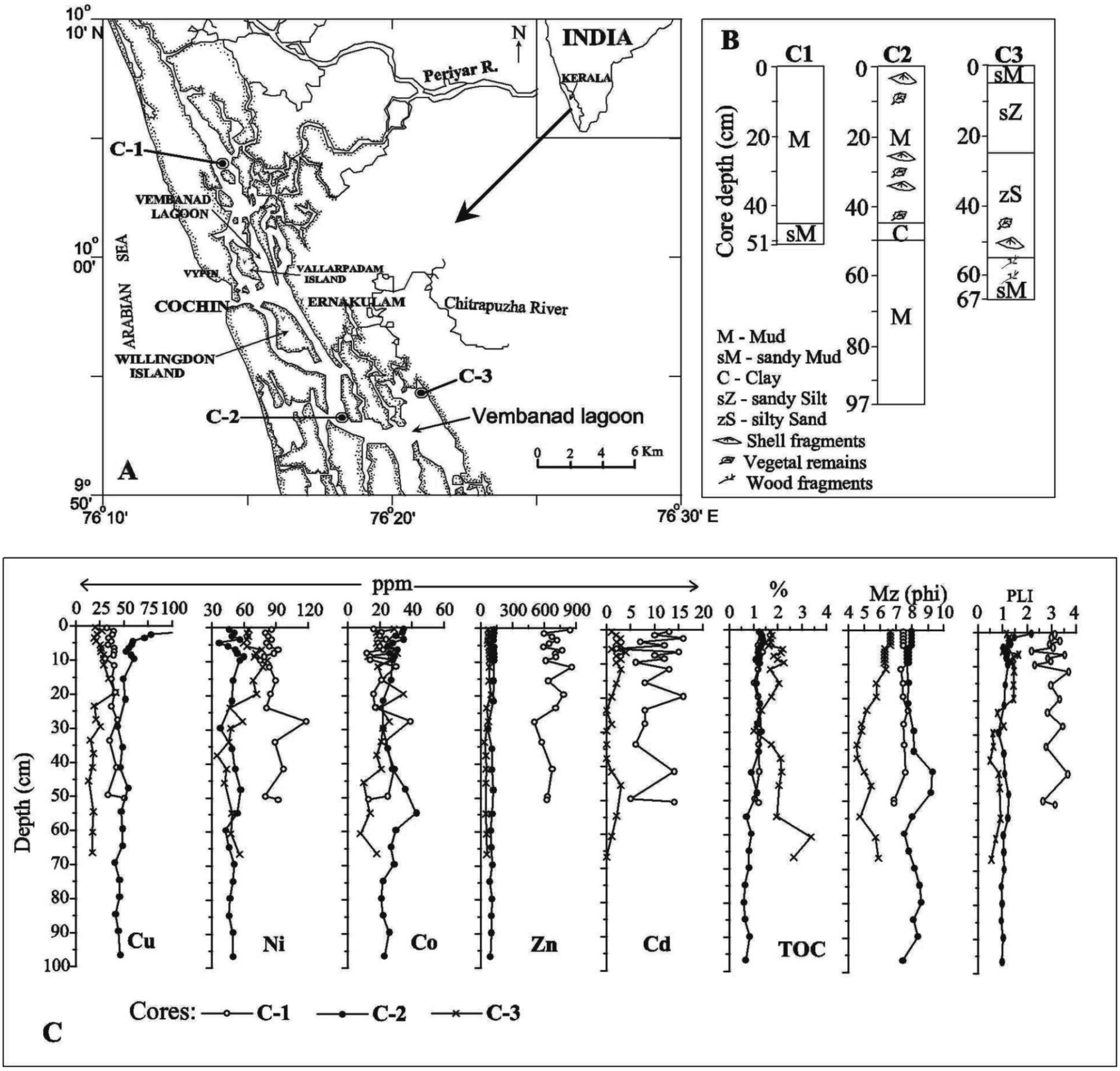

Figure 1. Map showing the study area with sample locations (A), downcore variation of texture (B) and heavy metals (C) in the sediment cores.

variable width, characterized by depositional features like spits, barrier islands and beach ridges or cheniers, (2) the zone of subsidence in the central part characterized by *yazoo drainage* zones, and (3) inland region of uplift with laterite cappings and ox-bow lakes and deserted channels as well as channel avulsion (NARAYANA *et al*., 2001). The watershed areas of the Vembanad lagoon are occupied predominantly by four major rock units. They are (1) Precambrian crystallines, (2) Tertiary sedimentaries, (3) Pleistocene laterites and (4) Recent-to-Subrecent sediments (GSI, 1995). The Precambrian crystallines are composed of mainly charnockites, khondalites, garnet-biotite gneisses, hornblende gneisses and other unclassified rocks. At many places, the Precambrian crystallines are intruded by acidic (granite and pegmatite) and basic (gabbro and dolerite) rocks. The tertiary sedimentary rocks are represented by Quilon beds and Warkalli beds, which in turn are composed of limestones, sandstones and clays. Laterites cover the Precambrian crystallines and the Tertiary sedimentaries at many places. Recent-to-Subrecent sediments (coastal alluvial and acid saline) constitute only a small portion of watershed areas of the Vembanad lagoon.

METHODS

Three sediment core samples were collected (Figure 1A) and subsampled at 1 cm interval. In total 67 samples were analyzed for texture, organic carbon and trace metal contents after drying the samples at 50ºC in a hot air oven. A part of the dried sample was used for textural analysis. The sediment texture of the cores was determined using settling tubes by pipette method (GALEHOUSE, 1971). The sand-silt-clay ratios were obtained and the lithologs were prepared (FOLK et al., 1970). Another part of the dried sample was powdered well and used for the determination of organic matter and trace metal contents. The total organic carbon (TOC) content of the samples was determined using wet oxidation method (GAUDETTE *et al*., 1974). For the trace metal analysis, 67 selected subsamples were decomposed using HF-$HClO_4$-HNO_3 acid mixture (SHAPIRO and BRANNOCK, 1962). The metal analyses were performed by atomic absorption spectrophotometry (AAS Model PE 2380). The precision and accuracy of the metal analyses were checked against the reference marine estuarine sediment, (MESS-1, NRC Canada) and we found that all the metal estimations were in agreement with the reported values (95% confidence level).

The heavy metal data, organic carbon content and mean size of the samples were subjected to statistical analysis (correlation coefficient) using the package SPSS to find out the interrelationships. Bivariate plots of metal contents were prepared and regression coefficients (r) were found out.

The Tomlinson's pollution load index (PLI) for the samples was calculated using the heavy metal data and metal concentration for the world shale average (WEDEPOHL, 1971) as the background value. The PLI is obtained as a concentration factor (CF) of each heavy metal with respect to the background value in the sediment (ANGULO, 1996). The equation applied is the following:

$$CF_{metal} = C_{metal} / C_{background}$$

$$PLI = {}^{n}\sqrt{(CF_1 \times CF_2 \times \ldots \times CF_n)}$$

The PLI represents the number of times by which the heavy metal concentrations in the sediment exceeds the background concentration, and gives a summative indication of the overall level of heavy metal toxicity in a particular sample.

RESULTS

Most of the samples texturally constitute mud, sandy mud and sandy silt (Figure 1B). In general, the mean size of the sediments varies from 4.54ϕ to 9.25ϕ. The mean size in the core sample C-1 varies from 6.87ϕ (at 49-51 cm depth) to 7.77ϕ (at 6-10 cm depth). In the core C-2, the mean size ranges from 7.39ϕ (at 96-97 cm depth) to 9.25ϕ (at 41-42 cm depth). In core C-3, the mean size range is 4.54ϕ (at 33-34 cm depth) to 6.65ϕ (at 0-5 cm depth). The cores C-1 and C-2 comprise of mostly muddy sediments. In the core C-3, the upper and lower portions are sandy mud and sandy silt; and the rest is silty sand.

The organic carbon content varies from 0.61-3.39% in the samples (Figure 1C). In general, there is not much variation in the vertical distribution of organic carbon except in core C-3. Organic carbon content shows an increasing trend downwards in the core C-3 except at 20-35 cm depth. The highest percentage (3.39%) of organic carbon is recorded at 60-61 cm depth of the core. The cores C-1 and C-2 show a similar trend of organic carbon content throughout down core. The organic carbon content of these cores ranges from 0.61-1.41%.

Spatially all the three cores show distinct variation in metal content as the core locations represent three distinct sites influenced by the different sources of effluent discharges i.e., the location of the core sample C-1 is influenced by the effluents of industries such as Fertilizers and Chemicals, Insecticides, Zinc, Rare Earths etc. on the southern limb of Periyar river. The core sample C-2 is predominantly influenced by the effluents discharged from urban sewage and the site 3, i.e. core C-3 is influenced by the Chitrapuzha river where petroliferous based industries are situated. In general, high concentrations of metals are observed in the top 20 cm of all the cores. The effluent discharge sites typically reflect the high concentration of certain metals especially in the surface portions of the cores.

TRACE METALS

Copper

Overall, the concentration of Cu in the sediments varies from 13-605 ppm with an average of 47 ppm. The highest Cu content is noticed in the top portion of the core C-2, just south of the Cochin city. Cu content is higher in the core C-2 compared to the other cores. The concentration of Cu in the core C-1 varies from 32 ppm in the surface to 50 ppm at the bottom portion of the core, where as in the core C-3 there is no much variation in its vertical distribution.

Nickel

Ni content varies from 35-118 ppm and averages about 64 ppm. The concentration of Ni is higher in the core C-1 than in the other cores. In core C-3 it varies from 35 ppm (at 37-38 cm depth) to 82 ppm (at 9-10 cm depth). The Ni content in the core C-2 varies from 37 ppm (at 4-5 cm depth) to 60 ppm (at 8-9 cm depth). It shows a similar downcore trend in the upper 20 cm of the cores C-2 and C-3.

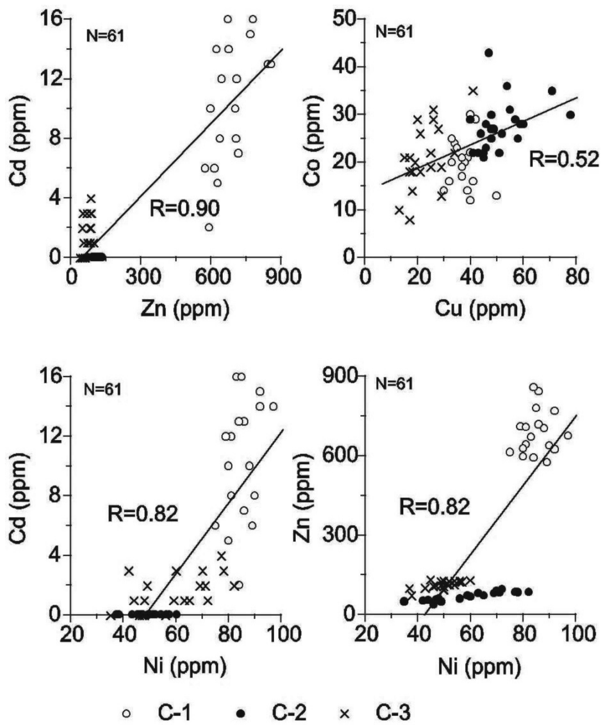

Figure 2. Scatter diagram of trace metal concentrations showing interrelationships among metals (C-1, C-2 and C-3 are core sample numbers).

Cobalt

The Co concentration in the cores varies from 8-39 ppm with an average of 24 ppm. The Co content distribution does not show much variation either laterally or vertically in the upper 40 cm of all the cores. The Co content has shown a little increase from 40 cm depth towards down core and remained stable in the lower portions of the core C-2.

Zinc

Spatially the Zn content shows marked high concentration in the northern part where the core C-1 is located. The Zn concentration varies from 39-858 ppm and the average Zn concentration is 259 ppm. The core C-1 shows higher values (508 - 858 ppm) of Zn throughout the core. In all the cores higher content of Zn is observed in the top 25 cm depth. The Zn content varies from 72-133 ppm and 39-97 ppm in the cores C-2 and C-3 respectively.

Cadmium

The highest Cd content (16 ppm) is recorded in the core C-1, whereas Cd is absent in the core C-2. In the core C-3, Cd content varies from 1-4 ppm and, however, no Cd is recorded in the middle portion of the core. There is a wide down core fluctuation of Cd values in the core C-1. Generally Cd concentration is higher in the upper 20 cm of cores C-1 and C-3.

Correlation Coefficients

Interrelationship of trace metals, organic carbon and mean size is shown in Table 1. Very good correlation is observed between Zn and Cd (0.90), Ni and Cd (0.81) and Ni and Zn (0.81). A good positive correlation is also noted between Cu and Co (0.51), and mean size (0.75). The correlation between mean size and Co, Zn, Cd is not significant.

Table 1. *Correlation coefficients of the trace elements, organic carbon and mean size of core samples (n=61).*

	Cu	Ni	Co	Zn	Cd	Mz	TOC
Cu	1.00						
Ni	-0.09	1.00					
Co	0.51	-0.16	1.00				
Zn	0.06	0.81	-0.28	1.00			
Cd	-0.07	0.81	-0.36	0.90	1.00		
Mz	0.75	0.11	0.33	0.29	0.11	1.00	
TOC	-0.57	-0.01	-0.35	-0.25	-0.07	-0.66	1.00

Scatter Diagram

Bivariate plots (Figure 2) between the heavy metals Zn and Cd, Cu and Co, Ni and Cd, and Ni and Zn show a good linear relationship. Core C-1 shows a distinct clustering of the values among Zn and Cd (R=0.90), Ni and Cd (R=0.82) and Ni and Zn (R=0.82). The scatter plot of Cu and Co exhibits a little scattering of values (R=0.52).

Pollution Load Index (PLI)

PLI values are plotted in the Figure 1C. Based on PLI values, it can be explained that the core C-1 is proximal to the potential source of contaminants, particularly the industrial effluents. It is found that in the core C-1 the PLI values vary from 2.2 to 3.7 and the pollutants are enriched 2 to 4 times higher compared to the background levels. In cores C-2 and C-3, the pollutants are found to be enriched by nearly two times in the upper 20 cm.

DISCUSSIONS

The trace metal (Cu, Zn, Ni, Co and Cd) concentrations and their down core variation in the sediment samples of the central Vembanad lagoon reveal that the metal enrichment is influenced by both the natural and anthropogenic sources. The different source rocks that occur in the hinterland region of the study area may be responsible for natural fluxes of heavy metals to the sediments in the Vembanad lagoon. The source rocks are - (1) Pre-Cambrian crystalline rocks (2) laterite deposits and (3) Cenozoic sediments adjacent to and carpeted in the lagoon. The Quaternary sediments of the central Kerala coast are rich in heavy minerals like zircon, ilmenite, rutile, monazite and amphiboles.

The potential anthropogenic sources of metal pollutants are identified as industrial and domestic wastes. The industrial sources are located near the banks of southern arm of the Periyar river, and along the Chitrapuzha river. The urban sewage is discharged into the lagoon through numerous canals. Ernakulam-Cochin is a vast urbanized area (~16,60,000 inhabitants) and second major city on the west coast of India.

The higher Zn concentration indicates potential contamination due to anthropogenic activities around Cochin (MANJUNATHA *et al*., 1998) with 70% of the chemical industries of Kerala are situated in the region. The industries are Fertilizers and Chemicals, Hindustan Insecticides, Indian Rare Earths, petroleum refineries and Zinc-Alumina ore smelting. About 260 million m^3/day of effluents from these industries are liberated into the Cochin backwaters. This eventually results in the increase of heavy metals such as Zn and Cd in the sediments. Co has been widely used in determining the source area characteristics of sedimentary rocks, because it has been considered as an immobile trace element. Enrichment of Co in sedimentary rocks is assumed to be derived from mafic sources. However, NATH *et al*. (2000) have attributed the secondary alteration for the enrichment of Co in the Vembanad lagoon sediments. Fuel terminals, oil refinery and heavy metal industry are enriching the Ni and Co metal contents. Nickel generally associated with the asphaltene component of petroleum. It is found that the metal concentrations are strongly influenced by the proximity to pollution sources.

Correlation coefficients and scatter diagrams suggest that Co and Cu content in all the cores were derived from a common source and both anthropogenic and natural fluxes equally control its distribution. Cu content is conspicuously higher in the surface sediments in the vicinity of urban sewage outfall. The Ni, Zn and Cd values show clustering in the scatter plots with their high concentrations compared to the background values indicating their distinct anthropogenic sources.

The metal enrichment in the uppermost layers of the cores is due to increased anthropogenic contamination of these metals through smelting, the burning of fossil fuels and the fabrication of metallic products and their subsequent introduction into the lagoonal environment during the recent past i.e., in the last few tens of years.

CONCLUSIONS

The industrialization, reclamation and rapid urban development during the recent period in and around Cochin area has led to the elevated metal concentrations in the lagoonal sediments. The enriched metal concentrations will have a direct bearing on the coastal ecosystem and periodic monitoring of effluent discharges is essential in the coastal zone management.

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