ACCUMULATION OF HEAVY METALS IN SEDIMENTS OF MARINE ENVIRONMENTS ALONG THE SOUTHWEST COAST OF INDIA

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Abstract

In order to estimate the rate of excessive sediment accumulation that causes navigational problems and the impacts of urban and industrial development on sediment quality, concentrations of Cu, Ni, Zn, Cr, Mn, Fe and Ca, and radioactivity levels of ^{210}Pb and ^{137}Cs have been measured in nineteen sediment cores from estuarine, lagoonal, marsh, backwater and inner shelf areas along the southwest coast of India. Sediment accumulation rates in estuarine, lagoonal, marshy areas of the Karnataka coast (ELMKC) and Cochin Backwaters (CBw) are three to six times higher than those in the adjacent inner shelf areas, consistent with the deposition of terrigenous sediments in the river-sea interaction zones. Hydrogen sulphide was detected in most of the samples; sediment colour varied from shades of gray to dark green. Sediments have lower elemental concentrations and element enrichment factors (EFs) particularly for redox sensitive elements such as Mn due to prevalence of reducing conditions in the sedimentary column. Sediments of ELMKC and CBw have a predominantly terrigenous source. They contain low Ca contents, characteristic of tropical river sediments. In contrast, a higher Ca content of inner shelf sediments off both Karnataka State (ISKS-1) and Kerala State (ISKS-2) implies the importance of additional sediment ($CaCO_3$) flux from the marine biota. Measured Cu, Ni and Zn concentrations are generally low, perhaps reflecting the pristine nature of sediments. However, higher concentrations of Cr at all stations and of Zn at CBw indicate the input of Cr enriched minerals like amphibole and pyroxene from the catchment as well as Zn from anthropogenic sources. Heavy metal accumulation rates are high in estuarine, lagoonal, marsh and backwater areas along the southwest coast of India. This is not only due to the proximity of sources, but also due to high sediment accumulation rates because of the reduction of river flow in river-sea interaction zones owing to particle aggregation and sedimentation processes.

1. INTRODUCTION

The input of river suspended matter to the coastal ocean has increased in recent years due to soil erosion, deforestation and changes in the landuse patterns. It is estimated that 65% of the 24.8 billion tons of suspended sediment added annually by rivers to the oceans is from anthropogenic source [1]. Many tropical countries like India are plagued by problems of land erosion and of high particulate matter concentration in rivers. Heavy rainfall over the west coast of India (>2000 mm/yr) and the neighbouring Western Ghats (~5000 mm/yr) [2], and drastic reduction of river flow during river-sea interactions trigger the deposition of suspended matter in nearshore areas causing problems

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for navigation. Flooding is also frequent in the lower reaches of rivers during rainy season. Although the severity of pollution has not yet reached the levels noticed in industrialized countries, marine sediments near industrial sites and cities along the west coast of India show noticeable contamination [3].

Enrichment of heavy metals, radionuclides, radioactive pollutants as fission products, hydrocarbons, fecal coliform bacteria, sulphates, etc. is noticed in sediments around major cities like Bombay, Goa, Cochin and Trivandrum [3-6]. There are proposals to double the production and the number of industries at some places along the west coast of India by the year 2002. The eastern Arabian Sea is one of the most productive seas in the world. Fisheries is the major source of food for native people and also drives the economy. Fishermen face problems of siltation in estuaries and navigational channels and fall in fish catch in nearshore water due to contaminant input from the land. The decreas in living resource in nearshore waters along the west coast of India probably reflects the increase of contaminants like organochlorine pesticides, HCHs, DDTs, aldrin, dieldrin, endrin etc. [7]

The main objectives of this study are to estimate the sediment and metal accumulation rates using ^{210}Pb and ^{137}Cs isotopes and heavy metal data respectively. This investigation was taken up in view of sedimentation processes causing navigational problems due to deforestation and soil erosion in the west-flowing river drainage basins along the south west coast of India and the impact of urban and industrial development on sediment quality.

1.1 The Study Area

The western continental shelf of India is one of the broadest in the world covering an area of 310,000 sq. km. The shelf is broad in the northern part (345 km off Bombay) and narrows down in the southern part (60 km off Cochin). The average shelf break occurs at 200m water depth. The inner shelf (<40-60 m water depth) is smooth, gentle, and blanketed by low carbonate, fine grained, organic-rich Holocene sediments. The outer shelf comprises of carbonate-rich sands of late Pleistocene age.

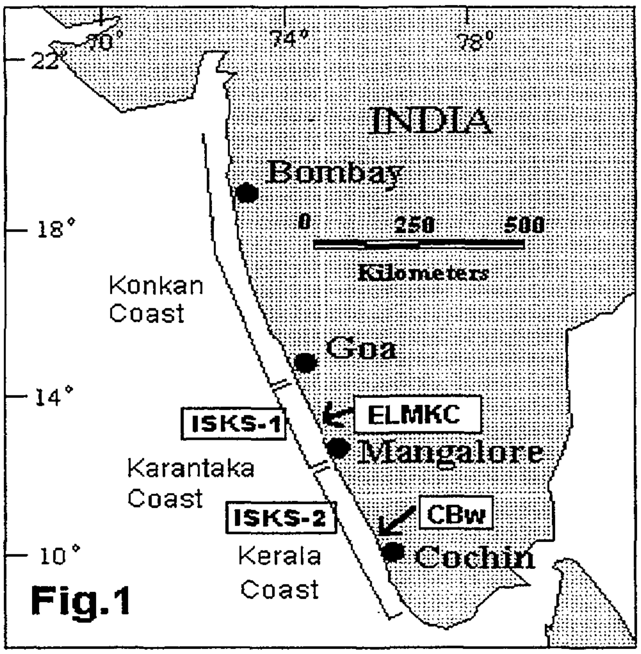

FIG. 1 The study area covers two southern states along the west coast of India which can be demarcated into: (i) Estuarine, lagoonal and marshy areas along the Karnataka coast (ELMKC), (ii) Inner shelf of Karnataka State (ISKS-1), (iii) Cochin Backwaters (CBw) and (iv) Inner shelf off Kerala State (ISKS-2).

2. MATERIALS AND METHODS

Nineteen sediment cores were collected from different marine environments along the southwest coast of India. Lead-210 was determined via its grand daughter ^{210}Po by alpha spectrometry, assuming secular equilibrium between them and negligible post-depositional migration in the sedimentary column [8]. Cesium-137 activities were measured by non-destructive gamma counting using hyper-pure germanium detectors [9].

The potential reactive metals like Cu, Zn, Cr, Mn and Fe, and Ca were measured in concentrated HNO_3 -leached samples by a Varian Spectra 250 AAS. Stream sediment reference materials (STSD 1 to 4) and duplicate samples were processed in a similar way to know the precision and accuracy of analysis. The errors of analysis are <4% for Cu and 6-12% for other elements. Sand content was measured by wet-sieving, and readily oxidizable organic matte in selected sample by Walkey-Black's method [10]. Carbon and nitrogen were measured in a few samples using a Perkin-Elmer CHN analyzer.

3. RESULTS AND DISCUSSION

3.1 Nature of sediments

The colour of sediment in all cores varied from shades of gray to dark green. Most of the sediment cores smelt of H_2S at the time of collection. Sand, partially/highly decayed vegetative matter and occasional gastropod and mollusc shells in deeper sediment layers are characteristic of estuarine, lagoonal and marshy sediments along the Karnataka coast (ELMKC). Due to the high sand percentage (20 - 93%), water and organic carbon contents are low (11 - 45%; 1.25 - 3.27%) in ELMKC sediment cores. In almost all the cores studied, sand content consistently increases downwards from surface indicating greater input of fine grained sediments from land in recent years Sediment cores from marshy areas have high vegetative matter, marshy plants, respiratory roots called pneumatophores and highly degraded calcareous shells suggesting severe reducing conditions that exist in deeper sedimentary layers. Carbon/nitrogen ratios are high (7.43-12.62) indicating the dominance of terrestrial organic matter.

In contrast to ELMKC, sediments from the inner shelf off Karnataka are fine grained (4 - 23%). Organic carbon was not measured in these sediments. However, the 2-3% organic carbon content at 20 m water depth does not much vary along the southwest coast of India [11]. Sediments from the Cochin Backwaters are relatively uniformly fine grained and rich in organic carbon (5.47 - 8.44%). Shells of macro-benthic organisms are rare. Organic carbon in Cochin Backwater sediments is 2-3 times higher when compared to that for inner shelf sediments off Kerala [11]. This is due to the discharge of effluents and organic wastes to the Backwater area [6]. As the sediment cores from the shelf off Kerala (ISKS-2) were collected from shallow depths (8-15 m) they contain a significant proportion of sand (2-64%) which is attributable to proximity to Pamba and Kallada rivers.

3.2 Sediment and heavy metal accumulation rates

The sediment accumulation rates along ELMKC range from 0.58 to 2.87 with an average of 1.21 ± 0.73 g cm^2 /yr (Table 1). As expected, the rates are high in estuaries of relatively large rivers when compared to smaller ones. The relatively large rivers in the study area are Kalinadi, Gangavalli, Sharavati, Gurpur and Netravati which annually discharge 6500, 5000, 9500, 2822 and 4600 million cubic meters of water and 0.48, 0.91, 0.27, and 0.44 million tons of suspended sediment to the coastal Arabian Sea [12-14]. The discharge from other small rivers is considered insignificant. Cesium-137 activity was measured in selected sub-samples. The average sedimentation rates deduced from the 1963 ^{137}Cs peak are in good agreement with the ^{210}Pb geochronology.

Sediment accumulation rate on the inner shelf (10-13 m water depth) off Karnataka is considerably lower (by 2.8 - 4.3 times) than the average estimated for ELMKC. This is due to the filtering of sediments in estuaries and adjacent wetlands which have contributed to a reduction in the

TABLE I. CONCENTRATION, ACCUMULATION AND ENRICHMENT FACTORS OF HEAVY METALS IN SEDIMENTS FROM VARIOUS MARINE ENVIRONMENTS ALONG THE SOUTHWEST COAST OF INDIA.

Parameters	ELMKC	ISKS -1	CBw	ISKS -2	R SPM[2]	G SPM[3]	Cont. Rocks[3]	Shale[4]
Sed. Rate[a]	1.21±0.73	0.38±0.1	2.77±1.33	0.46±0.24	-	-	-	-
Cu conc.[b]	51±18	29±1	91±33	22±2	71	100	32	45
accum.[d]	62±37	11±2.9	252±121	10±5	-	-	-	-
EF	0.75	0.7	0.99	0.45	1.14	-	-	-
Ni conc.[b]	54±19	50±1	67±3	43±3	173	90	49	68
accum.[d]	65±39	19±5	186±51	20±10	-	-	-	-
EF	0.53	0.8	0.67	0.57	1.84			
Zn conc.[b]	85±36	62±4	1496±314	65±5	90	250	127	95
accum.[d]	103±75	24±6.2	4144±1125	30±16	-	-	-	-
EF	0.6	0.71	10.7	0.63	-	-	-	-
Cr conc.[b]	212±112	125±22	172±8	155±7	-	100	71	90
accum.[d]	257±155	48±13	476±229	71±37	-	-	-	-
EF	1.58	1.51	1.3	1.6	-	-	-	-
Mn conc.[b]	242±124	447±194	472±205	186±10	724	1050	720	850
accum.[d]	293±177	170±45	1307±628	86±45	-	-	-	-
EF	0.19	0.57	0.38	0.2	0.62	-	-	-
Fe conc.[c]	7.01±2.34	4.33±0.17	6.9±0.3	5.07±0.36	6.5	4.8	3.59	4.7
accum.[e]	8.84±5.12	1.65±043	19±9.18	2.33±1.22	-	-	-	-
Ca conc.[c]	0.24±0.11	4.61±	0.57±0.37	4.68±0.81	0.26	2.15	4.5	1.6
accum.[e]	0.29±0.18	1.75±	1.58±0.76	2.15±1.12	-	-	-	-
EF	0.11	3.13	0.24	2.71	0.12	-	-	-

[a](g cm^2 /yr), [b](ppm), [c](%), [d](X10^{-6} g cm^2/yr) and [e](X10^{-3} g cm^2/yr).

width and draught of estuaries and navigational channels causing navigational problems and accumulation of land-transported contaminants.

For preliminary pollution assessment, elemental concentrations are compared with corresponding values for suspended particulate matter (SPM) from the study area [15], world river SPM (G SPM), average continental rocks [16] and shale [17]. Sediments of ELMKC have a predominantly terrigenous source and contain low Ca contents, a characteristic of tropical riverine sediments [15]. Manganese in ELMKC sediments is lower by factors of 2 to 4 when compared to that in continental rocks and shale, reflecting reducing conditions in the sedimentary column. The element enrichment factors (EFs; metal/Fe_{sample}/metal/Fe_{shale}) have been computed to infer anthropogenic accumulation of heavy metals. For most of the elements studied, the EFs are <1 with the exception of Cr suggesting that the sediments are not contaminated. The higher EF for Cr is due to Cr-enriched minerals like pyroxene and amphibole in the catchment material. In general, heavy metal accumulation rates are high in ELMKC than ISKS-1. This is not only due to proximity to the source but also to high sediment accumulation rates owing to particle aggregation processes like flocculation, agglutinization, biological uptake and fecal pelletization. The reduction of river flow due to river-sea interactions is the probable reason for high sediment accumulation rates along ELMKC. In ISKS-1 sediments, Cu, Ni, Zn, Cr and Fe are lower by factors of 1.1 to 1.7, but Mn and Ca are significantly higher by factors of 1.9 to 6 relative to ELMKC sediments. This suggests that the inner shelf sediments are relatively aerobic and receive carbonate flux from the marine biota.

In comparison with ELMKC, sediments of the Cochin Backwaters are relatively fine grained with sand content ranging from 3 to 66%. Sedimentation rate ranges from 2.67 to 3.20 with a mean of 2.77 ± 1.33 g cm^2 /yr. Probable reasons for high sediment accumulation rates are high river discharge, anthropogenic sediment input, development of harbours, dredging and the impact of sea-level rise. Among these, anthropogenic activities seem to be manipulating natural sedimentation processes in the backwaters. Periar and Muvattupuzha are important rivers and the former alone annually discharges 12,300 million cubic meters of water and 0.7 million tons of suspended sediment into the Backwaters [12, 13] .

The contents of Cu, Ni and Cr in sediments of CBw are relatively higher than those for average continental rocks and shale. However, EFs for these elements are <1. The higher concentration and EF of Zn indicate potential Zn contamination due to anthropogenic activities around Cochin, the second largest city along the west coast of India with a population exceeding one million and home to 70% of chemical industries of Kerala state [6]. The industries in and around Cochin are chemicals and fertilizers, insecticides, rare earths, petroleum products and aluminium and zinc or smelting. About 260 million cubic meters per day of partially treated or untreated effluents from these industries plus organic wastes, sewage and contaminants liberated by shipping activities in the Cochin port (established in 1936) are being added to the Backwaters. This eventually results in increase of contaminated heavy metals such as Zn, Cd, Pb, rare earths and radionuclides (Ra and Pb) in sediments [4, 18,19]

In contrast to CBw, sediment and metal accumulation rates are considerably lower in ISKS-2 (Table 1). As discussed earlier, terrigenous sediments are trapped in river-sea interaction zones which may explain this difference. The higher content and accumulation rate of Ca again reflect the contribution of Ca from marine biota.

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