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Source of sediments and response of clay minerals, organic matter and metals to fluctuating environmental conditions in western Bay of Bengal

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The sediment cores collected along three transects off the Mahanadi, Godavari and Krishna rivers were analyzed for spatial and temporal variations in grain size, clay minerals, total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), calcium carbonate, and selected metals (Al, Fe, Ti, Mn, Zn) to understand the provenance of sediments and the role of monsoons and dissolved oxygen in the preservation of organic elements and metals in recent past. Illite was the dominant mineral off Mahanadi and smectite off Godavari and Krishna that indicated their different sources, viz., felsic and mafic rocks, respectively. The high Fe/Al and Ti/Al content in shallow areas off Godavari and Krishna may have been added from the leaching of Red Beds and mafic rocks respectively. The TOC/TN molar ratio was above 8.00 in most samples that indicated the supply of organic matter from terrestrial sources. The sediment with less carbonate and organic matter revealed low biological productivity in the study area.

The relatively higher sand, elevated S/I+C ratio and metal content in the surface sediments and the lower section in majority of the cores indicated intensified rainfall and high runoff that brought increased oxygenated fresh water along with the higher metal influx. The reduced concentration of Mn/Al along with low S/I+C ratio and higher TOC and TN values in the 15 cm to 5 cm section in the cores off Godavari revealed weak rainfall which turned the water anoxic, as the available oxygen was consumed by the planktons. Under intensified OMZ, Mn/Al got depleted in reducing conditions and TOC, TN was better preserved.

[**Keywords**: Sediment provenance; Paleomonsoon; Productivity; Western Bay of Bengal]

Introduction

The earliest paleomonsoon interpretations were carried out in the African lakes[1] and from history of upwelling in the Arabian Sea[2]. Later, the Loess Plateau in China and South China Sea turned into a favorable location to understand the east asian monsoon variations[3,4,5]. High resolution analysis suggested that east asian monsoon system fluctuated considerably from a strong winter monsoon during the last glaciation (25,000-12,000 yr BP) to a moderate to weak winter and summer monsoons during the deglaciation

monsoon in the Holocene to present[6,7,8]. During the last glacial maximum (LGM), the snow cover over the Tibetan plateau and central Asia decreased the land-ocean temperature contrast during summer and increased during winter leading to weaker SW monsoon and strengthened NE monsoon[9]. Monsoon records from the Arabian Sea displayed similar patterns to the adjacent Asian and African regions[10,11,12] as inferred strong winter monsoon during LGM enhanced NE monsoon current. This was probably because the Indian and Chinese monsoons have similar sub-Milankovitch periodicities[13].

Unlike the Arabian Sea and South China Sea, paleomonsoon interpretations from Bay of Bengal sediment cores are limited. This is possibly because enormous sediment load enters the Bay through river discharge under high energy conditions and makes it very difficult to obtain an undisturbed, turbidity-free sediment core. Nevertheless, few recent reports[14,15,16,17] successfully explained variations in paleoclimate and geochemical cycles from LGM to late Holocene period in the Bay of Bengal. Less attention however is focused on the western expanse fluenced by the major monsoonal rivers of Mahanadi, Godavari and Krishna. The western continental shelf of Bay of Bengal along the east coast of peninsular India is dynamic in nature and drained by the major river systems of Mahanadi, Godavari and Krishna. These rivers introduce around 1.4 X 10^9 tons of suspended sediments into the region annually[18,19]. There is an imperative need to understand the response of proxies in different oceanic settings, particularly off these major rivers as they deliver huge amounts of freshwater and sediment to the ocean[20]. Therefore the objective of the present study was to understand the provenance of sediments, the influence of monsoons and the role of OMZ in the preservation of organic elements and metals in the recent times.

Further, a majority of the paleomonsoon records is based chiefly on foraminifera species (*Globigerina Ruber, Globigerina bulloides)*, magnetic susceptibility studies, sea surface temperature and salinity, but seldom upon lithogenous based proxies, such as grain-size, clay minerals, and major elements especially in studies of Bay of Bengal. These proxies are typical to the terrestrial sources and are directly linked to weathering and intensity of monsoon precipitation. The grain size of sediment helps to trace the sediment transportation pathways and the intensity of monsoon precipitation[21,22]. On the other hand, the bulk metals and clay mineral abundances in marine sediment are useful indicators of detrital provenance and dispersal patterns[23,24], as well as paleoclimatic conditions in the source areas[25,26,27,28, 29]. Further, the biogeochemical cycling of nutrients can be understood from carbon, nitrogen and phosphorus in ocean sediments as they are linked to the processes that occur in terrestrial ecosystems[30,31]. In addition, the C/N ratio has been frequently used to identify the source of organic matter in sediments which is ultimately related to monsoons[32,33,34,35]. In addition, earlier studies[36,37,38,39] have inferred past changes in bottom water oxygen content and extent of OMZ from variations in the sedimentary concentration of redox sensitive trace metals Mn and Zn.

The data on rate of sedimentation is not available for the sediment core samples used in the present study. However, at comparable latitudes and water depths, dates from earlier literature were utilized to get a broad idea on the sedimentation rates in this region. High sediment accumulation rates were reported during late Holocene in Bay of Bengal. Off Godavari[40,41], reported a sedimentation rate of 0.25 cm/yr for the cores between 30-100 m water depths which was measured using ^{210}Pb method. In the cores at deeper water depths of 600 to 1400 m[42,43,44], reported rates of 0.24 cm/yr off Mahanadi and 0.34 cm/yr off Krishna were measured from ^{14}C dates. The dating was carried out on the foraminifera species Globigerina Ruber and Globigerina Sacculifer.

Study area

The climatic setting in the coastal Mahanadi is sub-tropical with temperatures in summer of about 29 °C and winters 21 °C, while in the coastal Godavari and Krishna the climate is humid with the highest temperature at 35 °C[45]. The Mahanadi emerges from the Eastern Ghats and bulk of the geology along its course is composed of felsic rocks of khondalites, charnockites, granites, gneisses and the limestones, sandstones and shales of the Gondwanas[46]. On the other hand, Krishna and Godavari flow across the Indian peninsular shield passing along Precambrian, Deccan basalts and Dharwar formations which contribute to major portion of the sediments deposited along the coast. The bulk of the precipitation is received during the SW monsoon (June-September) intensifying sediment influx into coastal Bay of Bengal[47] with the prevalent wind direction favorable for upwelling. The sediment supply however, is largely by the river runoff as the upwelling is weaker in the east coast of India[48]. During the NE monsoon (October-January), due to the prevailing wind direction, no upwelling takes place along east coast of India.

Materials and Methods

The grain size, clay minerals, total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), $CaCO_3$ and selected metals were studied along three transects in 77 samples from 10 short cores of varying lengths (25 to 40 cm), namely, MC-(66, 65, 64) off Mahanadi, MC-(30, 31 ,33 ,35) off Godavari and MC-(27, 24, 22) off Krishna collected in the range from 40 to 1005 m water depth from the western part of the Bay of Bengal (Fig.1). The samples were selected from several sediment cores collected onboard RV Sagar Kanya (Cruise No. 308) in the January 2014, using a multi corer. It was ensured that there was no disturbance in the sediment column and the cores which were retrieved were undisturbed with the surface section intact. Post sub-sampling at 1 cm intervals, the samples were preserved in cold storage on board, packed in pre-numbered plastic bags.

In the laboratory, each sediment sample was dried in a hot air oven and used for further analysis. Sediment for grain size analysis was washed with distilled water to make it free from salts and later treated with 10 % sodium hexametaphosphate to dissociate clay particles, and hydrogen peroxide was added to oxidize organic matter. Sediment grain size was later determined using the pipette method[49] which is based on Stoke’s settling velocity principle. Part of the sub-sample was finely ground using pestle and mortar and packed in pre-weighed tin crucible for estimating the TC and TN contents that was determined using soil carbon-nitrogen elemental

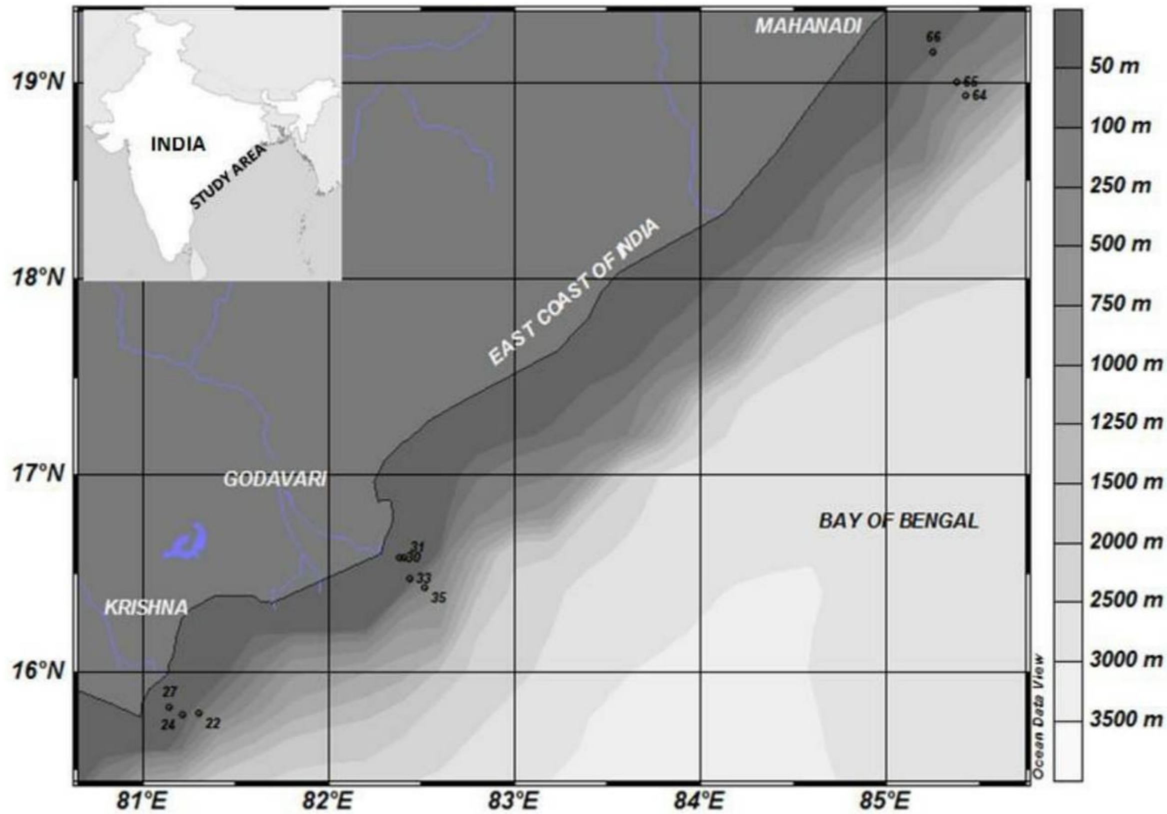

Fig. 1 — Locations of sediment samples with numbers

analyzer (Thermo flash 2000 model). Total inorganic carbon (TIC) was measured by using UIC carbon coulometer. The precision of the methods was monitored by carrying out replicate measurements and it was within ± 5 %. Accuracy was determined using a reference standard (soil NC) and obtained recoveries were 96 % for TC and TIC and 99 % for TN. TOC was calculated by subtracting TIC from TC. Calcium carbonate was computed from values of TIC by multiplying it to a factor of 8.33 (calculated from atomic mass of Ca, C and O). Total phosphorous was determined , where the intensity of the phosphomolybdenum blue complex was measured at 880 nm using UV-1800 (Shimadzu) visible spectrophotometer[50]. The digested sample of MAG-1 was used to determine the accuracy for the phosphorus analysis and obtained a recovery of 98 %. For the clay mineral analysis, the clay fraction was made free from carbonates and organics using glacial acetic acid and hydrogen peroxide respectively and the slides were prepared by pipetting 1 ml of the clay and spreading uniformly over a pre-numbered slide. The prepared slides were exposed to ethylene glycol vapors at 60 °C overnight. The slides were then scanned from 3° to 30°2 θ at 1.2°2 θ/min on Rigaku Altima IV using nickel-filtered CuKα radiation. The clay minerals were identified and quantified following the procedure given by Biscaye[51].

The sediment sub-samples for estimating the concentration of elements were finely ground and digested by using $HF–HClO_4–HNO_3$ mixture in Teflon beakers[52]. Complete digestion was censured by repeating the digestion steps until clear solutions were obtained. The concentration of major and trace elements (Al, Fe, Ti, Mn, Zn) was determined using Varian AA 240 FS flame atomic absorption spectrometry (AAS) with an air/acetylene flame for Fe, Mn and Zn, and for Al and Ti nitrous oxide/acetylene flame was employed at specific wavelengths. The instrument was calibrated at regular intervals by running standard solutions and the analysis was repeated at regular intervals to ensure that the precision of the results was within ± 6 %. Metal concentrations obtained were normalized with reference to Al. Together with the samples, the certified reference standard MAG-1 was digested and run to test the analytical accuracy of the method. The average recoveries for Al, Fe, Ti, Mn and Zn were 88, 94, 95, 95 and 96 %, respectively.

Results

Distribution of sediment components

The range and average of grain size along with clay minerals, TOC, TN, TP, calcium carbonate and Al normalized metals are presented in Table 1. The sediment in the study area was predominantly composed of clay except for MC-66 wherein sand was high and MC-27 wherein silt was high. In general, sand content decreased from shallow to deeper water depth except the highest value of 72.96 % obtained off Mahanadi. The silt content showed large range of variation in shallow regions compared to deeper regions. From shallow to deeper water regions, the average silt content increased off Mahanadi, fluctuated off Godavari and decreased off Krishna away from the coast. The clay content exhibited higher value towards deeper water depth as compared to the shallow depths in all transects. When the average sand value was compared from north to south, off Mahanadi sand content was the highest and reduced in concentration southward except for a core off Krishna at 55 m water depth (MC-27) where average sand content was slightly high (8.12 %). From north to south in the cores near the river mouths, the average silt distribution increased with the highest content (49.08 %) in core MC-27 off Krishna while in the cores from intermediate to deeper water depths off Godavari the silt content was slightly high. From north to south the average clay content in the cores close to the river mouths showed an increasing trend while in the cores at deeper water depths the clay content fluctuated but with overall decrease from north to south. Further, the data is graphically illustrated (Fig. 2) to understand the variation in the sediment components down the core.

Distribution of clay minerals

Illite was the dominant clay mineral off Mahanadi with the concentration varying between 52.73 and 62.52 % while its content was less off Krishna and Godavari and ranged between 11.77 and 17.92 %. On the other hand, smectite was the dominant clay mineral off Krishna and Godavari (52.46 to 74.21 %) while its concentration reduced to 11.10 to 17.40 % off Mahanadi. From shallow to deeper water regions, off Mahanadi and Godavari the smectite concentration increased while off Krishna its content was low towards deep waters and opposite distribution was seen in the case of illite. The kaolinite showed increasing trend off Mahanadi and Krishna but largely fluctuated off Godavari from the shallow to deep water areas. The chlorite content was

Table 1 — Range and average of grain size, clay minerals, TOC %, TN %, TP %, $CaCO_3$ % and Al normalized metals off Mahanadi, Godavari and Krishna used in present study

TRANSECT	CORE NO.	WATER DEPTH		SAND %	SILT %	CLAY %	SMECTITE (%)	ILLITE (%)	KAOLINITE (%)	CHLORITE (%)	TOC (%)	TN (%)	TP (%)	CaCO3 %	Al %	Fe/Al %	Ti/Al %	Mn/Al %	Zn/Al %
Mahanadi	MC-66	104	Min	42.43	1.44	12.24	6.59	53.04	18.35	4.16	0.34	0.00	0.035	30.77	1.60	0.820	0.051	0.014	0.0015
			Max	84.06	12.93	44.64	17.13	69.46	26.35	5.42	1.19	0.12	0.042	76.68	5.45	1.625	0.113	0.025	0.0030
			Average	72.96	4.66	22.38	11.10	62.52	21.53	4.90	0.57	0.05	0.038	65.69	2.73	1.263	0.073	0.020	0.0023
	MC-65	260	Min	0.16	15.66	65.92	6.59	45.96	13.41	3.35	1.06	0.10	0.039	1.38	8.61	0.579	0.050	0.008	0.0010
			Max	7.12	30.04	83.88	21.12	76.65	26.64	8.23	2.09	0.25	0.049	3.11	11.68	0.468	0.044	0.007	0.0006
			Average	1.40	21.03	77.58	15.19	57.62	21.90	5.29	1.60	0.17	0.044	2.14	9.76	0.579	0.050	0.008	0.0010
	MC-64	499	Min	1.57	15.65	75.24	14.93	50.25	20.46	3.47	1.63	0.17	0.033	3.37	8.17	0.543	0.049	0.006	0.0011
			Max	2.70	22.77	82.64	20.20	55.24	28.63	9.09	1.97	0.22	0.063	4.34	9.84	0.652	0.055	0.009	0.0012
			Average	2.07	20.16	77.76	17.40	52.73	24.04	5.83	1.78	0.19	0.040	3.89	9.28	0.580	0.051	0.007	0.0011
Godavari	MC-30	40	Min	0.25	29.05	35.20	44.31	10.17	8.90	2.97	0.96	0.07	0.021	2.51	7.96	1.048	0.078	0.019	0.0011
			Max	1.13	63.70	70.56	77.97	22.82	30.02	6.82	1.56	0.11	0.037	3.79	8.80	1.166	0.143	0.028	0.0013
			Average	0.71	37.94	61.35	55.83	17.92	22.05	4.21	1.15	0.09	0.034	3.31	8.29	1.105	0.123	0.025	0.0012
	MC-31	107	Min	0.10	23.85	62.88	36.14	7.31	15.92	3.76	0.87	0.07	0.035	2.03	7.13	0.732	0.082	0.021	0.0010
			Max	1.65	37.02	75.92	65.71	21.05	39.51	9.18	1.86	0.18	0.045	4.03	9.89	0.919	0.121	0.030	0.0014
			Average	0.47	31.09	68.44	52.46	13.15	28.10	6.30	1.26	0.11	0.039	2.99	8.83	0.807	0.101	0.025	0.0011
	MC-33	495	Min	0.20	22.39	40.16	49.50	7.52	16.69	1.98	1.10	0.09	0.036	2.53	7.91	0.811	0.080	0.013	0.0011
			Max	1.69	59.57	76.72	70.68	22.59	27.63	5.22	1.62	0.14	0.044	2.93	9.02	0.906	0.090	0.019	0.0014
			Average	0.63	36.39	62.99	57.62	16.36	22.01	4.01	1.30	0.11	0.040	2.78	8.58	0.857	0.083	0.015	0.0012
	MC-35	1005	Min	0.51	24.09	64.16	63.03	9.13	10.12	2.03	1.11	0.07	0.034	2.62	7.97	0.725	0.082	0.013	0.0012
			Max	2.86	33.45	75.12	76.26	15.65	21.08	4.52	1.63	0.14	0.044	3.52	8.67	1.091	0.124	0.031	0.0013
			Average	1.51	28.21	70.28	67.95	12.32	16.22	3.50	1.25	0.10	0.038	2.99	8.22	0.874	0.108	0.020	0.0013
Krishna	MC-27	55	Min	2.53	45.53	34.28	52.52	7.11	6.09	1.10	0.41	0.05	0.030	4.40	7.50	0.865	0.168	0.026	0.0012
			Max	15.45	55.33	51.12	80.44	18.71	24.94	3.84	1.85	0.11	0.041	5.21	8.51	1.031	0.236	0.037	0.0015
			Average	8.12	49.08	42.80	74.21	11.77	11.37	2.66	0.93	0.07	0.035	4.83	8.16	0.916	0.198	0.028	0.0013
	MC-24	202	Min	1.04	26.43	66.52	64.32	9.39	10.07	2.41	0.92	0.08	0.037	3.85	7.72	0.825	0.090	0.023	0.0012
			Max	2.36	31.45	71.48	75.15	15.32	20.45	5.84	1.30	0.11	0.045	5.10	8.46	0.977	0.117	0.024	0.0015
			Average	1.55	28.93	69.52	69.48	12.25	14.63	4.00	1.03	0.09	0.042	4.43	7.97	0.921	0.108	0.024	0.0013
	MC-22	767	Min	0.23	19.34	60.36	50.35	7.41	12.05	1.26	0.88	0.06	0.038	3.05	7.45	0.788	0.087	0.015	0.0011
			Max	2.89	39.32	80.08	75.00	23.53	26.60	5.67	1.61	0.16	0.044	4.61	8.67	0.959	0.149	0.034	0.0014
			Average	1.13	27.66	71.21	61.53	16.47	18.64	3.35	1.16	0.09	0.040	3.72	8.01	0.881	0.123	0.021	0.0013

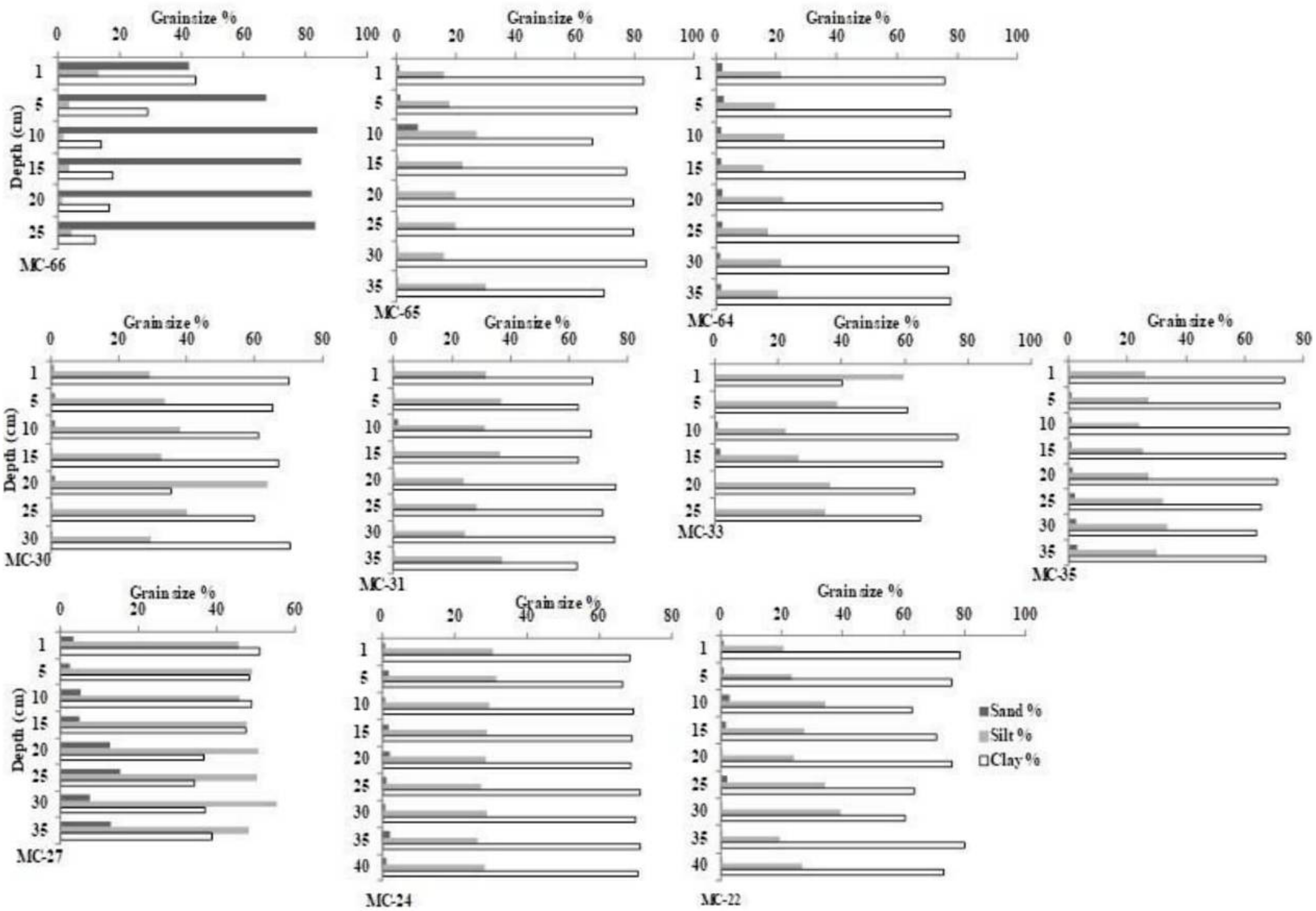

Fig. 2 — Vertical profiles of sand %, silt %, clay % in cores off Mahanadi, Godavari and Krishna

high off Mahanadi and fluctuated off Godavari and Krishna from the shallow to deep waters. When the average concentration of clay minerals was compared from north to south the smectite content increased and illite content decreased from off Mahanadi through off Godavari to off Krishna. Similar to illite, kaolinite and chlorite decreased from off Mahanadi through Godavari to off Krishna i.e. from north to south at different depth ranges with one or two exceptions. The data on the clay minerals down the core is graphically presented (Fig. 3) to understand the variation.

Distribution of TOC, TN, TP, $CaCO_3$

The TOC, TN and TP concentrations in the study area were rather low with average concentrations varying between 0.57-1.78 %, 0.05-0.19 %, and 0.034-0.044 % respectively. Along all three transects, TOC and TN contents showed an increasing trend from shallow to deep waters except in core MC-35 at 1005 m water depth where average TOC content was slightly reduced. Average TOC and TN concentrations in the cores at shallow areas decreased from off Mahanadi to off Krishna but off Godavari their concentration increased slightly, while in the cores from intermediate to deeper water regions TOC and TN contents decreased from north to south. Vertical variation in TOC and TN are presented in the graphs (Figs. 4 & 5). Total phosphorus was rather constant with no particular trend from shallower to deeper zones as well as from north to south. Also, in all the cores, the depth-wise variation in TP was largely constant (Fig. 5) throughout the length of the cores except in core MC-64 and MC-65 off Mahanadi at 30 cm where TP got slightly enriched. The average $CaCO_3$ content in the study area varied within a small range from 2.14 to 4.83 % except for core MC-66 at 104 m off Mahanadi transect where its concentration was exceptionally high (65.69 %). It may be noted that high content of sand was obtained for this core. Vertical variation in $CaCO_3$ content is presented in the graphs (Fig. 6).

Distribution of metals

The distribution of Al off Mahanadi increased from the shallow to deep waters with the average content of

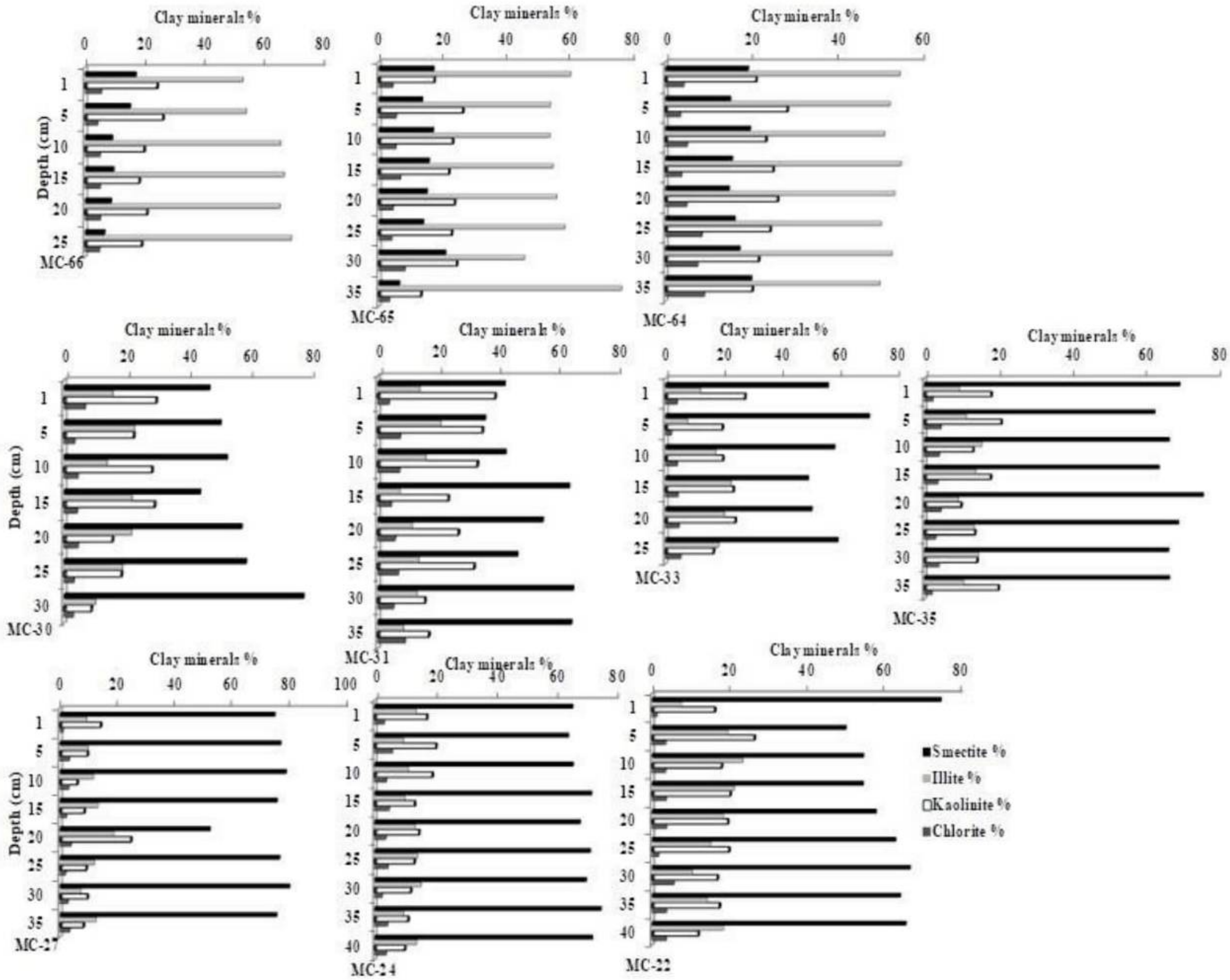

Fig. 3 — Vertical profiles of clay minerals in cores off Mahanadi, Godavari and Krishna

2.73 % in core MC-66 at 104 m water depth while in the cores collected from the deeper zones, the average Al content increased to about 9.00 %. Al average concentration was consistent at 8 to 9 % in the study area that indicated its uniform terrestrial source and suggested that changes in Al accumulation were limited. It was almost equal to the crustal PAAS value of 9.94 %. The metals were normalized with Al concentration. The average Fe/Al, Ti/Al and Mn/Al concentration was largely higher in shallow waters as compared to deep waters in all three transects. The Fe/Al, Ti/Al and Mn/Al content increased towards south from off Mahanadi through off Godavari to off Krishna in the shallow as well as deep sea cores. The average Zn/Al content was largely consistent from the shallow to the deep water regions as well as north to south in all transects. However, in core MC-66 at 104 m water depth off Mahanadi average Zn/Al content was high. The Fe/Al, Mn/Al, Ti/Al concentration in sediment was higher off Godavari and Krishna as compared to that off Mahanadi and their concentrations were higher than crustal PAAS values of 0.503 %, 0.060 % and 0.009 % (Taylor and McLennan, 1985) respectively in the samples, suggesting the presence of structurally unsupported hydroxides. The Zn/Al was higher than PAAS value of 0.0009% in all the samples. The data of Al normalized metal content is graphically illustrated (Figs. 7, 8 & 9), to understand the down core variation.

Discussion

Source and direction of transport with time

Sediment components: The distribution of sediments revealed that overall the sediment size decreased from the shallow to the deep water region

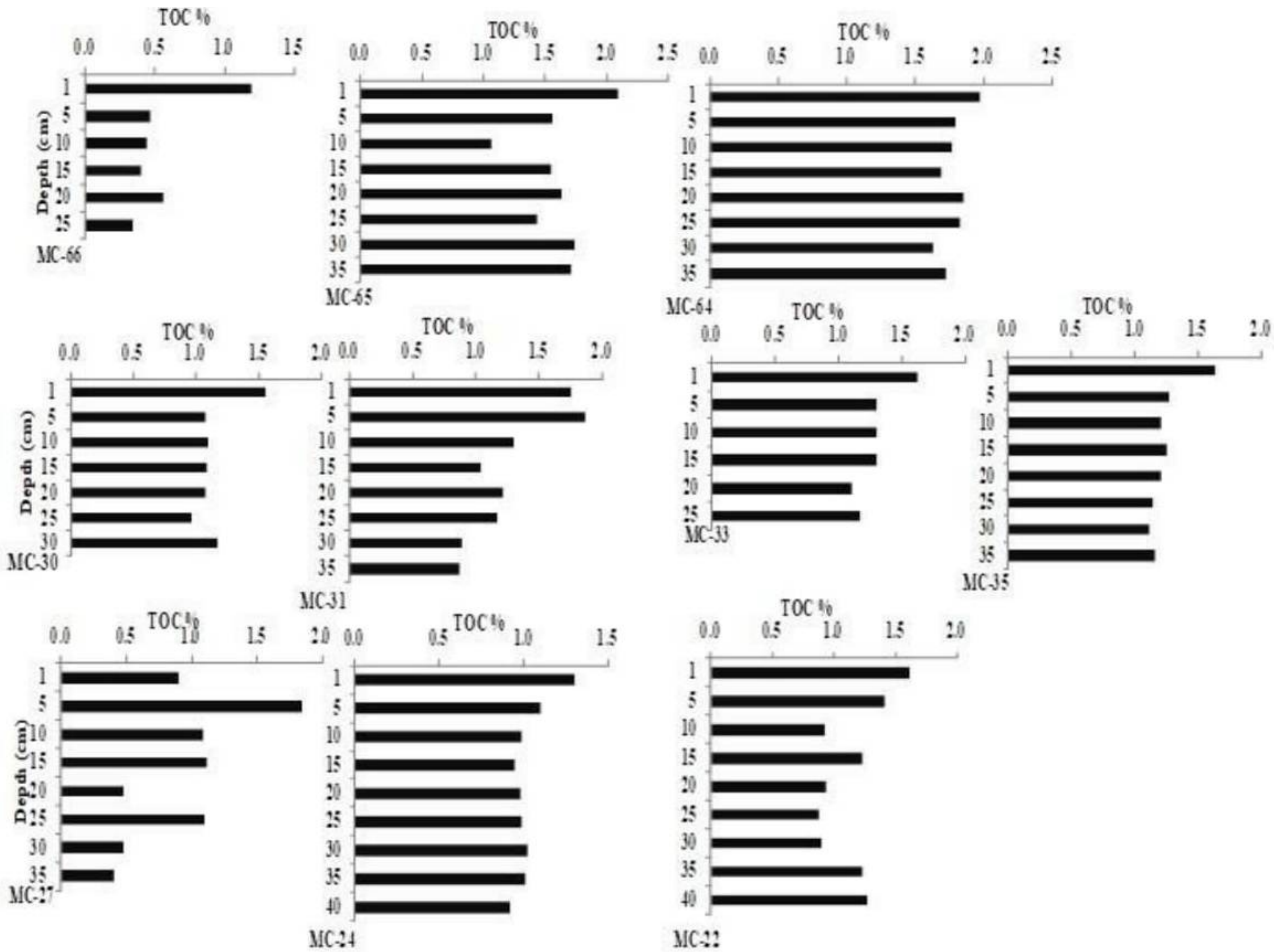

Fig. 4 — Vertical profiles of TOC % in cores off Mahanadi, Godavari and Krishna

and also from north to south in the study area. The coarser sediments were deposited in the shallow higher hydrodynamic environments near the coast, while finer sediments from the rivers must have been transported towards the slope and abyssal plains and were deposited later. The distribution of sediment components revealed land as a major source for the material. In Bay of Bengal, due to the narrow continental shelf most of the sediments are lost to the deeper regions[53,48]. Further, off Mahanadi, the higher sand content in the cores in shallow areas indicated high energy conditions that are prevalent near the river mouth. At the shallow water depths off Godavari, high silt content present indicated prevalent relatively low hydrodynamic energy conditions which enhanced the rate of silt accumulation. A probable loss of energy inhibited the transport of coarse grain sediments towards the south.

The high sand content observed in lower section between 35-20 cm (Fig. 2) of core MC-35 off Godavari and also from bottom up to a depth of 20 cm in core MC-27 off Krishna revealed flood event attributable to higher rainfall which must have brought abundant coarser terrestrial material. The relative change in the percentage of grain size was direct representation of monsoonal variation where an increase in coarser fraction indicated that the hinterland region received good monsoonal precipitation leading to enhanced weathering[5].

Clay minerals: Clay minerals generally form by hydrolytic decomposition of primary aluminosilicates[26]. While illite was the predominant clay mineral in stations off Mahanadi, abundant smectite characterized the sediment off Godavari and Krishna. Illite is a non-swelling clay that forms under cold climatic conditions as a product of mechanical weathering. Also, illite is formed from high grade metamorphic and felsic igneous rocks dominantly from the micas present in these rocks. Muscovite, a dominant clay mineral in the Himalayan region,

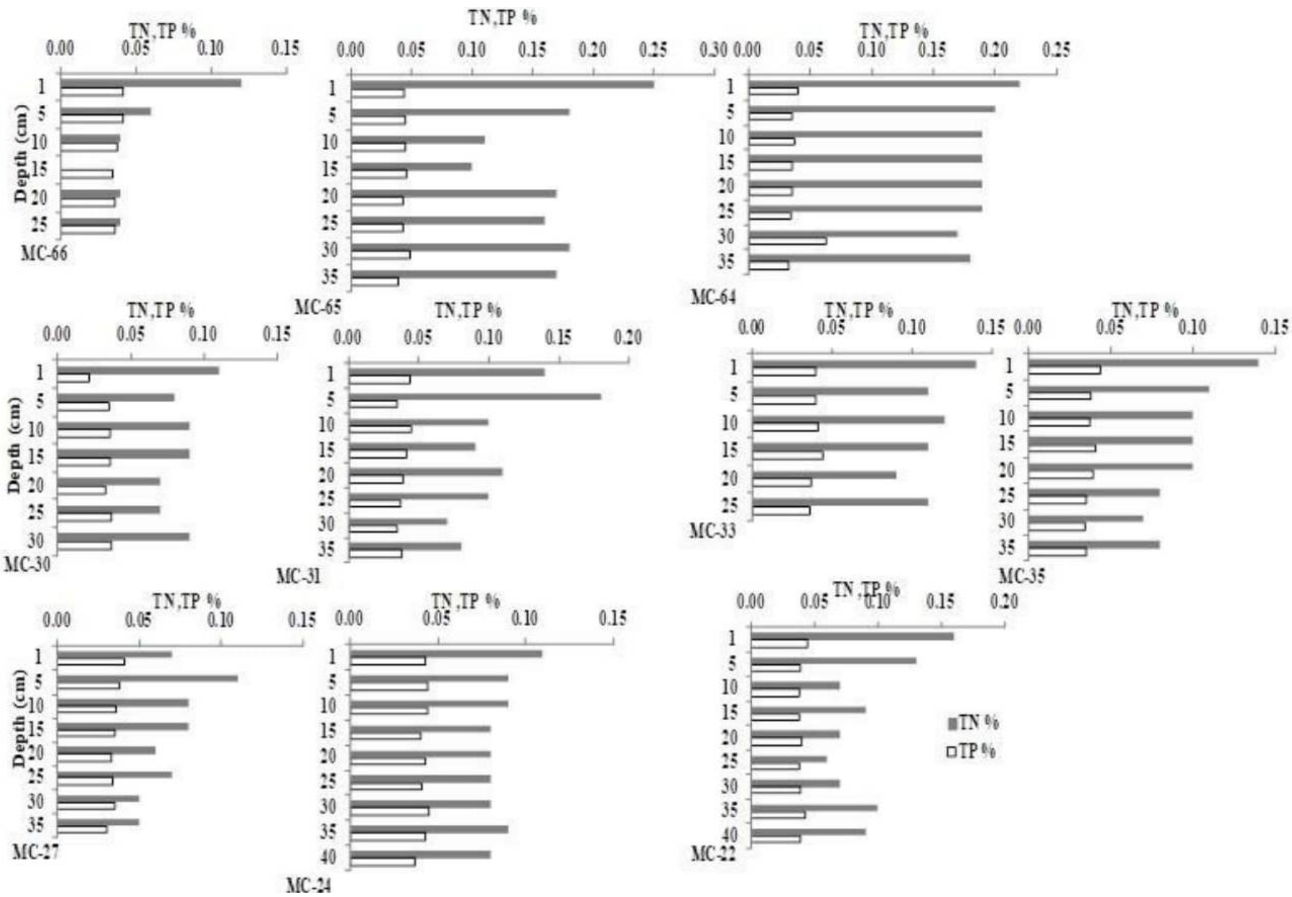

Fig. 5 — Vertical profiles of TN % and TP % in cores off Mahanadi, Godavari and Krishna

produces illite draining through Ganges-Brahmaputra reaching towards south[54]. Further, illite may have also leached from felsic rocks, granitic rocks, calc-granulites and pyroxene granulites from the Eastern Ghats draining through Mahanadi. Earlier Brass et at[55] reported higher illite off Mahanadi which they attributed to felsic and granitic rocks of Peninsular Gneissic Complex. The smectite increased considerably in stations off Godavari and Krishna (Fig. 3) that can be attributed to the weathering of basic volcanic igneous rocks mainly Deccan basalts under the prevailing climatic conditions and also from black cotton soils that drain through the peninsular rivers of Krishna and Godavari.

At 15 cm section in majority of the cores off Godavari and at 20 cm in cores off Krishna (Fig. 3), smectite decreased in concentration that indicated a reduced sediment discharge from land probably due to weaker rainfall during that period. Minor amount of illite was also present in few sections down core (Fig. 3) as the Krishna-Godavari flow over charnockites and granites of Archean age. These rocks weather under humid conditions and produce mixed clays[56]. Also, appreciable amount of smectite was observed in few sections in the cores off Mahanadi (Fig. 3) and may have been added from the eastern Deccan traps over which a tributary of Mahanadi passes through. In addition, higher kaolinite content in the cores located at shallower regions off Godavari may have been supplied from the ‘Red beds’ which is major rock type near the Visakhapatnam coast. Also, appreciable concentration of kaolinite observed at 30 cm, 20 cm and 5 cm in all the cores off Mahanadi (Fig. 3) must have been contributed after conversion of aluminosilicate minerals like feldspars leaching from Archean granites and gneisses and draining through Mahanadi during that time. Besides, the chlorite content was low from cores in the region due to prevailing humid tropical conditions which makes it unstable[28]. It has therefore been considered that source of clays in the study area is largely due to the weathering of rocks from terrestrial region. However, there were some exceptions that must be due to alternate processes.

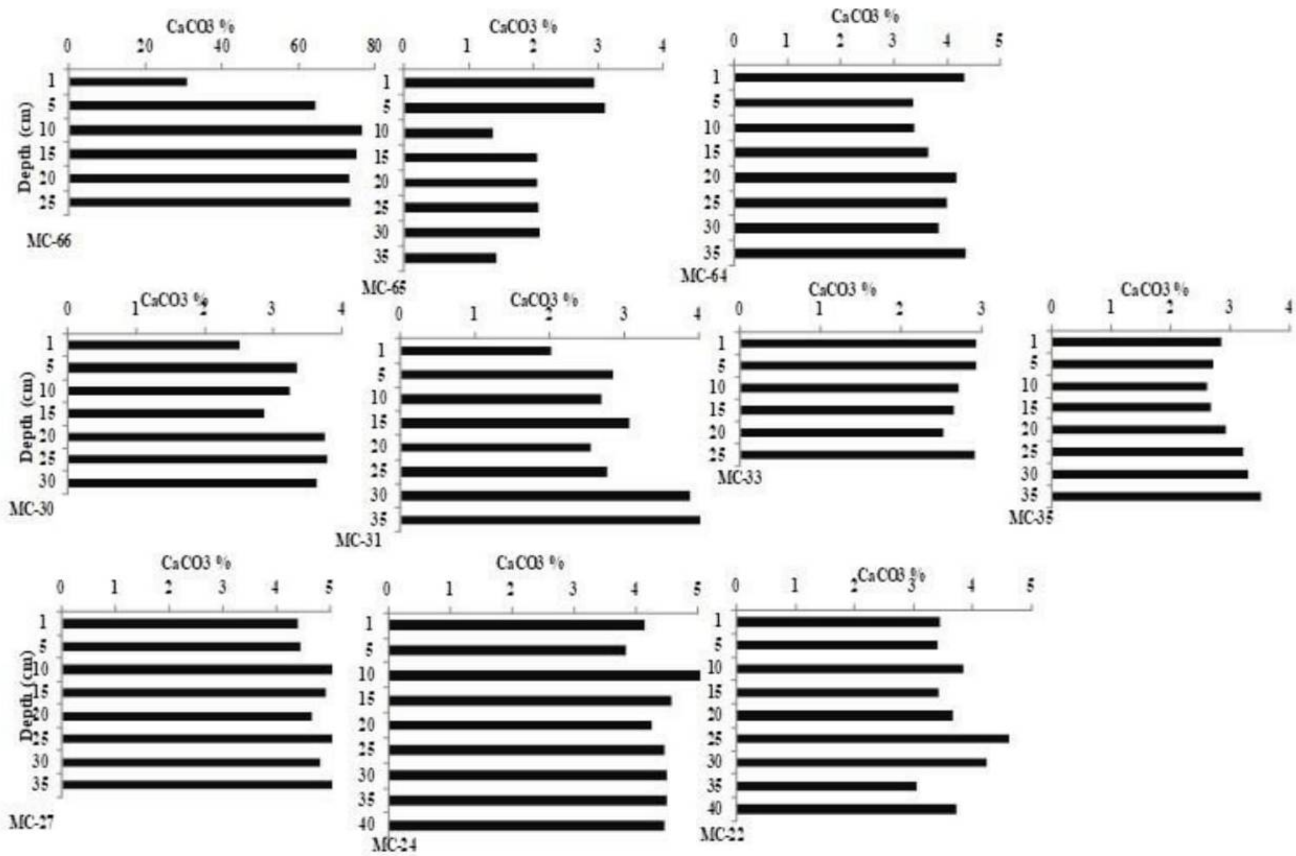

Fig. 6 — Vertical profiles of $CaCO_3$ % in cores off Mahanadi, Godavari and Krishna

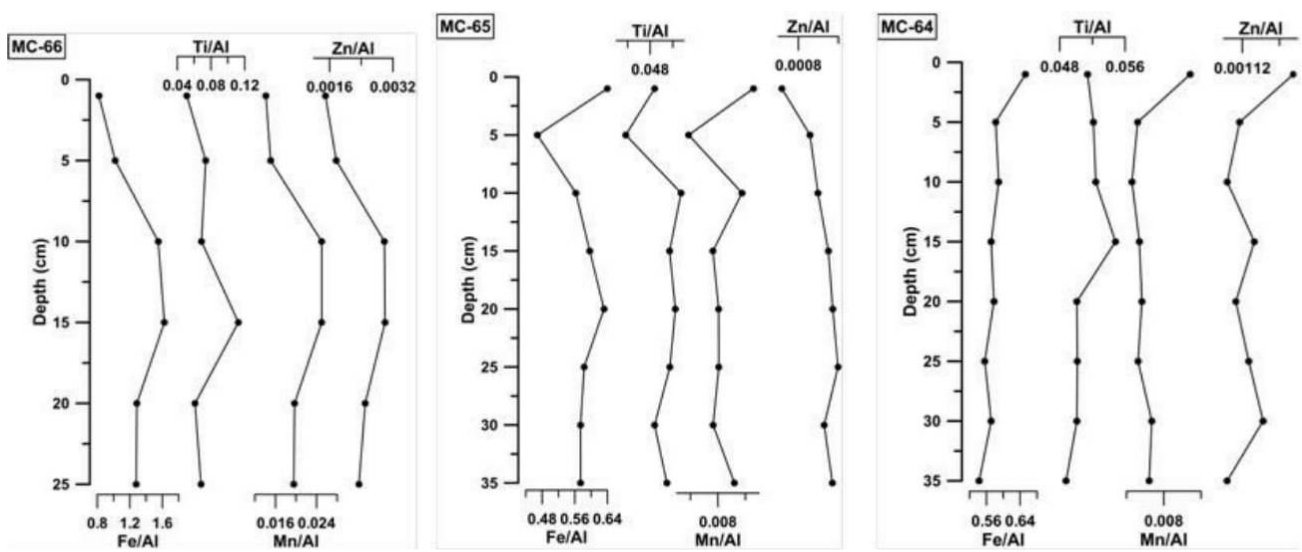

Fig. 7 — Vertical profiles of Al normalized metals in cores off Mahanadi

The differential settling of clays with respect to water depth[27,57,58] is responsible for the abundance of a particular clay type. Smectite is more enriched in finer fraction than illite[58]. In the cores off Mahanadi and Godavari with increasing water depth, average smectite increased which may be due to its finer size. Smectite associated with finer clay particles must have remained in suspension for longer time before

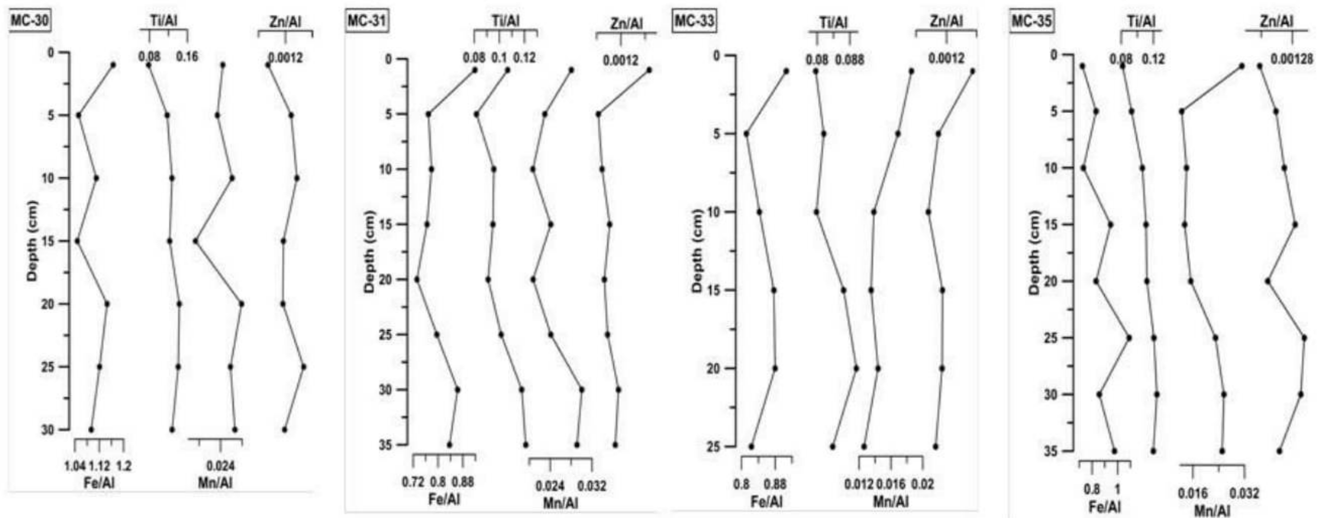

Fig. 8 — Vertical profiles of Al normalized metals in cores off Godavari

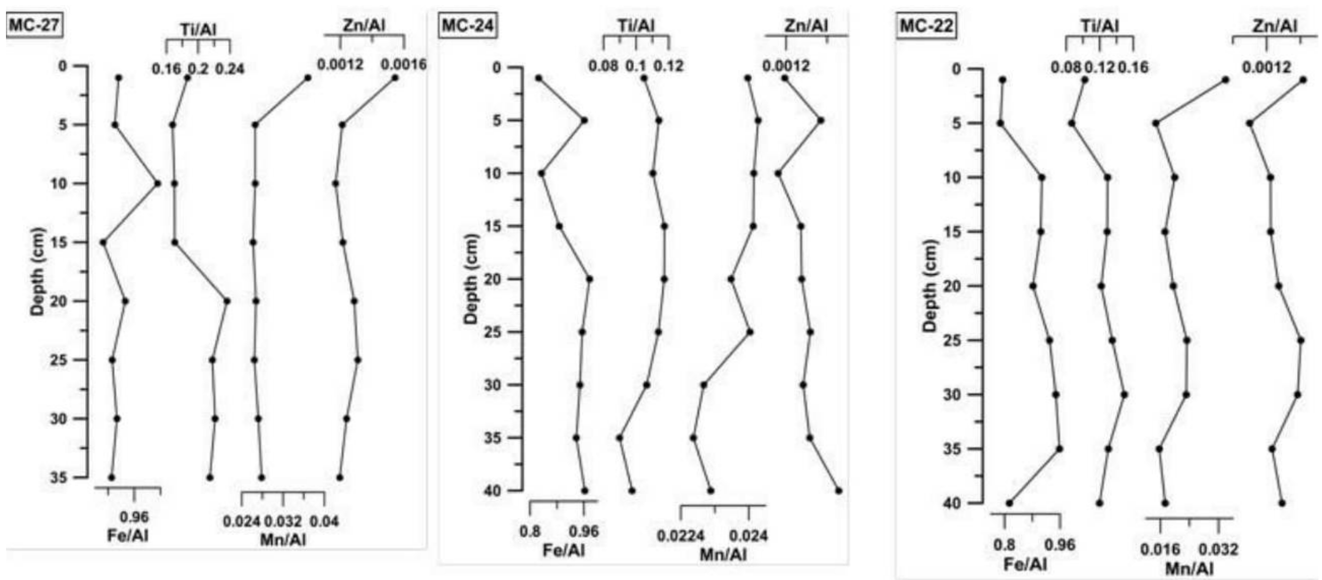

Fig. 9 — Vertical profiles of Al normalized metals in cores off Krishna

settling as even weak currents could transport it to deeper region. Smectite enrichment offshore with increasing water depth has been observed off Niger River and Kandalaksha Bay[58,59]. Illite on the other hand, due to its slightly coarser size was enriched in shallower regions. It was also noted that with increasing smectite, illite content decreased from shallow to deep waters and also depth-wise in majority of the cores. Such inverse relation was observed in many clay mineral studies worldwide due to their different settling rates[60].

Elements: Al is a major constituent of sediments attained from continents[61] commonly used to measure the extent of accumulation of the lithogenous component[62] and hence used for normalizing the elements. Higher Fe/Al, Ti/Al, Mn/Al and Zn/Al contents in the shallow regions indicated the abundant supply from lithogenous source rocks that were drained to the region via peninsular river runoff. The higher Fe/Al in the cores off Godavari may have been contributed from the leaching of iron rich sediments from ‘Red beds’, dominant rocks near Vishakapatnam coast. These red beds, composed of ferric hydroxide associated with appreciable amounts of kaolinite, explained its higher concentration in the samples in the shallow regions. Higher Ti content towards south may be contributed from mafic source, Deccan basalts, as supported by higher smectite in samples off

Godavari and Krishna. Furthermore, anthropogenic input contributing to the metal content in the sediments cannot be ruled out. Metal content higher than PAAS values in the cores off Godavari and Krishna may be coming from the industrial effluents in the recent years. The chemical factory 10 km from Godavari River manufacturing sulphuric acid situated in West Godavari district, zinc factory in Guntur district, the continuous ship activity at the Vishakhapatnam port and active oil rigs off Godavari which drill oil, may be the source of pollution. Also, aluminium and thermal power plants in Mahanadi basin and two fertiliser plants in Paradeep may be contributing to higher Zn/Al off Mahanadi.

Al, Ti and Fe can be used to trace the geology and weathering history of source rocks and their abundance varies conspicuously with the intensity of monsoonal precipitation[63,64]. Al normalized metals were enriched in upper few centimeters (Fig.7,8, & 9) in most of the cores that corresponded to higher clay values as compared to the lower section suggesting metal association with the clay fraction. Fe/Al was largely fluctuating within a small range down core (Fig. 7,8, & 9) with the exception of surface samples in upper 5 cm in majority of the cores where their concentration increased due to increased terrestrial input reflecting a probable intensification of SW monsoons in recent years. Earlier report[64] used Fe content as an indicator for climate change and stated that during intense monsoonal precipitation, breakdown and weathering of source rocks is more evident increasing the supply of dissolved Fe. The enrichment of Fe/Al towards the surface agreed mostly with higher clay and organic carbon in the surface samples suggesting the adsorption of organic matter on to the clay particles and binding together with iron oxides[65].

TOC/TN, TN/TP, TOC/TP molar ratios: The variations in C:N:P ratios are chiefly from changing proportions of terrestrially derived vs. marine-derived organic matter[66]. Phytoplanktons usually display TOC:TN ratio of 5-6[67,68] while a TOC:TN ratio of 12 to 14[69] is observed in the terrestrial plants which is enriched in cellulose and deprived of nitrogen. Earlier workers have also suggested that algae, freshwater and marine phytoplankton specifically have atomic C/N ratio < 10 and vascular land plants display C/N ratios of 20 and above[70,71,72,68]. However, for the present samples under study, the ratios given by Balakrishna, et al.[73] have been considered, as they represent the present environment setting. They have reported that C/N ratio of < 4 indicated organic matter derived from marine source (in situ) while ratios ranging from 8 to 14 indicated organic matter from terrestrial source. In the cores off Mahanadi, TOC/TN varied between 6.71 and 8.62 indicating a mixture of in situ derived marine organic matter with terrestrial matter. However, a sample at 20 cm in core MC-66 and 15 cm in core MC-65 showed high C/N ratio of 12.00 and 13.29, respectively (Table 2), denoting a higher input of terrestrial organic matter during that period. Illitic clays in the sediments may be associated with ammonium[74,68,75] that resulted in the lowering of C/N ratios below the ideal Redfield ratio in the upper section of the cores off Mahanadi. Off Godavari and Krishna, the molar C/N ratio was above 8 (Table 2) in majority of the samples indicating a terrestrial source of the organic matter. Off major river mouths, continental margins receive significant amount of organic matter of terrestrial origin[76]. Off Godavari in core MC-35 between 35 and 25 cm, the C/N ratio was higher than that on the surface which reveals increased terrestrial organic matter input in the past. This was supported by higher sand input from terrestrial region. Core MC-27 off Krishna showed decreased C/N ratios at 35 cm to 20 cm, except for a sample at 25 cm where C/N ratio was higher. Bacterial action might have caused degradation of organic matter thereby lowering the C/N ratio in the lower section of the core. Alternatively, high energy locally may be involved in suspending organic matter. Redfield ratios are used in oceanography to identify the extent of consumption of one nutrient on another[77,78]. TOC/TN molar ratios were higher than Redfield ratio (6.625) in all the sediment samples. On geologic time scales, the oceans are thought to be limited by P[79], but in much of the ocean on shorter time scales, N is the limiting nutrient[80,81]. The TN/TP molar ratios were < 3 in all of the samples significantly lower than Redfield ratio (Table 2). Earlier reports[82,83] revealed that N:P < 16 would indicate N limitation, while N:P > 16 would suggest P limitation. N:P ratio lower than 16 in the study area suggested the limitation of N. Minster, et al.[84] reported low N/P ratios in deep oceans probably as nitrogen is more labile than P. Also, phosphorus may be incorporated into sediments more rapidly than nitrogen thereby reducing the N/P ratios[85]. The TOC/TP molar ratios varied from 4 to 28, much lower than Redfield ratio (Table 2) and revealed significant

Table 2 — Molar ratios of carbon by nitrogen, nitrogen by phosphorus, carbon by phosphorus, S/I+C values off Mahanadi , Godavari and Krishna used in present study — (*Contd.*)

T	CORE NO.	WATER DEPTH	DEPTH	TOC/TN M	TN/TP M	TOC/TP M	S/I+C
Mahanadi	MC-66	104	1	8.50	1.29	10.97	0.29
			5	6.71	0.65	4.33	0.26
			10	9.43	0.48	4.48	0.13
			15		0.00	4.42	0.13
			20	12.00	0.50	6.02	0.12
			25	7.29	0.50	3.66	0.09
	MC-65	260	1	7.17	2.57	18.39	0.27
			5	7.43	1.81	13.42	0.23
			10	8.26	1.10	9.12	0.29
			15	13.29	0.98	13.04	0.26
			20	8.22	1.79	14.67	0.25
			25	7.66	1.68	12.87	0.23
			30	8.29	1.66	13.75	0.39
			35	8.62	1.97	16.97	0.08
	MC-64	499	1	7.68	2.48	19.06	0.33
			5	7.67	2.51	19.25	0.27
			10	7.98	2.32	18.52	0.35
			15	7.62	2.38	18.17	0.27
			20	8.35	2.38	19.89	0.25
			25	8.26	2.45	20.24	0.28
			30	8.22	1.22	10.02	0.29
			35	8.19	2.46	20.18	0.34
Godavari	MC-30	40	1	12.16	2.37	28.76	2.10
			5	11.57	1.03	11.94	1.94
			10	10.48	1.13	11.83	2.90
			15	10.38	1.13	11.72	1.69
			20	13.22	0.96	12.67	2.19
			25	11.76	0.85	10.04	2.69
			30	11.14	1.10	12.24	5.93
	MC-31	107	1	10.71	1.44	15.40	2.40
			5	8.86	2.32	20.57	1.26
			10	11.14	1.00	11.18	1.84
			15	9.90	0.99	9.82	5.44
			20	9.43	1.27	12.01	3.21
			25	10.03	1.22	12.24	2.29
			30	10.90	0.90	9.84	3.58
			35	9.32	0.95	8.86	3.68
	MC-33	495	1	9.92	1.58	15.68	3.53
			5	10.13	1.24	12.58	7.44
			10	9.29	1.32	12.27	2.75
			15	10.13	1.13	11.44	1.84
			20	10.48	1.10	11.51	2.04
			25	9.12	1.38	12.58	2.53
	MC-35	1005	1	9.98	1.44	14.34	5.91
			5	9.90	1.31	12.94	3.97
			10	10.37	1.22	12.66	3.41
			15	10.71	1.10	11.80	3.65
			20	10.37	1.16	12.01	5.60
			25	12.21	1.03	12.61	4.18
			30	13.59	0.93	12.64	3.57
			35	12.43	1.03	12.83	5.29

(*Contd.*)

Table 2 — Molar ratios of carbon by nitrogen, nitrogen by phosphorus, carbon by phosphorus, S/I+C values off Mahanadi , Godavari and Krishna used in present study — (*Contd.*)

T	CORE NO.	WATER DEPTH	DEPTH	TOC/TN M	TN/TP M	TOC/TP M	S/I+C
Krishna	MC-27	55	1	11.02	0.77	8.50	7.26
			5	14.42	1.31	18.85	5.97
			10	11.68	1.00	11.72	5.41
			15	12.00	1.03	12.39	4.95
			20	6.86	0.82	5.63	2.33
			25	13.47	0.93	12.52	5.57
			30	8.23	0.65	5.31	8.14
			35	7.03	0.75	5.29	4.80
	MC-24	202	1	10.13	1.16	11.70	3.90
			5	10.48	0.92	9.68	4.22
			10	9.43	0.92	8.71	4.42
			15	10.18	0.90	9.19	4.92
			20	10.50	0.84	8.82	4.00
			25	10.61	0.88	9.35	3.87
			30	10.93	0.80	8.77	3.96
			35	9.62	0.95	9.09	5.50
			40	9.86	0.98	9.63	4.10
	MC-22	767	1	8.63	1.64	14.16	8.65
			5	9.30	1.51	14.00	2.18
			10	11.39	0.83	9.47	2.03
			15	11.71	1.07	12.53	2.21
			20	11.51	0.79	9.10	2.63
			25	12.57	0.71	8.96	3.77
			30	11.02	0.81	8.93	4.19
			35	10.54	1.05	11.07	3.58
			40	12.10	1.04	12.61	2.99

generation of phosphorus relative to organic carbon. Low C/P ratios in bulk of the sediments suggested that the organic matter is not freshly deposited marine detrital material[86]. This was also supported by the higher C/N ratios in the sediments which indicated source of organic matter as terrestrial.

Paleomonsoon – through S/I+C ratio

Clay minerals in marine sediments provide information of overall climate impact[26]. Since smectite is formed under humid conditions and illite and chlorite are formed under arid, cold conditions, their ratios can be utilized as indicators of humidity[25,28,87]. To understand the possible paleomonsoon pattern, in addition to describing the abundances of individual clay minerals, the ratios of clay minerals (S/I+C) down core have been calculated (Table 2) to nullify dilution effects[88]. Based on the available sedimentation rates, the 35 cm of sediment in cores at deeper water depths may have been deposited in the last 145 years off Mahanadi and 102 years off Krishna while core MC-30 and MC-31 from shallower water depths off Godavari, the 35 cm sediment section probably represented material from last 140 years.

S/I+C ratio was slightly higher in the surface sediments compared to that of 5 cm level in majority of the cores indicating increased rainfall in recent years probably of SW monsoons. This was confirmed with the data of the Indian Meteorological Department (IMD) which reported higher than normal rainfall in the monsoon season of 2013, which is the period just before sampling. A cyclonic storm "Viyaru" developed in the Bay of Bengal in May 2013. As a result of the formation of Viyaru, the low level equatorial monsoon flow strengthened which allowed the early arrival of the SW monsoon to set in over the Bay of Bengal leading to higher precipitation during that season. Smectite is more stable during higher rainfall when parent rocks are basic igneous rocks[89]. The 25 cm to 10 cm section in core MC-66 showed lower S/I+C ratio. However, this lowering of the ratio cannot be considered due to weaker rainfall during this period as sand content is very high in this section denoting increased terrestrial matter input reflecting intensification of SW monsoon and this coarser material may be enriched in illite more than smectite thereby lowering the ratio. Further, the S/I+C ratio in the 25 cm to 10 cm section in other cores of the same transect is higher, supporting humid environmental conditions during that period. The rainfall data obtained from IMD for the coastal districts off Mahanadi i.e. Paradip, Puri and Cuttack from 1910 to 1973 revealed good rainfall above 1000 mm supporting the interpretation. Off Godavari, the S/I+C ratio slightly decreased between 15 cm to 5 cm in majority of the cores indicating a weaker monsoon during this period corresponding to about 80 to 20 years ago. In the lower section of core MC-35, the S/I+C ratio was higher from bottom up to a depth of 20 cm indicating an increase in monsoon intensity during that time. This was also supported by the higher sand content in this section of the core bringing in additional terrestrial matter probably during a flood event. In the peak monsoon season (June- September), when the SW monsoons winds are most prevalent, a low pressure monsoon trough is developed over the Bay of Bengal[90]. This low pressure zone moving landward accompanied by monsoon clouds brings high rainfall on the Indian sub-continent. Off Krishna, except for higher S/I+C ratio in the surface sample that reflected higher rainfall in recent years, the down core variation in S/I+C ratio was largely constant. However, at 20 cm depth, there was a change in the trend of S/I+C in all cores off Krishna that corresponded to about 60 years before present. A probable shift from wetter to drier i.e. SW summer monsoon to NE winter monsoon must have taken place that explained the relatively higher S/I+C ratio associated with higher sand up to a depth of 20 cm. According to earlier reports[47] , about 50 % of the total annual sediment flux reaching the Bay of Bengal is from the SW monsoons. Based on the available sedimentation rates the 20 cm section corresponds to the year 1953 and from the data of IMD the rainfall recorded in this year was 737 mm which was above normal in the Guntur district located off Krishna supporting the view of a good rainfall during SW monsoon season.

Productivity nutrients – factors involved

The TOC and TN content in marine sediment is controlled by numerous factors such as the grain size, productivity and oxygen content of the waters, water depth, intensity of monsoons, bacterial degradation, and sedimentation rates[91,76,92,93,77,94,95]. The TOC and TN content in the sediment increased with increasing distance from the coast. The enrichment of TOC and TN towards the surface in the cores (Figs.4 & 5) coincided with higher clay reflecting their association. Higher clay content associated with higher contents of organic matter results in a lower permeability of oxygen and a higher plankton oxygen uptake[96]. This might have reduced the oxygen content to some extent in the surface zone which was favorable for preservation of TOC and TN. Further, the organic matter content in the marine sediments serves as a proxy of surface water productivity[97,39]. The TOC, TN and TP concentrations are rather low in cores along western Bay of Bengal reflecting a poor biological productivity. In spite of the abundant nutrient influx from the Indian peninsular rivers, bulk of it may have been lost to the deep sea because of the narrow shelf[48,98,99]. Another possible reason for low organic matter in the region may be due to higher rate of sedimentation in the region which restricted the time the organic matter was captured within the sediments as seen from the study of Ramaswamy, et al. [100] at Ayeyarwady continental shelf. The TP values in the present core locations were lower than the PAAS (Post Archean Australian Shale) value of 0.07[61]. Phosphorus was almost absent in atmosphere and their only source is from organic debris via rivers[95]. Furthermore, some earlier studies[101,102] reported lack of upwelling in the waters and lack of vertical mixing of the surface layers due to the presence of strong stratification made Bay of Bengal less productive.

Low calcium carbonate (2 to 4%) was observed in the sediments. The presence of low $CaCO_3$ content was related earlier to probable dilution by higher terrigenous influx from the peninsular Indian rivers[103]. However, exceptionally high average $CaCO_3$ content (65 %) was obtained in core MC-66 at 104 m water depth off Mahanadi (Fig. 6). This is due to increased productivity probably during pronounced SW monsoon winds which churns up the nutrients in the water column towards the surface enhancing the intensity of upwelling. A portion of known quantity of sand fraction from core MC-66 was treated with 10 % HCl which dissolved the carbonate fraction. The percentage of sand obtained was only 40 % while 60 % of the sediment was composed of molluscan bivalve shell debris supporting the view of a high productivity during that period. The $CaCO_3$ enrichment was also observed in a majority of the cores at 25 to 20 cm depth (Fig. 6), while TOC and TN content was reduced at the corresponding depth thus revealing dilution of TOC and TN by the carbonate shell fragments. Conversely, the $CaCO_3$ concentration was low at 15 cm in most of the cores off Godavari corresponding to weaker rainfall period presumed from S/I+C ratios. Decreased $CaCO_3$ preservation is linked to the weakened monsoon leading to reduced upwelling[104]. In addition to weaker upwelling in Bay of Bengal, another possible reason for low $CaCO_3$ in bulk of the cores may be due to acidity produced from the remineralization of organic matter which releases carbon dioxide leading to dissolution of available carbonates[105].

Changing bottom water oxygen conditions

Organic elements: The burial rates and dissolved oxygen concentration also controlled the availability of TOC and TN content in the sediments[106,107]. In the Bay of Bengal the OMZ was found to be intensified at intermediate (60 to 1000 m) water depths[108,30,109]. The average TOC content was low (1 to 2%), even in sediments which were within OMZ. In core MC-35 at 1005 m water depth off Godavari transect, the average TOC value was slightly reduced as compared to shallow water depth sediments, as in Bay of Bengal dissolved oxygen was higher at water depths deeper than 1000 m[110]. Under the prevalent oxic conditions at deeper water depths generally TOC is less preserved. Furthermore, under low oxygenated waters, biochemical breakdown of nitrates to molecular nitrogen (i.e. denitrification) is evident. However, no significant enrichment of TN was observed in the samples at intermediate water depths. Earlier reports[30,111,109] found absence of secondary nitrates which are signatures for denitrification. Prasanna Kumar, et al.[101] also suggested that the river run-off was devoid of nitrates resulting in low primary productivity in western Bay of Bengal. TOC enrichment indicated weaker SW summer monsoon[112], while reduced TOC and TN contents at 35 to 30 cm in MC-31 and MC-35 and in the lower section of cores off Krishna up to 20 cm (Figs. 4 & 5) may be due to increased oxygenated water influx from the rivers during higher SW monsoon rainfall. The higher S/I+C ratios at corresponding depths also supported increased humid conditions during that time. Also, the Ti/Al values were slightly higher in the corresponding sections indicating higher terrestrial input during increased rainfall. Additionally, the efficiency with which phosphorus is buried relative to organic carbon can be used as an indicator of redox conditions in marine systems[113]. However, in the samples under study, the TP contents were largely constant with depth (Fig. 5) and also with increasing distance from shelf which limited the use of TP to identify the reducing environment.

Redox elements: Enrichment of Mn takes place under oxic conditions[114]. As the conditions became more reducing, Mn got depleted from the sediments[36,115,116,37,38]. Mn/Al distribution down core was largely stable in majority of the cores off Mahanadi and Krishna (Figs. 7 & 9) indicating no major shifts in the OMZ in recent years. However, in the cores off Godavari, a reduction in Mn/Al concentration in the 15-5 cm section (Fig. 8) coinciding with low S/I+C ratio and higher TOC and TN values was noted. This suggested that weaker rainfall turned the water anoxic as the available oxygen was consumed by the planktons. Under prevalent high OMZ, Mn breaks down under reducing conditions. Moreover, Mn/Al and Zn/Al enrichment in the surface samples of majority of the cores (Figs 7, 8 & 9) and in the lower section of most of the cores off Godavari from bottom up to 20 cm suggested increased metal influx during intensified SW monsoons as reflected in relatively higher S/I+C ratio in the corresponding samples. Also, a majority of the cores off Godavari enriched with respect to Ti/Al in the lower section of the cores up to a depth of 20 cm (Fig. 8) as compared to the upper section supporting higher terrestrial influx during increased rainfall.

Conclusion

Two distinct sediment provenances are identified with acid igneous source (granitic rocks) through Mahanadi River and basic igneous source (Deccan Traps) through Godavari and Krishna Rivers. Lithogenous source and presence of OMZ play an important role in the distribution of metals in the region. Effluents from industries in coastal region may have also contributed to the metal content. Mn/Al was largely consistent down core in most of the cores indicating no major shift in the OMZ in recent years. In spite of the abundant nutrient influx from the peninsular Indian rivers, the TOC, TN, TP and $CaCO_3$ concentrations were low both spatially and depth-wise in western Bay of Bengal that reflected poor biological productivity. The intensity of monsoons inferred from S/I+C ratios played a major role in the preservation of organic matter and metals. High S/I+C ratios reflected intensified SW monsoon in recent years while low S/I+C ratio indicated weaker rainfall.

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