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Source of sediment components and processes with time in middle regions of tropical estuaries along west coast of India

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To understand the source of materials and processes operating, the sediment cores collected from mudflats representing middle region of Sharavathi and Gurupur estuaries were analysed for grain size, organic carbon, clay mineralogy, bulk metals and clay chemistry. Relatively higher concentration of sand in the Sharavathi and higher clay and organic carbon content in the Gurupur estuary indicated variations in the depositional environment between the two estuaries. Further, higher sand in middle section and silt in the upper section in Sharavathi and Gurupur estuaries respectively indicated variations in the depositional conditions with time in both the estuaries. The kaolinite was the most abundant clay mineral, and the abundance and distribution of clay minerals in the two estuaries revealed the role of catchment area geology and river-sea water mixing conditions as major factors in sediment deposition. All the metals showed similar distribution pattern to finer sediments and organic carbon in the Sharavathi estuary, indicating their role in distribution of metals. Also, significant association of metals with Al suggested their natural source in this estuary. Similar distribution pattern of metals with Al in the clay fraction also supported lithogenic source of metals in the Sharavathi estuary. In the Gurupur estuary, role of sediment components was limited in the distribution of metals and insignificant association of metals with Al suggested their non-natural source. Non-similar distribution pattern of metals to that of Al in the clay fraction of the Gurupur estuary and their insignificant association with Al indicated metals source as anthropogenic.

[**Keywords:** Middle Estuary, Mudflats, Metals, Source, Processes]

Introduction

Estuaries are the transitional zones between the marine and terrestrial environments are divided into lower, middle and upper regions based on the variations in sea-river water mixing[1]. Lower estuary is in free connection with the open sea and is dominated by marine processes regulated by waves and tides[2], whereas the upper estuary is dominated by freshwater input derived from river and its tributaries. The middle estuary, however, is exposed to mixing of sea and river water and hence is subjected to greater variations in depositional processes. Therefore, the study of middle estuary is significant to understand the sea-river water mixing processes.

Mudflats are one of the prominent sub-environments found along the middle estuarine region of tropical estuaries. Mudflats primarily consist of fine sediment deposits originating from two main sources, namely land i.e. brought by river runoff and sea i.e. marine input[3]. Material brought by fresh water from catchment area when mix with saline waters, flocculation of suspended particulates occur which largely regulates settling and sediment deposition across the mudflats in the middle estuary. Metal ions adsorb onto the surface of these flocculated grains and/or get trapped within organic particles and get incorporated into the sediments. Therefore, grain size plays an important role in the distribution of metals in cohesive mudflat sediments[4]. Along with finer sediments, mudflats also favour deposition of higher organic matter content which further facilitates the deposition of metals. The variations in distribution and abundance of metals has been successfully used to reconstruct the changes in the sedimentary environment with time[5,6,7]. Mudflat sediments are also used in differentiating natural and anthropogenic sources, and associated processes[8,9].

In the present study an attempt has been made to understand source and processes in the sea-river water mixing zone using mudflat sediments collected from the middle region of the tropical estuaries, along west coast of India.

Study area

The Sharavathi and Gurupur rivers originate in the Western Ghats and drain into the Arabian Sea along the south west coast of India. These estuaries draining the region of the Karnataka state, represent humid tropical climate with an average annual rainfall of about 3750 mm of which around 90% falls during the monsoon (July and August) season. The Sharavathi River has a total length of 130 km, a catchment area of 3600 km^2 [10] and annual fresh water discharge of 4545 x 10^6 m^3 yr^{-1} [11] while, the Gurupur River is approximately 87 km long with a catchment area of 540.62 km^2 and annual fresh water discharge of 2,822 x 10^6 m^3 yr^{-1} [12,13]. The tidal range in Sharavathi is 1.41 and 0.66 m during spring and neap tides, respectively[14]; whereas, in the Gurupur the highest tide is 1.54 m which decreases to 0.25 m during neap tide[15]. In general, rock types consist of granites and granitic gneisses in the catchment area of these estuaries. The geological formations within Sharavathi catchment area include pre-Cambrian rocks rich in iron and manganese. On the other hand, the basin area of the Gurupur River is overlain by Pliocene to Recent laterite capped plateaus and alluvium[16]. Iron ore was mined in the catchment area of the Gurupur estuary by Kudremukh iron ore company limited (KIOCL). However, mines have not been in working condition for the past few years. Further, the Baikampady industrial estate is located on the bank of the Gurupur River which accommodates major refineries, storage of crude and finished petroleum products, LPG storage and bottling, fertilizer plant, pharmaceutical industry, brewery, edible oil processing units, sea food processing units, lead refining unit, cashew processing units, paint and dispersion unit, iron ore pelletization plant and pig iron plant apart from few engineering, fabrication, plywood plants and ready-mix plants[17]. The estuarine limits of these rivers are characterised by abundant intertidal mudflats and exhibit good coverage of mangroves. In recent years, the estuaries have received a large input from agricultural, dumping of garbage and disposal of sewage, industrial and mining wastes. In this study, an attempt has been made to understand source and processes regulating the metals in the middle region of two estuaries.

Materials and Methods

The sediment cores from intertidal mudflats representing middle estuarine region of Sharavathi S-2 (14°14'31.22"N; 74°31'22.03"E) and Gurupur GP-2 (12°56'34.31"N; 74°49'53.66"E), were collected from 16 km and 14 km from the estuarine mouths respectively during the field survey conducted in May 2013 (Fig 1). Sediment cores were collected using a hand operated PVC corer. The length of the core S-2 (Sharavathi) was 60 cm while that of core GP-2 (Gurupur) was 72 cm. Sub-sampling was done at 2 cm intervals with the help of a plastic knife. The sub-samples were sealed in clean plastic bags, labelled, stored in an ice box and transferred to laboratory. Sampling stations were located using a hand held Global Positioning System (GPS). In the laboratory, sub-samples were stored at 4^0C till further analysis.

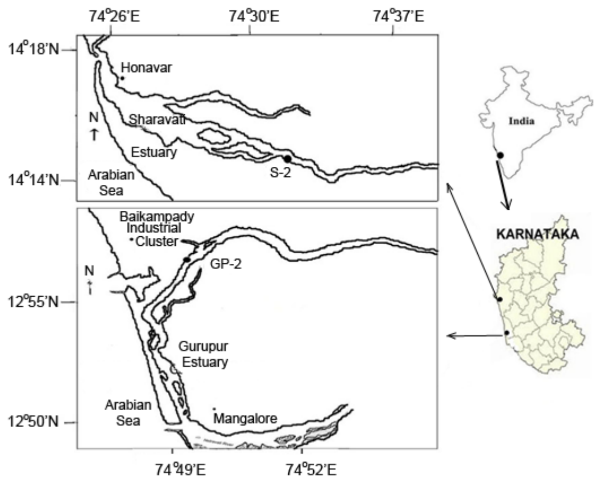


Fig 1 Map showing sampling locations.

Later, the sub-samples were oven dried at 60^0C. Sediment components (sand: silt: clay) were analysed following pipette method[18] and clay minerals in selected sub-samples were determined following the procedure given by Rao and Rao (1995)[19]. A portion of the dried samples was powdered and homogenized using an agate mortar and pestle. A part of powdered and homogenized samples was used for the estimation of organic carbon following modified Walkey-Black titration method[20]. The other part was used for metal analysis, in which, after complete digestion of known weight of sediment sub-samples with 7:3:1 HF:HNO_3:$HClO_4$ acid mixture[21], sample solutions were analysed for bulk metal chemistry (Al, Fe, Mn, Ni, Co, Cu, Zn, and Cr) using an atomic absorption spectrophotometer (AAS, Varian

AA240FS). Clay-sized fraction of selected sub-samples of both the cores was also digested and analysed for the above listed metals. The accuracy of the analytical method was tested by digesting standard reference materials 2702 obtained from National Institute of Standards and Technology (NIST) and was aspirated into the AAS. The average recoveries, ± standard deviations found for each metal were 96±12, 89±12, 91±15, 86±16, 74±12, 82±15, 84±16 and 79±14 for Al, Fe, Mn, Ni, Co, Cu, Zn and Cr, respectively. Also, the instrument was checked for its reproducibility by repeating the standard after every ten samples.

Statistical analysis

The Pearson's correlation analysis involving sediment components, organic carbon and major as well as trace metals in cores S-2 and GP-2 was performed. Additionally, factor analysis was attempted to understand source and association by using the software Statistica 7. In case of factor analysis, the numbers of factors were selected on the basis of criteria given by Kaiser (1960)[22], with eigenvalues greater than 1.

Results and Discussion

Sediment components and organic carbon

Table 1a Range and average concentration of sediment components and organic carbon in cores S-2 and GP-2

Sediment core	Sand (%)			Silt (%)			Clay (%)			Organic Carbon (%)		
	Range		Avg	Range		Avg	Range		Avg	Range		Avg
	Min	Max		Min	Max		Min	Max		Min	Max	
S-2	7.98	94.23	38.75	4.57	89.14	43.1	0.64	42	18.16	0.09	3.04	1.87
GP-2	4.91	50.2	14.89	27.37	63.77	45.24	21.24	54.72	39.87	0.41	4.28	2.26

Table 1b Range and average concentration of major metals in cores S-2 and GP-2

Sediment core	Al (%)			Fe (%)			Mn (ppm)		
	Range		Avg	Range		Avg	Range		Avg
	Min	Max		Min	Max		Min	Max	
S-2	1.84	10.69	8.02	1.51	7.23	4.87	123	2547	1181
GP-2	0.08	15.24	10.18	5.44	14.93	7.86	112	309	157

Table 1c Range and average concentration of trace metals in cores S-2 and GP-2

Sediment core	Ni (ppm)			Co (ppm)			Cu (ppm)			Zn (ppm)			Cr (ppm)		
	Range		Avg	Range		Avg	Range		Avg	Range		Avg	Range		Avg
	Min	Max		Min	Max		Min	Max		Min	Max		Min	Max	
S-2	37	148	103	5	54	27	65	190	141	21	100	72	66	183	132
GP-2	33	199	65	24	57	31	18	43	32	75	400	161	309	1602	680

The range and average concentration of sediment components and organic carbon in cores S-2 and GP-2 are given in the Table 1a. In both estuaries silt and clay contribute to more than 60% representing higher finer sediments with considerable organic carbon (~2%) of middle estuarine cores. Generally sand is predominant in the lower estuary indicating prevailing higher energy conditions and finer sediments are carried towards middle estuary from the lower estuary by the tidal currents. The finer sediments get settled in the quiet environment of middle estuary.

Table 2a Paired-samples t-test for the comparison of means

Pairs of variables	Difference of means	t	df	p (2-tailed)
Sand core S-2 - Sand coreGP-2	23.81423	4.320251	29	0.000
Silt core S-2 – Silt core GP-2	-2.92623	-0.56642	29	0.575
Clay core S-2- Clay core GP-2	-20.888	-10.3723	29	0.000
OC core S-2 - OC core GP-2	-0.2305	-1.24423	29	0.223
Al core S-2 – Al core GP-2	-2.72351	-3.56706	29	0.001
Fe core S-2 – Fe core GP-2	-3.20389	-5.68688	29	0.000
Mn core S-2 – Mn core GP-2	1027.662	7.711536	29	0.000
Ni core S-2 – Ni core GP-2	34.8	3.207088	29	0.003
Co core S-2 – Co core GP-2	-4.08333	-1.64513	29	0.110
Cu core S-2 – Cu core GP-2	110.05	13.99752	29	0.000
Zn core S-2 – Zn core GP-2	-86.475	-7.85948	29	0.000
Cr core S-2 – Cr core GP-2	-614.728	-7.79692	29	0.000

Table 2b Pearson's correlation table for core S-2 (n=30). Values in bold indicates significant correlation at $p<0.05$

	Sand (%)	Silt (%)	Clay (%)	Org C (%)	Al (%)	Fe (%)	Mn (ppm)	Ni (ppm)	Co (ppm)	Cu (ppm)	Zn (ppm)	Cr (ppm)
Sand (%)	1											
Silt (%)	**-0.93**	1										
Clay (%)	**-0.69**	**0.36**	1									
Org C (%)	**-0.81**	**0.65**	**0.75**	1								
Al (%)	**-0.77**	**0.61**	**0.75**	**0.97**	1							
Fe (%)	**-0.83**	**0.68**	**0.75**	**0.97**	**0.97**	1						
Mn (ppm)	**-0.79**	**0.72**	**0.56**	**0.89**	**0.87**	**0.92**	1					
Ni (ppm)	**-0.76**	**0.65**	**0.62**	**0.94**	**0.95**	**0.95**	**0.89**	1				
Co (ppm)	**-0.49**	**0.36**	**0.51**	**0.54**	**0.48**	**0.52**	**0.5**	**0.43**	1			
Cu (ppm)	**-0.83**	**0.68**	**0.75**	**0.97**	**0.97**	**0.98**	**0.93**	**0.95**	**0.54**	1		
Zn (ppm)	**-0.8**	**0.65**	**0.72**	**0.96**	**0.97**	**0.98**	**0.89**	**0.95**	**0.51**	**0.99**	1	
Cr (ppm)	**-0.86**	**0.72**	**0.74**	**0.92**	**0.9**	**0.95**	**0.91**	**0.89**	**0.54**	**0.96**	**0.93**	1

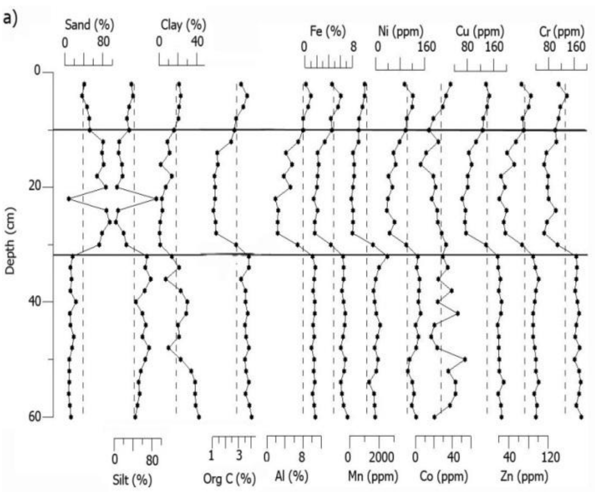
Table 2c Pearson's correlation table for core GP-2 (n=36). Values in bold indicates significant correlation at $p<0.05$

	Sand (%)	Silt (%)	Clay (%)	Org C (%)	Al (%)	Fe (%)	Mn (ppm)	Ni (ppm)	Co (ppm)	Cu (ppm)	Zn (ppm)	Cr (ppm)
Sand (%)	1											
Silt (%)	**-0.46**	1										
Clay (%)	**-0.38**	**-0.65**	1									
Org C (%)	**-0.41**	-0.01	**0.36**	1								
Al (%)	**-0.37**	0.05	0.27	-0.03	1							
Fe (%)	0.04	0.31	**-0.35**	-0.32	0.01	1						
Mn (ppm)	**0.49**	-0.27	-0.14	-0.19	-0.13	0.02	1					
Ni (ppm)	-0.15	**0.43**	-0.32	-0.14	0.14	0.06	-0.15	1				
Co (ppm)	**0.38**	0.11	**-0.44**	**-0.58**	0.08	**0.4**	**0.51**	-0.1	1			
Cu (ppm)	**-0.45**	0.25	0.13	**0.43**	-0.17	-0.25	-0.02	-0.03	-0.29	1		
Zn (ppm)	-0.32	0.14	0.13	0.25	0.19	-0.04	0.21	-0.04	0.21	**0.36**	1	
Cr (ppm)	0.07	**0.48**	**-0.57**	**-0.61**	-0.07	**0.57**	0.02	0.27	**0.63**	-0.22	-0.13	1

However, when the two estuaries are compared, sand shows relatively higher average value at S-2 whereas, clay and organic carbon show higher average values for GP-2. The percentage of silt is slightly higher in the core GP-2. The results of t test (2 tailed) show significant difference in sand

and clay between the two cores while difference of means is negligible in case of organic carbon and silt (Table 2a). Sand is higher in the core S-2 whereas, clay is present in higher concentration in the core GP-2.

On the basis of distribution pattern of sediment components (Fig. 2a), the core S-2 was divided into three sections, the lower (60 to 32 cm), middle (32 to 10 cm) and upper (10 to surface) sections. In the lower section of the core, sand is lower than average and not much variation in sand percentage is seen. The silt and clay show increasing and decreasing distribution pattern in this section, respectively. In the middle section of the core, sand percentage increases drastically from 32 to 10 cm with a sharp decreasing peak at 22 cm depth. Further, in the upper section, sand percentage decreases towards surface. The variations in sand percentage are compensated by silt and clay, more precisely; silt shows point to point variations opposite to that of sand in the upper two sections. Organic carbon shows a similar distribution pattern to that of finer sediments in all the sections. Based on the variations in the distribution pattern of sediment components with depth, the core GP-2 (Fig. 2b) was divided into two sections, viz. a lower section from bottom to 40 cm and the upper section from 40 cm to the surface. The sand does not show much variation from lower to upper section, except at 12 cm depth where a prominent increasing peak of sand is observed. Silt shows an overall slightly decreasing distribution pattern in the lower section, while in the upper section its percentage increases towards the surface, with fluctuations. In both the sections, the variation in silt percentage is compensated by clay. Organic carbon shows overall decreasing trend from lower to upper sections of this core with a sharp decrease at 12 cm depth.



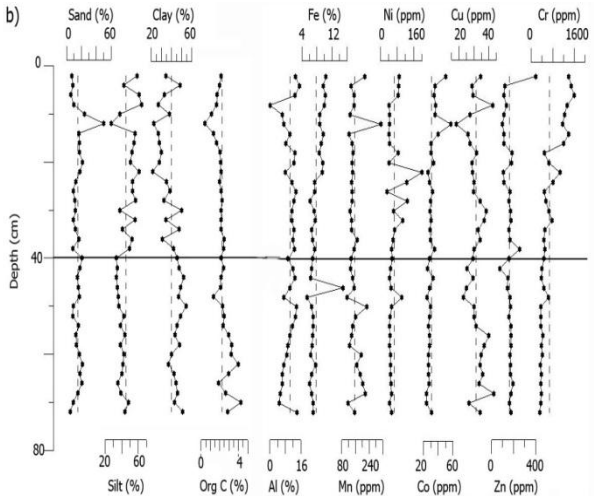


Fig 2 Down core variation of sediment components, organic carbon and metals with vertical lines of average values in cores S-2 (a) and GP-2 (b)

The grain size of sediment reflects prevailing hydrodynamic energy conditions[23]. The variations in the percentage of sand between the lower and middle sections of the core S-2 indicate change from a relatively low-energy depositional environment to high-energy environment[24]. The relatively higher coarser size particles in the middle section must have been brought by intense monsoon controlled runoff into the Sharavathi estuary. However, decrease in coarser sediments in recent years (top 10 cm) could be the result of diversion of river water for drinking and irrigational purposes by construction of small dams on tributaries (Nandihole, Haridravathi, Mavinahole, Hilkunji, Yennehole, Hurlihole and Nagodihole). The construction of dams must have led to changes in natural flow of fresh water affecting sedimentation patterns[25]. In core GP-2, sand is largely constant; however, the percentage of silt is slightly higher in the upper section than the lower section which suggests change in the hydrodynamic energy conditions with time from lower to higher energy environments.

Further, an attempt was made to understand hydrodynamic conditions prevailed during deposition of sediments by plotting sediment components on a ternary diagram proposed by Pejrup (1988)[26]. The majority of sediment components of the Sharavathi estuary (Fig.3a) fall in group III and IV indicating deposition of sediments under violent to extremely violent hydrodynamic conditions. In the case of core GP-2 (Fig.3b), sediment components vary from group II to III suggesting deposition of sediments in relatively violent to violent energy conditions from lower to upper sections. Distribution of sediment components with time therefore indicates difference in hydrodynamic conditions in the two estuaries, larger variation being in Sharavathi.

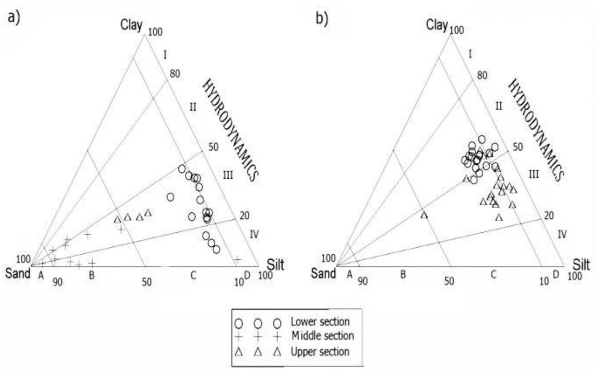


Fig 3 Ternary diagram for cores S-2 (a) and GP-2 (b)

The organic carbon in all the sections is associated with the finer sediments in the core S-2. The similar distribution pattern of organic carbon to that of finer sediments in the core S-2 reflects the incorporation of organic matter into the finer fractions of sediment by adsorption phenomena[27] due to similar settling velocity[28] and larger surface area of finer sediments. In the middle section, higher sand input must have diluted the organic matter content. In core GP-2, the distribution of organic carbon is similar to clay. The relatively higher percentage of organic carbon in the lower section in both the estuaries indicates higher deposition of organic matter in the past and/or partial decomposition and preservation of refractory organic matter in the sediments[8].

Clay minerals

In both the cores kaolinite is highly dominant. The abundance of clay minerals follows the order of kaolinite > illite > chlorite > smectite in the core S-2, while in the core GP-2 it follows the order of kaolinite > chlorite > illite > smectite. However, concentration of smectite and kaolinite when compared between the two estuaries, higher average percentage is noted in the Sharavathi estuary (Table 3) whereas illite and chlorite are higher in the Gurupur estuary. In core S-2, the concentration of smectite, illite and kaolinite fluctuates from bottom to 30 cm (Fig 4a). Further, smectite and illite show sharp increasing peak at 22 cm, while kaolinite exhibits decreasing peak. Above 22 cm, smectite and illite show overall decease towards the surface, whereas, kaolinite exhibits overall increase. Chlorite concentration fluctuates throughout the core S-2. The clay minerals fluctuate around average line from bottom to 30 cm in the core GP-2 (Fig 4b). Further, towards surface, all the minerals show overall increase with fluctuations.

Table 3 Range and average concentration of clay minerals in cores S-2 and GP-2

Sediment core	Smectite (%)			Illite (%)			Kaolinite (%)			Chlorite (%)		
	Range		Avg	Range		Avg	Range		Avg	Range		Avg
	Min	Max		Min	Max		Min	Max		Min	Max	
S-2	1.71	14.72	5.85	4.9	20.3	8.72	59.31	88.38	77.6	3.29	10.87	7.82
GP-2	2.53	7.62	4.96	8.84	19.79	12.93	63.91	79.85	72.38	5.57	13.34	9.73

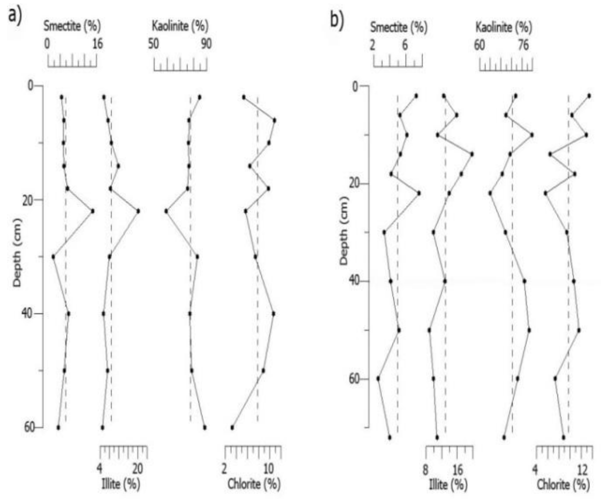


Fig 4 Variation in clay minerals with vertical lines of average values in cores S-2 (a) and GP-2 (b)

The clay mineral types and the proportions of the clay minerals in sediments depend on the nature of the source rocks[29] and climatic conditions. The dominance of Kaolinite in the sediments of both the estuaries indicates the role of catchment area geology in abundance of clay minerals. The weathering of granite and granite gneisses present in the catchment area of Sharavathi and Gurupur estuaries tend to release more kaolinite under a warm and humid climate[30].

Kaolinite is formed in the lithogenic environment from feldspars and, to a lesser extent, micas in sandstones[31]. In addition, change in salinity regulates the flocculation of clay minerals within an estuary. Rapid flocculation of kaolinite takes place under a 2 ‰ of salinity, leading to fast sedimentation in slightly saline waters[32] whereas, smectite flocculates in normal saline waters. The core S-2 was collected 16 km and core GP-2 from 14 km from the mouth of respective estuaries. Further, fresh water flow is much less in Gurupur estuary than Sharavathi estuary. Therefore, relatively higher salinity at the core location in Gurupur estuary is expected which must have facilitated adsorption of more metal on smectite. Therefore, sea-river water mixing conditions must have regulated the abundance of clay minerals.

Major metals (Fe, Mn and Al)

The range and average concentration of major metals in cores S-2 and GP-2 are given in the Table 1b. The percentage of Fe is higher in the core GP-2 whereas, Mn is present in very high concentration in the core S-2. This is also indicated by results of paired t test (Table 2a). The concentration of Fe and Mn is higher in the lower section of the core S-2 as compared to middle and upper sections (Fig. 2a). In the lower section, Fe and Mn do not show much variation in their distribution pattern. In the middle section, a sudden decrease in Fe and Mn concentration up to 28 cm is observed. Above this, Fe and Mn concentration remains nearly constant up to 14 cm followed by an increase towards surface of the core S-2 in the upper section. In core GP-2 (Fig. 2b), concentration of Fe is lower than average in the lower section as compared to the upper section. Fe does not show much variation in the lower section, except at 46 cm depth where it shows a prominent increasing peak. In the upper section, concentration of Fe increases gradually towards surface. Mn exhibits overall decrease from lower to upper sections with slightly higher values at 50, 12 cm depths and near surface. The distribution pattern of Mn is slightly similar to sand.

The higher concentration of Fe and Mn in the lower section and lower concentration in the middle section, similar to finer sediments and organic carbon in the core collected from the Sharavathi estuary, indicates their adsorption onto finer sediments and complexation with organic matter. The presence of higher percentage of coarser sediments in the middle section seems to have diluted metal concentration in sediments of the Sharavathi estuary. The change in particle size distribution must have resulted in variation in distribution pattern of metals in the sediments, with higher proportion of metals associated with finer fractions than coarser[33]. Further, a similar point-to-point variation of Fe and Mn is observed from bottom to 14 cm depth in core S-2. This is also supported by strong positive correlation observed between Fe and Mn (Table 2b), indicating strong association of the geochemical matrix between the two elements[34]. From the overall distribution pattern, a prominent increase in concentration of Fe from 14 cm towards surface is seen which may be the result of higher supply during recent years or remobilization of Fe which later associated with finer sediments and organic carbon in surface section. The gradual increase in Fe concentration towards surface in the core GP-2 may be due to additional supply from industrial input[35] in the recent years. Fe is associated with silt at this location. The slight similarity in Mn and sand distribution pattern along with a peak value at 12 cm depth in the core GP-2 indicates association of Mn with coarser sediments. This is also supported by the significant positive correlation of Mn with sand (Table 2c). In core GP-2, Fe and Mn exhibit a different distribution pattern and insignificant correlation (Table 2c), unlike the core S-2. The differences in Fe and Mn distribution pattern and their associations, could be due to difference in hydrodynamics, elemental behaviour with respect to physico-chemical conditions and source of supply[36].

The average concentration of Al is higher in the core GP-2 than core S-2 (Table 1b). The t values (Table 2a) are negative for Al, further indicating higher mean value of Al in the core GP-2. The concentration of Al is higher in the lower section and shows decrease in the middle section, similar to finer sediments, organic carbon and, Fe and Mn in the core S-2 (Fig 2a). In core GP-2, the distribution pattern of Al does not agree with sediment components, organic carbon and, Fe and Mn (Fig 2b). Al is the major component in the clay lattice and indicates terrigenous input. In the core collected from the Sharavathi estuary, Al exhibits significant positive correlation with finer sediments, organic carbon and, Fe and Mn (Table 2b), indicating its natural source. The association of Al with fine-grained sediments suggests that they are detrital minerals dominated by phyllosilicates[37]. On the other hand, insignificant relationship of Al with sediment components, organic carbon and, Fe and Mn in the core collected from the Gurupur estuary (Table 2c) indicates that these materials are derived from different sources.

Trace metals (Ni, Co, Cu, Zn and Cr)

The average percentage of Ni and Cu is higher in the core S-2 while, Co, Zn and Cr show higher average percentage in the core GP-2 (Table 1c). It is also indicated by the results of paired t test (Table 2a). In core S-2, the distribution pattern of Ni, Cu, Zn and Cr is similar to finer sediments, organic carbon, Al, Fe and Mn with higher concentration in the lower section (Fig. 2a). Co also shows overall increase with fluctuations in the lower section than the middle section. In case of core GP-2, Ni concentration does not vary in the lower section, except at 48 cm depth where it shows an increasing peak (Fig. 2b). In the upper section, Ni concentration shows large fluctuation from 34 to 16 cm depth followed by a constant trend up to 8 cm depth. Above 8 cm, Ni shows increase towards surface. Like Ni, the concentration of Co does not vary in the lower section. The concentration of Co is similar to sand and Mn in the upper section. Co concentration is highest at 12 cm and coincides with sand and Mn peaks at this depth. The fluctuating distribution pattern of Cu is observed in both the sections. Zn concentration remains nearly constant in the lower section with prominent decreasing peak at 42 cm depth. In the upper section, Zn shows overall decrease up to 4 cm depth followed by a sudden increase towards surface. Like the rest of the trace metals, Cr concentration does not vary in the lower section; however in the upper section it shows overall increase towards surface.

The distribution patterns of most of the trace elements agrees with the distribution patterns of finer sediments and organic carbon in the core S-2 which suggests that sediment grain size exerts a significant control on the vertical distribution of metals. Finer-grained sediments have a higher proportion of trace elements due to the larger surface area of smaller particles[38]. Also, the strong correlation between these trace metals and organic carbon (Table 2b) underlines an association in the form of organometallic complexes[39]. These trace metals, along with finer sediments and organic carbon, show significant positive correlation with Al. Al is a geochemical proxy and a strong correlation of it with metals further suggests that particle size contributes significantly to the variations of these elements[40]. Sand is positively loaded whereas finer sediments, organic carbon and metals are negatively loaded in the first factor of factor analysis (Table 4) which explains 76% of the total variance. The factor analysis results therefore indicate difference in the geochemical behaviour of coarser and finer sediments and support the role of finer sediments and organic carbon in distribution of metals in the Sharavathi estuary.

Table 4 Factor analysis matrix after varimax rotation for cores S-2 and GP-2. The bold values represent significant positive/negative correlation among the variables in each factor.

S-2	Factor 1	GP-2	Factor 1	Factor 2	Factor 3	Factor 4
Total variance (%)	73.3	Total variance (%)	32.1	18.98	12.32	11.29
Sand (%)	**0.885**	Sand (%)	0.058	0.512	-0.599	0.402
Silt (%)	**-0.739**	Silt (%)	**-0.799**	-0.282	0.441	0.009
Clay (%)	**-0.766**	Clay (%)	**0.784**	-0.146	0.055	-0.442

Org C (%)	**-0.966**	Org C (%)	0.494	-0.352	0.477	0.09
Al (%)	**-0.962**	Al (%)	0.006	-0.036	-0.008	**-0.893**
Fe (%)	**-0.984**	Fe (%)	-0.593	0.187	-0.145	-0.138
Mn (ppm)	**-0.925**	Mn (ppm)	0.105	**0.827**	0.048	0.228
Ni (ppm)	**-0.939**	Ni (ppm)	-0.493	-0.372	0.03	-0.032
Co (ppm)	-0.577	Co (ppm)	-0.488	**0.795**	-0.14	-0.139
Cu (ppm)	**-0.99**	Cu (ppm)	0.095	-0.136	**0.8**	0.214
Zn (ppm)	**-0.974**	Zn (ppm)	0.042	0.402	**0.735**	-0.312
Cr (ppm)	**-0.969**	Cr (ppm)	**-0.842**	0.196	-0.19	-0.024

The similar distribution pattern of Co to that of sand in the core GP-2 suggests its association with coarser sediments. This is well supported by the significant correlation of Co with sand (Table 2c). Also, significant correlation of Co with Mn is observed. Although metals are usually associated with finer fractions they have also been shown to accumulate on the surface of coarser materials like sand[41], possibly when received from non-natural sources. The coarser sediments stay in place for a longer period of time[42] and therefore sometimes develop oxide coatings which must have facilitated adsorption of Co onto the Mn oxide coatings on the sand grains[43]. The significant positive loading for Mn and Co, in addition to good loadings for sand in factor two (Table 4), supports the role of Mn in distribution of Co. Fe also shows good correlation with Co, however its poor correlation with sand limits its role in the regulation of Co. The increase in Cr concentration towards surface suggests its greater addition in the recent years, probably from anthropogenic sources. Cr shows good correlation with silt and Fe. Silt, Cr and Fe also have significant/good negative loadings (factor one) indicating their close association. Factor three shows significant positive loadings for Cu and Zn suggesting their similar source in the Gurupur estuary. The fourth factor along with results of correlation analysis indicate insignificant association of trace metals with Al supporting anthropogenic additions of metals into the Gurupur estuary. The core GP-2 is in close proximity to the Baikhampady industrial area. Although, industries located in the Baikhampady industrial area discharge their effluents through lined pipes into the Arabian Sea[44], there is no proper drainage system for storm water drains and surface runoff within the industrial cluster and the adjacent area. Since the topography of the area is sloping towards the river course, the storm water/surface runoff flow towards the Gurupur River through nalas/other natural drains[17]. This may have caused anthropogenic additions of metals. However, the absence of elevated concentrations of metals (except Fe and Cr) in the Gurupur estuary indicates not much change in industrial effluent discharge with time. This may be mainly due to the implementation of environmental protection policies, improvement in waste treatment systems and discharge of wastes into the Arabian Sea by the Karnataka state pollution control board (KSPCB) in co-ordination with the central pollution control board and Baikampady industrial cluster.

Metals in clay fraction

The range and average concentration of major and trace metals in the clay fraction in cores S-2 and GP-2 is given in Table 5a and b. Mn, Co and Cu are higher in the core S-2 whereas, Al, Ni, Zn and Cr are present in higher concentration in the core GP-2. Fe has almost equal concentration in both the cores. In core S-2, all the metals show similarity in their distribution pattern (Fig 5a). Higher peak values are noted in the middle section in this core. In core GP-2, Al and Zn show overall decrease from bottom to surface (Fig 5b). Cu also shows overall decrease with fluctuating distribution pattern. Fe, Mn, Ni, Co and Cr exhibit increasing distribution pattern from bottom to surface.

The similar distribution pattern of most of the metals with Al in the core S-2 suggests their similar source of lithogenic origin. Further, significant correlation of Al with all the metals supports the same (Table 6). The peak values of metals in the clay fraction obtained for the middle section reveals that the metals were brought to the estuary along with coarser sediments which got selectively associated with clay fraction. On the other hand, metals do not show similarity in their distribution pattern to that of Al in the Gurupur estuary. Also, Al shows insignificant correlation with other metals in this core (Table 6) indicating their anthropogenic source. Further, overall increase in concentration of Fe, Mn and Ni in the core S-2 and Fe, Mn, Co and Cr in the core GP-2 in the top 12 cm (Fig 5b) suggests greater deposition of clay fraction bound metals in recent years. Clay minerals, due to their large specific surfaces, possess the ability to adsorb cations[45]. However, in the present study only Fe and Ni show significant correlation with smectite in the core GP-2 (Table 6). Volvoikar and Nayak (2013)[36] stated that the clay fraction mainly holds metals within lattice structure of alumino-silicate minerals. Therefore, insignificant correlation of most of the metals with clay minerals in both the cores indicates that metals are merely adsorbed over the surface of the clay particles.

Table 5a Range and average concentration of major metals in clay fractions in cores S-2 and GP-2

Sediment core	Al (%) Range Min	Al (%) Range Max	Al (%) Avg	Fe (%) Range Min	Fe (%) Range Max	Fe (%) Avg	Mn (ppm) Range Min	Mn (ppm) Range Max	Mn (ppm) Avg
S-2	0.87	13.18	8.18	0.29	6.08	3.84	97	1106	692
GP-2	11.83	17.25	13.66	2.66	4.92	3.83	87	173	140

Table 5b Range and average concentration of trace metals in clay fractions in cores S-2 and GP-2

Sediment core	Ni (ppm) Range Min	Ni (ppm) Range Max	Ni (ppm) Avg	Co (ppm) Range Min	Co (ppm) Range Max	Co (ppm) Avg	Cu (ppm) Range Min	Cu (ppm) Range Max	Cu (ppm) Avg	Zn (ppm) Range Min	Zn (ppm) Range Max	Zn (ppm) Avg	Cr (ppm) Range Min	Cr (ppm) Range Max	Cr (ppm) Avg
S-2	12	183	81	7	95	42	51	418	204	60	428	227	27	440	236
GP-2	65	251	129	21	37	28	108	251	176	201	367	249	259	1517	714

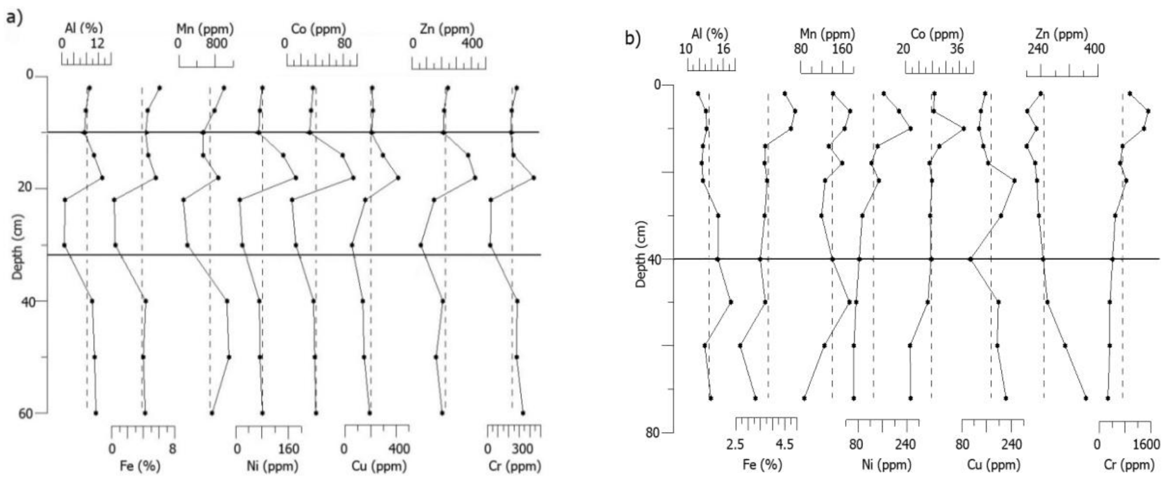


Fig 5 Down core variation of metals with vertical lines of average values in clay fractions in cores S-2 (a) and GP-2 (b)

Table 6 Correlation between clay minerals and metals in cores S-2 (n=10) and GP-2 (n=11). Values in bold indicate significant correlation at $p<0.05$

Core S-2	Smectite (%)	Illite (%)	Kaolinite (%)	Chlorite (%)	Al (%)	Fe (%)	Mn (ppm)	Ni (ppm)	Co (ppm)	Cu (ppm)	Zn (ppm)	Cr (ppm)
Smectite (%)	1.00											
Illite (%)	**0.83**	1.00										
Kaolinite (%)	**-0.92**	**-0.89**	1.00									
Chlorite (%)	-0.03	-0.19	-0.21	1.00								
Al (%)	-0.29	-0.56	0.40	0.15	1.00							

Fe (%)	-0.35	-0.60	0.45	0.19	**0.89**	1.00						
Mn (ppm)	-0.31	**-0.71**	0.45	0.31	**0.82**	**0.81**	1.00					
Ni (ppm)	-0.21	-0.26	0.19	0.17	**0.83**	**0.75**	0.47	1.00				
Co (ppm)	-0.19	-0.22	0.16	0.16	**0.80**	**0.69**	0.43	**0.99**	1.00			
Cu (ppm)	0.10	0.03	-0.10	0.13	**0.66**	**0.64**	0.27	**0.91**	**0.89**	1.00		
Zn (ppm)	0.04	-0.03	-0.04	0.12	**0.73**	**0.69**	0.34	**0.95**	**0.94**	**0.96**	1.00	
Cr (ppm)	-0.27	-0.57	0.40	0.16	**0.97**	**0.88**	**0.79**	**0.83**	**0.79**	**0.71**	**0.73**	1.00

Core GP-2	Smectite (%)	Illite (%)	Kaolinite (%)	Chlorite (%)	Al (%)	Fe (%)	Mn (ppm)	Ni (ppm)	Co (ppm)	Cu (ppm)	Zn (ppm)	Cr (ppm)
Smectite (%)	1.00											
Illite (%)	0.24	1.00										
Kaolinite (%)	-0.12	-0.42	1.00									
Chlorite (%)	0.14	-0.30	**0.62**	1.00								
Al (%)	-0.34	-0.57	0.43	0.18	1.00							
Fe (%)	**0.64**	0.23	0.12	0.56	-0.22	1.00						
Mn (ppm)	0.28	0.17	0.44	0.53	0.12	0.60	1.00					
Ni (ppm)	**0.62**	0.35	0.07	0.32	-0.49	**0.89**	0.53	1.00				
Co (ppm)	0.55	0.24	0.35	0.41	-0.14	**0.75**	0.56	**0.83**	1.00			
Cu (ppm)	0.03	-0.34	-0.57	-0.53	0.09	-0.42	-0.52	-0.41	-0.50	1.00		
Zn (ppm)	-0.44	-0.58	0.04	-0.11	0.20	**-0.61**	**-0.67**	**-0.62**	**-0.70**	0.44	1.00	
Cr (ppm)	0.58	0.36	0.00	0.30	-0.48	**0.90**	0.56	**0.98**	**0.72**	-0.40	**-0.63**	1.00

Conclusion

The sediment cores collected from the middle estuarine region of two tropical estuaries (Sharavathi and Gurupur) showed variations in percentage of sediment components. The clay and organic carbon were higher in the Gurupur estuary whereas, sand was higher in the Sharavathi estuary, indicating difference in the depositional environment between the estuaries. Further, data plotted on the ternary diagram revealed change in the depositional conditions with time in both the estuaries, larger variation being in Sharavathi. The abundance of clay minerals within studied tropical estuaries showed dominance of kaolinite in sediments which was attributed to catchment area geology and their distribution was due to river-sea water mixing conditions. Similar distribution patterns of finer sediments, organic carbon and metals suggested role of finer sediments in distribution of metals in the Sharavathi estuary. Further, significant association of metals with Al in bulk sediments and similar distribution of metals to Al in the clay fraction supported natural source of metals in the Sharavathi estuary. In the Gurupur estuary, however, insignificant correlation of metals with Al in bulk as well as clay fraction of the sediments suggested their non-natural source, possibly received from the Baikampady industrial estate. Further, insignificant association of most of the metals with clay minerals in both the estuaries indicated their mere adsorption onto the clay particles.

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