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Clay mineralogy and chemistry of mudflat core sediments from Sharavathi and Gurupur estuaries: Source and processes

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Clay minerals were investigated in mudflat core sediments representing lower and middle regions of the tropical estuaries, viz., Sharavathi and Gurupur, west coast of India to understand the source and the role of estuarine processes in clay mineral distribution. Clay chemistry of the sediments was also determined to understand the interaction of metals with clay minerals. Among the clay minerals, kaolinite was abundant in both the estuaries which reflected chemical weathering of source rocks, granites and granitic gneisses. Smectite was present in slightly higher concentration in the lower Sharavathi estuary than the middle region, while kaolinite was higher in the middle region of both the estuaries. Illite and chlorite were relatively higher in the lower region than the middle region of both the estuaries. Thus, the distribution of clay minerals within estuaries was regulated by salinity. Further, study of metals in the clay fraction from both the estuaries revealed higher concentration of metals in the middle region than the lower, which was attributed to mixing processes facilitating enhanced adsorption of metals onto suspended clay particles. The distribution of major elements, viz., Al, Fe and Mn in the lower Sharavathi estuary, and of all the metals in the lower Gurupur estuary indicated their association with kaolinite. On the other hand, distribution of Al, Fe, Ni, Co, Cu, Zn and Cr in the middle Sharavathi estuary and Al, Fe and Zn in the middle Gurupur estuary suggested their association with smectite and illite.

[**Keywords:** Estuary, Mudflats, Clay minerals, Clay chemistry, Source, Processes]

Introduction

Clay minerals are the weathering products of continental rocks[1]. The composition of clay minerals primarily depends on the source rock composition, climate and topography of the drainage basin of the river[2,3]. The parent rocks in the humid tropical regions undergo weathering and release clay minerals, which are transported to the estuary by rivers. In an estuarine environment, clay minerals undergo modifications by physical and bio-geochemical processes[4,5] and get accumulated in sediments. The relative abundance of clay minerals reaching the estuarine sediments therefore depends on source rock composition and estuarine processes. Hence, the study of composition of clay minerals will provide valuable information regarding the type and intensity of weathering in the catchment area. It has been demonstrated that clay mineral assemblages in estuarine sediments are particularly useful as sources of the sediments, especially in relation to the integral effect of provenance, lithology and climate[6,7,8]. Further, the distribution of clay minerals is complicated by various processes, viz., circulation patterns, size sorting, flocculation and organo-mineral interactions[9]. Hence, the study of clay minerals in a wide range of salinity in an estuary (lower to middle region) is most important. Clay minerals are among the major materials that interact with almost all soil contaminants in the natural environment[10]. They often represent a short-term sink of metals in sediments due to their large specific surfaces and the resulting ability to absorb cations[11]. These properties of clay minerals make them ideal for a large variety of environmental applications, such as water purification, waste treatment, mineral barriers for waste deposits, and slurry walls for the encapsulation of contaminated areas[12]. The determination of metals in the clay size sediments will be useful in understanding interactions of metals with the clay minerals. The processes regulating the distribution of clay minerals such as their flocculation/deflocculation with change in salinity as well as their diagenetic transformation with time can affect the association of metals with clay minerals which make it essential to study the distribution of clay minerals and metals in the clay fraction in the core sediments.

Most of the previous studies on clay mineral composition based on surface sediments as well as core sediments were carried out to understand the provenance and transport pathways of fine grained terrigenous sediments, and clay mineral utilities as paleo-climatic proxies in the Arabian Sea[13,14,15,16]. Several workers also reported clay minerals in suspended particulate matter and sediment of the Sundarban mangrove, major Indian Rivers and in Mandovi-Zuari estuaries[17,18,19,20,21]. The purpose of the present study is to report the distribution of clay minerals and metals in the clay size mudflat core sediments of the Sharavathi and Gurupur estuaries to better understand the source and the role of estuarine processes in clay mineral distribution and metal interactions with them. These estuaries are identical to each other with respect to their origin, but are different in terms of geomorphology, saline water intrusion and human activities.

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. The annual average rainfall in the Sharavathi estuary is 3521 mm[22], while the Gurupur estuary receives an annual average rainfall of 3900 mm[23]. Around 90 % of rainfall in these estuaries is received during the monsoon (July and August) season. The Sharavathi River has a total length of 130 km, with a catchment area of 3600 km^2 [24] and annual fresh water discharge of 4545 x 106 m^3 yr^{-1} [25]; 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 106 m^3 yr^{-1} [26,27]. The tidal range in Sharavathi is 1.41 m and 0.66 m during spring and neap tides, respectively[28]; whereas, in the Gurupur the high tide is 1.54 m which decreases to 0.25 m during neap tide[29].

Although these estuaries have narrow mouth, the estuarine channel width of the Sharavathi is larger than the Gurupur estuary.

Geology of the study area

The rock types consist of granites and granitic gneisses in the catchment area of the Sharavathi river, while the Gurupur river consists of gneisses and continental type of sedimentary deposits with dolerite and norite dikes[30]. The geological formations within the 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. The hinterland rocks are subjected to intense chemical weathering under humid tropical climate conditions. The minerals of granitic rock weather according to this sequence: Plagioclase feldspar, biotite, potassium feldspar, muscovite, and quartz. Biotite is a particularly active agent in the weathering process of granite. The feldspars break down by hydrolysis and hydration into clays and colloids. The hydrolysis of Na feldspar and K feldspar releases kaolinite[31].

Human induced activities along the Estuarine Region

In 1964, a dam was constructed near Linganamakki on the Sharavathi river for generation of hydroelectric power. This has led to changes in the natural flow of fresh water affecting sedimentation pattern. On the other hand, sedimentation pattern in the Gurupur estuary is regulated by seawalls and breakwaters constructed for impeding erosion of the Mangalore spilt in the recent years[32]. Further, the catchment area of these estuaries has been subjected to open cast mining activities for the last two decades; however, mines were not in working condition for the past few years. As ore handling (loading of ore onto barges, transport through river channel, and reloading at the port or midstream onto giant ships for export) is done in an open system, one would expect abundant spilled-over ore material into these estuaries. Further, located on the bank of the Gurupur river, is the Baikampady industrial estate, 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[33]. In addition, agricultural practice is also one of the anthropogenic activities carried out in the catchment area of these tropical estuaries.

Materials and Methods

Four sediment cores with lengths varying from 60 to 72 cm were collected from the mudflat regions (Fig. 1) of the Sharavathi and Gurupur estuaries, using a hand-driven PVC coring tube (1.5 m * 6 cm).

The core representing lower Sharavathi estuary (S-1) was 68 cm, while the core collected from the middle Sharavathi estuary (S-2) was 60 cm. The cores representing lower (GP-1) and middle (GP-2) Gurupur estuary were of length 60 and 72 cm, respectively. The cores were sub-sampled at 2 cm intervals, transferred to clean polyethylene bags, stored in an ice box and transported to the laboratory. Sampling stations were located using a hand-held global positioning system. In the laboratory, sub-samples were stored at 4 ^{0}C till further analysis. Later, the sub-samples were oven-dried at 60 ^{0}C. Clay minerals in sediment sub-samples (>2 µm) of cores S-1, S-2, GP-1 and GP-2 were determined following the procedure given by Rao & Rao (1995)[14]. The percentage of clay minerals was calculated by weighting the integrated peak area of basal reflection in the glycolated X-ray diffractograms by following the semi-quantitative method given by Biscaye (1965)[34]. Clay-sized fraction of sediment sub-samples of all the cores was digested with 7:3:1 HF:HNO_3: $HClO_4$ acid mixture and analyzed for metals, viz., Al, Fe, Mn, Ni, Co, Cu, Zn and Cr using an atomic absorption spectrophotometer (AAS, Varian AA240FS). The accuracy of the analytical method was tested by digesting standard reference materials 2702 obtained from the 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.

The data of clay minerals and metals bound to the clay fraction obtained for every 10 cm depth in each of the core sediment was used in this study.

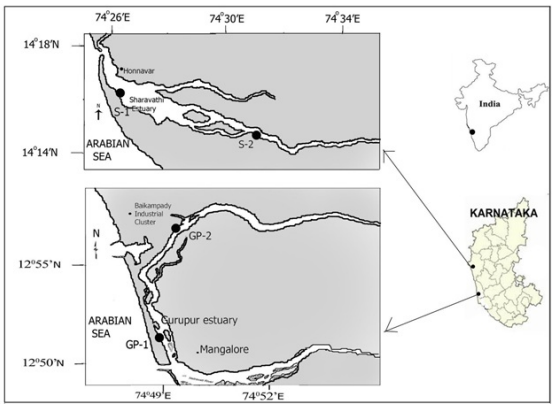

Fig. 1 ─ Map showing sampling locations

Results and Discussion

Clay minerals

The average concentration of clay minerals for every 10 cm depth in sediment cores S-1, S-2, GP-1 and GP-2 along with average value is given in Table 1a.

In case of the core S-1, concentration of smectite decreased from the bottom to 50-60 cm section, followed by an increase up to 30-40 cm section. Further, the value of smectite decreased towards the surface. The value of illite increased from the bottom to 50-60 cm section and then decreased towards the surface in this core. The concentration of illite was the highest at 50-60 cm section. The concentration of kaolinite exhibited fluctuating trend from the bottom

Table 1a ─ The average concentration of clay minerals for every 10 cm depth in sediment cores S-1, S-2, GP-1 and GP-2 along with average value.

S-1	Smectite (%)	Illite (%)	kaolinite (%)	chlorite (%)
0-10	3.51	7.27	78.97	10.25
10-20	3.52	9.16	76.18	11.15
20-30	4.18	9.78	76.85	9.19
30-40	11.11	18.39	59.68	10.81
40-50	7.59	18.48	68.53	5.39
50-60	4.64	23.71	66.78	4.87
60-68	5.97	13.37	76.16	4.51
Avg	5.79	14.31	71.88	8.02

S-2	Smectite (%)	Illite (%)	Kaolinite (%)	Chlorite (%
0-10	4.94	7.18	79.18	8.69
10-20	5.86	10.04	76	8.1
20-30	8.22	14.06	71.18	6.54
30-40	6.48	5.42	77.13	10.68
40-50	5.36	7.14	78.63	8.87
50-60	3.23	4.9	88.38	3.29
Avg	5.68	8.13	78.42	7.69

GP-1	Smectite (%)	Illite (%)	kaolinite (%)	chlorite (%)
0-10	5.21	16.70	71.13	8.82
10-20	5.06	19.91	64.43	8.98
20-30	4.73	12.77	67.85	10.89
30-40	4.31	9.39	76.98	15.91
40-50	2.59	10.48	72.53	13.99
50-60	4.64	9.71	71.78	12.87
Avg	4.42	13.16	70.79	11.91

GP-2	Smectite (%)	Illite (%)	kaolinite (%)	chlorite (%
0-10	6.18	13.11	74.48	12.16
10-20	4.71	18.39	70.00	8.60
20-30	5.47	11.86	66.83	7.49
30-40	4.08	12.88	76.88	10.68
40-50	5.11	8.84	78.63	11.56
50-60	2.53	9.90	74.38	7.29
60-72	3.97	10.77	69.16	8.81
Avg	4.58	12.25	72.91	9.51

to the surface of the core S-1. Chlorite showed an increase from the bottom to 30-40 cm depth, followed by fluctuating trend towards the surface. In the core S-2, smectite concentration increased from the bottom to 20-30 cm section and later decreased towards the surface. Illite showed fluctuating concentration from the bottom to 20-30 cm section and then decreased towards the surface. The concentration of kaolinite decreased from the bottom to 20-30 cm section, followed by an increase in concentration towards the surface. The chlorite concentration increased from the bottom to 30-40 cm section. Thereafter, its concentration decreased up to 20-30 cm section and then increased towards the surface of the core S-2.

In the core GP-1, smectite concentration decreased from the bottom to 40-50 cm section and further, showed increase towards the surface. Illite showed a fluctuating distribution pattern in this core with the highest value observed at 10-20 cm depth. Kaolinite increased from the bottom to 30-40 cm section and later showed decrease up to 10-20 cm depth. Further, its value increased towards the surface of the core GP-1. Chlorite increased from bottom to 30-40 cm section and thereafter, showed decrease towards the surface. In the core GP-2, the concentration of smectite showed a fluctuating distribution pattern throughout the core. Illite showed decrease from bottom to 40-50 cm section. Further, it exhibited fluctuating distribution pattern up to surface of the core GP-2. The highest value of illite was observed at 10-20 cm section. Kaolinite increased from bottom to 40-50 cm section and then exhibited decrease up to 20-30 cm section. Thereafter, its concentration increased towards the surface. Chlorite showed fluctuating trend from bottom to 30-40 cm depth. Further, its concentration decreased up to 20-30 cm section followed by an increase towards the surface of the core GP-2.

Among the clay minerals studied, the percentage of kaolinite was higher in all the cores collected from Sharavathi and Gurupur estuaries. The rock types in the catchment area of these estuaries consist of granites and granitic gneisses. Kaolinite is expected to be the most dominant mineral released from weathering of granites and granitic gneisses. Granitic rocks are rich in feldspar, which is a common source for kaolinite[35]. The weathering of granites and granitic gneisses might have released large amounts of kaolinite. Next to kaolinite, illite and chlorite were present in sediments of these estuaries. The granites and granitic gneisses exposed at places on the slopes of mountains, also release minor proportions of residual minerals like illite and chlorite to the clay fraction when they undergo breakdown[1]. Illite must have been formed by the weathering of non-layer silicate, such as feldspar, from granites under moderate hydrolysis conditions, and by the degradation of micas[36]. The decrease in smectite at 50-60 cm section corresponds to increase in illite concentration in the core S-1. Increase in illite was also observed at 40-50 cm and 10-20 cm sections in the cores GP-1 and GP-2, respectively, with corresponding lower values of smectite. Presence of smectite in relatively small amounts suggested diagenetic processes of transformation of smectite into illite[37]. According to Eberl (1984)[38] Al^{3+} ions substitute for Si^{4+} in the smectite tetrahedral sheets, thereby increasing the negative charge on smectite inter-layers. Upon achieving critical layer charge, the inter-layer potassium dehydrates expand smectite inter-layers into non-expanding illite inter-layers. Further, the weathering of igneous and metamorphic rocks might have released chlorite, as it is commonly found in igneous rocks as an alteration product of mafic minerals such as pyroxene, amphibole and biotite, and also associated with metamorphic rocks[39]. The abundant kaolinite together with considerable illite and chlorite present in sediments of Sharavathi and Gurupur estuaries reflected their source from the hinterland and indicated as weathering products of granites and granitic gneisses. As the rivers take the sediment load largely from mountainous regions during heavy rainfall, it appears that the river load from upstream contains abundant kaolinite.

Further, to understand variation in clay minerals within the estuary, the data was plotted on the isocon diagram (Fig. 2a). The comparison of two cores S-1 and S-2 revealed higher percentage of kaolinite in the middle region of the Sharavathi estuary than the lower estuarine region. On the other hand, illite and chlorite were higher in the lower estuarine region. Smectite was also slightly higher in the lower Sharavathi estuary. Similarly, the percentage of kaolinite was also higher in the middle Gurupur estuary than the lower estuarine region. Smectite was slightly higher in the middle Gurupur estuary, while illite and chlorite were higher in the lower Gurupur estuary.

In both the estuaries, the percentage of kaolinite was higher in the middle region. The variation in the percentage of kaolinite within the estuary was attributed to the processes governing flocculation of kaolinite. It is well known that rapid flocculation of kaolinite takes place under a 2% of salinity, leading to fast sedimentation in slightly saline waters[37]. Kaolinite responds rapidly and flocculates abundantly

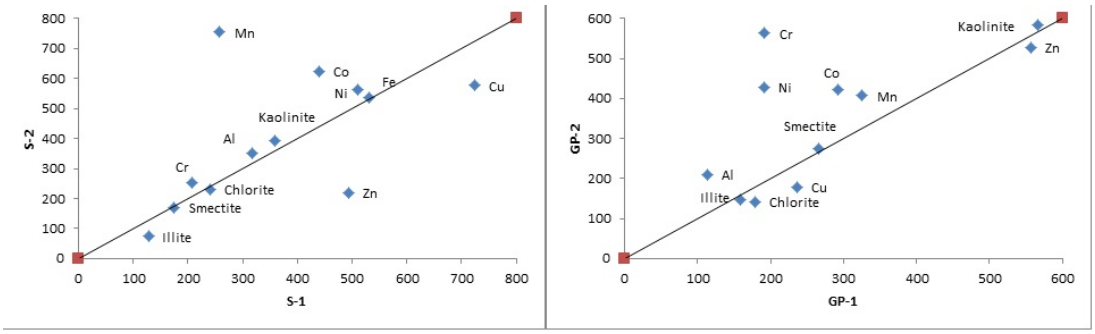

Fig. 2a — Isocon plots for clay minerals and clay chemistry, core S-1 v/s core S-2 and core GP-1 v/s core GP-2

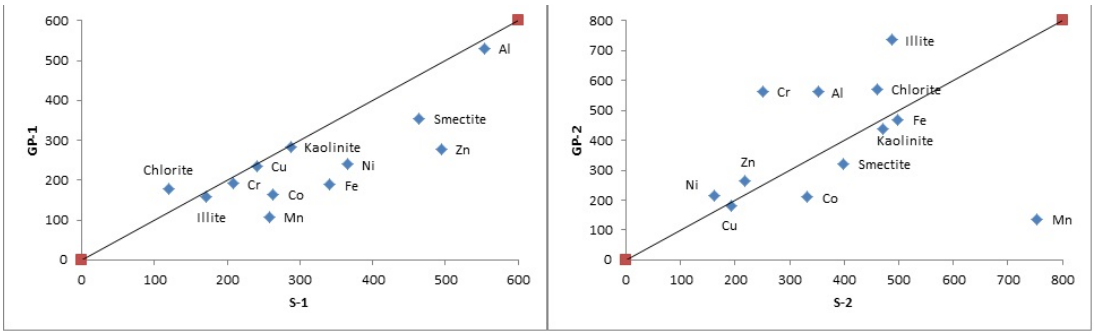

Fig. 2b — Isocon plots for clay minerals and clay chemistry, core S-1 v/s core GP-1 and core S-2 v/s core GP-2

at very low salinities[1]. The amount of kaolinite is therefore large in the nearly fresh water environment. This is very reasonable because the environment becomes considerably acidic and is suitable for the existence or in situ formation of kaolinite. Smectite, on the other hand, flocculates in normal saline water[40]. Keeping these in view, Gibbs (1977)[4] proposed early flocculation of kaolinite and winnowing of smectite away from the source. This might be a reason for slightly higher smectite in the lower Sharavathi estuary than the middle estuary. Degens & Ittekkot (1984)[41] suggested that because of smaller size and greater surface area of smectite, it bonds with organic compounds with greater intensity and sometimes flocculates in a wide range of salinity and organic matter conditions. Such a process might be responsible for slightly higher smectite in the middle Gurupur estuary. The higher illite and chlorite deposition in the lower region of the tropical estuaries might be the result of selective flocculation processes. The saline environment prefers deposition of illite and chlorite, in addition to smectite over kaolinite[42].

To understand the difference in clay minerals between Sharavathi and Gurupur estuaries, the data was plotted on the isocon diagram (Fig. 2b). On comparison of the cores S-1 and GP-1, smectite and illite were observed to be higher in the core S-1, while chlorite was higher in the core GP-1. Kaolinite was slightly higher in the core S-1. Further, when the cores S-2 and GP-2 were compared, higher smectite and kaolinite were seen in the core S-2; whereas, illite and chlorite were higher in the core GP-2.

Although both rivers receive sediment load from the mountainous regions of the Western Ghats, the geomorphology and lithological formations vary along their drainage basins. For instance, (a) the Sharavathi river (130 km) is longer than the Gurupur river (87 km); (b) The catchment area of the Sharavathi river (3600 km^2) is also higher than that of the Gurupur river (540.62 km^2); (c) The annual fresh water discharge of the Sharavathi river (4545 x 10^6 m^3 yr^{-1}) is much higher than that of the Gurupur river (2,822 x 10^6 m^3 yr^{-1}). In view of the large river length and catchment area, and higher annual fresh water discharge into the Sharavathi estuary, the sediment load into this estuary would dominantly be characteristic of rocks from mountain regions upstream, with chemical (kaolinite) weathering product concentration higher than that in the Gurupur estuary. Further, weathering of rocks depends upon various factors such as rock composition, climate, topography and vegetation[43]:

(a) Rocks in the Sharavathi basin are composed of granites and granitic-gneisses, while the Gurupur river consists of gneisses and continental type of sedimentary deposits with dolerite and norite dikes; (b) The amount of rainfall received is higher in the Gurupur estuary (3900 mm) than that in the Sharavathi river (3521 mm); (c) Estuarine channel of the Sharavathi river is wider than that of the Gurupur estuary; (d) Finally, due to the large catchment area of the Sharavathi estuary, bare surface area will be higher than in the catchment area of the Gurupur estuary. The rate and intensity of weathering of rocks vary with respect to properties of minerals and their resistance[44] which depends upon the factors mentioned above. These factors therefore might be contributing to variation in the percentage of clay minerals in the studied tropical estuaries.

Clay chemistry

The average concentration of metals bound to clay fraction for every 10 cm depth in sediment cores S-1, S-2, GP-1 and GP-2 along with average value is given in Table 1b.

In the core S-1, Al and Fe showed a decrease from the bottom to 50-60 cm section, followed by an increase up to 40-50 cm section, similar to smectite. Further, they exhibited decrease at 30-40 cm section and then showed an increase towards the surface.

Table 1b ─ The average concentration of metals bound to clay fraction for every 10 cm depth in sediment cores S-1, S-2, GP-1 and GP-2 along with average value

S-1	Al (%)	Fe (%)	Mn (ppm)	Ni (ppm)	Co (ppm)	Cu (ppm)	Zn (ppm)	Cr (ppm)
0-10	8.86	4.46	267.17	64.83	26.83	144.42	248.92	275.17
10-20	8.47	4.38	242.00	66.63	26.63	158.13	281.63	280.50
20-30	7.07	4.25	309.17	61.62	25.52	198.19	415.28	197.59
30-40	6.84	2.55	256.00	74.00	22.00	211.50	189.50	118.50
40-50	9.67	4.23	257.14	94.05	40.48	311.90	705.95	202.38
50-60	6.92	2.75	255.00	87.50	38.75	511.25	1337.50	195.00
60-68	7.55	3.88	219.25	62.25	24.75	151.25	283.25	188.50
Avg	7.91	3.79	257.96	72.98	29.28	240.95	494.57	208.23
S-2	Al (%)	Fe (%)	Mn (ppm)	Ni (ppm)	Co (ppm)	Cu (ppm)	Zn (ppm)	Cr (ppm)
0-10	8.11	4.98	774.18	74.73	34.59	211.65	223.72	241.48
10-20	11.81	5.10	705.37	163.31	87.21	357.28	403.46	342.79
20-30	1.02	0.36	142.69	16.45	9.51	105.20	105.75	31.01
30-40	9.99	4.31	1058.50	72.25	37.75	138.25	209.25	281.25
40-50	10.67	4.01	1105.50	73.75	39.25	148.75	163.25	275.25
50-60	11.12	4.24	737.25	81.50	41.00	191.25	204.75	336.25
Avg	8.79	3.83	753.91	80.33	41.55	192.06	218.36	251.34
GP-1	Al (%)	Fe (%)	Mn (ppm)	Ni (ppm)	Co (ppm)	Cu (ppm)	Zn (ppm)	Cr (ppm)
0-10	8.79	2.66	111.25	50.00	19.25	212.67	293.25	245.17
10-20	4.44	1.35	58.50	29.50	11.25	203.00	212.63	115.25
20-30	5.88	1.94	110.89	45.54	18.39	346.96	339.11	154.29
30-40	11.94	3.01	110.50	63.75	20.75	120.25	261.50	318.75
40-50	11.05	2.46	112.50	57.00	18.25	246.75	227.00	245.50
50-60	3.38	1.16	148.00	42.00	22.00	287.00	337.00	73.00
Avg	7.58	2.10	108.61	47.96	18.32	236.11	278.41	191.99
GP-2	Al (%)	Fe (%)	Mn (ppm)	Ni (ppm)	Co (ppm)	Cu (ppm)	Zn (ppm)	Cr (ppm)
0-10	12.72	4.73	159.25	209.42	31.33	144.42	223.42	1284.25
10-20	12.53	3.69	145.38	132.50	28.50	157.75	212.13	682.75
20-30	13.90	3.73	122.63	120.25	27.50	229.25	231.88	666.00
30-40	15.10	3.49	139.50	83.00	27.50	107.75	246.75	407.50
40-50	17.25	3.70	172.25	72.75	26.50	198.50	258.75	322.25
50-60	12.92	2.66	124.25	65.50	21.25	194.50	308.25	319.50
60-72	13.94	3.30	86.50	65.25	21.50	223.25	366.75	259.00
Avg	14.05	3.61	135.68	106.95	26.30	179.35	263.99	563.04

Their distribution in the top 20 cm was similar to kaolinite. The metals Mn and Co showed an increase from the bottom to 40-50 cm section, similar to chlorite. Thereafter, Mn concentration fluctuated towards the surface of the core and was similar to kaolinite in the top 30 cm, while the concentration of Co decreased from 40-50 cm section to 30-40 cm section and then increased towards the surface. The concentration of Ni and Cr increased from the bottom to 40-50 cm section, followed by decrease up to 30-40 cm section. Further, they showed an increase up to 10-20 cm section and then decreased towards the surface of the core S-1. To a large extent, distribution of Ni and Cr was similar to chlorite. The concentration of Cu showed large increase from the bottom to 50-60 cm depth and then decreased towards the surface of the core. A large increase in Zn was also observed from the bottom to 50-60 cm section. Thereafter, it decreased up to 30-40 cm section, followed by an increase at 20-30 cm section. Further, Zn exhibited decrease towards the surface of the core S-1.

In the core S-2, Al, Ni, Co and Cu showed a decrease from the bottom to 30-40 cm section, similar to kaolinite. Further, they showed a sudden decrease at 20-30 cm section, followed by an increase at 10-20 cm section and then decreased towards the surface. The distribution of these elements in the top 20 cm was similar to smectite and illite. Fe showed a minor variation from the bottom to 30-40 cm section and further, its distribution was similar to Al, Ni, Co and Cu. The metals Zn and Cr exhibited fluctuating distribution in this core. Their distribution was similar to smectite and illite in the top 20 cm of the core S-2. Similar to illite, Mn exhibited fluctuating distribution from bottom to 30-40 cm section. Its concentration decreased at 20-30 cm section, followed by an increase towards the surface. Its distribution in the top 30 cm was similar to kaolinite and chlorite.

In the core GP-1, the metals Al, Fe, Ni and Cr showed an increase from the bottom to 30-40 cm section, similar to kaolinite and chlorite. In case of Mn and Cu, decrease in concentration was observed from the bottom to 30-40 cm section, whereas the concentration of Co and Zn exhibited decrease from the bottom to 40-50 cm section, followed by an increase at 30-40 cm section. Further, all the metals showed decrease from 30-40 cm to 10-20 cm section and exhibited an increase towards the surface of the core GP-1. The distribution of all the metals in the top 30 cm was similar to kaolinite.

In the core GP-2, the metals Al and Fe showed fluctuating trend from the bottom to 40-50 cm section, followed by decrease up to 10-20 cm section and then increased towards the surface. Their distribution was similar to smectite. The concentration of Mn increased from the bottom to 40-50 cm section, followed by decrease up to 20-30 cm section and then increased towards the surface. Overall, the distribution of Mn was similar to kaolinite in this core. In addition, Mn distribution in the top 30 cm was also identical to chlorite. The metals Ni and Cr exhibited an increase from the bottom to surface of the core GP-2. The distribution pattern of Ni and Cr was largely similar to kaolinite. Like Mn, distribution of these elements was also similar to chlorite in the top 30 cm of the core. A decrease in Co was observed from the bottom to 50-60 cm section, followed by an increase towards the surface. Its distribution was similar to chlorite throughout the core and was also identical to kaolinite in the top 30 cm. A fluctuating distribution of Cu was observed from the bottom to 30-40 cm section, similar to chlorite. Further, it showed an increase at 20-30 cm section and then decreased towards the surface. The concentration of Zn decreased from the bottom to 10-20 cm section followed by an increase towards the surface. Its distribution was similar to illite from bottom to 40-50 cm section, whereas it was similar to smectite in the top 30 cm of the core GP-2.

In both Sharavathi and Gurupur estuaries, Al, Fe, Mn, Ni, Co and Cr were higher in the middle estuarine region, while Cu and Zn were the highest in the lower estuarine region (Fig. 2b). In general, in any given estuarine system, lower estuary with more marine influence, high waves, tides and currents maintains high energy and facilitates deposition of coarser sediments. On the other hand, the middle estuarine region is known for mixing of fresh and saline water, which facilitates calm conditions and therefore helps in deposition of finer sediments and organic matter. In the present study, higher concentration of Al, Fe, Mn, Ni, Co and Cr in the middle estuarine region was attributed to their retention on clay size sediments which remain in suspension for a longer period of time. In addition, Baikampady industrial area near Mangalore in the catchment area of the Gurupur estuary and mining related activities in the catchment area of the Sharavathi as well as Gurupur estuary are in proximity to the middle region of these estuaries. The middle region of these estuaries is therefore prone to maximum input of metals from such anthropogenic activities compared to

the lower estuarine region. The metals transported to the estuary via anthropogenic sources get adsorbed onto clay particles. In addition, metals in the lower estuary often get discharged into sea by strong tides and currents[45] that might have decreased their concentration in the lower estuarine region.

Further, to understand the difference in metals bound to the clay fraction between Sharavathi and Gurupur estuaries, the data was plotted on the isocon diagram (Fig. 2b). On comparison of the cores S-1 and GP-1, the metals, viz., Al, Fe, Mn, Ni, Co, Zn and Cr were observed to be higher in the core S-1. The concentration of Cu was also slightly higher in the core S-1. When the cores S-2 and GP-2 were compared, higher concentration of Fe, Mn, Co and Cu was observed in the core S-2, whereas, Al, Ni, Zn and Cr were higher in the core GP-2.

The percentage of clay minerals varies between the studied estuaries. The variation in clay minerals percentage is likely to cause a difference in the metals between Sharavathi and Gurupur estuaries. Additionally, human-induced activities, namely, open cast mining, agricultural practices and industrial waste release would also lead to variation in the percentage of metals.

Clay Minerals influencing distribution of Metals in the Clay Fraction

The distribution pattern of metals in the clay fraction suggested association of Al, Fe and Mn with kaolinite in the lower region of the Sharavathi estuary. The metals Ni, Co, and Cr were associated with chlorite, while Cu and Zn with illite. In the lower Gurupur estuary, all the metals were largely associated with the kaolinite. On the other hand, in the middle region of the Sharavathi estuary, the metals seem to be associated with smectite and illite, whereas in the middle Gurupur estuary Al, Fe and Zn were clays, due to their wide distribution and colloidal properties, are known to play an important role in the adsorption of metals[47]. Illite also has potential application as low-cost adsorbents for industrial waste treatment[48]. On the other hand, in the more dynamic conditions (lower estuary) smectite flocculates and also precipitates rapidly in high saline conditions, while kaolinite remain in suspension for longer duration and the metals tend to get adsorb onto kaolinite. The kaolinite derived from the tropical soils is generally associated with abundant iron oxides (goethite and sub-amorphous components), and often with gibbsite[34]. The iron oxide has a high affinity towards most of the metals in estuarine environment[49] which might have facilitated their adsorption onto Kaolinite. Although, it is kaolinite in the lower region, and smectite and illite in the middle region of the studied estuaries largely regulating distribution of metal, however, the difference in association of metals with clay minerals along the cores was also observed in the two estuaries. There is divergence of river water for drinking and irrigation purposes in the recent times to meet the growing needs of man. In addition, change in the Mangalore split, located at the mouth of the Gurupur estuary, with time led to change in the geomorphology of the estuary[50]. All these factors might be contributing to variation in salinity in these estuaries influencing flocculation of clay minerals regulating distribution of metals. The segregation of clay minerals due to salinity change might be one of the reasons for variation with time in association of metals with clay minerals in the tropical estuaries. Moreover, the small size of the clay minerals makes them prone to erosion, transport and redistribution within sediments by different media, such as wind transport, fluviatile transport, as well as transport and erosion by bottom currents or gravitational sediment movements[51], in addition to diagenetic transformation of clay minerals with time.

Conclusion

The study of clay minerals in mudflat core sediments of Sharavathi and Gurupur estuaries showed abundance of kaolinite in comparison to smectite, illite and chlorite. These minerals reflected their source from the hinterland geology and indicated weathering products of basin rocks, namely, granites and granitic gneisses. Further, the comparison of clay minerals within the estuary revealed higher concentration of kaolinite in the middle region of both the estuaries, while the slightly higher smectite value in the lower Sharavathi estuary was attributed to flocculation of these clay minerals under varying salinity conditions. The difference in the studied tropical estuaries namely, river length, estuarine channel width, catchment area, rainfall and annual fresh water runoff seemed to have contributed to the variation in percentage of clay minerals among them.

The higher concentration of most of the metals, viz., Al, Fe, Mn, Ni, Co and Cr in the middle region of Sharavathi and Gurupur estuaries than the lower estuarine region was attributed to mixing of fresh and saline water which facilitated enhanced adsorption of metals. The variation in percentage of clay minerals along with human-induced activities seemed to have

caused the difference in metal concentration among the tropical estuaries. In both the estuaries, kaolinite played a major role in distribution of metals in the lower region, while smectite and illite in the middle region.

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