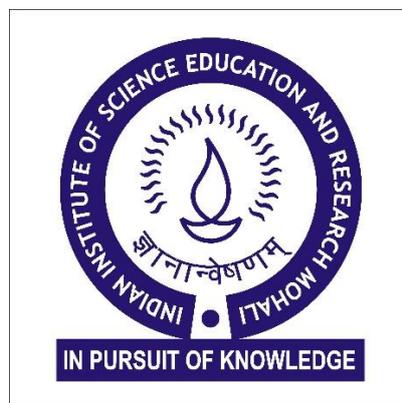


**Geochemical and sedimentological characterisation of
surface sediments from Ashtamudi Estuary, Southern
India: Provenance and paleoenvironmental implications**

Shah Parth Dharmendrabhai

*A dissertation submitted for the partial fulfilment of BS-MS dual
degree in Science*



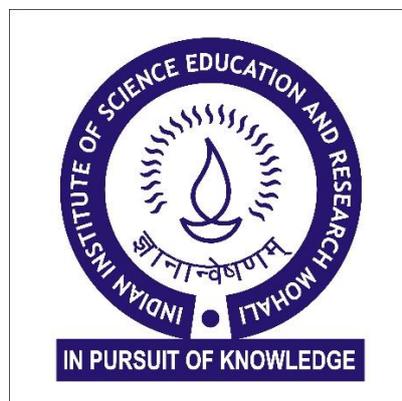
Indian Institute of Science Education and Research Mohali

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Shah Parth Dharmendrabbhai

MS13025

A dissertation submitted for the partial fulfilment of BS-MS dual degree in Science



Indian Institute of Science Education and Research Mohali

Certificate of Examination

This is to certify that the dissertation titled “Geochemical and sedimentological characterisation of surface sediments from Ashtamudi Estuary, Southern India: Provenance and paleoenvironmental implications” submitted by Shah Parth Dharmendrabhai (MS13025) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. Anoop Ambili

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Thesis Supervisor

Date: April 20, 2018

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Anoop Ambili at the Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contribution of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bona fide record of original work done by me and all sources listed within have been detailed in the bibliography.

Shah Parth Dharmendrabhai

Date: April 20, 2018

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Anoop Ambili

Thesis Supervisor

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Abstract

Geochemical and End-member mixing analysis (EMMA) of the grain-size distribution were conducted on modern surface sediments from Ashtamudi Estuary, Southern India to understand the hydrodynamic factors that influence modern depositional processes in the region. The complex interplay between natural (fluvial and marine) and anthropogenic influence on the Ashtamudi Estuary has been delineated based on the inter-relationship between geochemical elements and end members (EM) derived from the grain size parameters. The high contribution of Al, Fe, Cr and Ni combined with the EM1 and EM2 indicates fine-grained sediments derived from the fluvial input into the basin. Sediments from the lower end of the estuary are characterized by high concentration of Si, Ti, Ca, Sr and coarse end member (EM3) reveals evidence for strong marine/tidal influence. The elemental value of Cu, Zn and Co along with EM4 largely concentrated along the shore region, where dredging and construction activity has been active, suggests human interventions in the basin. This integrated geochemical analyses and EMMA from Ashtamudi Estuary present detailed knowledge of the controlling transport mechanisms of the particle supply and provides proxies for understanding the paleo land-ocean interactions from the region.

Keywords: End member modeling; Grain size; Estuary; Geochemistry; South India

Chapter 1

Introduction

1.1 Objective

1.2 Study Area

1.3 Methodology

Introduction

The estuaries, situated at the interface between land and ocean, are dynamic environment characterised by variable energy conditions and multiple sediment sources (Meade 1972; Zwolsman and Eck 1999). The sedimentary particles in estuary comprise of allochthonous river-borne terrestrial detritus and tidally advected marine inputs and autochthonous materials derived from planktonic and benthic primary production (Burton and Liss 1976; Ankit et al. 2017). The particle supply across the estuarine system is mostly controlled by physical energy responsible for sediment movement—from purely river currents to tidal and/or oceanic currents (Wright 1977). Sediments accumulating in estuarine environment offer an excellent opportunity to understand land-ocean interactions and can provide a valuable record of changing environmental conditions over time (Cronin et al. 2005; López-González et al. 2006; Zong et al. 2006). However, a detailed knowledge of the factors that control the source and transport mechanisms of the sediments is required to explore the paleoenvironmental changes from the estuarine sediments (e.g., Benninger and Wells 1993; Zhou et al. 2004).

The Ashtamudi Estuary, the second largest estuarine system in southwest coast of India, is characterised by unique hydrodynamic conditions with riverine influenced upper estuary, whereas marine/tidal processes dominate the lower estuary (Anooja et al. 2013; Ankit et al. 2017). Most surveys and studies from Ashtamudi Estuary have dealt with understanding the physiochemical characteristics (Divakaran et al. 1981; Sujatha et al. 2009; Babu et al. 2010; Antony and Ignatius 2016), estimation of organic matter sources (Nair et al. 1984; Jennerjahn et al. 2008; Reshmi et al. 2015; Ankit et al. 2017) and assessment of heavy metal concentration for enrichment and contamination (Babu et al. 2010; Krishnakumar et al. 2015; Nagendra et al. 2017). However, until now there has been a lack of information on the geochemical processes that control the behavior and transport of the particles across the estuary. In this study, surface sediment samples from Ashtamudi Estuary were analysed for their elemental composition and grain size distribution. The end-member mixing analysis (EMMA) was performed on the grain size parameters to understand the sediment mixtures in a series of sedimentary components (end members) reflecting the transport mechanisms and sediment sources.

1.1. Objective

The main objectives of the study are to discuss the hydro-dynamic factors that influence modern depositional processes in the study area. The geochemical distribution patterns of major, minor and trace elements constituents of Ashtamudi sediments have been described by multivariate analysis. Our goal is to acquire a better understanding of the modern processes that control the supply and composition of the inorganic sediment components in the Ashtamudi Estuary. We discuss the general trends within these deposits, assess how local variations affect sediment distribution and provide implications for paleoenvironmental interpretation. In addition, this study also attempted to delineate the natural (fluvial and marine) versus anthropogenic factors in governing the sediment distribution in the basin.

1.2. Study Area

1.2.1. Regional setting and climate

Ashtamudi Estuary (8°53'–9°02' N, 76°31'–76°41'E) is situated between the confluence of Kallada River in the north and Arabian Sea in the south (Fig. 1a). The estuary is ~16 km long with an average width of ~3.2 km and covers an area of ~51 km² (Sajan et al. 1992). The bathymetry survey of the Asthamudi Estuary shows a vent shaped depression in the proximity of Kallada River with a max depth of ~9 m (Ankit et al. 2017). The estuary is situated within the tropical climate zone, with mean annual temperature ranging from 26 °C to 33 °C (Divarakaran et al. 1981) and annual precipitation vary from ~1170 to ~2300 mm/year (source: Indian Meteorological Department based on the metrological data from 2012 to 2016 CE). The summer monsoon contributes ca. 53% of rainfall, whereas north east (NE) monsoon contributes ~24% of annual rainfall in the region (Fig. 1a). The hydrographic characteristics of the Asthamudi Estuary are controlled by monsoon fed Kallada River discharge and strong tidal influence in the lower estuary (Nair et al. 1984; Nair et al. 2001).

The human intervention in Ashtamudi Estuary has resulted in severe degradation of water quality and reduction of water spread area from 6,424 ha to 5,734 ha (data from 1999 to 2006 CE) (Sitaram 2014). The inputs from urban, agricultural and chemical industries, coconut husk retting from coir industry, contaminations from fishing and its processing industries as well as urban sewage discharges have affected the estuarine environment (Jennerjahn et al. 2008). In addition, a continuous dredging activity by the Port Department for navigation

purpose has altered the natural characteristics of sediment deposition in lower estuary (Nair et al. 1983; Krishnakumar et al. 2015).

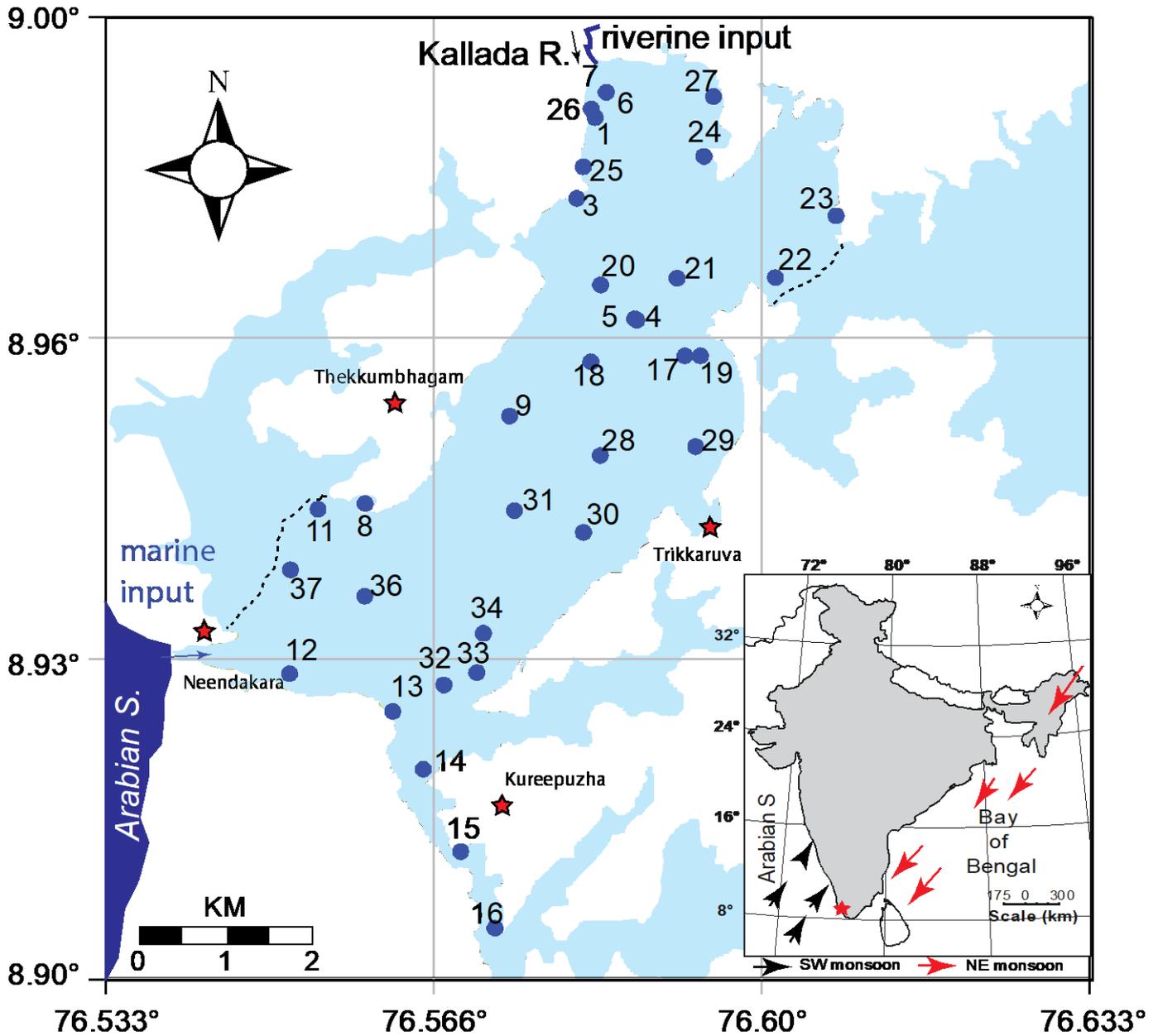


Fig. 1. Map showing study area and location of the retrieved surface sediment from Ashtamudi Estuary. The red star denotes the location of samples used to understand modern deposition in the estuary.

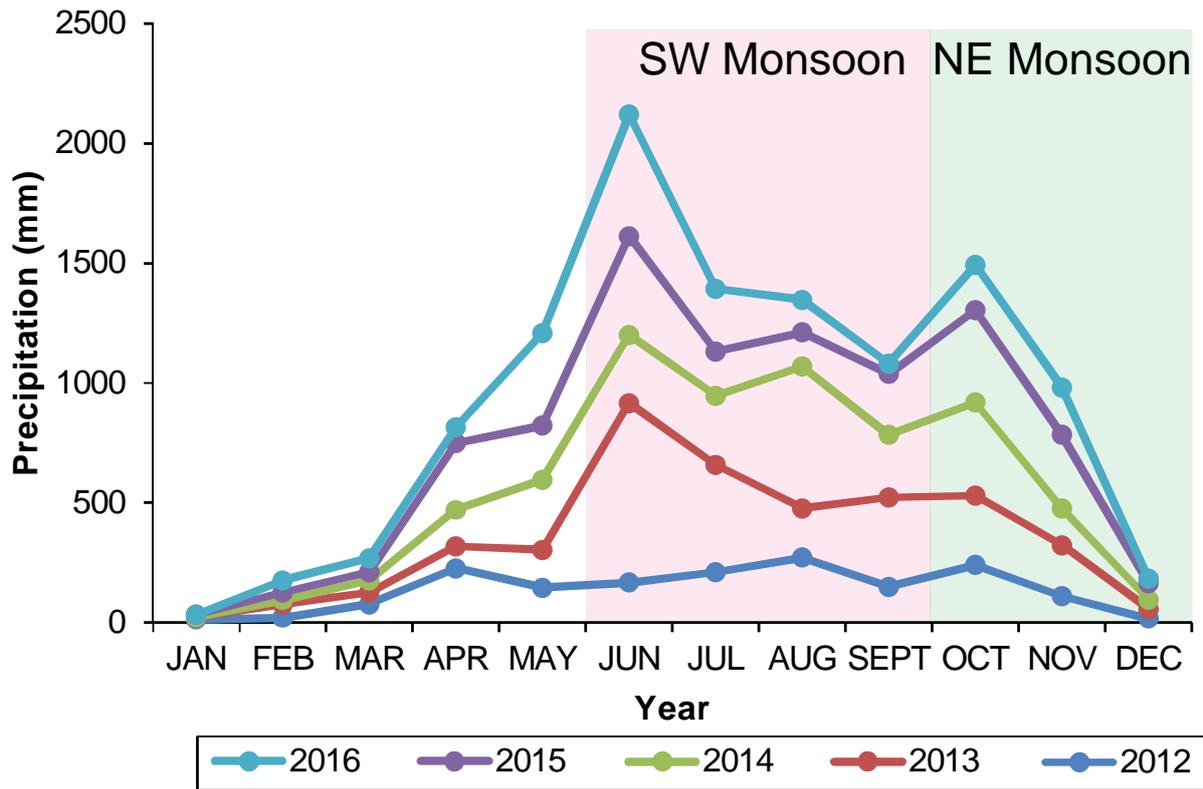


Fig. 2. Ashtamudi Estuary regional monsoon precipitation data.

1.2.2. Regional geomorphology and geology

Morphologically, the region consists of gently sloping valleys, coastal plains, channel fill deposits and tidal flats (Nair et al. 2010; Padmalal et al. 2011). The beaches and inner shelf environment of the region have been characterised with sandy sediments dominated by quartz and heavy minerals (Prakash 2000; Prakash et al. 2007). The major lithological units in the Ashtamudi region comprises of Archaean crystalline basement, Tertiary and Quaternary sedimentary sequences (Nair et al. 1984; Varghese 2014). The Archaean crystalline basement is represented by garnet biotite gneisses, khondalites and charnockites rock dominant in the eastern and south-eastern parts of the Kallada basin (Mohan et al. 2016; Vijith et al. 2016). The sedimentary sequences of Tertiary and Quaternary deposits occupy the lower end of the estuary (Varghese 2014).

1.3 Methodology

1.3.1. Sample collection

Total 34 surface sediment samples have been collected from the Ashtamudi Estuary to cover the entire basin. The samples have been collected using Van Veen Grab sampler with a penetration depth of 5-7 cm (Ankit et al. 2017). The samples were sealed in glass vials and *sent to laboratory for analysis*. The bathymetric map of the basin has been prepared using South SDE-28 Single Frequency Digital Echo sounder with a frequency 200 kHz (Ankit et al. 2017).

1.3.2 Laboratory analyses

1.3.2.1. Bulk elemental geochemistry

Total 21 powdered sediment samples have been analyzed for geochemical investigations. The samples were digested using a mixture of acids (HNO₃, HClO₄, HF, HCl) (conventional method — open system) for total elemental concentration measurements (Maxwell 1968). Specifically, ~0.2 g of each sediment sample in powdered form was transferred into a 50 mL Teflon tube and successively added 5 mL HF (48%) and 3 mL HClO₄ (70%). The solution was mixed using magnetic stirrer and heated first on a hot plate for 2 hr at 90 °C followed by 30 minutes at 130 °C. After cooling at room temperature, the digests were extracted with 10 mL HNO₃ (1:9) using the Millipore polycarbonate 0.45 µm filters. Finally, the solution was transferred to 100 mL volumetric flask and diluted up to factor 50 with ultra-pure water and kept at 4 °C for subsequent elemental analysis using ICP-AAS (Varian AA-30 model). The National Research Council Canada (NRC Canada; BCSS-1 and MESS-1) standards were analysed to check the accuracy of the results. The precision of the major and minor elements is < 2% and 5% for trace elements.

1.3.2.2. Grain size analysis

For grain size analysis (n=34), the pretreatment includes wet oxidation of organic matter at room temperature using 10 mL H₂O₂ (30%) in ~0.3 g of the sediments. Furthermore, the pretreated samples were centrifuged and washed several times to remove extra oxidizing agent. The solution was then treated with ultrasonic bath to prepare a homogenous solution for the analytical purpose. The grain size measurements were carried out using a Malvern Mastersizer

2000E laser grain size analyzer. The grain size distribution was calculated for 100 grain size classes (particles sizes between 0.02 and 2000 μm) and the analytical error was less than 1%.

1.3.3 Statistical analyses

1.3.3.1. Principle component analysis

Principal component analysis (PCA) is a data analysis tool used for reducing the multivariate data into fewer dimensions (Loska and Wiechula 2003; Zhou et al. 2008; Dempster et al. 2013). PCA transforms an original set of N-variables into a new set of N-principal components which are uncorrelated with each other (Xue et al. 2011). Each component is a weighted, linear combination of the original variables. PCA was performed using *princomp*-package in R-language based software (Mardia 1979; Venables and Ripley 2013). In this study, we have performed PCA on geochemical parameters of Ashtamudi estuarine sediments to understand the factors controlling the spatial distribution of sediments in the basin.

1.3.3.2. End Member mixing analysis

End member mixing analysis is a statistical technique to provide a meaningful solution in various mode of transportation of the sediments by unmixing polymodal grain size distribution (Weltje 1997; Prins et al. 1999; Dietze et al. 2012). The statistical analysis has been done using EMMAgeo-package, based on R-language (Weltje 1997; Dietze et al. 2012; Heinecke et al. 2017). To decipher the best-fit model for grain size distribution, the relation between the coefficient of determination (r^2) and a probable number of end member (q) has been used. This relation defines the stability of the model and explains the probable number of end members used to define the various mode of transportation in the basin (Zhou et al. 2004; Dietze et al. 2013; Borchers et al. 2016).

Chapter 2

Results and Discussion

2.1. Results

2.2. Discussion

2.3 Paleoclimatic implication

2.4. Conclusion

2.1. Results

2.1.1. Spatial distribution of elemental concentration

The geochemical concentration of 21 samples has been listed in Table 1. The sediments are mainly dominant in Si, Al and Fe except in the samples (EL31-33 and EL35-37) where Ca has significant contribution (6.3 to 14.9 wt %). The spatial distribution of the major elemental composition in the surface sediments shows large variability along the Ashtamudi basin. The distribution of major elements indicates that the upper end of the estuary is dominant in Mg, Fe, Na and Al (Fig. 3a), whereas Si, Ti and Ca are dominant in the marine-influenced lower estuary (Fig. 3b).

During the PC analysis, three end members have been extracted, explaining ~75% of the variability in the dataset (Fig. 4). The PC1 shows strong positive correlation with Ti, Sr, Ca, Co, Si and K, whereas negative correlation is observed for Ni, Al, Fe, Mg, Cu and Cr. Additionally, PC2 suggests its close association with P, Na, Cr and K. However, the PC3 shows a strong affinity with Cu and Zn indicating point source distribution in the basin near the south-eastern end of the estuary (Trikkaruva) (Fig. 1 and 3c).

2.1.2. Spatial distribution of grain size variability

The grain size distribution of the surface sediments from the Ashtamudi Estuary is largely characterized by silt with minor variation in the samples from north (dominant in clayey silt) and south (comprises of sand-sized particles) (Fig. 4a). The mean grain size of the Ashtamudi estuarine sediments ranges between 7.1 to 11.3 ϕ (average= 8.3 ϕ) and shows highest value towards the lower end of the estuary (Fig. 4).

The end member mixing analysis of grain size distribution in Ashtamudi estuarine sediments yielded an optimal model with four end members (Fig. 6) and explains 86% of the variability of the total dataset. EM1 (mode= 7.0 ϕ) and EM2 (mode= 6.0 ϕ) is highest near the confluence of Kallada river and south-eastern end of the estuary (Fig. 6). Similarly, EM3 with a mode of 4.5 ϕ lies in the range of coarser silt is highest towards the seaward side of the estuary near Neendakara (Fig. 6). The coarsest end member (mode= 3.3 ϕ) i.e. EM4 is highest near the shore of Thekkumbhagam and around the small islands in the southern end of the estuary (Fig. 6).

Sample name	Latitude	Longitude	Si (%)	Al (%)	Fe (%)	Ti (%)	Ca (%)	Mg (%)	Na (%)	K (%)	P (%)
EL 14	8.965	76.592	31.17	16.29	12.09	1.09	3.28	2.32	4.82	1.77	0.36
EL 15	8.964	76.582	30.9	16.35	11.49	1.05	3.82	2.32	5.53	1.82	0.32
EL 16	8.965	76.594	28.67	15.35	10.97	0.95	2.73	2.72	6.64	1.71	0.24
EL 17	8.972	76.583	29.94	15.55	10.61	0.92	3.16	2.63	6.91	1.74	0.32
EL 18	8.973	76.591	26.32	14.66	8.9	0.77	2.4	2.87	9.32	1.51	0.2
EL 19	8.973	76.601	34.11	15.8	14.33	0.94	3.61	2.12	3.78	1.07	0.1
EL 20	8.979	76.607	34.03	18.24	11.49	0.9	2.11	1.79	3.59	1.69	0.09
EL 21	8.986	76.594	27.32	18.75	10.47	0.8	1.84	2.51	6.03	1.51	0.24
EL 22	8.984	76.582	28.3	20.08	11.98	0.84	2.08	1.97	3.74	1.44	0.14
EL 23	8.990	76.582	33.1	21.41	12.94	1.09	1.08	0.99	2.43	1.74	0.18
EL 24	8.992	76.595	27.85	21.09	12.75	0.84	0.8	1.98	3.35	1.51	0.12
EL 25	8.954	76.583	32.09	14.24	12.24	1.14	5.31	2.23	4.94	1.85	0.29
EL 26	8.955	76.593	28.76	15.36	10.63	0.99	2.39	2.58	7.04	1.76	0.32
EL 27	8.946	76.582	31.95	14.12	10.66	1.14	3.48	2.54	6.61	1.86	0.36
EL 28	8.949	76.575	33.03	12.98	10.66	1.16	6.31	2.36	5.77	1.83	0.32
EL 29	8.931	76.567	34.65	9.09	8.61	2.35	12.15	1.67	4.93	1.58	0.28
EL 30	8.932	76.571	34.14	11.83	9.46	1.39	9.41	1.83	5.22	1.83	0.24
EL 31	8.936	76.572	33.76	13.88	10.97	1.21	4.29	2.08	5.97	1.83	0.24
EL 32	8.936	76.567	47.19	8.53	8.01	3.45	8.5	1.32	4.35	2.08	0.22
EL 33	8.940	76.559	43.01	8.81	7.92	3.3	11.54	1.23	4.26	1.98	0.2
EL 34	8.942	76.552	34.74	9.57	9.46	1.65	14.85	1.43	3.41	1.81	0.25

Table 1: Geochemical concentration of major and minor elements in Ashtamudi Estuarine sediments

Sample name	Latitude	Longitude	Cu (ppm)	Pb (ppm)	Zn (ppm)	Ni (ppm)	Co (ppm)	Cr (ppm)	Mn (ppm)	Sr (ppm)
EL 14	8.965	76.592	40	5	100	60	10	185	320	200
EL 15	8.964	76.582	35	5	95	60	10	175	290	200
EL 16	8.965	76.594	35	5	90	55	5	155	310	170
EL 17	8.972	76.583	35	25	100	60	5	195	490	220
EL 18	8.973	76.591	45	5	90	50	5	135	390	145
EL 19	8.973	76.601	45	5	90	45	5	100	550	80
EL 20	8.979	76.607	45	5	100	55	5	155	420	70
EL 21	8.986	76.594	60	5	90	65	5	200	580	100
EL 22	8.984	76.582	50	10	95	50	5	110	480	70
EL 23	8.990	76.582	55	10	100	55	5	120	430	85
EL 24	8.992	76.595	55	10	95	65	5	160	540	45
EL 25	8.954	76.583	35	5	90	55	2.5	170	250	135
EL 26	8.955	76.593	140	5	150	60	2.5	160	310	170
EL 27	8.946	76.582	35	5	100	65	2.5	200	260	210
EL 28	8.949	76.575	30	5	115	50	2.5	160	240	310
EL 29	8.931	76.567	35	5	85	35	10	130	350	500
EL 30	8.932	76.571	30	5	95	45	10	145	270	440
EL 31	8.936	76.572	35	5	95	50	10	165	220	235
EL 32	8.936	76.567	20	5	70	25	20	115	390	480
EL 33	8.940	76.559	30	5	85	25	20	120	390	540
EL 34	8.942	76.552	35	5	105	35	20	140	290	620

Table 2: Geochemical concentration of trace elements in Ashtamudi Estuarine sediments

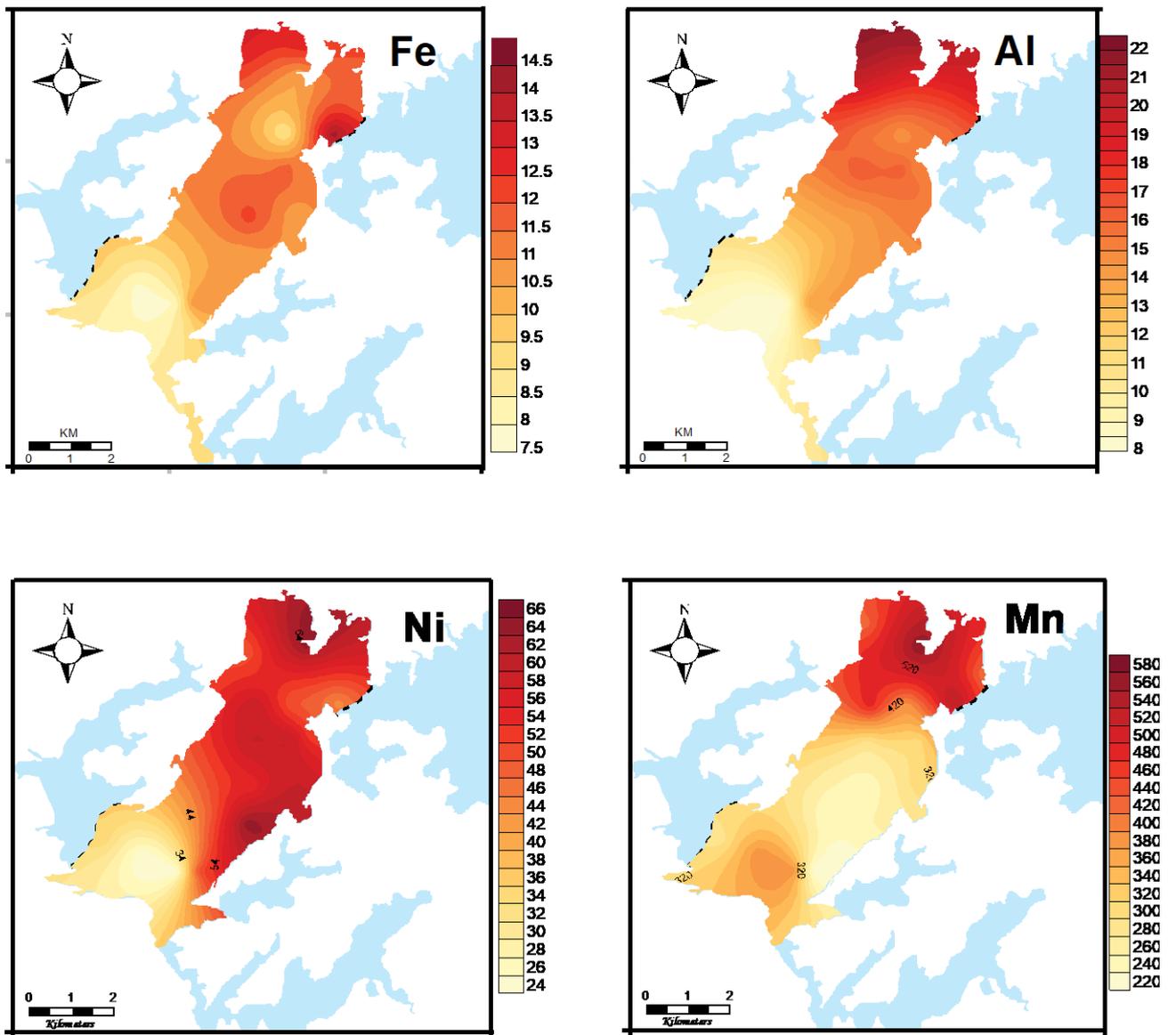


Fig. 3a. Spatial distribution of Fe, Al, Ni, Mg which are dominant in upper estuary.

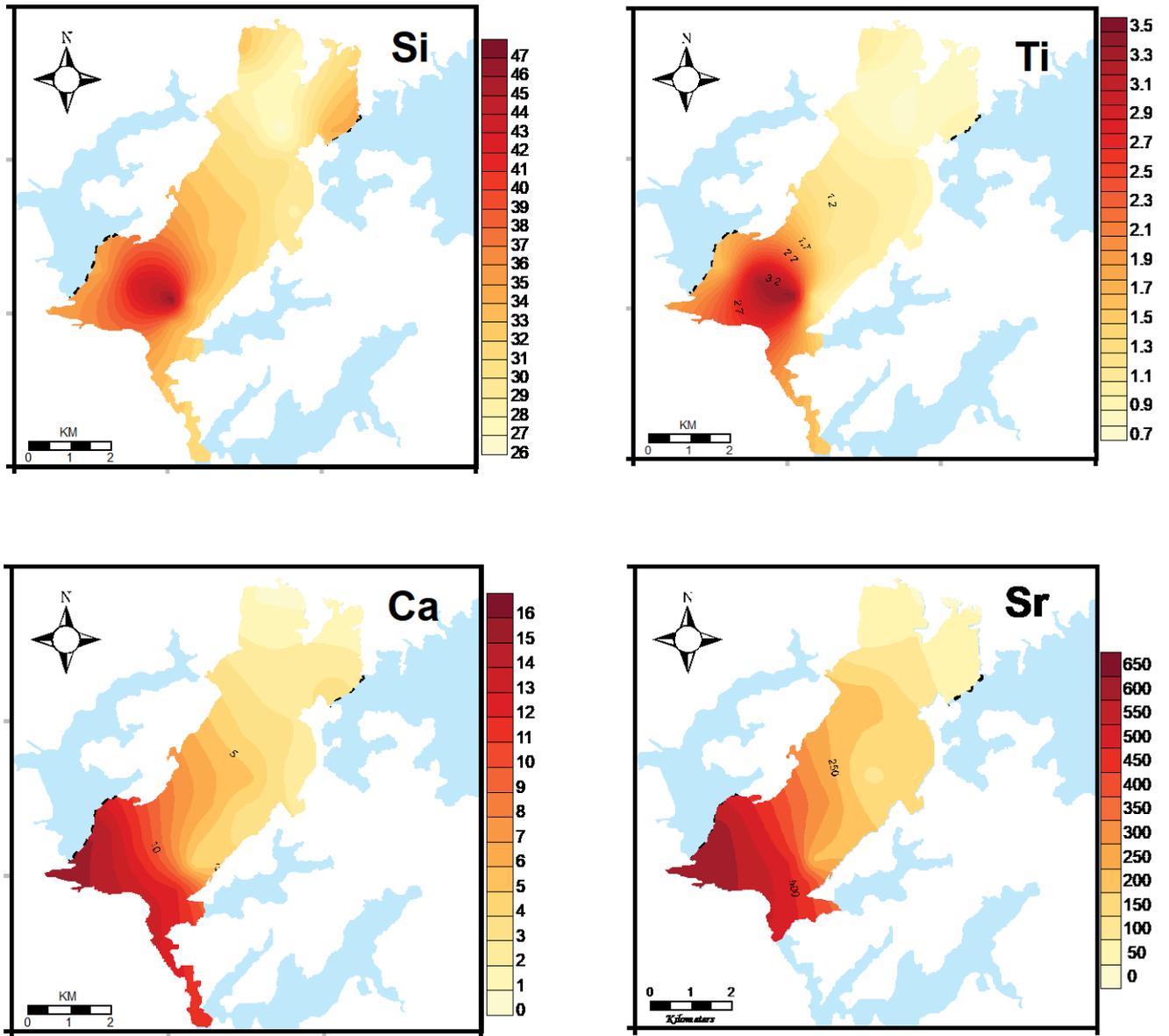


Fig. 3b. Spatial distribution of Si, Ti, Ca, Sr which are dominant in lower estuary.

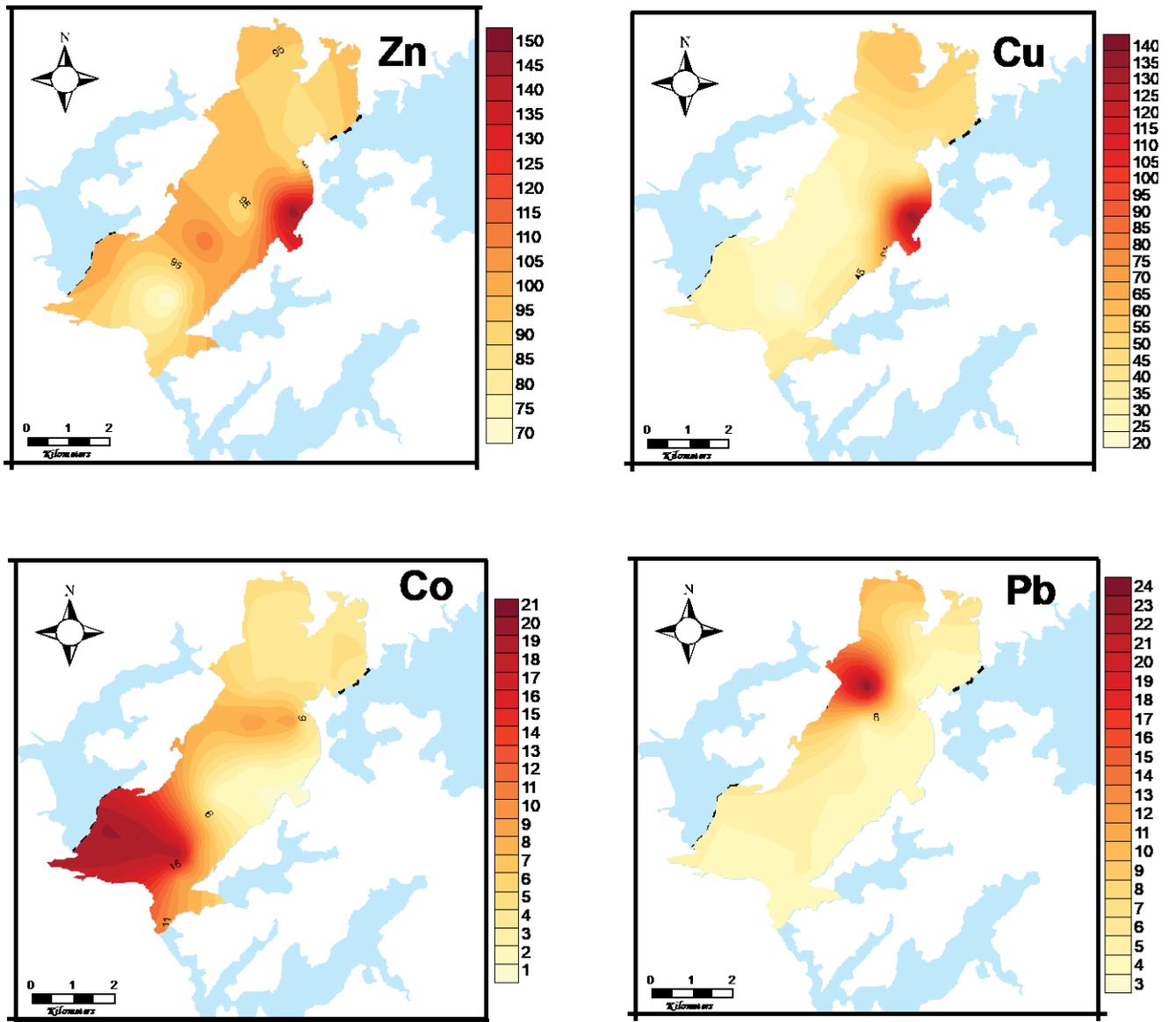


Fig. 3c. Spatial distribution of Zn, Cu, Co, Pb which are influenced by anthropogenic impact in estuary

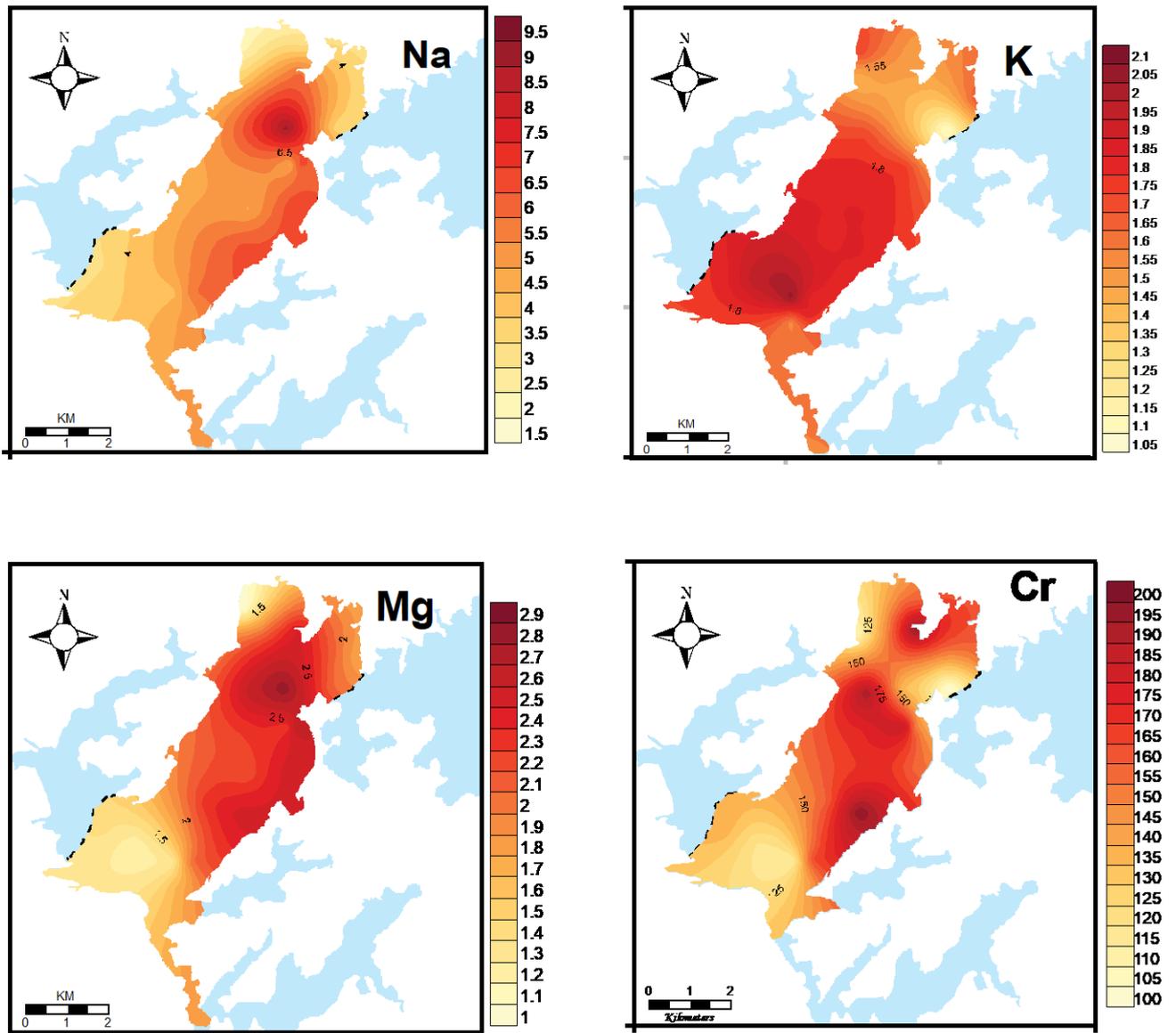


Fig. 3d. Spatial distribution of Na,K, Mg and Cr which are controlled by multivariate parameters

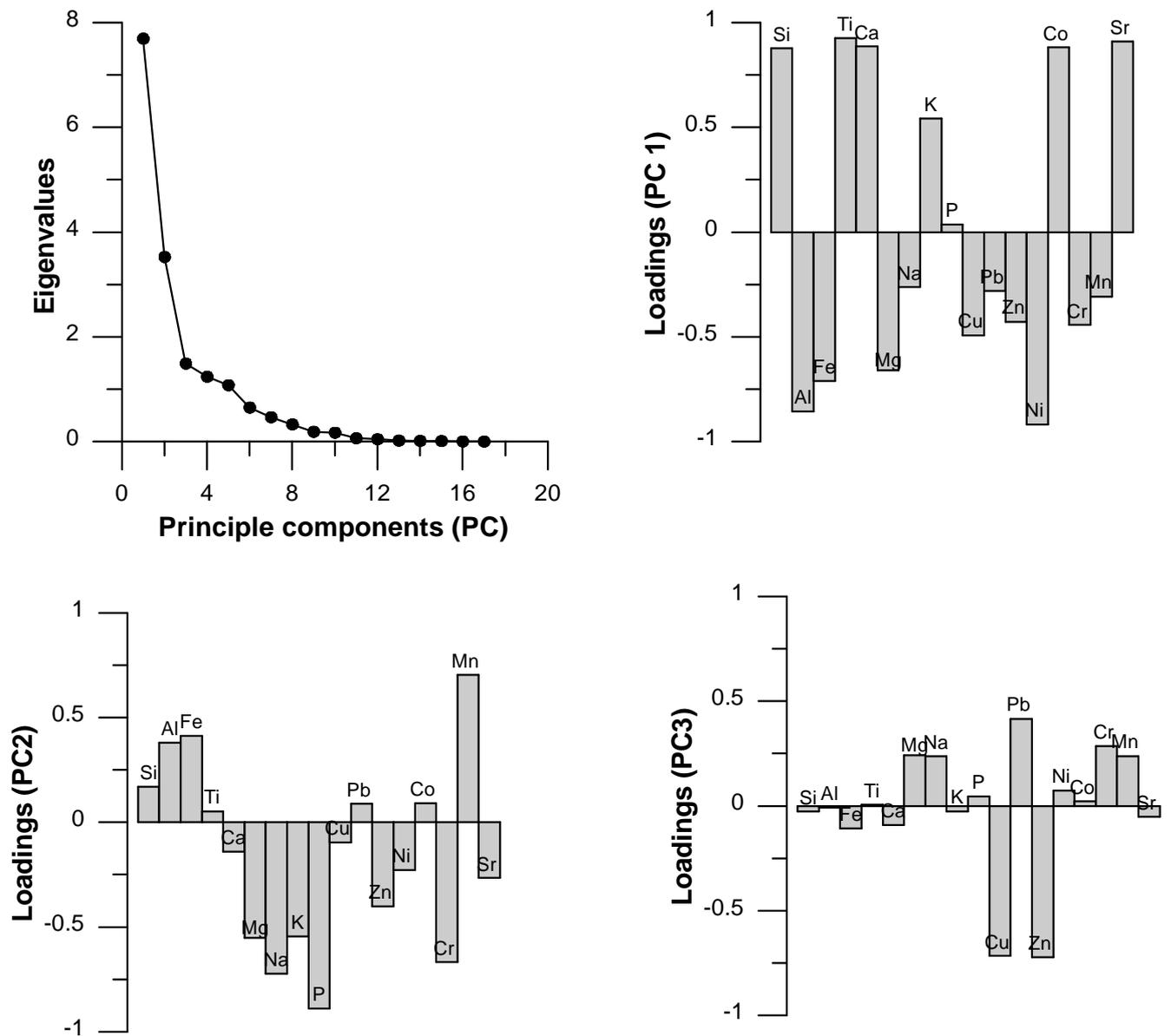


Fig. 4. Principal Component Analysis (PCA) of geochemical parameter

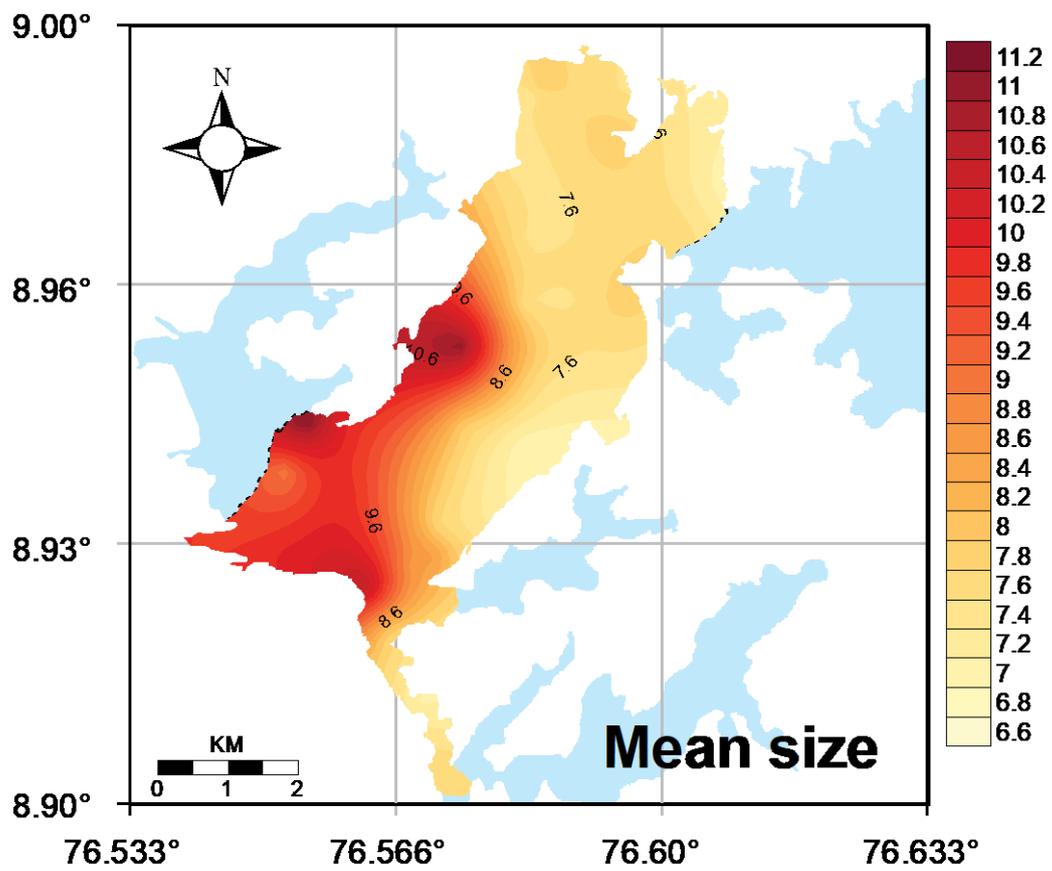
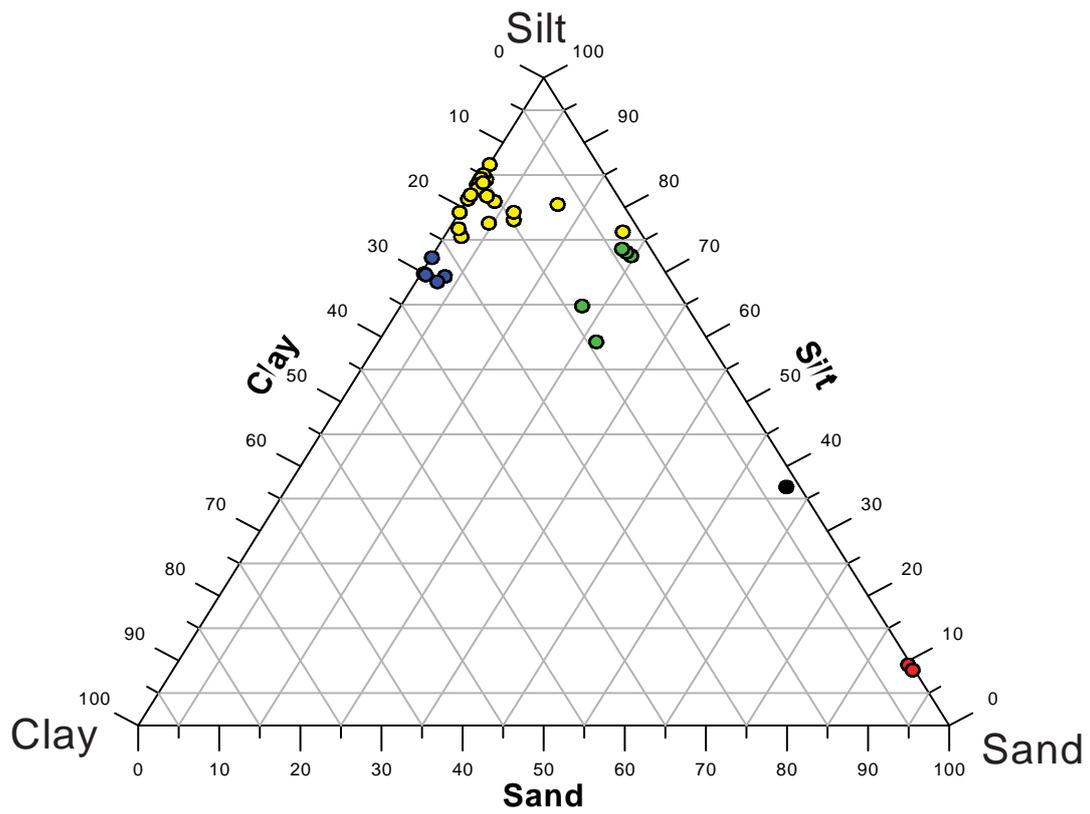


Fig. 5. Ternary diagram of grain size distribution of the Ashtamudi estuarine sediments and spatial distribution of mean grain size..

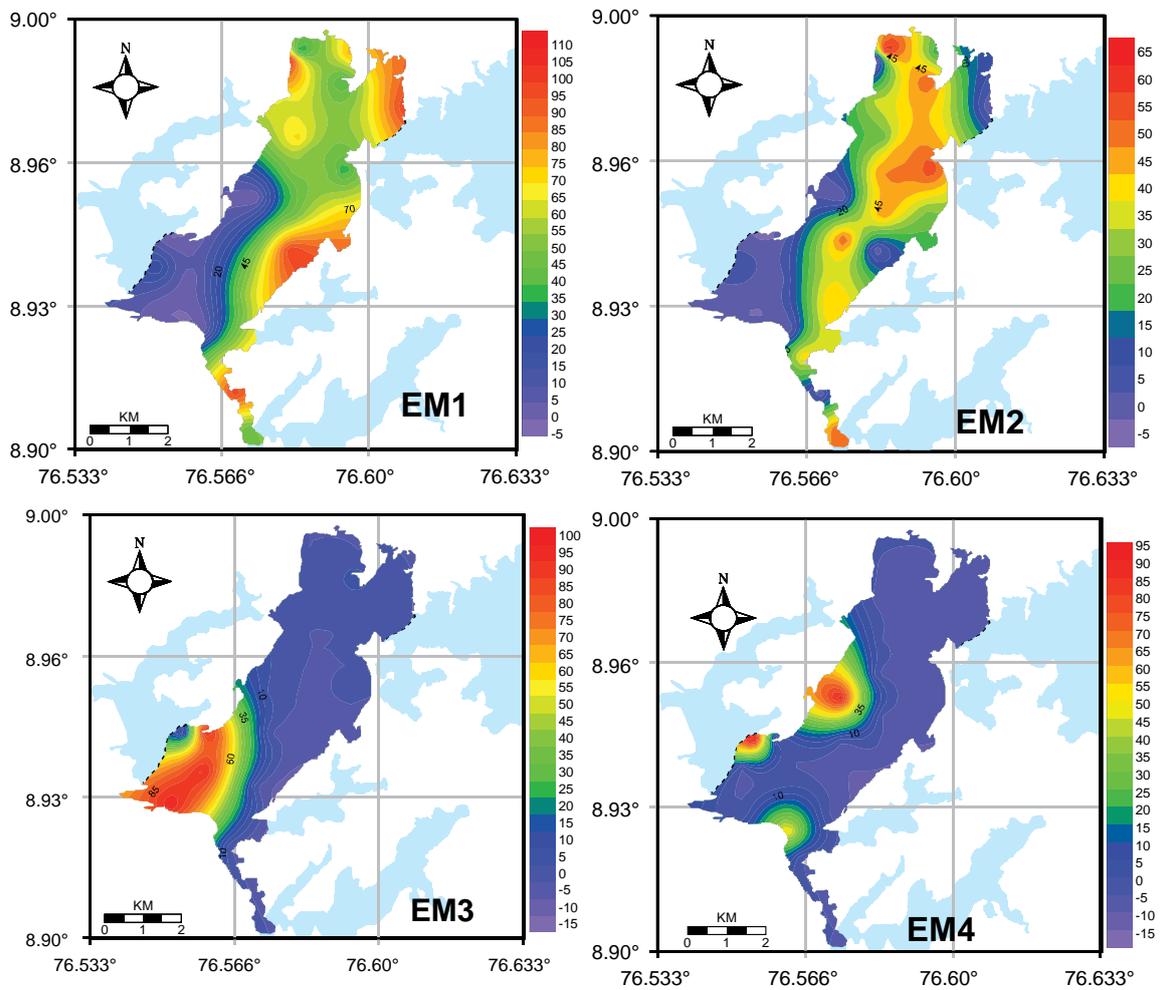
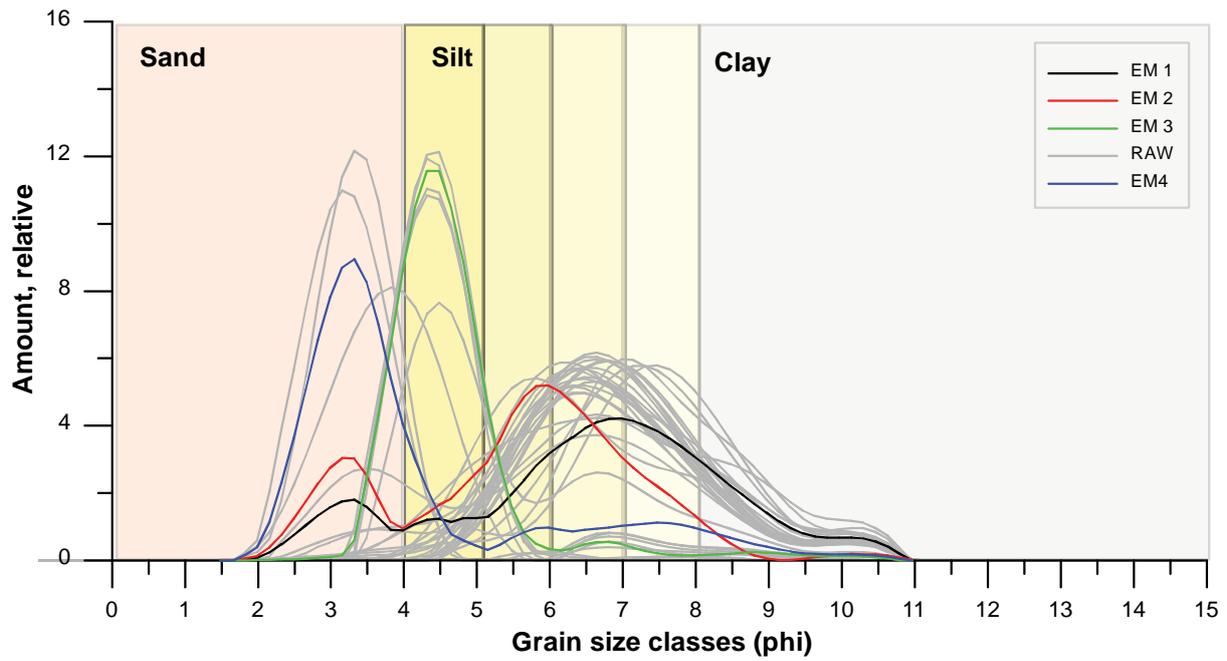


Fig. 6. End member End member loadings of grain size distribution and spatial distribution of EMs.

2.2. Discussions

2.2.1. Spatial distribution of geochemical and sedimentological parameters

The distribution of geochemical elements in estuarine environment are mostly governed by variability in riverine inputs, coastal and seafloor erosion, biological activities as well as anthropogenic influences (Zwolsman and Eck 1999; Liaghati et al. 2003; Zhou et al. 2004). The spatial distribution of geochemical concentrations in Ashtamudi Estuary is shown in Fig. 3a, 3b, 3c and 3d. PCA of the geochemical dataset provide information on the relationship among elements from the Ashtamudi sediments. The loading plot from the PC analysis revealed four groups of elements.

The first group comprises of Si, Ti, Ca, Sr and Co with higher values towards the lower end of the estuary (Fig. 3b and 3c). The high concentration of Si and Ti in the southern end of the estuary can be attributed to tidal advection of inner shelf sediments dominated in Quartz and heavy minerals (e.g., TiO_2). The calcium content increased from 0.8% to 14.9% from fluvial to marine end. The Ca and Sr indicate a non-detrital source due to its negative correlation with other detritals (e.g., Al and Fe). Interestingly, the lower end of estuary is characterized by the presence of bio-detritus which is largely composed of calcium carbonate (Jannerjahn et al. 2008; Ankit et al. 2017). Therefore, the high Ca and Sr values point to the high biological productivity observed in the marine influenced lower estuary. Furthermore, cobalt concentration (2.5 to 20.0 ppm) shows a decreasing trend from lower to upper end of the estuary with an average value of 7.9 ppm. The concentration of Co in the surface water of Lakshadweep sea shows an average value of 3.15 to 0.00315 ppm (Sanzgiri and Moraes 1979). However, in most of the stations, the values are below the detection limit (Sanzgiri and Moraes 1979). In an estuarine environment, Co is derived from both natural as well as anthropogenic factors including chemical factories, sewage effluents, urban runoff and agricultural activities (Sanzgiri and Moraes 1979; Nagpal 2004). The extremely high values of Co in Ashtamudi Estuary as compared to Lakshadweep Sea could be related to human activity as the lower end of estuary is heavily disturbed by the discharge of industrial effluents (Sitaram 2014).

The second group of elements (e.g. Al, Fe and Ni) is characterised by negative loadings of PC1 with higher values towards the upper end of the estuary (Fig. 4). The upper catchment of the estuary in the north is marked by Archean rocks with dominance of mafic minerals enriched in Fe and Ni. The high concentration of Fe and Ni in the upper estuary is attributed to the weathering in the upper catchment of the basin. Furthermore, the high concentration of Al

in upper estuary is related to the dominance of clay sized minerals. The result is also corroborated with the grain size distribution indicating fine grain sediments in the upper estuary.

The elemental group such as Mg, Cr, Na, P and K is characterized by high negative loadings of PC2 (Fig. 4). Since, P does not show much variability (variance = 0.007) in the basin, we have not considered this for our interpretation. The negative axis of PC2 shows the group of elements controlled by dual sources in the basin. For example, Mg is contributed by both the geogenic (from the mafic rocks) and biotritus (Mg^{2+} replaces Ca^{2+} in carbonates) sources (Mucci and Morse 1982; Mishra et al. 2014). However, in Ashtamudi Estuary, the spatial distribution of Mg shows high concentration towards the fluvial end (upper estuary).

We attribute weathering in upper catchment and fluvial processes as the key factor to control the Mg concentration in the basin. Additionally, evaporates and clay minerals constitute an important source for both Na and K. The higher concentration of these elements in the upper end of the estuary demonstrates that the contribution of K and Na is largely governed by the fluvial input into the basin. Likewise, Cr shows a high concentration towards the upper end of the estuary (Fig. 3d). Cr is a lithophile metallic element that readily substitute Fe and Mg because of similar atomic radii (White 2013). Therefore, Cr is enriched in mafic-ultramafic rocks which are dominant constituents in the upper catchment of the estuary. Additionally, in an estuarine environment, the high concentration of Cr is also related to various anthropogenic activities such as small scale industries (Krishnan and Jaya 2014; Karim and Williams 2015). In Ashtamudi Estuary, the bimodal source of Cr is linked to both the anthropogenic and fluvial process in the basin. However, the higher concentration of Cr towards the upper end of the estuary indicates that the Cr concentration is largely controlled by geogenic processes.

Elements (Cu and Zn) show low significant correlation with PC1 and PC2 and are only explained by PC3 (Fig. 4). The spatial distribution of these elements indicates a point source distribution which can be explained in terms of anthropogenic input into the basin. Copper and zinc are potential heavy metals used for copper based antifouling paints and Zn for galvanic anode in boats (Turner 2010). Near Trikkaruva, the high concentration of these elements indicates the role of anthropogenic activities in controlling their concentration. This interpretation is in line with human induced enrichment of Cu and Zn in Ashtamudi sediments (Krishnakumar et al. 2015).

2.2.1. Statistical approach to understand grain size distribution

The processes such as water mixing, the interplay between tidal and fluvial activities, bioturbation and anthropogenic influences have a significant effect on the grain size distribution in the estuarine system (Allen 1991; Anithamary et al. 2011; Oyedotun 2016). The combined effect of these processes result in a complex distribution with an uncertainty in the grain size variability. Therefore, it is essential to un-mix the grain size distribution in terms of the various depositional processes in the basin. The end member modeling analysis of the grain size provides genetically meaningful grain size end members that are representative for various physical and anthropogenic processes within the basin (Dietze et al. 2012). The EMMA of the grain size distribution in Ashtamudi sediments provides four EMs suggesting the various mode of deposition/sedimentation into the basin. The result of EMMA is shown in Fig. 6.

EM1 (mode= 7 ϕ) and EM2 (mode= 6 ϕ) with a dominant mode in fine silt shows higher values toward the upper and south-eastern end of the estuary (Fig. 6). The result is also corroborated with mean grain size distribution in the basin which shows finer concentration towards the riverine influenced upper end of the estuary (Fig. 5). In river channel, three factors i.e. variability in flow velocity, water turbulence, and the channel lengths are the most critical factors controlling the grain size distribution in the basin (Allen 1971). The fine particulates tend to accumulate in region where waves and currents velocity are absent or weak (Ip et al. 2007). The upper end of the Ashtamudi Estuary is characterized by the presence of several small islands separated by small river channels. Although the river channel is quite active, because of the small islands the river only carries sediment with low flow regime represented by the relatively finer sediments. This could probably explain by the long transportation of sediments from source to sink (i.e. Ashtamudi Estuary).

The EM3 concentration with a dominant mode of 4.5 ϕ (~45 μm) lies in the range of coarser silt. The EM3 shows higher values towards tidal dominated seaward side of the estuary (near Neendakara) (Fig. 6). The tidal induced enhanced erosion in the lower estuary has resulted in increased supply of coarser sediment into the Ashtamudi Estuary. Furthermore, EM4 (mode= 3.3 ϕ or 100 μm) shows the highest contribution near Thekkumbhagam (region with maximum human interventions). The anthropogenic activities such as construction and dredging exert considerable influence in grain size distribution of estuarine sediments (Wang et al. 2010; Liria et al. 2009). The area around Thekkumbhagam has been subjected to large scale construction

activities (Nair et al. 1983; Rajan and Bindhu, 2011) resulted in poorly sorted coarse sediments represented by EM4 (Fig. 6).

2.3. Paleoclimate implications

The present study highlighted the hydrodynamic processes that influence the sediment distribution in Ashtamudi Estuary. The inorganic geochemical compositions of the Ashtamudi sediments are primarily controlled by intensity of river discharge versus extent of tidal penetration and reworking. Our results suggest that the distribution of Fe, Al and Ni in surface sediments is mainly governed by river discharge and is closely associated with fine grained sediments. The elemental concentration of Fe and Al are well suited for estimating changes in the energy of terrestrial sediment supply through time and can be used to reconstruct past fluvial discharge. The distributions of Ti and Si are controlled by the tidal advection of marine sediments into the basin and can be used to interpret the ‘paleo’ sea level changes. Similarly, the grain size variability with relatively coarser (towards the marine end) versus finer sediments in the estuary can also be used to delineate marine versus fluvial activity in the basin. Applying these findings to well dated sediment records from the region will provide key information to develop an understanding of relative changes in the intensity of fluvial discharge and paleo sea level fluctuations in the region.

2.4. Conclusion

The integrated geochemical and sedimentological analyses on Ashtamudi surface sediments disentangle the natural (fluvial/marine) versus anthropogenic influence on sediment distribution in the basin. The sediments in the upper (north) estuary are characterized by Al, Ni, Cr, and Fe derived from the weathering of catchment rocks in the Kallada basin. Also, the high contribution of EM1 and EM2 indicates relatively fine grained sediments carried by the fluvial input in suspended form. The elemental concentration of Cr, Ni, Fe and Al are well suited for estimating changes in the intensity of terrestrial sediment supply through time. The high concentration of Si, Ti Ca, Sr and EM3 ($\phi = 4.5$) in the seaward side of the estuary indicates tidal interactions. The anthropogenic impact of the Ashtamudi Estuary is indicated by the high concentration of Cu, Zn, Co and EM4 ($\phi = 3.3$) in the basin. The several small scale industries, influx of domestic discharge, and pollution from the mechanized fishing boat in the lower estuary and vicinity of Thekkumbhagam are the region of high anthropogenic input in the basin. Application of these findings to chronologically well-constrained core sediments will provide insights into paleoenvironmental changes in the region.

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