

Spatial and temporal distribution of metals in suspended particulate matter of the Kali estuary, India

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Abstract

Major (Al, Fe, Mn, Ti, Mg) and trace (Cu, Zn, Pb, Cr, Ni, Co, Zr, Rb, Sr, Ba, Li, Be, Sc, V, Ga, Nb, Mo, Sn, Sb, Cs, Hf, Ta, Bi, Th, U) elements and particulate organic carbon (POC) concentrations in surface suspended particulate matter (SPM) of the Kali estuary, (central west coast of India) were studied during the pre-monsoon, monsoon and post monsoon seasons to infer estuarine processes, source of SPM and Geoaccumulation Index (I_{geo}) assigned pollution_{I_{geo}} levels. Distribution of SPM indicates the presence of the estuarine turbidity maximum (ETM) during all three seasons near the river mouth and a second ETM during the post monsoon time in the upstream associated with salinities gradient. The SPM during the monsoon is finer grained (avg. 53 μm), characterized by uniformly low normalized elemental concentration, whereas the post and pre monsoon are characterized by high normalized elemental concentration with coarser grain size (avg. 202 μm and 173 μm respectively) with highest ratios in the upstream estuary. The elemental composition and principal component analysis for the upstream estuary SPM support more contribution from the upstream catchment area rocks during the monsoon season; there is additional contribution from the downstream catchment area during the pre and post monsoon period due to the tidal effect. The Kali estuarine SPM has higher Al, Fe, Mn, Ti, Mg, Ni, Co, Ba, Li and V with respect to Average World River SPM (WRSPM). I_{geo} values for the SPM indicate Kali Estuary to be severely enriched with Mn and moderately enriched with Cu, Zn, Ni, Co, U and Mo in the upstream estuary during pre and post monsoon seasons. Seasonal changes in salinity gradient (reduced freshwater flow due to closing of the dam gates), reduced velocity at meandering region of the estuary and POC of 1.6 to 2.3 % resulted in co-precipitation of trace elements that were further fortified by flocculation and coagulation throughout the water column resulting in metal trapping in the upstream region.

Key words: Kali estuary, suspended particulate matter, metals, monsoon, organic carbon

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Introduction

The estuarine regions form connection between the rivers and ocean that are associated with changes in the biogeochemical behavior of elements by the action of various chemical and physical processes: like flocculation/coagulation precipitation, adsorption-desorption on suspended matter, re-suspension of bottom sediments, mixing of particulates from different sources (Turner et al., 1991; Bianchi, 2007) etc. In estuarine region, suspended particulate matter (SPM) acts as a major carrier as trace elements get adsorbed on to major elements like Fe-Mn oxy hydroxides and organic matter, and get precipitated, where coarse material may settle into the estuarine system (Kalpana et al., 2016) and finer material gets transported into the ocean. It is important to study major and trace elements as excess input of these metals may settle into the estuary due to salinity gradient (Bianchi, 2007; Shynu et al., 2012; Kessarkar et al., 2013) and/or can lead to degradation of the coastal environment (Gao et al., 2015). The presence of dam also influences estuarine environment, due to tidal asymmetry, increase in turbidity (Wolanski, 2007) as sediments are not flushed out.

There have often been questions whether the enrichment of the elements or the pollutants from estuarine region are fallout of anthropogenic input or natural contribution by the catchment rock (Huang et al., 1992; Chapman, 2007). Despite of numerous studies on SPM there are gaps in the studies on the special and temporal scale (Vercruysee et al., 2017). The contribution of SPM by the World Rivers to the ocean is mainly based on the major rivers (e.g. Milliman and Meade, 1983) but there is equal or more contribution by medium and minor rivers that goes unnoticed (Rodrigues et al., 2009) due to lack of data. It has been noted that the basic information on elemental concentrations are missing in many of the estuaries of the world leading to the miscalculation of the global budget (e.g. Huh et al., 1998; Rodrigues et al., 2009) where contribution of these elements to the sea still remains unresolved. Therefore there is a need to study SPM from the different estuarine environments in minor and small rivers that can contribute to the understanding of the SPM distribution, composition and behavior.

This work deals with distribution of SPM and metals (major and trace element) composition in surface SPM along the Kali Estuary, India. The major objective is to find seasonal variations in SPM quantity and composition and processes responsible for the enrichment of elements in relation to the changes in water discharge influenced by seasons and closing of the gates of six dams. During the monsoon there is excess runoff with dam gates open most of the time leading to lower salinities and most of the SPM being flushed out. Whereas, during the rest of the year, reduced discharge with dam gates closed most of the time leads to inflow of sea water increasing salinity, which can change the distribution and biogeochemistry of the SPM within the estuary. The Kali R. falls in the medium

river category with the SPM elemental concentrations much higher than some of the world's largest rivers and can contribute to the calculation of the budget of the elements to the ocean (e.g. Milliman and Meade, 1983; Huh et al., 1998; Rodrigues et al., 2009). The Kali estuary from the west coast of India is unique as there is no reported anthropogenic input, though we cannot rule out the input of domestic waste. Several baseline studies were conducted in the year 1993 and 1995 before construction of the Kaiga dam and nuclear power plant (Kaiga Generating Station). These studies mainly focused on anthropogenic and natural radionuclides in edible items, soils, water, SPM and river sediments (e.g. Karunakara et al., 2003; Rajashekara et al., 2008; Balakrishna et al., 2001). The studies based on SPM (two samples), sediments and water samples indicated no pollution in Kali River with reference to trace elements, whereas Uranium and Thorium nuclides were influenced by the lithology of the area (Manjunatha et al., 1996; Balakrishna et al., 2001). Other studies on the Kali estuary are restricted to the mouth area and coastal waters with emphasis on the bioaccumulation in oysters with metals like Zn (91.1 $\mu\text{g/g}$), Cu (38.6 $\mu\text{g/g}$) and Cd (1.82 $\mu\text{g/g}$) reported by Krishnakumar et al, (1990), Mn and Fe (Sharon and Rathod, 2015), dissolved and sediment organic carbon (~1.86 %) near the mouth (Pradhan et al., 2014; Krishna et al., 2015), biodiversity (Sowmya and Jayappa, 2016) and sediment transport offshore (along the coast) due to currents (Kunte, 1994).

1.1. Study area

1.1.1 Geology

The Kali River is ~180 km long and originates from the Western Ghats at an elevation of 900 m and drains through rocks of Dharwar Super Group covering a catchment area of 3,376 km² from the Karnataka state, India. The river passes through rocks like greywackes in the upstream, and granodiorite to tonalitic gneisses in the downstream, region before reaching the Arabian Sea (Figure 1a, b). There are also minor rock types like limestone, dolomites, manganese ore deposits, ultramafic rock complexes, orthoquartzites, argillites, banded magnetite/hematite quartzite and laterites within the catchment area. The soils in the catchment area are mostly lateritic (Manjunatha et al., 1996).

1.1.2 Hydrology

The Kali is a tropical estuary with its catchment area receiving high rainfall (3500 mm/yr) during the monsoon (June to September) and having an annual water discharge of $\sim 6213 \times 10^6 \text{ m}^3$ and sediment discharge of $\sim 0.7 \times 10^6$ tons (Subramanian et al., 1987). This river has six dams in the upstream (Supa, Bommanahalli, Kodsalli, Upper Kaneri, Tattihalla and Kadra). We restrict our study to the area that is between the last Dam (Kadra dam) and the end of the river meeting the Arabian Sea, and covering a length of about 26 km. The Kadara Dam was commissioned in 1999 (Karnataka

power Co. Ltd) and Atomic power plant (Kaiga Generating Station) was commercially operational from the year November 2000. The dam gates are opened during most of the monsoon period (June to September) with discharge from the upstream area while, for the rest of the season i.e. post monsoon (October to January) and pre monsoon (February to May), the water is discharged only during the power generation and is contributed to mostly by the tributaries connecting the rivers downstream of the dam. The river exhibit meandering in the upstream and there is a wider bay downstream. The average water depth ranges between 1.5 and 7.5 m (Nair et al., 1984). The salinity ranges between 0.24 and 33.4 and pH from 7 to 8.4 with higher values near the mouth (Nair et al., 1984). The Kali River estuary has a tidal amplitude of about 2 m (SanilKumar et al., 2001). On the southern side of the Kali R. mouth shoals/sand bar is present formed due to material supplied continuously by the Kali R. (Nayak, 1996). Because of the sand bar, estuary mouth is narrow and shallow with navigational channel almost closed during the monsoon season.

2. Materials and Methods

Surface water samples (10 to 20 liters) were collected along the midstream of the Kali estuary (Figure 1) using a motorized boat on spring tide. Eleven samples (K1-K11) were collected during the pre monsoon (6th May 2012), of which 9 samples were collected (K1-K9) using the boat. The depth of sampling stations ranged from 1.5 to 8 m. Beyond K9 the water level was too low to allow passage of the boat and could not take the boat. The Samples K10 and K11 (collected close to the Dam) were collected manually using a bucket. Ten samples (K1-K10) each were collected during the Monsoon (18th August 2012) and Post-monsoon (12th January 2013) seasons. All the samples were collected using a plastic bucket and transferred to acid cleaned carboys. The water samples after collection were transferred on the same day to the sedimentology laboratory of CSIR-National Institute of Oceanography, Goa, India and were filtered through pre-weighed 0.4 μm Polycarbonate membrane filter paper; particulate matter thus collected on the filter paper was dried and used for geochemical analysis. Salinity measurements for all samples were carried out using 8400 Guild Line Autosal Salinometer, as per the standard procedures given on <http://www.guildline.com/Datasheet/Guildline8400BDatasheet.pdf>. At each station we also deployed Laser In Situ Scattering and Transmissometry (LISST-25X) instrument for all three seasons to measure vertical distribution of grain size and particle concentration. This instrument uses laser diffraction technology and gives insitu particle volume concentration in $\mu\text{l/l}$ and particle size in μm (Sequoia Scientific Inc, 2008). The data was processed following the method given in Suja et al. (2016). The CTD (Sea-Bird Electronics) vertical profiler was used for measuring conductivity and temperature during the post monsoon season. The data was processed using software 7.23.2 copyright @ Sea-Bird Electronics,

Inc. 2014. (<http://www.seabird.com/software/sbe-data-processing>). The data represented in the figures is not corrected for tides.

For Major (Al, Fe, Mn, Ti, Mg) and Trace (Cu, Zn, Pb, Cr, Ni, Co, Zr, Rb, Sr, Ba, Li, Be, Sc, V, Ga, Nb, Mo, Sn, Sb, Cs, Hf, Ta, Bi, Th, U) element analysis, dried SPM from the filter paper was carefully removed and about 15 mg of the SPM was transferred into Teflon beakers. Acid mixture (5 ml) of suprapure (@Merk) HF(40%): HNO₃(65%): HClO₄(70%) in the proportion 6: 3: 1 was added into these beakers and kept overnight. The next day these Teflon beakers were transferred on to a hot plate for open vessel digestion at 180°C. Once the digestion was complete and the sample was dry, 1.2 ml of 1:1 HNO₃ was added to dissolve the residue, Rh was used as the internal standard and the solution was made to 30 ml (Govindaraju, 1994). All the samples were digested in metal free clean hood fitted with Hepafilters. Trace elements were measured on Thermo X series 2 ICP-MS at CSIR-National Institute of Oceanography, Goa, India. The calibration was achieved by comparing the unknown intensities to a curve prepared by the analysis of 3 multi-element standard references. The standards were run in sequence, blank followed by 3 standards, and then the samples. The samples were repeated to check the reproducibility. All the elements use a dwell time of 10000 ms with 40 sweeps and 2 replicates to determine the mean and standard deviation. The Internal standard element ¹⁰³Rh was added to compensate for matrix effects and instrument signal drift. For major elements the digested samples were run with the help of a Agilent 700 ICP-OES, at CSIR-National Institute of Oceanography, Goa, India, after calibration with suitable Merck elemental standards. Recalibration check was performed at intervals of 10 samples. Repeat sample analysis was also checked after 20 samples. Together with the samples, certified reference standard MAG1 was digested and run, to test the analytical and instrument accuracy of the method for ICP-MS and ICP-OES. The accuracy of the samples with reference to MAG-1 (Marine mud, United States Geological Survey, 1995) was found to be better than ± 10% and reproducibility was found to be better than ± 7% (Table 1).

For particulate organic carbon (POC) about 1 liter of water was filtered through GF/F filters (that were pre combusted at 300°C for 6 hours) under vacuum and dried at <45°C. These dried filters were exposed to HCl fumes for 12 hours. Samples were analysed using elemental analyzer (FlashEA; Thermo) coupled to an isotopic ratio mass spectrometer (IRMS, Delta V Plus, Thermo Electron, Germany) via ConFlo IV, at CSIR-National Institute of Oceanography, Regional Centre, India (Sarma et al al., 2014). Glutamic acid, alanine were used as laboratory standards and Organic Analytical Standard (OAS) as internal standards. Reoperation of the samples gave an error of ±0.008 %, for POC values which are reported in percentage (%) of dry weight.

The Principal Component Analysis (PCA) method has been applied to the data which, helps in describing a given multidimensional system by reducing large number of variables into a small set of variables (Tuncer et al., 2001; Loska and Wiechula, 2003; Soto-Jimenez et al., 2003; Mico et al., 2006). In the present study, the PCA was employed to judge and identify the metal sources of SPM and sediments in order to distinguish the sources. We could not apply PCA method on POC due to limited number of data points. The data processing was carried out using the software Statistica 10.0. The number of factors was chosen based on Eigen values >1 and degree of variation. Enrichment Factors (EF) were calculated (Taylor and McLennan, 1995) where $EF = \frac{[Element/Al]_{sample}}{[Element/Al]_{Background}}$, Average World River SPM (WRSPM) values given by Viers et al (2009) were used as the background. Geoaccumulation Index (I_{geo}) was calculated as per Muller (1969), $I_{geo} = \log_2 (Sample/1.5*Background)$. I_{geo} pollution levels (pollution_{I_{geo}}) were assigned based on Forstner et al. (1990), where I_{geo} >5 signify extreme pollution_{I_{geo}}, 3-5 signify strong pollution_{I_{geo}}, 1-3 denote moderate pollution_{I_{geo}} whereas $<0-1$ denotes uncontaminated.

3. Results

3.1. Variations in SPM, Salinity and POC along the Kali estuary

Kali estuary SPM content ranges between 0.02 and 2712 $\mu\text{l/l}$ (Figure 2), grain size between 0.1 and 343 μm and salinity values range between 0 and 34.9 (Figure 3, Table 2). Salinity profiles for the post monsoon season (Figure 2d) exhibit horizontal and vertical stratification with a pronounced salinity frontal zone at K7. Higher concentration of SPM is observed during all three seasons at the sea end stations K2 and K3 (SPM concentration up to 540 $\mu\text{l/l}$). High SPM at K2 and K3 stations is associated with high surface salinity (Figure 2, 3) during pre and post monsoon and low during the monsoon. There is another high SPM concentration zone (SPM up to 2712 $\mu\text{l/l}$) seen in the upstream stations centered on K6, K7, and K8 during the post monsoon time that is associated with vertical and horizontal salinity gradient in the water column (Figure 2d). The surface POC ranged between 0.6 and 5% with relatively higher values (1.8 to 5%) in the upstream region during the pre monsoon (K5, K7, K8) and post monsoon (K6, K8) and relatively lower values (0.6 to 1.4 %) during the monsoon time. The surface POC for downstream samples is relatively lower than the upstream samples for all the seasons.

3.2. Major and trace elements in the surface SPM

Most of the elements along the Kali Estuary exhibit narrow range in concentrations during monsoon compared to the pre monsoon and post monsoon (Table 2). The concentration of Rb and Th are higher (avg. 145.5 and 15.5 ppm) compared to the pre monsoon (63.8 and 8.4 ppm) and post

monsoon (80.8 and 9.4 ppm). To remove the source effect (Tribovillard et al., 2006), as distribution of metals can vary with provenance mineralogy, grain size, natural and anthropogenic effect (Ho et al., 2012), we have normalized the elemental concentrations with Al concentration (Figure 3, SM 5) and used for further discussions. The SPM is fine grained (avg. 53 μm) and associated with low element/Al ratios during the monsoon season. Whereas reverse trend is observed with coarser grained SPM during the pre monsoon (173 μm) and post monsoon (202 μm), and higher element/Al ratios (Figs. 3a, b). The downstream stations (K1-K6) exhibit lower element/Al ratios compared to the upstream stations (K7-K10) except for Li, Nb, Ta, Rb, Th, Cs and Mg. Most of the element/Al ratios show a peak at K7 station (Figures 3, SM 5). Relatively high element/Al ratios are observed at K6, K7 and K8 stations that are located at the meanders of the river (Figure 1a) and are also associated with horizontal and vertical salinity frontal zone during the post monsoon (Figure 2d)

The metal association in PCA plots exhibit seasonal changes with more distinct grouping (Table 3) observed in the upstream compared to the downstream stations (Figure SM 6a-f). During the monsoon, PCA plots exhibit more convergence of the groups in the upstream, most of the components correlating well and divergence for the downstream stations (Figure SM 6c-d). The post monsoon (Figure SM 6e-f) and pre monsoon (Figure SM 6a-b) upstream plot exhibits spreading up of groups (Table 3) that are not associated with the salinity or SPM concentrations whereas the downstream plot exhibits more separation of groups.

4. Discussion

4.1. SPM and Estuarine Turbidity Maximum (ETM)

High SPM concentrations were observed close to the sea end stations (K2 and K3) extending up to the bottom (4 m depth) for all three seasons that were associated with high surface salinity (26.1 to 34.9) during the pre and post monsoon and low (~ 0.5) during monsoon. High SPM was also observed centered between stations K5 to K8, covering a wider area extending up to a depth of 3 m during the post monsoon time (Figure 2). These high SPM zones at K2 and K3 are probably ETM that are associated with high salinity (19.3 to 34.9) during the dry season (pre and post monsoon) and lower salinity (0.5) during the monsoon (Figure 2; Table 2). Such zones of high SPM are reported in various estuaries as a result of salinity gradient leading to flocculation processes, tidal actions leading to re-suspension of bottom sediments or a combination of all these processes (Allen et al., 1980; Eisma, 1986; Uncles and Stephens, 1993; Brenon and Le Hir, 1999; Guézennec et al., 1999). The ETM zone in the estuaries may show seasonal shift seaward and landward depending on variation in salinity gradient (That may lead to settlement of SPM under gravitational sedimentation

and removal of elements from the water column), sediment discharge and river run off (Uncles et al., 1994; Mitchell et al., 1999; Downing-Kunz and Schoellhamer, 2013; Priya et al., 2015; Asp et al., 2016). Studies by Kessarkar et al (2009) have also observed ETM at sea end stations in Mandovi estuary during the monsoon related to runoff that carried high SPM leading to gravity sedimentation as soon as it came in contact with saline water; and during pre monsoon related to resuspension of bottom sediments with no ETM during the post monsoon time. In case of the Kali estuary we observe the ETM zone is fixed near the river mouth (K2 and K3 stations) during all the three seasons, which may be related to a very narrow and shallow mouth (as there is sand bar near the mouth) and high tidal influence keeping the SPM in suspension. The grain size of bottom sediments at stations K2 to K4 showed almost absence of finer fraction (Suja et al. 2017) which further confirms that finer fraction remains in suspension and is not deposited at these stations. During the post monsoon time there appears another ETM with high concentrations of SPM (K5 to K8 stations) in the upstream region (Figure 2c) associated with the vertical salinity gradient (4.5 to 13.8) and horizontal salinity gradient (4.0 to 17.2; Figure 2d). In this region as the salinity falls below 25 the SPM shows maximum precipitation with no precipitation seen for the salinities below 5. The grain size of SPM is high (avg. 202 μm) which confirms the process of flocculation and coagulation taking place leading to precipitation and settling of the SPM. Near ETM kinetics of particle concentration effect is high (Bianchi, 2007) leading to quicker coagulation.

4.2. Seasonal variations in elemental and POC concentrations of surface SPM

The SPM content exhibits high average concentration of Al, Fe, Ti, Cr, Rb, Li, Be, Sc, V, Ga, Nb, Cs, Ta, Bi and Th during the monsoon; Mg, Cu, Zn, Pb, Ni, Co, Sr, Ba, Sn, Sb and Hf during the post monsoon and Mn, Zr, Mo and U during the pre monsoon (Table 2). It is observed that there are higher concentrations of redox sensitive elements like Cu, Ni, Co, Mn, Mo and U during the post and pre monsoon seasons. The element/Al ratios are observed to be lower during the monsoon compared to the pre and post monsoon (Figure 3, SM 5). Similar low elemental concentrations have been observed in Yellow River, China (Huang et al., 1992; Hu et al., 2015) as a result of transportation of coarser sediments with low trace metals into the estuarine system. However, we observe that low element/Al ratios in SPM are associated with finer grain size (avg. 53 μm) for the monsoon season. Re-suspension of material also influences the SPM composition as observed in Humber and Thames estuaries, England (Turner and Millward, 2000). Thus, the finer grain size with low elements/Al ratio values during the monsoon in the present study may be contributed by the soils from the catchment area and further influenced by transportation of finer fractions as the river carries maximum water and moves with high velocity compared to pre and post

monsoon. The POC is low during monsoon ~ 0.6 to 1.4 % where as it is relatively higher during the pre monsoon (0.7 to 5%) and post monsoon (0.6 to 2.5 %) with higher values observed in the upstream stations (K6, K7, K8). Relatively higher POC in the upstream stations (K6, K7, K8) compared to down stream stations are associated with higher element/Al ratios (we could not perform PCA analysis due to limited POC data points). Increased POC can result from flocculation and coagulation and biogenic SPM (Shevechenko et al., 2005). There are several dams upstream with their gates opened during the monsoon time. The contribution from this upstream area (Greywakes, Granitoids etc; Devaraju et al., 2010) may have resulted in SPM with low trace elements/Al ratios. The higher element/Al ratio values during the pre-monsoon and post monsoon are associated with coarse grained material. Relatively less water is discharged through the dams during this period that can restrict the SPM coming from the upstream region. The reduced river flow due to closing of the dam may have served as a natural sieve depositing the coarser grained material upstream. Further, reduced velocity of the water may help in retaining the SPM within the estuary resulting in flocculation and coagulation (Figure 2c) under salinity gradient within vertical salinity frontal zone at K7 and horizontal frontal zone between K6 to K7 (Figure 2d) resulting in coarse grain size. The deposition of SPM depends on salinity (Shevchenko et al., 2005) with elements getting removed systematically with change in salinity from 2 to 15. Above changes observed in the study area may be responsible for removal of metals from the water column.

4.3.Sources of surface SPM

The lower elemental/Al values observed throughout the estuary during the monsoon compared to the post monsoon and pre monsoon season, suggest a change in source (Figure 3, SM 5). During the monsoon season, land runoff is contributed from a larger area covering different rock types and lateritic soils (Manjunath et al., 2001) in the drainage area. The gates of most of the dams in the upstream are open, that may also contribute to the SPM from the upstream drainage area and could be probable source of the elements. Overall, average elemental concentrations of Greywacke around the upstream stations (K6 to K10) are higher compared to Tonalitic gneisses in the downstream (Figure 1, Table 2). High Rb (upto 181 ppm) and Th (up to 21 ppm) are reported in the Greywacke formation (Devaraju et al., 2010) that indicates that high Rb and Th in the SPM may be contributed from the upstream. Further, the increase in water discharge due to rainfall and opening of the dam gates leads to strong flow of fresh water during the monsoon that avoids stagnation of water and dominance of more fresh water may have resulted in uniform distribution of the elements. The PCA plots in the upstream show most elements clubbing together in the group (Figure SM 6d) further supporting a single source, probably from the upstream. Whereas in the downstream PCA plots

separate groups (Figure SM 6c) can be identified that may be the result of additional contribution from the downstream catchment area during monsoon season.

The pre and post monsoon element/Al ratios can be classified into two zones along the estuary, the one with low values (K1 to K6) associated with high surface salinity (34.9 to 9.7) in the downstream of the estuary and the high values (K7 to K10) associated with low surface salinity (0 to 7.2) in the upstream (Figure 3, SM 5). These two zones are associated with two different rock types (Figure 1b), lower reaches dominated by tonalitic gneisses and laterites and upper reaches by greywackes (Radhakrishna, 1983; Jayram et al., 1983). The changes in the rock type may be one of the reasons for the change in the elemental concentration in the lower and upper reaches (Figure 1b). The lower estuary is associated with higher content of element/Al ratios of Li, Nb, Ta, Rb, Th, Cs and Mg compared to the upper estuary (Figure 3, SM 5). There is good inter elemental correlation (Figure SM 6a, e; Table 3), suggesting they may have been coming from the same source. These elements are generally associated with source rocks like granites and pegmatites (Selway and Breaks, 2005). The catchment area of lower estuary is dominated by tonalitic gneisses with pegmatite vein (see study area), that may contribute the above elements. The lower concentrations of other elements (Figure 3, SM 5b) may be a result of processes like mixing of marine (organic and/or carbonate rich) with land derived particles and re-suspension of non-cohesive coarse sediments under the influence of winds, waves and tides in the mouth of the estuary (Rao et al., 2011). Low POC and high salinity (Figure 2) in this region may not have supported flocculation and coagulation (Shevchenko et al., 2005), reducing the removal of elements (Pokovsky et al., 2014) from the water column. The PCA plots show spreading of the groups in the lower estuary indicating multiple sources (Figure 6a, e) like granites, pegmatites and laterites present in the catchment area.

The higher element/Al ratios are observed for most of the elements in the upstream (Figure 3, SM5) stations that may be related to the higher concentrations of these elements in rocks (Devaraju et al., 2010) from the upstream catchment area (e.g. Graywacke formations, Table 2). The element concentrations in the upstream SPM are observed to be much higher than the source rocks. It is noted that U is relatively higher at station K7 with concentrations higher than 26 ppm that is higher than the source rock (Table 2). Balakrishna et al (2001) have reported U values of about 2.2 ppm (2.2-4.2 ppm) in SPM for the samples collected in 1993 (in downstream estuary) during the post monsoon season, that is comparable to our results close to station K4 and K5 (See Table 2). To check if it is fallout from the Kadara Dam/Kaiga atomic power plant we have analysed the sample collected next to the Dam (water that has come out from the dam) at station K11. We observed that the U value of K11 is 2.4 ppm that is much lower than the K7 station, which suggests it is not

contributed by Kadara Dam. The catchment area U content of 3 ppm (Devaraju et al. 2010) is comparable to that of K11 station. Dissolved U in Kali estuary is reported to be higher in high salinity waters and decreases with the decrease in salinity (Balakrishna et al., 2001). Therefore, there is a possibility that U may be removed as river water comes in contact with sea water as suggested by Balakrishna et al. (2001). In Ganges-Brahmaputra R., U gets removed from the water in the mixing zone with decrease in the river discharge with salinity <12 (Carroll and Moore, 1993). Though Carroll and Moore (1993) could not figure out confirmed mechanism for U removal, they suggested that interaction of low salinity water with mangrove sediment and/or SPM to be probable reason. In the present study along with U, we also observed enrichment of most of the other elements around K7 station (sum trace elements, Figure 2). But elements like Mn, Cu, Ni, Cr, V, Mo, Zn, and U get precipitated and/or formed under low oxygen to anoxic conditions leading to enrichment of these elements in sediments (Calvert and Pedersen, 1993; Tribovillard et al., 2006). There are less chances of this SPM with high element/Al ratios entering from the reservoir (water stored in the dam) as the river was cut off from the dam during the pre and post monsoon sampling time. The morphology of the Kali estuary at K6 and K7 is such that it meanders (Figure 1) like a “U bend” separating the wider Bay stations K2 to K5 and upstream river stations K8 to K10. There can be additional input at the meandering caused due to upwelling with input of fine sediment (Wolanski, 2007) diffusing metals from porewater into the water column (Audry et al., 2007). During the post monsoon, the fresh water flow is relatively reduced as a result of end in rainfall and also closing of the dam gates, also seen by surface salinity low for monsoon and increase during the pre and post monsoon (Figure 3). As the fresh water flow reduces, the tidal influence is seen up to station K10 which indicates that there is intrusion of sea water. The salinity profiles (Figure 2d) show change in salinity 0 to 34.6 along the estuary, this change affects the metals from the solution and are removed from solution with decrease in salinity (Bianchi, 2007). We observed maximum vertical salinity gradient at K7 (4.5 to 13.8) and horizontal gradient between K6-K7 that may have led to gravitational settlement and co-precipitation of the elements with change in salinity. This precipitation of particulates is seen as high concentration of SPM in the water column profiler captured by LISST-25X at station K7 (Figure 2c). Further, comparing the sum of trace elements with the vertical SPM distributions along the estuary indicate high trace element values in the upstream stations (Figure 2c). Laboratory studies of the Kali River water samples have confirmed the co-precipitation of the elements (Balakrishna et al., 1997) with change in salinity (with rapid flocculation at salinity >25). Studies by Byrd (1990) and Pokrovsky et al., (2014) have also demonstrated removal of elements from solution, in the estuarine environment at lower salinity and/or with systematic change in salinities. There can also be aggregation of the SPM at lower

salinity and increase in floccules size for SPM concentrations higher than 4 mg/l (Verney et al., 2009). In the present study concentrations of SPM higher than 500 $\mu\text{l/l}$ (up to 2715 $\mu\text{l/l}$) could have resulted due to removal of metals from solution, flocculation/coagulation and may have increased leading to co-precipitation of elements. The adsorption/desorption of trace elements is controlled by Fe-Mn oxyhydroxides, POC, clays, carbonates (Bianchi, 2007). The elevated POC in the upstream (1.6 to 5.0 %) which contributes to micronutrients and Fe-Mn oxy hydroxides could have further accelerated sorption of elements (Turner and Millward 2002; Turner et al., 2004) leading to higher concentration (Tribovillard et al., 2006) that is seen in the present study (see Table 3, Figure 3). Later, by the time of pre-monsoon these particles may be getting settled into the sediments, tidal effect may have been stronger (due to reduced river flow) carrying the SPM with higher trace elements further upstream upto station K10 (Figure 3). The low water level during pre monsoon may have further aided resuspension of the SPM with high trace elements that were deposited during the post monsoon.

4.4. Degree of pollution_{geo}

The Al normalised concentration data was compared with the WRSPM to have a better picture of enrichment of the elements (SM Table 4). Enrichment of trace elements in more than one station is observed for Mn, Cu, Zn, Pb, Cr, Ni, Co Zr, Ba, Li, U and Mo during the pre monsoon season; Mn, Cr, Ni, Li and V during the monsoon and Fe, Mn, Ti, Cu, Zn, Pb, Cr, Ni, Co, Ba, Li Sc, V, Ga, Mo, Sn and U during the post monsoon season (SM Table 4). The Li and Mn exhibit higher enrichment during all three seasons. Most of these elements are enriched in the upstream region during all the three seasons. Enrichment of the metals in the other upstream estuaries (see Nelson and Lamothe, 1993; Fang and Lin, 2002) is related to anthropogenic input. But in the present study higher enrichment of elements are during the pre monsoon and post monsoon, where the source sediments are coming from the surrounding rocks (not much from the upstream as dam gates are closed) and with no anthropogenic input, makes Kali estuary different from the others. The elemental distribution can also be controlled by grain size and local hydrodynamic conditions in addition to the source rocks (Koukina et al., 2016). Comparing the present data with year 1993 (Balakrishna et al., 2001), the Kali estuary SPM exhibits increase in Cu and Co and decrease in Mg, Pb and Ba content for both monsoon and post monsoon seasons (Table 2). Further, when we compared our data with the Mandovi estuary (Table 2) that is affected by anthropogenic pollution (Shynu et al. 2012) and pass through similar rock types like that of Kali (Dharwad super group) higher concentration of Al, Mn, Cu, Zn, Ni, Co, Sr, Sc, V, Mo, U and Th are seen. Comparing the present data with that of the Yellow River containing high concentrations of the trace elements in SPM (Table 2) that are

enriched under natural condition (Huang et al., 1992) reveals that the Kali SPM elemental concentrations are much higher (except Al, Mg). The Li concentrations (up to 130 ppm, Table 2) in the Kali estuary SPM are much higher than those of the major rivers like the Amazon R. (71.6 ppm), the Xingu R. (63.9 ppm) and the Mississippi R. (49.3 ppm) SPM (Huh et al., 1998). Li is retained in the catchment area soils during clay mineral formation (Huh et al., 1998), it is also present in high content in the pegmatite that may be contributing to the SPM. Enrichment of Li could be further enhanced due to clays where Mg^{2+} is isomorphically substituted for Al in the octahedral layer where Li gets accommodated in the vacant space (Heier and Billings, 1978). During the post monsoon and pre monsoon, Li enrichment is higher and associated with the high Mg/Al ratios (Figure 3) which support isomorphous substitution. Whereas during the monsoon season Li enrichment is relatively low and associated with low Mg/Al ratios. The observed enrichment of Mn could be due to the high content from the upstream source rocks like Greywackes (Devaraju et al., 2010) with average of 2.2 % (Table 2), that could have further increased in concentration due to input from the precipitation taking place within the upstream estuary in the frontal zone (Station K7). Due to closing of the dam gates and relatively reduced run off, Kali estuary suggests tendency of enrichment of the metals (metal trapping) in the upstream region and out flow of these metals during the increased flow of river due to rainfall and opening of dam gates during the monsoon.

The Igeo values of Mn indicate moderate to strong pollution_{Igeo} in most of the stations for the pre and post monsoon season and moderate pollution_{Igeo} in the three stations for the monsoon season (Figure 4 a-c). Previous studies link high Mn content to the Mn mining in the catchment area (Manjunatha et al., 2001), mining has been stopped in most parts of the catchment area, as it is taken over by forest department and by 2011 mining was banned in the state of Karnataka (present study samples collected in the year 2012 and 2013). The mining reserves of Mn are in the upstream of Supa Dam and water/SPM coming from this area has to pass through 5 more dams to reach Kali estuary and seem to be difficult. If Mn had to come from the mining area and/or its dumps, the Igeo values would have been higher during the monsoon time, (as water moves from most of the catchment area and through the dams) but that is not the case here (See Figure 4). The high Mn Igeo values during post and pre monsoon may be a result of higher content in the source rocks and estuarine processes leading to its precipitation. Similar inverse relation of Mn with the river flow is reported for the Yaquina estuary in Oregon (Callaway et al., 1988). The Igeo values of Li also indicate moderate to strong pollution_{Igeo} in most of the stations for all the three seasons, with relatively higher values in the downstream areas. The Kali SPM is moderately polluted_{Igeo} with Cu, Zn, Ni, Co, U and Mo that are mostly restricted to the upstream region (Figure 3, SM 5). There are

no reported industries or industrial outputs from the surrounding areas in the estuary to account for the higher pollution_{Igeo} levels. The studies carried out on sediment and SPM by Manjunatha et al (2001) on the upstream of the Kadara dam have reported chemical weathering of source rocks from the catchment area mostly consisting of greywackes to be the major factor for higher concentration of the elements in the Kali R. SPM and sediment. Our study suggests that in addition to the chemical weathering there are changes in salinity (gradient in the frontal zone K7) and also stagnation of water due to reduced freshwater supply (may be due to closing of dam gates) leading to removal of elements from solution and co-precipitation with POC and Fe/Mn microcollides that leads to higher concentrations of elements in the SPM. The Igeo values for Mn, Zn, Ni and Mo indicate moderate pollution_{Igeo} at station K7 during the monsoon (Figure 4b), that may be a result of resuspension of the material (SPM that was accumulated in sediment during the post monsoon) due to stronger river flow towards the downstream.

Our results on seasonal changes in the SPM distribution in water column and elemental concentration in surface SPM can be helpful in understanding estuarine processes where water discharge is dominated by the monsoons. The river course and human controlled water discharge (by dams) can influence the grain size, distribution and composition of SPM. Our understanding suggests that medium river estuarine SPM can contain high Li concentrations compared to some of the largest rivers (Huh et al., 1998) of the world.

5. Conclusion

Seasonal changes in the SPM distribution and concentrations of Al, Fe, Mn, Ti, Mg, Cu, Zn, Pb, Cr, Ni, Co, Zr, Rb, Sr, Ba, Li, Be, Sc, V, Ga, Nb, Mo, Sn, Sb, Cs, Hf, Ta, Bi, Th, U and POC in surface SPM were observed during the pre monsoon, monsoon and post monsoon season along the Kali estuary. The SPM concentrations reveal presence of a consistent ETM near the mouth throughout the year, formed as result of re-suspension and one on the upstream during the post-monsoon mitigated by salinity gradient in the frontal zone. The Al normalized elemental concentrations during the monsoon season were uniformly low and fine grained SPM predominantly sourced from larger catchment area upstream with increased discharge through the dams. The pre and post monsoon SPM was coarser grained with high Al normalized elemental concentrations in the upper estuary SPM that may have resulted from precipitation of elements along with Fe-Mn oxy hydroxides, attached to organic matter microcollids; whereas, the lower estuary received additional input from source rocks like tonalitic gneisses and greywackes. Most of the Kali estuary SPM elemental concentrations are observed to be higher than the estuaries from regional (Mandovi R.) and global (Yellow R,) areas. The Igeo values are above threshold limit for Mn and Li. The enrichment of Cu,

Zn, Ni, Co, U and Mo in the upstream estuary during the post and pre monsoon probably resulted from co-precipitation attached to Fe-Mn oxyhydroxide and POC due to the combined effect of salinity gradient and meandering of river. Thus, natural and human generated changes in the river discharge and regional rock geochemistry combined with the estuarine hydrodynamics determines the composition of SPM in Kali estuary.

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Figure 1: (a) Location of the SPM sample collection along the Kali Estuary, K1 to K11 indicates station numbers. (b) Geology of the Kali river basin (http://www.indiawaterportal.org/sites/indiawaterportal.org/files/Map_Karnataka_State_Geology_and_Mineral_Map_Geological_Survey_of_India.pdf), filled dots indicate sample locations, note change in rock types from downstream stations (K1-5) to upstream (K6-9).

Figure 2: Bar graphs from top panel indicates the sum of trace elements from surface SPM at each station along the Kali estuary, just below the bar graphs are the SPM distribution in the water column with depth along the Kali estuary during (a) pre monsoon, (b) monsoon (c) post monsoon. (d) Salinity profiles during the post monsoon time, station numbers are given besides the profile. (salinity profiles for pre monsoon and monsoon not available).

Figure 3: Variation in surface salinity; POC and element/Al ratios in surface SPM along the Kali estuary during Pre monsoon, monsoon and post monsoon. On X axis “Sea” indicates seaward side and “Land” upstream side of the river samples. The dotted line with WR are element/Al values calculated from average world river SPM values (Viers et al., 2009). Only WR is given where the values does not fit on the axis.

Figure 4: Igeo values for selected elements ($I_{geo} > 1$) from surface SPM along the Kali estuary during (a) pre monsoon, (b) monsoon and (c) post monsoon.

SM Figure 5: Variation in element/Al ratios in surface SPM along the Kali estuary during Pre monsoon, monsoon and post monsoon. The dotted line with WR are element/Al values calculated from average world river SPM values (Viers et al., 2009) for respective element. WR is given where the values does not fit on the axis.

SM Figure 6: Principal Component Analysis of SPM content, Salinity and elemental composition of the surface SPM (a) Downstream estuary (stations K1 to K5) pre monsoon, (b) Upstream estuary (stations K6-K9) pre monsoon, (c) Downstream estuary monsoon, (d) Upstream estuary monsoon, (e) Downstream estuary post monsoon, (f) Upstream estuary post monsoon.

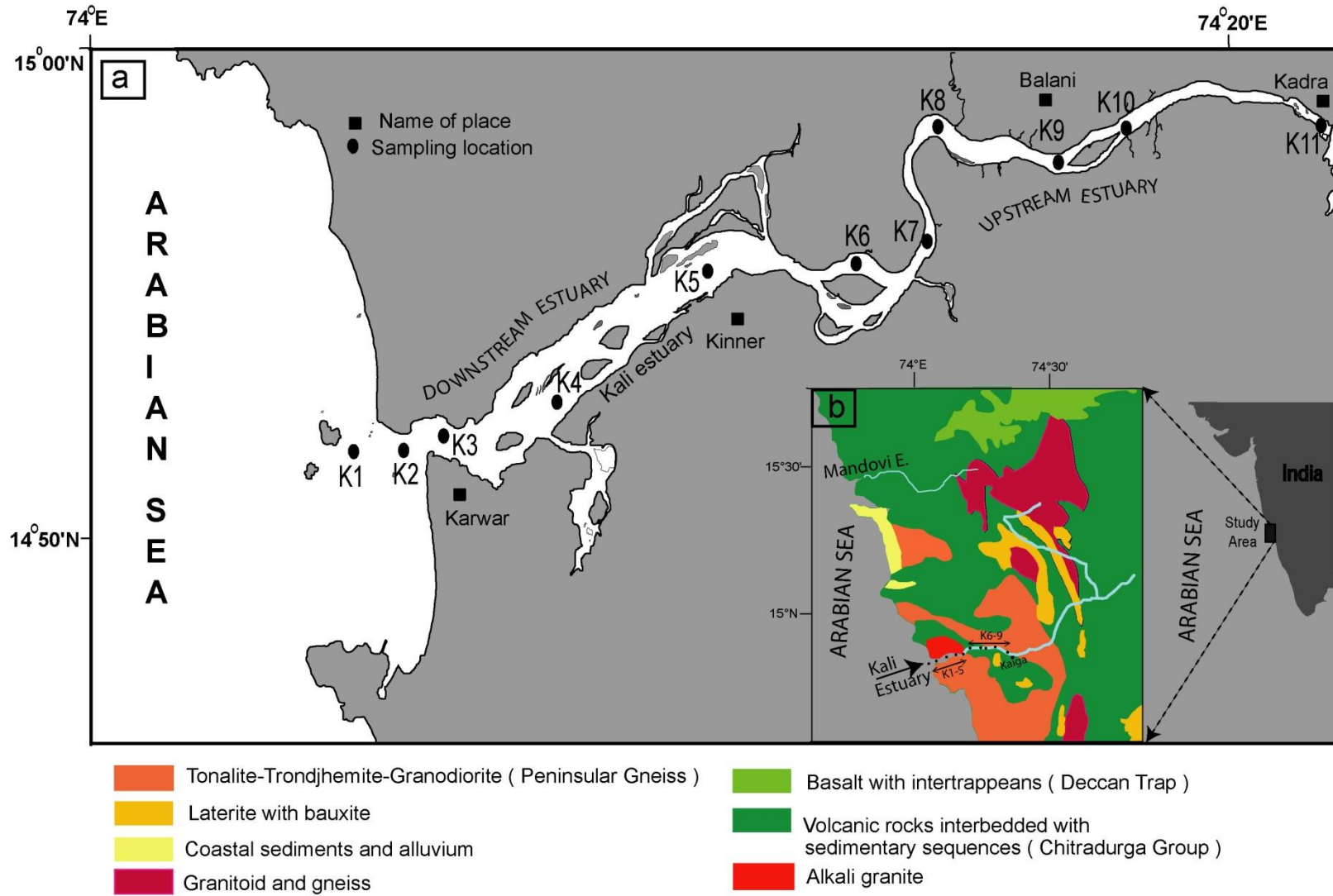


Fig. 1

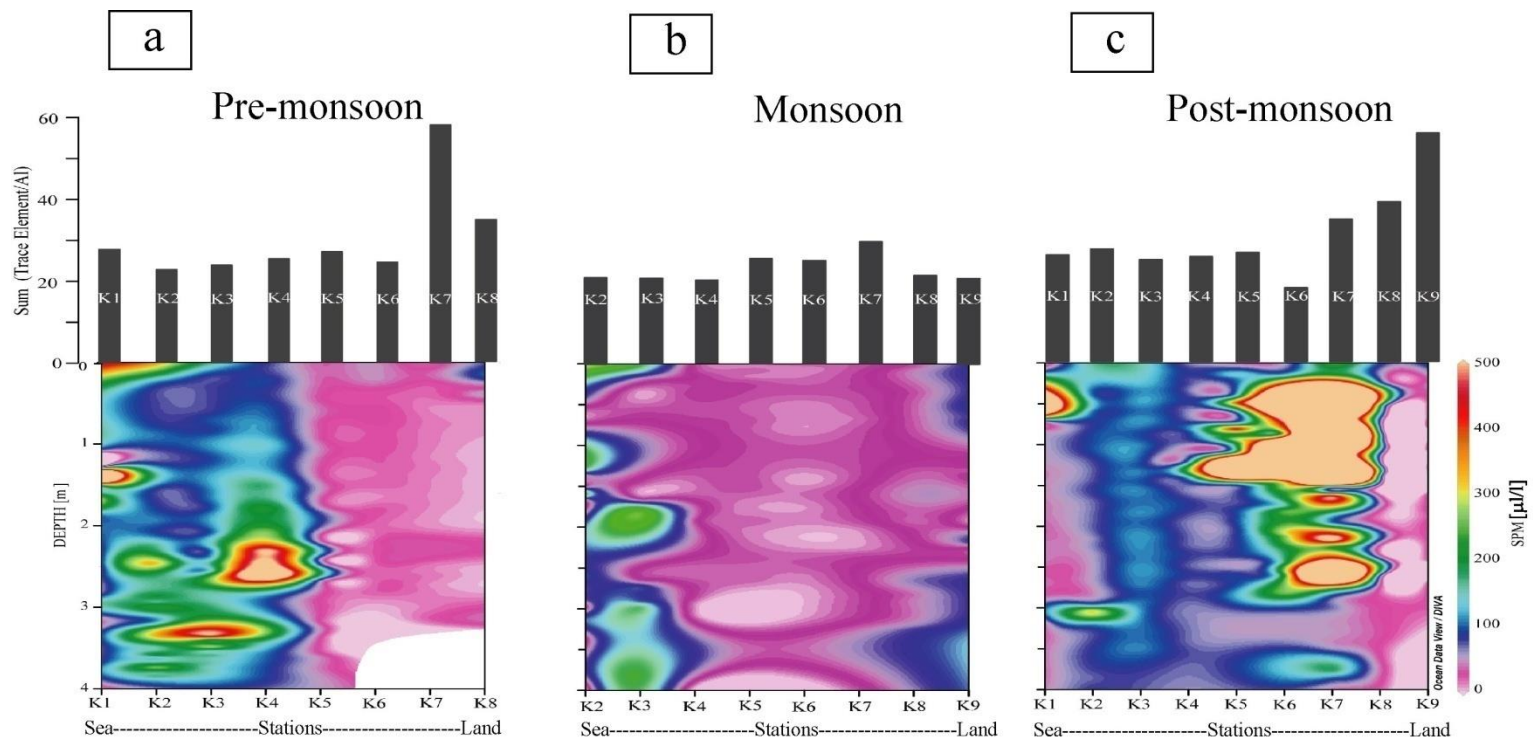


Fig. 2.

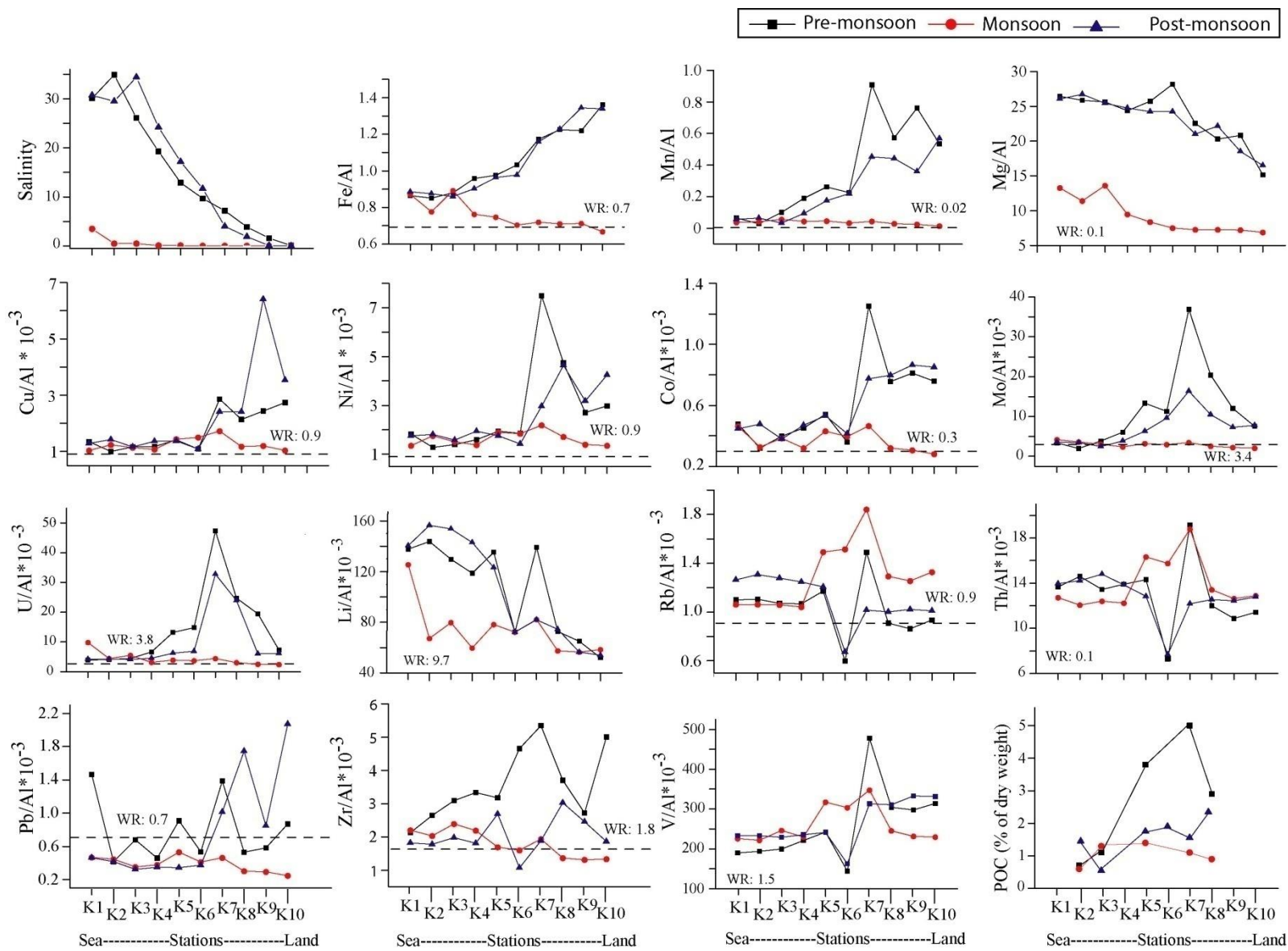


Fig. 3

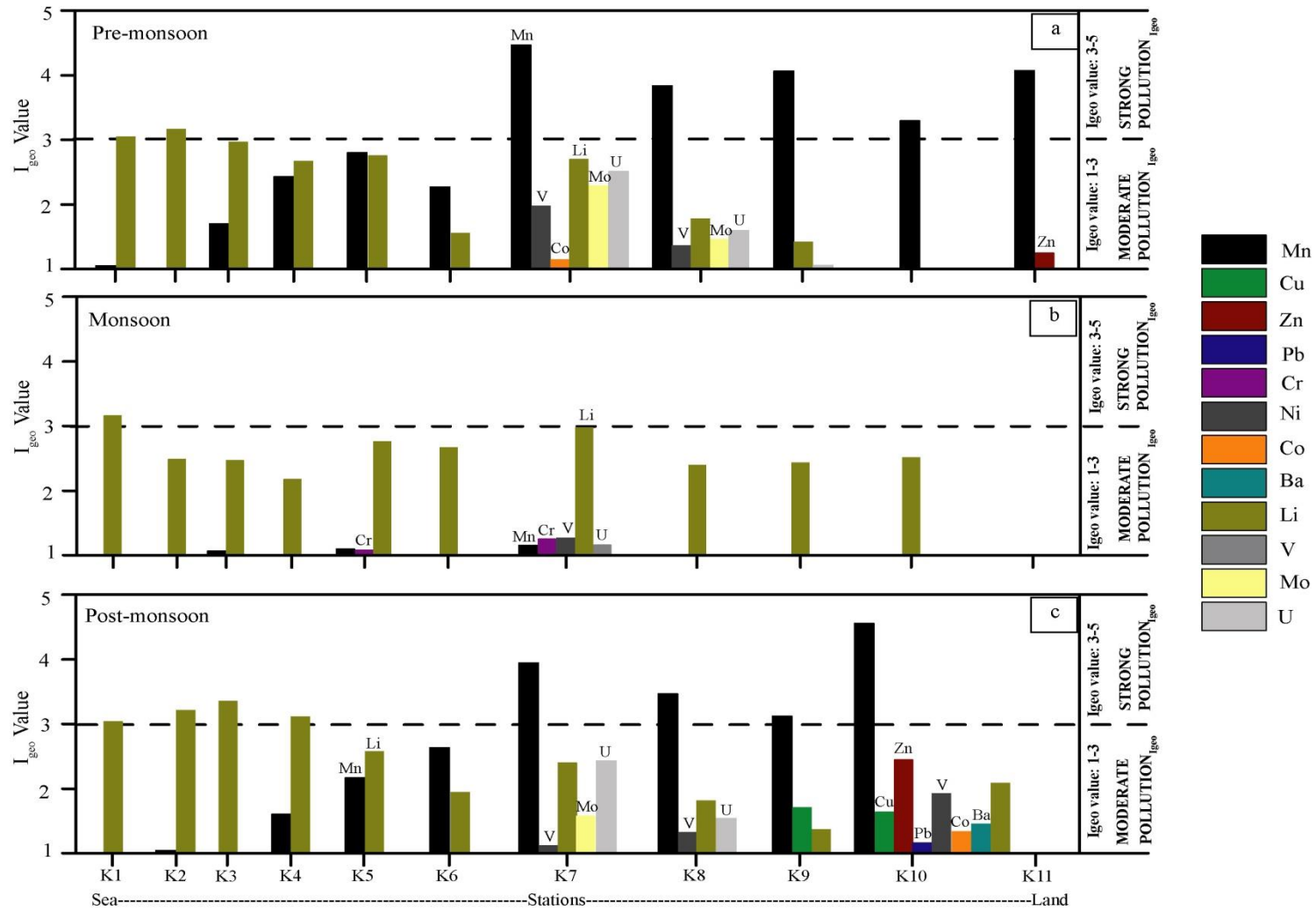


Fig. 4.

Table 1. Analytical results of USGS Recommended values of MAG-1 and the present study [trace elements values are in $\mu\text{g/g}$].

	USGS Certified Values		Present study		Accuracy (%)	Precision (%)
	Mean	SD	Mean	SD	\pm	\pm
Al (%)	8.66	± 0.30	8.28	± 0.14	4.37	1.21
Fe (%)	4.58	± 0.60	4.36	± 0.07	4.71	1.15
Mn (%)	0.08	± 0.01	0.07	± 1.6	0.22	1.27
Ti (%)	0.4	± 0.07	0.44	± 0.03	9.90	2.59
Mg (%)	1.8	± 0.1	1.9	± 0.03	4.90	0.51
Cu	30	± 3	32.5	± 1.8	8.3	1.1
Zn	130	± 6	130.6	± 2.54	0.46	1.52
Pb	24	± 3	23.37	± 0.54	2.6	3.51
Cr	97	± 8	97.5	± 8.63	0.51	3.06
Ni	53	± 8	52.05	± 5.31	1.78	3.51
Co	20	± 1.6	20.53	± 1.4	2.65	5.36
Zr	130	± 13	132.35	± 7	1.81	3.51
Rb	150	± 6	152.65	± 7.99	1.77	0.62
Sr	150	± 15	152.45	± 1.34	1.63	0.11
Ba	480	± 41	486.3	± 14.7	1.31	1.53
Li	79	± 4	84.69	± 7.71	7.2	1.01
Be	3.2	± 0.4	3.21	± 0.22	0.34	6.01
Sc	17.2	± 1	16.89	± 0.64	1.77	1.26
V	140	± 6	146.6	± 10	4.71	2.32
Ga	20	± 1.5	20.86	± 1.12	4.32	2.43
Nb	12		12.08	± 0.27	0.67	2.59
Mo	1.6		1.51	± 0.007	5.44	7.01
Sn	3.6		3.7	± 0.22	2.86	0.08
Sb	0.96	± 0.1	1	± 0.03	4.43	0.17
Cs	8.6	± 0.7	8.68	± 0.39	0.98	0.28
Hf	3.7	± 0.5	3.7	± 0.06	0.09	4.3
Ta	1.1		1.08	± 0.15	1.45	1.38
Bi	0.34		0.35	± 0.018	1.9	3.14
Th	12	± 1	11.97	± 0.52	0.21	4.97
U	2.7	± 0.3	2.8	± 0.04	3.85	4.28
POC (% of dry weight)	—	—	1.78	± 0.1	—	0.01

$$\text{Accuracy (\%)} = \left[\frac{\text{Mean} - \text{Certified value}}{\text{Certified value}} \right] \times 100 ; \text{Precision (\%)} = \left[\frac{\text{Measured 1} - \text{Measured 2}}{\text{Average}} \right] \times 100$$

Table 2: Concentrations of major and trace elements in SPM of the Kali estuary, source rocks in the catchment area-(tonalitic gneiss, greywacke), WRSPM- (Average World River SPM), SPM of Mandovi estuary and Yellow River.

	Present study (all stations)						Previous study ^a		Tonalitic gneiss ^b	Greywacke ^c	WRSPM ^d	Mandovi Estuary ^e	Yellow river ^f
	Pre-monsoon		Monsoon		Post-monsoon		Monsoon	Post-monsoon					
	Avg	Min-Max	Avg	Min-Max	Avg	Min-Max							
SPM (µl/l)	104	(1.0-778.2)	46.7	(0.02-395.3)	155	(24-2712.3)	—	—	—	—	—	—	
Salinity	13.9	(0.0-34.9)	0.7	(0.0-3.5)	15.7	(0.0-34.4)	—	—	—	—	—	—	
POC (% of dry weight)	2.7	(0.7-5.0)	1.1	(0.6-1.4)	1.6	(0.5-2.3)	—	—	—	—	—	—	
Al(%)	6.2	(4.3-7.9)	10.8	(8.8-12.4)	7.4	(5.7-9.8)	13.6	15.6	6.9	7.5	8.7	7.2	8.4
Fe(%)	6.4	(5.3-7.3)	8.1	(7.4-8.7)	8.0	(5.9-13.2)	11.5	10.4	1.6	4.9	5.8	11.3	4.4
Mn(%)	2.3	(0.2-5.3)	0.4	(0.2-0.5)	2.0	(0.3-5.6)	0.7	1.7	—	2.20	0.2	0.9	0.1
Ti(%)	0.5	(0.3-0.8)	0.7	(0.5-1.0)	0.6	(0.3-0.8)	—	—	0.2	0.3	0.4	—	—
Mg(%)	1.5	(0.7-2.1)	1.0	(0.8-1.2)	1.7	(1.1-2.2)	1.1	1.9	1.3	0.1	1.3	1.4	2.2
Concentration in ppm													
Cu	112.2	(55.7-181.7)	140.0	(93.5-209.3)	171.3	(74.3-365.7)	84.0	106.0	24.4	47	75.9	76.1	22.7
Zn	309.1	(133.4-730.7)	270.9	(142.3-414.9)	523.2	(177.6-1678)	400.0	328.6	—	78	208	327.7	52.8
Pb	54.8	(27.5-112.3)	42.4	(30.8-58.3)	69.1	(21.1-203.4)	69.2	84.4	12.1	12	61.1	60.9	14
Cr	218.9	(119.4-346)	338.2	(255.6-459.1)	265.3	(141-376)	—	—	27.2	108	130	341.6	94.9
Ni	182.7	(95.1-439.7)	181.6	(121.6-266.1)	198.6	(96.4-416.9)	152.0	242.2	16.5	52	74.5	94.8	52.2
Co	38.7	(18.5-73.4)	40.5	(30.8-56.5)	46.1	(28.2-83.6)	37.8	44.8	20.2	25	22.5	27.8	15.4
Zr	224.1	(141.3-313.5)	193.2	(159.2-235.7)	143.8	(72.9-182.8)	—	—	87.5	215	160	95.4	—
Rb	63.8	(30.6-87.9)	145.5	(93.4-223.6)	80.8	(45.8-108.3)	120.6	157.2	75.7	80	78.5	—	—
Sr	186.6	(89.6-348.3)	106.7	(81.4-138.4)	213.4	(148.4-280.4)	10.0	—	138	292	190	—	—
Ba	480.7	(168-1322.7)	490.8	(197-797.4)	646.8	(161.1-2105)	585.0	726.0	131	419	520	—	—
Li	70.4	(22.6-114.2)	78.8	(57.6-113.5)	78.3	(32.3-130.2)	—	—	—	—	8.5	—	—
Be	1.4	(0.7-2.0)	2.4	(1.8-3.4)	1.6	(1.0-2.1)	—	—	—	—	—	—	—
Sc	24.1	(12.1-37.2)	37.8	(26.4-56.8)	28.9	(16.5-40.4)	—	—	—	14	18.2	21.8	—
V	158.2	(73.9-279.9)	284.4	(204.3-422.6)	193.8	(110.7-325.6)	—	—	18	107	129	138.7	—
Ga	16.3	(8.4-32.4)	29.3	(18.3-45.7)	21.3	(9.6-52.1)	—	—	—	—	18.1	—	—
Nb	7.5	(3.6-10.5)	11.8	(8.8-17)	8.9	(5-12.1)	—	—	—	9	13.5	—	—
Mo	6.9	(1.6-21.6)	3.2	(2.4-4.3)	5.2	(2.1-13.3)	2.7	—	—	—	3	4.6	—
Sn	3.8	(2.0-11.9)	6.1	(3.6-9.2)	6.3	(2.2-14.3)	—	—	—	—	4.6	—	—
Sb	1.2	(0.6-2.3)	1.0	(0.7-1.5)	1.3	(0.7-3.1)	—	—	—	—	2.2	—	—
Cs	4.2	(1.9-6.0)	9.0	(6.0-13.6)	5.1	(2.9-7)	—	—	—	—	6.2	—	—
Hf	5.1	(3.3-7.3)	4.7	(3.9-5.8)	3.7	(1.8-4.8)	—	—	—	4	4	—	—
Ta	0.7	(0.1-1.0)	1.2	(0.8-1.8)	0.8	(0.4-1.3)	—	—	—	2	1.3	—	—
Bi	0.3	(0.1-0.4)	0.5	(0.3-0.8)	0.3	(0.2-0.6)	—	—	—	—	0.8	—	—
Th	8.4	(3.7-11.6)	15.3	(10.9-22.8)	9.4	(5.2-12.6)	—	8.2	—	8	12.1	7	—
U	8.6	(2.4-27.8)	4.5	(3.1-8.9)	7.2	(3.1-26.7)	—	3.2	—	3	3.3	3.4	—

Table 3: Factor loadings of SMP from Kali estuary

	Pre-monsoon								Monsoon								Post-Monsoon							
	Downstream				Upstream				Downstream				Upstream				Downstream				Upstream			
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 4		
Salinity	-0.98	0.18	-0.10	0.04	-0.21	0.79	-0.54	-0.03	0.93	-0.36	0.04	-0.09	-0.93	-0.35	-0.91	0.00	-0.37	0.17	0.69	0.56	0.46	0.01		
SPM	-0.60	0.71	0.28	0.25	-0.23	0.45	-0.27	0.82	-0.67	0.65	0.36	0.86	0.43	0.03	-0.73	-0.67	0.14	-0.07	0.64	0.76	0.08	0.08		
Al(%)	-0.95	0.19	-0.21	-0.14	-0.71	0.31	-0.05	0.60	-0.69	-0.68	-0.24	-0.08	0.90	-0.43	-0.97	-0.21	0.06	0.03	-0.81	0.42	0.41	0.02		
Fe(%)	-0.82	0.40	-0.40	-0.07	-0.71	-0.21	0.34	0.55	-0.08	-0.70	0.71	-0.24	0.61	-0.74	-0.92	-0.33	0.22	0.04	-0.97	0.07	0.25	0.02		
Mn(%)	0.98	-0.14	0.11	-0.01	-0.86	-0.36	0.28	0.05	-0.76	0.46	0.45	-0.88	-0.38	-0.22	0.91	-0.03	0.35	-0.20	-0.98	0.14	0.11	-0.12		
Ti(%)	-0.88	0.43	0.22	0.02	-0.97	0.17	0.10	-0.10	-0.24	-0.08	0.97	-1.00	-0.04	0.00	-0.88	-0.44	0.18	-0.07	-0.98	-0.01	-0.11	0.15		
Mg(%)	-0.97	0.01	-0.09	-0.21	-0.29	0.86	-0.24	0.15	0.27	-0.46	0.85	-0.24	-0.48	-0.84	-1.00	0.00	-0.10	0.01	-0.24	0.88	0.40	-0.10		
Cu	-0.23	-0.93	-0.17	-0.22	-0.65	-0.74	0.13	0.10	-0.78	-0.62	0.11	-0.97	0.20	0.02	-0.77	0.43	0.38	-0.29	-0.67	-0.59	-0.07	0.45		
Zn	-0.39	-0.80	-0.44	0.12	-0.32	-0.91	-0.19	-0.05	-0.66	-0.70	-0.29	-0.95	0.29	0.15	-0.18	0.63	-0.43	-0.62	-0.93	-0.15	0.33	0.03		
Pb	-0.32	-0.93	-0.15	-0.09	-0.69	-0.59	-0.39	-0.12	-0.05	-0.98	-0.17	-0.83	-0.55	-0.11	-0.63	0.61	-0.21	0.43	-0.91	-0.08	0.16	-0.37		
Cr	-0.88	-0.46	0.00	0.13	-0.98	0.08	0.11	-0.15	-0.63	-0.39	0.67	-0.98	-0.18	-0.09	-0.97	-0.20	0.00	0.11	-0.99	-0.07	-0.11	0.07		
Ni	-0.03	-1.00	-0.02	0.08	-0.98	0.10	-0.04	0.08	-0.74	-0.64	0.19	-0.94	0.10	0.16	-0.79	0.19	0.58	0.00	-0.93	-0.11	-0.02	-0.36		
Co	0.30	-0.94	-0.16	-0.04	-0.97	-0.16	0.16	-0.05	0.85	-0.48	0.21	-0.99	-0.10	-0.02	-0.22	0.61	0.68	-0.35	-1.00	0.01	-0.05	0.02		
Zr	0.38	0.85	-0.23	-0.27	-0.56	-0.26	-0.77	-0.02	-1.00	0.05	0.07	-0.99	0.08	-0.06	0.28	-0.90	-0.26	-0.21	-0.76	-0.23	-0.47	-0.37		
Rb	-0.97	0.06	0.14	-0.20	-0.99	-0.12	-0.03	-0.04	-0.66	-0.74	-0.16	-0.96	0.27	0.00	-0.99	-0.10	-0.02	-0.03	-0.98	0.20	0.00	0.03		
Sr	-0.77	0.40	-0.41	0.26	-0.82	0.40	-0.26	-0.22	0.54	-0.84	-0.05	-0.98	-0.11	0.05	-0.87	0.09	0.43	0.23	-0.86	0.47	0.21	-0.06		
Ba	-0.63	-0.78	-0.03	-0.01	-0.14	-0.96	-0.16	0.17	-0.94	0.14	-0.30	-0.74	0.59	-0.31	-0.92	0.12	-0.37	-0.01	-0.85	-0.42	0.32	0.08		
Li	-0.96	0.04	0.20	-0.18	-0.89	0.42	-0.15	-0.12	0.90	-0.42	0.15	-0.99	-0.14	-0.04	-0.99	-0.07	-0.04	-0.13	-0.37	0.93	-0.02	-0.04		
Be	-0.67	-0.21	0.64	0.32	-0.97	0.17	0.15	-0.10	0.52	-0.85	-0.10	-0.99	0.08	0.08	-0.96	0.13	0.24	0.01	-0.97	0.20	0.10	-0.04		
Sc	-0.94	0.26	0.12	-0.18	-0.97	0.14	0.16	-0.10	-0.97	-0.22	-0.04	-1.00	-0.02	0.03	-0.98	-0.16	0.05	-0.11	-0.97	0.16	-0.15	0.05		
V	0.28	0.65	0.60	-0.36	-0.97	-0.06	0.19	-0.07	-0.96	-0.29	0.00	-1.00	-0.06	0.04	-0.97	-0.22	0.13	0.02	-1.00	0.06	-0.07	0.03		
Ga	-0.87	-0.42	0.09	-0.23	-0.52	-0.84	-0.11	0.12	-0.93	-0.21	-0.29	-0.95	0.28	-0.02	-0.99	-0.01	-0.10	-0.06	-0.92	-0.29	0.24	0.06		
Nb	-0.91	0.19	0.37	0.00	-0.99	0.11	0.06	-0.07	0.94	-0.35	0.05	-1.00	-0.01	-0.09	-0.96	-0.26	-0.09	-0.04	-0.99	0.09	-0.08	0.10		
Mo	0.85	-0.30	0.42	-0.14	-0.93	0.36	-0.06	0.01	0.32	-0.91	0.25	-0.99	-0.07	0.03	0.96	0.06	0.26	-0.10	-0.35	0.89	-0.28	0.12		
Sn	0.29	-0.71	0.44	-0.47	-0.23	-0.87	-0.37	0.16	0.46	-0.83	-0.30	-0.93	0.01	0.26	-0.53	0.60	-0.49	-0.34	-0.91	-0.41	0.02	0.11		
Sb	-0.22	-0.97	-0.13	0.05	-0.84	-0.10	0.35	-0.12	-0.83	-0.56	-0.04	-0.82	0.13	0.42	-0.24	0.95	-0.09	-0.15	-0.95	-0.24	0.07	0.16		
Cs	-0.98	-0.02	0.12	-0.14	-0.99	0.07	-0.02	-0.11	0.35	-0.89	-0.29	-0.99	0.16	0.05	-0.99	-0.08	0.00	-0.13	-0.98	0.20	0.08	-0.01		
Hf	0.25	0.90	-0.25	-0.25	-0.70	-0.04	-0.64	-0.15	-0.85	-0.49	0.18	-1.00	-0.04	-0.02	0.44	-0.79	-0.31	-0.29	-0.84	-0.20	-0.41	-0.28		
Ta	-0.34	-0.18	0.75	0.54	-0.93	0.09	0.29	0.18	0.99	-0.16	-0.04	-0.99	-0.12	-0.06	-0.97	-0.09	-0.19	0.06	-0.63	0.44	-0.38	0.52		
Bi	-0.78	-0.46	0.30	-0.30	-0.99	-0.08	0.06	-0.09	-0.98	-0.18	0.04	-1.00	0.02	0.07	-0.92	-0.23	0.07	-0.33	-1.00	-0.01	0.02	-0.01		
Th	-0.95	0.30	0.12	0.00	-1.00	0.01	0.03	-0.03	-0.54	-0.79	-0.29	-0.99	0.10	0.00	-0.98	-0.21	-0.04	0.00	-0.99	0.13	0.00	-0.03		
U	0.79	-0.19	0.57	-0.11	-0.89	0.45	0.02	-0.04	0.89	-0.40	0.22	-0.98	-0.06	0.14	0.58	-0.72	0.23	-0.31	-0.18	0.72	-0.67	-0.08		
Eigen value	16.86	10.36	3.30	1.48	20.33	6.84	2.42	1.69	17.38	10.76	3.86	25.69	3.70	2.08	22.28	5.73	2.54	1.45	23.21	5.58	2.11	1.10		
% Variance	52.68	32.36	10.32	4.64	63.52	21.38	8.70	6.40	54.31	33.63	12.06	80.27	11.57	6.50	69.61	17.89	7.95	4.54	72.54	17.44	6.58	3.44		

