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

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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 Geo-accumulation Index (Igeo) assigned pollution$_{Igeo}$ 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). Igeo 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 1.6–2.3% 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.



## 1. 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 spacial and temporal scale (Vercruysse 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

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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 μg/g), Cu (38.6 μg/g) and Cd (1.82 μg/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., 2016), 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 3376 $km^2$ 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 (Fig. 1a and 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 catchemnt 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 ~6213 $\times$ $10^6$ $m^3$ and sediment discharge of ~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 (10–20 L) were collected along the midstream of the Kali estuary (Fig. 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 μl/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%): $HNO_3$(65%): $HClO_4$(70%) in the proportion 6: 3: 1 was added into these beakers and kept overnight. The next day these Teflon