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# Speciation of metals and their distribution in tropical estuarine mudflat sediments, southwest coast of India

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ABSTRACT

Two sediment cores collected from a mudflat sedimentary environment of Swarna estuary (S3) and Gurpur estuary (MF6), representing the middle estuarine region, Karnataka, India, were investigated to understand bioavailability of metals and their toxicity. The subsamples were analyzed for sand, silt, clay, organic carbon and total metal concentration of Aluminum (Al), Iron (Fe), Manganese (Mn), Nickel (Ni), Zinc (Zn), Copper (Cu), Cobalt (Co) and Chromium (Cr) at 2 cm intervals. Sediments (average) are relatively coarser in Gurpur estuary whereas silt, clay, organic carbon along with the studied metals (except Mn and Cu) is noted to be higher in the Swarna estuary. Significant correlations were observed of Al, Fe with finer sediments and most of the trace metals in both the cores indicating a mainly lithogenic source. Further, metal speciation analysis carried out for Fe, Mn, Ni, Zn, Cu, Co and Cr on selected samples of both the cores indicated that Fe was largely associated with the residual fraction with $93 \pm 0.5\%$ in Gurpur and $84 \pm 6\%$ in Swarna estuary. The concentration of studied metals in the residual fraction in the sediments of Gurpur estuary was in the order $Mn(90 \pm 5\%) > Cr(85 \pm 1\%) > Ni(72 \pm 5\%) > Zn(69 \pm 3\%) > Cu(57 \pm 5\%) > Co(55 \pm 2\%)$ and; $Cr(80 \pm 7\%) > Mn(77 \pm 10\%) > Ni(76 \pm 7\%) > Zn(67 \pm 10\%) > Cu(67 \pm 10\%) > Co(50 \pm 7\%)$ in Swarna estuary. When the total (bulk) metals were compared with the Sediment Quality Values (SQV) following Screening Quick Reference Table (SQUIRT), Co values of both the cores fell above Apparent Effect Threshold (AET) values. When the sum of the average bioavailable fractions in sediments was considered, Co values exceeded the AET in core S3 (Swarna estuary). When the variations are viewed with depth, bioavailability of Mn, Ni, Cu and Co in Gurpur estuary indicated anthropogenic addition in recent years whereas in Swarna estuary most of the studied metals showed diagenetic remobilization and diffusion to the water column from surface sediments. Metal speciation study indicated no harm to the aquatic life, except of Co, in Swarna estuary wherein it posed a high risk of toxicity to organisms associated with the sediments.



## 1. Introduction

Estuaries are the transition zones in which mixing of marine and fresh water occurs. The region receives sediments from different sources such as fluvial, marine, atmospheric and mixed sources (Wu et al., 2011). Mudflats are one of the major sub-environments along estuarine tidal flats in tropical region (Siraswar and Nayak, 2011) where low energy conditions facilitate the deposition of finer sediments. Along with finer sediments, these sub-environments also favor the deposition of higher organic matter which helps in trapping and accumulating the metals with time (Cook et al., 2004). Metals are essential to organisms but at higher levels become toxic. Metals once deposited within sediment, due to their long persistence nature may behave as pollutants and become toxic to the organism (Klavinš et al., 2000; Tam and Wong, 2000). Therefore it is necessary to understand the abundance and distribution of metals in mudflats as they are habitats for a number of macrofaunal species (Fujii, 2012). Further, the total metal concentration does not reflect the mobility and potential availability for biota. The remobilization of metals and their uptake by biota depends upon the chemical form in which they are attached to the sediment and thus respond differently when the environmental conditions changes (Fernandes et al., 2014). The mobility of metals associated with different sedimentary fractions is in the order: exchangeable > carbonate > Fe–Mn oxide bound (reducible) > organic and sulfide bound (oxidizable) > residual. Understanding of geochemical associations of metals will provide useful information concerning the origin, mobilization, mode of occurrence and bioavailability of metals (Almas et al., 2006; Dessai and Nayak, 2009). Earlier, researchers (Ashraf et al., 2012; Olutona

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et al., 2012; Akoto and Abankwa, 2014) have studied metals in sediments to understand the bioavailability of metals. Also, concentration of metals in organisms was attempted (Tuzen, 2003a,b; Mendil et al., 2010a,b). In this paper, an attempt has been made to study the distribution and abundance of sediment components, organic carbon and selected elements in sediments with time in two tropical estuaries, namely the Swarna and Gurpur estuaries, to understand the depositional environment, post depositional processes, bioavailability of metals and their toxicity.

## 2. Materials and methods

### 2.1. Study area

The Rivers Swarna and Gurpur, one of the major sources of sediment supply to the coastal zone, originates in the Western Ghats and flows westward. The upstream end of the Swarna River receives major freshwater influx during the southwest monsoon season. The Swarna River is the main source of drinking water to the Udupi and Karnala Talukas of Udupi district. Its major tributaries are Durga, Kada, Andar and Happanadka. The basin of Swarna River has an area of 603 $km^2$. Its basin is located on the southwestern part of the Western Dharwar Craton (WDC) underlain with metamorphic transition zone represented by green schist facies to granulite facies rock types, such as greenstone, amphibolites, and granulites of Precambrian age (Rogers et al., 1986). The major rock types exposed in the river basin include granitic gneiss, dolerite dyke, and laterite (Balasubramanyan, 1978; Tripti et al., 2013). Gurpur estuary is characterized by a mixed type of semidiurnal tides. Currents in the river mouth are controlled by fresh water discharge during the southwest monsoon and by tides the rest of the year. For this reason, ebb flow is dominant during the southwest monsoon and flood flow during winter and summer. Geologically the river basin is composed of rock types belonging to tertiary to quaternary periods in the lower catchments and older (Archean) gneissic complex in the upper catchments. The basin is located at the western part of the WDC with major lithounit as Peninsular Gneiss/Archean Tonalitic–Trondhjemitic–Granodioritic (TTG) gneiss. The greenstone-amphibolitic facies metamorphic rocks and granulites could be seen in patches. The basin is lithologically composed of about 83% migmatites and granodiorites, 5% of charnockites, about 6% metabasalts and 2% laterites and amphibolites. A 200 m long sand bar is present near the Netravati-Gurpur river mouth at a depth of 2–3 m (Reddy et al., 1979).

### 2.2. Sampling and analysis

Two shallow cores, S3 (56 cm) and MF6 (34 cm) were collected from the Swarna and Gurpur estuaries (Fig. 1) respectively, representing the mudflat sedimentary environment. In the field, the cores were sub-sampled at 2 cm intervals, transported to laboratory in ice box, frozen at 4 °C and later oven-dried at 60 °C. Sediment components (sand: silt: clay) were analyzed by pipette method (Folk, 1968). Organic carbon was determined by using the Walkey-Black method (Walkey, 1947), adopted and modified from Jackson (1958). All the sub samples of the mudflat cores were digested with HF, $HNO_3$ and $HClO_4$ acid mixture for total metal analyses. The samples were prepared in duplicates and analyzed. The metals viz. Al, Fe, Mn, Ni, Zn, Cu, Co and Cr were analyzed using Atomic Absorption Spectrophotometer (Varian AAS 240FS model, Australia). Together with the samples, certified reference standards (USGS standards) from the MAG-1(Marine Sediment), from the Wilkinson Basin of the Gulf of Maine and SGR-1(Green River Shale), from the Mahogany zone of the Green River Formation were digested and run, to test the analytical and instrument accuracy of the method. The average recoveries were around 90–97%. Suitable internal chemical standards (Merck Chemicals) were used to calibrate the instrument. Recalibration checks were also performed at regular intervals. Further, a modified sequential

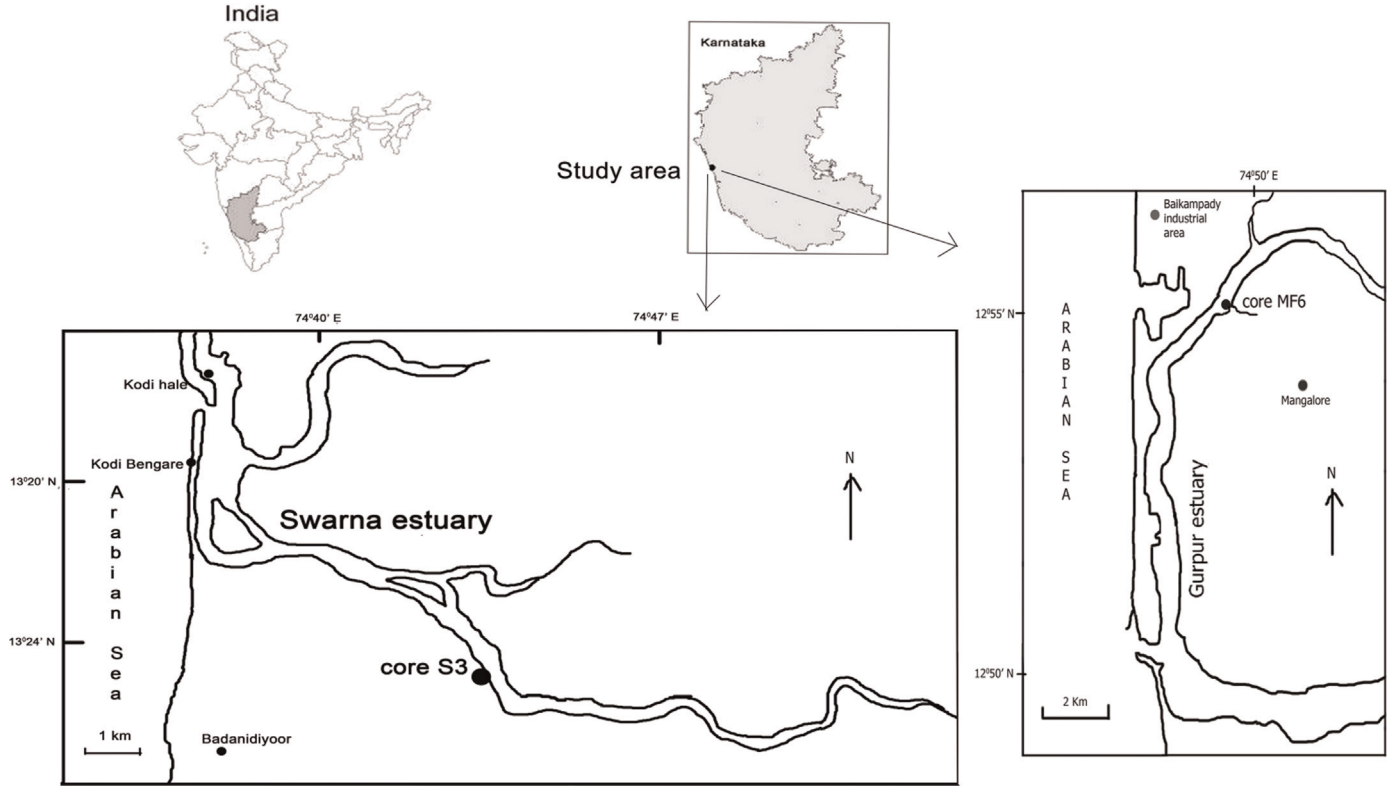


**Fig. 1.** Map showing location of sediment cores collection in the Swarna (core S3) and Gurpur (core MF6) estuary.