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REE in suspended particulate matter and sediment of the Zuari estuary and adjacent shelf, western India: Influence of mining and estuarine turbidity

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ABSTRACT

Concentrations of Al, Fe, Mn and rare earth elements (REE) were measured in 122 samples of suspended particulate matter (SPM) and 70 surficial sediments from the Zuari estuary and the adjacent shelf to understand their distribution, provenance and estuarine processes. Concentrations of SPM were low in the upper estuary, increased seaward with high values in the lower estuary and then decreased at stations in the bay in all seasons. The distributions of mean ΣREE, Al and Fe along transect imitate each other and resemble inverted bowl-shaped pattern, with high and identical values at the lower estuary. The mean ΣREE, Al and Fe of sediment along transect showed two peak high values, one in the upper estuary and another in the bay amid low values corresponding to the lower estuary. The variations in the mean ratio of $\Sigma REE_{SPM}/\Sigma REE_{SED}$ along transect resembled that of mean SPM at each station. The ΣREE of sediments in shallow shelf were close to that of the bay and, decreased seaward with increasing depth. PAAS-normalized REE patterns of every SPM/sediment sample revealed MREE- and HREE-enrichment with positive Ce and Eu anomalies. Ce /* Ce was inversely correlated with Eu /* Eu and salinity and, directly correlated with Mn concentrations. The results indicate that the REE of SPM/sediment is dominated by Fe, Mn ore dust and, its distribution along transect is controlled by the estuarine turbidity maximum (ETM). The ETM and seasonal circulation in the estuary controlled mixing and advective transport of particulates to the shelf during monsoon and, into the estuary during dry season. This study indicates sediment contribution to the shelf from tropical, minor rivers that are controlled by hydrodynamic conditions in the estuaries and should not be underestimated.

1. Introduction

Rare earth elements (REE) form a key group of trace elements whose properties change systematically and gradually across the series (from La to Lu). Because of their coherent and predictable behavior, they have been used as geochemical tracers to characterize igneous rocks of various types, determine detrital sediment sources and elucidate seawater circulation patterns, hydrothermal fluxes and past oxygenation of the oceans (Piper, 1974; Henderson, 1984). The major sources of REE to the ocean are fluvial, atmospheric and hydrothermal vent exhalations (Elderfield and Greaves, 1982; Fleet, 1984). REE transported through fluvial source are extensively modified in the estuaries before reaching the ocean. Estuarine processes that affect the distribution of REE are flocculation, salt-induced coagulation of river organic colloids, adsorption–desorption reactions, remobilization due to early diagenetic changes and re-suspension (Hoyle et al., 1984). The behavior of REE in estuarine water and sediments across salinity gradient has been reported (Sholkovitz, 1976, 1993, 1995; Elderfield and Sholkovitz, 1987; Elderfield et al., 1990; Bau, 1999; Chillou et al., 2006; Lawrence and Kamber, 2006; Censi et al., 2007; Marmolejo-Rodríguez et al., 2007). The distribution of REE in estuaries affected by acid mine drainage (Elbaz-Poulichet and Dupey, 1999; Johannesson and Zhou, 1999; Borrego et al., 2005) and geology of the hinterland (Prego et al., 2009, 2012) have also been reported. However, there are not many investigations on REE controlled by hydrodynamic conditions in the estuaries (Sholkovitz and Szymezak, 2000; Hannigan et al., 2010). Further, the studies on REE distribution in Indian estuaries are fewer, some examples being the Kaveri River estuary (Ramesh et al., 1999; Singh and Rajamani, 2001) and Mandovi River estuary (Shynu et al., 2011). We report here the REE distribution in the Zuari River (ZR) estuary that is located a few kilometers south of the Mandovi River (MR) on the west coast of India (see Fig. 1A). Unlike MR, the main channel of Zuari River is dammed upstream and its seasonal discharge (147 $m^3\ s^{-1}$) into the estuary is much less than that of the MR (258 $m^3\ s^{-1}$). Because of the low seasonal river discharge and funnel-shaped bay off ZR one would expect greater impact of the tidal and wind-induced currents in defining estuarine processes and sediment distribution. The purpose of the paper is to report the distribution of REE in SPM and surface sediments of the Zuari estuary and adjacent

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shelf for the first time and, relate their distribution with sources and hydrodynamic conditions in the estuary.

2. Geological and estuarine settings of the Zuari River

The Zuari River (ZR) is a major river of Goa in the central west coast of India (Fig. 1A). It is ~50 km long and originates in the Western Ghats (mountain regions) and drains through a narrow coastal plain. The main channel of ZR is connected to the Arabian Sea through a funnel-shaped, Mormugao Bay, which is ~10 km long, 5 m deep and has a maximum width of 5 km at its widest end (Fig. 1A). The ZR drains through rocks of Goa Group (Fig. 1B) belonging to the Dharwar Super Group of Archaean–Proterozoic age (Gokul et al., 1985). The basic rocks of Goa Group are green schists and gneisses and are largely covered by a residual weathered layer of rock (laterite), which is several tens of meters thick (Mascarenhas and Kalavampara, 2009). The original unweathered igneous and metamorphic rocks are, however, exposed only in coastal headlands or along steep slopes of high hill ranges. Sanvordem Formations (Fig. 1B) consisting of meta-greywacke, conglomerate and argillites occupy large area downstream of the Zuari River basin. The river runoff into the estuary is large in monsoon months and is regulated by a dam in the upper reaches (see Fig. 1A). The river runoff measured downstream of the dam during monsoon (June–September), post-monsoon (October–January) and pre-monsoon periods (February–May) are 147 $m^3 s^{-1}$, 7.3 $m^3 s^{-1}$ and 0.8 $m^3 s^{-1}$, respectively (Rao et al., 2011). The estuary of the Zuari River is classified as a monsoonal, meso-tidal estuary. The tide ranges are ~2.3 m and 1.5 m during the spring and neap tides, respectively (Shetye et al., 2007). Tidal circulation dominates during dry period (October to May). Tidal oscillations have been observed and saline waters penetrate ~45 km upstream from the river mouth during dry period (Manoj and Unnikrishnan, 2009). Recent measurements of currents made in the estuary at Cortalim (station Z4, see Fig. 1A) show maximum values of longitudinal component of currents reach up to 80 cm/s during spring tide (Dr. Unnikrishnan, personal communication).

The Mandovi and Zuari (Ma–Zu) River estuaries are inter-connected through Cumbarjua canal close to their mouths (see Fig. 1A). Several big open cast iron and manganese (Fe–Mn) ore mines operate in the drainage basins of the Ma–Zu Rivers. The ores brought from mines are stored on the shores of the estuaries (Fig. 1C), loaded on to barges (Fig. 1C) at loading points and transported through the estuary to the port or mid-stream point, from where the ore is exported in giant ships. Of the 30.7 million tonnes (mt) of pulverized ore material transported in the year 2004 (Nagaraj and Raghuram, 2005), 19.1 mt of ore was transported through the MR and 11.6 mt was through ZR. About 11 mt of ore carried through the Mandovi was diverted to the port through Cumbarjua Canal and bay of Zuari during the monsoon.

3. Materials and methods

3.1. Suspended particulate matter (SPM) sampling and chemical analyses

Two types of data were collected in the Zuari estuary during June 2008–May 2009: (1) Surface water was sampled every alternate day at one station (Z4) in the mid-channel of the estuary from June to September 2008. This station is referred to here as the "regular" station (Fig. 1A). (2) Surface water and bottom sediment were collected at stations along the main channel of the estuary every month during the spring tide. The stations are referred to as "transect" stations.5 l of surface water sampled at each station were filtered through 0.4 μm polycarbonate membrane filter. Three Millipore filtration units (Model No. X104-220-50) were used simultaneously to filter 5 l of water at each station, i.e., each filtration unit takes about 1.7 l of water. De-ionized water was used to clean the filters. The SPM retained on filter papers was dried and weighted. SPM is expressed as milligram per liter. Salinity of surface water was invariably measured at all stations using conductivity sensor of a portable CTD system (Seabird SBE19 plus). The accuracy of the system for temperature and conductivity are 0.005 °C and 0.0005 S/m, respectively.

A total of 122 samples of SPM were selected for determining the Al, Fe and Mn and, REE concentrations (Table 1A). This includes 16 samples from the regular station in addition, samples along transect stations. As we have sampled 6 stations (Z1 to Z6) during June–August, 8 stations (Z0 to Z7) in September and 10 stations (Z0 to Z9) during October–May, the total number of samples from transect stations are 106 (which can be summed up as: Z1–Z6: $6 \times 3_{(\text{June–August})} + $ Z0–Z7: $8 \times 1_{\text{September}} +$ Zo–Z9: $10 \times 8_{(\text{October–May})} =$ Total 106 samples). The procedure for preparing SPM for chemical analysis is as follows: The SPM on the filter was carefully weighed and transferred to teflon beakers. The samples were digested using ultra pure acids with $HF + HNO_3 + HClO_4$ mixture in a beaker, kept overnight and then dried on a hot plate. This treatment was repeated till the sample in the beaker was completely digested. The final residue was dissolved in 20 ml of 1:1 HNO_3. Subsequently, 5 ml of 1 ppm Rh solution was added as an internal standard and made up to the final volume (Govindaraju, 1994). These aliquots were analyzed for trace metals and REEs using Thermo X Series II Inductively-coupled plasma mass spectrometer (ICP-MS) at the National Institute of Oceanography, Goa, India. Major elements (Al, Fe and Mn) were analyzed using ICP-AES at the Department of Earth Sciences, Pondicherry University, India. MAG1 (Marine mud) was used as an internal standard to check the reliability of the analysis. Table 1B shows the certified values of major elements and rare earth elements of MAG1 and values obtained in our experiments. The reproducibility of the results was found to be better than 5% and 10% for major elements and REE, respectively. Table 2 shows the concentrations of major elements and REE in SPM at the regular station. Table 3 shows the average concentrations of major elements and REE in SPM at each station along with standard deviation (SD) on seasonal basis, i.e., the concentrations of elements at each station are obtained by averaging concentration values for four months — June to September (monsoon), October to January (post-monsoon) and February to May (pre-monsoon). The Ce ($Ce/^{*}Ce$) and Eu ($Eu/^{*}Eu$) anomalies were calculated, following Taylor and Mclennan (1985).

3.2. Sediment sampling and chemical analyses

Bottom sediment was collected along transect stations of the estuary, using Van Veen grab and the top centimeter of the surface sediment was carefully peeled off by opening one flap of the grab and dried. A total of 70 bottom sediment samples (50 from transect stations of the estuary and 20 from the continental shelf — Table 1A) were selected for chemical analyses. As we have chosen bottom sediments at 6 stations (Z1–Z6) each in August and September for monsoon period, 10 stations (Z0–Z9) each in November and December for post-monsoon and 10 stations (Z0–Z9) each in March and May for pre-monsoon, the total number of samples are 52 ($6 \times 2_{\text{August and September}} + 10 \times 2_{\text{November and December}} + 10 \times 2_{\text{March and May}}$). The sediments at stations Z2 during monsoon and Z0 during pre-monsoon were sandy with <9% silt and 5 to 6% clay. Since we could not collect enough <2 μm fraction of the sediment, these sediments were not analyzed. Therefore the number of samples at transect stations are 50. The <2 μm fraction of the sediment was separated from the sediments using Stoke's settling velocity principle and dried. Following the aforementioned procedure the <2 μm fraction of the sediment samples was digested and analyzed for major elements and REE concentrations. We have analyzed REE chemistry of the <2 μm of sediments because (a) fine fraction includes colloids, and coagulation of colloids is a dominant process for removal of REE from the dissolved load in low salinity regions of estuaries (Sholkovitz, 1995). (b) Fine fraction records re-suspension of REE due to adsorption–desorption related to changes