Estuarine, Coastal and Shelf Science 170 (2016) 173–185

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss

Distribution, provenance and early diagenesis of major and trace metals in sediment cores from the Mandovi estuary, western India

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ARTICLE INFO

Article history:
Received 2 April 2015
Received in revised form
27 December 2015
Accepted 5 January 2016
Available online 7 January 2016

Keywords:
Trace metals
Provenance
Diagenesis
Mandovi estuary
Western India

ABSTRACT

Major elements and trace metals were analyzed in four sediment cores recovered along a transect in the Mandovi estuary for their distribution, provenance and early diagenesis. The sediments were clayey silts in cores from the upper/lower estuary and sand-dominated in cores from the middle estuary/bay. Organic carbon (OC) content varied from 0.5 to 4%, with higher values in fine-grained sediments. The mean Fe and Mn contents of sediments from the upper/middle estuary were 3–5 times and 8–13 times, respectively higher than the reference sediment (RS) from the same estuary. The mean Fe and Mn contents of sediments from the lower estuary/bay were close to the RS. Strong inter-metal correlation among Ti, V, Cr and Zr in all the cores indicated their contribution from a common source, probably the laterites from hinterland. Trace metals were more enriched in fine-grained sediments than in sand-dominated sediments. Early diagenetic control on the redistribution of metal is evident in core sediments from the middle estuary to Bay. The distribution of Mo, U and Pb followed that of Fe and Mn in the upper estuary and OC in the lower estuary/bay. Our results indicated strong anthropogenic contribution of metals from ore deposits in the upper/middle estuary. The Mn and Cr contents of sediment in the upper/middle estuary and Fe in the middle estuary were highly enriched suggestive of 'significant pollution signal'. More trace metals from the middle estuary were moderately enriched. Speciation studies showed Mn and Pb occurred abundantly in non-residual phases. High Mn content and its high percentage in exchangeable and reductive phases indicate that it was susceptible to be mobilized. However, Fe, Cu and Ni occurred abundantly in residual phases and less percentage of them were expected to be bio-available.

1. Introduction

Trace metal concentrations in estuarine sediments are found to be different in different estuaries and largely depend on the geology of the area and weathering of rocks in the drainage basin of the rivers (Window et al., 1989; Bianchi, 2007). Estuaries also receive significant amounts of trace and toxic metals from anthropogenic sources such as mining activities and/or industries located on the shores of the rivers/estuaries (Tanner et al., 2000; Prego et al., 2008). This leads to the enrichment of trace metals compared to their background concentrations. On the other hand, physical processess such as re-suspension, sediment focusing and bioturbation may disturb the record of metal accumulation (Santschi et al., 1984; Kramer et al., 1991; Walling and He, 1992; Spencer et al., 2003). Mineralization of organic matter associated with the estuarine sediments leads to early diagenetic reactions near the sediment–water interface and changing redox conditions may have strong influence on mobilization and reprecipitation of trace metals (Millward and Moore, 1982; Tessier et al., 1985; Zwolsman et al., 1993; Chaillou et al., 2002). The turbidity maximum in estuaries can also influence trace metal mobilization by occurrence of oxidation–reduction processes in the water column similar to those taking place in surface sediments (Abril et al., 1999; Robert et al., 2004; Audry et al., 2006). In other words, biogeochemical and physical processes on estuarine sediments contribute to the complexity of trace metal distribution (Sholkovitz, 1976, 1978; Boyle et al., 1977; Shiller and Boyle, 1987; Santschi et al., 1997; Che et al., 2003). Therefore, the enrichment of trace metals in sediments does not necessarily reflect anthropogenic influence but could be of diagenetic origin as well (Cornwell, 1986; Gendron et al., 1986; Ridgway and Price, 1987; Finney and Huh, 1989; Shaw et al., 1990; Zwolsman et al., 1993; Zhou et al., 2004; Audry et al., 2006).

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http://dx.doi.org/10.1016/j.ecss.2016.01.014

Further, the metal mobility in sediments depends on chemical speciation of metals in the sediments. It is important to distinguish the sources of trace metals and processes contributing to their enrichment/depletion in the sediments. This study investigated the distribution of major and trace metals in 4 sediment cores recovered along a transect in the Mandovi estuary (Fig. 1). The purpose of the paper is to report the sources of major and trace metals, influence of early diagenesis on the redistribution of trace metals and metal distribution in different phases and their bioavailability.

1.1. Study area

The Mandovi estuary is a tropical, monsoonal estuary on the west coast of India, receiving abundant river runoff (~258 m^3 s^{-1}) during wet, monsoon period (June–September) and negligible river runoff (~6 m^3 s^{-1}) during dry, non-monsoon period (October–May; Vijith et al., 2009). The estuary acts as an extension of river during the monsoon because of abundant river discharge. During the dry period, the circulation in the estuary is dominated by tidal and wind-induced currents and as a consequence saline conditions extend 45 km landward from the mouth of the estuary (Sundar and Shetye, 2005). The estuarine turbidity maximum (ETM) is a consistent feature of the lower estuary/bay both during monsoon and pre-monsoon (Rao et al., 2011). The estuary receives sediments from the rocks of Goa Group, belonging to the Dharwar Super Group of Archean-Proterozoic age (Gokul et al., 1985). The Goa Group consists of quartzite, meta-conglomerate/breccias, meta-greywacke, quartz-chlorite-biotite-amphibole schist, carbonate-quartz-chlorite schist, banded iron and manganese formations (Dhoundial et al., 1987; Dessai et al., 2009). The basement rocks are, however, covered by thick laterites (Mascarenhas and Kalavampara, 2009). The Fe–Mn ore deposits are considered as natural wealth of Goa. The ore deposits brought from the mines are stored and loaded onto barges at several shore stations in the upper/middle estuary and transported through the estuary to the port for export.

Suspended and bottom sediments of the Mandovi estuary have been investigated for their organic carbon content, mineralogy, limited major and rare earth and trace metal chemistry, bio-accumulation of metals and Sr–Nd isotopes (Alagarsamy, 2006; Shynu et al., 2011, 2012, 2015; Rao et al., 2011, 2015; Kessarkar et al., 2013; Chakraborty et al., 2014, 2015). Previous investigations on sediment cores of the Mandovi estuary have not yielded important information on the sources of sediments as the studies were confined to specific locations, either mudflats (Siraswar and Nayak, 2011; Singh et al., 2014; Nasnodkar and Nayak, 2015) or mangrove ecosystem (Veerasingam et al., 2015). Prajith et al. (2015a,b) were the first to initiate detailed studies on mineralogy, rare earth elements (REE) and magnetic properties of sediments in cores recovered along a transect in the Mandovi estuary. The present study reports the distribution of major and trace metals in sediment cores to identify the sources and also the processes that control their distribution in the estuary.

2. Materials and methods

2.1. Sampling and laboratory analyses

Four gravity cores were recovered along a transect in the Mandovi estuary, using a mechanized boat and with the help of scuba diver who pushed the corer into the sediment at the bottom of the estuary. These sediment cores are one each from the upper, middle and lower estuaries and from the Aguada Bay (Fig. 1). The sediments recovered in the cores varied from 79 cm to 47 cm and the core length from the upper/middle estuary were longer than in the lower estuary/bay (see Fig. 2). The color of the sediment was noted, immediately after cutting the core. The sediments in cores were sub-sampled at 1 cm interval and were dried at <50 °C.

Grain size analysis of sediments was carried out on 130 sub-samples from the 4 cores. About 1.5 g of dried sediment was dispersed with distilled water and treated with 1N HCl and 30% H_2O_2 to remove carbonates and organic matter, respectively. Thereafter the sediments were washed thoroughly with de-ionized water until the pH became neutral. The sediments were then dispersed with 0.5 ml of 1% sodium hexa-meta phosphate solution and wet sieved, using ISTM 230 mesh sieve to separate sand fraction (<2000 μm – >63 μm) from clay and silt. The sand fraction retained in the sieve was collected, dried and weighted. The sediment fraction <63 μm was used for measuring size fractions of silt and clay, using Malvern Laser Particle size analyzer (Master sizer 2000). Thereafter the percentages of sand (<2000 μm – >63 μm),

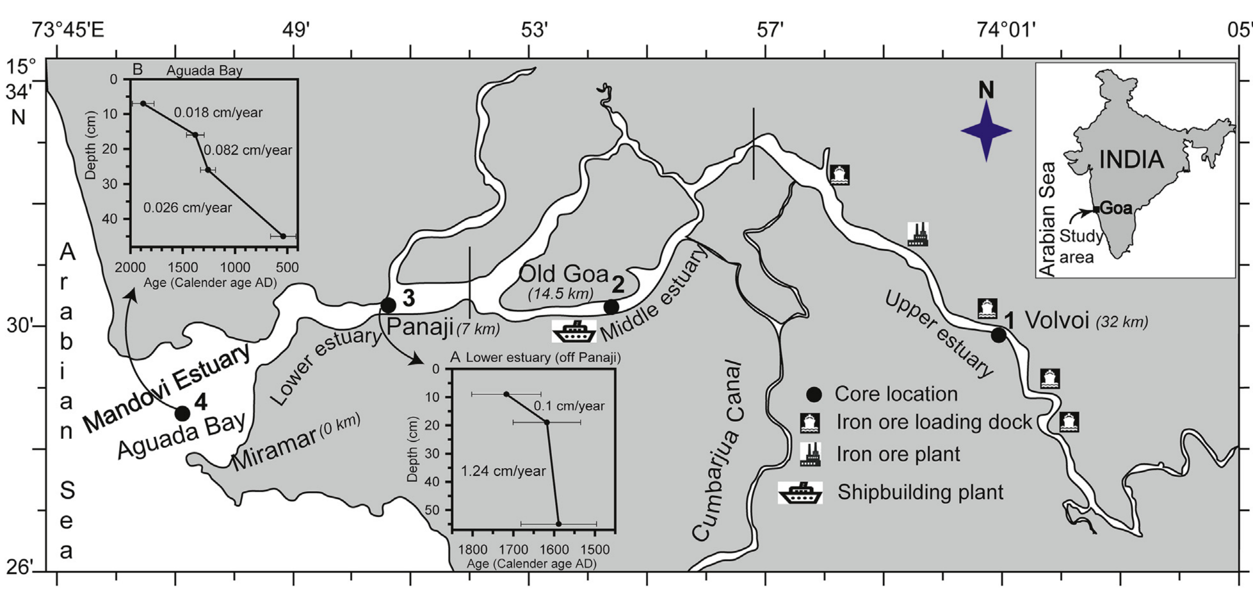

Fig. 1. Locations of gravity cores in the Mandovi estuary, western India. Number in parenthesis (next to the name of the sampling station) indicates distance of the core from the mouth of the estuary. Locations of iron ore loading docks, iron ore plant and ship building plant along the shore of the estuary are also shown. The plots of age (calibrated AMS age) vs. depth in the core for cores from the lower estuary and bay are also shown as insert figures at respective locations.