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Behaviour of trace metals in the anoxic environment of Veraval harbour, India

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ABSTRACT

The purpose of the present study is to investigate the behaviour of trace metals in anoxic environment. Water column of the harbour was found to be anoxic (DO < $0.2\ mg\ l^{-1}$) with high concentration of NH_4^+-N (av. 459 ± 21 $\mu mol\ l^{-1}$) and H_2S (av.73 ± 2.5 $\mu mol\ l^{-1}$) irrespective of season and tide. High concentrations of Fe, Mn in bottom water indicated that Fe, Mn were diagenetically mobilized under the anoxic conditions prevailing in the harbour. In harbour sediments significant correlation of metals with TOC and TS indicated their diagenetic immobilization in anoxic environment. Fe was positively correlated with TS suggesting FeS formation in anoxic condition. TOC/TN ratio of sediments was higher (16 ± 5.2) than the normal marine planktonic sediments suggesting an increased burden of terrestrial carbon in the harbour. A sediment core collected 10 km away from the shore indicated build-up of trace metals in recent years, showing diagenetically upward movement of metals.

1. Introduction

Due to advective impact, diagenetically mobilized elements travel to the surface of the sediment and in the presence of oxygen get oxidised and again precipitate, giving rise to their higher concentrations in the surficial sediments (Berner, 1980). However, when overlying water is anoxic, the reduced elements may escape to the water column and remain in dissolved form, giving rise to their higher concentrations in the overlying waters (Berner, 1980; Sakata, 1985; Lukawska-Matuszewska and Kielczewska, 2016). Substantial amount of work have been published on the behaviour of trace metals in surficial sediment as well as in core sediment beneath the oxic waters (Yuan et al., 2012; Xu et al., 2014; Ming et al., 2016). However, there is scarce work done on the sediment metal chemistry in the water body, which remains anoxic for all 365 days. Fishing harbours are widely distributed in coastlines of several countries. Fishing harbours also contain a special water area with high density of human activities, and thus the wastewater and oil, solid and house garbage from the fishing boats/ships are discharged into the harbours (Iduk and Samson, 2015). Harbours are also the recipients of contaminants from ship traffic, loading, repairs and dredging as well as rain water runoff, effluent discharge, dust, etc. (Schiff, 1997; Joksas et al., 2003; Guerra-Garcia and Garcia-Gomez, 2005). In addition, most are built in semi-enclosed coastal regions which are likely to decrease the seawater exchange ability (Owen and Sandhu, 2000; Dassenakis et al., 2003; Aly et al., 2013). As a result, the contaminants can dramatically increase in the harbour sediment (Lin et al., 2009; Xu et al., 2012). Out of these contaminants, pollution by trace metals in coastal environment has become a global phenomenon because of its toxicity, persistence for several decades in the environment, bioaccumulation and biomagnifications in the food chain (Chinnaraja et al., 2011).

Sediments function as a sink for metals in aquatic ecosystems; they also act as a source of metals when environmental conditions change (pH, Eh, redox, humic acids) (Guo et al., 1997; Burton, 2002; Woods et al., 2012; Chapman et al., 2013). Mn, Fe and Al play a crucial role in the removal of metal ions from sea water as well as their behaviour in sediments. The oxyhydroxides of Mn and Fe have a high adsorption capacity and large surface area and can adsorb cations such as Cr^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+} and Cd^{2+} (Forstner, 1979; Williams et al., 1994; Schulz and Zabel, 2005; Gasparatos, 2012).

The nature of the diagenetic change occurring in marine sediments largely depends on the influx of decomposable organic matter to the sediment and the metabolic rate of oxidation (Middelburg and Levin, 2009; Chakraborty et al., 2016). Three types of processes namely oxic diagenesis, suboxic diagenesis and anoxic diagenesis occur in sediments. When dissolved oxygen (DO) is present in the sediment porewaters, oxic diagenesis takes place and Mn concentrations in the porewaters remain extremely low (about $2\ \mu g\ l^{-1}$). When DO in porewater depletes to very low level, suboxic diagenesis dominates with a reduction of NO_3^--N followed by reduction of Fe and Mn

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oxyhydroxides. When this occurs, the concentration of dissolved Mn increases by several orders of magnitude ($> 1000\ \mu g\ l^{-1}$) compared to the ocean bottom water (about $0.2\ \mu g\ l^{-1}$) (Schulz and Zabel, 2005). In the sediment of oxic water, at a depth where oxygen diminishes, Fe and Mn oxyhydroxides are reduced to Fe (II) and Mn (II) ions and get dissolved in porewater along with other metals bound to Fe and Mn oxyhydroxides (Wijsman et al., 2001; Konovalov et al., 2007; Middelburg and Levin, 2009). Fe and Mn however, can migrate under redox gradients in sediments (Forstner, 1979; Soetaert et al., 2002). These metal ions migrate upward through the porewater and precipitate along with Mn and Fe at a depth in the sediment where oxidising conditions prevail (Berner, 1980; Fernex et al., 1984; Brannon and Patrick, 1987).

In the present work, dissolved oxygen (DO), biochemical oxygen demand (BOD), ammonia (NH_4^+-N), inorganic phosphate (PO_4^{3-}-P), hydrogen sulfide (H_2S) and dissolved metals such as Fe, Mn, Cr, Co, Ni, Cu, Zn, Cd, Hg, Pb were studied in overlying water to understand their variability and control on geochemistry of sediment in anoxic condition of the harbour. Sediment cores from polluted harbour as well as relatively clean offshore region were studied to find diagenetic behaviour of trace metals in different environment. Hence, the present study is a unique attempt to understand geochemical behaviour of trace metals in the sediment of Veraval harbour, the area where water remains anoxic throughout the year (NIO, 2014, 2015). The present work also helps in understanding the role of Fe, Mn, C, and S in vertical mobilization of toxic trace metals in anoxic waters. The ecological risk assessment of trace metal accumulation in sediments of Veraval harbour was carried out by Sundararajan et al., 2017 which showed the contamination levels of surface sediments of the harbour during the year 2006. In the present research, effort has been made to find the depth wise variation of trace metals and their behaviour with elements such as C, N and S in sediment core of Veraval harbour, which remains anoxic throughout the year (NIO, 2014, 2015).

2. Materials and methods

2.1. Study area

Veraval, located (20° 53′ N 70° 26′ E) on north-west coast of India (Fig. 1), is home to many textiles, chemicals and food processing industries and is the largest fishing harbour in Asia. The maximum temperature in the Veraval region varies between 30 and 39 °C. Being the coastal area, the humidity will not be below 55%. The annual rainfall in the area is around 729 mm. The maximum rainfall occurs during July–August and tapers off by the end of November. The winds are light to moderate with some increase in speed during southwest monsoon season. The main activities at Veraval include fish processing and export that provides significant economic source to its residents.

The harbour receives around $20{,}000\ m^3\ d^{-1}$ of anthropogenic waste from fish processing industries and about $24{,}000\ m^3\ d^{-1}$ of sewage from Veraval City (CPCB, 2009–2010). The harbour has the stagnant water condition, due to siltation at the mouth, lack of turbulence, wind action and tidal effect in and around the jetty because of the abrupt designing of it, making dilution an impossible task for tides coming towards the jetty. Due to fishing industries as well as domestic effluent discharge, and poor flushing, build-up of organic load has taken such an extent that Veraval harbour water has become anoxic giving rise to the high NH_4^+-N ($> 1000\ \mu mol\ l^{-1}$) concentration (NIO, 2014, 2015). Current direction of Veraval is parallel to the coast, hence water of Veraval harbour moves along the coast during low tide. Thus immediate rise of nutrient concentration in the water of Veraval is not noticed. As expected, the pH of coastal water varies in a narrow range (7.9–8.2) though lower values (7.3–7.8) are recorded in Veraval harbour due to environmental stress associated with the release of effluents from various sources in the harbour basin (NIO, 2014, 2015).

2.2. Sampling and analyses

For the present study, the samples were collected from three locations as shown in Fig. 2, during postmonsoon season of the year 2013. Overlying bottom water samples were collected using Niskin water

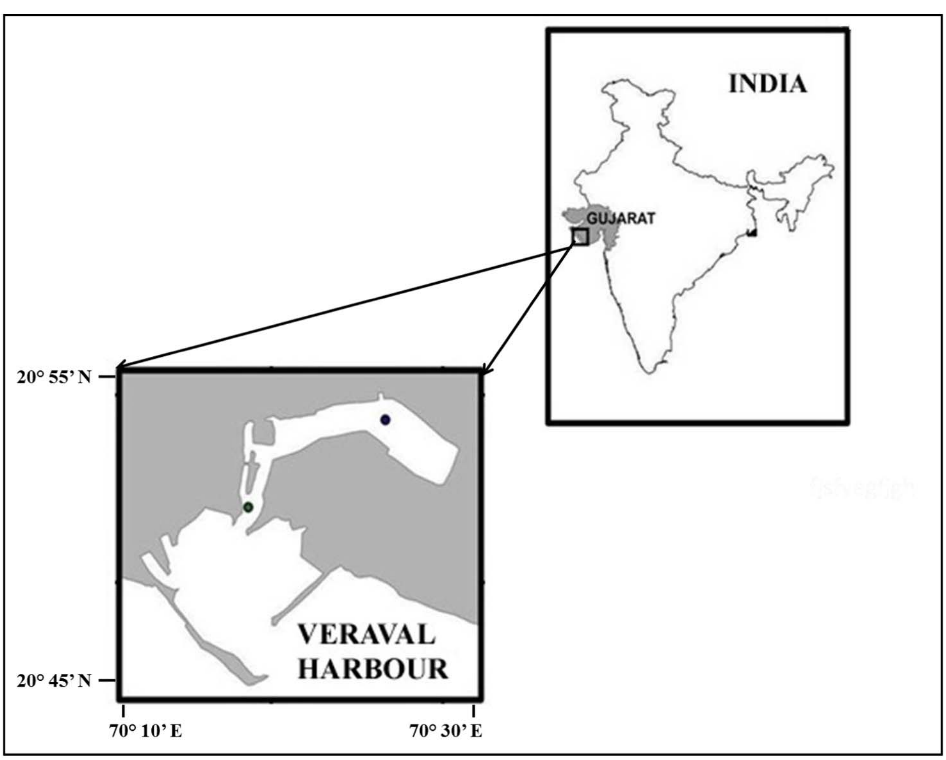

Fig. 1. Map showing study area.