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Ecological risk assessment of trace metal accumulation in sediments of Veraval Harbor, Gujarat, Arabian Sea

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ABSTRACT

In this study, different types of indices were used to assess the ecological risk of trace metal contamination in sediments on the basis of sediment quality guidelines at Veraval Fishery Harbor. Sediment samples were collected from three sectors in pre-, post-, and monsoon seasons in 2006. Trace metal concentrations were higher in the inner sector during post-monsoon, and it showed the highest statistical significance ($p < 0.01$) among the stations. Pollution load index was higher than unity, indicating alternation by effluent discharge from industries. Enrichment factor and geo-accumulation index showed that Cd, Pb, and Zn were enriched in the northern part of the harbor and Pb had accumulated in the harbor sediment. The ecological risk assessment index revealed that Ni, Zn, and Pb were higher than the effect range median values, indicating their potential toxicity to the aquatic environment in the Veraval Harbor. Hence, the harbor is dominated by anthropogenic activities rather than natural process.

In the past few decades, the rapid development of industries and economy in the coastal regions has resulted in the increase in trace metal concentration, thereby causing environmental pollution. Trace metal pollution in sediment is a global problem of the aquatic ecosystem (Zahra et al., 2014). Accumulation of trace metal pollutants in sediments can pose a serious environmental threat to the aquatic biota because of their toxicity, non-biodegradability, and bio-magnification in the food chain (Duman et al., 2007; Ho et al., 2010).

Sediment acts as a sink for organic and inorganic pollutants (heavy metal) from anthropogenic activities to the marine environment (Zahra et al., 2014). Metals enter the marine environment from natural (e.g., mineral weathering, volcanic eruptions, and dust deposition) and anthropogenic sources (e.g., mining, fossil fuel combustion, agriculture, industry, marine traffic, urban development, and sewage). Metals such as Pb, Cd, Zn, Cr, Cu, As, and Ni are primarily mobilized through human activity, whereas others such as Al, Fe, and Mn have lithogenic origin (Serrano et al., 2011). Thus, the seasonal and special distributions of metals in the sediment are important to evaluate the enrichment pattern and to assess any potential localized influences.

The assessment of trace metal is a complex process requiring physical, chemical, and biological data of estuarine and coastal sediment. However, the necessary biochemical data are not always available in environmental geochemistry. Therefore, the assessment of contamination status is normally based on sediment quality guidelines (SQGs) and quantitative pollution index of the respective metals (Ho et al., 2010).

The state of Gujarat has the longest coastline in India (1600 km) with a variety of aquatic fauna and ranks second in marine fish production in the country. It is one of the major fish producing-maritime states in India. Veraval Harbor is located on the southwest coast of Saurashtra, Gujarat coast, Arabian Sea. It is a port town with one of the largest fishing harbors in Asia. It contains several fish-processing factories that export high-quality seafood to the United States, Southeast Asia, Japan, Europe, and the Gulf, which is a significant source of economy to the population. Aditya Birla Nuvo Ltd. (one of India's largest rayon manufacturers), small industrial units, and fish-processing plants are located on the coast of Veraval, affecting the coastal water significantly by the anthropogenic pressure and industrial discharge (Borade et al., 2015; Bhadja et al., 2014). Therefore, studies on pollution are necessary to be carried out in this harbor.

To date, only few studies have been conducted in harbors worldwide regarding environmental risk assessment of metal pollution. Ceuta Harbor (Guerra-Garcı'a and Garcı'a-Go'mez, 2005), Boston Harbor (Bothner et al., 1998), Kaohsiung Harbor in Taiwan (Chen et al., 2007), Wellington Harbor in New Zealand (Dickinson et al., 1996), Port Elizabeth (Fatoki and Mathabatha, 2001), CuaOng Harbor, Ha Long Bay (Ho et al., 2010), Sydney Harbor in Australia (Mccready et al., 2006), and Bergen Harbor in Norway (Paetzel et al., 2003) are some of them. In India, environmental impact assessment studies were conducted by

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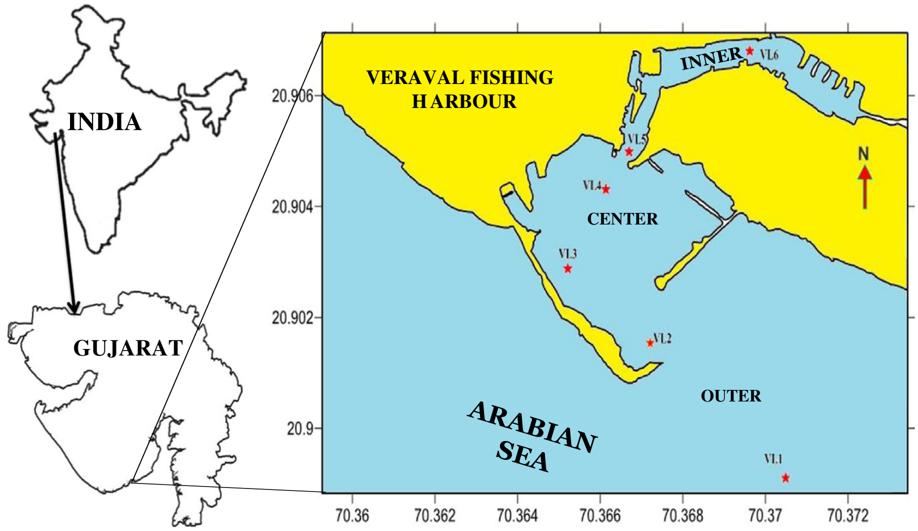

Fig. 1. Map showing the location of sampling points at Veraval fishing harbor.

Ganapati (1969), Ganapati and Raman (1973), Raman (1995), Sharma et al. (1996), and Senthilnathan and Balasubramanian (1999) in Visakhapatnam and Pondicherry harbors. In the west coast, extensive studies were conducted by Matkar et al. (1981) on trace metal concentration in Mumbai Harbor, Shirodkar et al. (2012) on seasonal changes in the water quality in Morumonga harbor, Bhadja et al. (2014) on the effect of seawater quality on industrial development in the coast of Gujarat, Mandal et al. (2015) on the occurrence of bloom in Veraval Fishery Harbor, and Borade et al. (2015) on the correlation between physicochemical parameters and a bacterial indicator in the Veraval coast. Even though the state Gujarat and Veraval Harbor in particular are the regions of concern, trace metal contamination studies have not been conducted in this area.

Therefore, this study attempts to determine the distribution of trace metal contamination in the surface sediment of Veraval Harbor by using different types of pollution indices and ecological risk assessment based on SQGs.

Veraval is located at 20.9°N and 70.37°E on the southwest coast of Gujarat, India, with many industrial units surrounding it. The main activities performed at the Veraval coast are processing and exporting of fish, which constitute a significant source of economy to the population. The fishing communities mostly depend on this coast. The seasonal data set from the study sites was integrated with the weather condition of this region, representing the periods of pre-monsoon (February to May), monsoon (June to September), and post-monsoon (October to January) seasons. Almost all precipitation occurs during the monsoon season from June to September (Bhadja et al., 2014). The trawling season starts from September to May, and the fishing is banned from June to August (Dineshbabu, 2003).

Sediment samples were collected from three sectors in the Veraval Harbor, inner (VL5 and VL6, anthropogenic input, and jetty area of harbor), center (VL3 and VL4, inside to mouth of harbor), outer (VL1 and VL2, mouth of harbor to open sea) (Fig. 1), in the months of May (pre-monsoon), August (monsoon), and December (post-monsoon) in 2006. The sediment samples were collected using the Van Veen Grab sampler and placed in plastic bags. The collected samples were preserved in ice box, which maintains the original condition of the samples. In the laboratory, the samples were dried in an oven at 105 °C for 24 h and stored until analysis.

In this study, the digestion and analytical procedures of the sediment were conducted using the US Environmental Protection Agency, Method (EPA 3052), 1996. For this analysis, 0.05 g of the fine powder sediment was weighed and digested in an ultrapure HNO_3–HCl mixture and heated up to 150 °C in an Anton Paar Multiwave 3000 (Graz, Austria) microwave oven. To verify the precision of the analytical procedures, the sediment samples were digested and analyzed in three replicates for each sample. After digestion, the clear solution was transferred into centrifuge tubes and made up to 10 ml by adding Milli-Q water (Cortada and Collin, 2013). The concentrations of trace metals in the final solutions were determined by inductively coupled plasma mass spectrometry (ICPMS, PerkinElmer, ELAN DRC e).

Average values of the triplicate analyses were taken as the final value. The results revealed good reproducibility of the instrument. Analyses of precision and accuracy of the metal including blank and standard reference material (SRM 1646a-estuarine sediment, NIST, USA) were run in the same way as the samples and trace metal concentrations were determined using standard solutions prepared in the same acid matrix. Sediment reference material (SRM 1646a-estuarine sediment, NIST, USA) was used ($N = 3$) to validate the data and quality control of the analytical method. The recovery of certified reference materials (SRM 1646a-estuarine sediments) varied from 90.19% to 104.28% (Table 1).

To assess the trace metal contamination in sediment, various parameters were considered such as enrichment factor (EF), contamination factor (CF), pollution load index (PLI), and geo-accumulation index (I_{geo}). These pollution indices were calculated using shale average values of metals (Turekian and Wedepohl, 1961).

Sinex and Helz (1981) used the EF to assess the degree of contamination and to understand the distribution of elements from the anthropogenic source in sites by individual elements in sediments (Chandrasekaran et al., 2014; Shang et al., 2015). Fe was chosen as the normalizing element while determining EF:

$$EF = (C_n/Fe)_{sample}/(C_n/Fe)_{background},$$

Table 1
Results analysis of standard reference materials (SRM) in comparison with certified values.

Trace metals	Certified value	Measured value, n = 3	Recovery (%)
Mn (μg g^{-1})	234 ± 2.8	231.2 ± 1.824	98.60
Ni (μg g^{-1})	23	21.36 ± 1.239	92.87
Co (μg g^{-1})	5	4.72 ± 0.088	94.32
Cu (μg g^{-1})	10.01 ± 0.34	9.69 ± 0.383	96.82
Zn (μg g^{-1})	48.9 ± 1.6	45.77 ± 0.430	93.59
Cd (μg g^{-1})	0.148 ± 1.9	0.13 ± 0.005	90.81
Pb (μg g^{-1})	11.7 ± 1.2	10.55 ± 0.234	90.19
Cr (μg g^{-1})	40.9 ± 1.9	40.03 ± 0.242	97.87
Fe (%)	2.008 ± 0.039	2.09 ± 0.034	104.28

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