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Baseline

# Bioavailable metals in tourist beaches of Richards Bay, Kwazulu-Natal, South Africa

E. Vetrimurugan [a], M.P. Jonathan [b,*], Priyadarsi D. Roy [c], V.C. Shruti [b], O.M. Ndwandwe [d]

[a] Department of Hydrology, University Of Zululand, Private Bag x1001, Kwa Dlangezwa 3886, South Africa
[b] Centro Interdisciplinario de Investigaciones y Estudios sobre Medio Ambiente y Desarrollo (CIIEMAD), Instituto Politécnico Nacional (IPN), Calle 30 de Junio de 1520, Barrio la Laguna Ticomán, Del. Gustavo A. Madero, C.P. 07340, Mexico D.F., Mexico
[c] Instituto de Geología, Universidad Nacional Autónoma de Mexico (UNAM), Ciudad Universitaria, C.P. 04510 Coyoacan, Mexico D.F., Mexico
[d] Department of Physics and Engineering, University Of Zululand, Private Bag x1001, Kwa Dlangezwa 3886, South Africa

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ABSTRACT

Acid Leachable Trace Metal (ALTMs) concentrations in tourist beaches of Richards Bay, Kwazulu-Natal, South Africa were assessed. 53 surface sediment samples were collected from five different beaches (Kwambonambi Long Beach; Nhlabane Beach; Five Mile Beach; Alkanstrand Beach and Port Durnford Beach). The results of ALTMs (Fe, Mn, Cr, Cu, Ni, Co, Pb, Cd, Zn, As, Hg) suggest that they are enriched naturally and with some local industrial sources for (avg. in $\mu g\ g^{-1}$) Fe (3530–7219), Mn (46–107.11), Cd (0.43–1.00) and Zn (48–103.98). Statistical results indicate that metal concentrations were from natural origin attributed to leaching, weathering process and industrial sources. Comparative studies of metal concentrations with sediment quality guidelines and ecotoxicological values indicate that there is no adverse biological effect. Enrichment factor and geo-accumulation indices results indicate moderate enhancement of Fe ($I_{geo}$ class 1 in FMB), Cd (EF > 50; $I_{geo}$ classes 2–4) and Zn ($I_{geo}$ classes 1 & 2).



Coastal environments like beaches are the most dynamic and complex landscapes forming critical habitats for plants and animals, providing recreational activities, storm protection and above all enhances the economic growth through tourism (Johns et al., 2001; Marshall et al., 2014). Rapid industrialization, urbanization and amplified human population shifting towards the coast have resulted in widespread modification of beach ecosystems. The most important threat posed to marine environment is the presence of heavy metals, due to their persistence and biogeochemical recycling nature (Liu et al., 2003; Qiao et al., 2013). Beach sediments are reservoirs of heavy metals derived from both natural weathering processes and anthropogenic sources as less than 1% of pollution remains dissolved in water whereas more than 99% are stored in sediments (Bartoli et al., 2012; Gaur et al., 2005; Bradley and Cox, 1986; Horowitz, 1991). Various factors such as nature of the sediments, grain size, properties of adsorbed particles and metal characteristics control the mobility and accumulation of metals in sediments (Bastami et al., 2014). The geochemical studies of heavy metals in marine beach environments near to the rapid developing coasts would aid in assessing natural and anthropogenic impacts as well as ecological risks are posed due to the presence of these metals.

The South African coastline is characterized by open water with high wave action. Approximately 30% of South Africa's population resides along coastline with high density coastal population along the east coast (Taljaard et al., 2006; Wepener and Degger, 2012). The KwaZulu-Natal coastline is one of the most valuable natural assets utilized for residential, commercial, natural conservation purposes and also attracts large number of tourists (Cooper, 1995). Among the northern coastal plain Richards Bay is very popular for fishing, scuba diving and surfing activities. It is characterized with high energy, coarse grained and sandy beaches are often subjected to large swells. Geologically the shore platforms of Kwazulu-Natal is composed of calcarenite beach rocks and aeolianites of Holocene and Pleistocene age exposed in the intertidal and supratidal regions and these form the part of Isipingo formation of the Maputaland Group (Cooper, 1991; Porat and Botha, 2008; Salzmann and Green, 2012).

Richards Bay situated in northern Kwazulu-Natal coast has the largest bulk cargo port exporting coal from South Africa which was constructed in the Mhlathuze estuary in 1976. Other exports handled by the port include ferro-alloys, chrome ore, steel and heavy metal groups of titanium, rutile, and zircon mined in the dunes north of Richards Bay (Fair and Jones, 1991; Greenfield et al., 2011). Apart from its economic importance Richards Bay Harbor serves as an important ecosystem function being a substitute for estuaries earlier present in this region which served as sheltered refuges, nurseries and feeding grounds for numerous marine and aquatic organisms (Cloete and Oliff, 1976; Forbes et al., 1996; Vermeulen and Wepener, 1999). Increased tourism,

* Corresponding author.
*E-mail addresses:* evetrimurugan@yahoo.co.in (E. Vetrimurugan), mpjonathan7@yahoo.com (M.P. Jonathan).

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development of port and other industrial activities present in this region insists on evaluation of metal concentrations in the sediments of Richards Bay and the surrounding beaches.

Surface sediment samples were collected from 53 sampling sites along the coastal area of Richards Bay during August 2014 including northern and southern regions (Fig. 1). The coastline was divided into five regions namely: 1) Kwambonambi Long Beach (KLB) (S.Nos. 1–4); 2) Nhlabane Beach (NB) (S.Nos. 5–14) [rural, agricultural, mining, sugarcane and timber plantations are the main economic activities in these two regions]; 3) Five Mile Beach (FMB) [(S.Nos. 15–34) Densely populated region close to Meer en See city and the presence of numerous hotels nearby this region]; 4) Alkanstrand Beach (AB) [(S.Nos. 35–43) Location of Richards Bay Harbor and the presence of coal terminal, paper mill, timber, aluminum and fertilizer industries] and 5) Port Durnford Beach (PB) (S.Nos. 44–53) [Input of Umlalazi river]. The sediment samples were collected from the inter-tidal zone using a plastic spatula and were placed in polythene plastic bag. The samples were oven dried below 40 °C for powdering and further analysis. ALTMs Fe, Mn, Cr, Cu, Ni, Co, Pb, Cd, Zn, As and Hg were analyzed based on modified EPA 3051A method. An acid mixture of $HNO_3$ + HCl (9:3 ratio) was used to digest the dry sediment samples on a modified closed autoclave method (Navarrete-López et al., 2012). The samples were digested using PFA [Poly(tetrafluoroethylene)] vessel at 119 ± 1.5 °C for 40 min and the final solution was made up to 50 ml after filtration. The filtered samples were introduced in Atomic absorption spectroscopy (AAS) (Perkin Elmer AAnalyst 100) for trace metal analysis and Graphite furnace (GFAAS) for As and Hg. All reagents used in the analysis were of analytical grade (J.T.Baker) and Standard Reference Material Loam soil B (SRM No.691029) and D (SRM No. 811221) was digested and analyzed along with the samples to check the recovery and precision of the analytical procedure. The procedure was validated using Marine Reference Standard (2702) and the recovery for the analyzed elements were: Fe 102% (±1.72 μg $g^{-1}$), Mn 96.2% (±0.09 μg $g^{-1}$), Cr 87.1% (±2.12 μg $g^{-1}$), Cu 99.71% (±3.22 μg $g^{-1}$), Ni 96.3% (±3.97 μg $g^{-1}$), Co 98.24% (±3.12 μg $g^{-1}$), Pb 99.04% (±2.82 μg $g^{-1}$), Cd 89.41% (±3.02 μg $g^{-1}$), Zn 99.79% (±1.12 μg $g^{-1}$), As 91.25% (±2.92 μg $g^{-1}$) and Hg 93.02% (±3.14 μg $g^{-1}$) respectively. Statistica (Version 8) was used to process the data and identify the relationship between different ALTMs.

The distribution patterns of ALTMs along the Richards Bay areas are presented in Fig. 2a–k. Based on the average concentration values of ALTMs (Table 1) the elements are ordered in the following order: 1) KLB: Fe > Zn > Mn > Pb > Cr > Ni = Co > As> = Cu > Cd > Hg; 2) NB: Fe > Zn > Mn > Cr > Pb > Ni > Co > Cu > As > Cd > Hg; 3) FMB: Fe > Zn > Mn > Pb > Cr > Ni > Co > As > Cu > Cd > Hg; 4) AB: Fe > Zn > Mn > Cr > Pb > Ni > Co > Cu > As > Cd > Hg; and 5) PDB: Fe > Mn > Zn > Cr > Ni > Pb > Co > Cu > As > Cd > Hg; respectively. The sequential order of elements in all the beaches are almost in the same pattern except for a few changes. All the values were compared with reference to the UCC values to have a general understanding on the enrichment pattern.

Higher values (in μg $g^{-1}$) of Fe (7145, 5044 and 7219) and Zn (77.18, 103.98 and 88.28) in the southern beaches FM, AB and PDB were observed compared to UCC. The higher values of Fe is mainly due to the sorption of Fe onto the surface particle or its substitution for Ca in the calcite crystals (Beltagy, 1984) and the higher values of Zn is due to the precipitation as $ZnCO_3$ resulting in higher values. The other sources adding to the increased concentrations of zinc are from the fiberglass boat factory and through the extensive use of the antifouling paints by shipping activities (Matthiessen et al., 1999; Turner and Huntingford, 2011). The Mn concentrations (in μg $g^{-1}$) in the analyzed samples were 46, 53.60, 59.99, 58.76 and 107.11, indicating a minor enrichment mainly due to the incorporation in the crystal lattice of calcite (Nawar and Shata, 1989). Apart from the natural sources, the influence from the city based activities, mining, development of Richards Bay Harbor, fishing activities and Port Durnford also will result in enrichment in the Southern Richards Bay. All other metals Cr, Cu, Ni, Co, Pb, Hg and As indicate lower values compared to the UCC values suggesting that the region is not affected by the external sources. The average concentrations of Cd for all the beaches were 1.00, 0.67, 0.93, 0.68 and 0.43 (all values in μg $g^{-1}$) respectively and slightly higher than the background UCC values (Cd = 0.102 ppm). Cadmium is closely associated with zinc where rock phosphates contain large contents of Cd and Zn as impurities (McMurtry et al., 1995). High Cd concentrations in the beach sediments are attributed to the terrigenous origin and increase of human activities in the coastal region such as tourism, landfilling, sewage and sludge disposal (Suresh et al., 2015). Exceptionally higher value (in μg $g^{-1}$) was observed in the sampling site 23 (FMB) for Fe

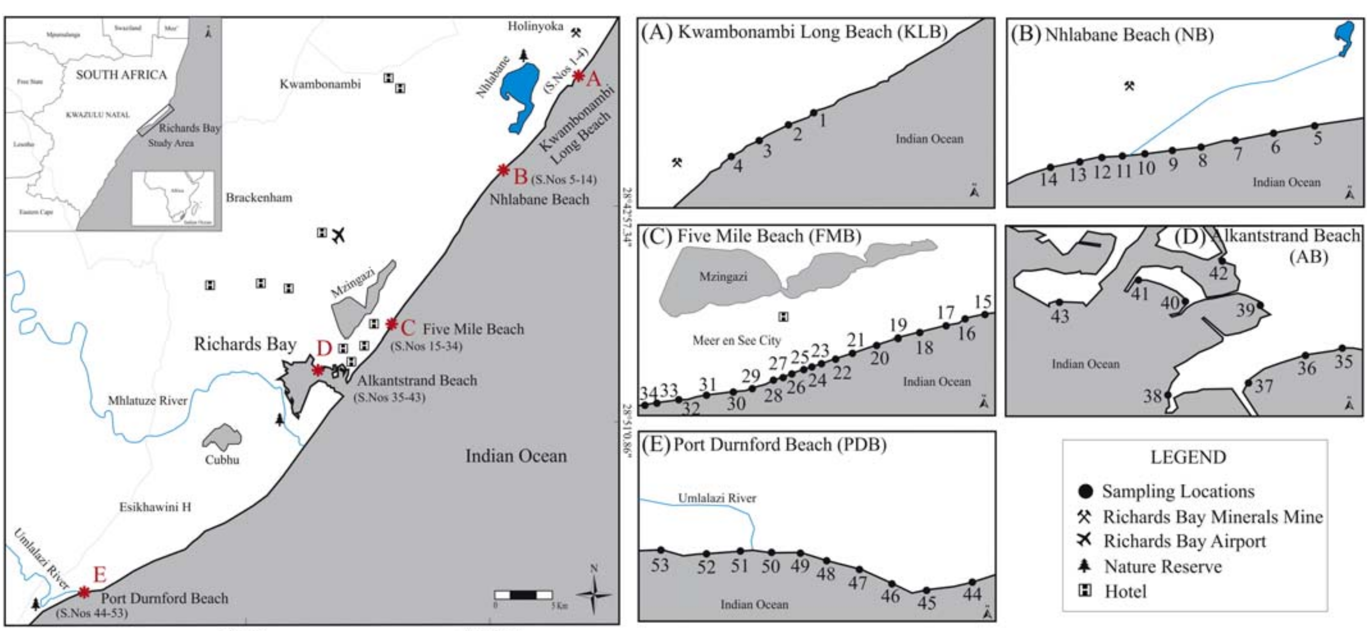


**Fig. 1.** Map showing the studied beaches of the Richards Bay, South Africa.