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Baseline

Comparison of heavy metal contamination during the last decade along the coastal sediment of Pakistan: Multiple pollution indices approach

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ABSTRACT

Heavy metals concentrations (Fe, Cu, Zn, Ni, Cr, Co, Pb, and Cd) were scrutinized during two monitoring years (2001 and 2011) in the coastal sediment of Pakistan. The status of metal contamination in coastal sediment was interpreted using sediment quality guidelines, and single and combined metal pollution indices. Ni, Cr, and Cd were recognized for their significant ($p < 0.05$) intensification in the sediment during the last decade. Sediment quality guidelines recognized the frequent adverse biological effect of Ni and the occasional adverse biological effect of Cu, Cr, Pb and Cd. Single metal pollution indices (*Igeo*, EF, CF, and ER) revealed that sediment pollution is predominantly caused by Pb and Cd. Low to moderate contamination was appraised along the coast by multi-metal pollution indices (CD and PERI). Correlation study specifies that heavy metals were presented diverse affiliations and carriers for distribution in the sediment during the last decade.

Heavy metal pollution has changed into a severe threat to the marine environments adjacent to highly industrialized and urbanized zones because of their toxicity, persistence, and non-biodegradable nature. Heavy metal originates from both natural and anthropogenic (agricultural runoff, mining activities, industrial effluents and atmospheric deposition) sources into coastal environments (Bryan and Langston, 1992; Callender, 2005). When heavy metals enter into the marine environment, a minute amount interact and mixed with the aqueous phase, however, the rest is deposited in the sediment by various physical and chemical processes (Hakanson, 1980; Bastami et al., 2014). Sediment acts as a sink for the several pollutants and the behavior of sediments reflects the historical deposition, sources, and effects of anthropogenic and lithogenic inputs of contaminants. Therefore, in comparison with water, the evaluation of sediment is more conservative and reliable to determine the intensity of contamination and toxicity in a marine environment (Marchand et al., 2006; Sany et al., 2013).

Some metals (such as Fe, Cu, Zn, Co, Mn, Cr, Mo, V, Se and Ni) are known to be essential for marine organisms but usually show toxicity if they are above the threshold level. Whereas a few other metals such as Ag, Hg, Cd, and Pb are particularly toxic to marine life, even if present in a minute amount (Bryan, 1979; Silva et al., 2014). Excessive levels of heavy metals in sediments affect marine benthic organisms, which are associated with sediments and may take up heavy metals through their food which play an important role in the food chain. Therefore, the adverse effects of heavy metals in aquatic environments may enhance further which may lead to public health concerns (Bryan and Langston, 1992; Siddique et al., 2009; Lin et al., 2013). Many studies revealed that heavy metal toxicity and accumulation in sediment not only depend on metal concentration, but may also be affected by various other factors including the system in which the metal component is present, the type and concentration of other materials and the level of integration with certain physicochemical parameters (temperature, salinity, pH, dissolved oxygen, organic carbon and grain size of sediment) (Hardman, 2006; Wang et al., 2002; Sany et al., 2013).

Coastal regions, adjacent to extensive industrial and urban territories have greater heavy metal levels which are five or ten times more than that 50 to 100 years ago (Cardoso et al., 2001; Santschi et al., 2001; Chaudhary et al., 2013). In this current situation, where a higher level of heavy metals was observed, it is necessary to use a specific and comprehensive method to assess the sediment capacity for the heavy metal acquisition and its adverse biological effect on associated marine organisms. To evaluate the contamination and ecological risks of metals, a number of studies have been conducted by many researchers that were based on the total concentrations and multiple indices. The Geo-accumulation index (*Igeo*), the enrichment factor (EF), contamination factor (CF) and ecological risk index (ER) were used to assess the single metal pollution, however, contamination degree (CD) and potential ecological risk (PERI) were used to evaluate the combined metal pollution (Hakanson, 1980; Siddique et al., 2009; Zhao et al., 2012; Mashiatullah et al., 2013; Xu et al., 2014; Zhuang and Gao, 2014).

The aims of the current study were: (1) to assess the spatial and temporal variations of the heavy metal distribution in sediments from four coastal areas of Pakistan in two monitoring years (2001 and 2011), (2) to apply indices for single metal pollution (Igeo, EF, CF and

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ER) and for combined metal pollution (CD and PERI) in order to recognize the pollution status, and (3) to evaluate the associations and sources of heavy metals in coastal sediment.

The entire coastline of Pakistan extends to about 990 km in length situated along the northern boundary of the Arabian Sea. About 320 km of coastline is covered by the Sindh province while the Baluchistan province covers approximately 670 km of coastline (Gondal et al., 2012). The Karachi coastline is situated in the Sindh province that comprises about 167 km long shoreline, is the most populated, mega city and main hub of industrial and commercial activities, and is threatened by pollution through domestic and industrial effluents, shipping and fishing traffic, and associated pollutants from agricultural runoff, which enter through various points and non-point sources (Rizvi et al., 1988; Saifullah et al., 2002; Qari et al., 2005). Lyari and Malir Rivers are the main point sources of coastal pollution in Karachi, are contaminated by various links of untreated urban and industrial wastes, and ultimately drain into the beaches of Karachi into the Arabian Sea (Rizvi et al., 1988; Siddique et al., 2009).

The coast of Baluchistan has many representative bays, one of them is Sonmiani Bay, which is located about 90 km away from Karachi on the eastern most part of Baluchistan coast. The bay is a 60 km long and 7 km wide convoluted and knotted body of water, which is connected to the sea at the southeastern end by a 4 km wide mouth (Saifullah and Rasool, 1995; Gondal et al., 2012). The sources of fresh water are the seasonal runoff of the Porali and Windor Rivers (Rasool et al., 2002; Saifullah et al., 2004). These rivers also contain effluents of approximately 122 industries, functioning at the Hub and Winder Industrial Trading Estate, which include textile weaving, plastic, chemical, food preservation, engineering, paper and paper product industries, etc., and contribute to coastal pollution (LGB, 2008; Saleem et al., 2013). On the basis of geography and exposure of contaminants, three sites from Sindh coast, i.e. Korangi Creek (24° 79′ N, 67° 20′ E), Phitti Creek (24° 65′ N, 67° 16′ E) and Sonari (24° 53′ N, 66° 42′ E) and one site from Baluchistan coast, i.e. Sonmiani Bay (25° 26′ N, 66° 35′ E) were selected for monitoring of heavy metal pollution during the last decade along the Pakistan coast (Fig. 1).

A total 45 sediment samples were collected from four coastal environments, Korangi Creek (KC), Phitti Creek (PC), Sonari (So) and Sonmiani Bay (SB). At each designated site 3 to 6, sediment samples were collected from 0 to 20 cm depth using a PVC core (diameter 5.6 cm) in both sampling years. Samples were placed in washed, clean and dry polyethylene bags, then transferred to the laboratory in an ice box and freeze dried at −4 °C until analysis. Physical (organic matter and grain size) and chemical (total metal concentration) characteristics of sediment samples were analyzed. Total organic matter (TOM %) was determined by loss on ignition at 500 °C for 4 h in a muffle furnace (Saher and Qureshi, 2010). To examine grain size distributions, all sediment samples were oven dried at 75 °C for 24 h. Dried sediment samples were ground and homogenized, then screened with US standard sieves (2.0, 1.0, 0.5, 0.3, 0.125 and 0.063 mm) following Folk and Ward (1957). Sediments were categorized into three main size classes, gravel (>2 mm), sand (<2.0 to >0.063 mm) and mud (<0.063 mm) fractions. Sediment <0.063 mm was used for determining the heavy metal concentrations. The previous work (grain size analysis and percent organic content of sediment) was done by Saher NU (2008) and stored sediment samples (<0.063 mm) were used in acid digestion for heavy metal analysis for a decade comparison.

Approximately 1.0 g of sediment sample was mixed with 10 ml mixtures of nitric acid and hydrochloric acid (1:3) and digested on a hot plate at 90 °C for an hour and then allowed to cool at room temperature. The sample was filtered (Whatman no. 42 μm) and diluted to 50 ml with distilled water (Qari et al., 2005). Samples were analyzed for the eight metals (Fe, Cu, Zn, Ni, Cr, Co, Pb, and Cd) by using Atomic Absorption Spectrometer (Perkin Elmer (USA), model A Analyst 700). Blank, standard solutions, and replicate samples were used to monitor the performance of equipment and data quality by developing calibration curves. Standard solutions were obtained by appropriate salts of corresponding metals dissolving in deionized water. The metal concentrations of each sample were expressed in $\mu g\ g^{-1}$ of the dry weight of sediment. In the present study, all heavy metals analyzed by AAS, achieved good precision (1 to 5% RSD), except for Co which (moderate) ranged from 1 to 15% RSD.

Numerical sediment quality guidelines (SQGs) are criteria usually applied in the evaluation of biological risk caused by toxic substances in sediments using two sets of guidelines i.e., effect range low (ERL) and effect range medium (ERM) and threshold effect level (TEL) and probable effect level (PEL) (Long and MacDonald, 1998). Mean quotients of these guidelines are a useful tool for reducing a lot of figures into a single digit for mixtures of contaminants associated with sediment (Long and MacDonald, 1998; Siddique et al., 2009; Zhuang and Gao, 2014).

$$\text{Mean X quotient} = \sum (C_n/X_n)/N \quad (1)$$

where C_n is concentration of metal 'n' in the sediment sample, X_n is the sediment quality guideline (ERL or ERM and TEL or PEL) value of metal 'n' and N is the sum of all examined metals.

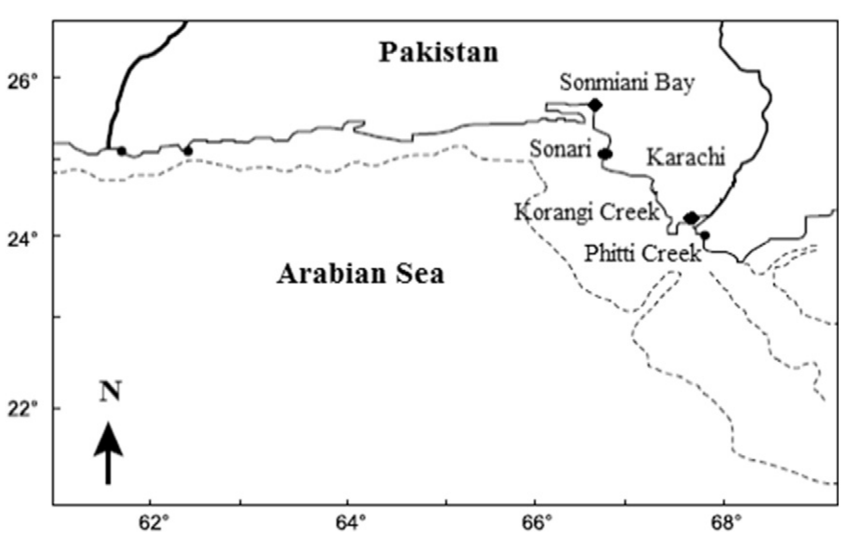

Fig. 1. Map showing the geographic locations of the monitoring sites along the coast of Pakistan.