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ORIGINAL ARTICLE

Distribution, speciation and risk assessment of heavy metals: geochemical exploration of Gulf of Kachchh, Gujarat, India

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Abstract

The present study includes analysis of six heavy metals, to determine spatial distribution and potential ecological risk at 10 stations of the Gulf of Kachchh, Gujarat, India. The geochemical exploration of toxic heavy metals on Gulf of Kachchh was evaluated using hierarchical cluster analysis (HCA). Pollution indices such as contamination factors (CF), pollution load index (PLI) and degree of contamination (D_c) were used to analyze the potential risk of Cu, Ni, Cr, Cd, Pb and Hg to the ecosystem of Gulf of Kachchh. The mean concentrations of six heavy metals were in the following order: Cr > Cu > Ni > Pb > Cd > Hg. Spatial distribution clearly indicated industrialization and domestic waste of major cities as sources of heavy metal contamination. Pollution indices revealed that Cu contamination at some of the stations was on the rise due to direct or indirect discharge from natural and anthropogenic sources which is of major concern. Despite episodic contamination by heavy metals on marine ecosystem of the Gulf of Kachchh, information obtained from geochemical characterization could be useful to develop effective management strategies to policy-makers and stake-holders.

Keywords Heavy metals · Sediment pollution · Gulf of kachchh · geochemical characterization · Pollution indices

Introduction

Due to aggressive industrialization and urbanization, coastal and estuarine regions are contaminated by persistent pollutants viz. polycyclic aromatic hydrocarbons (PAHs) (Dudhagara et al. 2016a,b; Rajpara et al. 2017; Gosai et al. 2018b,c; Sachaniya et al.2019), polychlorinated biphenyls (PCB) (Gosai et al. 2018a, b), and heavy metals (Zhu et al. 2011; Gosai et al. 2018c; Panseriya et al. 2019) leading towards reduced fertility in marine environment. Almost all heavy metals are a major threat to marine ecosystem because of their carcinogenic and mutagenic properties (Kim et al. 2015; Morales et al. 2016). Sediments play a key role in the transmission and deposition of heavy metals in marine ecosystem (Singh et al. 2005). Sediments are central carriers of heavy metals, acting as source and sink which are further diverted to hydrological cycle of marine ecosystem (Wu et al. 2014). Apart from sediments, heavy metals are also associated with water column phase that transforms them into hydrous iron, manganese oxides, sulphides, organic compounds and clay minerals. Thus, distribution and accumulation of heavy metals depend on their source, biochemical characteristics of the environment, geology of the location and physical transportation (Bastami et al. 2012; Tang et al. 2014; Kang et al. 2017).

Heavy metal contamination can alter valuable natural resources. These alterations lead to adverse effects on marine biota and human health. WHO (2004) surveyed cancer risk to humans through heavy metal contamination in developing and developed countries near the coastal region impacted with extensive industrialization (Steinnes et al. 1989; Zhang et al. 2007; Nedia et al. 2010; Vandieken et al. 2012). Above a threshold concentration, depending on the type of metal, animal species and environment, heavy metals are toxic to aquatic life (Sharifuzzaman et al. 2016). Toxicity of heavy

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metals considered to be harmful to marine biota is in the order Hg, Cd, Ni, Pb, Cu and Cr (Long et al. 1995; Freije 2015). Presence of heavy metals in tissues of aquatic organisms as fish, planktons, molluscs and algae inhabiting coastal areas has also been reported (Hossain and Khan 2001; de Mora et al. 2004; Naser 2013; Freije 2015). Bioaccumulation of heavy metals in marine organisms contributes to genetic damage by inducing double-strand breaks in DNA and inhibits critical proteins in DNA repair pathways (Kennish et al. 1996; Morales et al. 2016). Additionally, in benthic organisms, bioaccumulation eventually affects human health through the food chain (Jafarabadi et al. 2017). Many researchers have also documented that excessive bioaccumulation of heavy metals leads to health-related problems as infertility, problematic reproduction, damaged kidney, slow growth in developmental stages, organ deformities, abnormal behaviour, cancer, heart problem, nervous system disorder and liver diseases in aquatic and human populations (Li et al. 2014; Sfakianakis et al. 2015; Kamunda et al. 2016; Junaid et al. 2017; Tepanosyan et al. 2017).

Gulf of Kachchh is a unique marine ecosystem with the presence of corals. The Gulf is interspersed with large and small ports having various industries along its coastline. The central part of Gulf include about 37 large- and medium-scale industries having plants such as cement, fertilizers, woollen cloth, petrochemicals, oil refineries, solvents, bauxite, soda-ash and caustic soda. In addition, these industries are the major contributors of chemical effluents and inorganic waste released into the Gulf. Similar scenario has also been observed at Okha, western part of Gulf where eight large- and medium-scale industries such as metallurgical, agro-based, mineral-based and chemical industries are located. Land mining activities near Pindara (western part of Gulf) also are a major influencing factor for sediment contamination (MSME 2016–2017). Various locations at Gulf of Kachchh are relatively unexplored in context to heavy metal contamination. Few scientists have reported contamination of heavy metals at these sites. Chakraborty et al. (2014) reported Cd as the most abundantly found heavy metal at Sikka and Vadinar area (central Gulf). High concentrations of Cu and Cd in sediments of Gulf of Kachchh have been also reported by Kumar et al. (2015). However, there is dearth of research on the distribution, speciation and ecological risk assessment of heavy metals at the Gulf of Kachchh.

The current study was implemented with an aim to observe chemometric footprints in the surface sediment at Gulf of Kachchh. The main objectives of the present study were (i) assessment of heavy metal concentrations (ii) their distribution and speciation using hierarchical cluster analysis (HCA) (iii) determination of sediment quality using pollution indices such as contamination factor (CF), pollution load index (PLI) and degree of contamination (D_c) at various stations of Gulf of Kachchh. To the authors' best knowledge, this study may probably be considered as the first ever geochemical exploration to examine the potential risk assessment of heavy metals at the Gulf of Kachchh. The results of this study can be a meaningful reference in providing baseline information on heavy metal speciation, sediment quality determination and their risk on population inhabiting the coastal sediments.

Materials and methods

Study area and sampling strategies

The study area is located at latitude and longitude 22–23° N and 69° 90′–70° 45′ E as depicted in Fig. 1. It borders South Gulf covering Dwarka, Jamnagar and Rajkot districts. The locations considered for the study were Okha, Gopi, Pindara, Dhani, Salaya, Narara1, Narara2, Sikka, Rozi, and Jodiya. A random sampling technique was employed for the collection of sediments from the inter-tidal regions of mangroves during Nov, 2016. Three sediment samples at a distance of 500 m each were collected from each sampling station to obtain an overall representation of the contamination level at the sites (Kujawinski et al. 2011). Each sample from the corresponding station comprised of three pooled samples collected at a distance of 250 m each. Marine sediment samples were collected in polyethylene bags using clean plastic scoops. These samples were preserved in an ice box and transferred to the laboratory for further analysis.

Estimation of heavy metals concentration

For estimation of heavy metal concentration, collected sediment samples were dried at 105 °C for 3 h. Digestion was carried out using 0.5 g of sediment and heating with 12-mL aqua regia consisting of a 3:1 ratio of hydrochloric and nitric acids for 45 min which was then evaporated to dryness. To this hot residue, 2.5 mL of concentrated hydrochloric acid and 2.5 mL of hydrogen peroxide were added, followed by dilution to 50 mL with distilled water. The digested samples were filtered through 0.22 μm membrane filter and subjected to estimation of heavy metal concentration using inductively coupled plasma spectrophotometer (ICP, Perkin Elmer). Mean concentrations of heavy metals were used for further statistical analysis. Experimental data were analysed using Minitab Version 17. Unless otherwise mentioned, the experiments were conducted in triplicates.

Speciation of heavy metals

The sampling stations were dispersed around 150 km. Therefore, HCA was used to quantitatively identify specific areas

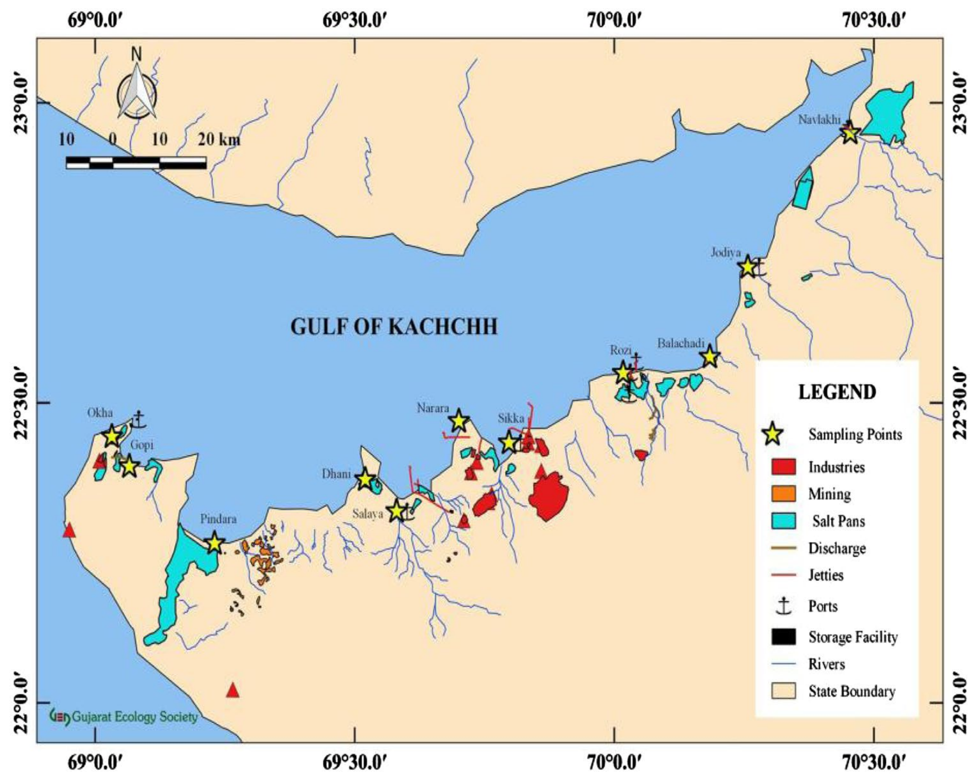

Fig. 1 Study area and sampling sites

of heavy metal contamination. HCA was performed using the mean concentration of individual heavy metals to determine their similarity along with various sampling stations. HCA was carried out using squared Euclidean distance method (Idris 2008; Tang et al. 2014).

Pollution indices

Pollution indices are valuable tools to determine sediment quality of contaminated regions. Indices used were contamination factor (CF), pollution load index (PLI), and degree of contamination (D_c) to examine heavy metal pollution in the sediment at the sites (Maanan et al. 2015; Begy et al. 2016; Gu et al. 2016; Guan et al. 2016; Jafarabadi et al.2017).

CF is an indicator used to assess contamination status of the sediment in an aquatic ecosystem. CF is defined as the ratio of analyzed heavy metal concentration (C_n) and its background value (B_n) (Kamunda et al. 2016). CF was computed as per Eq. 1 (Turekian and Wendepohl 1961).

$$\mathrm{CF}_n = \frac{C_n}{B_n}. \tag{1}$$

PLI is a robust tool to analyze heavy metal contamination. It summarizes different contaminants into a single value, being calculated for each station, and for the whole ecosystem. This index was developed by Tomlinson et al. (1980) for comparative analysis for assessing the level of heavy metal contamination. This index is calculated by the nth root of the CFs as given by Eq. 2 (Hussain et al. 2015; Maanan et al. 2015; Jafarabadi et al. 2017).

$$\mathrm{PLI} = \sqrt[n]{\mathrm{CF}_1 \times \mathrm{CF}_2 \times \mathrm{CF}_3 \times \ldots \times \mathrm{CF}_n} \tag{2}$$

where CF is a contamination factor and n is the number of metals. PLI > 1 is indicative of higher level and < 1 lower level of pollution.

D_c was calculated using summation of CFs of all heavy metals at each station as per Eq. 3 (Laribi et al. 2017).

$$D_c = \sum_{i=1}^{i=n} \mathrm{CF}. \tag{3}$$

$D_c < 7$ indicates low degree of contamination, $7 \le D_c < 14$ moderate degree of contamination, $14 \le D_c < 28$ considerable degree of contamination and $D_c \ge 28$ is indicative of very high degree of contamination.

Potential ecological risk assessment (ERI)

Ecological risk assessment ERI was carried out from sedimentological perspective to investigate the ecological impact of heavy metals in marine ecosystem. E_r has been computed for individual element of each station using Eq. 4 (Maanan et al. 2015).

$$ERI = \sum_{i=1}^{n} E_r^1 = \sum_{i=1}^{n} T_r^1 \times CF, \quad (4)$$

where ERI and E_r indicate sum of all potential ecological risk and monomial risk of individual heavy metal contamination, respectively. T_r and CF represent toxic-response factor and contamination factor, respectively. The toxic response (T_r) values were Cr = 2, Cd = 30, Cu = 5, Pb = 5, Ni = 5, and Hg = 40 as per Hussain et al. (2015). The monomial ecological risk (E_r) for individual heavy metals is classified as < 40 (low ecological risk), $40 \le E_r < 80$ (moderate ecological risk), $80 \le E_r < 160$ (considerable ecological risk), $160 \le E_r > 320$ (high ecological risk), $E_r \ge 320$ (very high ecological risk). ERI values were categorized as 150 < ERI low ecological risk, 150 < ERI < 300 moderate ecological risk, 300 < ERI < 600 considerable ecological risk, ERI > 600 very high ecological risk (Chowdhury and Maiti 2016).

Ecotoxicological significance of heavy metals

U.S. National Oceanic and Atmospheric Administration (NOAA) sediment quality guidelines (SQGs) have also been used to find out ecotoxicological significance of heavy metals in coastal sediments. Ecotoxicological significance has been represented as TELs (threshold effect level), PELs (probable effect level), ERL (effect low range) and ERM (effect medium range) as described by Long et al. (1995).

Results and discussion

Estimation of heavy metal concentration

The concentration of heavy metal in the sediments at 10 sampling stations, covering the Gulf of Kachchh is summarized in Table 1. Their concentrations were: Cu 17.83–61.41 μg/g; Ni 11.31–37.43 μg/g, Cr 32.26–67.44 μg/g, Cd 0.01–0.28 μg/g, Pb 7.90–16.40 μg/g and Hg—BD, 0.014 μg/g. Maximum concentration of heavy metals was detected at Pindara, followed by Jodiya and Rozi (Table1). Least concentration was detected at Sikka (Table 1). Elevated concentrations of heavy metals at Pindara may be due to land mine activities and its geographical location being bay located at the mouth of Gulf of Kachchh (Fig. 1). Also, the effluents of industries located between Jamnagar and Salaya which contain heavy metals are discharged in the muddy area of Pindara leading to their elevated concentrations. Moreover, agriculture run-off of surface sediments from the nearby locations during monsoon also may have led to their elevated concentrations. Domestic waste and effluents of small scale industries are the major contributors to the high concentration of heavy metals at Jodiya. Strikingly, the magnitude of heavy metal concentration at Jodiya reported by Kumar et al. (2015) was higher as compared to the present study. Elevated level of heavy metal contamination at Rozi could be due to anthropogenic activities and release of domestic waste as it is located near Jamnagar city. Moreover, inconsequential contributions of total heavy metal concentrations at most of the sites can be explained by the presence of large-scale industries, release of domestic waste, existence of ports and cup-shaped geographical location of Gulf of Kachchh.

Among heavy metals, mean concentration of Cr was found to be maximum ranging from 32.26 ± 0.35 to

Table 1 Heavy metal concentration (μg/g) in sediments at Gulf of Kachchh during Nov, 2016

Sampling stations	Cu	Ni	Cr	Cd	Pb	Hg
Okha	36.42 ± 1.23	14.43 ± 0.98	64.83 ± 2.12	0.16 ± 0.01	16.40 ± 0.98	0.011 ± 0.00
Gopi	32.21 ± 2.20	25.36 ± 0.49	36.18 ± 1.52	0.06 ± 0.00	8.42 ± 0.56	BDL
Pindara	61.41 ± 3.22	21.72 ± 0.14	58.15 ± 2.00	0.06 ± 0.00	11.63 ± 0.45	0.013 ± 0.00
Dhani	28.35 ± 1.10	16.28 ± 0.25	67.44 ± 2.98	0.28 ± 0.01	10.48 ± 0.23	0.010 ± 0.00
Salaya	53.10 ± 0.99	17.34 ± 0.82	32.26 ± 0.35	0.14 ± 0.01	12.71 ± 0.78	BDL
Narara1	17.83 ± 0.58	18.75 ± 0.65	52.63 ± 0.45	0.01 ± 0.00	12.24 ± 0.82	0.010 ± 0.00
Narara2	19.42 ± 0.42	26.16 ± 0.47	61.59 ± 0.42	0.04 ± 0.01	9.15 ± 0.49	0.010 ± 0.00
Sikka	24.36 ± 0.86	11.31 ± 0.96	38.36 ± 0.38	0.07 ± 0.00	7.90 ± 0.44	BDL
Rozi	59.76 ± 1.43	28.65 ± 0.42	42.32 ± 1.57	0.05 ± 0.00	11.32 ± 0.21	BDL
Jodiya	42.64 ± 1.46	37.43 ± 0.38	54.70 ± 1.17	0.08 ± 0.01	12.80 ± 0.78	0.014 ± 0.00
Standard value	33	56.1	77.2	0.11	19	0.02

Standard value: Sharifuzzaman et al. (2016)

BDL below detected level

67.44 ± 2.98 µg/g of sediments. Maximum concentration of Cr was found at Dhani (67.44 ± 2.98 µg/g), followed by Okha (64.83 ± 2.12 µg/g) and Narara2 (61.59 ± 0.42 µg/g). Least concentration was recorded at Salaya (32.26 ± 0.35 µg/g). Elevated concentration of Cr could be due to the effluent released by the large- and medium-scale industries such as metallurgical, agriculture and chemicals situated along the Gulf of Kachchh (MSME 2016–2017). Also, higher clay content in the sediments could be responsible for the accumulation of Cr (Kumar et al. 2015). In the previous study carried out by NIO (2009), similar pattern has also been reported for Cr.

Apart from Cr, Cu is also a major contributor of heavy metal contamination at most of the sites. The average concentrations of Cu at all the sites ranged from 17.83 ± 0.58 to 61.41 ± 3.22 µg/g of sediments. Maximum concentration of Cu recorded was at Pindara (61.41 ± 3.22 µg/g), followed by Rozi (59.76 ± 1.43 µg/g) and Salaya (53.10 ± 0.99 µg/g). Least concentration was recorded was at Narara1 (17.83 ± 0.58 µg/g). NIO (2009) has also reported Cu content to be in range 12.00–78.00 µg/g in the sediment of Gulf of Kachchh. Despite differences in the geographical locations, the concentrations of Cu remained similar at Salaya and Rozi. Possible reason for similar pattern of Cu concentration could be domestic waste released by manmade activities at the above sites. Moreover, almost all the sites are exposed to domestic waste and inorganic chemical wastes with the presence of old ports (Kumar et al. 2015). Thus, elevated concentration of Cu seems to be logical.

Heavy metal contaminations in the sediment of Gulf of Kachchh were compared with studies reported by researchers from globally (Table 2). Concentrations of most of the heavy metals at Gulf of Kachchh were lower as compared to rest of the coasts. Kumar et al. (2015) have reported decrease in heavy metals concentration during 2014–2016 which could be due to a decrease in anthropogenic activities and flushing out of sediment by hydrodynamic forces. Lower concentration of heavy metals can also be explained by the particle size of the sediments; as the collected samples did not have > 80% sand (Cantillo and O'connor 1992). However, moderate contamination of heavy metals can prove to be harmful to marine biota and subsequently to human health through the food chain, causing serious health impact (Adakole and Abolude 2009; Hussain et al. 2015).

Speciation of heavy metals

Geographical association of heavy metals is mainly restricted to local environmental features, geological processes, and their characteristics. Thus, an examination of the relationship between heavy metal concentration and their geographical location was carried out using hierarchical cluster analysis (HCA). Figure 2 represents HCA for heavy metal concentrations in the sediments at 10 different stations. Geographical associations were roughly clustered based on similarity of heavy metals concentration pattern at 10 stations with two distinct clusters viz., A and B. Cluster A included Okha, Gopi, Dhani, Narara1, Narara2 and Sikka. Okha and Gopi lie at the mouth of Gulf where sediments are influenced by domestic waste whereas, Dhani, Narara1, Narara2 and Sikka are located in the inner region of Gulf that receives treated and untreated effluents. In a study on Sunderbans that receive treated or untreated effluents from the industries and the urban cities of the coastal area also showed higher heavy metal concentration (Aloupi and Angelidis 2001; Micó et al. 2006; Nibo et al. 2010; Chowdhury

Table 2 Comparative global scenario of heavy metals (µg/g) at different coasts

Locations	Cd	Cr	Cu	Ni	Pb	Hg	References
Gulf of Kachchh, India	4.8	163.00	86.00	69.00	20.00	NA	Chakraborty et al. (2014)
Gulf of Kachchh, India	**0.10**	**50.84**	**37.55**	**21.74**	**11.23**	**0.01**	**Present study**
Gulf of Mannar, India	0.16	177	57.00	24.00	16.00	NA	Jonathan et al. (2004)
Coastal Bohai Bay, China	0.22	101.40	38.50	40.70	34.70	NA	Gao and Chen (2012)
Daya Bay, China	0.05	NA	20.80	31.20	45.70	NA	Gao et al. (2010)
Sundarbans Biosphere, India	33.80	NA	1.70	37.31	41.57	NA	Chowdhury and Maiti (2016)
Pearl River Estuary, China	NA	88.97	46.15	41.73	59.26	NA	Zhou et al. (2004)
South East Coast, India	6.50	194.80	506.20	38.60	32.30	NA	Raj and Jayaprakash (2008)
Coast of southwestern Taiwan	0.56	73.00	32.00	35.00	44.00	NA	Chen and Kandasamy (2008)
Jiaozhou Bay, China	0.15	NA	27.30	NA	30.90	0.08	Xu et al. (2005)
Western Xiamen Bay, China	0.33	75.00	44.00	37.40	50.00	NA	Wu et al. (2014)
Bay of Bengal, India	0.21	57.00	20.00	30.00	16.00	0.21	Selvaraj et al. (2004)
Izmit Bay, Turkey	4.90	74.30	67.60	NA	102.00	NA	Pekey (2006)
Masan Bay, Korea	1.24	67.10	43.40	28.80	44.00	NA	Hyun et al. (2007)

The values of present study as compared to other studies are shown in bold

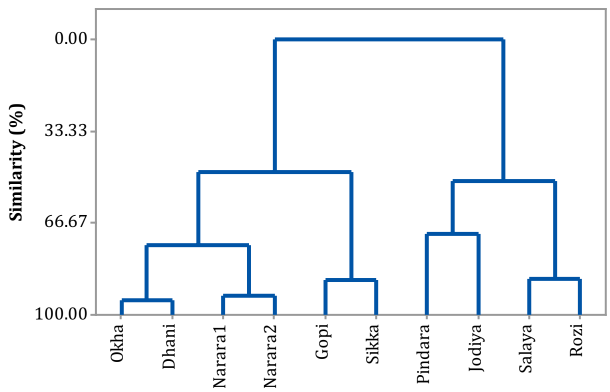

Fig. 2 Hierarchical cluster analysis (HCA) of metal contains stations at the 10 stations

and Maiti 2016). Cluster B include stations Pindara, Salaya, Rozi and Jodiya which were more polluted compared to the sites included in cluster A. Here, Pindara has geographic bay location having open cast and open cut land mining activities. This leads to deposition of heavy metals within the bay with their low flushing out in the open sea. On the other hand, stations Salaya, Rozi and Jodiya lie in a creek with coal unloading and receives domestic and industrial sewage from cities like Salaya, Jamnagar and Jodiya (Kumar et al. 2015). Another possible explanation for heavy metal accumulation in cluster B could be their geographic location. These stations are located at the receiving end due to transportation and deposition of the contaminated sediments from Navlakhi through the water column (Kunte et al. 2005).

Assessment of pollution load using pollution indices

Contamination factor (CF), pollution load index (PLI) and degree of contamination (D_c)

The CF, PLI and D_c, are indicators used widely to assess contamination status of the sediments in the marine ecosystem. Pollution load based on CF is categorized as; CF < 1: low contamination; 1 ≥ CF < 3: moderate contamination; 3 ≥ CF < 6: considerable contamination; CF ≥ 6: very high contamination (Turekian and wendepohl 1961). Results of the present study have shown that the CF values of Cr, Ni, Pb, Cd and Hg in the study area were < 1 indicating low contamination of these metals at the Gulf of Kachchh. However, the values of Cu at Pindara, Salaya and Rozi recorded were 1 ≥ CF < 3 summarizing moderate contamination level (Table 3). Major contribution of Cu is due to reprocessing industries established at Jamnagar GIDC for recycling of copper and brass scraps. Kumar et al. (2015) have reported anthropogenic activity as the major source of heavy metal contamination at the Gulf.

PLI values were in low range (< 1) from 0.24 to 0.50 at all stations indicative of low contamination and hence, the study area can be categorized as unpolluted (Table 3). A higher value of PLI, i.e., 0.50 was recorded at Salaya, which could be attributed due to Cu (CF = 1.18), Cd (CF = 0.49) and Pb (CF = 0.63) detected in the sediments. While in the case of Rozi, PLI value observed was 0.31 also due to the presence of Cu (CF = 1.32) and Pb (CF = 0.56) in sediments. Results indicated that there is a spatial distribution of PLI values and higher values were reported in the central part of Gulf of Kachchh, where pH of the sediment was recorded to be in the range 8.1–8.3 during post-monsoon. Accumulation of heavy metals in sediment might be due to anoxic conditions that become oxidized, precipitated, and carries metals with it (Li et al. 2013). This is a matter of concern as the only Marine National Park on the west coast of India lies in

Table 3 Contamination factor (CF), pollution load index (PLI) and degree of contamination (D_c) at Gulf of Kachchh

Sampling stations	Contamination factor of metal (CF)						PLI value and pollution load		Degree of contamination (D_c)	
	Cu	Ni	Cr	Cd	Pb	Hg				
Okha	0.80	0.21	0.72	0.56	0.82	0.02	0.33	Unpolluted	3.14	Low
Gopi	0.71	0.37	0.40	0.21	0.42	NA	0.39	Unpolluted	2.12	Low
Pindara	1.36	0.31	0.64	0.20	0.58	0.03	0.32	Unpolluted	3.14	Low
Dhani	0.63	0.23	0.74	0.94	0.52	0.03	0.34	Unpolluted	3.12	Low
Salaya	1.18	0.25	0.35	0.49	0.63	NA	0.50	Unpolluted	2.91	Low
Narara1	0.39	0.27	0.58	0.05	0.61	0.02	0.28	Unpolluted	1.94	Low
Narara2	0.43	0.38	0.68	0.13	0.45	0.02	0.24	Unpolluted	2.12	Low
Sikka	0.54	0.16	0.42	0.26	0.39	NA	0.33	Unpolluted	1.78	Low
Rozi	1.32	0.42	0.47	0.19	0.56	NA	0.31	Unpolluted	2.98	Low
Jodiya	0.94	0.55	0.60	0.27	0.64	0.03	0.35	Unpolluted	3.05	Low

the Gulf of Kachchh and has good coral diversity. The PLI provided a clear view of the less hazardous effect of heavy metals on coastal area and ecosystem compared with previous studies (Chakraborty et al. 2014; Kumar et al. 2015). D_c values at each station were observed to be < 7also indicative of a low level of Dc.

Potential ecological risk index (ERI)

The potential ecological risk index is used to evaluate ecological risk of individual heavy metal and their cumulative impact.

Table 4 indicates the results of spatial trends of individual heavy metal summarized as $E_r < 40$ at all stations indicating low impact of ecological risk. E_r value of heavy metal Cd was found to be 28.40, 16.80 and 14.70 at stations Dhani, Okha and Salaya, respectively. Cd contamination at Okha could be due to heavy domestic as well as minimal industrial wastes, whereas at stations Dhani and Salaya, it could be due to discharge of paint and fuel for boat, transportation of metalloid components, agricultural and domestic wastes of Salaya city and near areas, indicating comparative higher heavy metal accumulation at these stations. Luo et al. (2010) reported that higher concentration of Cd leads to inhibition of photosynthesis in the marine diatom *Phaeodactylum tricornutum* by inhibition of diatoxanthin epoxidation to diadinoxanthin in the xanthophyll cycle. Generally, heavy metal toxicity is related to oxidative stress induced in living systems and promotes oxidative damage (Luo et al. 2010). E_r of Cd was found in a range of 1.6–8.3 suggesting low value in five of the sampled stations as compared to other three stations viz., Okha, Salaya and Dhani. However, rest of heavy metals (Pb, Cr, Cu, Ni and Hg) apparently showed less potential ecological impact on living biota as E_r value of individual heavy metals at every station is 1–7 for Cu, 1–3 for Ni, 0–2 for Cr, 1–5 for Pb and 0–2 for Hg. The trend of E_r in the study area for heavy metals in the environment is in the order of Cd > Cu > Pb > Ni > Hg > Cr.

Present study also evaluates potential ecological risk index (ERI) for each station. The ERI indicates the cumulative impact of heavy metals on ecosystem. ERI is used to evaluate the ecological risk degrees for toxic heavy metals in soils (Hussain et al. 2015). ERI values were calculated by summation of E_r values of all heavy metals for the station or zone. ERI for cumulative heavy metal was observed < 150 indicating low level of risk due to heavy metals in the Gulf of Kachchh. Comparative study between stations revealed ERI at Dhani (ERI = 38.12) followed by Okha (ERI = 28.53) and Salaya (ERI = 25.76), indicating high ERI values compared to the other study stations. High ERI of these three stations was mainly due to high agriculture, industrial and domestic wastes of heavy metals accumulation in sediment. Both stations Dhani and Salaya are located near marine sanctuary and marine national park, where corals, fishes and other type of biodiversity are present indicating no harsh impact on these biota. However, ERI results at other seven stations were < 21 which indicates no potential ecological risk on marine biota due to low contamination and less accumulation of heavy metals in sediment. ERI also indicates that the pollution level is controlled and monitored by responsible authorities.

Ecotoxicological significance of metal concentrations in sediments

Concentrations of heavy metals were evaluated for ecological risk assessment, by comparing sediment quality guidelines (SQGs) such as TELs (threshold effect level) and PELs (probable effect level), ERL (effect low range) and ERM (effect medium range). A low-range value of heavy metal concentration than the ERLs and TELs indicates adverse effects on environment. In contrast, the ERMs and PELs above concentrations of heavy metal indicate adverse effect is likely to occur. The US NOAA guidelines provide two values for each heavy metal, classifying the sediment either

Table 4 Potential ecological risk index (ERI) at Gulf of Kachchh

Sampling stations	Risk assessment by individual heavy metal (E_r)						ERI	ERI grade
	Cu	Ni	Cr	Cd	Pb	Hg		
Okha	4.04	1.06	1.44	16.80	4.10	1.08	28.53	Low risk
Gopi	3.57	1.86	0.80	6.40	2.10	NA	14.75	Low risk
Pindara	6.82	1.59	1.29	6.10	2.9	1.34	20.06	Low risk
Dhani	3.15	1.19	1.49	28.40	2.62	1.26	38.12	Low risk
Salaya	5.90	1.27	0.71	14.70	3.17	NA	25.76	Low risk
Narara1	1.98	1.37	1.16	1.60	3.06	1.01	10.20	Low risk
Narara2	2.15	1.92	1.36	4.10	2.28	1.17	13.01	Low risk
Sikka	2.70	0.83	0.85	7.80	1.97	NA	14.16	Low risk
Rozi	6.64	2.10	0.94	5.90	2.83	NA	18.41	Low risk
Jodiya	4.73	2.75	1.21	8.30	3.20	1.46	21.67	Low risk

Table 5 Sediment quality guidelines (SQGs) for trace metals as per Long et al. (1995)

Heavy metals	Average HM concentration (mg/kg)	TEL	PEL	ERL	ERM
Cu	37.55	18.70	110.00	34.00	270.00
Cr	50.84	52.30	160.00	81.00	370.00
Cd	0.10	0.68	4.20	1.20	9.60
Pb	11.23	30.20	110.00	46.70	218.00
Ni	21.74	15.90	43.00	20.90	51.60
Hg	0.01	0.174	0.48	0.15	0.71

HM heavy metal, *TEL* threshold effect level, *PEL* probable effect level, *ERL* effect low range, *ERM* effect medium range

rarely (< ERL), occasionally (≥ ERL and < ERM) or frequently (≥ ERM) associated with adverse biological effects (WHO 2004).

The SQG values for heavy metals based on these guidelines are shown in Table 5. The results based on concentration of heavy metals in the sediment samples and the SQG suggest that Cd, Pb and Hg in sediments would rarely be expected to cause adverse effects on biota. Only a small percentage of sediments would be classified as possibly presenting an occasional threat to organisms due to concentrations of Cu which is found to be between TEL-PET and ERL-ERM. Study sites near the cities would be expected to be occasionally associated with adverse biological effects. None of the heavy metals exceeded either ERM or PEL values indicating no adverse biological effects. However, concentrations of two metals Cu and Ni in sediment samples exceeded the TEL value indicating occasionally adverse biological effects. Cr was also less than TEL and ERL indicating a rare adverse a biological effect in the environment. Overall, results revealed that low contamination of heavy metals were found in the study area as per SQGs.

Conclusion

The present study is the first comprehensive geochemical exploration of the entire Gulf of Kachchh to assess the heavy metals concentration, sediment quality and their ecological risk in the coastal sediments. The impact of heavy metals pollution at Gulf of Kachchh was evaluated using HCA, pollution indices CF, PLI and D_c for toxic heavy metals. Generally, the mean concentrations of six heavy metals were in the following order: Cr > Cu > Ni > Pb > Cd > Hg. HCA revealed heavy metals contamination pattern between the geographical locations indicative of sediment quality similarities between each site. The results of pollution indices, ERI and ecotoxicological significance revealed lower sediment contamination of heavy metals at Gulf of Kachchh. Taken together, these results indicate that Cu and Cd have become a major environmental problem in future for the ecosystem of the entire Gulf of Kachchh. Various researchers stated that heavy metals such as Cu and Cd were transferred from sediment to water and accumulate in the food chain which can be directly or indirectly affect human health (Christophoridis et al. 2009; Kumar et al. 2015). Thus, this study can be footprint for future remediation studies to develop policies and strategies for restoration of entire Gulf of Kachchh.

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