Heavy metals fractionation in surface sediments of Gowatr bay-Iran

F. Moore · M. J. Nematollahi · B. Keshavarzi

Abstract In this study, the chemical speciation of heavy metals and their distribution in surface sediments of Gowatr bay, southeast Iran, are investigated. Modified Bureau Commune de Reference of the European Commission (BCR) sequential extraction technique was applied to assess Cu, Pb, Zn, Mn, Ni, Co, Cr, V, and Fe in the four fractions of five surface sediment samples. Calculated contamination factors (C^i_f) indicate considerable to very high degree of contamination for Cu and Cr, and very high degree for Zn and Ni. Maximum contamination degree (C_d) also suggests serious anthropogenic pollution at two sites. The dominance of average concentration of Cu, Pb, Zn, and Mn in non-residual fractions indicates higher ecological risk within Gowatr bay. Conversely, Ni, Co, Cr, Fe, and V mainly exist in residual phase and hence pose no immediate ecological risk. Calculated individual contamination factors (ICFs) indicate the highest risk of Cu, Pb, Zn, and Mn at two investigated sites. Global contamination factor (GCF) reveals that Pasabandar harbor is highly impacted by metal pollutants.

Keywords Heavy metals · Pasabandar harbor · Surface sediment · Fractionation · Gowatr bay

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Introduction

Estuaries and bays are two important environments for many persistent pollutants to accumulate in organisms and bottom sediments. Since the Industrial Revolution, a tremendous amount of toxic pollutants has been discarded into coastal environment, and hence, harbor sediments have become large sinks of heavy metals (Fukue et al. 1999; Turner 2000; Billon et al. 2002; Fan et al. 2002; S. Wang et al. 2010). Therefore, bay sediments are ecologically important components of the marine environment and have been contaminated by inorganic and organic materials (Uluturhan 2010).

Heavy metals because of their toxic effects on life in aquatic system, high enrichment factor, and slow removal rate are generally considered as serious inorganic pollutants (Alloway and Ayres 1997; Fu and Wang 2011). Occurrence of elevated levels of trace metals especially in sediments is a good indicator of man-induced pollution, while high level of heavy metals is often attributed to anthropogenic influences (Bloom and Ayling 1977; Shriadah 1999). Industrial development has brought the risk of heavy metal contamination in coastal zones (Esen et al. 2010). In addition, coastal traffic especially in and close to harbors and repair of marine vessels are also suspected to be responsible for elevated concentration in the upper reaches of harbors (Okoro et al. 2012).

Surficial sediment geochemistry is helpful in assessing pollution accumulation and mobilization of trace elements in the aquatic environment (Holm 1988; Geetha et al. 2008; Chibunda et al. 2010; Ahmad et al. 2010). Sediments, depending on environmental

conditions, can act as either a sink or a source for trace metals in aquatic environments (Salomons and Förstner 1984; Qiu et al. 2011). During sediment transport, trace metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption, and complexation phenomena which affect their behavior and bioavailability. The accumulation of metals from the overlying water to the sediment is dependent on a number of additional environmental factors such as pH, Eh, ionic strength, anthropogenic input, type and concentration of organic and inorganic ligands, and the available surface area for adsorption (Davies et al. 1991). Sediments integrate contaminants over time and are in constant flux with the overlying water column. Analysis of heavy metals in the sediments permits detection of pollutants that are present in low concentrations in the water column (Davies et al. 1991). Furthermore, their distribution in coastal sediments provides a record of the spatial history of pollution in a particular region or ecosystem.

Total metal content usually does not provide sufficient information about mobility, bioavailability, and toxicity of metals (Yuan et al. 2004). It is very imperative to study different forms of heavy metal mobility and bioavailability rather than the total concentration in order to obtain an indication of the bioavailability of metals. Heavy metal properties depend not only on their total concentration but also on the physicochemical form they occur (Davidson et al. 1994), generally described as "speciation" (Ure et al. 1993). The speciation of metals in sediments is therefore a critical factor in assessing the potential environmental impacts. For this reason, classical and modified sequential extraction procedures are commonly applied because they provide information on the fractionation of metals in the different lattices of the solid sample (Margui et al. 2004; Nádaská et al. 2009). The aim of this study is the identification of surficial distribution, bioavailability, and fractionation of heavy metals in the surface sediment samples taken from Gowatr bay.

Study area

Gowatr bay (a part of the Oman sea) in southeast Iran (25° 01′–25° 14′ N, 61° 20′–61° 40′ E), is a semi-closed water body with the average depth of 8.5 m and total surface area of 350 km^2 (Fig. 1), with 30.6 % of it falling in the Iranian territory (western sector) and the rest to Pakistan. Three rivers including Kajou, Nahang, and Bahoukalat discharge into the Iranian sector of Gowatr bay. The bay is a natural reserve with unique ecological values. *Aveccinia marina*, the sole mangrove species in Iran, together with two halophile herbaceous species occupies more than 400.000 ha of Gowatr area. Mangrove muddy flats have a high capacity to retain heavy metals from tidal water, freshwater rivers, and storm water runoff, and they often act as sinks for heavy metals (Tam and Wong 1995).

Geologically, the study area is a part of coastal Makran and dates from late Cretaceous to Holocene (Farhoudi and Karig 1977). The basement is mostly intertidal deposits, alluvial terraces, and alluvial fan deposits including sandstone and conglomerate with shell fragments, and greenish gray gypsiferous and fossiliferous marls. Makran ophiolite upstream of the study area is an important geogenic source supplying heavy metals to Gowatr bay through Bahoukalat river. There are also several shipbuilding, plants along with shrimp, fish, and various fowl breeding farms in Gowatr bay coast that can act as potential anthropogenic sources.

Materials and methods

Sampling, sample treatment, and analysis

In September 2012, sediment samples were collected from 16 sites along with a local background sample (N27) in the Iranian sector of Gowatr bay (Fig. 1). Intertidal and inside water sediments were sampled using clean plastic spoon and Van veen grab, respectively, and then immediately transferred to polyethylene plastic bags and refrigerated. In each station, subsamples were mixed to obtain a composite representative sample. Preliminary treatment of the samples was carried out at the geology lab of Iranian National Institute for Oceanography and Atmospheric Science (INIOAS)– Chabahar research station, and after being transferred to the geochemistry lab at Shiraz University, the samples were air dried and sieved and the size smaller than 63 μm was retained and kept in clean polythene bags for further analysis.

Heavy metal concentrations in sediment samples were determined using inductively coupled plasma–mass spectrometry (ICP-MS, Agilent 7500, Agilent, USA), at the ACME Analytical Laboratories following Aqua Regia Digestion. Total organic matter content was estimated by measuring loss on ignition weight using a
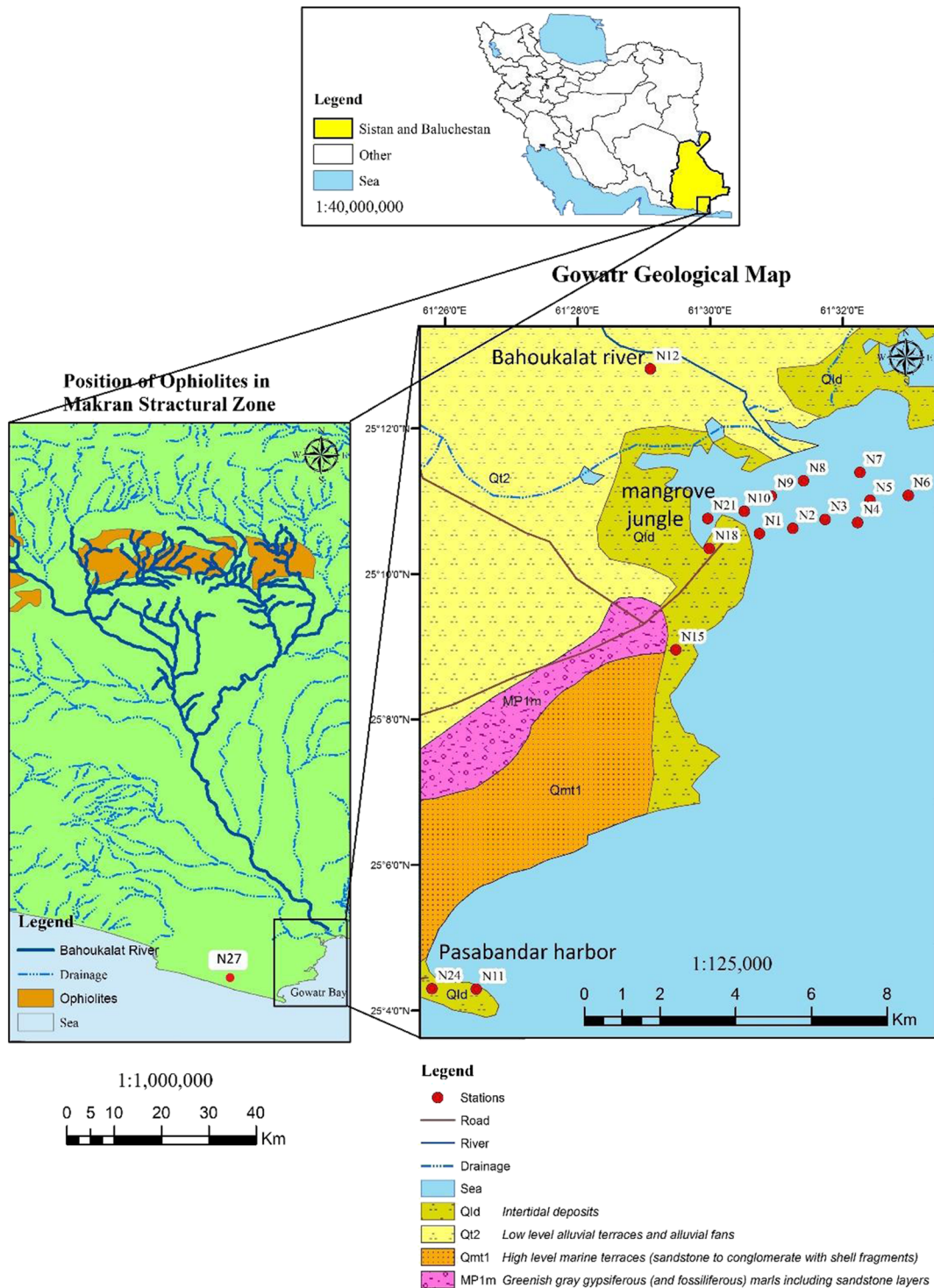
Fig. 1 Map of Gowatr bay and position of sampling sites

high-temperature furnace (Carbolite, Sheffield, UK) at 550 °C for 4 h (Heiri et al. 2001) at geochemistry lab, Shiraz university. pH was measured in situ using a portable pH meter (WTW pH 330i, Germany). The results of heavy metal analysis, pH, and TOC are presented in Table 1.

Table 1 Results of heavy metal analysis, pH, and TOC of Gowatr bay sediment samples

Site	Element and parameters Position	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Co (mg/kg)	Mn (mg/kg)	V (mg/kg)	Cr (mg/kg)	Fe (mg/kg)	S (%)	TOC (%)	pH
N1	Inside Gowatr Bay	19.25	12.37	53.70	77.90	13.60	616.00	29.00	49.50	2.69	0.09	1.90	8.19
N2		19.68	14.76	53.00	78.80	14.10	620.00	29.00	49.60	2.76	0.08	2.87	8.19
N3		23.89	17.74	63.40	91.80	16.60	680.00	35.00	57.20	3.28	0.13	2.40	8.19
N4		25.59	15.58	67.60	95.50	17.00	672.00	34.00	58.30	3.32	0.13	2.78	8.17
N5		16.83	13.22	53.10	74.90	13.20	611.00	30.00	49.40	2.69	0.05	1.49	8.17
N6		17.62	12.67	52.20	77.00	13.90	612.00	29.00	47.30	2.65	0.07	1.96	8.19
N7		20.62	12.80	56.50	84.70	16.10	564.00	36.00	52.40	3.06	0.09	1.94	8.16
N8		15.76	11.65	42.60	66.00	12.10	631.00	32.00	44.50	2.41	0.05	1.92	8.19
N9		17.31	11.84	48.20	70.10	12.40	582.00	34.00	48.00	2.52	0.05	1.20	8.22
N10		30.27	17.69	72.60	102.90	18.60	726.00	36.00	59.10	3.43	0.11	4.15	8.15
N11	Pasabandar harbor	68.17	16.78	113.90	109.40	17.50	496.00	38.00	60.10	3.61	0.35	5.28	8.02
N12	Bahoukalat river	28.29	17.12	66.90	96.90	17.80	619.00	33.00	54.20	3.13	0.05	3.40	7.70
N15	channel of shrimp breeding	23.80	24.70	57.90	87.30	16.50	660.00	30.00	45.40	2.73	0.04	2.21	8.06
N18	Mangrove muddy flats	32.11	24.53	79.90	115.80	19.70	638.00	40.00	64.00	3.80	0.10	3.86	7.32
N21	Mangrove muddy flats	27.95	20.39	68.70	98.50	17.70	674.00	35.00	55.00	3.27	0.10	1.75	7.90
N24	Pasabandar sandy coast	19.71	24.70	41.40	25.00	9.40	467.00	62.00	73.90	2.13	0.09	1.29	8.09
N27	Between Lipar and Beris	4.16	14.66	6.70	10.30	8.60	318.00	17.00	9.40	1.23	0.05		

Sequential extraction technique

It has been demonstrated that metal speciation and solubility have a profound effect on the mobility, bioavailability, and toxicity of metals (Griscom et al. 2000; Yap et al. 2002; Amiard et al. 2007). The most widely used procedures among a long list of procedures using various extraction reagents and experimental conditions to investigate the distribution of heavy metals in sediments and soils, the five-step Tessier et al. (1979) and the six-step Kersten and Förstner (1986) extraction methods, are more favored. Considering the many schemes and diversity of existing procedures and the lack of uniformity in the different protocols used by the various authors, the European countries (EC) Standards, Measurement and Testing Programme launched a project to harmonize measurements of the extractable trace metal content in soils and sediments and also to improve original (three-stage) Bureau Commune de Reference of the European Commission (BCR) procedure (Quevauviller et al. 1994). It harmonized differential extraction schemes for sediment analysis. Modification of three-stage BCR

sequential extraction procedure including changes to the concentration of the reagent and pH of the second step, which has resulted in better precision for the extraction of reducible metals, was carried out (Rauret et al. 2000). Also, the addition of a fourth step, an aqua regia digest on the solid residue remaining after step 3, has provided the opportunity for quality assurance by comparison of the sum of the four BCR steps to an independent aqua regia analysis on a second portion of sample (Rauret et al. 2000).

Hence, in this research, in order to access the mobility and bioavailability of heavy metals, the BCR four-step (modified BCR) sequential extraction scheme (including the residual fraction) was used (Guevara-Riba et al. 2004; Arain et al. 2008; Malferrari et al. 2009; Yan et al. 2010). All extractions were carried out for 16 h (overnight), at room temperature, using a mechanical shaker (Ratek MP4, Australia). The extract was then separated from the solid residue by centrifugation (KUBOTA 5100, Japan) for 20 min, at 3000 rpm, and the resultant supernatant liquid was transferred into a

Table 2 Modified BCR sequential extraction technique scheme

Step	Fraction	Reagents	Volume (ml)	Temperature (°C)	Extraction time
1	Easily exchangeable (bound to clay minerals and carbonates)	0.11 mol/l CH_3COOH	20	22±5	Shaking for 16 h (overnight)
2	Reducible (Fe-Mn)	0.5 mol/l $NH_2OH \cdot HCl$ acidified with 2 mol/l $HNO3$	20	22±5	Shaking for 16 h (overnight)
3		8.8 mol/l H_2O_2	5	22±5	Digest for 1 h (occasional manual shaking)
	Oxidizable (organic matter+sulfides)			85±2	Digest for 1 h
			5	85±2	Digest for 1 h
		1 mol/l NH_4OAc (pH=2)	25	22±5	Shaking for 16 h (overnight)
4	Residual	Aqua regia (ISO 466 protocol)			

polyethylene volumetric flask. The residue was washed by adding 20 ml of deionized water, shaking for 15 min on the end-over-end shaker, and centrifuging for 20 min at 3000 rpm. Subsequently, the supernatant was decanted. The extractant solutions as listed in Table 2 were prepared from analytical grade reagents (Merck, Darmstadt, Germany). Extremely, heavy metals in each sediment fraction were carried to Zar Azma lab-Tehran, Iran, and determined using inductively coupled plasma–optical emission spectrometry (ICP-OES, PerkinElmer Optima 3300, USA).

Quality control

The quality assurance and control were monitored by using blanks and sample duplicates. To preclude uncertain contaminations, all laboratory equipment used was washed with phosphate-free soap, double rinsed with distilled water, and left in 10 % HNO_3 for 24 h. Then, they were rinsed two times with double-distilled water and left semi-closed to dry at room temperature. The recovery of the sequential extraction procedure was accounted as follows:

$$Recovery = [(step 1 + step 2 + step 3 + step 4)/pseudototal] \times 100$$

The recovery rates for heavy metals ranged from 79.40 % for Pb at site N18 to 116.5 % for Cr at site N15 (Table 3).

Results and discussion

Geochemical maps of elements are used to display heavy metal surficial distribution (Fig. 2). It can be seen that the maximum concentration of Cu, Zn, and V, and Cr, Ni, Co, and Fe are related to Pasabandar and mangrove muddy flats, respectively. Also, Mn has the maximum concentration at site N10. Marine traffic, and ship yard activity at and close to Pasabandar harbor and mangrove jungle, along with transported weathered material from ophiolites, are apparently responsible for the observed elevated concentration of heavy metals in Gowatr bay (Moore et al. 2014).

Hakanson (1980) suggested a contamination factor (C_f^i) and the degree of contamination to describe the contamination of a given toxic substance in a basin given by

$$\left(C_f^i\right) = C_{0-1}^i / C_n^i \quad \text{and} \quad C_d = \sum_{j=1}^{P} C_f^i$$

Table 3 Recovery percent of heavy metals in sediment samples of Gowatr bay

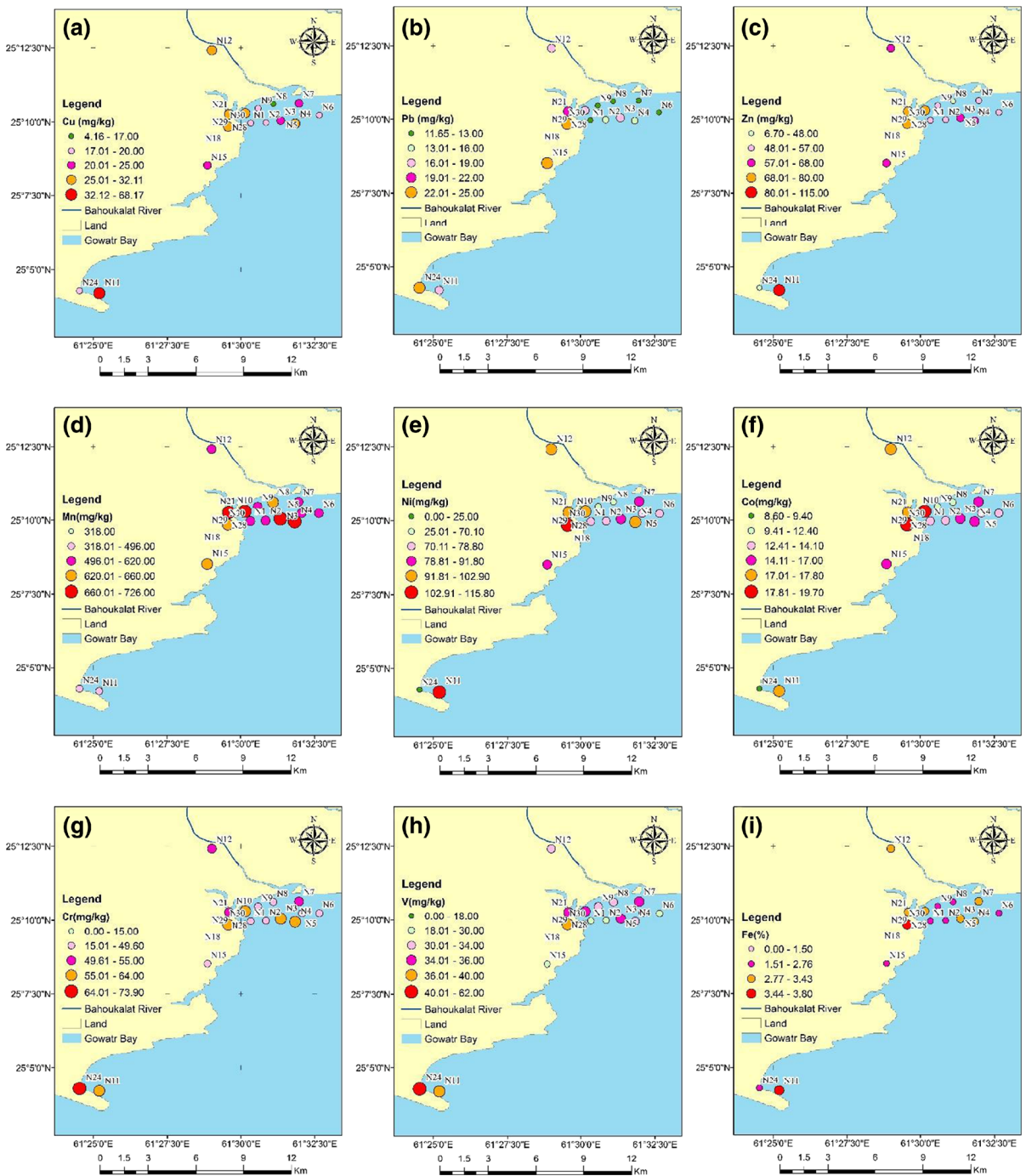| Element	N11	N18	N10	N12	N15
Cu	99.38	99.66	90.00	90.00	88.54
Pb	82.33	79.40	90.42	83.46	80.36
Zn	99.27	108.09	107.88	110.96	96.42
Ni	87.83	88.61	87.25	80.93	92.46
Co	83.70	87.50	85.95	83.25	82.81
Mn	95.94	93.51	93.22	89.44	87.24
V	104.05	107.63	92.86	97.88	91.72
Cr	106.11	106.32	96.40	102.45	116.50
Fe	98.53	93.85	90.07	89.58	83.57

Fig. 2 Schematic maps showing geochemical distribution of **a** Cu, **b** Pb, **c** Zn, **d** Mn, **e** Ni, **f** Co, **g** Cr, **h** V, and **i** Fe in surficial sediments of Gowatr bay

where, C_{0-1}^i is the mean content of the substance from at least five sample sites, and C_n^i is the reference values for the substance. The terminologies in Table 4 are used to describe the contamination factor and the degree of contamination. Heavy metal contamination factors for the sediment samples are indicated as boxplots in Fig. 3. The calculated contamination factor (C_f^i) values of heavy metals for surficial sediment samples of Gowatr

Table 4 Terminologies used to describe the contamination factor and contamination degree

C_f	C_d	Description
$C_f<1$	$C_d<7$	Low degree of contamination
$1<C_f<3$	$7<C_d<14$	Moderate degree of contamination
$3<C_f<6$	$14<C_d<28$	Considerable degree of contamination
$C_f>6$	$C_d>28$	Very high degree of contamination

bay are moderate for Pb, Mn, Co, V (except of site N24), and Fe, considerable to very high for Cu and Cr, and very high for Zn and Ni.

Figure 4 displays the contamination degree (C_d) trend in Gowatr bay. C_d values indicate very high degree of heavy metal contamination at all sites, especially at sites N11 and N18, suggesting serious anthropogenic pollution at these two sites.

Metal speciation in sediments

Since contamination degree values for samples N11, N18, N10, N12, and N15 were relatively high, they were selected for sequential extraction analysis. Fractionation patterns of elements in the bay sediments, based on sequential extraction procedure, are indicated as bar diagrams in Fig. 5.

Exchangeable fraction

It is widely accepted that exchangeable metal in sediments is labile, highly toxic, and the most bioavailable fraction. The results of this study also showed that the exchangeable fraction of Mn accounted for 52.62, 55.29, 67.37, 61.24, and 65.71 % of total Mn content in the sediments at sites N11, N18, N10, N12, and N15, respectively. Manganese concentration in the Earth's crust and carbonatic rocks (950 and 620 mg/kg, respectively) is high (Huheey 1983; Batley 1989; Caplat et al. 2005). With respect to abundance of carbonate pearls and minerals in the bay, elevated percentage of exchangeable Mn is assumed to have derived from these minerals. Furthermore, Mn^{2+} ionic radius is similar to that of Ca^{2+} (0.91 and 1.08 Å, respectively), and with respect to similar charge, ionic potential of Mn^{2+} for substituting Ca^{2+} is high. Mn is generally weakly bound to the surface of carbonate minerals. Hence, Mn may easily be released via ionic exchange and dissociation processes (Tessier et al. 1979; Yuan et al. 2004). On the other hand, only a small amount of other heavy metals was extracted by acetic acid solution, and exchangeable Cu, Pb, Zn, Co, Ni, Cr, V, and Fe are negligible (Fig. 5).

Reducible fraction

Due to the large surface area, amorphous hydrous Fe-Mn oxides are important geochemical phases impacting the mobility and behavior of trace metals (Turner 2000). Large numbers of studies have been conducted to remove organic or inorganic pollutants by utilizing the strong adsorption capacity of hydrous Fe or Mn oxides (L. Wang et al. 1997; Choo and Kang 2003; Root et al. 2007). Due to their chemical characteristics, Fe and Mn extracted by
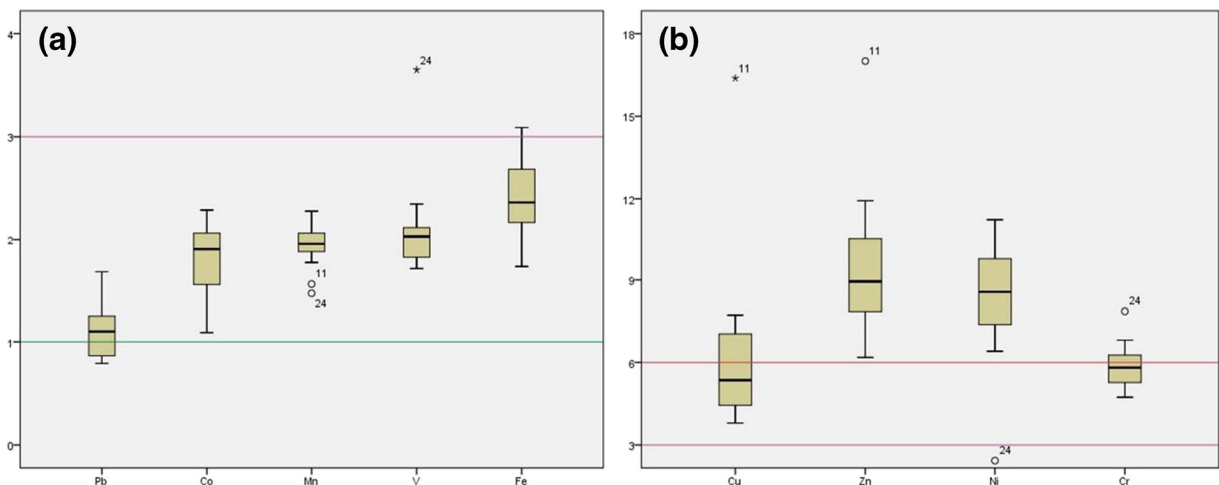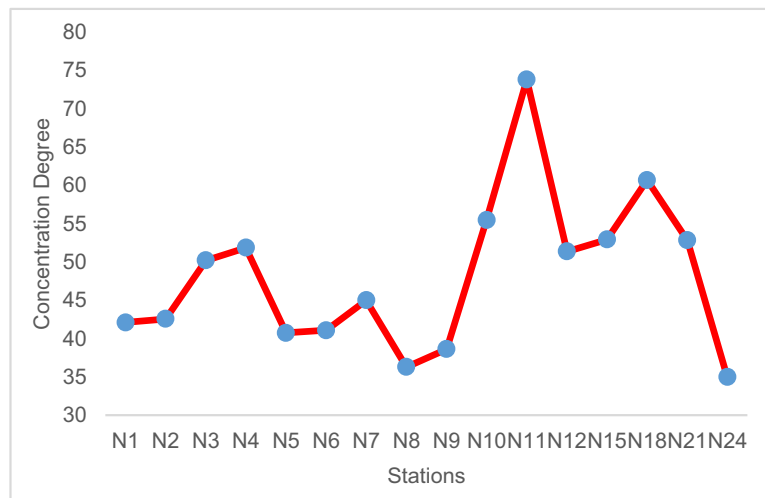

Fig. 3 Boxplots showing **a** Pb, Co, Mn, V, and Fe and **b** Cu, Zn, Ni, and Cr contamination factors at sampling sites

Fig. 4 Trend of contamination degree values at sampling sites

hydroxylamine hydrochloride solution are regarded as amorphous hydrous Fe-Mn oxides in sediments or soils (Gomez Ariza et al. 2000). Our results showed that 37.65–55.11 % of Cu, 33.18–61.45 % of Pb, and 13.84–50.60 % of Zn (averagely 46.29 % of Cu, 42.36 % of Pb, and 23.05 % of Zn) occur as amorphous Fe-Mn oxides in sediments of Gowatr bay. Occurrence of Cu, Pb, and Zn in reducible fraction is considerable at site N11. Occurence of other heavy metals in this fraction is not significant. Cu and Pb adsorption on Fe-Mn oxy-hydroxides surface increases in alkaline pH (Kabata and Pendias 2001). Thus, alkaline pH of Gowatr bay (Table 1) is probably appropriate for Cu and Pb associa-tion in reducible fraction. In polluted sediments, Pb also mostly occurs in reducible and carbonate phases. This suggests that hydrous Fe-Mn oxides may play a major role in controlling the fate and transport of Pb and Cu in the sediments of Gowatr bay. Previous investigations demonstrated that reductive dissolution of iron oxy-hydroxides and subsequent release of adsorbed Pb are potential sources of Pb in porewater (Gallon et al. 2004). Several authors (Hong and Förstner 1984; Szefer et al. 1995; Li et al. 2001; Korfali and Davies 2004) have indicated that Zn is mainly associated with the reducible phase, mostly due to strong binding and formation con-stant of Zn with hydrous Fe-Mn oxides (Korfali and Davies 2004). Zn can be adsorbed on and precipitated with hydrous Fe-Mn oxides. According to Li et al. (2001), Zn also constitutes a multiple oxide like Franklinite through the following reaction:

$$Zn^{2+} + 2Fe^{2+} + H_2O \rightarrow ZnFe_2O_4 + 8H^+$$
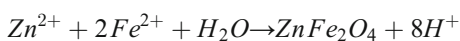
Reducible fraction of sediment at site N11 plays a major role in Pb, Cu, and Zn speciation (Fig. 5). Thus, in anoxic condition, Pb, Cu, and Zn bound to hydrous Fe-Mn oxides may contribute a fraction to interstitial or above water in the bay. Finally, moderate percentage of V at sites N11 (25.97 %) and N18 (20.54 %) was found binding to hydrous Fe-Mn oxides. Other reducible heavy metals were negligible.

Oxidizable fraction

Organic matter and sulfides are important factors that control the mobility and bioavailability of heavy metals. Current opinions differ on the toxicity of heavy metals influenced by organic matters. For example, Höss et al. (2001) proposed that Cd complexation by organic matter, serving as food, might elevate the toxicity of Cd to nem-atode in sediment. In contrast, Besser et al. (2003) suggest that amendments of humus shifting the partitioning of Cd and Cu toward greater concentrations in sediments and lesser concentrations in pore waters reduce the toxicity of Cd and Cu. In the present study, relatively low percentage of metals was found bound to organic matter and sulfides, probably due to relatively low contents of organic matter (1.2–5.28 %) and sulfide (0.04–0.35 %) in the sediments (Table 1). Only moderate amounts of Zn (26.15 and 28.30 % at sites N18 and N10, respectively) and Cu (20.12 % at site N11) were found binding to oxidizable fraction. Maximum concentration of Cu, organic matter, and sulfide at site N11 is also the reason for high percent-age of Cu in oxidizable fraction at this site. Even though
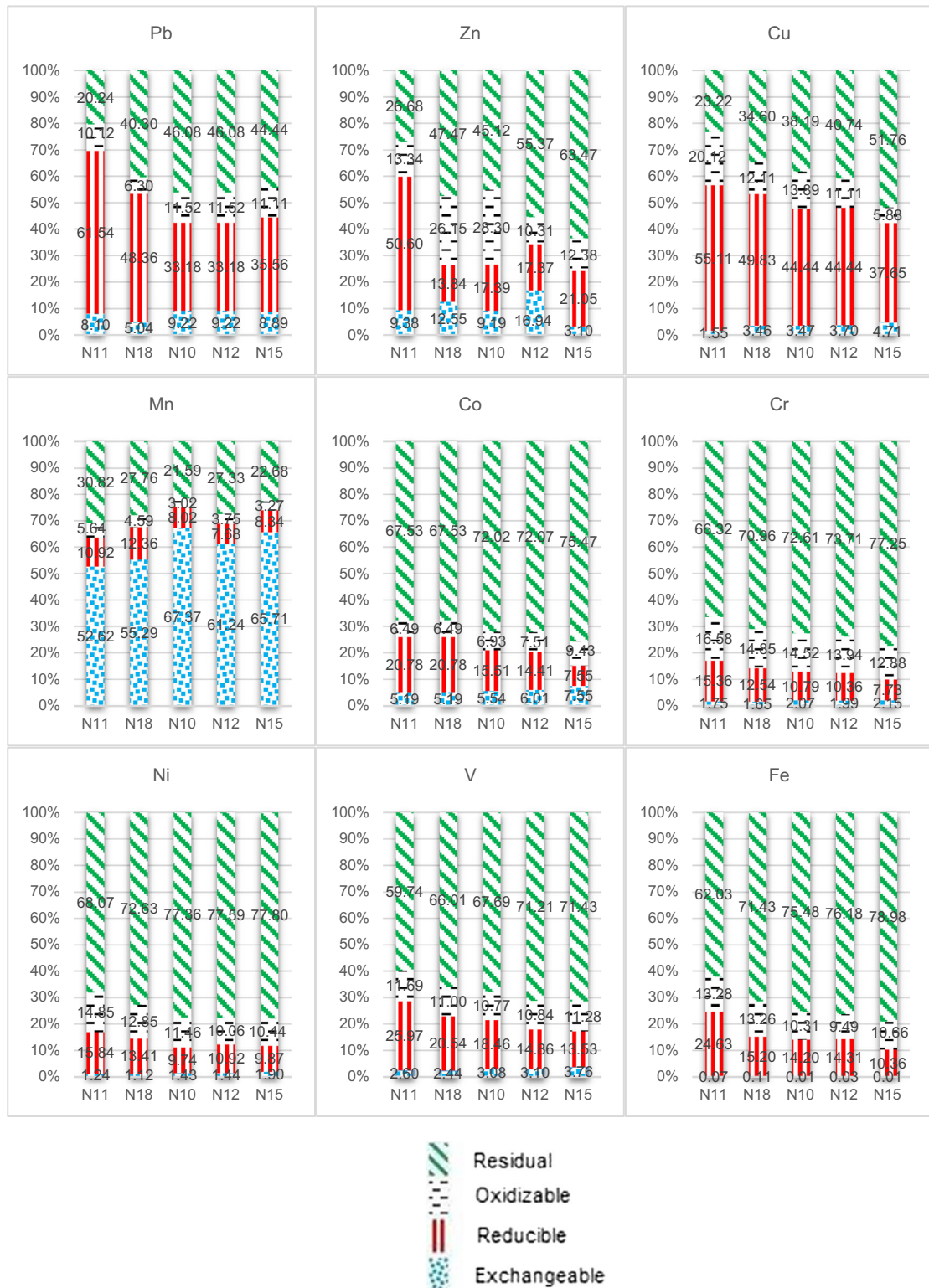
Fig. 5 Percentage of Cu, Pb, Zn, Mn, Ni, Co, Cr, V, and Fe removed in each step of the sequential extraction procedure in the sediments of Iranian sector of Gowatr bay

the aforementioned is not true for Zn at sites N18 and N10, oxidizable fraction in adsorbing Zn is more efficient than reducible fraction. On the whole, low percentage of metals in oxidizable fraction (Fig. 5) indicates that organic matter and sulfide content are not the primary factor impacting the behavior of heavy metals in the study area.

Residual fraction

Residual phases of metals are generally much less toxic for organisms in aquatic environment. In Gowatr bay, dominant fractions of Fe (62.03–78.98 %), V (59.74–

71.43 %), Cr (66.32–77.25 %), Ni (68.07–77.80 %), and Co (67.53–75.47 %) were found residing in residual fraction while Zn at sites N12 and N15, Pb at sites N10, N12, and N15, and Cu at site N15 were dominant (Fig. 5). Apparently, weathering of Makran ophiolites and oceanic crust supplies the above heavy metals.

Heavy metal content relative to other localities

Average total heavy metal concentrations (wt. mg/kg) and average percentages of heavy metals in each sediment fraction are compared with selected similar

Table 5 Heavy metal content (wt%) in different fractions in Gowatr bay compared with that in selected localities in the world

| Location	Fraction	Cu	Pb	Zn	Ni	Co	Mn	V	Cr	Fe
Gowatr bay	1	3.38	8.09	10.23	1.42	5.9	60.45	2.99	1.92	0.05
	2	46.29	42.36	24.05	11.96	15.81	9.46	18.67	11.35	15.74
	3	12.62	10.11	18.1	11.93	7.37	4.06	11.11	14.55	11.4
	4	37.7	39.43	47.62	74.69	70.93	26.04	67.22	72.17	72.82
	Total content	25.43	16.78	61.98	84.53	15.39	616.75	35.13	54.24	2.97
	Non-Residual	62.3	60.57	52.38	25.31	29.07	73.96	32.78	27.83	27.18
East China Sea (Yuan et al. 2004)	1	1.51	0.08	7.46	3.23	4.18	9.54	0.06	0.53	
	2	8.73	40.05	12.59	12.37	58.2	56.22	6.54	2.4	
	3	13.93	26.16	19.89	31.02	17.98	19.72	11.2	17.1	
	4	75.83	33.75	60.05	53.41	19.64	14.52	82.19	79.98	
	Total content	20.13	28.98	52.05	28.65	13.31	945.23	97.93	134.19	
	Non-Residual	24.17	66.29	39.94	46.62	80.36	85.48	17.81	20.02	
Daya bay (Gao et al. 2010)	1	2.36	4.73	1.96	6.12	6.46	48.75			
	2	8.08	32.17	9.65	5.77	13.15	14.93			
	3	5.05	3.13	5.42	10.22	9.45	6.03			
	4	84.13	60.18	82.74	77.88	70.94	30.23			
	Total content	20.8	45.7	113	31.2	12.7	837			
	Non-Residual	15.48	40.02	17.03	22.12	29.06	69.71			
Coast of Kranji, Singapore (Cuong and Obbard 2006)	1	5.5	2.9	12.4	16.2				0.3	
	2	20.6	40	30.7	13.6				6.5	
	3	41.5	1.2	38	15.5				14.3	
	4	32.5	55.9	18.9	54.7				78.9	
	Total content	17.27	26.13	62.12	26.12				47.27	
	Non-Residual	67.6	44.1	81.1	45.3				21.1	
Manchar lake, Pakistan (Arain et al. 2008)	1	15.81	2.32	34.12	12.43				2.45	
	2	46.76	50.51	32.84	40.47				41.42	
	3	20.67	9.7	16.67	17.38				33.87	
	4	16.86	37.68	16.27	29.91				22.17	
	Total content	20.9	19.8	100	21.4				21.2	
	Non-Residual	83.24	62.53	83.63	70.28				77.74	
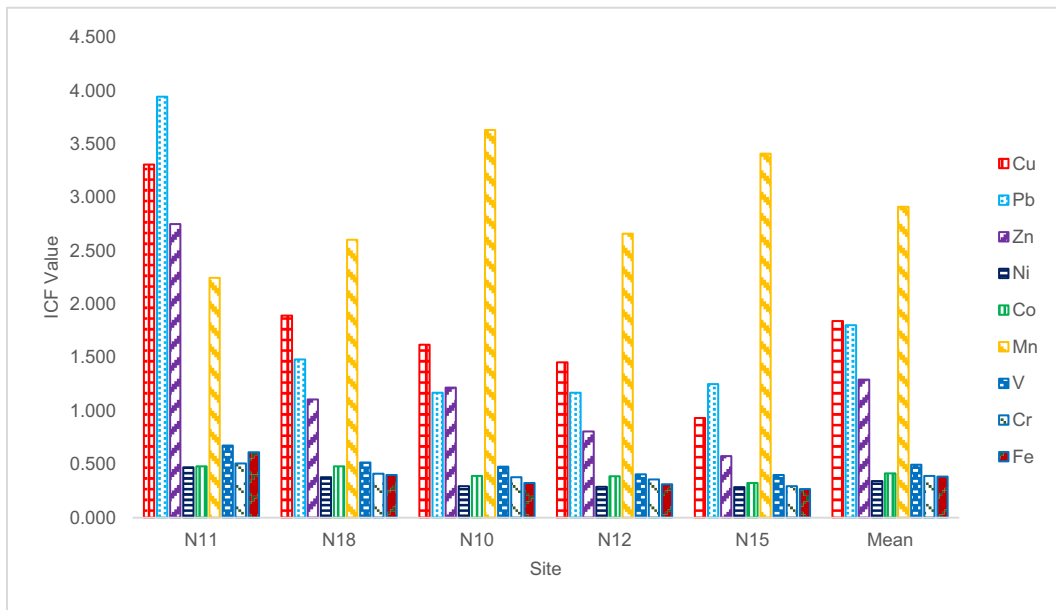
Fig. 6 Bar diagrams indicating individual contamination factor at surficial sediments of Gowatr bay

analyses in the world (Table 5). Average total concentrations of Cu, Ni, and Co of the sediment samples are greater when compare with those of other regions, while Pb content is lower. As well as average total Zn content of sediments is mostly similar to that from the coast of Kranji (Cuong and Obbard 2006). The predominance of Mn in non-residual fractions of the sediment samples obtained from the current study is similar to that from East China Sea (Yuan et al. 2004) and Daya bay (Gao et al. 2010). Cu, Pb, and Zn in

both the study area and Manchar Lake of Pakistan (Arain et al. 2008), Cu and Zn in coast of Kranji, and Pb in East China Sea are mostly found in non-residual fractions of sediments, reflecting high mobility of these metals. The data indicate that fractional distribution of vanadium and chromium in East China Sea, and nickel and cobalt in Daya bay is mainly similar to that in the study area, suggesting the dominance of these heavy metals in residual fraction and hence their immobility.

Fig. 7 Trend of global contamination factor at surficial sediments of Gowatr bay
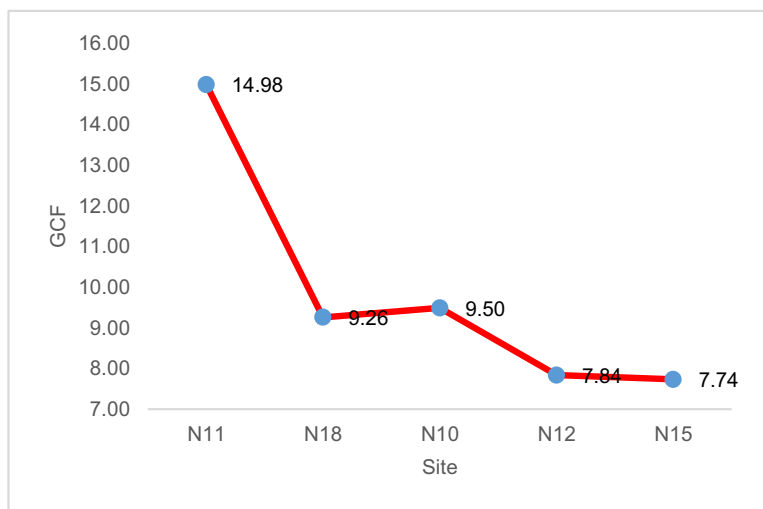
Risk assessment

Individual and global contamination factor

The distribution of metal speciation associated with different geochemical fractions is a critical parameter to assess the potential mobility and bioavailability of heavy metals in sediments. The determination of contamination factor of heavy metals is an important aspect that indicates degree of risk of heavy metals to the environment in relation with its retention time. The individual contamination factors (ICFs) for various sampling sites were calculated from the result of the fractionation study by dividing the sum of the first three extractions (i.e., exchangeable, reducible, and oxidizable-organic forms) by the residual fraction for each site. The global contamination factor (GCF) for each site was calculated by summing the ICFs for heavy metals obtained for a site (Ikem et al. 2003). The ICF and GCF were computed for each station using the following equation:

$$ICF_{\text{metal}} = \frac{C_{\text{non-residual}}}{C_{\text{resistant}}} \quad GCF = \sum_{i=1}^{n} CF_i$$

The individual contamination factors for heavy metals in the surface sediments of the bay are indicated as bar diagrams in Fig. 6. The highest individual contamination factor for Cu, Pb, Zn, Ni, Co, V, Cr, and Fe occurs at site N11, while site N10 indicates the highest ICF for Mn. ICF reflects the risk of contamination of a water body by a pollutant (Ikem et al. 2003). Therefore, the highest risk of heavy metals except for Mn was computed at site N11 and for Mn at site N10. The average individual contamination factors in surface sediment of sampling stations range in the order of Ni (0.343)<Fe (0.383)<Cr (0.389)<Co (0.413)<V (0.494)<Zn (1.292)<Pb (1.802)<Cu (1.840) <Mn (2.909).

The global contamination factor analyzed from ICF values showed that site N11 is highly impacted by metal pollutants (Fig. 7). The tendency of trace metals to accumulate in sediments, contamination from each source tends to be localized in a hotspot near the input, and then disperses regionally in lower concentrations (Luoma et al. 2008). Hence, the results obtained in this investigation revealed that site N11 located at Pasabandar fishing-commercial harbor is a high potential risk to fauna and flora of the Gowatr bay.

Conclusion

The present study indicates that Pasabandar harbor in Gowatr bay is highly impacted by metal pollutants and the highest risk of Cu, Pb, and Zn is seen at this harbor. The results of modified BCR fractionation scheme revealed that Cu and Pb mainly occur in reducible fraction, while Mn mostly occurs in exchangeable fraction. Cu, Pb, Zn, and Mn dominance in non-residual phases poses a higher ecological risk within Gowatr bay. The results of this investigation also revealed that Fe-Mn oxy-hydroxides play a positive role in complexing Cu, Pb, and Zn in the surface sediment of Gowatr bay.

In the northwest Arabian Sea, upwelling occurs each summer by strong southwest monsoon winds. Upwelling areas generally display natural geochemical anomalies. In the process of upwelling, marine deep water rises to the surface, bringing with it dissolved heavy metals and eventually leads to heavy metal accumulation in marine organisms. On the other hand, continuous erosion of Makran ophiolites will also supply Ni, Co, Cr, Fe, and V to Gowatr bay. Thus, in time, geogenic processes together with anthropogenic activity will lead to elevated heavy metal accumulation in the study area. The analytical data of this study indicated that current strategies on Gowatr bay utilization especially in Pasabandar harbor should be reviewed due to poor environmental quality. Total heavy metal content in most sites investigated does not display extreme enrichment in the surface sediments and hence does not pose a serious threat to the local fauna and flora. However, it is recommended to reduce and regulate anthropogenic sources of pollution.

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