Assessment of Mineralogical Composition and Heavy Metal Pollution in the Surface Sediment of North West Persian Gulf

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ABSTRACT: In this study, the mineralogical composition and concentration of heavy metals in surface sediment of North West Persian Gulf (Musa estuary and Hendijan coastline) were investigated. Fifteen sampling sites were selected and the sediment samples were collected using Peterson grab sampler in August 2013. XRD analyses demonstrated that the sediments of study area are principally composed of calcite, quartz and dolomite. The high concentration of calcium carbonate can be derived from limestone and frequency remains of benthic organisms. The metal concentrations compared with values of these metals in the average shale, indicated that all the sampling sites are contaminated with Pb and Ni. The results of enrichment factor and geoaccumulation index demonstrated that at sites 3, 4, 5, 6 (near Emam port and petrochemical plant site), 14 and 15 (adjacent Bahregan port) have high metal concentrations due to anthropogenic activities such as discharge of industrial, agricultural and residential wastewaters and shipping. Based on the average shale contents, the result of EF are more reliable than the Igeo index.

Key words: XRD, Metals, Sediment, Enrichment factor, Geoaccumulation index, Persian Gulf

INTRODUCTION

Sediments are important indicators for assessment of pollution in aquatic environments. In the aquatic ecosystem, most anthropogenic chemicals and waste materials containing toxic organic and inorganic chemicals finally accumulate in sediments (Miller, et al. 2000, Ghrefat *et al.,* 2011). Pollutants such as heavy metals are potentially accumulated in marine sediments and organisms and subsequently transferred to man through the food chain. (Chen *et al.,* 2007, Suresh *et al.,* 2012).Heavy metals enter the aquatic environment through point sources such as industrial, municipal and domestic waste water effluents as well as natural sources which include land runoff, rock weathering, atmospheric deposition and emissions from terrestrial (Balls *et al.,* 1997, Abdolahpur Monikh *et al.,* 2013, Zahra, *et al.,* 2014). Metal content and accumulation sediment are identified as an appropriate bioindicator for estimation the degree of contamination in marine ecosystems (Alahverdi and Savabieasfahani, 2012). Sediments also perform an important role in the remobilization of pollutants in aquatic systems under favorable conditions and in interactions between water and sediment (Ghrefat *et al.,* 2011). Sediments are habitats for many aquatic organisms and also a major repository for many of the dangerous chemicals elements that can migrate back into the water (Feng, *et al.,* 2004, Adekola and Eletta, 2007, 2013). Heavy metals are adsorbed onto organic matter and mineral surfaces in inorganic or organic forms (Wang *et al.,* 2010). The minerals composition in marine sediments can be influenced and changed due to anthropogenic activities. Accumulation and distribution of heavy metals are affected by mineralogical composition, sediment texture, adsorption, desorption processes and different physico-chemical characteristics (Zahra, *et al.,* 2014). In marine environment, high concentrations of metals in sediments are often detected near the industrialized harbors and coastal regions (Wang, *et al.,* 2007). The aims of this study are, (1) to determine and evaluate the mineralogical composition of sediments, (2) to investigate the concentration of heavy metals in surface sediment of Musa estuary and Hendijan coastline.

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MATERIALS & METHODS

The Persian Gulf is shallow basin with an average depth of 30-45 m and a total area of round 240 sq . The Persian Gulf is polluted by several anthropogenic activities such as shipping and tanker traffic, industrial output, fishing and collecting, mining, power plants and agriculture development (Haidari Chaharlang *et al.,* 2012, Abdolahpur Monikh *et al.,* 2013). The turnover and flushing time have been estimated to be in the range of 3–5 year suggesting that contaminants are likely to reside in the Persian Gulf for a considerable time (Pourang *et al.,* 2005). The study area including Musa Estuary and coastline Hendijan is located in the North western of Persian Gulf. Along the coast of Musa Estuary, there are agriculture lands and industrial plants (petrochemical plants, LPG plants, oil transfer docks and cargo ship's ballasts water).

Fifteen sampling sites were selected for assessing mineralogical composition in the study area (Fig.1). The sediment samples were collected using Peterson grab sampler in August 2013. The samples were transported to the laboratory in polyethylene bags and dried at 60 °C. The mineralogical analysis of the sediments was carried out by x-ray diffraction using a Philips PW-1800 diffractometer equipped with a copper cathode, nickel filter and operating at 40 kV and 30 mA. For the measurement of total metal concentrations, 1g of sediment samples were digested with HNO_3, H_2O_2 30% and HCL using USEPA (1996) 3050B method. The metals concentration was measured by inductively coupled plasma atomic emission spectrometry. Total organic matter content was determined by loss on ignition method at 525 °C for 4 h. (Caeiro *et al.,* 2005).

RESULTS & DISCUSSION

The results of mineralogical analysis including major and minor mineral phases in sediment samples from 15 site of study area are represented in Table 1. All the major mineral phases from the XRD results revealed that, the sediments of north western of Persian Gulf contained predominantly calcite. Calcite, Quartz and Dolomite are the dominant minerals respectively in all sediment samples. Albite, Chlorite, Orthoclase, Halite, Montmorillonite and Muscovite-illite minerals are minority components. Calcite and dolomite are derived from limestone. Furthermore, the high concentration of calcium carbonate can be correlated significantly with a high abundance of organisms (benthic foraminifer and Coccolithophores) (Valdes *et al.,* 2005) which indicates that the calcite content in surface sediments is controlled by the abundance of such biogenic debris. All the samples demonstrated approximately similar diffractographs, especially in the major mineral phase, except sites 1, 2, 3 and 9. Fig. 2 depicts 4 different diffractographs. X-ray diffraction peak at $2\theta = 29.406°$, $2\theta = 26.652°$, $2\theta = 30.939°$ and 2θ
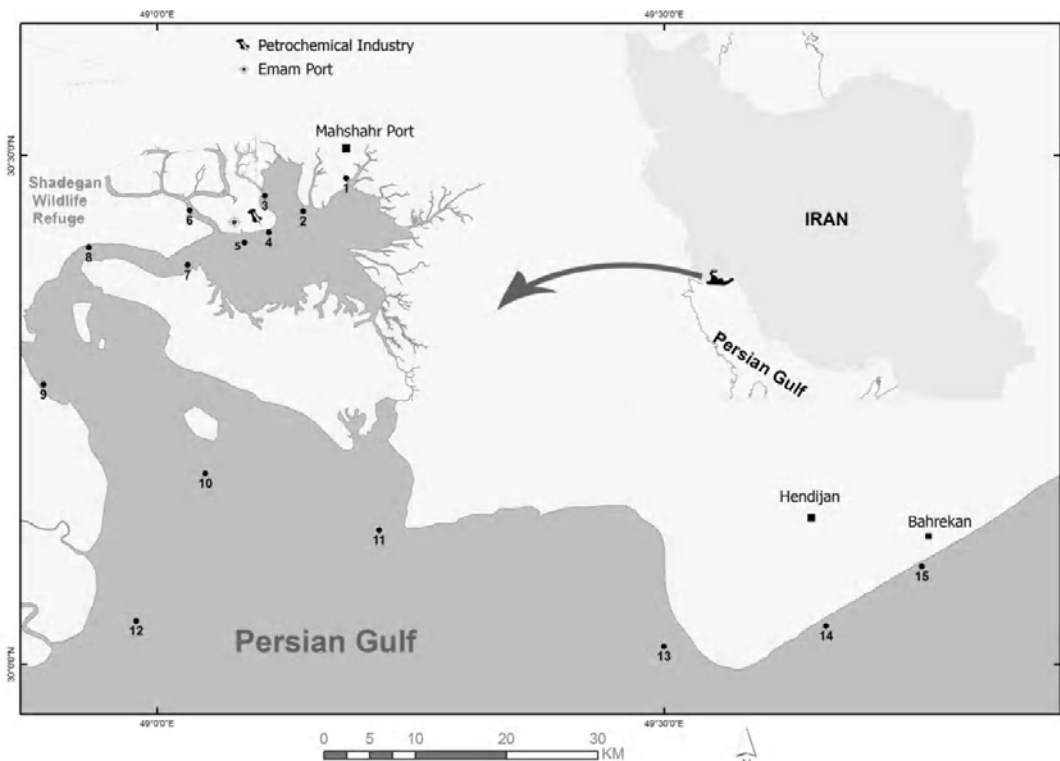

Fig. 1. Map of the study area and sampling sites in the north western of Persian Gulf

Table 1. Major and minor mineral phases in sediments

Sites	Major mineral				Minor mineral			
1	Calcite	Dolomite	Quartz	-	Albite	Microcline	Chlorite	Montmorillonite
2	Calcite	Quartz	-	-	Dolomite	Halite	Chlorite	-
3	Calcite	Quartz	Dolomite	-	Chlorite	Albite	-	-
4	Calcite	Quartz	-	-	Chlorite	Dolomite	Albite	-
5	Calcite	Quartz	Dolomite	-	Chlorite	Microcline	Halite	Albite
6	Calcite	Quartz	-	-	Albite	Dolomite	Chlorite	Halite
7	Calcite	Quartz	Dolomite	-	Albite	Orthoclase	Chlorite	Montmorillonite
8	Calcite	Quartz	Dolomite	-	Albite	Orthoclase	Chlorite	Muscovite-illite
9	Calcite	Quartz	Dolomite	Albite	Muscovite-illite	Chlorite	Halite	-
10	Calcite	Quartz	Dolomite	-	Albite	Orthoclase	Chlorite	Halite
11	Calcite	Quartz	Dolomite	-	Chlorite	Albite	Chlorite	Halite
12	Calcite	Quartz	Dolomite	Albite	Chlorite	Orthoclase	Halite	-
13	Calcite	Quartz	Dolomite	-	Chlorite	Orthoclase	Albite	-
14	Calcite	Quartz	Dolomite	-	Chlorite	Albite	Halite	Orthoclase
15	Calcite	Quartz	Dolomite	-	Chlorite	Albite	Halite	-

=27.893° suggest presence of calcite ($CaCO_3$), quartz (SiO_2), dolomite ($CaMg(CO_3)_2$) and albite ($NaAlSi_3O_8$), respectively. Little peaks at various values of 2θ suggesting the presence of other minerals such Chlorite, Orthoclase, Halite, Montmorillonite and Muscovite-illite and etc.

Total concentrations of metals and total organic matter content in surface sediments for the 15 sites in study area are shown in Table 2.

The metal concentrations in this research compared with values of these metals in the average shale exhibits that approximately all the sampling sites are contaminated with Pb and Ni. The highest concentration of Pb and Ni were detected at location 6 and 4 respectively. The presence of organic matter can potentially increase metal concentrations in sediment by adsorption of metals from surrounding environment onto organic material (Erdogan, 2009). The total organic matter content (TOM) in surface sediments of these 15 sites, ranges between 8.4% and 13.2%, with an average of 10.71%. The relatively high concentration of TOM in sediments of the study area is principally related to the high organic content of bituminous limestone and organisms remains.
The higher concentration of TOM was at the site 4 which might be due to direct discharge of industrial sewage. In general, the highest contents of metals were found around of petrochemical industry zone due to wastewater discharge.

In this study, the geoaccumulation index (Igeo) and enrichment factor (EF) are used to assess the level of contamination in the sediments of study area. The background concentrations of metals in the average shale procured from Turekian and Wedepohl (1961) are used in this study. To recognize irregular metal concentrations, the geochemical normalization of the metal data to a conservative element, such as Al, Fe, or Si, is used (Ghrefat *et al.*, 2011). In this research Fe is defined as the normalization element. The EF is calculated using the following formula,

$$EF = \frac{(C_n/C_{Fe})\ Sample}{(C_n/C_{Fe})\ Background}$$

Where, C_n and C_{Fe} are the concentrations of heavy metal and iron, respectively. The classification of EF value as follows: EF<1 indicates no enrichment, 1–3 is minor, 3–5 is moderate, 5–10 is moderately severe, 10–25 is severe, 25–50 is very severe, and >50 is extremely severe (Acevedo-Figueroa *et al.*, 2006). The Geoaccumulation index (Igeo) was developed by Muller (1969) to evaluate metal pollution. The formula of Igeo is defined as the following:

$$I_{geo} = Log_2\left(\frac{Cn}{Bn \times 1.5}\right)$$

Where Cn is the measure concentration for metal n, Bn is the average shale, and factor 1.5 is used to contain possible variations of the background values due to lithogenic effects (Christophoridis *et al.*, 2009). This index includes 7 classes. (Igeo≤ 0: practically unpolluted;
0 < Igeo < 1: Unpolluted to moderately polluted; 1 < Igeo < 2: Moderately polluted; 2 < Igeo < 3: Moderately
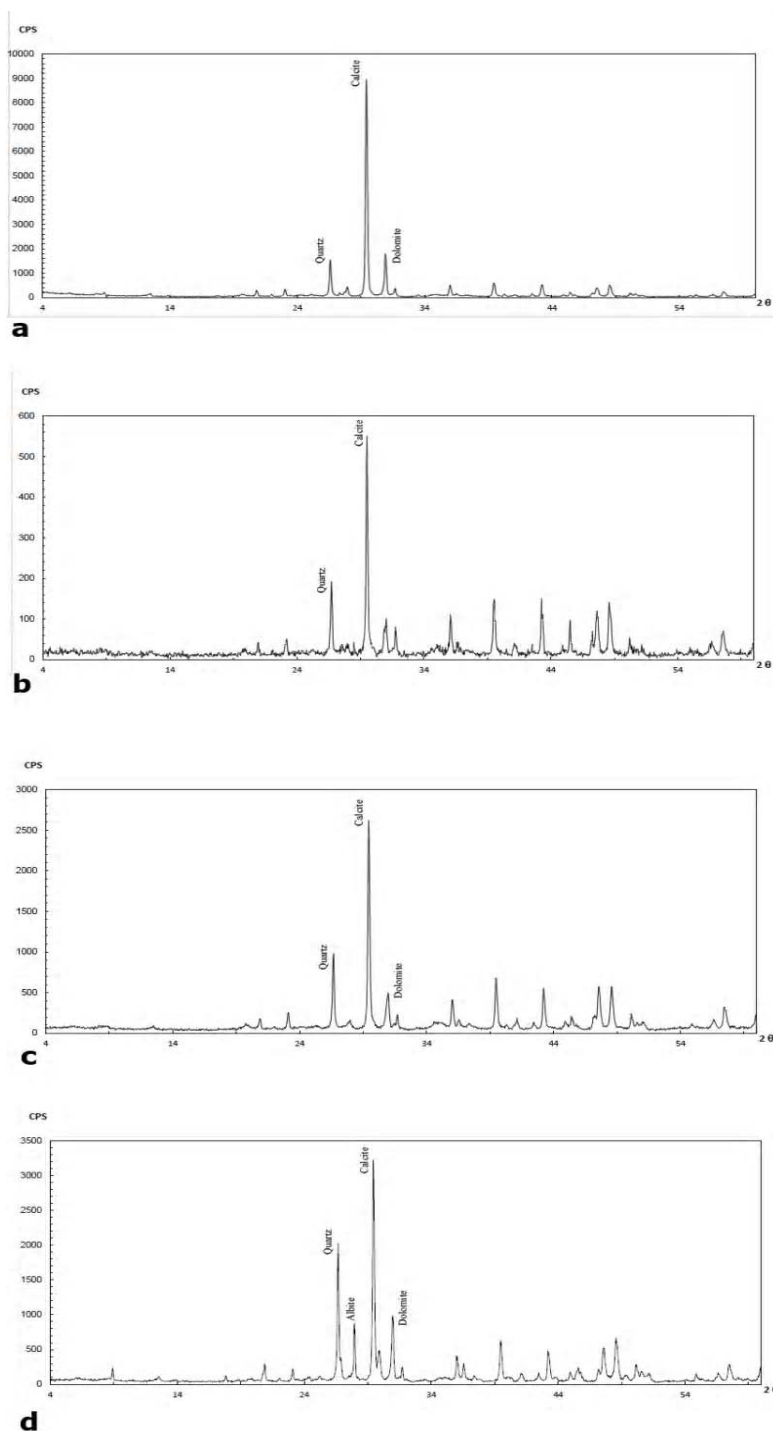
Fig. 2. Result of X-ray diffraction. a): Diffractograph of site 1; b). Diffractograph of site 2; c) Diffractograph of site 3; d) Diffractograph of site 9

to strongly polluted; 3 < Igeo < 4: Strongly polluted; 4 < Igeo < 5: Strongly to extremely strongly polluted; 5 < Igeo: Extremely polluted (Varol, 2011). The results of Igeo and EF values are depicted in Fig 3. According to Zhang and Liu (2000), EF values between 0.05 and 1.5

suggest that the metal is totally from crustal materials or natural processes, while EF values higher than 1.5 indicate that the sources are more likely to be anthropogenic. The EF values of Cu and Zn at all sites are lower than 1.5 and EF values for Ni and Pb at all

Table 2. The results of chemical analysis for metals and TOM contents

| Site	Fe (%)	Cu (mg/kg)	Zn (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	V (mg/kg)	TOM (%)
1	3.2	24.3	58.9	74.5	81.3	40.7	0.28	76.7	11.4
2	3.8	23.5	52.8	81.8	119	45.9	0.64	131	13.3
3	3.9	42.8	72.6	123	134	57.5	1.1	130	12.7
4	4.1	45.8	87.6	132	180	72.5	1.7	193	13.5
5	4.3	45.3	94.2	129	143	74.8	0.97	141	12.6
6	4.4	47.9	98.3	112	178	94.6	1.7	165	13.2
7	3.9	29.8	72.1	97.6	123	38.5	0.65	112	11.3
8	4.0	32.3	69.2	81.2	118	32.0	0.41	109	9.8
9	4.2	35.5	67.4	74.7	132	38.4	0.60	89.2	12.7
10	3.5	32.5	62.9	72.3	96.3	32.5	0.26	95.4	11.0
11	3.3	24.7	57.1	80.1	78.2	23.1	0.23	82.8	10.6
12	4.2	28.2	74.2	86.9	93.6	26.5	0.22	104	12.2
13	3.7	21.8	52.4	70.2	106	35.0	0.32	109	10.6
14	4.1	23.7	55.2	93.3	148	80.1	1.6	118	10.5
15	3.9	29.8	56.5	86.2	136	91.5	2.1	136	11.1
Max	4.4	47.9	98.3	132	180	94.6	2.1	193	13.5
Min	3.2	21.8	52.4	70.2	78.2	23.1	0.22	76.7	9.8
Mean	3.9	32.56	68.76	92.99	124.43	52.24	0.85	119.47	11.77
SD	0.35	9.02	14.78	21.11	30.81	24.23	0.64	31.22	1.18
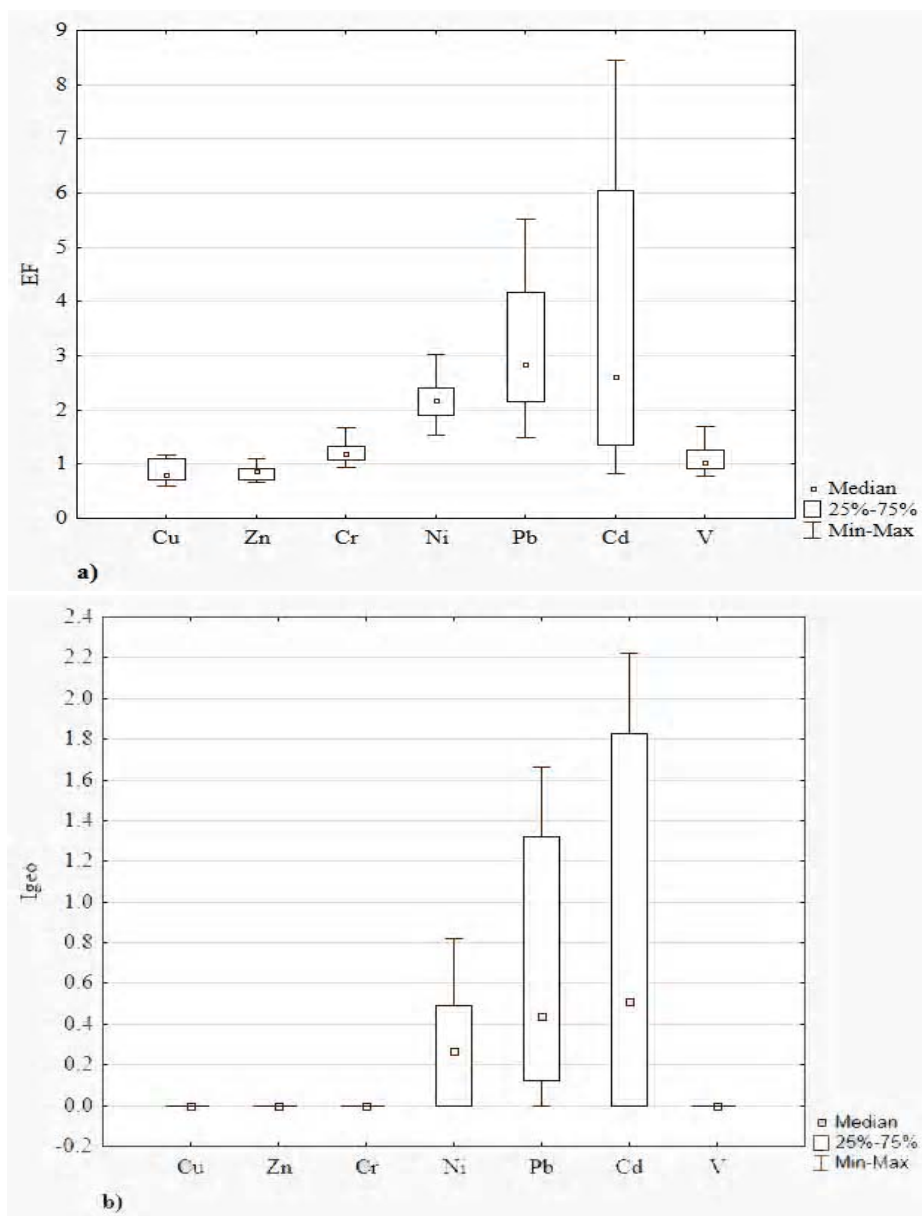
Fig. 3. Results of Enrichment Factors (a) and geoaccumulation index (b)

locations are greater than 1.5, which suggesting anthropogenic impact. The EF content of Ni at site 4 (near the petrochemical industry) is higher than 3, indicating "moderate enrichment" while the EF values for this metal at all sites are between 1 and 3, showing "minor enrichment". The EF values for Pb and Cd in the sediment of sites 6, 14 and 15 are greater than 5, suggesting "moderately severe enrichment". The Igeo values of Cu, Zn, Cr and V at all sites are less than zero indicating that these sites are not polluted by these metals. Among seven metals studied, Pb and Cd have the highest Igeo values. The Igeo values of Pb at

sites 4, 5, 6, 14 and 15, Cd at sites 3, 4, 5, 6, 14 and 15 are greater than 1 indicating that the sediments of these locations are moderately polluted.

In general, the highest EF and Igeo values are calculated at sites 3, 4, 5, 6, 14 and 15 due to wastewater discharges from the anthropogenic activities such as petrochemical industry, tanker traffic and shipping.

CONCLUSION

The investigation of mineralogical composition revealed that calcite, quartz and dolomite are the dominant minerals respectively in all sediment samples of study

area (Musa estuary and coast of Hendijan). The high concentration of calcium carbonate can be derived from limestone as well as frequency remains of benthic organisms. The metal concentrations compared with values of these metals in the average shale, indicated that all the sampling sites are contaminated with Pb and Ni. The results of enrichment factor and geoaccumulation index demonstrated that at sites 3, 4, 5, 6 (near Emam port and petrochemical plant site), 14 and 15 (adjacent Bahregan port) have high metal concentrations due to anthropogenic activities such as discharge of industrial, agricultural and residential wastewaters and shipping. The EF results exhibited that Pb and Cd in the sediment of sites 6, 14 and 15 in the study area are enriched. Based on the average shale contents, the result of EF are more reliable than the Igeo index.

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