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# Fractionation of heavy metals in sediments and assessment of their availability risk: A case study in the northwestern of Persian Gulf

Amirhossein Pejman<sup>a,\*</sup>, Gholamreza Nabi Bidhendi<sup>a</sup>, Mojtaba Ardestani<sup>a</sup>, Mohsen Saeedi<sup>b</sup>, Akbar Baghvand<sup>a</sup>

<sup>a</sup> Graduate Faculty of Environment, University of Tehran, P.O. Box 14155-6135, Tehran, Iran

<sup>b</sup> Environmental Research Laboratory, Department of Water and Environmental Engineering, School of Civil Engineering, Iran University of Science and Technology, P.O. Box 16765-163, Narmak, Tehran, Iran

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## ABSTRACT

Sequential extraction procedure was applied to determine the chemical forms of heavy metals in sediments in order to assess their mobility and availability in the aquatic environment. The mean concentrations of Cr, Ni, Pb, Cd, Cu and Zn in exchangeable and carbonate fractions were 14.9, 30.9, 17, 0.37, 4.4 and 14.4 mg/kg, respectively. Based on the sediments quality guidelines (SQGs), the adverse biological effects caused by Ni, can occur frequently across the study area. Risk assessment code (RAC) suggested that the Cd has the highest level of environmental risk compared with other studied metals. Modified risk assessment code (mRAC) demonstrated a high potential adverse effect in the many of sampling sites. According to the fractionation results, the concentration of Ni in exchangeable and carbonate fractions was very considerable and more than other metals, hence, the potential risk of nickel release can be much more than other investigated metals.

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## 1. Introduction

Sediments are considered as the main repository for many contaminants such as heavy metals in the aquatic environment, (Alonso Castillo et al., 2013) hence analysis of sediments is known an appropriate procedure for monitoring pollution (Suresh et al. 2012). Diffusion of heavy metals within marine and coastal environments can be extremely damaging for marine ecosystem due to their toxicity, persistence in environments, bioaccumulation and entering the food chain (Yang et al. 2014; Zhang et al. 2014; Wang et al. 2015; Pejman et al. 2015). Toxic metals can be released within marine and coastal environments through natural and anthropogenic processes (Carman et al. 2007; Duyusen and Gorkem 2008; Hosono et al. 2010; Nazeer et al. 2014). The activities of industrial, agricultural, urbanization, coastal development, recreation and shipping can be as the major sources of pollution in coastal and marine environments (Alonso Castillo et al., 2013). A serious risk for aquatic environments is the release of accumulated heavy metals in sediments into the overlying water column (Soares et al. 1999; Bastami et al. 2012; Liu et al. 2013; Pejman et al. 2014). This event can occur through alteration of physico-chemical characteristics (Wu et al. 2016; Hamdoun et al. 2015).

The mobility of heavy metals depends on the various factors such as changing pH and redox potential, the amount of organic matter and ion exchange processes (Filgueiras et al. 2004).

Measurement of the total concentration of heavy metals is not sufficient for providing an appropriate evaluation of mobility and availability of metals in aquatic environments (Sundaray et al. 2011). The behavior of metals depends to a great extent on their chemical forms and various geochemical phases in sediments (Passos et al. 2010; Islam et al. 2015). In fact, the most reliable criteria for assessing the mobility and availability of metals, is metal speciation into different fractions. Application of sequential extractions procedures is very beneficial to determine the concentration of metal in different geochemical fractions (Sundaray et al. 2011; Gu et al. 2015).

The proposed indices based on the geochemical fractionation, are as the common tools to assess mobility and availability of heavy metals. The indices such as the risk assessment code (RAC) and modified its (mRAC) are used in this research.

The objectives of this study are: (1) to assess the concentration of heavy metals in different fractions, (2) To evaluate the negative effects of heavy metals on marine organisms using sediment quality guidelines, (3) to investigate the mobility and availability of heavy metals in the marine environment of the study area.

## 2. Materials and methods

### 2.1. Study area

The Persian Gulf is a shallow basin with average depth of 35–40 m and an area of approximately 226,000 km<sup>2</sup> (Mokhtari et al. 2015). Various factors such as limited circulation, shallow depth, high temperature

\* Corresponding author.

E-mail address: [ahpejman@ut.ac.ir](mailto:ahpejman@ut.ac.ir) (A. Pejman).

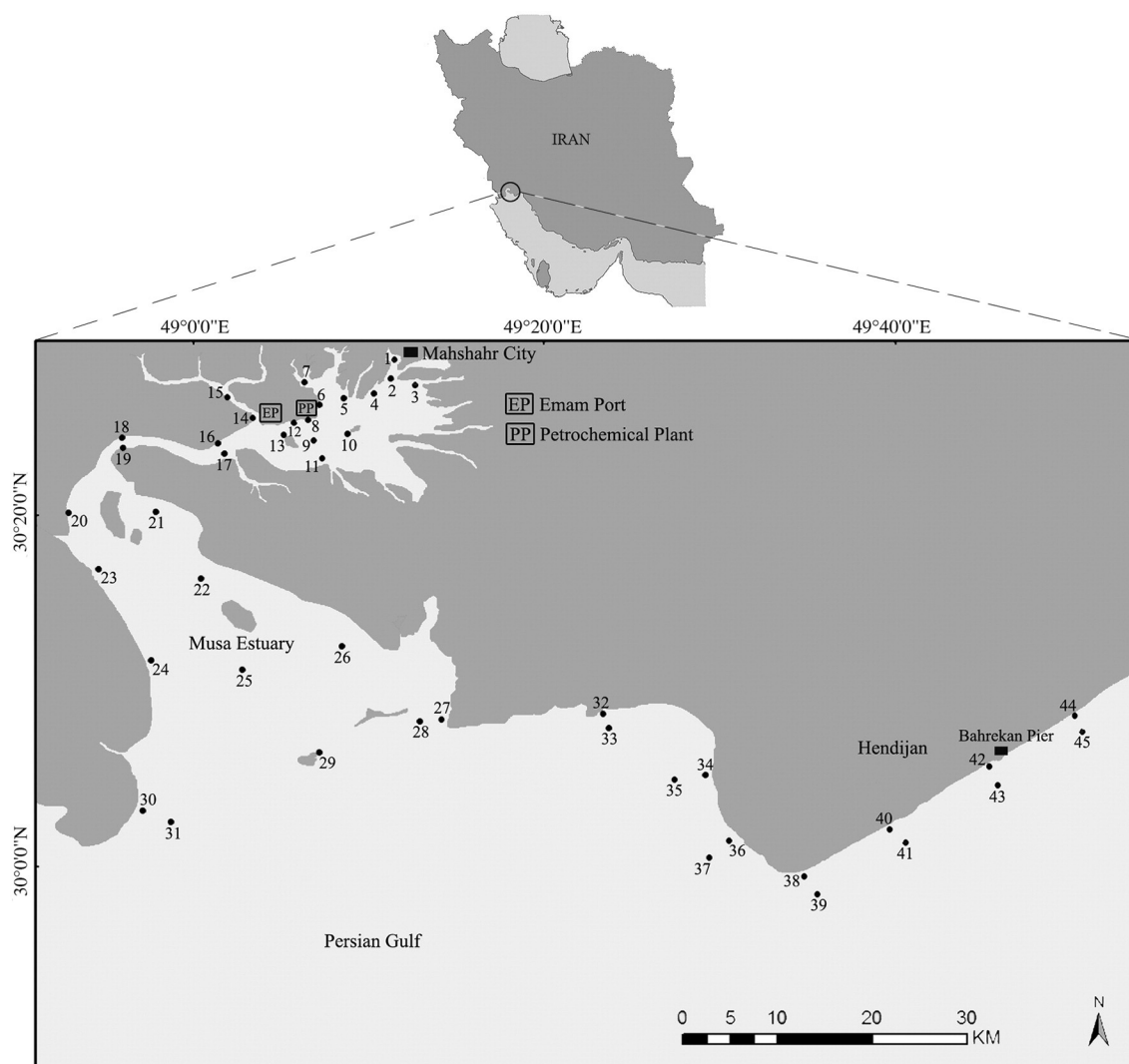


Fig. 1. Map of the study area and location of sampling sites.

and high salinity have caused the pollutants have a relatively long persistence in this region (Kazemi et al. 2012; Fard et al. 2015). The Musa estuary and a part of the Hendijan coast as case study areas are located in the northwest of Persian Gulf. A huge harbor, several piers and various industries such as petrochemical plant are located on the shores of Musa estuary. In the coastal area of Hendijan, the maintenance zone and traffic of fishing boats are considerable. The mentioned regions are privileged habitat for various and unique species of marine creatures (Pejman et al. 2015).

Calcite, Quartz and Dolomite were reported as the dominant minerals in the sediments of study area, according to the results of mineralogical analysis by Pejman et al. (2014). Other minerals such as Albite, Montmorillonite, Chlorite, Muscovite-illite, Orthoclase and Halite were identified as the minority components.

## 2.2. Sample collection

Sampling locations were selected based on the proximity and remoteness of anthropogenic activities (some stations around the industrial zone, harbor and piers and some others far from them). The study area and sampling locations are shown in Fig. 1. Surface sediments samples (top 10 cm) were collected from 45 sampling sites in August 2013, by a Peterson grab sampler. Three subsamples were taken at each station within an area of about 16 m<sup>2</sup> and were mixed

together and finally a composite sample was obtained for each site. Samples were stored into polyethylene bottles and transported to the laboratory under 4 °C.

**Table 1**  
Five-step of fractionation procedure.

Fraction	Extraction procedure
(F1) Exchangeable	8 mL of 1 M MgCl <sub>2</sub> (pH = 7) was added to 1 g sample at room temperature for 1 h with continuous agitation.
(F2) Bound to Carbonates	8 mL of 1 M NaOAc was added to residue from step 1 and adjusted to pH 5.0 with HOAc and continuous agitation for 5 h.
(F3) Bound to Fe-Mn oxides	Residue from step 2 was extracted with 20 mL 0.04 M NH <sub>2</sub> OH·HCl in 25% (v/v) in 25% (v/v) HOAc at 96 ± 3 °C with occasional agitation for 5 h.
(F4) Bound to Organic Matter	3 mL of 0.02 M HNO <sub>3</sub> and 5 mL of 30% H <sub>2</sub> O <sub>2</sub> adjusted to pH 2 with HNO <sub>3</sub> were added to residue from step 3 and the mixture was heated to 85 ± 3 °C for 2 h with occasional agitation. Then 3 mL of 30% H <sub>2</sub> O <sub>2</sub> (pH 2 with HNO <sub>3</sub> ) was added to the mixture and the sample was heated again to 85 ± 3 °C for 3 h. After cooling, 5 mL of 3.2 M NH <sub>4</sub> OAc in 20% (v/v) HNO <sub>3</sub> was added and the sample was diluted to 20 mL and shaken for 30 min.
(F5) Residual	Residue from step 4 was digested with a HF-HClO <sub>4</sub> mixture.

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