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# Geochemical distribution, fractionation and contamination assessment of heavy metals in marine sediments of the Asaluyeh port, Persian Gulf

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## ABSTRACT

In this study, total concentration and speciation of heavy metals in sediments of the Asaluyeh, one of the Iran's largest commercial ports, are investigated. 48 sediment samples were collected and analyzed for trace and major elements. Sediment quality guidelines along with calculated enrichment factors and trace metal profiles indicate that Asaluyeh port is threatened by contamination, especially with respect to Hg and Cu. Normalization to Sc indicated high enrichment factors in the sediments following the decreasing order of: Hg > Cu > As > Ni > Zn > Pb ≈ Cr ≈ Mn > Co ≈ V ≈ Fe ≈ Al. Hg displayed the greatest potential ecological risk factor among sampling stations. The results of sequential extraction procedure revealed that in some stations >50% of Mn, V, Cu and Zn occur in potentially mobile phases and therefore are more readily mobilized in the sediments of the study area.

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## 1. Introduction

Metal contamination in aquatic ecosystems has become a considerable concern due to its toxicity, abundance, and persistence in the environment, and its subsequent accumulation in aquatic habitats (Lin et al., 2013). Heavy metals discharged into an estuarine environment, either by natural or anthropogenic sources, are distributed between the aqueous phase and sediments through adsorption, hydrolysis, and coprecipitation (Gaur et al., 2005). Sediments are important sinks for various pollutants such as heavy metals and also play a useful role in the assessment of metals contamination (Ikem et al., 2003; Moore et al., 2011; Raeisi-Sarasiab et al., 2014). Various studies have demonstrated that sediments from coastal areas are prone to be greatly contaminated by heavy metals (Bellucci et al., 2003; Pekey et al., 2004; Buccolieri et al., 2006; Qiao et al., 2013; Wang et al., 2015); therefore, the evaluation of metal distribution in surface and deep sediments is useful to assess the pollution in the marine environments (Kumar et al., 2013). In addition, metal-contaminated sediments may release metals into the overlying water column and thus pose a risk to aquatic life and ecosystems (Calmano et al., 1990).

Information on the total concentrations of metals alone is not sufficient to assess the environmental impact of polluted sediments, as

heavy metals are present in different chemical forms in sediments, which determine their mobilization capacity and bioavailability (Usero et al., 1998; Filgueiras et al., 2002; Zemberyova et al., 2006; Rao et al., 2008; Keshavarzi et al., 2014). Metals are generally present in a variety of chemical forms in sediments and exhibit different physico-chemical behaviors in terms of chemical interaction, mobility, bioavailability and potential toxicity (Alvarez et al., 2011). Many different sequential extraction schemes have been proposed in literature (Schramel et al., 2000; Kaasalainen and Yli-Halla, 2003; Anju and Banerjee, 2010). The most employed procedure is the European Community Bureau of Reference (BCR) three-step sequential extraction technique which harmonizes the various sequential extraction procedures (Cuong and Obbard, 2006; Yan et al., 2010; Oyeyiola et al., 2011; Moore et al., 2015).

By having one of the highest records of loading and unloading among all Iranian ports, Asaluyeh has become one of the busiest marine areas in the Persian Gulf (Alipour et al., 2014). Accelerated development of urbanization and industrialization and dense maritime activities in the area and the existence of a huge petrochemical industry in the margins of this port may be responsible for the high-level accumulation of pollutants in the region (Alahverdi and Savabieasfahani, 2012). The main objectives of the present study are: (1) to determine spatial variation of potentially toxic trace elements in the Asaluyeh port sediments; (2) to identify probable pollution sources of the sediments; (3) to assess metals bioavailability in the sediments.

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## 2. Materials and methods

### 2.1. Study area

The Persian Gulf is a shallow and semi-enclosed marginal sea resulting from continuous deposition in a once deep basin (Emery, 1956). Asaluyeh port is located in 28°28'24.48" N and 52°36'49.79" E on the edge of the Persian Gulf (Fig. 1). Besides pollution through riverine inputs, the study area has been exposed to various additional contaminants as a consequence of marine accidents and wars in recent years. Population of about 60,000 inhabitants has been settled or is working in Asaluyeh, mostly due to the development of South Pars gas field (Alipour et al., 2014). Natural gas from the South-Pars field is transported to Asaluyeh gas processing plant by pipelines where liquid hydrocarbons are separated. The pattern of water circulation in the Asaluyeh region representing two local stream flows, including west - east and west - southeast (Reynolds, 1993). West-east currents flow along the coast in the depth of less than ten meters; while west - southeast currents flow in the more than ten meters depth. Therefore, any effluent and pollutant that discharges in the shallow waters ( $\leq 10$  m), by west-east flows will be transferred to the Asaluyeh and Nayband coasts. In the case of effluent discharge at depth of more than ten meters, because of west-southeast currents, any pollutant moves to the Oman Sea.

The surrounding geological formations include Kazhdumi, Sarvak, Ilam, Gachsaran and Surgah (Fig. 1). The Kazhdumi Formation lies above the main gas and condensate reservoirs at South Pars. This and its equivalents represent an influx of clastics during the Albian following

emergence and erosion of shallow-water Aptian carbonates. In the South Pars field the Kazhdumi Formation is 40–50 m thick and comprises grey to greenish and brownish shales with occasional marl intercalations. A few sandstone layers occur in the lower parts of the formation in two of the wells studied in the western part of the field (Ghasemi-Nejad et al., 2009).

### 2.2. Sampling and analysis

The studied sites are areas of importance in seaweed harvest and areas close to sources of anthropogenic pollution. Sampling sites were selected considering the morphology of the main channel and location of the urban and industrial discharges. In this study, a total of 48 composite sediment samples were collected in October 2014. In order to obtain bulk composite samples, two individual sub-samples were collected for achieving to ideal weight of sample. Because of the existence of large shells in some stations, more sub-samples were taken. Samples were mixed thoroughly and approximately 2 kg of fresh samples were collected. Locations of sampling sites were recorded using a global positioning system (GPS) and are plotted in Fig. 2 and Table 1. Sediments were collected using a Van Veen stainless steel grab (a cable-operated sediment sampler) from a boat. After each sampling, grab sampler is carefully washed with sea water. Samples were collected from water depth of  $< 1$  m (tidal zone) to a maximum depth of 37 m in the aquatic region. Sediments were placed in sealed polyethylene plastic bags, labeled and stored at 4 °C until analysis. In the laboratory, shells were removed. The preparation of the sediment samples for inorganic compounds includes different techniques of drying: air-drying,

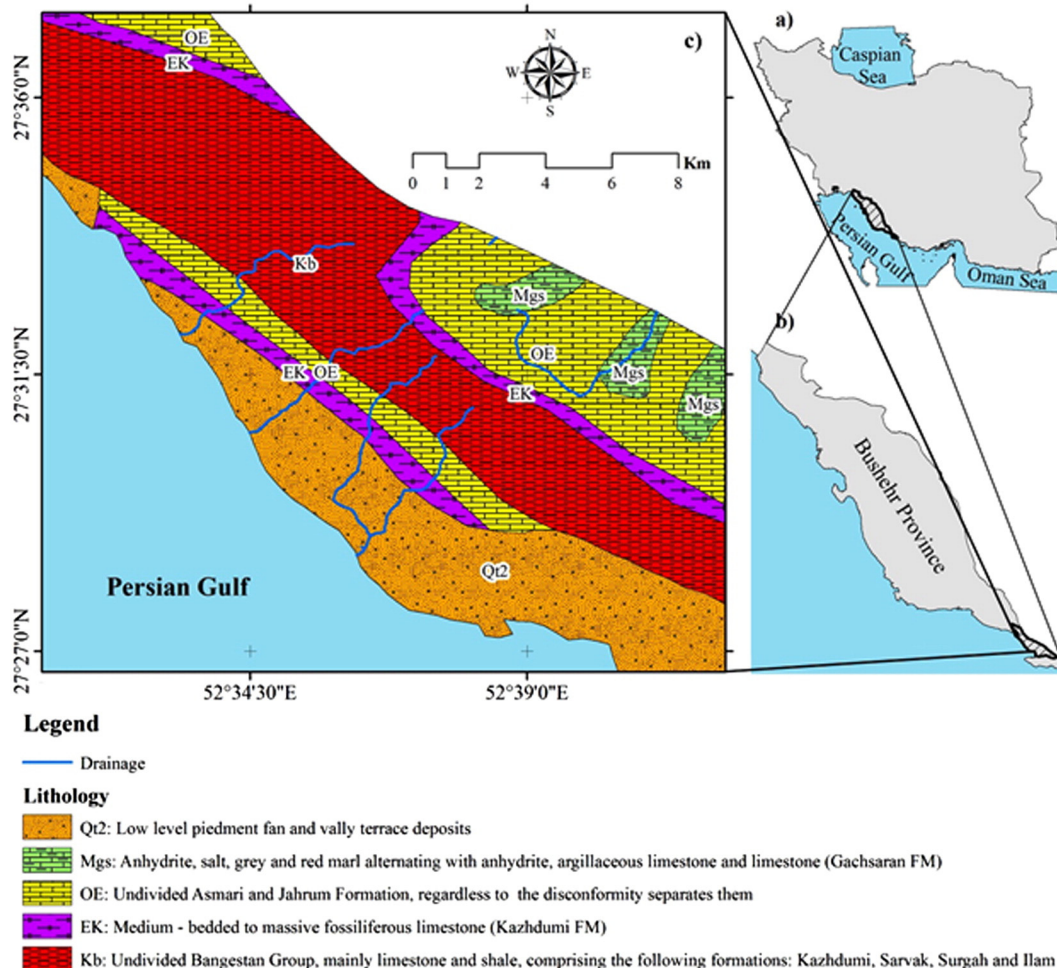


Fig. 1. (a) Location of the study area in south of Iran. (b) Location of the Bushehr province. (c) Geological map of the study area.

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