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Evaluation of metal contamination in the Mand River delta, Persian Gulf

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Keywords: Trace metal Contamination Geochemistry Surface sediments Mand River	Mand River is one of four permanent rivers flowing into the Persian Gulf. Intense industrial activities have significantly impacted its watershed and estuary. In order to evaluate metal contamination and their provenance nine sediment samples were taken from the Mand Delta. Enrichment factors were employed to detect anthropogenic contributions to levels of metal pollution. We also calculated weathering indices in order to identify the source of the metals, related to geological units. Pollution levels were assessed using the modified degree of contamination. Geological units, oil combustion, aerosols and industrial activities are the main factors controlling the abundance of Cr, As, Ni and Pb. Wave action, coastal currents, grain-size parameters, mineralogy, bio-accommodation and organic matter are the factors affecting the distribution and concentration of metals in the study area. More studies are needed to evaluate the impact of metal pollution on the fisheries industry and public health

The Persian Gulf is a semi-enclosed tropical sea with limited water exchange with the Indian Ocean through the Strait of Hormuz. In recent decades, the Gulf countries have experienced an unprecedented boom in population and industry. One of the consequences of these developments is a considerable increase in trace metals in aquatic ecosystems, with both short and long-term impacts. In addition to anthropogenic sources, trace metals released into the environment also result from the physical and chemical weathering of parent rock in surrounding watersheds (Callender, 2005).

Organic matter abundance, physical and chemical basin properties (pH, Eh, basin energy), trace metal mobility and sediment particles ability to absorb and accumulate the metals are significant factors in explaining the distribution and depletion of metals in aquatic systems (Ip et al., 2007; Christophoridis et al., 2009; Liu et al., 2016; Li et al., 2017). The toxicity of the trace metals and their persistence in the environment pose a tremendous threat to human health, fauna and flora. Many native species of the Gulf have attained their natural environmental range of tolerance (Price et al., 1993).

Several studies have been conducted to determine the impacts of industrial activities in different environmental contexts of the Persian Gulf, including river mouths (Diagomanolin et al., 2004), bottom sediments (Grimalt et al., 1985), fish species (Khoshnoud et al., 2011), coastal areas (Kazemi et al., 2012), estuaries (Dehghan Madiseh et al., 2008) and coral reefs (Rezai et al., 2004). However,

few investigations have been carried out on contamination resulting from anthropogenic activities and the erosion/weathering of geological outcrops.

The sedimentological and geochemical characteristics of sediments can be used as tools to probe the natural and/or anthropogenic sources of metal concentrations in coastal waters (Fedo et al., 1996; Nath et al., 2000).

The Mand shrimp farm is one of the most important producers of marine food in the Bushehr Province. It harvests 3 tons of shrimp per acre twice a year, with plans to increase production to 6 tons per acre. This study aims to assess the risk of metal pollution on present and future fishery activities around the Mand Delta.

The Mand River is one of the main permanent rivers of the Persian Gulf. It has a river supply of 1308.8 million m^3/yr and is located in the northern part of the Gulf. The study area has a semi-arid climate characterized by flash-floods during the wet season. The main weather phenomenon is the NW Shamal wind which blows during November and December. The main sediment transport direction in the study area is from the NW to the SE (Uchupi et al., 1996). A wide variety of sedimentary and igneous rocks, and oil and gas fields are present in the Mand River watershed (Fig. 1). Pars Special Economic Energy Zone (PSEEZ) are the most important examples of oil and gas industries in the area.

Nine surficial samples were collected from the study area using a

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Fig. 1. Map of the study area, denoting the sampling locations, geological units in the hinterland, the Mand shrimp farm and oil and gas industrial zones.

Van Veen grab sampler. Organic Matter (OM) and carbonate content was measured based on the methods outlined by Heiri et al. (2001). Grain-size data were obtained using a Horiba Laser Particle Size Analyzer LA-950. Arc GIS 10.3 was used for data processing and geospatial visualization. Geochemical analyses were carried out using X-ray fluorescence spectrometry. We used the matrix correction methods described by Leoni et al. (1982). The detection limit for trace elements, according to the analytical conditions, was about $3 \ \mu g \ g^{-1}$.

To identify weathering/alteration of geological outcrops in the source area, the Chemical Index Alteration (CIA) (Nesbitt and Young, 1982) and the Chemical Index of Weathering (CIW) (Harnois, 1988) were applied. Both the CIA and CIW were used to measure the extent of feldspar conversion to clays such as kaolinite. CIA and CIW are very sensitive to subtle changes in geochemistry (Price and Velbel, 2003). The CIA index reflects the integrated weathering history of the watershed. Furthermore, it shows negative correlation with sediment yield and weathering history and also the chemical weathering of parent rocks (McLennan, 1993; Hamdan and Burnham, 1996; Li and Yang, 2010). CIA and CIW were calculated based on Eq. (1) and Eq. (2), respectively.

$$CIA = [Al_2O_3/(Al_2O_3 + CaO + Na_2O + K2O)] \times 100$$
 (1)

$$CIW = [Al_2O_3/(Al_2O_3 + CaO + Na_2O)] \times 100$$
 (2)

The Enrichment Factor (EF) is an indicator used to evaluate

anthropogenic contributions to trace elements in the sediments. This method was used to estimate anthropogenic impacts on the sediment, via Al or Fe, in order to reduce the variations produced by heterogeneous sediments.

Al is a conservative element and a major constituent of clay minerals that has been successfully used by several workers to normalize the metal content of a sediment sample (Ryan and Windom, 1988; Sinex and Wright, 1988; Balls et al., 1997). In this study, we used Al to normalize metal concentration as a proxy for grain size.

The enrichment factor (EF) was calculated using the following Eq.uation (4) (Tanner et al., 2000)

$$EF = \frac{X/Al(sediment)}{X/Al(background)}$$
(3)

where X is the element concentration and X/Al is the ratio of the element concentration in relation to aluminum. The concentration of Al in the background reference (after Turekian and Wedepohl, 1961) was implemented to normalize all metal concentration values. According to Taylor (1964), sediments can be classified into different groups of contamination based on the EF (Table 1).

The degree of contamination (Abrahim and Parker, 2008; Hakanson, 1980) was calculated for the samples based on Eq. (4).

$$mC_{\rm D} = \sum Cf/n \tag{4}$$

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