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## Geochemical partitioning and pollution assessment of Ni and V as indicator of oil pollution in surface sediments from Shadegan wildlife refuge, Iran



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#### ABSTRACT

The total concentrations and chemical partitioning of Ni, V and Fe have been assessed in surface sediments from 160 sites along the Shadegan wildlife refuge. The results showed that the average total level of Ni, V and Fe in surface sediments were  $45.08 \pm 12.09, 25.25 \pm 20.8$  and  $25,979.01 \pm 6917.91 \,\mu$ g/g dw, respectively. On the average, the chemical speciation of Ni, V and Fe in most stations were in the order of residual > oxidisable-organic > acid-reducible > exchangeable. In all fractions, the residual was accounted the highest proportion for the metals analyzed. Among the non-residual phases, the proportion of heavy metals in organic matter fraction was higher than other phases collected from all locations. The comparison between measured values in this study and some fresh water sediment quality guidelines indicated that the levels of nickel would be expected to sporadically cause harmful biological impacts on biota in the Shadegan wildlife refuge.

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#### 1. Introduction

Nowadays, the discharge of great amounts of oil combustion related pollutants has become very acute in oilfields and their surrounding aquatic ecosystems in Iran (Karbassi et al., 2015). Shadegan international wetland is one of the 18 international wetlands registered in UNESCO's natural heritage list and the 34th largest of the 1201 designated Ramsar sites in the world (Zamani-Ahmadmahmoodi et al., 2010: Nasirian, 2014). It is known as Iran's largest wetland and considered as one of the most wonderful natural attractions of the world because of its unique biodiversity (HosseiniAlhashemi et al., 2012). Shadegan wetland is located in the adjacent of an oil field (HosseiniAlhashemi et al., 2011), during the last few decades, the establishment of various pollution sources including petrochemical complexes, oil pressure boosting station, oil pipelines and petroleum refineries along the boundaries of Shadegan wetland (Zamani-Ahmadmahmoodi et al., 2014) has led to irreparable damages to natural resources of wetland and human health hazard consequences (Kaffashi et al., 2012). Introduction of residual atmospheric hydrocarbons, products of burning furnaces in refineries occurs regularly and oil pipelines accidents are known to cause damage to Shadegan wetland through introduction of petroleum-related hydrocarbons (Zare-Maivan, 2012). Unprotected oil conveying pipelines that cross the whole wetland in an east-westerly direction makes drastic corrosion and repeated breakages. Pipeline breaks this past decade emitted oil over the area, resulting in great bird deaths, and threatening the wetland ecosystem in other ways (Kaffashi et al., 2011). In addition to all these threats, during the oilwar in Persian Gulf region and discharging crude oil from Kuwait's oil wells into wetland of Shadegan, almost 20% of vegetation coverage in this wetland which is vital for livestock food without any cost, has been extensively decremented (Davodi et al., 2011; Zare-maivan, 2011; Kaffashi et al., 2012). The main contaminants, originating from oil activities or oil spills and recognized to cause detrimental effects to aquatic life and to human consumers contain heavy metals such as nickel (Ni) and vanadium (V) (Barbour et al., 2009). Nickel (Ni) and vanadium (V) are available in the majority of crude oil sources (generally at levels much higher than any other metal) (Zhang et al., 2015; Doyle et al., 2015). Hence, they can be known as an indicator of crude oil pollution (Vieira et al., 2016). Nickel is a common and omnipresent metal in most aquatic systems (Asadpour et al., 2013), with input from natural origins (e.g., weathering of rocks or soils, forest fires, vegetation and erosion of land surfaces by water) and anthropogenic ones (e.g., industrial discharges from electroplating, refining operations and melting) (Attig et al., 2010). Ni is observed in sedimentary rocks in the range of 5 to 90 mg/g, sandstones contain the lowest levels of Ni while terrestrial rocks including sulfides and arsenide's harbor Ni mostly in



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ferromagnesian rocks replacing Fe (Zare-maivan, 2010). Ni is also accompanied with carbonates, phosphates and silicates and especially with petroleum. Every year, 26,000 tons of Ni is dispersed in the atmosphere from natural sources whereas anthropogenic activities are responsible for an input of 47,000 tons (Amiard et al., 2008). Vanadium is a component of many magmatic rocks and is present in shale's within the concentration of 100-250 ppm (Zare-maivan, 2010). Despite the fact that vanadium (V) is between the 20 most abundant elements in the earth's crust (Zhang et al., 2015) and it is found as abundant as nickel and zinc in the earth's crust, it is not a common pollutant (Zaki et al., 2010). Vanadium does not occur as the free metal, but as relatively insoluble minerals and organo-metallic complexes (Beusen and Neven, 1987). Vanadium presents naturally in about 65 different minerals and they contain >1% vanadium (Ringelband, 2001), therefore a large fraction of vanadium releases the aquatic systems through natural rock weathering (Beusen and Neven, 1987). However, anthropogenic input has led to a substantial enrichment of vanadium in the environment more than the levels of vanadium of biogenic origin (Asadpour et al., 2013). Vanadium exists in rather high concentrations in crude oils and coals and burning of these fossil fuels organizes the mainsource of vanadium emissions to the aquatic environment (Osuji and Adesiyan, 2005) with an estimated input of 12,000 to 24,000 tons per year, 10 to 15% of which being due to atmospheric fallout (Amiard et al., 2008). Although, in small quantities, Ni and V has proved to be an essential metal for the function of many organisms, accumulations in some areas from both anthropogenic discharge and naturally differing contents can be harmful to aquatic biota (Escudero et al., 2014). Vanadium and nickel are not very ambulant in fuel oil, and thus their transfer to the aqueous ambient is highly slow (Pourang et al., 2005). Bacterial decomposition, dissolution, oxidation and remineralization of the organic matter are the mechanisms recommended for the release of trace metals such as V and Ni from the spilt oil to the environment (MacõÂas-Zamoraa et al., 1999). As a result of this, a comprehensive survey is required for these metals since there may be a transfer from seawater and sediments (Lavilla et al., 2006). Heavy metals introduced from natural and anthropogenic sources in the aquatic ecosystem are insoluble in water but bound to sediments; they are usually associated to particles (Kazemi et al., 2013; Wang et al., 2015). These particles are often very small, and can therefore stay in solution for a very long time (Al-Husaini et al., 2014). Nevertheless, they will end up in the sediments; therefore concentrations in the sediments are often 10 to 100 times higher than those in solution (Al-Husaini et al., 2014; Keshavarzi et al., 2015). In hydrological cycle far <1% of metals are found dissolved in the water column; >99% are stored in the sedimentary environment (HosseiniAlhashemi et al., 2011). Hence, sediments commonly act as a source and as a sink for various extraneous chemicals in aquatic systems (Wang et al., 2015). Sediments are preferred monitoring tools, since contaminant concentrations are orders of magnitude higher than in water, and they show less variation in time and area, permitting more consistent assessment of spatial and temporal contamination (Dadolahi and NazarizadehDehkordi, 2013; Diop et al., 2015). On the other hand, heavy metals are not stabilized continually to sediments (Salahshur et al., 2014) and changes in biogeochemical and physical properties of the environment can convert the reactions and result in the release of the contaminants from the sediments to overlay waters which pose a major risk to benthic habitants (Al-Husaini et al., 2014; Emili et al., 2015). Thus, contaminated sediment can play an important role in destroying water quality as a secondary source (Palma et al., 2015). It is now well known that total metal concentrations for any metal are not a controlling factor to the understanding metals environmental behavior or in developing remedies for its safe management (Venkatramanan et al., 2013; Jara-Marini et al., 2015). Although it is essential to site characterization and management, they offer no insight into risk (HosseiniAlhashemi et al., 2011). Rather, it is the metals bioavailability which plays a significant role in the risk assessment of contaminated media (Yang et al., 2015). In aquatic systems, heavy metals are accompanied with sediments in a number of chemical species, and their association characterizes the mobility and availability (Mohiuddin et al., 2011; Baran and Tarnawski, 2015). For instance, they can be settled on clay surfaces, or iron and manganese oxyhydroxides, and or, also adsorb in the lattice of residual primary mineral phases (e.g., silicates) and or, secondary mineral phases, including carbonates, sulfates, and oxides. Metals may also be bound in amorphous substances, such as iron and manganese oxyhydroxides, or complexes with organic matter (Kennou et al., 2015). The behavior, fate and environmental impacts of heavy metals extremely depends on their chemical forms, mobility and bio-accessibility (Xu et al., 2015) and only those with high bioavailability may be incorporated by organisms, and then, they can cause harmful effects to organisms and human beings (Venkatramanan et al., 2013; Cai et al., 2014). Therefore, surveys on the fractionation and distribution of heavy metals in sediments could supply beneficial information on the degree of pollution, mobility, toxicity, biological and physiochemical bioavailability as well as their input (Li et al., 2013; Jara-Marini et al., 2015; Garcia-Pereira et al., 2015). Unfortunately, Ni and V receive relatively few attentions in the scientific research on soil and sediment geochemistry (Cappuyns and Swennen, 2014). There are still significant gaps in the awareness on the effect of Ni and V sediment pollution on aquatic biota, but it is known that they can be harmful and toxic to plants, animals and human health (Al Rashdi et al., 2015). Chemical extraction is an accepted technique for designation of principal phases of metals, when they concentrate in solid samples and offer more realistic estimate of true environmental impact (Shirneshan et al., 2013; Bagheri et al., 2014; Garcia-Pereira et al., 2015; Abdel-Satar and Goher, 2015). In this research, the sequential extraction technique (SET) was used to differentiate the anthropogenic metals from those of natural origin. The geochemical forms investigated in this study were the 'easily, freely, leachable or exchangeable' (EFLE), 'acid-reducible', 'oxidisable-organic' and 'resistant' types. The sum of three phases of the EFLE, 'acid-reducible' and 'oxidisable-organic' makes the 'nonresistant' phase (Yap et al., 2002; Bagheri et al., 2014). This 'nonresistant' fraction is representative of anthropogenic contamination, while the resistant fraction derives from the dissociation of the silica lattices of rocks (Shirneshan et al., 2013). The main objectives of the present study were as follows:

- 1. To assign the total concentrations of nickel, vanadium and iron in surface sediments from Shadegan wildlife refuge, as well as to estimate the fractionation of these metals using a sequential extraction technique (SET) in order to provide information about identification of natural and anthropogenic shares and their potential bioavailability.
- 2. To quantify the metal contamination degree and potential ecological risks by indexes of enrichment factor (EF), geo-accumulation index (I<sub>geo</sub>), individual and global contamination factor (ICF and GCF) and potential ecological risk index (PER).
- 3. To assess the quality of the sediments based on freshwater sediment's quality guidelines published by US EPA (US EPA, 2002), U.S. Public Health Service (USPHS, 1997), Ministry of Environment of Ontario criteria (MEO, 1990), soil standards for Serbia (Official Gazette of Serbia, 1990) (Sakan et al., 2007) and the LEL/PEL SQGs (Malik et al., 2012) which relate the pollution condition of sediments, taking into attention the total metal level.

#### 2. Materials and methods

#### 2.1. Description of the study area

Shadegan international wetland with an area of 537,700 ha (Taravati et al., 2012) is an environmental system comprising of fresh, brackish and saline waters, which is located in Khuzestan Province, south western of Iran (Karimi et al., 2012). About 296,000 ha of wetland area are established as a wildlife refuge that surrounds the main wetland area (Karimi et al., 2012). It is important to note that, Ramsar site involves Download English Version:

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