# Geochemical speciation, bioavailability and source identification of selected metals in surface sediments of the Southern Caspian Sea

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## ARTICLE INFO

## ABSTRACT

Geochemical speciation of As, Cd, Co, Cr, Cu, Ni, Pb, V and Zn were determined in the surface sediments of the southern Caspian Sea. A five-step sequential extraction technique was used to determine the chemical forms of metals. Mean concentrations (ppm) of heavy metals were (mean ± S.D.) As: 9.94 ± 1.71, Cd: 0.87 ± 0.23, Co: 14.85 ± 2.80, Cr: 72.29 ± 19.48, Cu: 18.91 ± 4.48, Ni: 32.87 ± 5.25, Pb: 12.48 ± 3.22, V: 86.07 ± 20.71 and Zn: 66.85 ± 10.11. Among the metals, Cu, As, Pb and Zn exhibited relatively higher mobility, while Cd, Co, Cr, Ni and V were found mainly in the residual fractions. Cu and As showed the highest percentages in the exchangeable phase while Co and Cr had the lowest percentages in the phase. The Risk Assessment Code (RAC) values indicated that As, Cu and V had medium risk at some sampling sites. According to pollution load index (PLI), sediments from some sampling sites were polluted.

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## 1. Introduction

Heavy metal pollution of the aquatic ecosystems has globally received tremendous significance due to its toxicity, abundance, persistence and subsequent accumulation (Dong et al., 2010). As a result of their solubility and mobility metals would cause serious ecological and health hazards throughout accumulation in marine food chains (Iyer et al., 2005). The toxicity of metals and their compounds largely depends on their bioavailability which encompasses the mechanisms of uptake through cell membranes, intracellular distribution, and binding to cellular macromolecules (Beyersmann and Hartwig, 2008).

Bottom sediment, specifically as a tool for monitoring of heavy metals in the sea, represents advantageous results of pollutant distribution. Sediments are accumulated over the years and can be regarded as fixators of contamination level. After being discharged into bodies of water, pollutants are gradually deposited on bottom in various forms. When the pollution level of sediment exceeds than specific amounts, this would disturb the ecosystem equilibrium and consequently would make it downfall. Monitoring of heavy metal deposition in

sediments provides a continuous surveillance of pollution in the studied area and sediment analysis could make the specification of pollution type easier in order to adopt any management decisions for advisable controlling (ElNemr et al., 2007; Bastami et al., 2015).

Heavy metals are ubiquitous environmental contaminants derived mainly both natural (like as physical and chemical weathering of parent rocks) and anthropogenic sources. Complex processes including anthropogenic activities or natural procedures including riverine or atmospheric inputs, floor erosion, biological activities, water drainage and discharge of urban and industrial wastewater are important parameters controlling the distribution of metals within the aquatic environments.

A minor fraction of metals remains dissolved in water whereas large quantities of free metal ions are stored in sediments. Therefore, sediments in aquatic environments can either retain metals or release them to the water column by various remobilization processes (such as both biological and chemical activities). Sediment parameters (mineralogy, texture), metal characteristics, pH, organic matter and oxidation–reduction potential are important factors managing accumulation and availability of heavy metals in the sediment.

Trace metals in sediments are mainly associated with silicates and primary minerals and therefore they have limited mobility. However, metals introduced by human activities show greater mobility and are
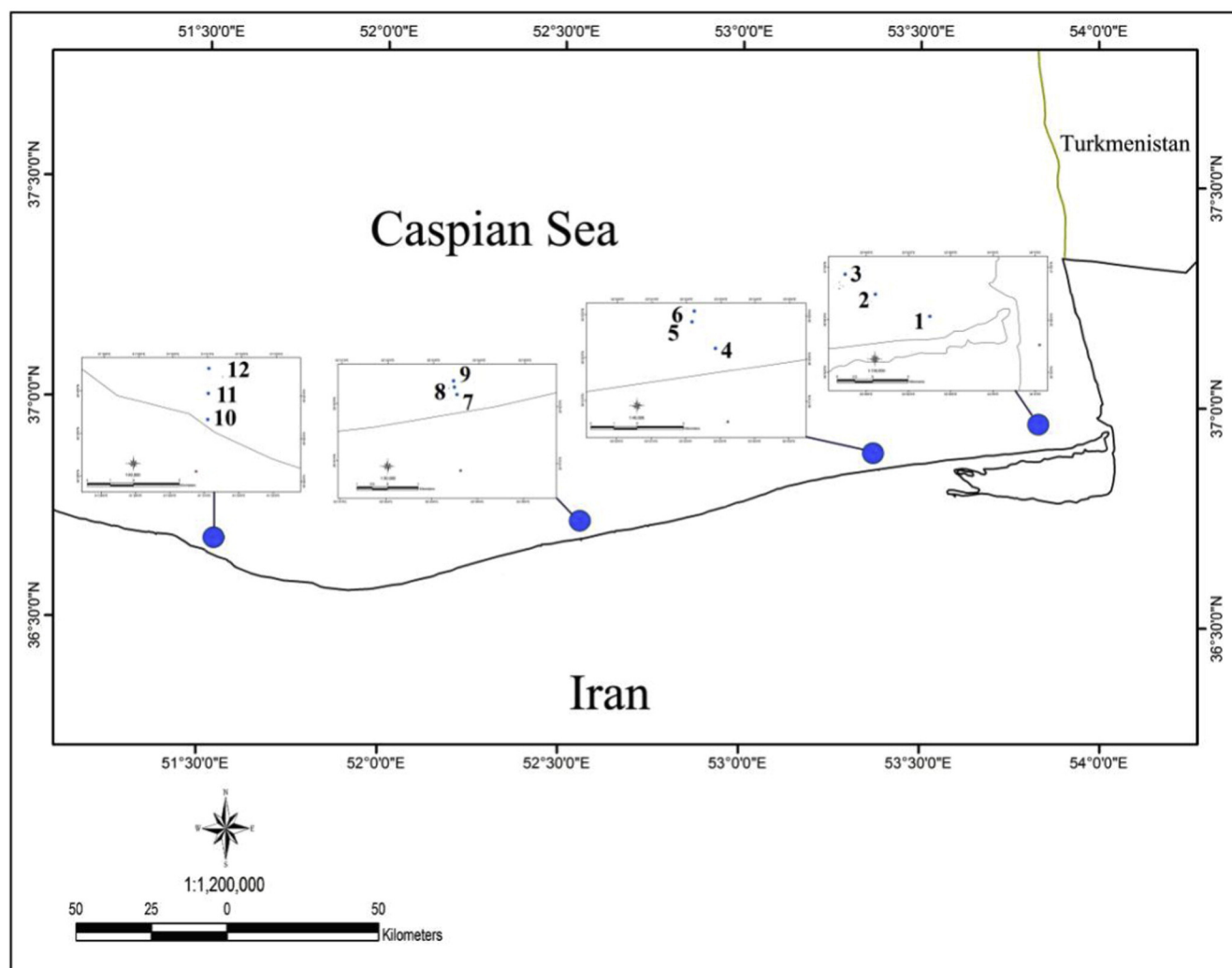
Fig. 1. The locations of the sampling sites at the southern Caspian Sea.

associated with other sediment phases such as carbonates, oxides, hydroxides and sulfides (Passos et al., 2010; Heltai et al., 2005).

Total heavy metal concentrations are often used to assess heavy metal pollution in sediments, but poorly reflect the mobility and bioavailability of these metals (Nemati et al., 2011).

Investigations on chemical partitioning of metals in sediment and water column are important to distinguish the bioavailable fraction. Among metal fractions (Exchangeable, Carbonates, Reducible, Oxidizable, Residual), exchangeable and carbonate bound fractions are considered to be bioavailable, and determine both the bioaccumulation and biomagnification in aquatic food web (Tessier and Campbell, 1987; Sundaray et al., 2011).

The Caspian Sea, which accounts for 40–44% of total lacustrine waters of the world, is denoted as a sea or lake. Because of high biodiversity in the Caspian Sea and its coastal zone, it is one of the most valuable ecosystems on the earth. As this region has been isolated from other bodies of water for a long time, a high level of endemism is remarkably evident in its fauna. Several specific features in this unique region such as the existence of shallow areas, several deep depressions and a wide range of salinities varying from 0.1‰ to 13‰ provide different ecological niches, which highly raise its species diversity.

Regarding the high ecological significance of the Caspian Sea, its heavy metal pollution status has been studied by several researchers so far (De Mora et al., 2004; Tabari et al., 2010; Bastami et al., 2012;

Bastami et al., 2014; Raeisi et al., 2014; Bastami et al., 2015; Naji and Sohrabi, 2015; Pakzad et al., 2016). But heavy metals mobility and their bioavailability in this area has not been yet recognized. Therefore, the objectives of the present work were (i) to assess heavy metal dynamics and their mobility in different geochemical fractions of sediment and (ii) to identify the bioavailability and ecological risk of these metals in surface sediment of the southern Caspian Sea.

## 2. Materials and methods

### 2.1. Sediment samples collection and analytical methods

Surface sediment samples from twelve different sites in southern part of the Caspian Sea were collected using Van-Veen grab during autumn (November) 2015 (Fig. 1). Then, samples were packed and carried to the laboratory in iced-boxes and stored at −4 °C until analysis. After drying in an oven, sediment samples were ground by using a hand mortar followed by screening with a 0.5 mm sieve to remove large particles.

For chemical partitioning of metals, sediment samples were analyzed using Tessier sequential chemical extraction procedure (Tessier et al., 1979). The sequential extraction procedure was divided into five operationally defined chemical fractions: (F1) the exchangeable fraction: readily soluble and exchangeable; (F2) the carbonate bound and specifically adsorbed fraction: carbonate-bound, specifically adsorbed