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Baseline

Heavy metal pollution assessment in relation to sediment properties in the coastal sediments of the southern Caspian Sea

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ABSTRACT

This study aimed to evaluate major elements and heavy metal concentrations of Arsenic (As), Copper (Cu), Chromium (Cr), Cobalt (Co), Vanadium (V), Nickel (Ni), lead (Pb) and Zinc (Zn) in surface sediments of the southern Caspian Sea. Metal contents in the sediment were observed in the order of: V > Cr > Zn > Ni > Co > Cu > Pb > As. Correlations between elements showed that sediment TOM, grain size and chemical composition are the main factors that influence the distribution of heavy metals. According to the pollution load index (PLI), sediments from some sampling sites were polluted. Concentrations of Ni, As, Cr and Cu were higher than sediment quality guidelines at some sampling sites, implying potential adverse impacts of these metals.

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Heavy metal pollution in marine ecosystems is a serious concern due to the toxic and long lasting effects (Zhan et al., 2010; Gao and Chen, 2012). Heavy metals in coastal sediment originate from both natural (physical and chemical weathering of parent rocks) and anthropogenic sources (Callender, 2005). Wastewater discharge, urban effluent and fertilizer application constitute the major anthropogenic inputs.

Heavy metals are discharged into aquatic systems during transport, and distributed between the aqueous phase and sediment. Because of adsorption, hydrolysis and co-precipitation of metal ions, a large quantity of free metal ions are deposited in the sediment while only a small portion of ions remain dissolved in the water column. Therefore, sediments in aquatic environments can either retain metals or release them to the water column by various remobilization processes. Sediment parameters (mineralogy, texture), metal characteristics, pH, organic matter and oxidation–reduction potential are important parameters controlling the accumulation and the availability of heavy metals in the sediment (Hakanson 1980; Wright and Mason 1999; Tam and Wong 2000; Buccolieri et al., 2006; ElNemr et al., 2007; Bastami et al., 2012).

Therefore, sediments are considered sources of heavy metals in marine environments and play a key role in transmission and deposition of metals.

Generally, normal metal concentrations found in sediments are not detrimental to inhabiting organisms. For normal metabolism, live organisms essentially require some metals, such as zinc. However, these metals can have toxic effects above a critical threshold.

The Caspian Sea, which accounts for 40–44% of the 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 earth. Because 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. The existence of shallow areas, several deep depressions and a wide range of salinities, varying from 0.1‰ to 13‰, provide different ecological niches, giving rise to high species diversity.

The main goal of this study is to investigate heavy metals distributions in different compositions of surficial sediments from the southern Caspian Sea, and to discover relationships between the distributions and sediment characteristics.

Sediment samples from twelve different sites were collected in autumn for heavy metal analysis using a Van-Veen grab sampler (November) 2013 (Fig. 1). Then, samples were packed and carried to the laboratory in iced-boxes and stored at 4 °C until analysis.

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After drying in an oven, sediment samples were ground using a hand mortar, followed by screening with a 0.5 mm sieve to remove large particles. Then, samples (0.5 g) were digested using a mixed solution of HF–HCl–HNO₃–HClO₄ according to ASTM standard practice D5258-92 (ASTM, 2013). Samples were analyzed for Al, As, Cu, Ni, Pb, Co, Cr, V and Zn by using inductively coupled plasma-optical emission spectrometry (ICP-OES; Varian VISTA-MPX). The analytical results of the quality control samples showed good agreement with the certified values (Table 1). Additionally, major element contents (SiO₂, CaO, Fe₂O₃, Al₂O₃, MgO, K₂O, Na₂O, TiO₂, P₂O₅ and MnO₂) were measured using an X-ray fluorescence spectrometer (Bruker Model). For determination of total organic matter, sediment samples were dried at 70 °C for 24 h and then combusted in the oven at 550 °C for 4 h. Total organic matter, as described by Abrantes et al. (1999), was measured by the following equation:

$$\text{Total organic matter (TOM, \%)} = [B - C/B] \times 100 \quad (1)$$

where *B* and *C* are the weights of dried sediment before and after combusting in the oven, respectively.

Grain size analysis was performed using a laser particle size analyzer (HORIBA-LA950, France and Japan). Before analysis, approximately 4 g samples were combusted in the oven at 550 °C for 4 h and 950 °C for 2 h to remove organic matter and biogenic carbonate, respectively.

An enrichment factor, which is an appropriate tool for determining sedimentary metal sources as being either anthropogenic or natural events, normalizes metal concentrations according to sediment texture properties (Selvaraj et al., 2004; Vald'es et al., 2005; Bastami et al., 2014a). In this index, aluminum is widely used, indicating aluminum silicate at coastal areas where this element is predominant. The enrichment factor was also applied as a degree of sedimentation (Lee et al., 1998; Woitke et al., 2003) and determined as follows:

$$\text{Enrichment factor} = (H_s/Al_s)/(H_c/Al_c) \quad (2)$$

where *H_s* and *H_c* are heavy metal concentrations in the sample and reference data, respectively. *Al_s* and *Al_c* are the aluminum contents in the sample and reference data, respectively. In this study, we used reference concentrations of metals in sediment from Iranian waters of the Caspian Sea, which are 12.5, 51.5, 18, 34.7, 85.3, 116, 15.9, 85.2 ppm and 6.05% for As, Ni, Pb, Cu, Zn, V, Co, Cr and Al, respectively (De Mora et al., 2004).

To assess the sediment's environmental quality, an integrated pollution load index of eight metals was calculated, as suggested by Suresh et al. (2011).

$$\text{PLI} = (\text{CF}_1 \times \text{CF}_2 \times \text{CF}_3 \times \dots \times \text{CF}_n)^{1/n} \quad (3)$$

Table 1

Certified vs. measured concentrations of selected metals in standard reference material.

Metals	Reference material	Expected value	Measured ± SD
Al	OREAS 72b	47,900 ± 1870	46,750 ± 1546
As	OREAS 72b	146 ± 9.1	136 ± 5.2
Cu	OREAS 72b	222 ± 8.5	207 ± 3.1
Ni	OREAS 72b	6860 ± 250	5849 ± 241
Pb	OREAS 72b	14.9 ± 1.7	19 ± 1.8
Zn	OREAS 72b	99 ± 6.7	112 ± 7.2
Co	OREAS 72b	131 ± 5.5	125 ± 6.5
Cr	OREAS 72b	771 ± 127	742 ± 121
V	OREAS 72b	73.6 ± 2.6	69.8 ± 1.4

where CF_{metals} is the ratio between the concentration of each metal and the reference values,

$$CF_{\text{metals}} = CH_{\text{metal}}/CH_{\text{back}} \quad (4)$$

where CH_{metal} is the concentration of the sampled heavy metal and CH_{back} is the reference value of the heavy metal, respectively.

The potential ecological risk index (PER) was also introduced to assess the contamination degree of heavy metals in the studied sediments. The equations for calculating the PER were proposed by Hakanson (1980), as follows:

$$E = TC \quad (5)$$

$$C = C_a/C_b \quad (6)$$

$$\text{PER} = \sum E = \sum TC \quad (7)$$

where *C* is the single element pollution factor, *C_a* is the content of the element in the samples and *C_b* is the reference value of the element. The sum of *C* for all the metals examined represents the integrated pollution degree (*C*) of the environment. *E* is the potential ecological risk factor of an individual element. *T* is the biological toxic factor of an individual element, which is set at Cu = Pb = 5, Zn = 1, As = 10, Cr = 2 and Ni = 6 (Hakanson 1980). PER is a comprehensive potential ecological index, which equals the sum of *E*. It represents the sensitivity of a biological community to toxic substances, and illustrates the potential ecological risk caused by contamination.

A Pearson correlation analysis was performed to test the relationship between various heavy metals and environmental parameters.

Differences in heavy metal concentrations were indicated by a non-metric multidimensional scaling ordination (nMDS), which was derived from Bray-Curtis similarity matrices and a fourth root

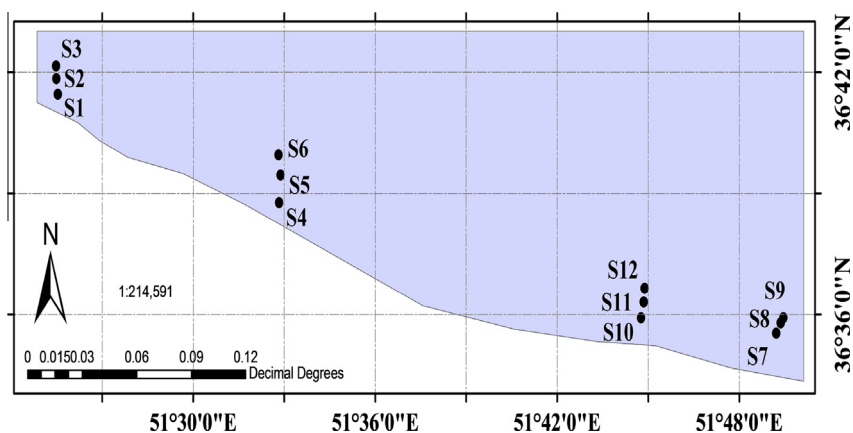


Fig. 1. The locations of the sampling sites at the southern Caspian Sea.

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