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Distribution and ecological risk assessment of heavy metals in surface sediments along southeast coast of the Caspian Sea

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ABSTRACT

The present study aimed to evaluate heavy metal concentrations of Arsenic (As), Copper (Cu), Nickel (Ni), Lead (Pb) and Zinc (Zn), their spatial distribution, enrichment factor index (EF), the pollution load index (PLI) and potential ecological risk (PER) in two different seasons of the year (winter and summer) in surface sediments along southeast coast of the Caspian Sea. The results indicated that there were significant differences between concentrations of As, Ni and Pb in two different seasons. Considering PER, sediments from southeast Caspian coast had low ecological risk. According to PLI, sediment from the southeast coast had no pollution. Risk assessment showed that As threshold concentrations to occasionally be exceeded in the study area.

Heavy metal elements in coastal sediment originate from physical and chemical weathering of parent rocks, wastewater discharge and atmospheric deposition (Callender, 2005). Heavy metals discharged into aquatic system during their transport are distributed between the aqueous phase and sediments. Because of adsorption, Hydrolysis and co-precipitation of metal ions, a large quantity of them are deposited in the sediment while only a small portion of free metal ions stay dissolved in water column. The accumulation and mobility of heavy metals in sediments controlled by various factors such as nature of the sediment particles, properties of adsorbed compounds, metal characteristics, redox reactions and biodegradation of sorptive substance under specific conditions (Hakanson, 1980; Maher and Aislabie, 1992; Rivail Da Silva et al., 1996; Wright and Mason, 1999; Tam and Wong, 2000; Buccolieri et al., 2006; ElNemr et al., 2007; Bastami et al., 2012). Hence, sediments are enumerated as sources of heavy metals in marine environments and play a key role in transmission and deposition of metals. Accumulated heavy metals in sediment can be chemically altered by organisms and converted into organic complexes, some of which may be more hazardous to animal and human life, via the food chain.

Coastal ecosystems surrounded by industrialized communities continuously receive much more heavy metal loadings by river discharges, inlets and estuaries filled with run-off from adjacent grounds (Bloom and Ayling, 1977; Unnikrishnan and Nair, 2004). Up to now, heavy metal pollution in coastal ecosystems and estuary has been studied by many worldwide researchers (Maanan et al., 2004; Zhang et al., 2007; Yu et al., 2008; De Mora et al., 2004; Bastami et al., 2012).

The Caspian Sea is the largest inland water body on the earth and debate still exists whether this water body should be referred to as a sea or as a lake. The biodiversity of the Caspian Sea and its coastal zone makes the region one of the most valuable ecosystems in the world. Due to its long-term isolation from other water bodies, one of the remarkable aspects of its fauna is the high level of endemism. The existence of shallow areas, several deep depressions, and a wide range of salinities varying from 0.1‰ to 13‰ pro-

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vide different ecological niches which gives rise to a high species diversity. Although the distribution of several heavy metals have been previously described by De Mora et al. (2004) but there is no information about ecological risk assessment of heavy metals in sediment from the southeast coast of the Caspian Sea.

With the above scenario, the objectives of the present study were to assess the extent and ecological risk assessment of heavy metals in the surface sediments along southeast coast of the Caspian Sea.

Sediment samples from seven different sites were collected using Van-Veen grab for heavy metals analysis during winter (March) and summer (September) 2012 (Fig. 1). After sampling, sediment 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. Sediment sample (1 g) was digested using a mixed solution of 1:3 nitric acid: hydrochloric acid for 3 h. The solution was cooled, filtered through Whatman – 42, diluted and then adjusted to 50 ml volume using distilled water (APHA et al., 2005). Samples were analyzed (Cu, Ni, Pb, Zn and Al) by using Inductively coupled plasma-optical emission spectrometry (ICP-OES; Varian 735 ES series). Arsenic (As) analysis was carried out by using atomic absorption spectrometry (model SOLAAR M5, Shimadzu, England). Standard samples were used to monitor the performance of the instrument and data quality. The analytical results of the quality control samples showed good agreement with the certified values (Table 1).

For determination of total organic matter, sediment samples were dried at 70 °C for 24 h and then combusted in an oven at 550 °C for 4 h. Total organic matter, as described by Abrantes et al. (1999), was measured by the following equation:

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

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

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

Enrichment factor which is an appropriate tool to determine sedimentary metals source produced by anthropogenic events or natural origin, normalizes metals concentrations according to the sediment texture properties (Morillo et al., 2004; Selvaraj et al., 2004; Adamo et al., 2005; Vald'es et al., 2005). In this index, aluminum is widely used, indicating aluminum silicate at coastal areas where this element is predominant. Enrichment Factor was also applied as a degree of sedimentation (Lee et al., 1998; Huang and Lin, 2003; Woitke et al., 2003) and determined as follows:

$$\text{Enrichment Factor} = (H_s/\text{Al}_s)/(H_c/\text{Al}_c)$$

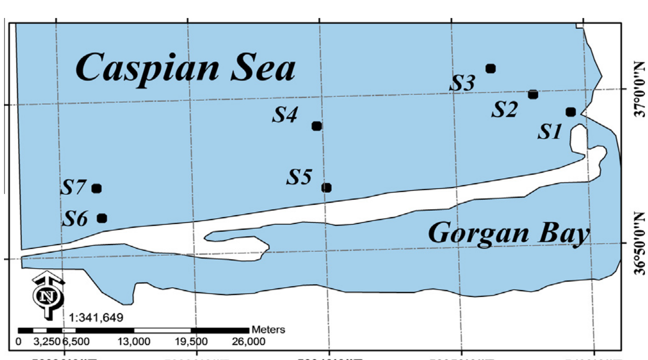

Fig. 1. The locations of the sampling sites at the southeast coast of Caspian Sea.

Table 1
Certified vs. measured concentrations of selected metals (ppm) in standard reference material.

	Reference material	Expected value	Measured ± SD	Recovery (%)
As (ppm)	MESS-3	21.2	19.5 ± 1.1	91.98 ± 1.4
Cu (ppm)	DS7	109	108.75 ± 2.75	99.7 ± 2.53
	DS8	110	114.56 ± 9.31	104.15 ± 8.46
Ni (ppm)	DS7	56	56.90 ± 0.56	101.60 ± 1.01
	DS8	38	39.50 ± 2.42	103.94 ± 6.38
Pb (ppm)	DS7	60.6	71.85 ± 5.16	101.77 ± 7.31
	DS8	123	123.20 ± 5.40	100.16 ± 4.39
Zn (ppm)	DS7	411	395.00 ± 5.16	96.07 ± 1.72
	DS8	312	320.66 ± 4.16	102.77 ± 1.33

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

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

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

where CF metals is the ratio between the content of each metal to the background values,

$$\text{CF}_{\text{metals}} = \text{CH}_{\text{metal}}/\text{CH}_{\text{back}}$$

Potential ecological risk index (PER) was also introduced to assess the contamination degree of heavy metals in the present sediments. The equations for calculating the PER were proposed by Guo et al. (2010) as the following:

$$\text{PER} = \Sigma E$$

$$E = \text{TC}$$

$$C = C_a/C_b$$

where C is the single element pollution factor, C_a is the content of the element in 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 index of an individual element. T is the biological toxic factor of an individual element, which is determined for Cu = Pb = 5, Zn = 1, As = 10 and Ni = 6 (Guo et al., 2010; Fu et al., 2009). PER is a comprehensive potential ecological index, which equals to the sum of E. It represents the sensitivity of biological community to toxic substances and illustrates the potential ecological risk caused by the overall contamination.

The significant differences in the calculated parameters among different seasons were determined by t-test analysis using the SPSS statistical package program (Ver. 19). Prior to the analysis, the normality and homogeneity variance assumptions were checked and, when necessary a log $(1 + x)$ transformation data was utilized. A Pearson correlation analysis was performed to test the relationship amongst environmental parameters.

General characteristics of sediments (average ± SD) sampled along southeast coast of the Caspian Sea in different seasons are shown in Table 2.

Average value for Sand, mud (silt + clay) and TOM during winter and summer seasons varied from 39.90% to 46.73%, 60.10% to 53.06% and 4.12% to 4.70%, respectively. Sampling sites 1 and 7