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## Baseline

## Preliminary evaluation of heavy metal contamination in the Zarrin-Gol River sediments, Iran

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## ABSTRACT

The major objectives of the study were to test the hypothesis of the Zarrin-Gol River as a reference site for ecotoxicological studies and to assess the contamination degree of heavy metals and metalloids in the river using four contamination indices. For these purposes, eleven heavy metal and metalloid concentrations were analyzed. The average concentrations ( $\text{mg kg}^{-1}$ ) in the sediments were: 37.67 (chromium) 286.28 (manganese), 13,751.04 (iron), 8.79 (cobalt), 12.39 (nickel), 32.68 (zinc), 21.91 (arsenic), 40.59 (selenium), 2923.86 (aluminum), ND (silver) and 785.96 (magnesium). Contamination factor, enrichment factor, pollution load index, and geoaccumulation index were calculated to evaluate the contamination degree and influence of human activities on heavy metal levels. The contamination indices of the sediment samples showed that arsenic and selenium were the highest pollutants. The results indicated that the Zarrin-Gol River could not be used as a reference site at least for arsenic and selenium.

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Pollution in the aquatic ecosystems has received much concern due to the abundance, toxicity, persistence, ubiquity, and non-degradability in the ecosystem, and subsequent bio-accumulation, of heavy metals (Liu et al., 2016; Varol, 2011). Heavy metals in polluted habitats may accumulate in the aquatic ecosystems, especially in fish tissues, which, in turn, may enter into the human food chain and eventually lead to health risks (Ahmed et al., 2015; Islam et al., 2015a; Zhu et al., 2013). Heavy metals and metalloids discharged into an aquatic system by both anthropogenic and natural sources are distributed between different compartments of these ecosystems, such as water, sediment and biota (Ali et al., 2016; Maanan et al., 2015). After entering into the aquatic ecosystem, only a small portion of free metal ions stay dissolved in water because of the particularities of heavy metals and metalloids, the rest gets deposited in the sediments (Varol, 2011; Zhuang and Gao, 2015). Therefore, sediments are an ecologically important component of the system and play a significant role in the transport and storage of potentially hazardous metals (Antizar-Ladislao et al., 2015; Diop et al., 2015). River sediments are suitable for the monitoring of man-made pollution, as they not only act as a carrier of pollutants, but also the potential secondary sources of pollutants in the water body (Ma et al., 2016; Mekonnen et al., 2015; Singh et al., 1997). Therefore, the analysis of river sediment samples is a suitable technique to investigate the metal contamination in an area (Islam et al., 2015b; Thuong et al., 2013).

The Zarrin-Gol River is one of the rivers in northern Iran. In some studies, particularly in ecotoxicological studies, it is assumed that this

river is a reference river although no studies have been done to test this assumption until now. Here we report the results of the first comprehensive study on the distribution and concentration of heavy metals and metalloids in sediments of the river carried out through systematic monitoring during the sampling period from different sites along the river.

The major objectives of the present study were (i) to determine the concentration of eleven heavy metals and metalloids in surface sediments of the Zarrin-Gol River, (ii) to assess the degree of contamination of heavy metals and metalloids in the river using four contamination indices (iii) to estimate the relationship between heavy metals and metalloids (Cr, Mn, Fe, Co, Ni, Zn, As, Se, Al, Ag, and Mg) and their possible sources (iv) to create baseline data of heavy metal distribution for this ecosystem, which may help future researchers, managers and policy makers.

The Zarrin-Gol River is a small river situated in the eastern Elburz Mountains (Golestan province in northern Iran) (Fig. 1). The Zarrin-Gol River originates in the Golestan District of Aliabad Katoul city and joins the Gorganrood River and eventually flows into the Caspian Sea. The Caspian Sea ecosystem is unique and the largest inland body of water in the world and includes many endemic species such as types of sturgeon fish, Caspian seal. The survival of these species is threatened due to the arrival of contaminants such as heavy metals and persistent organic pollutants in the ecosystem.

Table 1 shows the 6 sites selected for sampling. Surface sediment samples were collected in spring and summer, 2014. The samples collected from each site consisted of 5–6 composite samples (from the

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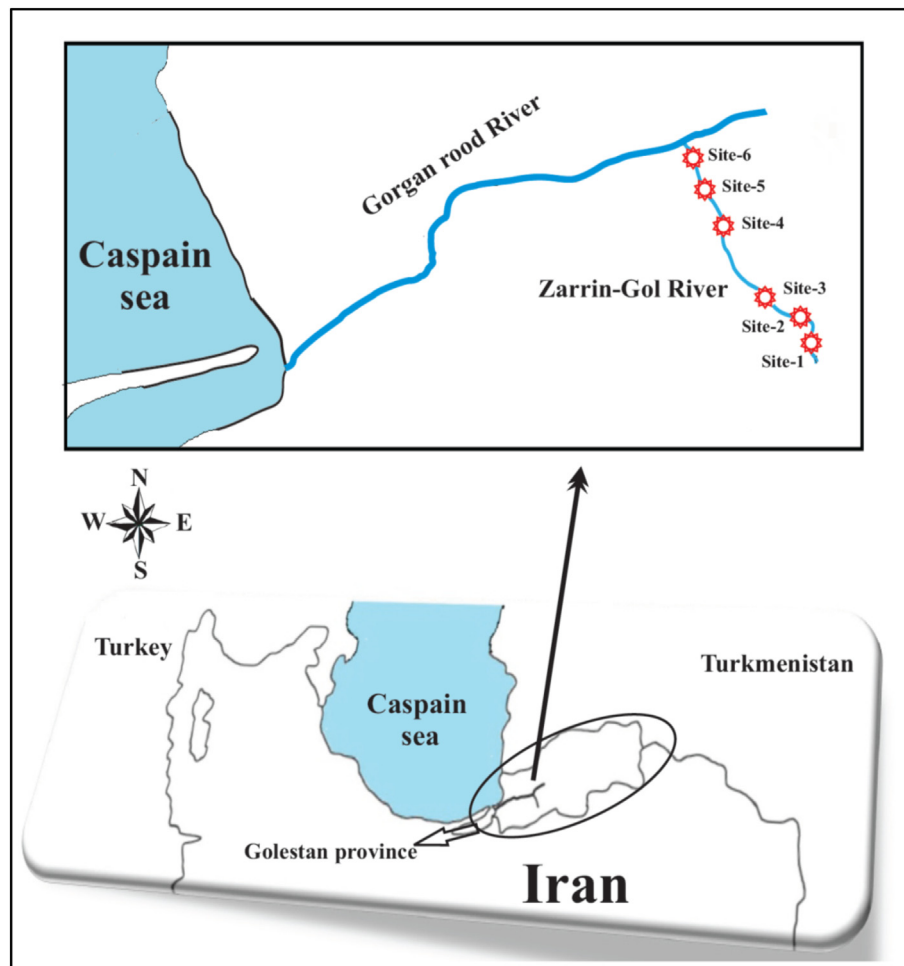


Fig. 1. The location of the study area and sampling sites in the Zarrin-Gol River.

top 0–10 cm of the riverbed and were sealed in clean polyethylene bottles and kept at 4 °C until further analysis).

Sediment samples were air dried; and mixed thoroughly, and then sieved through a 230 ASTM sieve mesh (mesh size 63  $\mu\text{m}$ ) and ground to a fine powder (Zhao et al., 2012). For total heavy metal determinations, 1 g sediment samples were digested by  $\text{HNO}_3$ – $\text{HClO}_4$ –HF mixture (8, 5 and 3 mL, respectively) in Teflon tubes at 160 °C for 6 h in an oven. After digestion, the extracted solutions were filtered and diluted with double deionized water to 25 mL (Hu et al., 2015). The sediment extracts were analyzed for Cr, Mn, Fe, Co, Ni, Zn, As, Se, Al, Ag, and Mg by Spectro Genesis inductively coupled plasma optical emission spectroscopy spectrometer (made in Germany, Petrolab part number: 76004551).

**Table 1**  
Locations of sampling sites along the Zarrin-Gol River.

Sites	Coordinates		Altitude (m)
	Latitude	Longitude	
S-1	36° 48' 51.0156"	55° 1' 52.3482"	530
S-2	36° 52' 25.5318"	54° 57' 16.5198"	515
S-3	36° 49' 33.2760"	55° 00' 41.1546"	291
S-4	37° 0' 8.5206"	54° 54' 18.1116"	60
S-5	37° 4' 29.8884"	54° 53' 3.1950"	26
S-6	37° 7' 37.2786"	54° 52' 46.6320"	15

In this study, analytical data quality was ensured through the implementation of laboratory quality assurance and quality control methods, including the use of calibration with standards, standard operating procedures, recovery of spiked samples, analysis of reagent blanks, and analysis of replicates. The precision and accuracy of the analytical methods were evaluated by recovery measurements on spiked sediment samples. The percentage recoveries of the elements ranged from 90.7% to 108.5%. The precision of the analytical procedures, expressed as the relative standard deviation (RSD), ranged from 3 to 8%.

In the present study, several different indices were used to estimate the degree of heavy metal pollution in surface sediments of the Zarrin-Gol River. The CF index values were obtained by dividing the concentration of each metal in the sediment by baseline or background level (Hakanson, 1980). The background values used were 90.0 for Cr, 850.0 for Mn, 47,200.0 for Fe, 19.0 for Co, 68.0 for Ni, 95.0 for Zn, 13.0 for As, and 0.6 for Se, and 80,000  $\text{mg kg}^{-1}$  for Al, respectively (Buccolieri et al., 2006; Chabukdhara and Nema, 2012; Díaz-de Alba et al., 2011; Harikumar and Jisha, 2010; Turekian and Wedepohl, 1961; Tuttle, 1996).

$$\text{CF} = \frac{C_{\text{Heavy metal}}}{C_{\text{Background}}}$$

CF values were interpreted as follows: low contamination at  $\text{CF} < 1$ ; moderate contamination at  $1 < \text{CF} < 3$ ; considerable contamination at  $3 < \text{CF} < 6$ ; and very high contamination at  $\text{CF} > 6$ , according to Hakanson, 1980.

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