

## Research Article

# Evaluating arsenic and heavy metal contamination in estuarine sediments of the Southern Caspian Sea, Iran

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Coastal and estuarine ecosystems face increasing threats from heavy metal pollution originating from industrial and agricultural activities, presenting significant environmental and public health risks. This study investigates arsenic and heavy metal contamination within surface sediments of eight major rivers discharging into the southern Caspian Sea: Gorganrud, Qarasu, Tajan, Babolrud, Sardabrud, Safarud, Cheshmeh Kileh, and Sefidrud. Twenty-four surface sediment samples, collected from upstream, river mouth, and near-shore zones, were analysed to assess spatial variations. A sediment core from Gorgan Bay, providing a ~1400-year depositional record, was also examined to understand historical trends. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to determine trace metal concentrations, along with grain size distribution and organic matter content analyses. Arsenic concentrations varied spatially, ranging from 0.3 to 18.45 mg/kg. Pollution indices, including modified contamination degree (mCd) and Pollution Load Index (PLI), revealed slight-to-moderate pollution in several rivers, while the Ecological Risk Index (RI) indicated consistently low ecological risk. Enrichment Factor (EF) analysis identified both natural and anthropogenic influences contributing to heavy metal accumulation. These results underscore the complex interplay of factors driving heavy metal contamination in the Caspian Sea estuaries, emphasising the need for long-term monitoring programs to support effective coastal management and mitigation efforts within this ecologically vital region.

[**Keywords:** Arsenic, Caspian Sea, Ecological risk, Enrichment factor, Pollution, Sediment]

## Introduction

Geochemical investigations of sediments from rivers, estuaries, and coastal areas are essential for determining the sources of pollutants, their transport pathways, and associated ecological dangers<sup>1</sup>. When environmental conditions change such as shifts in redox status or microbial activity heavy metals that were previously trapped in sediments can be released into the water column and eventually enter food webs<sup>2-4</sup>. This release becomes more pronounced in coastal environments, where increased salinity facilitates the detachment of metals from clay surfaces<sup>5</sup>.

Heavy metals present in aquatic systems originate either from natural rock weathering or from human activities<sup>6,7</sup>. For hazardous elements like arsenic (As), lead (Pb), and cadmium (Cd), anthropogenic sources frequently dominate in coastal regions<sup>8</sup>. Arsenic is especially concerning because of its intricate geochemical behavior, elevated toxicity, and tendency to accumulate in living organisms<sup>9</sup>. Although natural weathering contributes to arsenic

mobilization, human inputs have significantly changed its environmental cycle<sup>10</sup>.

Sediments act both as reservoirs and as secondary sources of pollutants, with remobilization presenting ongoing threats to ecosystem health<sup>11,12</sup>. The Caspian Sea, which is experiencing rising anthropogenic stress, serves as a clear example of these challenges<sup>13</sup>. Earlier research on rivers that flow into the Caspian (including the Tajan, Gorganrud, and Neka) has documented elevated heavy metal concentrations, with spatial patterns reflecting human influence near estuarine zones<sup>14</sup>. Specifically, arsenic and zinc levels in Gorganrud River sediments exceeded recommended thresholds<sup>14,15</sup>, while enrichment factors calculated for the Neka River indicated severe contamination from silver and cadmium<sup>15</sup>. Nevertheless, information on comprehensive evaluations of arsenic distribution and its chemical forms is essential for risk assessment remain limited<sup>16</sup>. This knowledge gap is especially concerning given the Caspian Sea's ecological significance as a habitat for endemic species and as a support for commercial fisheries<sup>17</sup>.

The present study examines geochemical signatures in sediments collected from eight major rivers draining into the southern Caspian Sea: Gorganrud, Qarehsu, Tajan, Babolroud, Sardabroud, Shiroud, Cheshmeh Kileh, and Sefidrud. A sediment core obtained from Gorgan Bay was also analyzed. Through analysis of heavy metal distribution with a particular emphasis on arsenic, this research introduces a novel element: the application of a historical baseline derived from the K5 core sample (dated to approximately 1400 years before present) to evaluate recent anthropogenic effects on sediment composition.

This approach allowed for a more robust determination of the extent of enrichment of various elements compared to natural background levels, (2) identify anthropogenic vs. natural contributions, and (3) evaluate ecological risks. The findings provide critical data for regional monitoring programs and inform management strategies tailored to the Caspian's unique biogeochemical conditions.

## Materials and Methods

### Study area

The study area is located in the southern part of the Caspian Sea, extending from Astara in the far west to the Hussein-Quli Gulf in the far east, encompassing 8 important rivers and parts of the coastal lines of 3 provinces: Golestan, Mazandaran, and Gilan. It has unique geological structures and characteristics that are primarily influenced by factors such as geology, wave and current regimes, basin water level, physicochemical water status, and types of biological

processes (Fig. 1). Geologically, the Gorgan schists, metamorphic rocks of eastern Masuleh, Lahijan granites, evidence of multiple volcanic activities, and mafic and ultramafic igneous rocks are situated in the central and western parts of the region within an area called the Gorgan-Rasht zone<sup>18</sup>.

The prevailing climate in the region varies from warm and humid Mediterranean to warm and dry desert, influenced by its geographical position and natural features. Due to the Caspian Sea's location at relatively low latitudes, it receives significant solar radiation. The Alborz and Caucasus mountain ranges in the southern and western parts, and the steppes and deserts in the northern and eastern sections of this sea, have led to very different atmospheric processes, with the most significant atmospheric systems affecting the region's climate being the Siberian high-pressure system in Asia and the North Atlantic oscillations (caused by the Icelandic low-pressure and Azores high-pressure systems)<sup>19,20</sup>. The maximum precipitation throughout the year (around 800 mm) occurs in the western parts of the region, particularly in the Anzali area, and the amount of precipitation decreases towards the east, reaching approximately 450 millimetres in Gorgan and about 125 – 195 mm in the eastern parts<sup>19,20</sup>.

### Sediment sampling and analysis

Considering the ecological and fisheries importance of the rivers and river mouths in the southern Caspian Sea, surface sediment samples were collected from eight key rivers: Gorganrud, Qarasu, Tajan, Babolrud, Sardabrud, Safarud, Cheshmeh

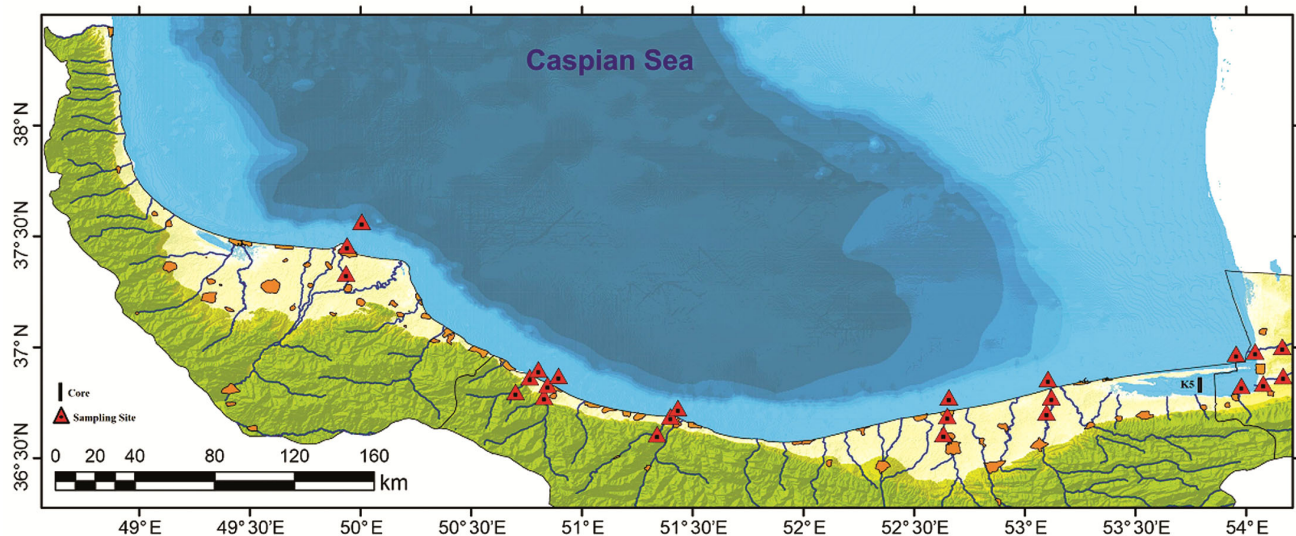


Fig. 1 — Location of sediment sampling in the southern Caspian Sea

Kileh, and Sefidrud. Sampling was carried out at three distinct points: (1) upstream sections of the rivers, (2) estuarine zones, and (3) offshore areas at water depths ranging from approximately 1 to 10 meters. In order to determine natural background levels of heavy metals, a sediment core was collected from Gorgan Bay using a gravity corer. The precise geographic positions of all sampling sites were recorded using a handheld GPS unit (eTrax, Garmin) to support subsequent geostatistical modeling (Fig. 1). Once collected, the sediment samples were immediately placed in coolers filled with ice and transferred to the laboratory, where they were stored at 4 °C pending further processing. Each sample was then split into two subsamples: one subsample was designated for particle size analysis, organic matter content, and calcium carbonate measurement, while the other was kept for arsenic and heavy metal analysis.

For preparation, sediment samples were oven-dried, and any visible gravel or debris was manually removed. The dried material was subsequently pulverized to a fine powder using a hand mortar. For chemical digestion, 0.5 g of the ground sediment was mixed with a solution containing hydrochloric acid (HCl), nitric acid (HNO<sub>3</sub>), and deionized water in a 1:1:1 volumetric ratio. This mixture was then heated at 95 °C for 60 minutes. After digestion, the samples were analyzed using ICP-MS (Perkin-Elmer ELAN9000). To verify analytical precision and reliability, certified reference materials (Oreas 45Pa, DS7, and DS8) were used to assess instrument calibration and data quality. The obtained results showed strong agreement with certified values, achieving recovery rates between 94.04 % and 107.89 %. The method's detection limit was determined to be 0.1 ppm.

For the assessment of Total Organic Matter (TOM), sediment samples were initially dried at 70 °C for 24 h, followed by combustion in an oven at 550 °C for 4 h. The TOM content was quantified in accordance with the methodology outlined by Abrantes *et al.*<sup>21</sup>, utilising the prescribed equation. This rigorous approach ensured the precision and validity of the analytical results.

$Total\ Organic\ Matter\ (TOM\%) = (B - CB) \times 100$   
(Before combustion);  $Total\ Organic\ Matter\ (TOM\%) = (BB - C) \times 100$  (After combustion).

Where, *B* and *C* represent the weights of the dried sediment before and after combustion in the oven, respectively. For grain size analysis, 4 g of sample was dispersed in a dispersion solution, and the grain

size distribution was determined using a laser particle sizer (Horiba LA-950).

#### Assessment of heavy metals pollution

To evaluate current heavy metal pollution levels (specifically arsenic, As) and compare them to historical conditions, Enrichment Factor (EF) analysis was employed. This established method effectively distinguishes between sedimentary metal sources of anthropogenic or natural origin by normalising metal concentrations relative to sediment texture properties, using a reference element such as aluminum (Al)<sup>22-25</sup>. EF serves as a key indicator of environmental contamination status. Following Sutherland's (2000) classification<sup>26</sup>, EF values are categorised as: EF < 2 (deficiency to minimal enrichment), EF = 2 – 5 (moderate enrichment), EF = 5 – 20 (significant enrichment), EF = 20 – 40 (very high enrichment), and EF > 40 (extremely high enrichment). Aluminum is commonly used as the normalising element in coastal areas due to its prevalence in aluminosilicates. The EF, also reflecting sedimentation degree<sup>27</sup>, was calculated using:

$$EF = (H_s / Al_s) / (H_c / Al_c)$$

Where, *H<sub>s</sub>* and *H<sub>c</sub>* represent the heavy metal concentrations in the sample and background reference sediment, respectively, and *Al<sub>s</sub>* and *Al<sub>c</sub>* represent the corresponding aluminium concentrations. This study utilised background metal concentrations for sediments from the Iranian sector of the Caspian Sea: As (12.5 ppm), Cr (85.2 ppm), Pb (18 ppm), Cu (34.7 ppm), Zn (85.3 ppm), and Al (6.05 %) <sup>28</sup>. To assess overall sediment environmental quality, the Pollution Load Index (PLI) for six metals was calculated according to Suresh *et al.*<sup>28</sup>:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$$

Where, *CF<sub>1</sub>*, *CF<sub>2</sub>*, ..., *CF<sub>n</sub>* are the contamination factors; *CF* (Contamination Factor) for each metal is the ratio of its concentration in the sample (*CH metal*) to its background concentration (*CH back*):  $CF = CH\ metal / CH\ back$ .

The Potential Ecological Risk Index (PER) was also applied to evaluate the contamination level and associated ecological risk from heavy metals in the sediments, based on the methodology of Guo *et al.*<sup>29</sup>:

$$PER = \sum E$$

The ecological risk factor for an individual element (*E<sub>i</sub>*) is calculated as:

$$E_i = T \times C_i$$

Where,  $C_i$  is the single-element contamination factor ( $C_i = Ca_i / Cb$ ),  $Ca_i$  is the concentration of element  $i$  in the sample, and  $Cb$  is its reference background value. The biological toxic response factor ( $T_i$ ) for each element was assigned as: Cu = 5, Pb = 5, Zn = 1, As = 10, and Cr = 6. PER represents the cumulative potential ecological risk, integrating the sensitivity of biological communities to toxicants and the overall contamination level.

Significant differences in calculated parameters (EF, PLI, PER, CF) between seasons were identified using  $t$ -tests in SPSS (Version 19). Data normality and homogeneity of variance were verified beforehand, applying  $\log(1+x)$  transformation where necessary. Relationships among environmental parameters were examined using Pearson correlation analysis. Background metal concentrations used for the CF and PER calculations (As: 5 ppm, Pb: 6 ppm, Cu: 10 ppm, Zn: 31 ppm, Cr: 17 ppm, and Al: 1.09 %) were derived from a sediment sample collected at a depth of 1 m<sup>(ref. 30)</sup>.

#### Sediment Quality Guidelines (SQG)

Concentrations of individual heavy metals (As, Cr, Pb, Cu, Zn) were compared to established SQG benchmarks, specifically the Threshold Effect Level (TEL) and Probable Effect Level (PEL)<sup>31</sup>, as well as the Effects Range-Median (ERM) and Effects Range-Low (ERL) values<sup>32,33</sup>. These guidelines provide empirically derived thresholds to estimate the likelihood of adverse biological impacts (e.g., toxicity to benthic organisms) based on sediment metal concentrations.

#### Results

The chemical composition of sedimentary rocks is influenced by processes such as source rock type, weathering conditions, tectonics, and climate changes<sup>30,31</sup>. Analysing sediment origins aids in reconstructing sedimentation history, including source-area distance, direction, size, and regional climate. Elemental geochemistry is crucial for determining paleoenvironmental conditions, allowing investigation of climate and depositional characteristics. Sedimentological analysis of 24 samples obtained from 8 key rivers in the southern Caspian Sea region revealed a diverse range of facies. The compositional distribution, as determined by laboratory examination, indicates a prevalence of silty

sand (zS) and sandy silt (sZ) facies, each accounting for six samples. Further analysis identified five samples as representing gravelly sandy mud (gmS) facies, while four samples exhibited characteristics consistent with mud-sand facies containing minor gravel ((g)mS). The remaining samples comprised two examples of gravelly sand (gS) and a single instance of mud (M) facies, collectively illustrating the heterogeneous sedimentary environment prevailing within the river systems under investigation, as summarised in Figure 2. The average composition was 3.59 % gravel, 52.46 % sand, 41.48 % silt, and 2.27 % clay, with organic matter averaging 6.93 %, peaking in Gorganrud (Gor-3) and lowest in Sardabroud upstream (SD-1) (Fig. 2). Arsenic concentrations were elevated in Gorganrud and Qarasu Rivers, while chromium, cobalt, lead, and vanadium peaked in Ramsar River (Safaroud), and zinc was highest in Qarasu (Fig. 3). The lowest metal concentrations were found in Cheshmekileh (cobalt), Sefidroud (arsenic), Sardabroud (copper, chromium, zinc), Babelroud (nickel), and Qarasu (lead). Maximum concentrations included arsenic (49.6 mg/kg) in Gorgan River (Gor-2), copper (52.6 mg/kg) in Sefidrud (Sf-3), nickel (60 mg/kg) in Qarasu (Gh-01), and lead (56.7 mg/kg), cobalt (32.67 mg/kg), and chromium (142.8 mg/kg) in the Ramsar's Safaroud estuary (Ram-2, Ram-3). Pollution indices (Cd and mCd) indicated all rivers were polluted, with Gorganrud, Qarasu, Tajan, Ramsar, and Sefidrud classified as significantly polluted ( $24 \geq Cd \geq 12$ ). Modified indices ranged from low ( $2 \geq mCd \geq 1.5$ ) to moderate pollution ( $4 \geq mCd \geq 2$ ). The Pollution Load Index (PLI) exceeded 1 in most cases, indicating slight to significant pollution. Urbanisation, fishing boats, and vehicular traffic along Mazandaran and Gilan Rivers likely contributed to sediment pollution, especially in estuaries (Table 1). The establishment of a historical baseline, derived from the analysis of the K5 core sample obtained at a depth of 85 cm and dated to approximately 1400 years before present, offers a crucial framework for the evaluation of contemporary anthropogenic impacts on sediment geochemistry within this region and enabling a nuanced understanding of the temporal evolution of sediment composition under the influence of human activities (Table 1).

According to the enrichment factor, it was observed that arsenic is highly enriched in Gorganrud and Qarasu Rivers, and in other rivers it is normal

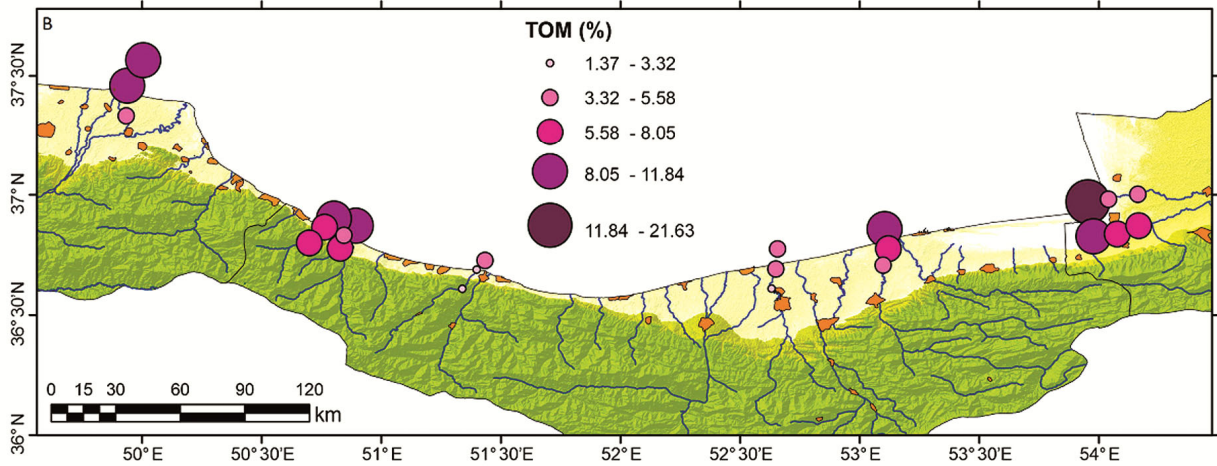
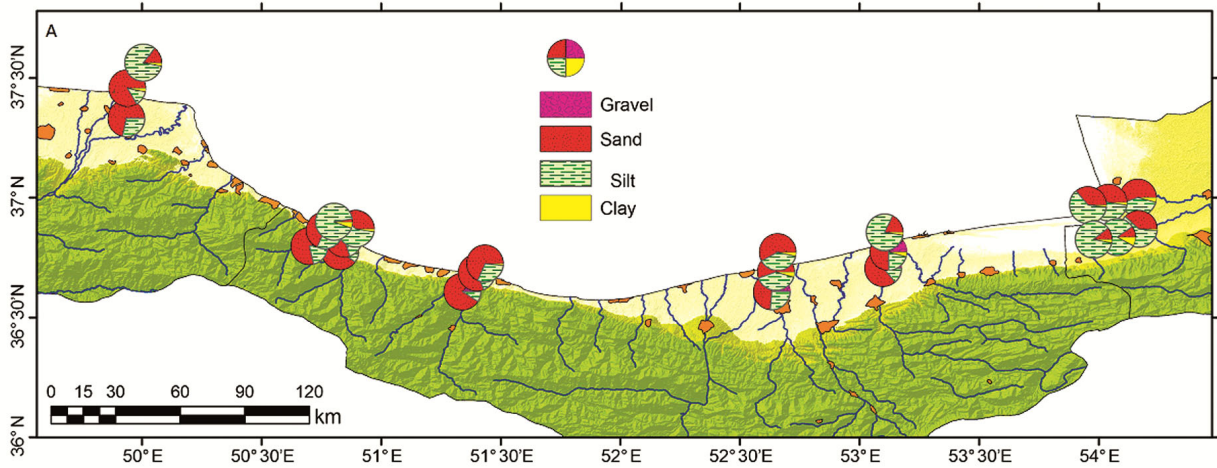


Fig. 2 — Results of grain size and total organic matter results for different stations

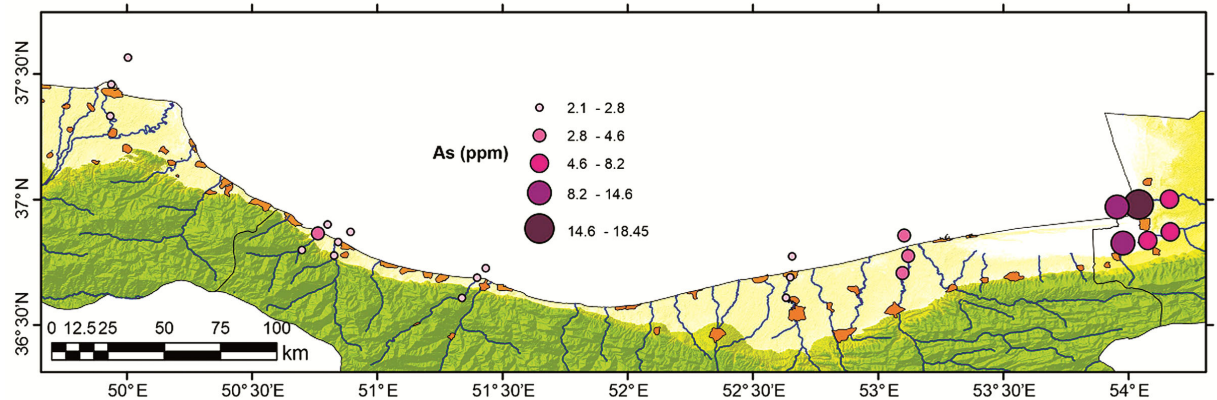


Fig. 3 — Distribution of arsenic in different stations

(Fig. 3). In the samples of most rivers chromium showed normal level and the highest enrichment is related to Ramsar and upstream of the river, where the enrichment factor reaches more than two to three times its natural value. Zinc is also contaminated in all the samples, and its enrichment

factor ranged from two to more than four times. Nickel, cobalt and copper elements also showed contamination in most of the samples (Fig. 4). One of the factors for the enrichment of arsenic and some heavy metals can be the geology of the region<sup>32</sup>.

Table 1 — Concentrations of heavy metals and arsenic compared to background values (ppm)

Sample	As (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Fe (%)	Al (%)	Cd	mCd	PLI	RI
Gor-1	6.76	11.2	39	13.5	28.2	14.3	80.5	2.43	2.7	9.11	1.30	1.20	35.08
Gor-2	18.45	19.5	86	35.4	59.1	22.4	110.3	2.74	6.5	9.11	1.30	1.20	35.08
Gor-3	14.6	15.3	48.5	9.5	20.4	21.6	36.6	3.40	2.0	18.73	2.68	2.39	87.42
GH-01	7.8	26.0	65.0	34.0	60.0	14.0	90.0	3.81	3.2	11.29	1.61	1.25	63.60
GH-02	8.2	26.0	63.0	47.0	59.0	16.1	99.0	2.64	3.1	14.03	2.00	1.92	46.60
Gh-03	11.8	19.2	52.0	31.2	50.4	18.3	72.1	3.19	2.2	15.39	2.20	2.07	53.30
Tajan-1	4.6	21.2	63.2	33.8	49.5	25.4	79.9	1.47	4.2	13.94	1.99	1.83	60.47
Tajan-2	3.7	24.6	81.8	34.5	47.6	29.3	78.6	1.17	6.2	12.83	1.83	1.79	40.48
Tajan-3	3.1	25.1	84.2	32.8	48.9	31.3	78.5	1.28	5.9	13.44	1.92	1.87	40.02
Babol-1	2.1	11.6	34.2	22.8	19.2	33.7	65.2	0.82	1.9	13.43	1.92	1.84	38.36
Babol-2	2.3	11.0	35.0	24.0	18.0	24.2	56.0	1.77	1.4	9.08	1.30	1.13	30.62
Babol-3	2.3	14.0	34.0	32.0	28.0	27.3	64.0	2.90	2.3	8.12	1.16	1.06	27.72
SD-01	2.3	10.9	29.0	14.2	25.5	28.2	47.0	1.31	1.3	9.74	1.39	1.25	31.79
SD-02	2.8	14.0	37.0	18.1	32.2	29.4	64.0	0.81	1.7	7.72	1.10	1.00	25.84
SD-03	2.2	10.2	29.0	12.3	22.6	23.8	43.0	0.92	1.1	9.33	1.33	1.24	29.63
CH-01	2.4	11.0	38.0	16.4	26.6	25.5	57.0	2.22	1.2	6.91	0.99	0.91	22.90
CH-02	2.2	9.6	37.0	15.0	26.3	26.1	51.0	2.05	1.1	8.13	1.16	1.09	26.07
Ch-03	.3	10.2	38.3	17.2	25.7	24.7	52.2	4.14	1.3	7.72	1.10	1.02	25.12
Ram-1	2.4	18.0	42.0	31.0	48.0	28.3	72.0	4.16	5.4	7.88	1.13	1.06	25.78
Ram-2	3.0	32.7	142.8	31.4	47.9	25.2	87.8	4.50	6.1	11.21	1.60	1.48	32.50
Ram-3	2.2	25.8	88.0	48.2	55.3	56.7	96.2	2.19	7.4	14.74	2.11	2.01	37.20
Sf-1	2.3	10.0	31.0	32.1	28.3	15.4	49.0	2.79	7.0	17.14	2.45	2.13	51.61
Sf-2	2.1	26.4	81.0	48.2	47.9	19.1	73.9	1.98	6.0	7.99	1.14	1.05	26.67
Sf-3	2.2	24.9	86.5	52.6	58.6	24.0	89.6	2.48	6.0	13.03	1.86	1.70	35.06
Min	0.3	17.85	56.90	28.63	38.88	25.18	70.56	2.38	3.63	6.91	0.99	0.91	22.9
Max	18.45	32.67	142.78	52.62	60.00	56.70	110.30	4.50	7.40	18.73	2.68	2.39	87.42
Average	9.60	9.60	29.00	9.47	18.00	14.00	36.59	0.81	1.10	11.25	1.61	1.48	38.71
Crust	1.8	25	100	55	75	13	70	5.00	8.10	-	-	-	-
Shale	13	19	90	45	68	20	95	4.72	8.00	-	-	-	-
K5 Core	2.96	11.60	53.01	14.33	27.43	20.85	41.60	2.25	3.13	-	-	-	-

## Discussion

Monitoring heavy metal pollution in coastal sediments provides a critical indicator for assessing the health of coastal ecosystems. The current study results present a comprehensive geochemical analysis of sedimentary rocks collected from eight major rivers draining into the southern Caspian Sea, revealing insights into sediment provenance, paleoenvironmental conditions, and anthropogenic pollution. The investigation analyses the chemical composition of 24 sediment samples collected from various locations along these rivers, identifying six distinct facies: silty sand (zS), sandy silt (sZ), gravelly sandy mud (gmS), muddy sand with gravel ((g)mS), gravelly sand (gS), and mud (M). The analysis of grain sizes, organic matter content and heavy metal concentrations provides valuable information about

the source rocks, weathering processes, and anthropogenic inputs affecting these river systems. The eastern parts of the Caspian Sea are particularly vulnerable to heavy metal contamination due to the region's underlying geology. The Gorgan metamorphic complex (Gorgan shales), a prominent geological feature in this area, contributes significantly to the heavy metal load<sup>18</sup>. Notably, a substantial portion of the source rock of this metamorphic complex is of basic igneous origin.

Basic igneous rocks, such as basalts and gabbros, are naturally enriched in a variety of heavy metals, including chromium, nickel, cobalt, and vanadium. As these rocks undergo weathering and erosion, these metals are released into the surrounding environment, eventually finding their way into the Caspian Sea (Fig. 5). The combination of heavy metal-rich igneous

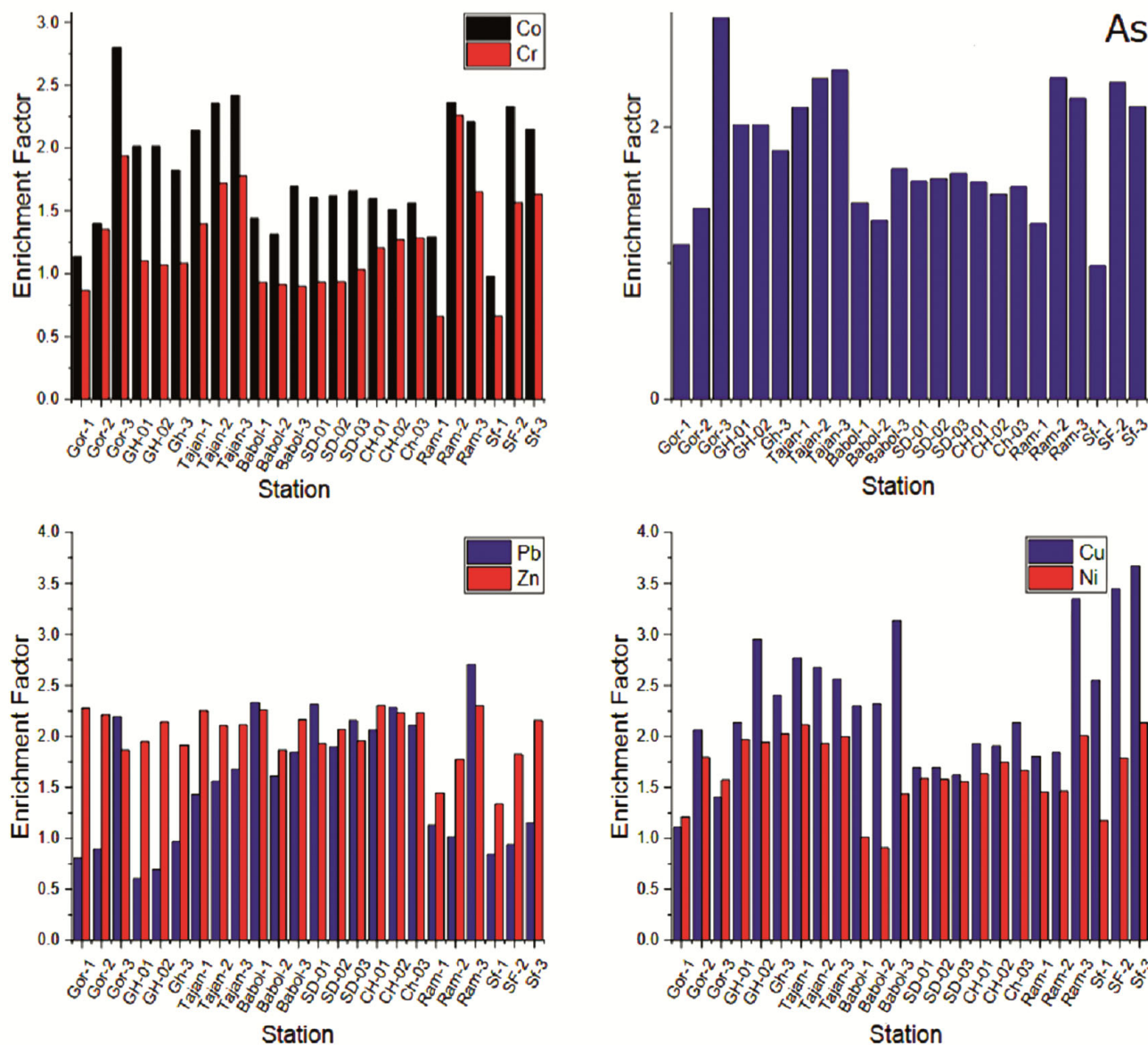


Fig. 4 — Enrichment chart of heavy metals in different stations

source rocks and the adsorption capacity of clay-rich sediments creates a scenario where the eastern Caspian Sea is naturally predisposed to elevated heavy metal concentrations. In the central and western parts of the Caspian Sea, the presence of ultramafic rocks contributes to the heavy metal burden. Ultramafic rocks, characterised by their high magnesium and iron content and low silica content, are often rich in elements such as iron, chromium, nickel, cobalt, and manganese. The hot, humid climate in this region promotes the weathering and erosion of these ultramafic rocks, leading to the release of these elements into the environment. This

release further contributes to the overall heavy metal load in the Caspian Sea sediments.

While natural geological processes undeniably contribute to the heavy metal burden in the Caspian Sea, anthropogenic activities are responsible for the majority of heavy metal pollution. Industrial discharges, agricultural runoff, and domestic wastewater introduce a variety of pollutants, including heavy metals, into the sea. Further evidence supporting the role of natural sources comes from correlation analyses of heavy metal concentrations in river sediments feeding into the Caspian Sea. According to Table 2 and Figure 6, the results note

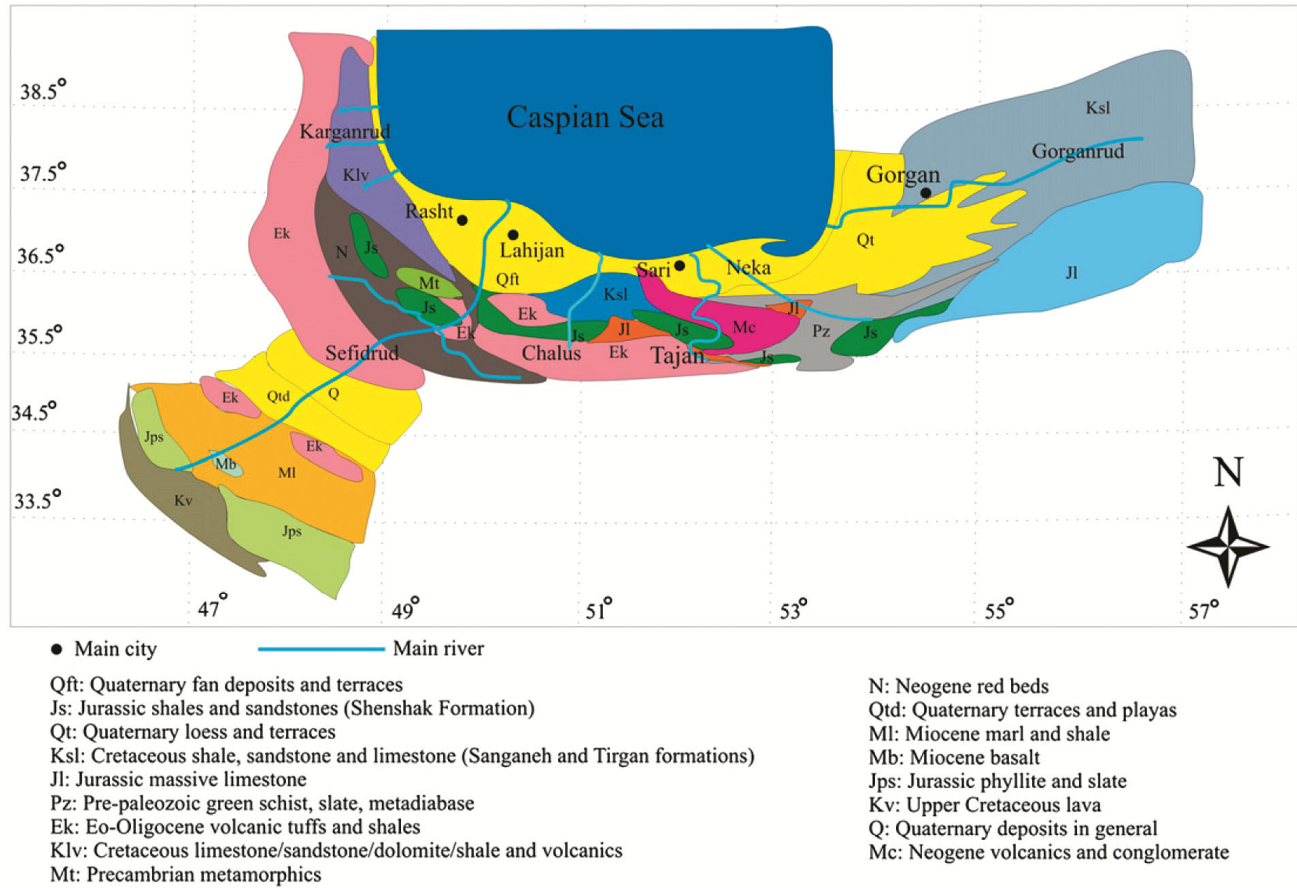


Fig. 5 — Geological map of study area (Taken from Lahijani & Tavakoli, 2012)<sup>43</sup>

Table 2 — Correlation of different elements and grain size

	Fe	AL	As	Co	Cr	Cu	Ni	Pb	Zn	V	Sand	Silt	Clay
<b>AL</b>	.749**												
<b>As</b>	.224	.044											
<b>Co</b>	.770**	.677**	.140										
<b>Cr</b>	.683**	.706**	.153	.901**									
<b>Cu</b>	.758**	.744**	-.013	.763**	.611**								
<b>Ni</b>	.859**	.678**	.294	.855**	.711**	.815**							
<b>Pb</b>	-.056	.220	-.352	.111	.171	.142	.025						
<b>Zn</b>	.863**	.617**	.308	.750**	.696**	.741**	.871**	.095					
<b>V</b>	.604**	.756**	.032	.657**	.814**	.590**	.457*	.323	.597**				
<b>Sand</b>	-.325	-.235	-.380	-.440*	-.326	-.475*	-.506*	-.186	-.490*	-.253			
<b>Silt</b>	.344	.259	.403	.432*	.331	.464*	.500*	.114	.462*	.244	.983**		
<b>Clay</b>	.320	.193	.177	.383	.253	.501*	.372	.052	.488*	.245	-.610**	.598**	
<b>Tom</b>	-.101	.082	.358	.268	.234	.041	.090	-.049	-.125	.017	-.417*	.458*	.215

that nickel, cobalt, vanadium, copper, lead, and zinc exhibit a positive and significant correlation with iron and aluminium in river samples. This correlation suggests that these elements originate from the same source and exhibit similar behaviour in the environment. The association with iron and aluminium further supports the hypothesis that these

elements are derived from the weathering of iron-rich and aluminium-rich rocks, such as the ultramafic and metamorphic rocks found in the Caspian Sea basin. In contrast, arsenic shows a negative correlation with most other elements, suggesting a different origin or behaviour<sup>14</sup>. This finding is consistent with the understanding that arsenic's solubility and mobility in

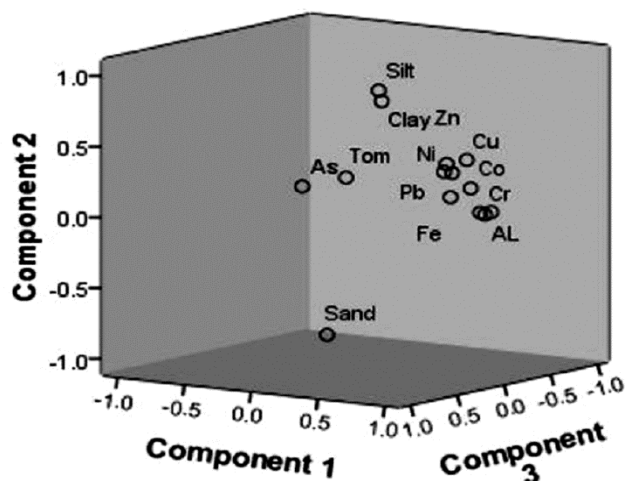


Fig. 6 — PCA of heavy metals

aquatic environments differ from those of other heavy metals. The availability of diverse climatic and structural conditions for weathering in the Caspian Sea basin results in soils with a high potential to contain natural metal elements. These metal-rich soils, subjected to erosion and transport, contribute to sediment enrichment in the Caspian Sea.

#### Comparison with other regions

It's important to compare the geochemical characteristics of the Caspian Sea river sediments with those observed in other river systems worldwide. Studies in major Asian rivers, such as the Yellow River in China<sup>33,34</sup> and the Ganges River in India<sup>35,36</sup>, have revealed significant heavy metal contamination stemming from industrial discharge, mining activities, and agricultural runoff. The Yellow River, for example, carries high loads of sediment and pollutants due to intensive agriculture and industrial development in its basin<sup>37</sup>. The Ganges River suffers from severe pollution due to untreated sewage, industrial waste, and agricultural runoff<sup>36</sup>. The levels of pollution in these rivers, like those found in the Caspian Sea, emphasise the impact of anthropogenic activities on aquatic environments. In Europe, the Rhine River, which flows through several industrialised countries, has historically suffered from heavy metal pollution. Extensive remediation efforts have improved water quality over the past decades, but legacy contamination remains a concern<sup>38</sup>. Other European rivers, such as the Danube, also experience pollution from industrial sources, agriculture, and urbanisation<sup>39</sup>. Although

the sources are different, the underlying issues of industrial and urban contributions to heavy metal pollution are observed in the Caspian Sea's rivers as well. Many North American rivers also face challenges related to sediment pollution. The Mississippi River, for instance, is heavily impacted by agricultural runoff, particularly nutrient loading that leads to hypoxia in the Gulf of Mexico<sup>40</sup>. While the Caspian Sea river studies primarily focus on heavy metals, the impact of agricultural activities is similar.

#### Sediment quality guidelines

Concentrations of selected elements in the collected sediments were evaluated against established sediment quality standards and compared with findings from relevant studies in other locations. Internationally recognised benchmarks, including the NOAA Sediment Quality Guidelines<sup>41,42</sup> and the Canadian Sediment Quality Guidelines, were applied. These define critical thresholds: NOAA: Effects Range-Low (ERL) – the concentration below which adverse biological effects are rarely observed; and Effects Range-Median (ERM), the concentration above which adverse effects frequently occur. As per Canadian SQG, Threshold Effect Level (TEL) is concentration below which adverse effects are unlikely, and Probable Effect Level (PEL) is the concentration above which adverse effects are likely. Analysis revealed that the sediment element concentrations in the study area consistently fell below the PEL and ERM thresholds (indicating probable/severe effects) and were generally positioned between the TEL/ERL and PEL/ERM levels. Comparative analysis (Table 3) showed that while concentrations in the southern rivers were generally lower than those reported for the Volga River, certain elements (notably cobalt, chromium, nickel, and to a lesser extent, lead) were higher than levels documented in the Red, Suwa, and Han Rivers<sup>43</sup>. Field observations indicate that both the region's distinct geological characteristics and anthropogenic activities are significant contributors to riverine pollution. Given the ecological and economic importance of these areas, particularly the estuaries for tourism and fisheries resources, implementing preventive measures, rigorous management protocols, and continuous monitoring is essential to mitigate potential threats to environmental health and local ecosystems.

Table 3 — Comparison of results of this study with other studies and quality guidelines

Region	Fe (ppm)	Pb (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Ni (ppm)	Co (ppm)	Cr (ppm)	Reference
Gorganrud	3.17	19.43	19.47	75.80	13.27	35.90	15.33	57.83	This study
Qarasu	3.93	16.13	37.40	87.03	9.27	56.47	23.73	60.00	This study
Tajan	3.33	28.67	33.70	79.00	3.80	48.67	23.63	76.40	This study
Babolroud	2.67	28.40	26.27	61.73	2.23	21.73	12.20	34.40	This study
Sardabroud	2.33	27.13	14.87	51.33	2.43	26.77	11.70	31.67	This study
Cheshmeh Kileh	2.13	25.43	16.20	53.40	2.30	26.20	10.27	37.77	This study
Ramsar	4.27	36.73	36.87	85.33	2.53	50.40	25.50	90.93	This study
Sefisroud	3.60	19.50	44.30	70.83	2.20	44.93	20.43	66.17	This study
Gorgan Bay	2.1- 7.3	9.88- 43.8	6.01- 45.2	23.8- 106	2.89- 10.15	8.78- 105.4	5.37- 44.8	15.3- 149.6	Bagheri <i>et al.</i> , 2020
SE Caspian Sea	5	13	9.09	28	4.11	17.42	-	-	Bastami <i>et al.</i> , 2014
Volga	-	38	53	152	-	67	-	69	Winkels <i>et al.</i> , 1998
Red river	3.76	66	83	127	-	38	-	-	Nguyen <i>et al.</i> , 2016
Han River	3.26	35.1	29.7	126	-	25.3	19.2	-	Kim <i>et al.</i> , 2011
Sova River	3.13	55.3	42.8	303	-	49.38	15.7	-	Bilinski, 2008
ERL <sub>a</sub>	-	46.7	34	150	8.2	21	-	81	Long <i>et al.</i> 1995
ERM <sub>b</sub>	-	218	270	410	70	52	-	370	Long <i>et al.</i> 1995
TEL <sub>c</sub>	-	30.2	18.7	124	7.24	-	-	52.3	ISQG
PEL <sub>d</sub>	-	112	108	271	41.6	-	-	160	ISQG

## Conclusion

This research offers a thorough evaluation of the geochemical characteristics and contamination status of sediment samples collected from major rivers that flow into the southern basin of the Caspian Sea. The findings reveal widespread contamination, especially concerning heavy metals, and emphasize the combined influence of natural geological processes and human activities on sediment pollution. By employing a historical baseline to calculate enrichment factors, the study presents a useful approach for assessing the extent of anthropogenic impacts. These results carry significant implications for environmental governance and policy-making, pointing to the necessity for more stringent regulations, enhanced waste management systems, and focused remediation efforts to safeguard the Caspian Sea ecosystem's health. Additional investigations are essential to pinpoint the exact origins of pollutants, determine their respective contributions, and evaluate the bioavailability and potential ecological threats linked to the detected metal pollution.

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## Conflict of Interest

The author declares that there are no conflicts of interest regarding the publication of this manuscript. No financial, personal, or professional relationships have influenced the research, analysis, or interpretation of the data presented in this study.

## Ethical Statement

This study did not involve any human participants, animal experiments, or the use of protected or endangered species. All sediment samples were collected in accordance with local environmental regulations and guidelines. No ethical approval was required for this research.

## References

- 1 Shajan K P, Geochemistry of bottom sediments from a river-estuary-shelf mixing zone on the tropical southwest coast of India, *Bull Geol Surv Japan*, 52 (8) (2001) 371-382.
- 2 Karbassi A R & Shankar R, Geochemistry of two sediment cores from the west coast of India, *Int J Environ Sci Technol*, 1 (4) (2005) 307-316.
- 3 Ahdy H H & Khaled A, Heavy metals contamination in sediments of the western part of Egyptian mediterranean Sea, *Aust J Basic Appl Sci*, 3 (4) (2009) 3330-3336.
- 4 Abadi M, Zamani A, Perizanganeh & Khosravi H, Investigation of heavy metal concentrations in the sediments

- of four important rivers of south Caspian Sea, *Sci J Wetland Ecol Biol*, 40 (2019) 67-82.
- 5 Herve R P, Andriamalala R, Yves M, Marcellin R, Christine R & Andriamandimboisa N, Assessment of heavy metals concentrations in coastal sediments in north-western cities of Madagascar, *Environ Sci Technol*, 4 (2) (2010) 51-60.
  - 6 Bastami K, Neyestani M, Raecisi H, Shafeian E, Baniamam M, *et al.*, Bioavailability and geochemical speciation of phosphorus in surface sediments of the Southern Caspian Sea, *Mar Pollut Bull*, 126 (2018) 51-57.
  - 7 De Mora S, Sheikholeslami M R, Wyse E, Azemard S & Cassi R, An assessment of metal contamination in coastal sediments of the Caspian Sea, *Mar Pollut Bull*, 48 (1) (2004) 61-77.
  - 8 Bagheri H, Mahmodi Gharaei M H, Mossavi Harami R & Khanebad M, Trace metal environmental contamination records in core sediments of Gorgan Bay in southeast of Caspian Sea, *Appl Ecol Environ Res*, 17 (4) (2019) 9547-9559.
  - 9 Sinderman C J, *Coastal Pollution: Effects on Living Resources and Humans*, 1<sup>st</sup> edn, (CRC Press, Boca Raton), 2005, pp. 312. <https://doi.org/10.1201/9781420036411>
  - 10 Buccolieri A, Buccolieri G, Cardellicchio N, Atti A D, Leo A D, *et al.*, Heavy metals in marine sediments of Taranto Gulf (Ionian Sea, Southern Italy), *J Mar Chem*, 99 (2006) 227-235.
  - 11 Bastami K, Bagheri H, Haghparast S, Soltani F & Hamzehpoor A, Distribution and ecological risk assessment of heavy metals in surface sediments along southeast coast of the Caspian Sea, *Mar Pollut Bull*, 81 (2014) 262-267.
  - 12 Duodu G, Goonetilleke A & Ayoko G, Potential bioavailability assessment, source apportionment and ecological risk of heavy metals in the sediment of Brisbane River estuary, Australia, *Mar Pollut Bull*, 117 (1-2) (2017) 523-531. <https://doi.org/10.1016/j.marpolbul.2017.02.017>
  - 13 Azizpour J & Ghaffari P, Low-frequency sea level changes in the Caspian Sea: long-term and seasonal trends, *Clim Dyn*, 61 (2023) 2753-2763. <https://doi.org/10.1007/s00382-023-06715-9>
  - 14 Bagheri H, Mahmodi Gharaei M H & Mossavi Harami R, Study of arsenic distribution in sediments of the southeastern Caspian Sea, *Int J Basic Appl Sci*, 4 (1) (2015) 57-65.
  - 15 Maghsoudi A, Vanai M & Yazdi M, Heavy metals and study of enrichment and geochemical intensity indices in Nekarood river, *Q J Earth Sci*, 24 (2015) 167-174 (in Persian).
  - 16 Alizadeh H, Naderi Beni A & Tavakoli V, Heavy metals in coastal sediments of South Caspian Sea: natural or anthropogenic sources, *Caspian J Environ Sci*, 16 (1) (2018) 45-61. [https://cjes.guilan.ac.ir/article\\_2781.html](https://cjes.guilan.ac.ir/article_2781.html)
  - 17 Gandhi K S, Pradhap D, Saravanan P, Krishnakumar S, Kasilingam K, *et al.*, Metal concentration and its ecological risk assessment in the beach sediments of Coromandel Coast, Southern India, *Mar Pollut Bull*, 160 (2020) p. 111565. <https://doi.org/10.1016/j.marpolbul.2020.111565>
  - 18 Darvishzadeh A, *Geology of Iran*, 5<sup>th</sup> edn, (Amirkabir Publication, Tehran), 2003, pp. 312.
  - 19 Lahijani H, *Introduction to the Caspian Sea*, (Nourbakhsh Publications), 2003, pp. 119.
  - 20 Terziev S F, Hydrometeorology and hydrochemistry of seas, In: *Hydrometeorological Conditions*, Vol 6.1, (Gidrometeoizdat, Leningrad), 1992.
  - 21 Abrantes A, Pinto F & Moreira M, Ecology of Polychaete *Nereis diversicolor*: population dynamics, production and oogenic cycle, *Acta Oceanol*, 20 (4) (1999) 267-283.
  - 22 Aloupi M & Angelidis M O, Geochemistry of natural and anthropogenic metals in the coastal sediments of the island of Lesvos, Aegean Sea, *J Environ Pollut*, 113 (2001) 211-219.
  - 23 Morillo J, Usero J & Gracia I, Heavy metal distribution in marine sediments from the southwest coast of Spain, *Chemosphere*, 55 (2004) 431-442.
  - 24 Selvaraj K, Ram Mohan V & Szefer P, Evaluation of metal contamination in coastal sediments of the Bay of Bengal, India: geochemical and statistical approaches, *Mar Pollut Bull*, 49 (2004) 174-185.
  - 25 Valdés J, Vargas G, Sifeddine A, Ortlieb L & Guinez M, Distribution and enrichment evaluation of heavy metals in Mejillones Bay (23°S), Northern Chile: geochemical and statistical approach, *Mar Pollut Bull*, 50 (2005) 1558-1568.
  - 26 Sutherland R A, Bed sediment associated trace metals in an urban stream, Oahu, Hawaii, *Environ Geol*, 39 (2000) 611-627.
  - 27 Woitke P, Wellnitz J, Helm D, Kube P, Lepom P, *et al.*, Analysis and assessment of heavy metal pollution in suspended solids and sediments of the river Danube, *Chemosphere*, 51 (2003) 633-642.
  - 28 Suresh G, Ramasamy V, Meenakshisundaram V, Venkatachalapathy R & Ponnusamy V, Influence of mineralogical and heavy metal composition, *Appl Radiat Isot*, 69 (10) (2011) 1466-1474.
  - 29 Guo J, Wang J, Cui D, Wang L, Ma F, *et al.*, Application of bioaugmentation in the rapid start-up and stable operation of biological processes for municipal wastewater treatment at low temperatures, *Bioresour Technol*, 101 (17) (2010) 6622-6629. <https://doi.org/10.1016/j.biortech.2010.03.093>
  - 30 Chen F H, Chen J H, Holmes J, Boomer I, Austin P, *et al.*, Moisture changes over the last millennium in arid central Asia: a review, synthesis and comparison with monsoon region, *Quat Sci Rev*, 29 (2010) 1055-1068.
  - 31 Maghsoudi A, Vanai M & Yazdi M, Heavy metals and study of enrichment and geochemical intensity indices in Nekarood river, *Q J Earth Sci*, 24 (2015) 167-174 (in Persian).
  - 32 Hug S J, Leupin O X & Berg M, Bangladesh and Vietnam: different groundwater compositions require different approaches to arsenic mitigation, *Environ Sci Technol*, 42 (2008) 6318-6323.
  - 33 Wang Z, Lin K & Liu X, Distribution and pollution risk assessment of heavy metals in the surface sediment of the intertidal zones of the Yellow River Estuary, China, *Mar Pollut Bull*, 174 (2022) p. 113286. <https://doi.org/10.1016/j.marpolbul.2021.113286>
  - 34 Ren J, Hao J & Tao L, Concentrations, spatial distribution, and pollution assessment of heavy metals in surficial sediments from upstream of Yellow River, China, *Environ Sci Pollut Res Int*, 28 (2021) 2904-2913. <https://doi.org/10.1007/s11356-020-10349-3>
  - 35 Chakraborty P, Mukhopadhyay R & Chatterjee D, Assessment of heavy metal pollution in sediments of the Ganges River, *Environ Monit Assess*, 186 (11) (2014) 7787-7798.
  - 36 Hao J X, Ren J, Tao L, Fang H, Gao S & Chen Y, Pollution evaluation and sources identification of heavy metals in surface sediments from upstream of Yellow River, *Pol J Environ Stud*, 30 (02) (2021) 1161-1169. <https://doi.org/10.15244/pjoes/125485>

- 37 Salomons W & Förstner U, *Metals in the Hydrocycle*, (Springer-Verlag), 1984, pp. X, 352.
- 38 Liška I, Wagner F & Slobodnik J, Quality of the River Danube: chemical pollution, transboundary effects, and water quality management, *Water Res*, 35 (1) (2001) 1-23.
- 39 Rabalais N N, Turner R E, Diaz R J & Justić D, Hypoxia in the northern Gulf of Mexico: nutrient loadings and coastal water quality, *Estuaries*, 25 (6B) (2002) 1286-1300.
- 40 Long E, MacDonald D D, Smith S L & Calder F D, Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments, *J Environ Manage*, 19 (1995) 81-97.
- 41 NOAA, *Sediment quality guideline developed for the national status and trends Program*, (National Oceanic and Atmospheric Administration, Center for Coastal Monitoring and Assessment), NOAA Technical Memorandum NOS NCCOS CCMA 0137P, 1999.
- 42 Ghanbarpour M R, Goorzadi M & Vahabzade G, Spatial variability of heavy metals in surficial sediments: Tajan River Watershed, Iran, *Sustain Water Qual Ecol*, 1 (2013) 48-58.
- 43 Lahijani H & Tavakoli V, Identifying provenance of South Caspian coastal sediments using mineral distribution pattern, *Quat Int*, 261 (2012) 128-137.