Distribution and contamination pattern of heavy metals from surface sediments in the southern part of Caspian Sea, Iran

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This study concentrates on the speciation and distribution patterns of some heavy metals (Pb, Ni, Cd, Zn, and Cu) in surface sediments in the southern part of the Caspian Sea, the biggest lake in the world, to obtain an overall classification for the origins of metals in the area using a sequential extraction technique. At all sampling stations, Pb, Ni, Zn, and Cu were mostly (>50%) accumulated in the resistant fraction, which indicated that there were no significant anthropogenic inputs of Pb, Ni, Zn, and Cu into the surface sediments of the south Caspian Sea. Guilan province on the west coast of Caspian Sea accumulated higher percentages of non-resistant fractions of Pb and Zn, while Mazandaran and Golestan provinces in the middle and western parts of the Caspian Sea, in the Iranian zone, accumulated higher percentages of non-resistant fractions of Ni and Cu. The present study revealed that the coastal area of the south Caspian Sea is still not seriously contaminated. Cadmium in Guilan and Golestan provinces were dominated by non-resistant fractions (55–69%), which indicated more anthropogenic inputs of Cd on the south coast of the Caspian Sea in comparison with other metals.

Keywords: trace metals; chemical speciation; surface sediment; Caspian Sea

Introduction

There are two main sources of metals that enter coastal waters: natural sources from rock weathering within the catchment's area and anthropogenic sources resulting from human activities.[1] The main aim of most contamination-oriented searches and research of sediments was to estimate whether the aquatic ecosystems have been anthropogenically or naturally affected. Low concentrations of many heavy metals occur naturally in the earth's crust. Large amounts of numerous heavy metals, including toxic metals, are discharged into marine environments as contaminants from anthropogenic activities.[2] Inappropriate and illegal disposal of industrial and municipal waste products and ignorance of their management can result in severe environmental problems, such as contamination of receiving waterways and associated sediments by heavy metals.[1]

Coastal sediments are one of several environmental compartments in which heavy metals and organic pollutants accumulate. Sediments represent the most concentrated physical pools of metals in aquatic environments.[3–5] When heavy metals are released into the water column, they may be transferred rapidly into the sediment phase by adsorption as suspended particulate matter, followed by sedimentation.[1] Under favorable conditions, that is, appropriate pH, salinity, redox reactions, temperature, and organic ligand concentrations, metals in sediments can be released from a solid to a liquid phase and have adverse effects on aquatic biota.[6]

Studies of trace metal contamination of sediments often rely on the analysis of total metal content. However, information about total concentration is not sufficient to understand the environmental behavior of trace metals, as only a fraction of the total metal is available for biological processes. The form of metal available in the sediments (distribution among substrates) is important for determining the metal eco-toxicological risk to biota.[7] The behavior of heavy metals is closely related to their chemical forms, and only those with high bioavailability can be absorbed by organisms, and then, they can do great harm to organisms and human beings.[8] Therefore, studies on the speciation and distribution of heavy metals in sediments could provide information on the degree of contamination, metal bioavailability and mobility, as well as their origin.[9]

Important aspects of the present study are as follows: (1) To our knowledge, most studies have been done in the northern part of the Caspian Sea, no results have yet been reported based on the bioavailability of heavy metals in southern parts of the Caspian Sea; (2) there are more than ten million people living in coastal areas of the Caspian Sea. Their life greatly depends on the Caspian Sea as a source of food, that is, cheap and healthy protein as part of their diet. Most bioavailable fractions of heavy metals are transferred through the food chain via the following route: sediment – zoo benthos – benthonic sarcophagi – humans. Therefore, the present study on sediment, as one of most important compartments of the aquatic environment, could provide baseline data for

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the environmental behavior of trace metals in order to protect the Caspian Sea and avoid a health risk to humans from anthropogenic contamination.

The main objectives of this study were as follows: (1) to identify the distribution of Pb, Ni, Cd, Zn, and Cu contamination in surface sediments of the Caspian Sea using some pollution indices and established sediment quality guidelines (SQG); (2) to determine the anthropogenic degree, mobility, and bioavailability of Pb, Ni, Cd, Zn, and Cu in surface sediments in order to obtain preliminary baseline data for monitoring contamination in the Caspian Sea.

Materials and methods

Study area

The Caspian Sea, bounded by the five littoral states of Iran, Azerbaijan, Federation of Russia, Kazakhstan, and Turkmenistan, is the largest inland body of water in the world, with an average depth of 180 m and a total capacity of 77,000 km^3.[10] It is a landlocked sea with brackish water, having a surface area of about 436,000 km^2, a length of 1,200 km, and a width of between 204 and 566 km, with an average of 330 km.[11] There are three distinct basins: the central and southern basins are quite deep, with maxima of 788 and 1,025 m, respectively; however, the northern part is shallow, with an average depth of about 5 m and a maximum depth of only 20 m. The sea level is presently about 26 m below the level of the world's oceans.[11, 12] The average salinity in the south part of the sea is 12–13 ppt.[12] About 400,000 tons of fish are caught each year by the different bordering countries, with sturgeon fishing especially representing 90% of the world's catch.[12] The sea hosts about 126 different fish species of which 44 have commercial importance.[11, 12]

Sources of pollution

As a closed environment with no outlets, various pollutants from coastal catchment areas and leakage from offshore oil production have accumulated in the Caspian Sea.[13] The main sources of pollution of the Caspian natural environment are the trans-border atmospheric and water transfer of pollutants from other regions, runoff from river flow, discharge of untreated industrial and agricultural waste water, municipal domestic waste water from cities and settlements in the coastal zone, notably the Volga River, which is the main river in the north, and from rivers at the western border coming from the Republic of Azerbaijan and Kazakhstan.[14] Coastal zone settlement may be due to an insufficient number of treatment facilities, the operation of oil and gas wells on land and offshore, oil transportation via sea, navigation by both rivers and sea and secondary pollution during bottom-dredging works.[10,14,15] Due to excessive pollution in some western Caspian Sea areas, there are no traces of aquatic life, especially in coastal areas near Baku Harbour (Azerbaijan) and Kazakhstan. Industrial effluents from over 40 factories in Baku Bay have caused serious local contamination of the area [14] (Table 1). The ecology of the Caspian Sea, which depends on the input and diversity of pollutants, is determined by the economic development of littoral states and the condition of the Caspian watershed basin. On the Iranian coastline, there are over 350 small and large rivers flowing into the Caspian Sea.[11] All these rivers receive raw sewage discharges from urban, industrial, and agricultural areas. The Caspian is a non-tidal sea, the bulk of discharged contaminants remains trapped within its basin. Sea currents transport and circulate the entrapped pollutants along the Iranian coast of the Caspian Sea. The limited water exchanges with the open sea and long-term dumping of different kinds of waste, industrial, and municipal garbage are the main reasons for the appearance of an anthropogenic impact in the Caspian Sea.[16]

Sampling and storage

Randomly selected stations were established along the south of the Caspian Sea, between 37°38′N, 49°5′E and 36°53′N, 54°02′E (Figure 1). Zero to 5 cm of surface sediment from each station was collected using a plastic spatula.[17] This layer is usually permanently oxidized and thus acts as a barrier to metals migrating from deeper layers toward the surface and is retained by organic matter, iron, and manganese oxides. The surface layer of sediments controls the exchange of metals between sediments and water and constitutes a reserve of metals to which benthic organisms are exposed. Polyethylene bags were used to store the sediment samples. Samples were kept in an icebox at 4 °C to reduce biochemical reactions. In the laboratory, the sediment samples were kept in a freezer at −20 °C for further analysis.

Speciation of Pb, Ni, Cd, Zn, and Cu in sediment samples

Geochemical fractions of Pb, Ni, Cd, Zn, and Cu in surface sediments were obtained using a modified sequential extraction technique (SET) as described by Badri and Aston [18] and Naji et al. [19] The four-fraction solution and conditions applied were as follows:

Step 1. *Easily, freely, or leachable and exchangeable (EFLE):* About 10 g of each sample was continuously shaken for 3 h with 50 ml of 1.0 M ammonium acetate (NH$_4$CH$_3$COO), pH 7.0, at room temperature.

Step 2. *Acid-reducible*: The residue from step 1 was continuously shaken for 3 h with 50 ml of 0.25 M hydroxyl ammonium chloride (NH$_2$OH.HCl) acidified to pH 2 with HCl at room temperature.

Step 3. *Oxidisable-organic*: The residue from step 2 was first oxidized with 30% H$_2$O$_2$ in a water bath at 90–95 °C. After cooling down, the metal released from the

Table 1. Positions and descriptions of sampling sites for coastal sediments collected from the southern part of Caspian Sea.

| No.	Station	Latitude	Longitude	Designation
1	Astara	38°26′	48°52′	Industrial effluents from over 40 factories from Azerbaijan, Urban, Tourism
2	Parasar	37°38′	49°05′	Wood industry, Urban
3	Anzali	37°28′	49°27′	Urban, port, fishery, discharge from lagoon, industrial activity, such as nylon and polyester, paints, varnishes and medicines, iron and steel processing
4	Kiashahr	37°26′	58°75′	Urban, port, dairy products
5	Chamkhale	37°12′	50°16′	Refinery, urban, industrial activity such as carpet industry and soap processing
6	Chaboksar	36°59′	50°32′	Agriculture, aquaculture
7	Vazivar	36°34′	51°54′	Urban, tourism
8	Noshahr	36°39′	51°30′	Recreational area, urban, port, agriculture, industrial area
9	Neka	36°39′	53°18′	Wood industry, urban, oil refinery, electrical power plant
10	Babolsar	36°42′	52°39′	Tourism, urban, industries of food, paper, and plastics
11	Khazarabad	36°48′	53°6′	Tourism, urban, food products, basic chemicals industry
12	Goharbaran	36°47′	53°56′	Tourism, urban, power plant, agriculture
13	Bandar Gaz	36°47′	53°56′	Port, urban, agriculture
14	Bandar Torkman	36°53′	54°02′	Agriculture, urban, animal husbandry, fishery, tourism
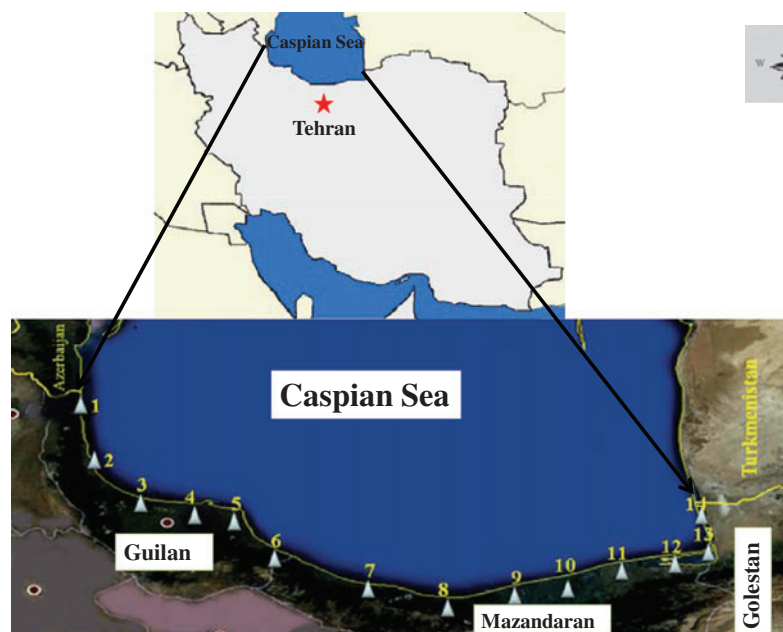
Figure 1. Sampling locations along the southern coastline of the Caspian Sea.

organic complexes was continuously shaken for 3 h with 1.0 M ammonium acetate (NH$_4$CH$_3$COO) acidified to pH 2.0 with HCl at room temperature.

Step 4. *Resistant*: The residue from step 3 was digested in a 10 ml combination (ratio of 4:1) of concentrated HNO$_3$ (AnalaRgrade, R&M Chemicals 65%) and HClO$_4$ (AnalaR grade, R&M Chemicals 70%).

The residue used for each fraction was weighed before carrying out the next fractionation. The residue was washed with 20 ml of DDW. It was filtered through a Whatman No.1 filter paper. The supernatant liquid of each fraction after filtration was stored for metal determination, except fraction 1 that was sensitive and had to be analyzed immediately to minimize any loss of volatile elements. For each fraction of the sequential extraction procedure, a blank using the same procedure was employed to ensure that the samples and chemicals used were free of metal contaminants.

Determination of Pb, Ni, Cd, Zn, and Cu and total organic carbon

After filtration, the samples were determined for Pb, Ni, Cd, Zn, and Cu using an air-acetylene flame atomic absorption spectrophotometer (FAAS, Perkin-Elmer Model AAnalyst 800). The data are presented in µg/g dw. Multiple-level calibration standards were analyzed to generate calibration curves against which sample

concentrations were calculated. To avoid any possible contamination, all glassware in the experiment was previously acid-washed, and the percentage of recovery of metals in the samples was analyzed. The wavelengths used were 228.8, 213.9, 232.0, 324.8, and 283.3 for Cd, Zn, Ni, Cu, and Pb, respectively. The detection limits of the studied metals were calculated based on the IUPAC detection limit. Moreover, the detection limits of the FAAS for Cd, Zn, Ni, Cu, and Pb were 0.009, 0.007, 0.003, 0.01, and 0.009 mg/L, respectively. Concentrations of organic matter (loss on ignition, 8 h, 550 °C) were used to estimate the total organic carbon (TOM) following the specific procedure of Tam and Wong.[20]

Quality control

To avoid uncertain contamination, all laboratory equipments were washed with detergent, double rinsed with distilled water and left in 10% HNO3 for 24 h and all equipment was then rinsed twice with double-distilled water and left semi-closed to dry at room temperature. Certified reference material (CRM) (International Atomic Energy Agency, Soil-5, Vienna, Austria) was determined as a precision check. About 1 g of CRM was weighed and placed in a hot-block digester and digested in a 10 ml combination (ratio of 4:1) of concentrated HNO_3 (AnalaRgrade, R&M Chemicals 65%) and $HClO_4$ (AnalaR grade, R&M Chemicals 70%), first at low temperature (40 °C) for 1 h and then at 140 °C for at least 3 h.[21] The digested samples were diluted with double-distilled water. The sample was then filtered through Whatman No.1 filter paper, and the filtrate was stored in 80-ml polypropylene bottles until metal determination. The concentrations of Cd, Zn, Ni, Cu, and Pb in the CRM samples were determined by FAAS. Percentages of recovery ($n = 3$ for each metal) for certified and measured concentration of those metals ranged from 95% for Cu to 108% for Cd (Table 2). Calibration curves for each trace element were determined with 1,000 mg/l (BDH Spectrosol®) stock solution. The reagent and procedural blanks were monitored for each fraction after five samples during the analysis, as part of the quality accuracy program.

Sediment quality assessment

Numerical SQGs were used to estimate the possible environmental consequences of the analyzed metals at the study sites and to conduct ecological risk assessments. Concentrations of the metals studied were compared to the SQG of the effect range low (ERL: lower 10th percentile of the effects data) and the effect range median (ERM: the median, 50th percentile of the effects data) in marine and estuarine sediments.[22] For chemical concentrations of less than the ERL, rare adverse biological effects are expected. For those between the ERL and ERM, occasionally adverse biological effects are expected and for concentrations higher than the ERM, frequently adverse effects are expected.[22]

Individual and global contamination factors

Determination of metal contamination is one of the most important aspects to reduce and control pollution in the aquatic ecosystem. The bioavailability and toxicity of metals depend on their type of chemical form. Determination of the contamination factor of metals is an important aspect that indicates the degree of risk from heavy metals to the environment in relation to their retention time.[19,23,24] Individual contamination factors (ICF) for the sampling stations were calculated from the results of the speciation study by dividing the sum of the first three extractions (i.e. exchangeable, acid-reducible, and oxidisable-organic forms) by the residual fraction for each site. The global contamination factor (GCF) for each site was calculated by summing the ICF obtained for the metals studied at each site.[23] The ICF and GCF were measured for each station using the following equation:

$$ICF_{metal} = \frac{Cnonresistant}{Cresistant}$$

$$GCF = \sum_{i=1}^{n} CF_i$$

Statistical analysis

All statistical analyses were computed using Statistical Package for Social Science (SPSS) version 16. Pearson's correlation analysis was applied to test the relationship between the heavy metals analyzed. Graphs were drawn with Microsoft Excel for Windows.

Table 2. Measured and certified concentrations of International Atomic Energy Agency, Soil-5, Vienna, Austria. (Mean ± SD; $n = 5$).

Element	Measured concentration (µg/g)	Certified concentration (µg/g)	Percentage of recovery (%)
Cd	1.62 ± 0.05	1.5 ± 0.06	108
Zn	359.9 ± 2.1	368 ± 3.2	98
Ni	12.75 ± 0.09	13 ± 0.3	98
Cu	73.09 ± 0.8	77.1 ± 1.2	95
Pb	24.6 ± 0.2	25.7 ± 0.6	96

Prior to the statistical analysis, all data were tested for basic assumptions of normality and homogeneity of the variance inherent in the linear model statistics using normal probability plots generated by the univariate procedure in SPSS. All statistical significances were considered at $p < 0.05$. A Kolmogorov–Smirnov test was performed to analyze the normality of the data distribution. Non-parametric statistical tests were used for data analysis if the data were not normally distributed.

Results and discussion

Speciation of heavy metals in surface sediments

The EFLE fractions for Pb, Ni, Cd, Zn, and Cu ranged from 0.36 to 1.14 μg/g, 1.07 to 1.81 μg/g, 0.01 to 0.17 μg/g, 0.36 to 1.53 μg/g, 0.03 to 1.37 μg/g, respectively, (Table 3). The highest concentrations of EFLE fractions for Pb, Ni, Cd, Zn, and Cu were found in Parasar (1.14 ± 0.03 μg/g dry weight), Astara (1.81 ± 0.07 μg/g dry weight), Bandar Gaz (0.17 ± 0.005 μg/g dry weight), and Astara (1.53 ± 0.2 μg/g dry weight). Bandar Torkman (1.28 ± 0.05 μg/g dry weight) and Kiashahr (14.39 ± 0.55 μg/g dry weight), respectively. The highest EFLE fraction concentration of heavy metals (Pb, Ni, Cd, Zn, and Cu) was recorded in Guilan province in the western Caspian Sea, in comparison with other provinces (Mazandaran and Golestan). The EFLE fraction contributed only a small portion of the total concentration of Pb, Ni, Cd, Zn, and Cu in sediments from all stations, suggesting poor bioavailability of these metals. The percentage of the EFLE fraction was very low when compared to other fractions. This fraction might be a model for what is "bioavailable" to sediment-ingesting animals and the biota of overlying water such as fish.[7,25]

The acid-reducible fractions ranged from 1.27 to 3.61 μg/g, 1.03 to 3.48 μg/g, 0.03 to 0.08 μg/g, 0.55 to 2.50 μg/g, and 0.12 to 0.95 μg/g for Pb, Ni, Cd, Zn, and Cu, respectively, (Table 4). Bandar Torkman recorded the highest concentrations of acid-reducible fractions for Pb, Ni, and Cu (3.61 ± 0.14, 3.48 ± 0.14, and 0.95 ± 0.03 μg/g dw, respectively). Meanwhile, Astara in the western Caspian Sea recorded the highest concentrations of Cd and Zn (0.08 ± 0.01 and 2.50 ± 0.11 μg/g dw, respectively). The percentages of acid-reducible fractions for all metals were also low indicating that the affinities of these metals in the acid-reducible fractions of sediments were also low. According to Calmano and Frostner [26] a reducing condition is mainly caused by the decomposition of organic matter that is mediated by microorganisms. This finding is still comparable to previous studies on the west coast of Peninsular Malaysia which found 3–17% of the total fraction and 10–30% in Chile.[7,28] Less than 20% of the metals in the sediment were in the acid-reducible fraction, and therefore, as mentioned by Yap et al. [27] this fraction was not considered a major binding portion for metals in sediments.

The oxidisable-organic fractions ranged from 2.54 to 9.50, 2.35 to 8.19, 0.21 to 0.55, 2.61 to 8.90, and 1.05 to 7.45, for Pb, Ni, Cd, Zn, and Cu, respectively. According to Table 5, Bandar Torkman found the highest concentrations of oxidisable-organic for Ni and Cu (8.19 ± 0.17 and 7.45 ± 0.32 μg/g dw, respectively). The highest concentrations for the oxidisable-organic fraction of Cd (0.55 ± 0.02) and Zn (6.45 ± 0.19) were found in the western Caspian Sea in the Astara area. The higher percentage of organically bound Pb found in the present study could be due to physicochemical properties of the sediments. The higher percentage probably indicates that these areas have received more anthropogenic inputs of metals.[29] According to Sadiq [30] Cd adsorption in the marine sediment is probably mixed up by organic matter and the carbonate surface and also strongly influenced by their respective chemistries. The high concentrations for oxidisable-organic fractions for Zn and Cu indicate that their adsorption was mainly involved in organic matter.[31] It might be due to the high affinities of these metals for humic substances, which are fractions of organic matter and chemically very active in complex elements such as heavy metals. Moreover, heavy metals may be associated with various forms of organic materials, such as living organisms, detritus, or the coating on mineral particles.[32]

The resistant fractions for Pb, Ni, Cd, Zn, and Cu ranged from 11.54 to 24.60 μg/g dw, 14.76 to 65.87 μg/g dw, 0.23 to 0.53 μg/g dw, 38.35 to 91.24 μg/g dw, and 7.80 to 31.55 μg/g dw, respectively (Table 6). The highest concentrations of the resistant fractions of Ni (65.87 ± 0.32), Cd (0.53 ± 0.06), Zn (91.24 ± 0.51), and Cu (31.55 ± 1.26) were recorded in Golestan province in the eastern Caspian Sea, while Neka in the middle of the Caspian area showed a high concentration of oxidisable-organic fraction of Pb (24.60 ± 0.56). The resistant fractions of Pb, Ni, Zn, and Cu (but not Cd) in coastal surface sediments in the southern Caspian Sea accounted for more than 50% of the total amount of metals, indicating that Caspian coastal sediments are not heavily contaminated. The resistant fractions of these metals in the sediments were probably due to natural sources such as chemical weathering of igneous and metamorphic rocks, as well as the decomposition of biota detritus. These metals, originating from non-anthropogenic inputs, were considered to be trapped within silicate minerals, and incorporated into the crystalline lattice positions of minerals.[18,27]

Comparison of non-resistant and resistant fraction between stations

The mathematical summation of EFLE, acid-reducible and oxidisable-organic fractions constitutes the non-resistant fraction (non-lithogenous).[18] The non-resistant fractions (the sum of fractions 1, 2, and 3) found in surface sediments are an ecotoxicological concern. Besides posing a threat to living organisms, these non-resistant

Table 3. Concentrations (μg/g dry weight ± SE) of EFLE fraction of Pb, Ni, Cd, Zn, and Cu from 14 stations in the southern part of Caspian Sea.

No	Station	Pb			Ni			Cd			Zn			Cu		
		Mean	SE	%	Mean	SE	%	Mean	SE	%	Mean	SE	%	Mean	SE	%
1	Astra	1.07 ±	0.03	(3.24)	1.81 ±	0.07	(4.06)	0.03 ±	0.006	(2.67)	1.53 ±	0.20	(2.56)	0.78 ±	0.09	(2.14)
2	Parasar	1.14 ±	0.03	(4.37)	1.67 ±	0.05	(3.87)	0.02 ±	0.006	(2.69)	0.87 ±	0.04	(1.62)	0.46 ±	0.04	(1.93)
3	Anzali	1.13 ±	0.08	(3.19)	1.70 ±	0.08	(2.64)	0.02 ±	0.003	(3.35)	0.86 ±	0.04	(1.61)	0.52 ±	0.02	(1.31)
4	Kia	0.95 ±	0.07	(4.11)	1.41 ±	0.04	(4.66)	0.03 ±	0.009	(3.84)	0.56 ±	0.04	(0.97)	0.38 ±	0.02	(2.25)
5	Cahmkhaleh	0.85 ±	0.07	(3.28)	1.26 ±	0.03	(5.47)	0.02 ±	0.003	(3.19)	0.55 ±	0.05	(0.75)	0.33 ±	0.06	(2.56)
6	Chaboksar	0.48 ±	0.03	(2.24)	1.23 ±	0.05	(6.14)	0.01 ±	0.003	(2.34)	0.55 ±	0.09	(0.97)	0.26 ±	0.02	(1.41)
7	Vazivar	0.94 ±	0.04	(3.35)	1.54 ±	0.08	(5.12)	0.02 ±	0.006	(2.50)	0.55 ±	0.08	(1.03)	0.31 ±	0.05	(1.69)
8	Noshahr	0.82 ±	0.08	(2.37)	1.45 ±	0.07	(3.18)	0.02 ±	0.003	(3.10)	0.17 ±	0.01	(0.32)	0.20 ±	0.02	(2.20)
9	Neka	0.63 ±	0.04	(1.72)	1.27 ±	0.04	(2.64)	0.04 ±	0.005	(4.41)	0.45 ±	0.00	(0.74)	0.06 ±	0.02	(0.63)
10	Babolsar	0.59 ±	0.04	(2.63)	1.31 ±	0.04	(3.11)	0.03 ±	0.009	(3.56)	0.43 ±	0.01	(0.82)	0.06 ±	0.03	(0.65)
11	Khazar Abad	0.36 ±	0.06	(1.88)	1.26 ±	0.02	(3.80)	0.06 ±	0.006	(6.59)	0.36 ±	0.03	(0.85)	0.05 ±	0.01	(0.42)
12	Gohar	0.91 ±	0.03	(3.04)	1.19 ±	0.01	(2.46)	0.09 ±	0.008	(12.44)	0.38 ±	0.01	(0.67)	0.03 ±	0.01	(0.19)
13	Bandar Gaz	0.74 ±	0.03	(3.61)	1.07 ±	0.04	(1.54)	0.17 ±	0.005	(16.11)	0.45 ±	0.02	(0.48)	0.74 ±	0.01	(3.31)
14	Bandar Torkmen	1.12 ±	0.08	(3.57)	1.59 ±	0.13	(2.01)	0.15 ±	0.005	(12.23)	1.42 ±	0.11	(1.53)	1.28 ±	0.05	(3.31)

Table 4. Concentrations (μg/g dry weight ± SE) of acid-reducible fraction of Pb, Ni, Cd, Zn, and Cu from 14 stations in the southern part of Caspian Sea.

No	Station	Pb			Ni			Cd			Zn			Cu		
		Mean	SE	%	Mean	SE	%	Mean	SE	%	Mean	SE	%	Mean	SE	%
1	Astara	3.55 ±	0.14	(10.74)	1.56 ±	0.04	(3.49)	0.08 ±	0.01	(0.08)	2.50 ±	0.11	(4.17)	0.73 ±	0.05	(2.01)
2	Parasar	2.53 ±	0.07	(9.71)	1.44 ±	0.07	(3.33)	0.03 ±	0.01	(0.03)	1.17 ±	0.08	(2.17)	0.58 ±	0.03	(2.44)
3	Anzali	1.95 ±	0.06	(5.49)	1.41 ±	0.07	(2.19)	0.03 ±	0.00	(0.03)	1.19 ±	0.05	(2.24)	0.38 ±	0.01	(1.27)
4	Kia	1.64 ±	0.09	(7.08)	1.26 ±	0.05	(4.17)	0.03 ±	0.00	(0.03)	0.74 ±	0.03	(1.28)	0.36 ±	0.03	(2.12)
5	Cahmkhaleh	1.57 ±	0.02	(6.05)	1.47 ±	0.03	(6.38)	0.05 ±	0.01	(0.05)	1.09 ±	0.03	(1.49)	0.26 ±	0.01	(1.46)
6	Chaboksar	1.16 ±	0.04	(5.46)	1.40 ±	0.09	(6.99)	0.03 ±	0.00	(0.03)	0.71 ±	0.06	(1.26)	0.34 ±	0.02	(1.88)
7	Vazivar	3.41 ±	0.14	(12.19)	1.83 ±	0.06	(6.07)	0.05 ±	0.01	(0.05)	0.60 ±	0.06	(1.11)	0.36 ±	0.02	(1.95)
8	Noshahr	2.98 ±	0.04	(8.59)	1.83 ±	0.01	(3.98)	0.08 ±	0.01	(0.08)	0.68 ±	0.03	(1.24)	0.31 ±	0.04	(3.33)
9	Neka	1.93 ±	0.01	(5.28)	1.03 ±	0.05	(2.14)	0.07 ±	0.01	(0.07)	0.60 ±	0.04	(0.99)	0.33 ±	0.03	(3.27)
10	Babolsar	2.11 ±	0.09	(9.37)	1.41 ±	0.06	(3.35)	0.07 ±	0.01	(0.07)	0.67 ±	0.03	(1.27)	0.39 ±	0.02	(4.14)
11	Khazar Abad	1.27 ±	0.03	(6.62)	2.45 ±	0.05	(7.39)	0.08 ±	0.01	(0.08)	0.55 ±	0.02	(1.29)	0.37 ±	0.02	(2.85)
12	Gohar	3.07 ±	0.05	(10.21)	3.05 ±	0.08	(6.28)	0.05 ±	0.01	(0.05)	0.78 ±	0.04	(1.34)	0.12 ±	0.02	(0.63)
13	Bandr Gaz	3.35 ±	0.03	(16.27)	1.59 ±	0.03	(2.29)	0.07 ±	0.01	(0.07)	0.60 ±	0.04	(0.63)	0.31 ±	0.01	(1.36)
14	Bandar Torkmen	3.61 ±	0.14	(11.45)	3.48 ±	0.14	(4.39)	0.08 ±	0.01	(0.08)	1.46 ±	0.14	(1.57)	0.95 ±	0.03	(2.30)

Table 5. Concentrations (μg/g dry weight ± SE) of oxidisable-organic fraction of Pb, Ni, Cd, Zn, and Cu from 14 stations in the southern part of Caspian Sea.

No	Station	Pb			Ni			Cd			Zn			Cu		
		Mean	SE	%	Mean	SE	%	Mean	SE	%	Mean	SE	%	Mean	SE	%
1	Astara	9.22 ±	0.16	(27.87)	6.47 ±	0.29	(14.53)	0.55 ±	0.02	(48.96)	8.90 ±	0.47	(14.84)	5.04 ±	0.13	(13.81)
2	Parasar	8.20 ±	0.36	(31.49)	7.19 ±	0.46	(16.67)	0.33 ±	0.03	(43.95)	6.53 ±	0.15	(12.10)	1.33 ±	0.03	(5.60)
3	Anzali	7.34 ±	0.05	(20.72)	4.71 ±	0.16	(7.35)	0.35 ±	0.02	(49.30)	6.54 ±	0.19	(12.31)	2.05 ±	0.00	(6.91)
4	Kia	3.22 ±	0.03	(13.89)	2.35 ±	0.01	(7.79)	0.26 ±	0.01	(39.11)	3.32 ±	0.12	(5.78)	1.45 ±	0.03	(8.59)
5	Cahmkhaleh	3.89 ±	0.14	(15.03)	2.40 ±	0.01	(10.43)	0.36 ±	0.01	(50.70)	4.03 ±	0.18	(5.51)	1.52 ±	0.06	(8.73)
6	Chaboksar	3.59 ±	0.08	(16.91)	2.68 ±	0.19	(13.36)	0.21 ±	0.02	(36.84)	3.51 ±	0.10	(6.23)	1.22 ±	0.03	(6.69)
7	Vazivar	8.53 ±	0.33	(30.50)	6.02 ±	0.13	(19.98)	0.33 ±	0.01	(39.92)	3.06 ±	0.04	(5.71)	1.35 ±	0.06	(7.24)
8	Noshahr	9.06 ±	0.18	(26.09)	5.03 ±	0.12	(10.97)	0.22 ±	0.01	(29.20)	3.11 ±	0.13	(5.66)	1.05 ±	0.02	(11.21)
9	Neka	9.50 ±	0.10	(25.92)	5.06 ±	0.12	(10.53)	0.46 ±	0.01	(44.24)	2.97 ±	0.08	(4.92)	1.08 ±	0.04	(10.74)
10	Babolsar	7.20 ±	0.03	(32.04)	4.31 ±	0.20	(10.22)	0.32 ±	0.01	(45.33)	3.17 ±	0.09	(6.04)	0.94 ±	0.03	(9.98)
11	Khazar Abad	6.21 ±	0.27	(32.44)	6.54 ±	0.38	(19.69)	0.45 ±	0.02	(50.85)	3.15 ±	0.09	(7.42)	1.12 ±	0.04	(8.72)
12	Gohar	8.34 ±	0.29	(27.77)	5.99 ±	0.08	(12.35)	0.39 ±	0.00	(50.53)	3.12 ±	0.05	(5.40)	1.09 ±	0.02	(5.83)
13	Bandar Gaz	2.54 ±	0.06	(12.31)	3.96 ±	0.07	(5.69)	0.28 ±	0.03	(26.91)	2.61 ±	0.04	(2.76)	5.08 ±	0.20	(22.62)
14	Bandar Torkmen	7.76 ±	0.23	(24.62)	8.19 ±	0.17	(10.35)	0.53 ±	0.01	(43.21)	3.58 ±	0.21	(3.85)	7.45 ±	0.32	(18.02)

Table 6. Concentrations (μg/g dry weight ± SE) of resistant fraction of Pb, Ni, Cd, Zn, and Cu from 14 stations in the southern part of Caspian Sea.

No	Station	Pb			Ni			Cd			Zn			Cu		
		Mean	SE	%	Mean	SE	%	Mean	SE	%	Mean	SE	%	Mean	SE	%
1	Astara	18.45 ±	1.85	(55.75)	34.72 ±	0.61	(77.92)	0.46 ±	0.04	(41.25)	47.04 ±	0.37	(78.43)	29.97 ±	1.07	(82.05)
2	Parasar	14.23 ±	0.47	(54.68)	32.85 ±	0.21	(76.13)	0.37 ±	0.01	(49.33)	45.37 ±	1.65	(84.11)	21.26 ±	0.69	(89.32)
3	Anzali	24.48 ±	0.92	(69.12)	56.30 ±	1.00	(87.81)	0.30 ±	0.01	(42.72)	44.56 ±	1.05	(83.84)	26.86 ±	0.58	(90.51)
4	Kia	17.37 ±	0.61	(74.93)	25.14 ±	0.39	(83.38)	0.36 ±	0.01	(52.97)	52.72 ±	2.01	(91.96)	14.68 ±	0.28	(87.03)
5	Cahmkhaleh	19.49 ±	1.22	(75.26)	28.12 ±	0.26	(77.73)	0.28 ±	0.00	(38.97)	67.38 ±	0.84	(92.24)	15.20 ±	0.56	(87.25)
6	Chaboksar	16.16 ±	0.91	(76.06)	14.76 ±	1.19	(73.51)	0.32 ±	0.02	(56.14)	51.49 ±	0.67	(91.54)	16.24 ±	0.75	(89.09)
7	Vazivar	14.57 ±	0.16	(52.09)	20.74 ±	0.43	(68.83)	0.43 ±	0.01	(51.61)	49.44 ±	0.07	(92.15)	16.57 ±	0.39	(89.12)
8	Noshahr	22.12 ±	1.76	(63.71)	37.54 ±	0.60	(81.87)	0.43 ±	0.01	(57.52)	51.09 ±	0.44	(92.79)	7.80 ±	0.11	(83.26)
9	Neka	24.60 ±	0.56	(67.09)	40.76 ±	0.40	(84.69)	0.46 ±	0.01	(44.24)	56.43 ±	1.02	(93.35)	8.55 ±	0.26	(85.36)
10	Babolsar	14.18 ±	1.26	(63.14)	35.16 ±	1.31	(83.33)	0.29 ±	0.01	(41.12)	48.13 ±	1.62	(91.87)	8.07 ±	0.44	(85.23)
11	Khazar Abad	11.54 ±	0.63	(60.34)	22.96 ±	0.80	(69.12)	0.30 ±	0.00	(33.90)	38.35 ±	0.88	(90.44)	11.31 ±	0.63	(88.02)
12	Gohar	17.71 ±	0.63	(58.98)	38.28 ±	0.73	(78.92)	0.23 ±	0.01	(30.06)	53.61 ±	0.41	(92.59)	17.37 ±	1.18	(93.36)
13	Bandar Gaz	13.87 ±	0.52	(67.31)	62.93 ±	1.40	(90.48)	0.53 ±	0.06	(50.02)	91.24 ±	0.51	(96.13)	16.31 ±	1.11	(72.72)
14	Bandar Torkmen	19.02 ±	0.30	(60.36)	65.87 ±	0.32	(83.25)	0.47 ±	0.04	(38.04)	86.56 ±	0.25	(93.05)	31.55 ±	1.26	(76.37)

fractions are most likely due to anthropogenic inputs rather than having natural origins.[33] The first fractions are potentially toxic for organisms because they are removed and used by organisms, while fractions 2 and 3 can be solubilized depending upon their physical and chemical parameters, such as pH, oxygen content, and bacterial activity.[34] Assuming that bioavailability is related to solubility, then metal bioavailability decreases in the order of exchangeable forms > acid reduction forms > organic forms > residual forms.[23,24,35] The residual phase represents metals largely embedded in the crystal lattice of the sediment fraction and should not be available for remobilization except under very harsh conditions.[23]

Figure 2 compares non-resistant with resistant fractions in the surface sediments of the southern part of the Caspian Sea. The non-resistant fraction accounted for 23.94–47.91% of Pb, 9.52–31.17% of Ni, 42.45–69.75% of Cd, 3.38–21.57% of Zn, and 6.64–27.28% of Cu at 14 stations. The resistant fraction accounted for 52.09–76.06%, 68.83–90.48%, 30.67–57.52%, 78.43–96.17%, and 72.72–93.36% of Pb, Ni, Cd, Zn, and Cu, respectively. All the metal concentrations in the sediments at 14 sampling stations (Pb, Ni, Zn, and Cu), except for Cd, were dominated by resistant fractions. The non-resistant fractions were lower than the resistant fractions across the whole study, which indicates no significant anthropogenic inputs of Pb, Ni, Zn, and Cu to the surface sediments of the south Caspian Sea. The findings for resistant and non-resistant geochemical fractions in the surface sediments at the different sampling stations of the present study generally showed that

sources of Cd in surface sediments of the south Caspian Sea mainly came from anthropogenic sources. This was indicated by the higher percentages of non-resistant Cd compared to resistant Cd. Non-resistant Cd contributed 50 to 70% of the total concentrations in sediments from Spain [34] 57% in sediments from the Suez Canal,[36] 50–70% in sediments from Singapore,[29] and 82% in sediments from the Yangtze estuary, China.[37] The dominance of residual or resistant fractions of heavy metals is probably due to the low levels of total metals in sediments.[38] Similarly, Davidson et al. [39] mention that sediments are relatively unpolluted. Metals in this form (resistant) are not soluble under experimental conditions and may therefore be considered to be tightly bound.[40] The higher percentages of resistance in comparison with non-resistant geochemical fractions for Pb, Ni, Zn, and Cu suggest that the sources of these metals in surface sediments come mainly from geological processes under natural field conditions. The resistant fractions of Pb, Ni, Zn, and Cu were probably due to natural sources, such as the chemical weathering of indigenous and metamorphic rocks and the decomposition of biota detritus.[18] The high concentrations of Pb, Ni, Zn, and Cu in the residual fractions may also indicate that these metals were less mobile than Cd. This ability, therefore, makes them (Pb, Ni, Zn, and Cu) less bioavailable for uptake by organisms.[38] The levels of non-resistant fractions of the metals examined in the present study might be due to sea currents. Overall, speciation of the all metals studied in the surface sediments of the Caspian Sea was in the order of residual > oxidisable-organic > -acid-reducible > exchangeable.
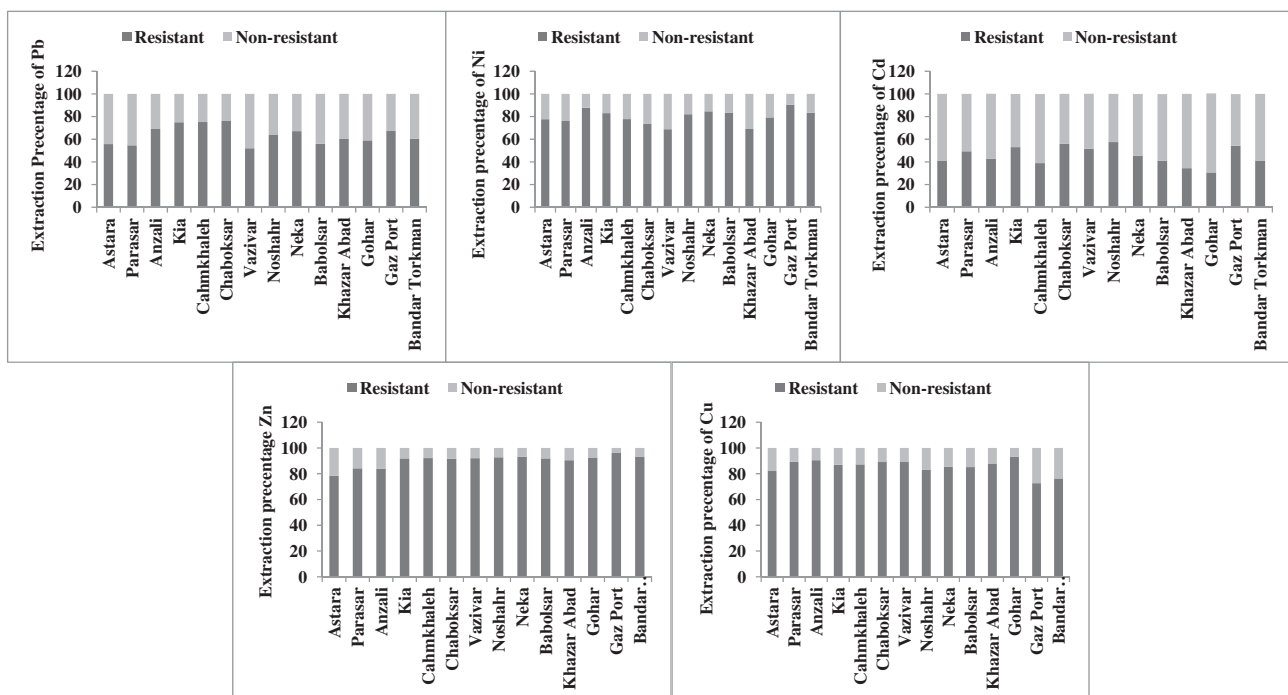

Figure 2.   Percentages (%) of resistant and non-resistant fractions of metals from 14 stations in the southern part of Caspian Sea.

Relation between oxidation-organic (fraction 3) and TOM

The TOM content of sediment samples was measured at 14 stations. The TOC varied between 1.2 and 3.9, with high values in the west and east parts and lower concentrations in the middle part of the study area. It has been widely reported [19,41,42] that there is heavy metals uptake by the organic carbon content of sediments. Organic content is recognized as a useful tool to obtain quantitative and qualitative information from both absolute values and variation trends; it comes from natural and anthropogenic sources, and even if it is not directly responsible for dangers to human health,[19] particulate organic materials have a high cation exchange capacity and strongly sequester metal ions.[7]

A relationship between concentrations of Pb, Ni, Cd, Zn, and Cu in the oxidation-organic fraction with TOM in surface sediments of the Caspian Sea was identified. The results showed that there was a significant and positive linear correlation between Cu ($r^2 = 0.45$, $p < 0.05$) and TOM. The correlations of the rest of metals were positive but not statistically significant ($p > 0.05$). TOM had a positive function that was complex, involving Cu, in surface sediments of the Caspian Sea. Organic matter is a most significant sink for Cu in sediments.[43] Cu in the oxidisable-organic fraction is associated with biogenic carriers, which settle through the water column.[44,45] The number and intensity of binding sites vary among types of organic matter. Some types of organic material have a few sites per unit surface (e.g., lignins) and others have many (e.g., humic and fulvic acids). The intensity of complexation also appears to vary progressively with metal concentration, with high-intensity sites being filled first, followed by sites of progressively lower intensity.[7] Clay colloid reveals a significant trend for adsorbing organic matter, and the concentration increases as the average grain size decreases,[46] whereas entire of stations were dominated by sand particles. This could therefore be for reasons suggested in this study, as there was no significant positive correlation between the metals studied in the oxidation-organic fraction and TOM. Some characteristics of sediments, such as pH, redox reactions, and chemical forms of the metals in a binding capacity, which control the solubility, availability, and mobility of metals, are also important.[19]

Correlation of heavy metals between fractions

According to Rubio et al. [47] a simple correlation statistical analysis can be performed in order to explore the possible association existing between different variables of metals. From Table 7, most metals were strongly and positively correlated. Significant correlations ($p < 0.01$) were found in the total concentrations between Pb and Cd ($r = 0.5$), Pb and Cu ($r = 0.4$), Ni and Cd ($r = 0.74$), Ni and Zn ($r = 0.76$), Cd and Zn ($r = 0.68$), Cd and Cu ($r = 0.65$), and Zn and Cu ($r = 0.7$). Similar results have been observed previously [48] and were related to a similar source and distribution pattern of these metals. Soto-Jiménez et al. [49] indicate that these metals are bioavailable simultaneously and also indicate a common source of metal contamination. On the other hand, this might be due to similar uptake and release mechanisms by organisms living in or overlying the sediments [50]. According to previous studies, Pb, Cu, and Zn are positively correlated among these metals, suggesting a common origin for these metals in the study area.[51,52] The correlation between total metals with resistant fractions might also be used to estimate the degree of natural origin of the metals analyzed (Table 7). The resistant fraction of Pb did not significantly correlate to the total concentrations of other metals, except for total Pb ($r = 0.614**$ $p < 0.01$). The resistant fractions of Ni also correlated significantly to the total concentrations of Ni, Cd, and Zn ($r = 0.846**$, $0.537**$, and $0.751**$, $p < 0.01$, respectively). The resistant fraction of Zn correlated significantly to the total concentrations of Ni, Cd, and Zn ($r = 0.625**$, $0.470**$, $0.785**$, $p < 0.01$, respectively). Meanwhile, the resistant fractions of Cd and Cu correlated significantly ($p < 0.01$) to Pb, Ni, Cd, Zn, and Cu. Total Cd and Ni correlated strongly ($p < 0.01$) to naturally occurring Pb, Ni, Cd, Zn, and Cu. Moreover, total Cd and Ni also correlated strongly to anthropogenic Pb, Ni, Cd, Zn, and Cu. This indicates that when total Cd and Ni concentrations are elevated in the sediment, this is mostly due to both anthropogenic and naturally occurring Pb, Ni, Cd, Zn, and Cu. Total Pb was strongly related to resistant Pb ($r = 0.614$, $p < 0.01$) and non-resistant Pb ($r = 0.659$, $p < 0.01$). Similarly, for Cu, when total Cu correlated strongly ($r = 0.909$, $p < 0.01$) with naturally occurring (resistant) Cu, total Cu also correlated strongly ($r = 0.816$, $p < 0.01$) with anthropogenic Cu. This indicates that when Pb and Cu concentrations are elevated in the sediment, this is mostly due to both Pb and Cu of natural origin and from anthropogenic sources.

Contamination assessment

The individual and GCFs for Pb, Ni, Cd, Zn, and Cu in surface sediments of the Caspian Sea are shown in Table 8. The highest levels of ICF for Pb and Ni were found at sites 1, 2, and 7. The highest levels of ICF for zinc were found at sites 1, 2, and 3. The highest levels of ICF for copper were measured at sites 1, 13, and 14. The highest levels of cadmium were identified at sites 4, 6, 7, 8, and 13. ICF reflects the risk of contamination to a water body by a contaminant.[19,23] The differences between contamination factors in the sediments of different stations might be related to physicochemical parameters which control the rate of adsorption and desorption of heavy metals,[2] and also sea currents. The highest risk from the metals studied was computed at stations

Table 7. Pearson's correlation coefficient variables for total concentration (sum of four fractions, Tot), non-resistant (NR) and resistant (R) Pb, Ni, Cd, Zn, and Cu based on their log_{10} transformed concentrations in µg/g in the southern part of Caspian Sea.

	R-Pb	R-Ni	R-Cd	R-Zn	R-Cu	NR-Pb	NR-Ni	NR-Cd	NR-Zn	NR-Cu	Tot-Pb	Tot-Ni	Tot-Cd	Tot-Zn	Tot-Cu
R-Pb	1														
R-Ni	0.327*	1													
R-Cd	0.128	0.416**	1												
R-Zn	0.033	0.656**	0.473**	1											
R-Cu	0.137	0.435**	0.21	0.225	1										
NR-Pb	0.297	0.259	0.27	−0.172	0.288	1									
NR-Ni	−0.097	0.343*	0.203	0.016	0.474**	0.714**	1								
NR-Cd	0.019	0.529**	0.286	0.384*	0.441**	0.406**	0.622**	1							
NR-Zn	0.174	0.135	0.105	−0.202	0.756***	0.380*	0.281	0.27	1						
NR-Cu	0.01	0.663**	0.571***	0.674***	0.738***	0.194	0.454**	0.663**	0.430**	1					
Tot-Pb	0.614**	0.336*	0.259	0.043	0.494***	0.659***	0.386*	0.428***	0.455***	0.330*	1				
Tot-Ni	0.024	0.846***	0.510***	0.625***	0.489***	0.404***	0.620***	0.733***	0.167	0.738***	0.348*	1			
Tot-Cd	0.087	0.537***	0.619***	0.470***	0.556***	0.464***	0.604***	0.877***	0.407***	.850***	0.501***	0.742**	1		
Tot-Zn	0.067	0.751***	0.552***	0.785***	0.676***	0.01	0.24	0.531***	0.357*	0.902***	0.255	0.762**	0.682**	1	
Tot-Cu	0.006	0.308*	0.396***	0.268	0.909***	0.235	0.469***	0.417***	0.695***	0.816***	0.404**	0.442**	0.653**	0.692**	1

*significant at $p<0.05$; **significant at $p<0.01$.

Table 8. Individual and GCFs of Pb, Ni, Cd, Zn, and Cu in the southern part of Caspian Sea.

Stations	ICF					GCF
	Pb	Ni	Cd	Zn	Cu	
Astara	0.75	0.28	0.70	0.27	0.22	2.22
Parasar	0.83	0.31	0.97	0.19	0.11	2.42
Anzali	0.43	0.14	0.75	0.19	0.11	1.62
Kia	0.33	0.20	1.13	0.09	0.15	1.90
Cahmkhaleh	0.32	0.18	0.65	0.08	0.14	1.38
Chaboksar	0.32	0.36	1.28	0.09	0.11	2.17
Vazivar	0.88	0.45	1.08	0.09	0.12	2.62
Noshahr	0.58	0.22	1.34	0.08	0.20	2.42
Neka	0.49	0.18	0.81	0.07	0.17	1.72
Babolsar	0.70	0.20	0.69	0.09	0.17	1.85
Khazar Abad	0.68	0.45	0.51	0.11	0.14	1.88
Gohar	0.70	0.27	0.43	0.08	0.07	1.55
Bandar Gaz	0.48	0.11	1.02	0.04	0.38	2.02
Bandar Torkman	0.66	0.20	0.62	0.07	0.31	1.86

1, 2, and 7. Average ICF values in surface sediments at the sampling stations were ranged in the order Cd > Pb > Ni > Cu ≈ Zn.

The GCF analyzed from ICF values determined that the western and middle sections of the southern part of the Caspian Sea were highly affected by metal pollutants. The result shows that those stations close to the berth line, highly populated and industrialized areas, posed a high potential risk to the Caspian Sea. The tendency of trace metals is to accumulate in sediments, and contamination from each source tends to be localized in a hotspot near the input, and then, this is dispersed regionally in lower concentrations.[7] Hence, the results obtained during this investigation show that the stations located in the vicinity of a municipal area pose a high potential risk to the fauna and flora of the Caspian Sea environment. The GCF value is significant because it reflects the overall potential risk posed by toxic elements.[23]

Comparison with previously reported studies

Table 9 shows a comparison of data reported by this study with the results of other researchers for marine sediments. Pb concentrations were higher than Caspian Sea regions in Kazakhstan,[14] Russia,[14] Azerbaijan, [14] the Persian Gulf, Bahrain [53] and Uluabata Lake, Turkey.[54] However, they are still much lower than in the northern part of the Persian Gulf.[55] Concentrations of Ni were also comparable or lower than some reported values, but higher than samples from the west coast of Malaysia,[56] the southwest coast of Spain [34] Caspian Sea regions in Kazakhstan,[14] Russia,[14] Azerbaijan, [14] the Dumai coast, Indonesia [57] and the Persian Gulf, Bahrain.[53] Cd concentrations were found to be still within the range found in other studies, but were higher than the Caspian Sea regions in Kazakhstan,[14] Russia,[14] Azerbaijan,[14] coastal sediments in India, [58] or Uluabat Lake, Turkey.[54]

Zn concentrations were still within the range found off the west coast of Malaysia [56] or Kaoshiung Harbour, Taiwan,[59] but lower than in the Caspian Sea, Azerbaijan,[14] Sandy area, Chile,[28] or Kaoshiung Harbour, Taiwan.[59]

Cu concentrations were comparable or even much lower than concentrations reported in other geographical areas, but higher than samples from Caspian Sea regions in Kazakhstan,[14] Russia,[14] or Uluabat Lake, Turkey.[54]

Comparison with SQGs

In the present study, the concentrations of heavy metals were compared with ERL and ERM values to estimate the possible toxic effects of heavy metals at different stations. The results of the present study showed that Ni was distributed between the < ERL (7.1%), ERL-ERM (71.4%), and > ERM (21.43%). Ni at stations 3, 13, and 14, which

Table 9. Comparison of heavy metals in surface sediments of the Caspian Sea with previously reported studies.

Location	Pb	Ni	Cd	Zn	Cu	Reference
The west coast of Malaysia	3.59–25.36	–	0.1–1.42	4.00–79.05	0.25–13.80	Yap et al. [27,56]
Izmit Bay, Turkey	23.80–178	38.40–70.7	3.3–8.9	500–1190	60.6–139	Pekey [41]
Southwest coast of Spain	20–197	10–61	0.19–2.5	141–649	41–336	Morillo et al. [34]
Caspian Sea, Azerbaijan	19.6	34.5–68	0.14	83.2	31.9	De Mora et al. [14]
Caspian Sea, Kazakhstan	5.75	1.8–54.8	0.05	11.1	6.4	De Mora et al. [14]
Caspian Sea, Russia	4.19	5.42–34.2	0.06	17.1	8.3	De Mora et al. [14]
Caspian Sea, Iran	18.00	29.4–67.8	0.16	85.3	34.7	De Mora et al. [14]
Persian Gulf, northern part	90.48		2.89			Pourang et al. [55]
Uluabat Lake, Turkey	1.42		0.078	0.75		Barlas et al. [54]
Sandy area, Chile	9.47–18.50	5.67–13.6	0.8–1.09	55.30–519	1259–1896	Ramirez et al. [28]
Kaohsiung Harbour, Taiwan	9.5–470	–	0.1–6.8	52–1369	5–946	Chen et al. [59]
Dumai coast, Indonesia	14.63–84.90	7.26–19.97	0.46–1.89	31.49–87.11	1.61–13.48	Amin et al. [57]
Persian Gulf, Bahrain	12.3		0.4		9.6	ROPME [53]
Coastal sediments, India	13.7–24.9	26.5–44.5	0.1–0.2	26–162	21.5–64.1	Reddy et al. [58]
South Caspian Sea, Iran	13.06–33.48	18.01–69.63	0.62–1.5	30.11–87.88	5.86–38.89	Present study
*ERL	47	21	1.2	150	34	Long et al. [22]
**ERM	218	52	9.6	410	270	Long et al. [22]

*ERL = effect range Low, dry weight.
**ERM = effect range median, dry weight.

are located in industrialized areas, showed frequent adverse effects that were expected. Cd was distributed between the < ERL (92.85%) and ERL-ERM (7.15%), whereas Cu was distributed between the < ERL and ERL-ERM ranges (14.28% and 85.72%, respectively). Finally, 100% of Zn and Pb concentrations were distributed in the first concentration range (<ERL). Overall, none of the metal concentrations (except for Ni at stations of 3, 13, and 14) in these sediments were as high as ERM values. Therefore, frequent adverse effects were not expected (Table 9).

Conclusion

What is important is that the Caspian Sea is a shared water body surrounded by countries that potentially affect the aquatic environment. This is due to the Caspian Sea currents and the influence of uncontrolled pollution in the area. Sediment quality assessment revealed that the potential toxicity of the marine environment could not cause adverse biological effects on the biota directly. The levels of trace metals in the surface sediments did not show severe enrichment. Nevertheless, it is still strongly recommended that further investigations and ongoing monitoring focus on heavy metals contamination in order to assess the long-term effects of anthropogenic discharge into the Caspian Sea ecosystem. These results will help facilitate the development of new strategies for the control of contamination in the Caspian Sea.

Disclosure statement

The present study was the first study of anthropogenic assessment of some metals in southern part of Caspian Sea. The result showed the health situation of the area. And also, such this kind of data will answer those questions of people who are concerning about their health and environment.

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