

Distribution and Normalization of some Metals in Surface Sediments from South Caspian Sea

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Abstract Surface sediments along the south of Caspian Sea were collected to evaluate the contamination of heavy metals. The result ranged ($\mu\text{g/g}$, Fe% dw): Pb(13.06–33.48); Ni(18.01–69.63); Cd(0.62–1.5); Zn(30.11–87.88); Cu (5.86–26.37) and Fe(1.8–4%) respectively. Cadmium showed higher EF when compared to other sites. Geoaccumulation Index value for Cd in most stations was classified as moderately contaminated and moderately to strongly contaminated, as well as the average of I_{geo} of Cd (1.77 ± 0.35) suggested that surface sediments of Caspian coast were moderately polluted by this metal. The result of the Pearson correlation showed that there were significant positive associations between Ni, Cd and Zn ($r = 0.44$ – 0.76 ; $p < 0.01$).

Keywords Caspian Sea · Enrichment factor · Geoaccumulation index · Pollution load index

The Caspian Sea, surrounded by the five littoral states of Azerbaijan, Federation of Russia, Islamic Republic of Iran, Kazakhstan and Turkmenistan, is the principal inland body of water in the world. As a closed-environment without an outlet, various pollutants caused by effluents from coastal catchment areas and leakages from off shore oil production

have accumulated in the Caspian Sea. On the other hand, sea currents transport and circulate the entrapped pollutants along the Iranian coast of the Caspian Sea. A large percentage of the more than 10 million people who reside in the Iranian coastal provinces bordering the Caspian Sea are expected to be exposed to high concentrations of toxic contaminants like the coastal residents who regularly eat sturgeon and other fish from the Caspian Sea (Parizanganeh et al. 2007).

Heavy metals have great ecological significances due to their toxicity and tendency to accumulate in both sediment and biota. Trace metals derived from natural inputs and anthropogenic emissions are ubiquitous in the global environment. These elements are not biodegradable and undergo a global ecological cycle. They are present in streams as a result of chemical leaching of bed rocks, water drainage and discharge of urban and industrial waste waters (Ahmed et al. 2007). Sediments serve as a pool of metals that could be released to the overlying water from natural and anthropogenic processes such as bioturbation and dredging, resulting in potential adverse health effects (Long et al. 1995). It is important that sediment contamination by trace metals be evaluated, and that natural versus anthropogenic contribution be distinguished for effective remedial actions against metal pollution (Chapman and Wang 2001). The enrichment rate of pollutants in sediments reflects the contamination sources. The most heavily polluted layers tend to accumulate during the most intensive production of metals, whereas, in the period prior to industrial activity, concentrations of heavy metal are more similar to geochemical back-ground values.

The main purposes of this study were (1) to assess the heavy metals concentration in surficial sediments of the south coast of the Caspian Sea, (2) to identify the non-lithogenous degree of metal in surface sediments to provide

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preliminary data for control of pollution in south of the Caspian Sea and (3) to evaluate correlation between total organic matter (TOM) and trace metal concentration in the surface sediment of Caspian Sea. The extent of metal pollution was assessed using Enrichment Factor (EF), Geoaccumulation Index (I_{geo}) (Chen et al. 2007), Effective range Low (ERL) and Effective Range Median (ERM) (Ramirez et al. 2005).

Material and Method

Fourteen sampling stations were established along the south of the Caspian Sea, between 37°38'N, 49°5'E and 36°53'N, 54°02'E (Table 1; Fig 1). Surface sediments (0–5 cm) were collected from each station. Three samples from each station were collected using a plastic spatula, placed in clean plastic bags and kept frozen prior to analysis as described by Ismail (1993). The samples were transported to the laboratory, dried to constant weight at 80°C (Ismail 1993) and sieved through a stainless steel sieve.

As a qualify control, the metals certified references material was processed at the same time as the other samples. To avoid possible contamination, all glassware and equipment used acid-washed. To check for contamination, procedural blanks were analyzed in every five samples. Quality control samples, made from standard solutions of Cd, Cu, Pb, Ni, Zn and Fe were analyzed in every five samples to check for the metal recoveries. The percentage of recoveries were 108%, 98%, 98%, 95%, 96%, 94% for Cd, Zn, Ni, Cu, Pb, Fe respectively.

The direct Aqua regia method was used for the analyses of total Cd, Cu, Ni, Pb, Zn and Fe concentration in sediment samples. About 1gr of each dried sample was weighted and digested in a concentration composed of nitric acid 69% and perchloric acid 60% in the ratio of 4:1 first at low temperature 40°C for 1 h. Then, the temperature was increased to 140°C for at least 3 h (Ismail 1993). The digested samples were diluted to an exact volume with double distilled water (DDW) and was filtered through Watman No. 1 filter paper, and the filtrate was stored until metal determination. After filtration, the prepared samples were determined for Cd, Cu, Ni, Pb, Zn and Fe by using an air-acetylene flame atomic absorption spectrophotometer (AAS) Perkin-Elmer Model 4100. The data are presented in µg/g dw basis. Multiple-level calibration standard were analyzed to generate calibration curves against which sample concentrations were calculated. To avoid any possible contamination, all glassware in the experiment were previously acid-washed. The detection limits of the FAAS for Cd, Zn, Ni, Cu, Pb and Fe were 0.009, 0.007, 0.003, 0.01, 0.009 and 0.007 mg/L, respectively.

According to Mucha et al. (2003), sediments were dried in the air circulated oven at 80°C until constant weights, and then ignited in the furnace at 500°C for 4 h. The difference of weight before and after ignition was considered as total organic matter of samples. The enrichment factor for each metal is calculated by dividing its ratio to the normalizing element by the same ratio found in the chosen baseline. EF represents the actual contamination level in the sediment and is a good tool to differentiate the metal source between anthropogenic and naturally occurring

Table 1 Sampling position and human activity near sampling location

No	Station	Latitude	Longitude	Designation
1	Astara	38° 26'	48° 52'	Main pollution comes from Azerbaijan, urban, tourism
2	Parasar	37° 38'	49° 05'	Wood industry, canning, urban
3	Anzali	37° 28'	49° 27'	Urban, port, discharge from lagoon, canning, industry of animal food, nylon and polyester processing, paints, varnishes, medicines, iron and steel
4	Kiashahr	37° 26'	58° 75'	Urban, port, dairy products, wearing apparel industry
5	Chamkhale	37° 12'	50° 16'	Refinery, carpet industry, textile, soap processing, machinery and equipment
6	Chaboksar	36° 59'	50° 32'	Agriculture, aquaculture, silk
7	Vazivar	36° 34'	51° 54'	Urban, tourism
8	Noshahr	36° 39'	51° 30'	Tourism, ship transport, agriculture, food processing, timber treatment and steel industries
9	Neka	36° 39'	53° 18'	Wood industry, oil reservation, electrical power plant
10	Babolsar	36° 42'	52° 39'	Tourism, urban, industries of food, sugar, canning, carpet and rugs, textile, paper, plastic
11	Khazarabad	36° 48'	53° 6'	Tourism, urban, food products, textile, basic industry of chemicals, fertilizers and pesticides, paint, structural metal products
12	Goharbaran	36° 47'	53° 56'	Tourism. Power plant
13	Gaz port	36° 47'	53° 56'	Port, urban, agriculture
14	Torkman port	36° 53'	54° 02'	Agriculture, handicrafts, animal husbandry, fishing, and tourism

Fig. 1 Sampling locations along the south of Caspian Sea



(Valdés et al. 2005). The EF was calculated according to the following equation:

$$EF = (\text{Metal/Fe})_{\text{sample}} / (\text{Metal/Fe})_{\text{Background}}$$

where M_x and Fe_x are the sediment sample concentrations of the heavy metal, while M_b and Fe_b are their concentrations in a suitable background or baseline reference material (Salomons and Forstner 1984). In this study, the geochemical normalization was obtained using Fe as the reference element. According to (Zhao et al. 2007), Fe was used for the following reasons: (1) Fe is associated with fine solid surfaces; (2) its geochemistry is similar to that of many trace metals; and (3) its natural sediment concentration tends to be uniform.

Chen et al. (2007) interpreted the value of EF into seven classes. $EF < 1$ indicates no enrichment, $EF < 3$ is minor enrichment, $EF = 3\text{--}5$ is moderate enrichment, $EF = 5\text{--}10$ is moderately severe enrichment, $EF = 10\text{--}25$ is severe enrichment, $EF = 25\text{--}50$ is very severe enrichment and $EF > 50$ is extremely severe enrichment.

Geochemical index (I_{geo}) was originally stated by Muller (1969) in order to determine and define metal contamination in sediments by comparing current concentrations with pre-industrial levels (Muller 1969). I_{geo} is calculated as follows:

$$I_{\text{geo}} = \log_2(C_n / 1.5n)$$

where, C_n is the concentration of metals examined in sediment, and B_n geochemical background concentration

of element (n). Factor 1.5 is the background matrix correction factor due to lithogenic effects. Muller determined the following descriptive classes for increasing I_{geo} Values (Muller 1969) available in Table 2.

Result and Discussion

The Range and average heavy metal concentrations in sediments from all stations are presented in (Table 3). Metal concentrations ($\mu\text{g/g}$; except Fe%) showed variations with Pb, 13.06–33.48; Ni, 18.01–69.63; Cd, 0.62–1.5; Zn, 30.11–51.45; Cu, 5.86–26.37; Fe, 1.8–4. Concentration of heavy metals in surface sediment were found to be higher

Table 2 Description of sediment quality I_{geo} classification (Muller 1969)

I_{geo}	I_{geo} class	Description of sediment quality
>5	6	Extremely contaminated
4–5	5	Strongly to extremely strongly contaminated
3–4	4	Strongly contaminated
2–3	3	Moderately to strongly contaminated
1–2	2	Moderately contaminated
0–1	1	Uncontaminated to moderately contaminated
<0	0	Uncontaminated

All statistical analyses were computed by using Package for Social Science (SPSS) version 16

Table 3 Mean metal concentrations ($\mu\text{g/g}$; except Fe %)

No	Station	Pb	Ni	Cd	Zn	Cu	Fe %	TOM
1	Astara	32.70	43.39	1.38	68.35	38.89	2.07	3.4
2	Parasar	14.29	38.29	0.79	39.54	24.89	2.7	1.9
3	Anzali	31.78	40.66	0.72	60.49	24.02	2.5	2.4
4	Kiashahr	23.78	18.01	0.71	51.89	16.74	2.2	1.3
5	Chamkhale	26.62	21.95	0.75	55.29	15.04	2.2	1.5
6	Chaboksar	16.30	24.01	0.62	46.38	13.44	2.4	1.2
7	Vazivar	13.06	30.12	0.84	30.11	6.41	1.8	1.3
8	Noshahr	27.05	29.88	0.78	38.28	8.07	1.9	1.4
9	Neka	33.48	45.69	1.07	52.97	7.97	2.4	1.6
10	Babolsar	22.25	33.72	0.75	41.06	7.10	2.0	1.4
11	Khazarabad	22.27	41.59	0.92	34.25	5.86	2.5	3.7
12	Goharbaran	28.27	44.47	0.78	44.65	7.86	2.2	2.1
13	Gaz Port	21.63	63.58	1.04	87.88	17.75	4.0	2.4
14	Torkman port	27.23	69.63	1.50	86.18	26.37	4.0	3.9
Mean		23.69	38.58	0.9	51.45	13.96	2.52	
Min		13.06	18.01	0.62	30.11	5.86	1.8	
Max		33.48	69.63	1.5	87.88	26.37	4	
Aver. sediment ^a		19	52	0.1	95	33	4.1	
ERL ^b		46.7	20.9	1.2	150	34	–	
ERM ^b		218	51.6	9.6	410	270	–	

^a Salomons and Forstner (1984)^b Long et al. (1997)

in some sites closed to ports, urban areas and ship transport areas in the west and East Caspian with anthropogenic activities. High concentrations of Ni, Zn and Fe were found in sediments from station 12 (Gaz Port) to station 13 (Torkman Port) which is located in the Golestan Province. Ni concentration ($69.63 \mu\text{g/g}$) was found highest in Torkman Port. According to De Mora et al. (2004), the distribution of Ni in the Caspian Sea reflecting the high natural background is due to mineralization. The hot spot for Zn and Fe concentration were noted at station 13 ($87.88 \mu\text{g/g}$, 4%) in Gaz port.

Moreover The high concentration of Zn in this area concurs with studies of Caspian Sea Environment Program which demonstrated the zinc concentration, at a short distance away from the Cheleken Peninsula in Turkmenistan, exceeding by 7.2 times. The reason of this finding is probably that Zn is the influenced of some activities stretching from Cheleken Peninsula area to Iranian coast in Torkman.

High concentration of Cu ($26.37 \mu\text{g/g}$), Pb ($33.48 \mu\text{g/g}$) and Cd ($4.48 \mu\text{g/g}$) were observed in Golestan and Mazandaran provinces, whilst Guilan Province had high concentrations of Cu. Pb is found in Anzali port while Cd is in Astara. According to Caspian Environment Program studies, Copper in the northern Caspian exceeds the maximum permissible level by 3.9 times. Golestan province especially the areas of sites 13 and 14 are under the influence of numerous sources of pollutants which are discharged from industries into the near shore area by the Behshahr. Heavy

metals distribution among the 14 stations can be seen in (Table 3). Higher concentrations were found in stations 1, 2, 12 and 13 which were probably due to port terminal and oil development zones. The Anzali area (station 2) is affected by massive amount of contaminants from anthropogenic sources. Anzali lagoon discharges into the near shore of this area contaminated agriculture, food processing and urban wastes which have been collected from various sources (Parizanganeh et al. 2007). Gaz and Torkman Port are near to the eastern side of the Caspian Sea. The industrial center of Torkman Port is a major source of polluting heavy metals around this station. According to Chen et al. (2007), Port and industrial activities have been reported to contribute to heavy metal contamination (Chen et al. 2007).

The mean concentration of Pb, Cd, in sediment of the south of the Caspian Sea exceeded the average sediment concentrations (Salomons and Forstner 1984). Concentration of Ni, Zn and Cu were below average sediment concentrations presented in Table 3. When compared to metal concentrations, sediments though out the coast of Caspian Sea, all metals especially Pb and Cd in Azerbaijan and Iran were higher than those from Russia and Kazakhstan. De Mora et al. (2004) reported that mean concentrations of Cd, Cu, Ni, Pb, Zn and Fe in sediments ranging from West to East of the Caspian Sea were 0.2, 34.7, 51.6, 18, 85.3, 3.5(%) $\mu\text{g/g}$ respectively (De Mora et al. 2004). The mean concentration of total heavy metals in sediments represented the next decreasing order

Fe > Zn > Ni > Pb > Cu > Cd. Cadmium and Copper showed the lowest concentrations at most studied locations. The coastal area of the Caspian Sea is becoming increasingly polluted with massive load of contaminants discharged into the Caspian Sea from various anthropogenic sources. The World Bank predicted that a million cubic meters of untreated industrial wastewater is discharged directly into the Caspian, with the bulk coming from oil and mining operations (Parizanganeh et al. 2007).

The mean EF value of metals with respected to average sediment is showed in Table 4. The result showed that the range of EF values were 1.15–3.4; 0.66–1.65; 5.71–16.04; 0.58–1.42; 0.29–2.33 for Pb, Ni, Cd, Zn, Cu respectively.

EF value for Zn and Cu were less than which indicated no enrichment of the two metals. The lowest EF values were determined in Zn and Cu which originated from natural weathering process. The average enrichment factor of Pb 0.76 ± 2.22 and Ni 0.3 ± 1.23 were determined, indicating that this metal had minor enrichment. The highest EF values for Pb, Ni, Cd, Zn and Cu were found in Astara, Parasar and Anzali in the West of the study area, so, in these stations, Pb (3.45) value could be classified as moderately enrichment whilst Ni, Zn and Cu were minor enrichment. According to De Mora et al. (2004), the stations in Guilan coasts were affected by heavy metal contaminants from the numerous oil extractions, petrochemical and industrial area in Azerbaijan. The average enrichment factor of cadmium (8.71 ± 2.86) was determined to be

higher than 5 in surface sediment of the south Caspian, which indicated that Cd contamination, had moderately severe enrichment. It is known that the greatest concentrations are likely to be found close to the major coastal industries (e.g. the Absheron peninsular in Azerbaijan Astara and Anzali in Iran) and the mouths of rivers which have mining, chemical industries and agriculture on their catchments. According to (Table 4), the results of the calculated I_{geo} values from this study are -0.4 to 0.23 for Pb, -2.12 to (-0.13) for Ni, -2.8 to (-0.15) for Cu, 1.28 – 2.44 for Cd and -1.9 to 0.65 for Zn. The Geoaccumulation Index (I_{geo}) of heavy metals in this study exhibited that 70.76% of the metals belonged to I_{geo} classes 0 (Uncontaminated), 15.3% ranged in I_{geo} class 2 (Moderately contaminated), 7.69% located in class 1 (Uncontaminated to moderately contaminated) and 6.15% in class 3 (Moderately to strongly contaminated). I_{geo} value for Cd in most station was high which can be classified as moderately contaminated and moderately to strongly contaminated, and the average of Geoaccumulation Index of Cd (1.77 ± 0.35) suggested that surface sediments of Caspian coast were moderately polluted by this metal, whereas the average of geoaccumulation indexes of Pb in some stations (Astara, Anzali, Vazivar, Neka and Torkman) were uncontaminated to moderately contaminated by this metal. In contrast, I_{geo} of Ni, Zn, Cu in all stations was of class 0 that suggested the surface sediments can be considered as uncontaminated for these metals. According to Long et al. (1997), concentration of Pb, Ni, Cd, Cu and Zn were

Table 4 EF and I_{geo} values for sediments from the South of the Caspian Sea

No	Station	Pb		Ni		Cd		Zn		Cu	
		EF	I_{geo}	EF	I_{geo}	EF	I_{geo}	EF	I_{geo}	EF	I_{geo}
1	Astara	3.40	0.19	1.65	-0.85	16.04	2.44	1.42	-1.06	2.33	-0.35
2	Parasar	1.15	-0.16	1.13	-0.85	11.37	1.63	0.64	-1.26	1.16	-0.90
3	Anzali	2.79	0.15	1.30	-0.94	7.06	1.50	1.06	-1.24	1.21	-1.04
4	Kiashahr	2.39	-0.26	0.66	-2.12	7.93	1.47	1.04	-1.46	0.97	-1.56
5	Cahmkhaleh	2.58	-0.10	0.78	-1.84	8.16	1.56	1.07	-1.37	0.84	-1.72
6	Chaboksar	1.44	-0.32	0.78	-1.87	5.71	1.28	0.82	-1.53	0.69	-1.14
7	Vazivar	1.58	0.04	1.33	-1.31	5.76	1.73	0.73	-1.71	0.45	-1.19
8	Noshahr	3.12	-0.09	1.26	-1.38	10.05	1.61	0.88	-1.90	0.54	-2.62
9	Neka	3.03	0.23	1.51	-0.77	11.99	2.21	0.96	-1.43	0.42	-2.64
10	Babolsar	2.39	-0.36	1.32	-1.25	9.05	1.56	0.88	-1.80	0.44	-2.80
11	Khazarabad	1.89	-0.40	1.29	-1.21	6.61	1.85	0.58	-1.88	0.29	-1.95
12	Goharbaran	2.77	-0.01	1.59	-0.81	8.54	1.61	0.87	-1.67	0.44	-2.66
13	Gaz Port	1.17	-0.40	1.26	-0.29	6.31	2.03	0.95	-0.70	0.55	-1.48
14	Torkman Port	1.46	0.20	1.37	-0.13	7.31	2.36	0.93	-0.65	0.82	-0.15
Mean		2.22	-0.09	1.23	-1.11	8.71	1.77	0.91	-1.4	0.79	-1.58
Min		1.15	-0.40	0.66	-2.12	5.71	1.28	0.58	-1.9	0.29	-2.8
Max		3.40	0.23	1.65	-0.13	16.04	2.44	1.42	-0.65	2.33	-0.15
S.d		0.76	-	0.3	-	2.86	-	0.2	-	0.52	-

Table 5 Pearson correlations

	Pb	Ni	Cd	Zn	Cu	Fe	%TOM
Pb	1						
Ni	.348*	1					
Cd	.501**	.742**	1				
Zn	.255	.762**	.682**	1			
Cu	.404**	.442**	.653**	.692**	1		
Fe	.031	.564**	.500**	.550**	.378*	1	
%TOM	.284	.300	.484**	.567**	.843**	.407*	1

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

compared to the sediment quality Guidelines of Effect Range Low (ERL) and Effect Range Median (ERM) to estimate the possible environmental concentrations of the analyzed metals at the studied stations. The results showed that concentration of Pb, Cd, Zn and Cu in most of the stations were still below the values for ERL and ERM. Astara and Torkman Port exceeded the ERL but still well below ERM value for Cu. The distribution indicated that the influence of pollution from Azerbaijan to Iranian coast is an important source. This contamination may be derived from mining activities in the catchment area and moved by water current to Iranian coast.

However, concentrations of Cd in all stations were above the background concentration of non-contaminated sediment (0.17 µg/g) suggested by Salomons and Forstner 1984, but the concentration of Cd has never exceeded the ERL value except for Astara and Torkman port. The maximum concentration of Pb (33.48 µg/g) was found in Neka station, but the Pb levels have never exceeded the ERL value. Ni concentration exceeded the ERL but still below ERM value. Ni values in two stations have exceeded the ERM (63.58, 69.63 for Gaz and Torkman Port). This result is in agreement with Kirlov (1987) that mentioned about the concentration of Ni which was as high as 100 µg/g but rarely <21 µg/g. According to De Mora et al. (2004) the investigated Ni levels reflected the high natural background in the Caspian Sea.

Inter -element relationships in sediment provide information on heavy metal sources and pathways in the geo-environment (Dragovi et al. 2008). According to the values of Pearson correlation coefficient in Table 5, Pb, Ni, Cd, Zn and Cu were positively correlated with each other ($r = 0.40\text{--}0.74$; $p < 0.01$). All metals were correlated with Fe except Pb (0.56, 0.5, 0.55, and 0.37 for Ni, Cd, Zn, and Cu respectively). This result suggested that Pb was not strongly controlled by natural weathering processes (Zhang et al. 2009).

The significantly positive correlation of Ni, Cd, Zn and Cu with Fe indicates that the elements were derived from similar sources and also moving together (Bhuiyan et al. 2009). There were significant correlation between TOM and Cd (0.48; $p < 0.01$), Zn (0.56; $p < 0.01$) and Cu (0.84;

$p < 0.01$), whereas Pb and Ni had low association with total organic matter with low positive correlation.

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