Assessment of Heavy Metal and oil pollution in surface sediments of South Eastern Caspian Sea using Indices

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Extended Abstract

As the largest lake, the Caspian Sea is one of the most important lakes in the world from ecological, political and natural resources points of view. The Caspian Sea is increasingly being under environmental threats and pressures because of residential, industrial and agricultural areas, oil exploitation and production activities within and in the vicinity of long coastlines of this lake. Studying the bottom sediments as the final sink of the fated pollutants has been of interest to evaluate the overall quality of the aquatic environments. Much attention has been paid to the study of the water and sediment quality and ecology of the Caspian Sea. In the present study, heavy metals and petroleum hydrocarbon contents in surface sediment samples of a large area from east to central coasts of southern Caspian sea (from Miankaleh bay in Golestan province to Ramsar coasts in Mazandaran province, Iran) are studied. Twenty sediment samples from different depths in 7 zones along coastline are taken and analyzed for metals (Fe, Al, Ba, Ni, Cu, Zn, V, Cr, Sn and Pb), Total Petroleum Hydrocarbons (TPH) and Polycyclic Aromatic Hydrocarbons (PAHs). Sampling points coordinates; water depths and percentile of fine materials (< 63 μm) in sediment samples are presented in Table 1. Samples are taken by a Van Veen grab sampler and preserved, prepared and analyzed for hydrocarbons according to U.S.EPA SW-846 using gas chromatography. Samples for metal analysis aere prepared according to MOOPAM and measured by atomic absorption spectrometry. Hydrocarbons in marine environments may either be originated from biogenic or petrogenic sources. Results of the present study showed that the contents of TPH fall in the range of 10-64 μg/g of sediments with more enriched (40-64 μg/g) sediments of central part of Mazandaran province coasts. It should be pointed out that TPH contents of some other parts of the world that are recognized as polluted areas are as follows: 60-464 μg/g in Hong Kong, 35-2900 μg/g in New York Bay, 11-690 μg/g in Persian Gulf and 0.059- 34.09 μg/g in northern Caspian sea. Based on some published works, TPH content in sediments more than 500 μg/g is indicative of pollution while sediments containing less than 10 μg/g of TPH may be considered as unpolluted.

According to this rule of thumb, sediments of the study area may be unpolluted in most of the region except for coasts of Mahmudabad to Tonkabon which may have low pollution of hydrocarbons (30<TPH<64 μg/g). PAHs content variations in sediments of the study area show that the concentrations fall in the range of 150-1600 μg/kg while more concentrated sediments are those in Sari to Chalus coasts and lower PAHs content sediments are those for eastern part of Miankaleh bay at south eastern Caspian.

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Table1. Location of sampling points, water depth and percent of fine materials in sediment samples

Sampling Station	Longitude	Latitude	Fine materials (<63 μm) %	Water Depth (m)
1	50° 46′ 881"	37° 14′ 133"	79.9	10
2	50° 46′ 892"	37° 15′ 111"	64.6	27
3	50° 48′ 991"	37° 19′ 126"	61.5	46
4	50° 80′ 006"	37° 04′ 778"	47.7	11
5	50° 81′ 124"	37° 05′ 672"	45.5	27
6	50° 83′ 234"	37° 07′ 665"	43.4	48
7	51° 51′ 149"	36° 48′ 151"	46.6	27
8	51° 51′ 266"	36° 49′ 788"	37.2	67
9	51° 52′ 122"	36° 51′ 556"	34.1	76
10	52° 30′ 004"	36° 35′ 234"	60.3	12
11	52° 33′ 111"	36° 37′ 228"	58.1	30
12	52° 41′ 377"	36° 40′ 311"	42.8	45
13	53° 15′ 122"	36° 51′ 898"	24.8	10
14	53° 13′ 133"	36° 54′ 592"	60.3	19
15	53° 07′ 441"	39° 49′ 105"	63.9	28
16	53° 32′ 062"	37° 01′ 377"	50.7	15
17	53° 23′ 661"	37° 09′ 691"	34.1	20
18	53° 46′ 661"	36° 58′ 283"	76.8	10
19	53° 47′ 022"	37° 09′ 052"	69.7	12
20	53° 41′ 912"	37° 11′ 053"	74.2	16

PAHs contents in sediments of the study area seems relatively high in comparison with Black Sea coastlines 7-638 µg/kg, coastal area of the Adriatic Sea 24-501 µg/kg, Victoria harbor in Hong Kong 350-450 µg/kg, Antarctica in adjacent of South Orkney Islands 8-280 µg/kg, Gironde estuary in France 19-252 µg/kg, Balearic Islands in Mediterranean Sea 30 µg/kg, Russian coast of Caspian Sea 6-345 µg/kg and Kazakhstan coast of Caspian Sea 7-294 µg/kg. Comparing the results of this study with those mentioned above and NOAA guidelines on sediment quality (4000 µg/kg PAHs) shows that sediments of the central coasts of southern Caspian Sea may be relatively low polluted to PAHs. This particularly can be observed for central parts in the vicinity of coastal cities. Major (Fe, Al and Ba) and trace metals (Ni, Cu, Zn, V, Cr, Sn and Pb) in fine (<63µm) sediments analyses showed that metals contents in samples fall in the following ranges in the study area: Fe; 22200-44000 mg/kg, Al; 43600-71000 mg/kg, Ba; 200-512 mg/kg, Ni; 35-67 mg/kg, Cu; 15-50 mg/kg, Zn; 56-104 mg/kg, V; 90-140 mg/kg, Cr; 60-92 mg/kg, Sn; 3-4 mg/kg and Pb; 22-25 mg/kg. In order to have a better assessment on the sediments metal pollution, it is necessary to have studied metals background concentration or the metals concentration of preindustrial era in sediments for the area. Since core sediments sampling and dating analyses are usually required to achieve these information and these experiments are not included in the present study, some public applied geochemical indices are used. These indices are geochemical accumulation index (Igeo), Enrichment Factors (EF), Degree of Contamination (Cd) and modified degree of contamination index (mCd). Mean Fe content (36000 mg/kg) in the area of study sediments observed about 22% and 12% lower than that of mean world sediment (46000 mg/kg) and mean crust (41000 mg/kg), respectively. Mean Al content (59500 mg/kg) in the area of study sediments is about 17% and 27% lower than that of mean world sediment (72000 mg/kg) and mean crust (82000 mg/kg), respectively. Mean Zn content (85 mg/kg) in the area of study sediments is about 7% lower than that of mean world sediment (95 mg/kg) and 20% more than that of mean crust (75 mg/kg).

Mean Cr content (81 mg/kg) in the area of study sediments is also lower than that of mean crust (100 mg/kg) and shale (90 mg/kg). Mean Cu content (35 mg/kg) in the area of study sediments is about 7% more than that of mean world sediment (33 mg/kg), 30% less than that of mean crust (50 mg/kg) and 22% less than that of shale (45 mg/kg). Mean Ni content (49 mg/kg) in the area of study sediments is about 5% more than that of mean world sediment (52 mg/kg), 38% less than that of mean crust (80 mg/kg) and 28% less than that of shale (68 mg/kg). Mean Pb content (19 mg/kg) in the area of study sediments is approximately equal to that of mean world sediment and shale (20 mg/kg) and 35% more than that of mean crust (14 mg/kg). As it is obvious, evaluation of the contamination of the studied sediments using just mean world sediment, mean crust and shale concentrations to compare seems impossible. So mentioned geochemical indices were applied to have a better assessment of contamination. Enrichment Factor analyses showed that most of metals in the sediments are relatively low enriched while amongst them Pb, Sn and Zn enrichment in sediments seemed to have a higher rate. Indices of geochemical accumulation (Igeo) for V, Cr, Cu and Ni were about zero showing no contamination using this index as assessment tool. Igeo for Pb and Sn in sediments of the central part of the study area is higher than that for other metals and areas showing low contamination of sediments with these metals. Modified degree of contamination index for studied metals in the study area also showed no major metals contamination of sediments. To achieve a better understanding of correlations of different studied contaminates behavior and origins within the study area; statistical analyses (correlation coefficients and cluster analysis) have been performed. Result of the cluster analysis is indicative of high correlations among Fe, Al, Cu and Ni contents in sediments. High correlations of V, Zn, Pb and Cr and to some extent Ba and Sn contents with hydrocarbon contents in sediments may be indicative of existence of some same sources of releasing these contaminants into the coastal environment of the studied area though it is hard to determine that these sources are lithougenous or anthropogenic. Regarding the nature of the geology and anthropogenic activities in coastal and inland boundaries of the studied area both kinds of sources may contribute discharging the contaminants into the sediments.
Results, reveal that no extreme contamination of sediments are observed in the area, having in mind that sediments of central part of the southern Caspian is being enriched by some metals and hydrocarbons which highlights the need for more detailed and extensive researches on the nature of contaminant sources and trend of pollution in sediments of the southern part of the Caspian Sea. Need for determining the background concentration of metals in sediments and historical changes of metal contents through core sediment sampling and analyses is also noticeable.

Key words

Oil pollution, Heavy metals, Enrichment Factor, Geochemical Accumulation Index, Caspian Sea, sediments.