

Environmental Assessment of Heavy Metals Contamination of Bottom Sediments of Oman Gulf, United Arab Emirates

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Abstract

To investigate the bottom sediments pollution characteristics and environmental assessments, twenty three samples were collected from Khor Kalba, Fujairah, Khor Fakkan and Dibba coastal areas, Oman Gulf, United Arab Emirates (UAE). The concentrations of copper, zinc, lead, iron, manganese, chromium, arsenic nickel, cobalt, cadmium, molybdenum and vanadium are varied between (9.00, 17. 15, 11.62, 19812.8, 254.85, 156.57, 15.14, 497.46, 24.46, 5.02 and 19.40 ppm) respectively were obtained using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) at Geology Departments, UAE University. The levels of all heavy metals in all 23 samples collected do not exceed the safety limits set by the Dutch guidelines except of Ni. The levels of heavy metals enrichments in the bottom sediments were determined using contamination indices: the Contamination Factor (CF), Enrichment Factor (EF), Geo-accumulation Index (Igeo), and Pollution Load Index (PLI). Geochemical analysis of the study area could be considered lightly or no polluted by heavy metals. This indicating a clear pattern of anthropogenic impact on Oman Gulf.

Keywords: Heavy metals; Environmental assessment; Bottom sediments; Oman Gulf; UAE

Introduction

The study area is undergoing massive infrastructure development on an unprecedented scale. The shoreline is increasingly dissected by many harbors, major power and desalination plans in addition to the construction of oil and gas pipelines, road construction and shipping canals. Terrestrial- and marine-derived sediments are excavated and transported over considerable distances for use in land reclamation projects. These anthropogenic impacts processes deteriorate sediment and water quality. Therefore, contaminations of heavy metals studies help us to know the determination of the degree of anthropogenic impact on Oman Gulf water and sediments.

The heavy metals assessment includes namely enrichment factor, geo-accumulation index, pollution load index and sediment quality guidelines were often used to screen the potential for contaminants within sediment. The main objective of this study is to assess the contamination factors that can be used as appropriate indicators and benchmarks for future assessment of the impacts on the coastal areas. This is carried out through studying the geological environments and evaluation of the pollution quality of the coastal zone of the Gulf of Oman and implement it areas within United Arab Emirates and to provide the required scientific and technological advice and support for ensuring the sustainability and property oriented research activities.

The UAE is in southwest Asia. It is surrounded by the Gulf of Oman to the east, the Kingdom of Saudi Arabia to the west and south, and the Arabian Gulf to the north. It extends from the Qatar to Oman over a distance 725 km along the Arabian Gulf Coast. An additional 75 km of the Eastern coast borders the Gulf of Oman immediately south the Musandam Peninsula, in Oman [1,2].

The UAE can be divided into two different geographic, oceanographic and morphological regions. The Arabian Gulf side which is a flat area of dunes and the Gulf of Oman coast which has narrow, alluvial plains. The Arabian Gulf is a shallow sea with a maximum depth of only 60 m, while the eastern coast faces Open Ocean. The soil in UAE is mainly infertile and sandy with high concentrations of quartz and carbonates [3]. Behind the Arabian Gulf shore line lie the extensive salt flats known as 'sabkha' that are only covered by the sea during freak storm conditions. This coastal complex is backed by recently abandoned salt flats and a series of low escarpments of Tertiary rocks (called the Lower Fars limestones) that can be seen along the Abu Dhabi-Tarif road.

Behind these low escarpments, stretch the vast trains of sand dunes that slowly move south eastwards blown by the ever-present northwest winds. The dunes vary in size and color. Near the coast they are cream to buff but towards the interior they become a deep red-brown color, as at Al Ain, along the Al Ain-Dubai road and towards Al Dhaid city.

The coastal area of UAE bordering Gulf of Oman (study area) is a long range of stark, jagged mountains zone is a separate and distinct geological entity. It comprises an unusual suite of oceanic rocks (ultrabasic and basic igneous rocks). These rocks (lavas, oozes and oceanic crustal rocks) are believed to have formed at the site of a midoceanic ridge (where the Indian Ocean now lies) more than 70 million years ago.

Overall, the coastal region of the United Arab Emirates can be divided into the Arabian Gulf Coastal region and the Eastern Coast of UAE region (study area). The main objective of this study is determine the levels of concentration of heavy metal in the bottom sediments of Khor Kalbaa, Fujairah, Khor Fakan and Dibba areas to create assessment and awareness of human health risks on the present status of the study areas.

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Material and Methods

Sample collection and analysis

Twenty three bottom sediment samples were collected from the Oman Gulf (six samples from Khor Kalba, seven samples from Fujairah), three samples from Khor Fakkan and seven samples from Dibba) (Figure 1). By using a grab sampler from each station and using GPS to determine the coordinates of each one and immediately transferred to sampling containers. The studied areas lie between 25°00' and 25°36' North and 56°18' and 56°22' East.

The samples were left to dry in Petri dishes at room temperature. The dry samples were divided into two portions. On the first portion, the size and distribution of the sand and gravel fractions were determined solely by sieve analyses. The second portion was used for chemical analysis. Sub sample of the air dried sediments was homogenized with a pestle and mortar in order to normalize for variations in grain size distribution. The dried homogenized sediment samples were sieved through a 63 μ m screen and kept in clean plastic containers ready for heavy metals analysis.

Analytical procedures

Twenty three samples from bottom powdered sediments of Oman Gulf (approximately 1 g each) were dissolved in 15 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid (3:1 ratio aquaregia). The mixture was digested at 120°C for l-2 h. Upon cooling, the solution (the leachate) was diluted to 30 ml with deionized water and filtered using Whitman No.1 filter paper, [4].

Concentrations of heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, As, Mo and Zn) (Table 1) were analysis in an aliquot using inductively coupled plasma-mass spectrometry (ICP-MS) at Geology Departments, UAE University. Under the following conditions: reflected power 0 W, incident power 1350 W, coolant flow 1.1 slpm, nebulizer gas flow 0.874 slpm, and nebulizer pressure 2.4 bar. Along with the samples, system and method blanks were run with standard material for background

correction and quality control.

Result

Grain size analyses

Grain size is the most fundamental physical property of sediment. We used information on marine sediment grain size to study trends in surface processes related to the dynamic conditions of transportation, deposition and to study reactions and the affinities of fine-grained particles and contaminants [5,6]. The mean size of 23 samples which taken from the Khor Kalba, Fujairah, Khor Fakan and Dibba areas were studied by Eltokhi et al. [7]. These results revealed that most of the samples in Khor Kalbaa area are muddy sand to sand while most of the samples in Dibba area are sandy to gravelly sand texture, in Khor Fakan sand texture and the samples from Fujairah area range from muddy sand to sand (Figure 2).

Heavy metalsconcentration

Natural background levels of heavy metals: Some heavy metals may be considered a "contaminant" if it occurs where it is unwanted, or in a form or concentration that causes a detrimental human or environmental effect. Metals include lead (Pb), cadmium (Cd), arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), cobalt (Co), and zinc (Zn). Therefore, knowing their natural background levels or at least their permanent concentrations in a marine environment, is essential for detecting and assessing trace metal pollution [8].

Heavy metal contaminations of land resources continue to be the focus of numerous environmental studies and attract a great deal of attention worldwide. This is attributed to no-biodegradability and persistence of heavy metals in soils. In order to identify spatial relationship of heavy metals in soil-rice system at a regional scale.

Table 1 shows the analysis of the bottom sediment samples of the studied areas. The concentrations of copper, zinc, lead, iron, manganese, chromium, arsenic nickel, cobalt, cadmium, molybdenum and vanadium are varied between (9.00, 17.15, 11.62, 19812.8, 254.85, 156.57, 15.14,



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S No	Δs	Cd	Co	Cr	Сц	Fe	Mn	Mo	Ni	Ph	Zn	v	TCC wt %	TOM wt %
KK1	0.01	7 79	28.91	217.8	40.73	57314	299.6	1 72	567.6	21.94	41 15	45.7	56.6	7.4
	10.00	0.20	20.01	217.0	45.04	00764	200.0	0.06	000.7	12.04	24.24	40.7	66.9	2.5
<u> </u>	10.96	0.30	37.4	244.3	15.94	23764	309.5	0.20	000.7	13.01	24.24	42.5	00.0	2.5
KK3	25.52	7.86	33.37	203.7	13.48	35549	376.4	1.76	676.7	12.47	22.98	41.85	64	2.6
KK4	14.53	7.5	31.64	186	13.46	34677	361.3	0.62	622.5	12.77	18.52	38.07	64.2	3.4
KK5	10.18	6	25.65	161.7	11.57	39572	328.2	0.45	537.8	9.68	22.55	34.14	61	3.3
KK6	4.84	6.75	27.64	179.2	10.69	28482	335.2	0.61	564.2	9.27	18.6	34.45	59.6	3.5
D11	8.05	1.18	7.42	24.1	1.2	3997	56.4	7.43	102.8	5.85	10.11	5.37	6.2	2
D12	L.D	1.04	3.9	16.3	0.07	1598	21.9	4.73	41.9	5.49	3.97	2.17	1.4	2.6
D13	L.D	0.55	7.22	21.8	0.05	3940	50	3.31	150.6	14.85	3.48	3.01	4.6	0.4
D14	L.D	1.39	16.17	24.3	0.48	6637	80.5	1.7	258.9	3.86	1.63	2.68	25.4	1.7
D15	5.59	4.21	31.98	81.4	1.26	18433	236.2	1.14	738.2	2.38	11.33	5.63	24	1.6
D16	2.08	3.6	35.01	124.4	1.75	17757	251.7	1.2	703.5	9.89	17.17	7.11	41.4	1.4
D17	L.D	1.62	12.23	38.5	1.19	6205	83.6	0.5	225.1	7.29	7.15	3.68	18	0.5
F1	19.2	4.4	21.65	203.6	9.53	18780	276	0.009	450	12.61	18.12	19.55	48.8	4.4
F2	20.2	4.93	22.9	181.1	8.46	20246	289	0.005	459	10.39	15.55	15.82	48.8	3.6
F3	21.5	5.95	24.77	297.3	9.71	20537	318	0.009	490	8.42	25.57	23.88	54.6	2.6
F4	10.7	5.52	20.14	165.2	10.81	20326	286	0.005	467	23.36	26.15	18.43	52.4	5.6
F5	19.6	7.19	26.93	190.1	15.08	23207	318	0.005	509	7.52	20.08	18.95	50.4	5.2
F6	22.8	7.5	38.8	298.7	10.71	29733	395	0.005	830	21.45	16.1	17.66	57.6	2.4
F7	26.1	6.3	29.96	207.4	8.53	24077	334	0.04	641	15.11	16.84	21.74	49.8	9
KF1	9.6	1.23	5.44	6.1	2.13	1370	18	0.04	13	7.26	9.01	4.07	2.8	4
KF2	37.1	7.56	37.17	227.2	11.17	28764	371	0.04	792	25.28	19.73	19.07	52.6	3.6
KF3	19.1	7.11	36.38	300.8	9.1	28843	386	0.009	792	7.17	24.54	20.71	53.8	4.2

Khor Kalba-KK, Fujairah-F, Khor Fakkan-KF, Dibba-D–D

Table 1: Concentration of heavy metals in bottom sediments in the study area.



497.46, 24.46, 5.02 and 19.40 ppm) respectively which are being less than safe limit of Dutch guidelines except of Ni [9].

Table 2 shows a summary of the concentrations recorder in the sediments as guidelines for the natural background levels in the bottom/ surface sediments in the different regions in Arabian and Oman Gulf in the comparison with the studied area. Al-Abdali et al, De Mora et al and Shriadah [10-12] calculated the average values of the heavy metals in the Arabian-Oman Gulf.

The results obtained from the present study of bottom sediments in the offshore areas of the Oman Gulf suspected to be contaminated by each individual heavy metal in the Gulf region. The most heavy metals in the studied samples are shown to be high level of concentrations rather than the values of shoreline sediments of Arabian Gulf after Shriadah [12] (except Pb and Ni) and higher than the values of costal sediments of Oman Gulf after De Mora et al. [11]. The high levels of Ni and Cd in the study areas are supported by the average analyses of heavy metals in Arabian and Oman Gulf after Al-Abdali et al. (Figure 3) [10].

The distribution patterns of heavy metals in the study area are shown in Figure 4. From this concentration maps, it is clear that high concentration of heavy metals in the study samples are located near heavy industrial activities and lie inside marine traffic area. This anthropogenic activates including Fujairah and Khor Fakan ports and

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Reference Areas		Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cd	Sb	Cr	v
Safe limit of Dutch guidelines (ppm) [9].		190	530	720	210	240	-	-	55	12	15	380	250
Average of concentration Arabian-Oman Gulfs (ppm) [10].		15-30	15-30	30-60	70-80	-	300- 600	10000- 20000	-	1.2-2	-	-	20-30
Average of concentration (µg/g) of AI Sawadi, Oman Gulf. [11].		1.6	1.82	4.92	50.9	2.45	70.4	3500	4.22	0.1	0.12	96.2	12.8
Mean concentration (µg/g) shoreline of Arabian Gulf [12].		7.21	28.1	11.3	36.4	10.2	84.1	-	-	4.82	-	11.9	-
Continental crust average (ppm) Taylor & Mclennan 1995 [13].		25	20	71	20	10	600	35000	1.5	0.098	0.2	35	60
Average of the study area (ppm).		9	11.62	17.16	497.46	24.46	254.85	21469.9	15.14	5.02	-	156.57	19.4



Table 2: Compression between the average concentrations of heavy metals in the study area.

Figure 3: Histogram showing the concentrations of the heavy metals in the studied area (VI) in comparison with the sediments in the different regions in Arabian and Oman Gulf.



major Power and Desalination Plans. In addition to the construction of oil and gas pipelines (Fujairah Oil refinery), marine activities (khor Kalba fishing charter, Fujairah marine club and waiting area of ships at Dibba (Figures 5a-5f).

Heavy metals enrichment contamination assessment

In view of geochemistry results, the heavy metals in the bottom sediments may be show anomalous concentrations which are derived from natural inputs and human activities. For a better estimation of anthropogenic input, several indexes were considered to assess the metal status for the sampled sediments: the Contamination Factor (CF), Enrichment Factor (EF), Geo-accumulation Index (Igeo) and Pollution Load Index (PLI) should be considered. Since the bedrocks in the study area were terrigenous sedimentary and shell fragments, quantitative indexes values were calculated with respect to background values of the upper continental crust (as ppm) described by Taylor and McLennan [13] (Table 3) (0.098 for Cd, 35.0 for Cr, 25.0 for Cu, 600 for Mn, 20.0 for Ni, 20.0 for Pb, 60.0 for V, 10.0 for Co, 1.5 for As and 71.0 for Zn).

Contamination factor (CF)

The level of contamination expressed by the Contamination Factor (CF) and it was calculated as follows [14]:

$$CF = \frac{(metal \ concentration \ in \ the \ sediment)}{(metal \ concentration \ in \ a \ natural \ reference \ sediment \ *)}$$

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Figure 5: Satellite image showing the some polluted locations along Oman Gulf. A: Ships waiting area, Dibba; B: Fujairah International Marine Club; C: Khor Fakan Port; D: Ships Waiting area, Port of Fujairah; E: Power Station, Fujairah and F: Oil Refinery, Fujairah.

Sample ID	As	Cd	Co	Cr	Cu	Fe	Mn	Мо	Ni	Pb	Zn	v
Average of CF in Khor Kalba	7.34	75.31	3.08	5.68	0.71	1.04	0.58	0.6	31.48	0.66	0.35	0.66
Average of CF in Fujairah,	13.34	60.92	2.65	6.3	0.42	0.64	0.53	0.01	27.47	0.71	0.28	0.32
Average of CF in Khor Fakkan	14.62	54.08	2.63	5.09	0.3	0.56	0.43	0.02	26.62	0.66	0.25	0.24
Average of CF in Dibba	3.49	19.81	1.63	1.35	0.03	0.24	0.19	1.91	15.86	0.35	0.11	0.07
Average of CF in the study area	9.70	52.53	2.50	4.6	0.36	0.62	0.43	0.63	25.36	0.6	0.25	0.32
Average of EF in Khor Kalba	7.88	78.25	3.24	5.93	0.66	1.00	0.61	0.55	33.34	0.65	0.34	0.67
Average of EF in Fujairah	20.96	95.04	4.10	9.89	0.66	1.00	0.83	0.01	42.48	1.10	0.45	0.52
Average of EF in Khor Fakkan	69.68	167.52	7.61	7.59	1.05	1.00	0.77	0.24	37.61	3.75	1.33	0.85
Average of EF in Dibba	18.93	101.39	7.12	6.15	0.16	1.00	0.78	20.42	61.28	2.78	0.63	0.43
Average of EF in the study area	29.36	110.55	5.52	7.39	0.63	1.00	0.74	5.30	43.68	2.07	0.69	0.62
Average of Igeo in Khor Kalba	1.47	15.11	0.62	1.14	0.14	0.21	0.12	0.12	6.32	0.13	0.07	0.13
Average of Igeo in Fujairah	2.68	12.23	0.53	1.26	0.08	0.13	0.11	0.00	5.51	0.14	0.06	0.06
Average of Igeo in Khor Fakkan	2.93	10.85	0.53	1.02	0.06	0.11	0.09	0.00	5.34	0.13	0.05	0.05
Average of Igeo in Dibba	0.70	3.98	0.33	0.27	0.01	0.05	0.04	0.38	3.18	0.07	0.02	0.01
Average of Igeo in the study Area	1.95	10.54	0.50	0.92	0.07	0.12	0.09	0.13	5.09	0.12	0.05	0.07
Average of Pollution Load Index (PLI) in Khor Kalba=1.93, Fujairah=1.25, Khor Fakkan=1.15, Dibb=0.59												

Table 3: Average concentration of heavy metals in bottom sediments in the study areas The Enrichment Factor (EF), Concentration Factor (CF) and Geo-accumulation Index (Igeo) for all metals concentered in the study areas.

The contamination factor was classified into four groups, CF<1 refers to the low contamination factor 1<CF<3 refers to moderate

contamination factor 3<CF<6 refers to the considerable contamination factor and CF>6 refers to very high contamination factor. The values

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of Contamination Factor (CF) are present in Table 3. The values of contamination factor show low levels for the most elements (Mo, Cu, Pb, Zn, Co, Mn, Fe, and V) in the study areas. As, Ni, Cd and Cr are higher than the most elements in the study areas. The contamination factor for study areas are low to moderate for Mo, Cu, Pb, Zn, Co, Mn, Fe, V and between moderate to high for Ni, As, Cd and Cr.

Enrichment factor (EF)

The enrichment factors (EF) were evaluated by computing the ratios of metal concentrations to Fe concentration. The enrichment factor for each metal was calculated from the formula stated by Rubio $(Matel + E_2)$ complete

et al. [15].
$$EF = \frac{(Metal / Fe)sample}{(Metal / Fe)crust^*}$$

To calculated the ratio of Enrichment Factors (EF's) of average of heavy metals in bottom sediments at Khor Kalbaa, Dibba, Khor Fakan and Fujairah areas to the crustal average of the upper continental [13] (Table 3). The EF categories are based on the classifications [16], where EF<1 indicates no enrichment, EF=1-3 moderate severe enrichment, EF=10-25 is severe enrichment, EF=25-50 is very severe enrichment and EF> 50 is extremely severe enrichment.

In Table 3, the Enrichment Factors (EF's) of heavy metals in the Oman Gulf bottom sediments at Khor Kalbaa, Dibba, Khor Fakan and Fujairah areas divided into two groups, the first one revealed that they were high enriched in As, Cd, Cr and Ni for all the studied areas. The mean EF values of heavy meals from first group follows the sequence: Cd (110.55)>Ni (43.68)>As (29.36)>Cr (7.39). The average enrichment factors for this group of metals are greater than >50 for cd and from 25-50 for Ni and As and <10 for Cr and Co, suggesting various degrees of metal enrichment according to the recommendation by Yongming et al. [17].

On the other hand, the second group shows low enrichment factor lower than 3 (EF<3) to EF>5 and reflect moderate to minor enrichment. The mean EF values of heavy meals from second group follows the sequence: Co (5.52)>Mo (5.30)>Pb (2.07)>Mn (0.74)>Zn (0.69) >Cu (0.63)>V (0.62). The contamination of the first group of metals could be correlated to local point discharges.

According to Zhang and Liu [18], EF values smaller than 1.5 suggest that heavy metals derived from mainly natural source such as weather processes while EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic. In general, the highest to moderate enrichment factor for all trace metals in the sediment samples were recorded at all the areas under consideration. This high value of enrichment factors suggesting that a significant portion of heavy metals in study sediment is delivered anthropogenic (related to the industrial wastes from the power and desalination plants) effect from several sources.

Geo accumulation index (Igeo)

Commonly, Igeo index is employed in order to determine and define metal contamination in sediments by comparing current concentrations with background levels [19]. Geo accumulation index is expressed as in

followed equation:
$$Igeo = log 2 \left[\frac{Cn}{1.5 \times Bn} \right]$$

Where,

 $\mathrm{C_n}$: The measured concentration of the examined metal (n) in the sediment samples

1.5: The background matrix correction factor due to lithogenic effects

Based on the Igeo value, Muller [19] has distinguished seven classes: Igeo<0, unpolluted, 0<Igeo<1, unpolluted to moderately polluted, 1<Igeo<2, moderately polluted, 2<Igeo<3, moderately to strongly polluted, 3<Igeo<4, strongly polluted, 4<Igeo<5, strongly to very strongly polluted, Igeo>5, very strongly polluted.

The most samples in Table 3, on average were categorized under class "0" (the values of Igeo varied from 0.00 to 0.53, the most samples are uncontaminated with exceptionally from moderately to strongly contaminated with As, Cd, Cr and Ni.

Pollution load index (PLI)

Another commonly used criterion to evaluate the heavy metal pollution in sediments is the Pollution Load Index (PLI). The Pollution Load Index (PLI) proposed by Tomlinson et al. [20] is obtained as a Concentration Factor (CF) of each metal with respect to the background value in the sediment [21], by applying the following equation:

CF = C metal/C background

$$PLI = (CF1 \times CF2 \times CF3 \times \dots \times CFn)^{1/n} CF1$$

Where n: number of metals

The PLI value of >1 is polluted whereas <1 indicates no pollution. The values of PLI obtained in studied sediments. Table 3 show a different range of PLI from 0.59 of Dibba area to 1.93 of Kohr Kalba with average (1.23) indicating of semi polluted grade [22-27].

Conclusion

The rate at which natural and anthropogenic (domestic) wastes are released into bottom sediments of Khor Kalbaa, Dibba, Khor Fakan and Fujairah at Oman Gulf has been of great concern. The study attempted to assess the status of several heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, As, Mo and Zn) in the bottom sediments of Oman Gulf. High levels were found undergoing massive infrastructure development on an unprecedented scale. Many ports and major power and desalination plans increasingly dissect the shoreline in addition to the construction of oil and gas pipelines, road construction and shipping canals. The concentrations of copper, zinc, lead, iron, manganese, chromium, arsenic nickel, cobalt, cadmium, molybdenum and vanadium are varied between (9.00, 17. 15, 11.62, 19812.8, 254.85, 156.57, 15.14, 497.46, 24.46, 5.02 and 19.40 ppm) respectively. The levels of all heavy metals in all 23 samples collected do not exceed the safety limits set by the Dutch guidelines except of Ni. Thus, the area is safe and focus should be on preventing possible future contaminations.

The study showed that the total heavy metals concentrations in the bottom sediment samples followed the order: Fe>Ni>Mn>Cr>Co >V>Zn>As>Pb>Cu>Cd>Mo. Useful indexes Contamination Factor (CF), Enrichment Factor (EF), Geo-accumulation Index (Igeo) and Pollution Load Index (PLI) were used to assess the bottom sediment quality in the Oman Gulf system. Based on average of pollution load index in the study sediments (1.23) was treated as semi polluted. Based on CF, EF factors Igeo index, the contamination degree can be defined as uncontaminated to low contaminated for Mo, Cu, Pb, Zn, Co, Mn, Fe and V and moderate to considerable for As, Cd, Cr and Ni. Geochemical analysis showed significant heavy metal concentration in

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sediments indicating a clear pattern of anthropogenic impact on Oman Gulf.

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