RESEARCH ARTICLE



Heavy metal contamination in sand and sediments near to disposal site of reject brine from desalination plant, Arabian Gulf: Assessment of environmental pollution

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Abstract Accumulation of heavy metals in environment may cause series potential risk in the living system. This study was carried out to investigate heavy metal contamination in sand samples and sediments along the beach near to disposal site of reject brine from Alkhobar desalination plant, which is one of the oldest and largest reverse osmosis desalination plants in eastern Saudi Arabia, Arabian Gulf. Fourteen heavy metals (U, Ca, Fe, Al, Ti, Sr, Rb, Ni, Pb, Cd, Cr, Cu, As, and Zr) were measured using gamma-ray spectrometry, atomic absorption spectrometer (AAS) and energy dispersive X-ray fluorescence spectrometer (EDX). The obtained data revealed that the concentrations of these metals were higher than the values in sediment and soil for other studies in Arabian Gulf. Furthermore, the mean values of Fe, Mn, Cr, Cu, As, Sr, and Zr concentrations in sand and sediments were higher than the geochemical background values in shale. The contamination factor (CF), modified degree of contamination (mC_d) and pollution load index (PLI) were assessed. According to contamination factors (CF > 1), the results showed elevated levels of Cu, Cr, Mn, Zr, and As in all samples. The highest value of contamination factor was found for As. Based on PLI (PLI > 1), the values of all sampling sites indicate a localized pollution in the study area. Current study could be useful as baseline data for heavy metals in sand and sediments nearby a desalination plant.

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Fatimh Alshahri faalshehri@uod.edu.sa **Keywords** Heavy metals · Sand and sediments · Pollution · Reject brine · Arabian Gulf

Introduction

The desalination process is one of the mankind's earliest designs to separate freshwater from a salt-water solution (Einav et al. 2002). Desalination involves several processes to remove the excess salt and other minerals from the water to obtain potable water for human usage. Desalination of sea or ocean water is a widespread technology used in many countries around the world.

Essentially, a desalination plant is a system to separate saline water into two streams: one with a low concentration of dissolved salts and inorganic materials and the other containing the remaining dissolved salts (brine). The amount of flow discharged to waste as a brine discharge varies from 20 to 70 % of the feed flow, depending on the technology used in the plant. Brine discharge is the fluid waste from a desalination plant, which contains a high percentage of salt and dissolved minerals, such as Cu, Cd, Pb, Hg, U, Ni, Cr, and As (Mohamed et al. 2005). The brine returns to the sea and distributes according to different aspects. Desalination plants could have several impacts on the surrounding environment. The major concern of these impacts surrounds the outfall brine discharge due to its physical and chemical features (Younos 2005; Abdul-Wahab 2007; WHO 2007).

Toxic metals might be produced if the discharge brine has contact with the metallic materials used in the plant facilities (Mohamed 2005; Abdul-Wahab 2007). The release of high amounts of heavy metals into water bodies creates serious health and environmental problems. The impacts of toxic metals on animals (marine life) include reduced growth, development, cancer, organ damage, nervous system damage,

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and, in extreme cases, death (Ogoyi et al. 2011; Rahman et al. 2012; Kim et al. 2015).

Saudi Arabia is the world's largest producer of desalinated seawater. The Saline Water Conversion Office (SWCO) constructed 24 desalination plants across the Saudi Arabian coasts, including the 12 major plants on the western coast on the Red Sea and another three on the eastern coast on the Arabian Gulf (Murakami 1995). There are three major desalination plants in Saudi Arabia; Al-Jubail and Al-Khobar plants are located on Arabian gulf coast and Shoaiba plant on the Red Sea coast.

The beach near to Al Khobar desalination plant is famous for its large number of palms. In addition, this beach is constantly frequented by general population and many fishermen. Therefore, this study aims to achieve the following objectives:

- Determine uranium concentration and heavy metals in sand and sediment.
- Identify areas that may be chemically hazardous for population.
- Evaluate the environmental pollution in this public area.

Finally, the data of this study will be useful in future to provide an environmental baseline information to evaluate and control the increase of heavy metals in the study area.

Materials and methods

Beach sand and sediment samples were collected from different locations along Al Azizia beach near to Al Khobar desalination plant with a length interval of 6500 m (Fig. 1). From different locations near to desalination plant, 24 sand samples were collected at 2 m from the shoreline (Table 1). These samples were taken from surface and at 30 cm depth from the surface. From the same locations, 12 sediments were collected from sea water during low tide. In this study, three techniques were used for the analysis: a gamma-ray spectrometer for uranium concentration, atomic absorption spectrometry (AAS), and energy dispersive X-ray fluorescence spectrometer (EDX) for trace metals.

Gamma-ray analysis

Sample preparation

For gamma-ray measurements, sand samples were bulked as a single sample and dried in an oven at 70 °C for 24 h. After that, sand samples were prepared for radiation counting by sieving through 2 mm mesh size. Each sand sample was packed into 152-ml standard size beakers and tightly sealed and stored for 28 days to acquire secular equilibrium. Two

reference materials were packed into the same standard size beakers for efficiency calibration.

Experimental setup

A Hyper pure Germanium detector (HPGe), coaxial type, Ptype with relative efficiency of 20 % was exploited. The detector was shielded with a low-level background lead shield. The HPGe was calibrated for efficiency using the reference material RGU-1 from IAEA. The certified activity of uranium is 400 ppm which refers to 4960 Bq kg⁻¹. The energy transitions of the ²²⁶Ra daughters (²¹⁴Pb and ²¹⁴Bi) were used to develop the efficiency calibration curve. A fourth degree polynomial fitting was performed to reach the best R^2 value (≈ 0.987).

Out of the three naturally occurring isotopes of uranium $(^{234}\text{U}, ^{235}\text{U}, \text{ and } ^{238}\text{U})$, 99 % is ^{238}U which has a half-life of 4.46 × 10⁹ years. Therefore, ^{238}U was measured. After subtracting the background, uranium concentration was measured using its progenies ^{214}Pb with energy 351.93 keV (37.6 %) and ^{214}Bi with energies 609.31 keV (46.1 %), 1120.29 keV (15.1 %), and 1764.49 keV (15.4 %). Uranium was determined based on the above-mentioned energy transitions after achieving secular equilibrium for 28 days after sample packing. The average values were calculated in ppm unit (mg/kg).

Heavy metal analysis

For AAS analysis, the sand samples and sediments were digested in 10 % HNO₃ solution. The digestion solution was performed by adding 3 g of sample with 30 ml of 10 % NHO₃ in a beaker. After standing for 24 h, the solution was heated at 75 °C for 3 h. Then, 25 ml of 5 % HNO₃ was added again to the remaining solution. After digestion, the obtained extract was filtered and transferred to 40-ml polyethylene volumetric flask for analysis. The trace metals were determined in the obtained filtrate using atomic absorption spectrometer (AAS).

The elements with high concentrations such as Ca, Fe, Al, Ti, Sr, and Rb were measured using EDX-8000 spectrometer. EDX-8000 is rapid, non-destructive technique, and sensitive for heavy and light elements. The system has a large boxshaped chamber, high visibility led lamp, X-ray tube, semiconductor camera, high-performance silicon drift detector (SDD), and PCEDX Navi software. The supply voltage is 100–240 V AC and a frequency of 50/60 Hz. Before EDX measurements, the samples were prepared in a cylindrical container of polyethylene (cell) with a diameter of 3 cm. After the sample is irradiated with X-rays inside the chamber, the qualitative and quantitative analysis can be performed by measuring the amount of X-rays at the wavelength specific to each elements. **Fig. 1** Location map of the collected samples along the beach near to desalination plant



Results and discussion

Uranium and heavy metal concentrations in sand samples and sediments collected along the beach near to disposal site of reject brine

The concentrations of heavy metals in sand samples and sediments at 12 sites near to a disposal site of reject brine and the average values of geochemical background in shale are given in Tables 2, 3, and 4. These metals included U, Ca, Fe, Al, Ti, Sr, Rb, Ni, Pb, Cd, Cr, Cu, As, and Zr. Heavy metals are a special group of trace metals which have been shown to create definite health hazards (Singare et al. 2013). The obtained results are recorded as follows:

 Table 1
 Locations of sand and sediment samples collected from different sites along the beach near to disposal of reject brine from desalination plant

Sample site	Latitude	Longitude
1	N: 26°10′54.03″	E: 50°13′01.03″
2	N: 26°10′57.29″	E: 50°13′05.83″
3	N: 26°10′00.88″	E: 50°13'52.72"
4	N: 26°11′01.92″	E: 50°13'08.44"
5	N: 26°11′07.15″	E: 50°13'07.74"
6	N: 26°11′11.05″	E: 50°12'54.19"
7	N: 26°11′12.07″	E: 50°13'03.56"
8	N: 26°11′17.35″	E: 50°13'10.21"
9	N: 26°11 [′] 19.12 [″]	E: 50°12 ['] 49.47 ["]
10	N: 26°11′22.07″	E: 50°13'00.48"
11	N: 26°11′30.07″	E: 50°13'11.24"
12	N: 26°11′33.87″	E: 50°13'05.14"

Uranium

For sand samples, the average concentrations of uranium in sand ranged between 0.98 and 2.94 mg/kg for surface samples and between 1.58 and 2.54 mg/kg for subsurface samples. For sediment samples, uranium concentrations ranged from 1.48 to 3.04 mg/kg. The mean values of uranium in sand and sediment were within the global average in soil (0.3–11.7 mg/kg) (UNSCEAR 1993).

Nickel and copper

The concentrations of Ni and Cu ranged between 1.16 and 16.2 mg/kg and between 623 and 1022 mg/kg, respectively, for surface sand and ranged between 0.91 and 2.72 mg/ kg and between 680 and 1001 mg/kg, respectively, for subsurface sand. Similarly, the concentrations of Ni and Cu for sediments ranged between 1.99 and 4.19 mg/kg and between 620 and 964 mg/kg, respectively. The results show high concentrations of Cu which were higher than the permissible value in sediment (18.7 mg/kg) (USEPA 1996). The highest concentration of Cu was found in site 7 for surface sand. Copper was recorded high concentrations in all sites for sand and sediments. High levels of Cu in sediments and sand along the shoreline may due to the use of copper-nickel alloys as heat exchanger materials in desalination plant. Brine contamination with copper is due to corrosion in these materials (Dawoud and Al Mulla 2012). Copper is an essential micronutrient for most organisms, and it might only become toxic if excess amounts become biologically available (Hoepner and Lattemann 2002).

 Table 2
 Heavy metal concentrations (in mg/kg unless % indicated) in sand samples collected from surface

•			-			-									
Sample code	Ca%	Ti%	Sr%	Rb%	Fe	Al	Mn	Pb	Cr	Cu	As	Zr	Ni	Cd	U
SS1	14.5	0.33	0.09	0.032	20,600	17,350	1012	5.37	1100	902	738	390	3.23	ND ^a	0.98
SS2	48.8	1.20	0.37	0.030	60,860	32,490	1605	10.3	7011	822	1054	901	1.71	ND	1.73
SS3	38.1	1.40	0.44	0.025	52,260	25,590	2013	14.6	7800	922	793	3211	1.45	ND	2.94
SS4	29.7	0.52	0.40	0.031	37,770	22,620	970	8.51	2800	870	674	421	1.16	ND	1.74
SS5	38.0	1.44	0.38	0.030	63,470	27,130	1560	8.42	3205	772	561	912	1.24	ND	2.37
SS6	38.7	1.10	0.44	0.028	56,580	31,860	1350	8.08	3550	790	793	504	1.91	ND	1.22
SS7	33.8	0.66	0.54	0.035	38,480	29,020	900	9.61	1400	1022	867	504	1.63	ND	1.47
SS8	41.7	0.74	0.36	0.030	40,350	27,460	1500	10.1	2170	623	377	811	1.35	ND	1.75
SS9	30.2	1.31	0.38	0.025	52,740	28,420	1450	8.85	6800	960	540	1513	8.85	ND	2.26
SS10	40.8	0.88	ND	0.024	56,240	32,590	1600	11.1	2120	812	625	811	11.1	ND	2.48
SS11	35.9	1.03	0.37	0.025	46,510	28,991	1480	16.2	4490	780	604	1213	16.2	ND	1.82
SS12	35.5	1.09	0.38	0.025	54,490	30,560	1530	9.02	4502	890	763	960	9.02	ND	1.30
Min	14.5	0.33	0.09	0.024	20,600	17,350	900	5.37	1100	623	377	390	1.16	ND	0.98
Max	48.8	1.44	0.54	0.035	63,470	32,590	2013	16.2	7800	1022	1054	3211	16.2	ND	2.94
Mean	35.5	0.98	0.38	0.028	48,363	27,840	1414	10.0	3912	847	699	1013	4.90	ND	1.84
Background in Shale (mg/kg)	22,100	4600	300	140	47,200	80,000	850	20	90	45	4.72	160	68	0.3	3.7

^aND: Not detectable.

Lead and chromium

The content of Pb and Cr in sand samples ranged between 5.37 and 16.2 mg/kg and between 1100 and 7800 mg/kg, respectively, for surface sand and ranged between 6.89 and 12.2 mg/kg and between 1550 and 9860 mg/kg, respectively, for subsurface sand. Similarly, the contents of lead and chromium for sediment ranged between 4.52 and 26.5 mg/kg and from 1040 to 5818 mg/kg, respectively. The highest value of

Cr was in site 10 from subsurface sand. High contents of Cr were observed in all sand and sediment samples which are higher than the permissible value in sediment (25 mg/kg) (WHO 2004), while low contents of Pb were observed in most of the samples. Generally, concentrations of Pb in all samples were lower than the permissible value of 40 mg/kg in sediment (USEPA 1999). However, all lead compounds are potentially harmful or toxic (Jenkins 1989). The high concentrations of Cr may be due to the corrosion products in brine water

Table 3 Heavy metals concentrations (in mg/kg unless % indicated) in sand samples collected from subsurface

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Sample code	Ca%	Ti%	Sr%	Rb%	Fe	Al	Mn	Pb	Cr	Cu	As	Zr	Ni	Cd	U
SB1	32.2	0.89	0.16	0.020	48,610	32,400	1610	6.89	1550	913	741	424	1.32	ND	1.58
SB2	53.2	0.94	0.47	0.030	49,920	24,210	1221	9.62	3700	1001	922	1022	2.61	ND	1.68
SB3	41.2	1.24	0.37	0.028	45,410	32,590	1203	12.2	2500	810	956	710	1.58	ND	1.67
SB4	31.0	0.47	0.45	0.030	30,540	23,880	830	8.25	1550	890	781	504	1.60	ND	1.56
SB5	47.5	1.11	0.61	0.024	51,860	26,690	1280	8.51	3430	800	466	707	1.35	ND	1.94
SB6	37.5	1.74	0.21	0.027	68,000	42,620	1900	8.51	5020	680	500	1401	0.91	ND	1.80
SB7	39.6	1.35	0.42	0.027	54,130	32,360	1150	8.76	5470	870	399	1107	1.37	ND	1.98
SB8	51.9	1.15	0.59	0.029	49,400	25,170	1270	8.76	2800	740	457	504	1.08	ND	2.54
SB9	31.3	0.58	0.36	0.031	30,180	22,100	570	11.6	2110	911	466	608	1.32	ND	2.21
SB10	39.5	1.96	0.59	0.023	61,610	30,800	1750	11.9	9860	790	723	1022	1.53	ND	2.36
SB11	41.6	0.87	0.48	0.030	39,800	25,190	920	7.91	2811	830	637	608	1.72	ND	2.44
SB12	35.4	1.27	0.48	0.027	45,900	26,530	1160	8.84	6930	850	989	804	1.40	ND	1.98
Min	31.0	0.47	0.16	0.020	30,180	22,100	570	6.89	1550	680	399	424	0.91	ND	1.58
Max	53.2	1.96	0.61	0.031	68,000	42,620	1900	12.2	9860	1001	989	1401	2.72	ND	2.54
Mean	40.2	1.13	0.43	0.027	47,947	28,712	1239	9.31	3978	840	700	785	1.48	ND	1.94
Background in Shale (mg/kg)	22,100	4600	300	140	47,200	80,000	850	20	90	45	4.72	160	68	0.3	3.7

Table 4 Heavy metal concentrations in sediments (in mg/kg unless % indicated)

Sample code	Ca%	Ti%	Sr%	Rb%	Fe	Al	Mn	Pb	Cr	Cu	As	Zr	Ni	Cd	U
SD1	18.8	0.41	0.11	ND	29,360	18,480	1260	5.71	2248	760	194	380	4.19	ND	1.90
SD2	37.3	0.57	0.38	ND	27,560	17,990	1195	7.57	3456	781	240	242	4.09	ND	1.85
SD3	35.5	0.84	0.32	0.02	48,620	27,110	1130	6.47	2971	675	175	621	3.08	ND	2.07
SD4	33.7	0.43	0.40	0.03	31,940	27,590	1235	6.90	3214	852	233	344	2.80	ND	1.48
SD5	39.2	1.28	0.30	0.02	55,450	30,670	1480	6.56	3940	677	298	732	2.22	ND	1.95
SD6	35.8	0.57	0.49	0.03	41,250	32,250	990	8.08	1040	870	86.6	330	1.99	ND	2.13
SD7	39.9	1.60	0.41	0.03	60,980	29,910	1720	4.52	6592	811	374	1142	2.90	ND	2.58
SD8	42.4	0.18	0.55	ND	13,780	28,970	1760	26.5	5818	620	405	241	3.34	ND	1.94
SD9	42.7	1.47	0.49	0.03	67,820	41,460	1800	8.25	5043	731	466	1172	2.59	ND	3.04
SD10	32.5	0.23	0.30	ND	15,580	38,565	1010	6.81	5431	964	252	274	3.72	ND	1.85
SD11	41.2	0.89	0.48	0.03	37,420	35,670	1260	15.5	5237	716	390	692	2.89	ND	2.86
SD12	37.6	0.85	0.40	ND	41,740	31,520	1405	7.53	4879	848	359	723	2.79	ND	2.87
min	18.8	0.18	0.11	0.02	13,780	18,480	990	4.52	1040	620	86.6	241	1.99	ND	1.48
max	42.7	1.60	0.55	0.03	67,820	41,460	1800	26.5	5818	964	466	1172	4.19	ND	3.04
mean	36.3	0.77	0.38	0.03	39,292	30,015	1354	9.35	4090	769	283	561	3.07	ND	2.14
Background in Shale (mg/kg)	22,100	4600	300	140	47,200	80,000	850	20	90	45	4.72	160	68	0.3	3.7

resulting from the effect of water flow, dissolved gases, and treatment chemicals (acids) on the alloys utilized in the construction of desalination pipes and equipment (Dawoud and Al Mulla 2012).

Arsenic and zirconium

The concentrations of As and Zr for sand samples ranged from 377 to 1054 mg/kg and from 390 to 3211 mg/kg, respectively, for surface samples and ranged from 399 to 989 mg/kg and ranged from 424 to 1401 mg/kg, respectively, for subsurface samples. The concentrations of As and Zr for sediment ranged from 86.6 to 466 mg/kg and from 241 to 1172 mg/kg, respectively. The highest value of As was in site 2 for sand sample from surface. Generally, high concentrations of As were observed in all samples which are higher than the allowed limit (1–40 mg/kg) (WHO 2001).

Cadmium and manganese

From Tables 2, 3, and 4, it can be observed that Cd was not detected in all samples. The concentrations of Mn in sand samples ranged from 900 mg/kg for surface sand and ranged from 570 to 1900 mg/kg for subsurface sand, whereas the average concentration for sediments ranged from 990 to 1800 mg/kg. The highest concentration of Mn was observed in surface sand at site 3. However, the concentrations of Mn in sand and sediment for all sites were higher than the average of background in shale (Turekain and Wedepohl 1961) except two sites in subsurface sand (sites 9 and 4).

Iron and aluminum

In case of Fe and Al, the concentrations of Fe in sand ranged between 20,600 and 63,470 mg/kg for surface samples and ranged between 30,180 and 68,000 mg/kg for subsurface samples, while the concentrations of Al in sand ranged between 17,350 and 32,590 mg/kg for surface sand and ranged between 22,100 and 42,620 mg/kg for subsurface samples. For sediment samples, the concentrations of Fe and Al ranged between 13,780 and 67,820 mg/kg and between 18,480 and 41,460 mg/kg, respectively. The highest value of Fe was found in subsurface sand at site 6.

The mean values of Ca, Ti, Sr, and Rb were 35.5, 0.98, 0.38, and 0.028 %, respectively, for sand samples from surface, and the mean values for subsurface samples were 40.2, 1.13, 0.43, and 0.027 %, respectively. Similarly, the mean values of Ca, Ti, Sr, and Rb for sediments were 36.3, 0.77, 0.38, and 0.03 %, respectively. These results show high concentrations of Ca and Ti in sand and sediment samples which constitute major elements in soils. This study found high concentrations of Sr, which may be due to the high concentration of Sr in reject brine (Mohamed et al. 2005).

From Tables 2, 3, and 4, the mean values of Fe, Mn, Cr, Cu, As, and Zr concentrations for sand samples were higher than the geochemical background values in shale (Turekain and Wedepohl 1961). Similarly, the result for sediments is close with that in sand, except the mean value of Fe which was lower than the background value in shale.

Generally, the data shows a variation in the concentrations of heavy metals in surface and subsurface sand near to disposal site of reject brine that could be attributed to the intrinsic

Table 5 Comparison of heavy metals (in mg/kg) in sediment and soil for this study and other local and regional studies in Arabian Gulf coast	y metals (in mg/kg) in	sediment an	d soil for this study	y and other lo	cal and region	nal studies in	Arabian Gu	lf coast			
Country	Type of sample	Depth	Fe	Al	Mn	Pb	Cr	Cu	As	Ni	Ref
Kuwait	Sediments	1	353-32,150	1	3–579	2.60-37.6		3.60-56.5	-	2.10–96	Al-Abdali et al. 1996
Bahrain	Sediments	1		1	1	111.6	1	15.1	1	40.5	Akhter and Al-Jowder 1997
Dammam, Saudi Arabia	Sediment	1	372.4	-	5.9	2.1	6.5	6.3	1	4.4	AlKahtany et al. 2015
Dammam, Saudi Arabia	Soil	Surface	<1	1	0.0063	<0.001		<0.001	1	0.035	Almahasheer et al. 2014
		Subsurface	< <u></u>	1	<0.007	<0.001		<0.001	-	0.0127	
Saudi Arabia	Soil from tide zone 0–30	0-30	1800		36	4	34	5	-	1	Fahad et al. 2014
		30-60	1800	1	38	5.2	42	5	1	2	
Qatar	Sediment	1	123.04–2368.46	-	4.42-54.66 0.67	0.67		0.52-6.87	1	8.55	Al-Naimi et al. 2015
Iran	Sediment	1		1.01 %	351	-	43	22	10.5	62	Vaezi et al. 2015
Qatar	Sediments	1	305-5680	484-18,000 13.2-127	13.2-127	0.43 - 3.88	11.5-40.8 1.22-8.17	1.22-8.17	1.0 - 6.3	0.74 - 20.8	0.74-20.8 de Mora et al. 2004
United Arab Emirates (UAE)		1	874-29,600	534-26,000 32.9-360	32.9–360	0.69-5.88 17.6-303 0.64-3.58	17.6–303	0.64-3.58	0.7–9.6	2.0-1010	
Bahrain		1	471–6475	601-8954	22.6-84.3	0.673-99.0 3.36-41.8 2.38-48.3	3.36-41.8	2.38-48.3	3.16 - 6.88	2.46-23.2	
Oman		-	334-11,600	632-18,300 27.8-265	27.8-265	0.253-1.82 6.46-133		0.602-6.66	0.602-6.66 0.740-5.01 1.84-77.8	1.84-77.8	
Al Khobar beach, Saudi Arabia Sand	Sand	Surface	48,363	27,840	1414	10.0	3912	847	669	4.90	Present study
		Subsurface	47,947	28,712	1239	9.31	3978	840	700	1.48	
	Sediment		39,292	30,015	1354	9.35	4090	<i>769</i>	283	3.07	

Table 6 Categories of sedimentpollution based on the calculatedindexes of CF and mC_d

CF	Contamination level	mC _d	State of pollution
CF < 1	Low contamination	mC _d < 1.5	Zero to very low degree contamination
$1 \le CF < 3$	Moderate contamination	$1.5 < mC_d < 2$	Low degree of contamination
$3 \le CF < 6$	Considerable (high) contamination	$2 < mC_d < 4$	Moderate degree of contamination
CF > 6	Very high contamination	$4 < mC_d < 8$	High degree of contamination
		$8 < mC_d < 16$	Very high degree of contamination
		$16 < mC_d < 32$	Extremely high degree of contamination
		$mC_d \ge 32$	Ultra high degree of contamination

nature of its geological formations and the different depositional processes of heavy metals along the shoreline during the high tide. Depositional processes of heavy metals in surface and subsurface sand may be affected by sand processes such as dissolution, sorption, migration, precipitation, binding by organic matter, absorption, and volatilization. In addition to depositional processes, the accumulation of heavy metals in sand depends on different physicochemical factors such as type of pH, organic matter contents, grain size, and others. These parameters are thought to play an important role in controlling the concentration of heavy metal in surface and subsurface sand (Al-Abdali et al. 1996).

Comparison of Fe, Al, Mn, Pb, Cr, Cu, As, and Ni concentrations with other local and regional studies in Arabian Gulf coast

The concentrations of heavy metals in sand and sediment samples of this study were compared with other local and regional studies in Arabian Gulf as given in Table 5. By comparing this study with the other studies in Arabian Gulf coast, it is evident that the concentrations of Fe, Al, Mn, Cr, Cu, and As were higher than the values of those studies. The mean values of Ni in sand and sediment were lower than the values in all coastal sediment and soil from Bahrain, Qatar, Iran, United Arab Emirates and Kuwait, Arabian Gulf, whereas it was higher than the values of local studies, Saudi Arabia. The mean values of Pb in sediment and sand were higher than the values along the shoreline of the other countries in Arabian Gulf, except the concentrations of Pb in the sediment of Bahrain and Kuwait coast. From the local studies, the data of Fe, Al, Mn, Pb, Cr, Cu, and As were within the limits of geochemical background values, while the current study found high concentrations of the selected metals in sediment and sand samples at the immediate vicinity of the disposal site of reject brine from desalination plant. However, AlKahtany et al. (2015) and Almahasheer et al. (2014) found these metals in low levels away from the outfall, which indicates a localized pollution in the study area.

High concentrations of Fe, Al, Mn, Pb, Cr, Cu, and As in beach sand and sediments near to desalination plant, pollutant source, may be associated with the fluid waste discharges from desalination plant which contains elevated levels of heavy metals (Sadiq 2002; Naser 2013). These metals were deposited from the seawater during high tide (Mohamed et al. 2005; Dawoud and Al Mulla 2012). Even the essential trace elements create a toxicity problem if high levels are present in the environment (Dissanayake and Chandrajith 2009).

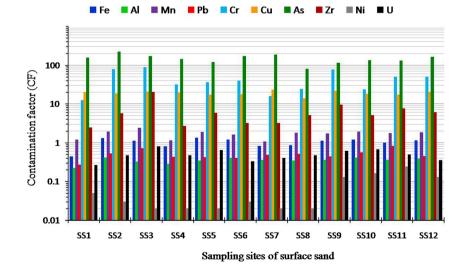
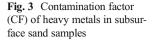
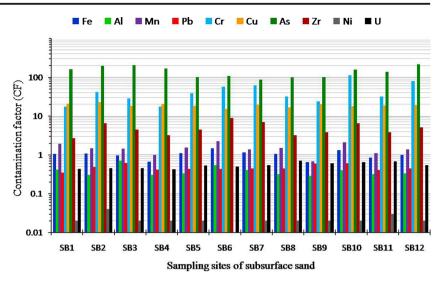


Fig. 2 Contamination factor (CF) of heavy metals in surface sand samples





Generally, most of the local and regional studies indicated that levels of heavy metals in the Arabian Gulf for sediments are within the natural background levels found in offshore and onshore areas. However, elevated levels of heavy metals in Arabian Gulf coast are associated with the human activities such as oil refiners and desalination plants (Naser 2013).

Assessment of environmental pollution

To evaluate the degree of contamination of metals in sediments and sand in the study area, contamination factor (CF) for each metal in the site, the modified degree of contamination (mC_d) and pollution load index (PLI) for each site were calculated. The contamination factor (CF) is calculated using the following equation:

$$CF = C_m \text{ sample}/C_m \text{ background}$$
 (1)

where C_m sample is the concentration metal in sample and C_m background is the background value of metal in shale (Turekian and Wedepohl 1961).

Fig. 4 Contamination factor (CF) of heavy metals in sediment samples The modified degree of contamination (mC_d) was calculated using the following relationship (Abrahim and Parker 2008):

$$mC_d = \frac{\sum_{i=1}^n CF^i}{n} \tag{2}$$

The CF and mC_d categories are listed in Table 6 (Vaezi et al. 2015; Hakanson 1980; Turekian and Wedepohl 1961).

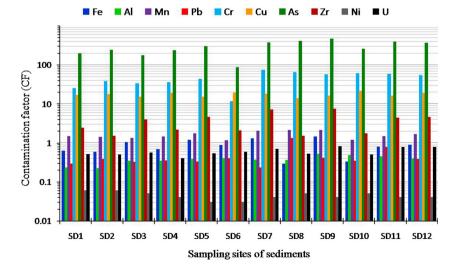
Pollution load index (PLI) was calculated with the following formula (Tomlinson et al. 1980; Ra et al. 2013):

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times \dots \times CF_n}$$
(3)

where n is the number of metals. The PLI > 1 means the presence of pollution, whereas $PLI \le 1$ suggests the absence of pollution (Cabrera et al. 1999).

Contamination factor (CF)

Contamination factors (CFs) of Fe, Al, Mn, Pb, Cr, Cu, As, Zr, Ni, and U in sediments and sand are shown in Figs. 2, 3,



Sample code	mC_d	State of pollution	Sample code	mC_d	State of pollution	Sample code	mC_{d}	State of pollution
SS1	19.3	Extremely high degree of contamination	SB1	20.1	Extremely high degree of contamination	SD1	24.1	Extremely high degree of contamination
SS2	32.9	Ultra high degree of contamination	SB2	26.8	Extremely high degree of contamination	SD2	30.0	Extremely high degree of contamination
SS3	30.1	Extremely high degree of contamination	SB3	25.7	Extremely high degree of contamination	SD3	23.1	Extremely high degree of contamination
SS4	19.9	Extremely high degree of contamination	SB4	20.8	Extremely high degree of contamination	SD4	29.3	Extremely high degree of contamination
SS5	18.2	Extremely high degree of contamination	SB5	16.3	Extremely high degree of contamination	SD5	36.6	Ultra high degree of contamination
SS6	23.2	Extremely high degree of contamination	SB6	19.1	Extremely high degree of contamination	SD6	12.3	Very high degree of contamination
SS7	22.9	Extremely high degree of contamination	SB7	17.5	Extremely high degree of contamination	SD7	47.7	Ultra high degree of contamination
SS8	12.7	Very high degree of contamination	SB8	15.1	Very high degree of contamination	SD8	49.0	Ultra high degree of contamination
SS9	22.5	Extremely high degree of contamination	SB9	14.9	Very high degree of contamination	SD9	55.1	Ultra high degree of contamination
SS10	18.4	Extremely high degree of contamination	SB10	29.2	Extremely high degree of contamination	SD10	33.9	Ultra high degree of contamination
SS11	20.7	Extremely high degree of contamination	SB11	19.2	Extremely high degree of contamination	SD11	47.3	Ultra high degree of contamination
SS12	24.2	Extremely high degree of contamination	SB12	31.5	Extremely high degree of contamination	SD12	44.1	Ultra high degree of contamination

Table 7 mC_d index for heavy metal in sand and sediments

and 4. For all sites, the values of CF were less than 1 for U, Ni, Pb, and Al in sand and sediment, with the exception of Pb in sediment at site 8. Based on Hakanson classification in Table 6, the classification of U, Ni, Pb, and Al in all sites was low contamination except site 8 for Pb in sediment that showed moderate contamination. The contamination factors of Mn, Zr, Cu, Cr, and As ranged between 1.06 and 466 for all sites, with the exception of Mn in subsurface sand at two sites 4 and 9. The classification of Mn, Zr, Cu, Cr, and As for sand and sediment samples in all sites ranged between moderate contamination and very high contamination except sites 4 and 9 that showed low contamination. The results showed that the contamination levels of Cu, Cr, and As in all sites are very high contamination. The CF values of Fe were higher than 1 for surface sand in all site except sites 1, 4, 7, 8, and 11which were lower than 1. Similarly, the contamination levels of Fe in subsurface samples were moderate contamination in all sites except sites 3, 4, 9, 11, and 12 which showed low contamination. The CF values of Fe in sediment indicate low contamination in most of the sites. The highest value of contamination factor was found in sediment for As. Consequently, the high contamination levels for Cu, Cr, and

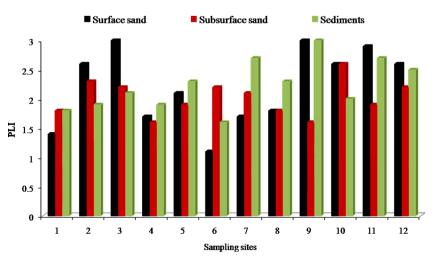


Fig. 5 Variations of pollution load indices for sediment and sand in all sampling sites

As in sediments and sand along the shoreline indicate the presence of a pollutant source.

Modified degree of contamination (mC_d)

The values of modified degree of contamination of the studied metals in sand and sediment for all sites are shown in Table 7. According to Hakanson classification in Table 6 (1980), the results showed that the modified degree of contamination ranged from very high degree to ultra high degree in all sites. The highest degree of contamination was recorded in sediment at site 9. The values of mC_d in sand and sediment indicate high level of pollution in the area of study.

Pollution load index (PLI)

Figure 5 shows the variations of pollution load indices for sediment and sand in all sampling sites. The values of PLI ranged between 1.1 and 3.0 for surface sand and between 1.6 and 2.6 for subsurface sand. Similarly, PLI ranged between 1.6 and 3.0 for sediment. The highest value of PLI was in sites 3 and 9 (PLI > 3) for surface sand and site 9 for sediment. PLIs were found to be higher than 1 in all sites. According to the results of PLI, all sites are considered polluted. The main contributors in PLI values are Cu, Cr, As, and Mn as it is revealed by contamination factors.

Conclusions

In this study, the concentrations of U, Ca, Fe, Al, Ti, Sr, Rb, Ni, Pb, Cd, Cr, Cu, As, and Zr were measured in 36 sand and sediment samples at different sites along Al Azizia beach near to disposal site of reject brine from desalination plant, Arabian Gulf, using gamma-ray spectrometry, atomic absorption spectrometer (AAS), and energy dispersive X-ray fluorescence spectrometer (EDX). The data showed that the mean values of Fe, Mn, Cr, Cu, As, Sr, and Zr concentrations in sand and sediments were higher than the geochemical background values in shale. Based on the contamination factor, modified degree of contamination (mC_d), and pollution load index (PLI), the results showed elevated levels of Cu, Cr, Mn, As, and Zr in the studied area. These toxic elements have a wide range of health issues associated with their contamination. Furthermore, long-term exposure to the naturally occurring radioactive isotopes of Sr and Zr may have serious health implications if living organisms are exposed to them.

In view of the current study, the analysis of heavy metals in sand and sediments near to disposal site of reject brine from desalination plant provided evidence of a localized pollution in the study area.

The regulations and policies related to reject brine discharges and chemical composition disposal must be implemented and enforced. Generally, the available information from this study indicates the need for an environmental management plan to reduce and control the input of high concentrations of Cu, As, Cr, Mn, and Zr from further pollution in the environment nearby a desalination plant. However, if the pollution problem is neglected in the area of study, Arabian Gulf, this will be a cause of great concern that can cause for irreparable ecological damage in the long term.

Abbreviations

AAS, Atomic absorption spectrometry; EDX, energy dispersive X-ray fluorescence spectrometer; UNSCEAR, United Nations Scientific Committee on the Effects of Atomic Radiation; WHO, World Health Organization; USEPA, United States Environmental Protection Agency

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