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Baseline

Metal pollution in Al-Khobar seawater, Arabian Gulf, Saudi Arabia

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ABSTRACT

In order to assess heavy metals pollution along the Al-Khobar coastline, 30 seawater samples and 15 sediment ones were collected for Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Hg and Pb analysis by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). The analysis indicated a southward decreasing pattern in most heavy metal concentrations and the average values of Zn, Fe, Mn, Cu, As and Cr were higher than the ones reported from some worldwide seas and gulfs. Most of the highest levels were recorded within the bays and were related with in situ under sediments especially that composed of clays and very fine sands, and in localities characterized with anthropogenic activities like landfilling, desalination plants, fishing boats, oil spills and solid rubbish. The results of the present study provide useful background for further marine investigation and management in the Arabian Gulf region.

The increase in the levels of trace metals in the marine environment, as a result to rapid development of industrialization and urbanization along the coasts is a worldwide problem (Shriadah et al., 2004). Many obvious impacts have resulted from the increase in residue levels in water, sediments, and biota such as decrease productivity, and increase in exposure of humans to harmful substances (El-Sorogy et al., 2012, 2013). The high concentrations of some metals in seawater are indicative of anthropogenic sources. However, natural sources and processes were also investigated and remain a potential source (Al-Taani et al., 2014, El-Sorogy et al., 2016a, 2016b, 2016c).

In the Arabian Gulf region, which is one of the most arid regions of the world, the typical sources of metal contamination are represented by oil industry, platforms, housing projects, industrial cities, oil terminals, offshore oil, ships, stainless steel, and cement industries, in addition to power stations and many industries expanded along the coastline and adjacent to nearby small cities from 1970 to 1990, and continued to the present (Loughland et al., 2012).

The present study is designed to assess the current status and spatial distribution of heavy metals along the Al-Khobar coast, on the Arabian Gulf of Saudi Arabia to identify the potential sources of contamination and compare between the rate of pollution in Al-Khobar coastal area and other neighboring and worldwide coasts. This evaluation helps develop effective coastal management guidelines and strategies for better management of coastal activities, where the Arabian Gulf is an important area in terms of marine waterways, tourism and various commercial and industrial activities.

The Al-Khobar coast is located in the south of Saudi Arabian Gulf between longitudes 49°58′–50°14′ E and latitudes 25°56′–26°18′ N (Fig. 1). The studied coast is distinguished into three types (Fig. 2): 1) Sandy-dominated shores, composed of coarse sand, sandy mud and very few biogenic materials (e.g. sediment samples 13 and 20). Biogenic materials include abundance of bivalves, gastropods, echinoids, foraminifers, ostracods and sea grass. 2) Biogenic-dominated shores composed of seashells and calcareous sands (e.g. samples 22, 27 and 30). Seashells are represented by accumulations of gastropods (mostly cerithiids) and bivalves (mostly venerids). Calcareous sands showed abundant foraminiferes (*Peneroplis*, *Sorites*, *Quinqueloculina*, *Spiroloculina*, *Triloculina*, *Ammonia* spp.), ostracods, bryozoans (*Membranipora*, *Holloporella* spp.) echinoid fragments and embryonic stages of molluscs. 3) Artificial and natural rocky shores. The artificial ones were constructed to protect cities and tourist villages from high tides and sea erosion. The natural rocky shores composed of highly consolidated sands and found in limited areas, especially in the southern part (e.g. samples 24 and 28).

Thirty surface seawater and fifteen representative sediment samples were collected from Al-Sahil, Al Buhairah and Half Moon bays and from the coastline of Al-Khobar coast in April 2016 (Fig. 1). Unfiltered samples were collected in 1-liter pre-acidified polyethylene containers, kept in an icebox (at 4 °C) and transported to the water laboratory for subsequent chemical analyses. Total dissolved solids (TDS), redox potential (Eh) and electrical conductivity (EC) were directly measured in-situ. Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Hg and Pb

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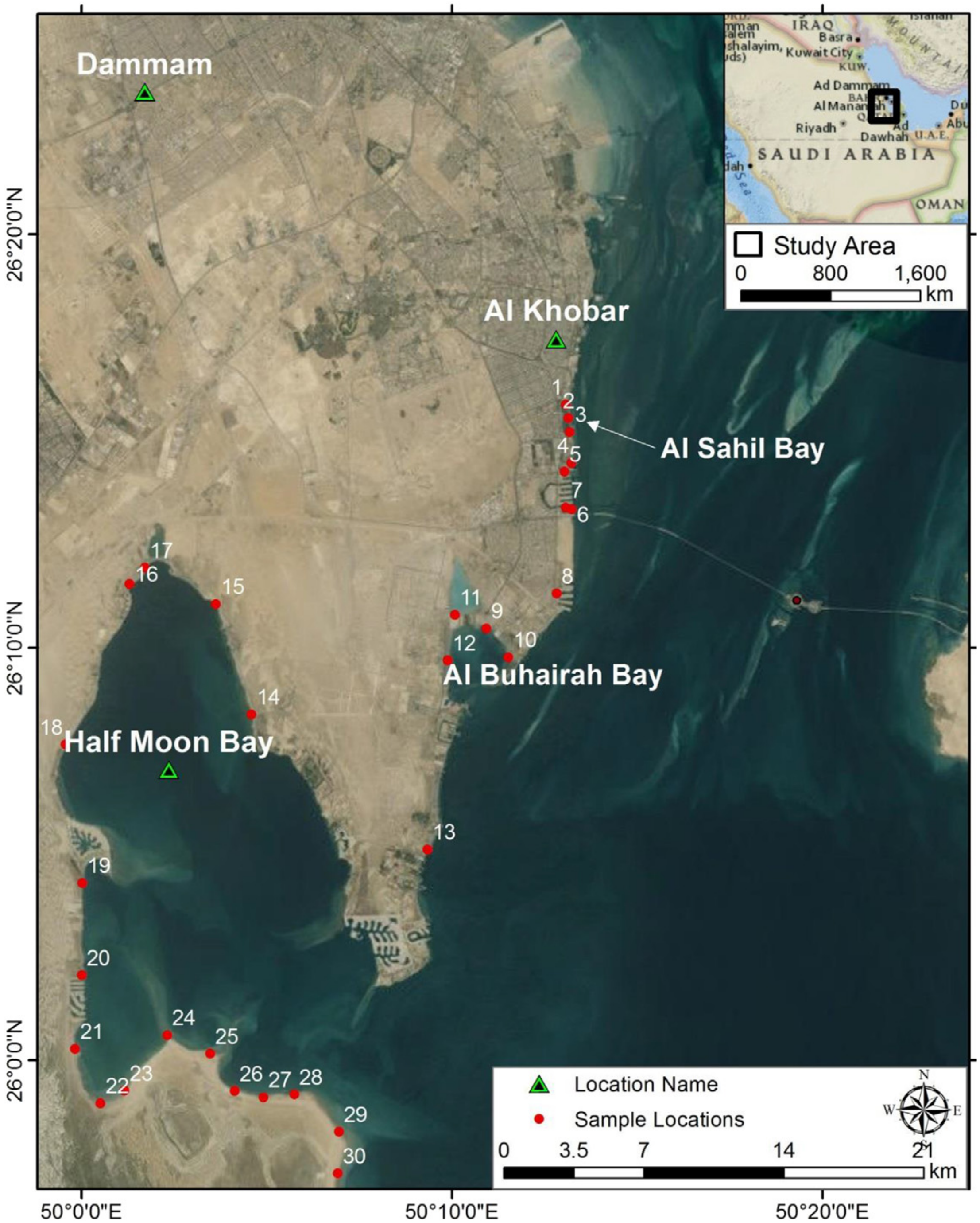

Fig. 1. Location map of Al-Khobar coastline and the locations of the collected samples.

were measured with Inductively Coupled Plasma Mass Spectrometer (ICP-MS): NexION 300 D (Perkin Elmer, USA). Triplicate samples were collected and analyzed.

The sediment samples were ground and sieved through 2 mm sieve. 200 mg of samples were placed in a dry and clean Teflon digestion beaker, and 6 mL of HNO_3, 2 mL HCl and 2 mL HF were added to the Teflon beaker (Trabzuni et al., 2014). Samples were digested on the hot plate at 120–150 °C for approximately 40 min. The resulting digest was filtered through Whatman filtered paper No. 42. The filtrate was transferred to volumetric flask and the volume was adjusted to 50 mL with deionized water. A blank digest was carried out in the same way. 500 mg of rock-powdered samples were placed in a dry and clean Teflon digestion beaker and 2 mL of HNO_3 and 6 mL HCl were added. Samples were digested, filtered and diluted with deionized water similar to soil samples.

Table 1 shows the coordinates of the collected samples and the results of the in situ physical properties (pH, Ec and TDS). Tables 2 and 3 show the results of the heavy metal analyses in seawater and representative sediment samples respectively. The pH ranges from 7.82 in sample 26 to 8.10 in sample 8. EC values of surface seawater ranged between 67,900 and 81,400 μS/cm. The TDS values showed spatial variability, with concentrations ranging between 45,490 and 54,540 mg/L. The higher TDS levels observed in the southward side in general, indicating dissolution and leaching of the adjacent deposits. Mineral dissolution primarily occurred due to wave activity and irregular flash floods, where salts (and trace elements) are transported coastward (Al-Taani et al., 2014).

The spatial distribution of Zinc in seawater samples showed decreasing pattern towards the southward direction, except sample 20 which

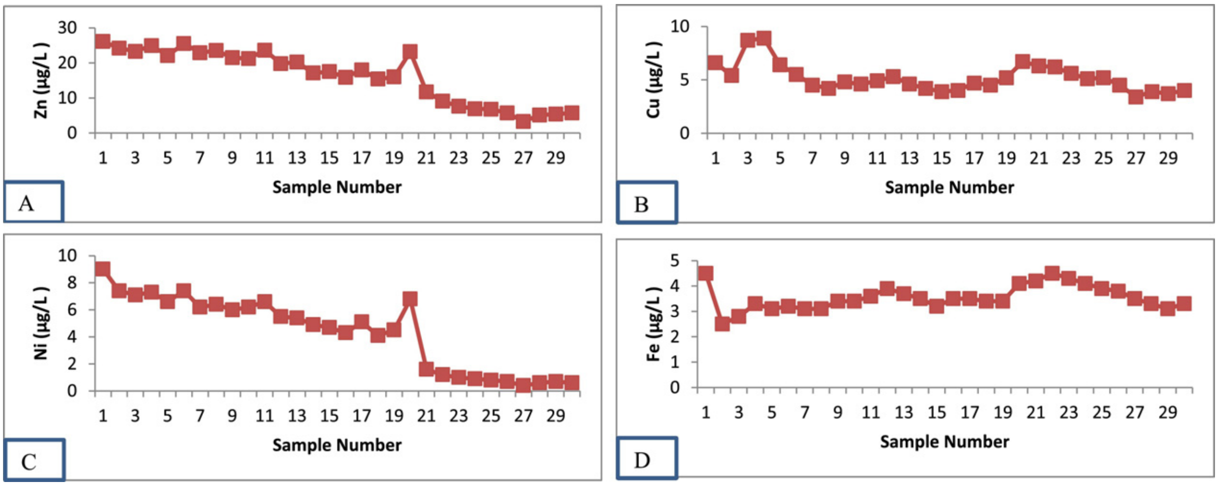

Fig. 2. Spatial distribution of Zn (A), Cu (B), Ni (C) and Fe (D) in seawater samples of Al-Khobar coastline.

anomalies this general trend (Fig. 2A). In seawater samples, Zn ranged from 3.30 μg/L in sample 27 to 26.10 μg/L in sample 1 (within Al-Sahil Bay), while it ranged from 25 to 78 μg/g in sediment samples. Copper levels in seawater samples exhibited slightly elevated values in the northern part and decrease southward with somewhat anomaly in sample 20 within the Half Moon Bay (Fig. 2B). Cu values varied from 3.40 μg/L in sample 27 to 8.90 μg/L in sample 4, while ranged from 96 to 330 μg/g in sediment samples. Nickel exhibited a general trend greatly resemble Zn distribution (Fig. 2C). Ni values varied from 0.4 in sample 27 μg/L to 9.00 μg/L in sample 1 (within Al-Sahil Bay), while ranged from 32 to 111 μg/g in sediment samples. Iron values fluctuated without general trend, but the higher concentrations were recorded in the samples located within the three bays (Fig. 2D). These values varied from 2.50 μg/L in sample 2 to 4.50 μg/L in samples 1 and 22 (within Al-Sahil and Half Moon bays respectively). In sediment samples, Fe ranged from 664 to 14,368 μg/g.

The lowest Manganese values were recorded to the southward while the highest one was recorded near the desalination station of the Al-Khobar City (Fig. 3A, Fig. 8C). Mn varied from 1.30 μg/L in sample 27 to 8.50 μg/L in sample 9 (within Al Buhairah Bay) and ranged from 12 to 202 μg/g in the representative sediment samples. Strontium levels showed a fluctuated pattern without a general obvious trend (Fig. 3B). These values varied from 70 μg/L in sample 27 to 299 μg/L in sample 20. In sediment samples, Sr values ranged from 48 to 2614 μg/g. Lead distribution showed relatively decreasing pattern southward, except few samples within the Half Moon Bay (Fig. 3C). Pb concentrations ranged from 0.017 μg/L in sample 27 to 0.095 μg/L in sample 2 (within Al-Sahil Bay). Pb values ranged from 2.1 to 8.2 μg/g in sediment samples. Distribution pattern of Aluminum is fluctuated within the study area, but in general, the high values were recorded within the Half Moon Bay (Fig. 3D). Al values ranged from 0.60 μg/L in sample 27 to 10.60 μg/L in sample 24, and from 688 to 3224 μg/g in sediment samples.

Distribution of Cadmium showed a deceasing pattern southward, except some beaks in samples 8, 11, 13, 18 and 20 within Al Buhairah and Half Moon bays (Fig. 4A). These values varied from 0.01 μg/L in sample 28 to 0.26 μg/L in sample 20 and ranged from 0.09 to 0.44 μg/g in sediment samples. Vanadium did not exhibit an obvious distribution pattern within the study area but in general the highest value was recorded northward while the lowest one was recorded southward (Fig. 4B). It ranged from 0.60 μg/L in sample 27 to 1.60 μg/L in sample 4 and ranged from 11 to 472 μg/g in sediment samples. Selenium showed fluctuated up and down within the study area (Fig. 4C). These values ranged from 0.14 μg/L in sample 18 to 0.71 μg/L in sample 10 (within Al Buhairah Bay), while ranged from 0.18 to 0.84 μg/g in sediment samples. Arsenic exhibited a decreasing southward trend, except sample 5 (Fig. 4D). It varied from 0.10 μg/L in sample 5 to 3.50 μg/L in sample 3 and ranged from 48 to 2614 μg/g in sediment samples.

Molybdenum concentrations were fluctuated with a decreasing southward trend (Fig. 5A). The values ranged between 0.30 μg/L in sample 27 and 1.80 μg/L in sample 1 (within Al-Sahil Bay), and ranged from 1.3 to 12.1 μg/g in sediment samples. Chromium exhibited small variation along the study area, except the anomaly in sample 1 (Fig. 5B). It varied from 0.80 μg/L in sample 27 to 3.30 μg/L in sample 1 and ranged from 14 to 77 μg/g in sediment samples. Cobalt concentrations in

Table 1
Coordinates of the collected seawater samples and the results of some situ physical properties.

Sample no.	Location	pH	EC	TDS	Sample no.	Location	pH	EC	TDS
1[a]	50°12′59.852″E, 26°15′49.556″N	8.02	69,400	46,498	16[a]	50°1′18.526″E, 26°11′32.802″N	8.01	75,025	50,265
2[a]	50°13′8.187″E, 26°15′33.497″N	7.95	68,200	45,690	17	50°1′42.787″E, 26°11′56.197″N	7.93	78,560	52,635
3	50°13′10.487″E, 26°15′13.804″N	8.02	70,100	46,965	18[a]	49°59′34.5″E, 26°7′38.995″N	7.84	81,400	54,540
4[a]	50°13′13.313″E, 26°14′28.8″N	7.91	69,350	46,460	19	50°0′1.813″E, 26°4′17.898″N	7.95	79,825	53,480
5[a]	50°13′1.7″E, 26°14′15.8″N	7.93	67,900	45,490	20[a]	50°0′0.6″E, 26°2′4.302″N	7.84	78,330	52,480
6	50°13′13.887″E, 26°13′21.098″N	7.96	70,050	46,930	21	49°59′50.113″E, 26°0′16.797″N	7.78	80,040	53,625
7	50°13′4.187″E, 26°13′23.197″N	7.86	68,880	46,150	22[a]	50°0′30.661″E, 25°58′57.802″N	7.92	79,000	52,930
8	50°12′49.5″E, 26°11′18.598″N	8.1	70,800	47,435	23	50°1′10.013″E, 25°59′16.302″N	7.98	77,800	52,125
9[a]	50°10′55.613″E, 26°10′28.102″N	7.98	71,500	47,900	24[a]	50°2′19.213″E, 26°0′36.798″N	8.02	79,110	53,000
10[a]	50°11′30.974″E, 26°9′46.098″N	7.95	71,680	48,025	25	50°3′29.026″E, 26°0′9.902″N	7.95	80,050	53,630
11	50°10′4.587″E, 26°10′47.797″N	7.9	70,890	47,495	26	50°4′8.326″E, 25°59′15.4″N	7.82	78,800	52,800
12	50°9′52.913″E, 26°9′41.598″N	7.95	73,000	48,910	27[a]	50°4′55.039″E, 25°59′6.6″N	7.93	76,940	51,550
13[a]	50°9′19.974″E, 26°5′6.698″N	8.02	75,832	50,805	28[a]	50°5′44.939″E, 25°59′10.803″N	7.96	77,890	52,190
14	50°4′35.587″E, 26°8′23.503″N	7.92	72,990	48,900	29	50°6′57.226″E, 25°58′15.998″N	7.89	78,220	52,410
15	50°3′38″E, 26°11′3.195″N	7.99	74,655	50,010	30[a]	50°6′55.226″E, 25°57′15.497″N	7.99	78,900	52,860

[a] Sediment samples, as well as seawater ones.

Table 2
Metal concentrations in seawater samples in Al-Khobar coastline.

S. no.	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Cd	Hg	Pb
1	1.1	1.5	3.3	7.5	4.5	0.79	9	6.6	26.1	3.2	0.62	246	1.8	0.12	0.91	0.084
2	0.8	0.9	0.8	4.1	2.5	0.68	7.4	5.4	24.2	2.5	0.48	222	1.5	0.16	0.69	0.095
3	1.3	1.3	1.1	8	2.8	0.65	7.1	8.7	23.3	3.1	0.64	253	1.6	0.16	0.78	0.072
4	1.9	1.6	1.3	6.7	3.3	0.64	7.3	8.9	24.9	3.5	0.51	267	1.6	0.18	0.98	0.068
5	3.1	1.5	1.4	5.2	3.1	0.48	6.6	6.4	22.1	0.1	0.27	204	1.2	0.16	0.9	0.066
6	1.1	1.5	1.5	3.2	3.2	0.54	7.4	5.5	25.5	3.2	0.27	237	1.1	0.16	0.84	0.06
7	1.2	1.3	1.3	4.3	3.1	0.42	6.2	4.5	22.9	2.7	0.49	190	1.2	0.11	0.79	0.057
8	1.4	1.4	1.3	5.8	3.1	0.34	6.4	4.2	23.5	2.8	0.59	202	1.4	0.1	0.81	0.053
9	1.9	1.5	1.4	8.5	3.4	0.43	6	4.8	21.5	2.7	0.61	224	1.2	0.16	0.89	0.044
10	1.2	1.4	1.4	5.5	3.4	0.33	6.2	4.6	21.2	2.8	0.71	229	1.3	0.1	0.98	0.053
11	0.8	1.5	1.5	4.7	3.6	0.45	6.6	4.9	23.6	3	0.36	267	1.5	0.23	0.72	0.042
12	0.8	1.4	1.5	4.1	3.9	0.43	5.5	5.3	19.8	2.9	0.44	241	1.1	0.08	0.96	0.032
13	1.5	1.4	1.4	3.5	3.7	0.37	5.4	4.6	20.2	2.8	0.19	213	1	0.15	1.01	0.028
14	4.5	1.3	1.3	5.8	3.5	0.3	4.9	4.2	17.1	2.6	0.17	178	1	0.1	0.82	0.023
15	1.5	1.3	1.3	3.1	3.2	0.36	4.7	3.9	17.5	2.5	0.24	182	1.1	0.1	0.68	0.03
16	4.3	1.2	1.2	5.8	3.5	0.32	4.3	4	15.9	2.5	0.49	176	0.6	0.1	0.55	0.038
17	2.4	1.3	1.4	5.3	3.5	0.3	5.1	4.7	18	2.6	0.19	204	1.2	0.08	0.39	0.025
18	1.3	1.2	1.2	3.5	3.4	0.32	4.1	4.5	15.4	2.3	0.14	171	0.9	0.18	0.49	0.028
19	1.2	1.3	1.4	4	3.4	0.35	4.5	5.2	16	2.6	0.56	216	1	0.16	0.74	0.028
20	2.7	1.5	1.6	4.1	4.1	0.58	6.8	6.7	23.2	2.8	0.29	299	1.4	0.26	0.68	0.036
21	3.6	1.3	1.5	3.8	4.2	0.21	1.6	6.3	11.7	2.5	0.29	254	0.8	0.08	0.82	0.045
22	8.1	1.4	1.5	3.3	4.5	0.24	1.2	6.2	9.1	2.6	0.34	243	0.9	0.08	0.57	0.04
23	4.3	1.3	1.4	3.5	4.3	0.17	1	5.6	7.6	2.5	0.17	226	0.9	0.1	0.55	0.023
24	10.6	1.3	1.3	3.3	4.1	0.24	0.9	5.1	6.9	2.4	0.17	176	0.8	0.1	0.25	0.057
25	1.5	1.1	1.2	2.1	3.9	0.12	0.8	5.2	6.8	2.2	0.56	170	0.7	0.05	0.41	0.021
26	1.4	1	1.1	2.2	3.8	0.16	0.7	4.5	5.7	1.9	0.33	140	0.7	0.02	0.35	0.023
27	0.6	0.6	0.8	1.3	3.5	0.1	0.4	3.4	3.3	1.2	0.26	70	0.3	0.05	0.49	0.017
28	1.8	0.8	0.9	2.3	3.3	0.1	0.6	3.9	5.1	1.7	0.18	121	0.7	0.01	0.62	0.028
29	1.6	0.9	0.9	2.7	3.1	0.17	0.7	3.7	5.4	1.7	0.42	129	0.8	0.02	0.43	0.019
30	1.2	0.8	0.9	1.7	3.3	0.15	0.6	4	5.7	1.6	0.28	109	0.7	0.02	0.55	0.032
Min	0.6	0.6	0.8	1.3	2.5	0.1	0.4	3.4	3.3	0.1	0.14	70	0.3	0.01	0.25	0.017
Max	10.6	1.6	3.3	8.5	4.5	0.79	9	8.9	26.1	3.5	0.71	299	1.8	0.26	1.01	0.095
Average	2.56	1.25	1.38	4.33	3.54	0.36	4.36	5.24	16.21	2.41	0.38	200.88	1.07	0.11	0.68	0.04

seawater showed obvious decreasing trend from north to south, except sample 20 in the western side of the Half Moon Bay (Fig. 5C). The levels varied from 0.10 μg/L in samples 27 and 28 to 0.79 μg/L in sample 1, while they ranged from 0.6 to 8.8 μg/g in the representative sediment samples. Mercury took a general decreasing pattern from north to south (Fig. 5D). The levels varied from 0.25 μg/L in sample 24 to 1.01 μg/L in sample 13, and ranged from 0.05 to 1.61 μg/g in sediment samples.

The average value of Zinc in seawater samples of the Al-Khobar is 16.21 μg/L. It increased the average values of 3.323, 0.22, 0.21, 0.22, 0.21, 0.013, 3.44 and 0.4 μg/L recorded in the surface water of the Gulf of Aqaba, the Red Sea, the Mediterranean Sea, southern Yellow Sea and the average oceanic concentration respectively (Al-Taani et al., 2014; Shriadah et al., 2004; El-Sorogy and Attiah, 2015; He et al., 2008; Broecker and Peng, 1982). Also Zn values increased the ones ranged from 18.01 to 22.62 μg/L in the Gulf of Chabanhar, the Oman Sea (Bazzi, 2014) and decreased the 23.62 and 26.90 μg/L recorded from Dingzi Bay and Tianjin Bay (Pan et al., 2014; Meng et al., 2008). Copper average value (5.24 μg/L) is higher than 0.12, 0.11, 1.12, 2.02, 2.54 and 0.2 μg/L of the mean oceanic level, Gulf of Aqaba, the Red Sea, southern Yellow Sea, the Dingzi Bay, Tianjin Bay and from the Mediterranean Sea (Broecker and Peng, 1982; Shriadah et al., 2004; He et al., 2008; Pan et al., 2014, Meng et al., 2008; Laumond et al., 1984; Boyle et al., 1985). Also Cu values increased the ones ranged from 3.37 to

Table 3
Metal concentrations in representative sediment samples in Al-Khobar coastline.

S. no.	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Cd	Hg	Pb
1	2892	236	51	171	10,928	6.5	95	134	52	1.6	0.41	2314	9.9	0.24	0.75	5.8
2	2910	251	66	182	12,102	7.1	105	145	61	2	0.62	2510	10.8	0.3	0.92	7.1
4	3224	302	77	202	14,368	8.8	111	158	70	2.6	0.84	2614	12.1	0.44	1.2	8.2
5	2931	264	65	190	12,205	7.2	108	132	63	2.1	0.6	2490	10.6	0.31	0.94	7.5
9	3004	248	68	185	12,207	7.3	107	144	60	1.9	0.66	2501	11.4	0.33	0.9	7.3
10	688	386	46	12	664	0.6	44	250	36	0.8	0.18	48	4.2	0.09	0.05	2.1
13	2882	230	50	172	11,044	6.6	93	130	55	1.5	0.44	2320	9.8	0.25	0.72	5.9
16	894	472	60	25	1266	1.3	62	310	68	2	0.39	88	8	0.19	1.31	4.8
18	880	470	63	24	1250	1.2	62	307	69	1.9	0.38	86	8.1	0.18	1.2	4.5
20	924	404	72	28	1439	1.1	66	330	78	2.3	0.51	102	9.5	0.22	1.61	5
22	3005	246	64	180	12,107	0.6	106	146	60	2.2	0.62	2490	11	0.31	1.12	3.8
24	1237	12	15	70	5220	3.6	32	98	27	0.9	0.6	1742	1.5	0.11	0.44	3.4
27	2798	218	40	156	10,192	6	84	115	48	1	0.33	2102	7.5	0.18	0.62	4.3
28	1304	21	23	90	5377	5.1	40	140	35	1.1	0.72	1993	2.7	0.2	0.71	5.1
30	1212	11	14	72	5192	3.8	33	96	25	0.8	0.58	1730	1.3	0.12	0.42	3.6
Min	688	11	14	12	664	0.6	32	96	25	0.8	0.18	48	1.3	0.09	0.05	2.1
Max	3224	472	77	202	14,368	8.8	111	330	78	2.6	0.84	2614	12.1	0.44	1.61	8.2
Average	2041	250.24	50.88	116.06	7681.9	4.48	75.94	180.06	53.53	1.65	0.52	1634.82	7.75	0.24	0.86	5.22

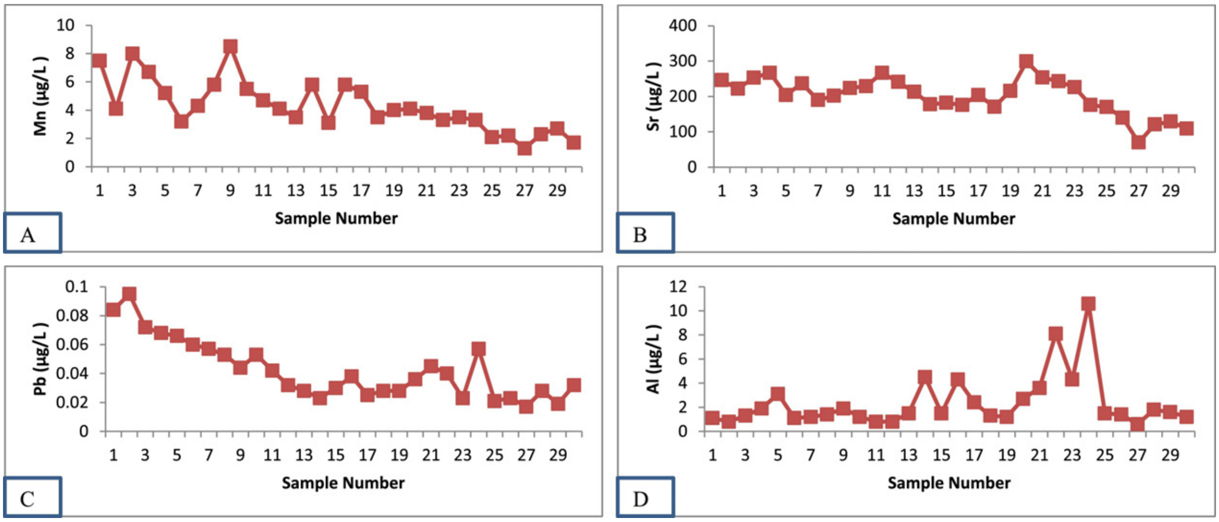

Fig. 3. Spatial distribution of Mn (A), Sr (B), Pb (C) and Al (D) in seawater samples of Al-Khobar coastline.

5.74 μg/L in the Gulf of Chabanhar, the Oman Sea (Bazzi, 2014) and decreased the mean value of 6.183 μg/L from the Gulf of Aqaba (Al-Taani et al., 2014).

Present Nickel average value (4.36 μg/L) is higher than the 0.19, 0.12 and 0.006 μg/L reported from the Gulf of Aqaba, the Red Sea and the Mediterranean Sea (Shriadah et al., 2004; El-Sorogy and Attiah, 2015) and decreased the ones ranged from 16.42 to 17.14 μg/L in the Gulf of Chabanhar, the Oman Sea (Bazzi, 2014). The average value of iron (3.54 μg/L) increased the values of 1.58, 1.11, 0.22 and 0.04 μg/L reported from the Gulf of Aqaba, the Red Sea, the Mediterranean Sea and the mean oceanic concentration (Shriadah et al., 2004; El-Sorogy and Attiah, 2015; Broecker and Peng, 1982) and decreased the ones ranged from 7.06 to 8.67 μg/L in the Gulf of Chabanhar, Oman Sea (Bazzi, 2014). Manganese average value (4.33 μg/L) is higher than those of 0.010, 0.259 and 0.11 μg/L from the Mediterranean Sea, the Gulf of Aqaba and the Red Sea respectively (El-Sorogy and Attiah, 2015; Al-Taani et al., 2014; Shriadah et al., 2004) and decreased the ones ranged from 15.43 to 24.74 μg/L in the Gulf of Chabanhar, Oman Sea (Bazzi, 2014). The average value of Strontium is 200.88 μg/L. It highly greater than 2.09 μg/L, which recorded from the surface water of the Mediterranean Sea (El-Sorogy and Attiah, 2015). The average value of Lead is 0.04 μg/L. It is considerably higher than 0.001 and 0.006 μg/L of the mean oceans and Mediterranean Sea (Broecker and Peng, 1982; El-Sorogy and Attiah, 2015). Pb decreased the values of 0.202, 0.36, 0.30, 1.07, 7.18 and 4.24–4.52 μg/L reported from the Gulf of Aqaba, the Red Sea, southern Yellow Sea, Dingzi Bay, Tianjin Bay and the Oman Sea respectively (Shriadah et al., 2004; Al-Taani et al., 2014; He et al., 2008; Pan et al., 2014; Meng et al., 2008; Bazzi, 2014).

The average value of Aluminum is 2.56 μg/L. It is greater than 0.11 μg/L, which recorded from the surface water of the Mediterranean Sea (El-Sorogy and Attiah, 2015). Cadmium average value (0.11 μg/L) is higher than 0.030, 0.053 and 0.07 μg/L from the Gulf of Aqaba, southern Yellow Sea and the mean oceanic concentration respectively (Al-Taani et al., 2014; He et al., 2008; Broecker and Peng, 1982). This value decreased the 0.53, 0.37, 0.36 and 0.15–0.19 μg/L from the Red Sea, Dingzi Bay, Tianjin Bay and the Oman Sea respectively (Bazzi, 2014) (Shriadah et al., 2004; Pan et al., 2014; Meng et al., 2008; Bazzi, 2014). Selenium average value of Al-Khobar seawater samples (0.38 μg/L) is higher than those of 0.295 reported in Gulf of Aqaba (Al-Taani et al., 2014) and north Atlantic and north Pacific oceans (Donat and Bruland, 1995). Concerning the arsenic, its average value (2.41 μg/L) is higher than the mean value of 0.82, 1.66, 1.33, 1.26 and 0.30 μg/L recorded

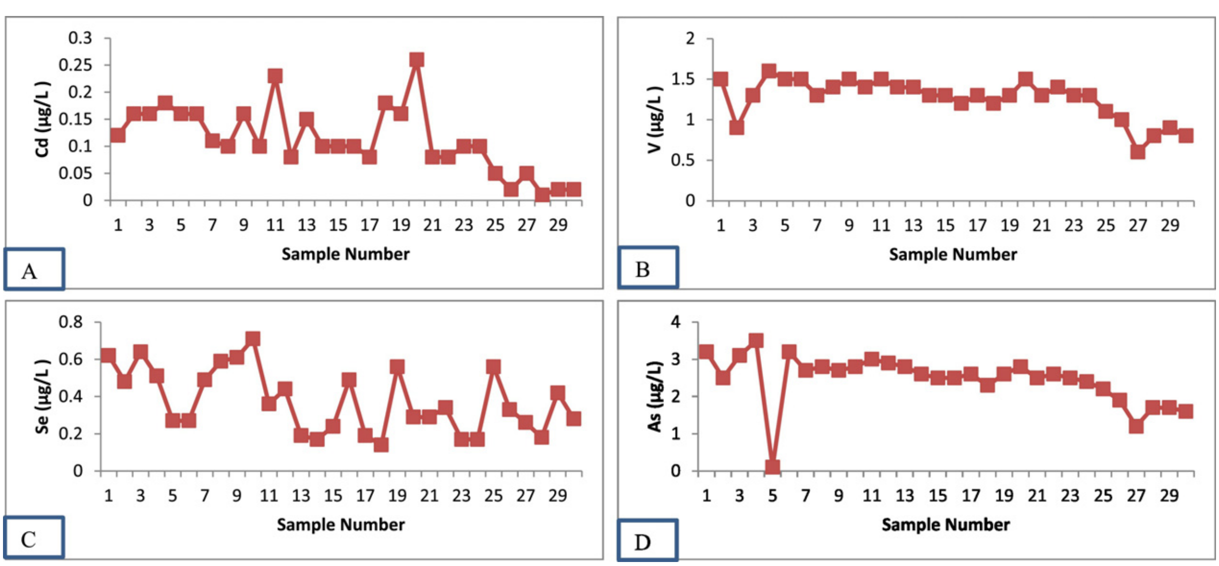

Fig. 4. Spatial distribution of Cd (A), V (B), Se (C) and As (D) in seawater samples of Al-Khobar coastline.

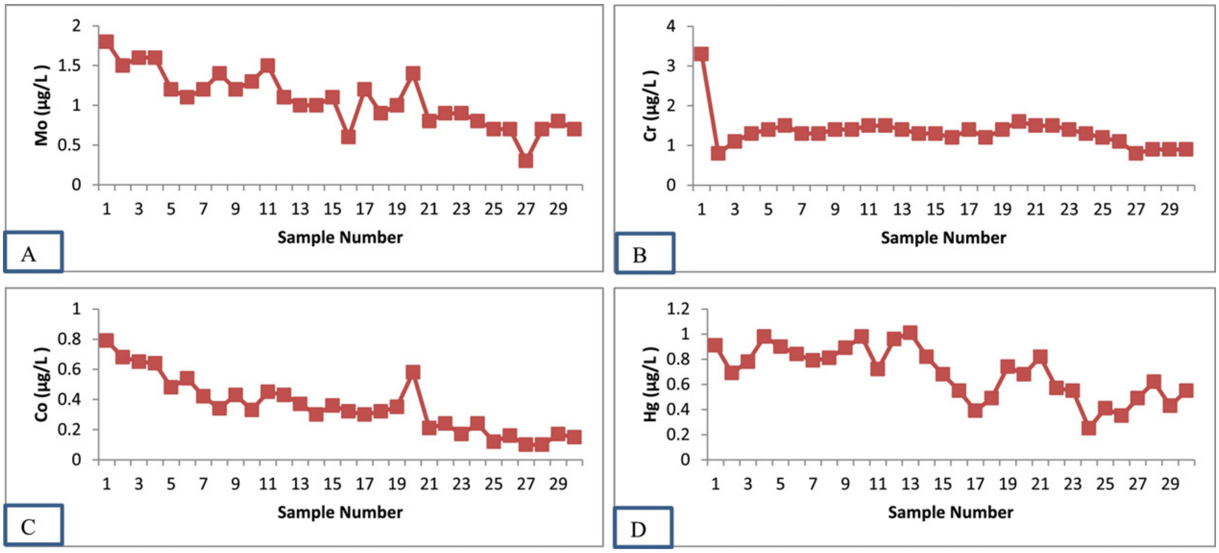

Fig. 5. Spatial distribution of Mo (A), Cr (B), Co (C) and Hg (D) in seawater samples of Al-Khobar coastline.

from the surface water of the Gulf of Aqaba, southern Yellow Sea, Dingzi Bay, Tianjin Bay and from the Mediterranean Sea (Al-Taani et al., 2014; He et al., 2008; Pan et al., 2014; Meng et al., 2008; El-Sorogy and Attiah, 2015). It is less than those from north Atlantic and north Pacific oceans (Donat and Bruland, 1995). Average level of Molybdenum is 2.08 µg/L. It decreased the mean value of 6.499 µg/L of the surface water of the Gulf of Aqaba (Al-Taani et al., 2014), mean oceanic concentrations (Broecker and Peng, 1982) and the average seawater concentrations in the Pacific Ocean (Collier, 1985; Millero, 1996).

Chromium average value (1.38 µg/L) is higher than 0.40 µg/L from Tianjin Bay (Meng et al., 2008), the mean value of 0.957 µg/L of the Gulf of Aqaba (Al-Taani et al., 2014), 0.004 µg/L from the Mediterranean Sea (El-Sorogy and Attiah, 2015). It decreased the ones ranged from 20.16 to 21.46 µg/L in the Gulf of Chabanhar, Oman Sea (Bazzi, 2014). Cobalt average value is 0.36 µg/L. It decreased 0.17 and 0.13 µg/L from the Gulf of Aqaba and Red Sea (Shriadah et al. 2004), 0.004 µg/L from the North Atlantic (Kennish, 1994) and 0.236 µg/L of the Gulf of Aqaba (Al-Taani et al., 2014), while it decreased the 1 µg/L from the Mediterranean Sea (Migon and Nicolas, 1998). The average value of mercury (0.68 µg/L) is higher than 0.0086 µg/L from southern Yellow Sea (He et al., 2008), 0.05 µg/L from Dingzi Bay (Pan et al., 2014), 0.04 µg/L from Tianjin Bay (Meng et al., 2008) and comparable to 0.063 µg/L which reported from Gulf of Aqaba (Al-Taani et al., 2014).

The analyses of heavy metals from the Al-Khobar coastline indicated the following order for the seawater samples: Sr > Zn > Cu > Ni > Mn > Fe > Al > As > Mo > Cr > V > Hg > Se > Co > Cd > Pb and Fe > Al > Sr > V > Cu > Mn > Co > Zn > Cr > Mo > Pb > Co > As > Hg > Se > Cd for the sediment ones. Fig. 6 illustrates the dendrogram of the heavy metal concentrations in seawater samples using HCA analyses. The heavy metals are classified into two different clusters: 1st cluster includes all the studied

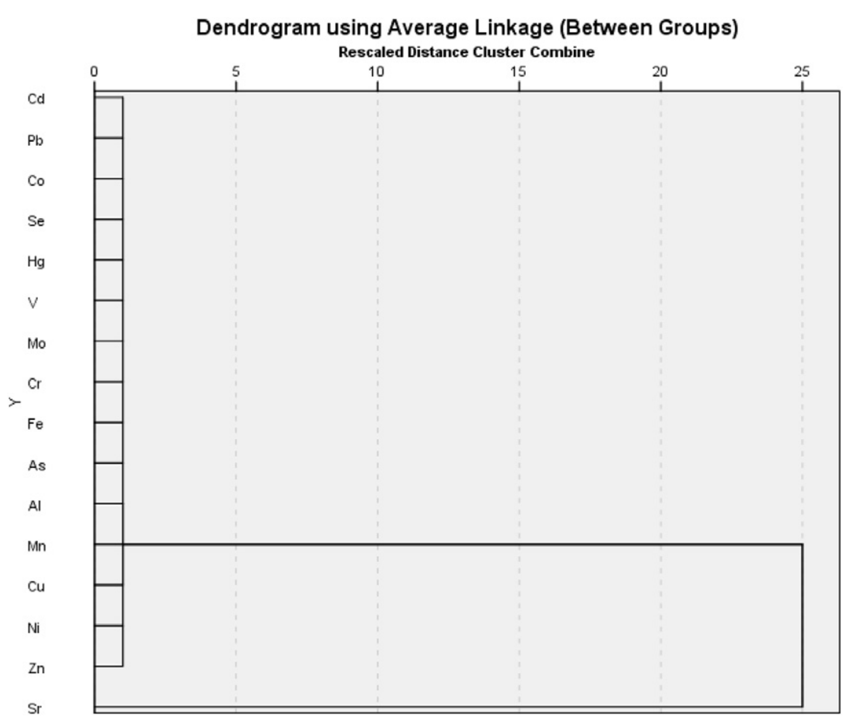

Fig. 6. Dendrogram for hierarchal clusters analyses of 16 metals in surface seawater samples collected from Al-Khobar coastline.

metals, except Sr. The 2nd cluster includes Sr only. The seawater samples are divided into three main groups (Fig. 7): Group 1, includes seawater samples 2, 5, 7, 8, 9, 10, 13, 14, 15, 16, 17, 18, 19, 23, 24 and 25, which recorded the lowest values of Se, Fe, Hg, As, Hg and the highest values of Al, Pb, Mn, Se. Group 2, includes samples 1, 3, 4, 6 and 11, 12, 20, 21 and 22, which recorded the highest values of V, Cu, As, Cr, Fe, Co, Ni, Zn, Sr, Cd and Mo. Coastal sediments under seawater samples in the last two groups are composed mostly of very fine sands and clays with rare biogenic materials. As well as, they situated mostly within the three bays which observed many human activities such landfilling, new building construction, crowded fishing boats and solid rubbish (Fig. 8). Group 3, includes seawater samples 26, 27, 28, 29 and 30, which recorded the lowest values of almost metals, except Fe, As, Se, and Hg. Beach in the last group is of biogenic dominated origin and rocky shore ones. Field survey indicated no human contribution in such studied areas and therefore evidenced by recording the lowest values of the most analyzed metals.

Table 4 illustrates the correlation coefficients among dissolved heavy metals in seawater as well as their correlation with physical parameters. The correlation matrix performed strong correlations between Al and Mg, Ti, K, Fe, P, Cr, Cu, Ni, Co, V and Ga indicating a similarity in their geochemical source. Also, significant positive correlations were found between several pairs of heavy metals; Sr with V, Cu and Zn concentrations ($r = 0.842$, 0.716 and 0.722 respectively), Mo with Zn, Co, Ni, Sr and Mn($r = 0.866$, 0.881, 0.871, 0.750 and 0.723 respectively), Pb with Co and Zn ($r = 0.792$ and 0.656, respectively). Hg with Ni and As ($r = 0.711$ and 0.734, respectively), Cd with Co, Ni, Zn and Sr ($r = 0.724$, 0.730, 0.750 and 0.733 respectively). This indicating a local high concentration for one metal as a result of possible contamination does not necessarily indicate high values for other metals. This also reflects different sources and different biogeochemical behaviors (Fahmy et al., 1997).

Field survey during collecting samples has stated anthropogenic stresses on some localities of Al-Khobar coastline (Fig. 8). Landfilling, seawater desalination plant of Al-Khobar City, fishing boats, and different solid rubbish on the beach are the representatives of theses human activities. Table 5 illustrates the average values of the analyzed heavy metals in seawater and sediment samples and a comparison in-between. Recorded metals in all sediment samples (except As) are higher than those recorded in seawater ones, where coastal sediments are always the final repository of contaminants driving from multiple sources and usually act as functional sinks for trace elements through adsorption and subsequent sedimentation (Chapman et al., 1998; Zwolsman et al., 1997; Pan et al., 2014). Heavy metals in sediment samples ranged from 2170 times in Fe to 1.4 times in Se, in comparison with seawater samples. However, sediments release more heavy metals into the seawater when local environment conditions (e.g., salinity, pH and redox potential) have changed (Hill et al., 2013).

In general, Al-Khobar coastline is characterized by the absence of major industrial activities and low population. As well as, it is being fairly remote from the Industrial City of Al-Jubail to the north. Accordingly the high levels of some studied elements in comparison with those in other worldwide coasts may attribute primarily to the last mentioned anthropogenic activities, releasing of traces from bottom in situ

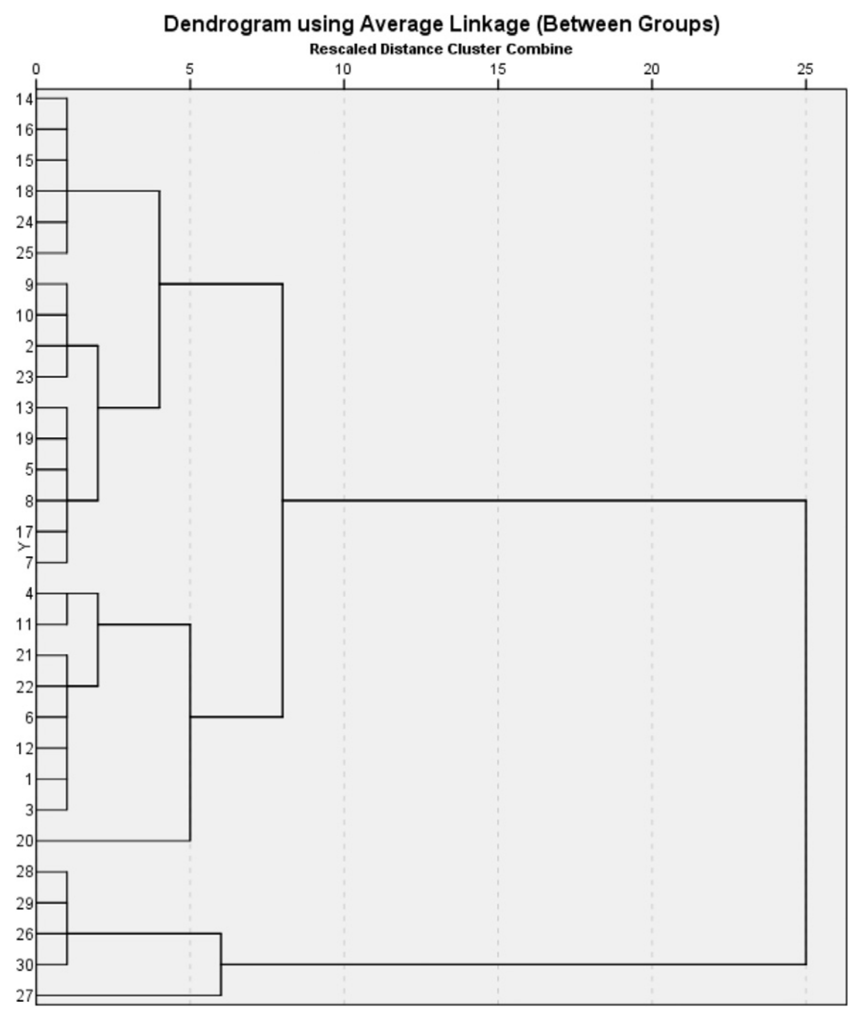

Fig. 7. Dendrogram for hierarchal clusters analyses of 30 seawater samples collected from Al-Khobar coastline.

Fig. 8. A, Landfilling, construction remains and solid rubbish in the intertidal zone of the site 3, Al-Khobar coastline; B, landfilling by rock blocks of the sand beach of site 11; C, Al-Khobar desalination and power plants, between sites 9 and 10; D, Crowded fishing boats in the intertidal zone of site 5.

sediments, oil spills off the Arabian Gulf and dust storms from the surrounding deserts.

The distribution pattern of Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Hg and Pb in Al-Khobar seawater samples indicated that Mn, Co, Ni, Cu, Zn, As, Mo, Cd, Hg and Pb exhibited a decreasing pattern towards the southward, except one or more samples that anomalies this general trend, especially within the bays. The highest value of Mn was recorded near the desalination station of the Al-Khobar City. Fe, Sr, V, Se and Cr fluctuated within the study area without general trend, but also with exceptions here and there.

The average values of Zn, Fe, Mn, and Cr were higher than the ones reported from the Gulf of Aqaba, the Red Sea and the Mediterranean Sea, while the values of Cu and As were higher than the ones reported from the Gulf of Aqaba, the Red Sea, southern Yellow Sea, Dingzi Bay, Tianjin Bay and from the Mediterranean Sea. Most of the highest values were recorded in seawater samples within the three bays, where characterized in localities with landfilling, new constructions, crowded fishing boats and solid rubbish.

The lowest values of most metals were recorded in seawater samples from stations with biogenic dominated sediments or of rocky shore ones and without human contributions. The recorded heavy metals in sediment samples were higher than those recorded in seawater samples, especially in Fe, Al, V, Pb, Cr, Cu, Mn, Ni, Co and Sr. Accordingly, the high levels in some heavy metals in the Al-Khobar seawater in

Table 4
Correlation matrix among analyzed metals.

	pH	EC (μS/cm)	TDS (mg/L)	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Cd	Hg	Pb
pH	1																		
EC (μS/cm)	−0.302	1																	
TDS (mg/L)	−0.302	1.000	1																
Al	0.066	0.307	0.307	1															
V	0.082	−0.412	−0.412	0.168	1														
Cr	0.124	−0.242	−0.242	0.039	0.608	1													
Mn	0.287	−0.618	−0.618	−0.037	0.639	0.452	1												
Fe	−0.155	0.459	0.459	0.488	0.253	0.566	−0.127	1											
Co	0.151	−0.731	−0.731	−0.241	0.586	0.513	0.676	−0.206	1										
Ni	0.198	−0.788	−0.789	−0.358	0.665	0.473	0.727	−0.309	0.914	1									
Cu	−0.070	−0.319	−0.319	0.101	0.541	0.344	0.498	0.131	0.638	0.432	1								
Zn	0.166	−0.777	−0.777	−0.323	0.719	0.445	0.716	−0.293	0.889	0.989	0.445	1							
As	0.152	−0.240	−0.240	−0.043	0.559	0.408	0.472	0.159	0.506	0.508	0.377	0.546	1						
Se	0.262	−0.466	−0.466	−0.342	0.218	0.229	0.552	−0.205	0.415	0.428	0.289	0.413	0.356	1					
Sr	−0.057	−0.377	−0.377	0.064	0.842	0.522	0.579	0.231	0.697	0.666	0.716	0.722	0.663	0.302	1				
Mo	0.176	−0.701	−0.701	−0.247	0.656	0.517	0.723	−0.178	0.881	0.871	0.603	0.866	0.562	0.469	0.750	1			
Cd	−0.059	−0.397	−0.397	−0.084	0.661	0.283	0.483	−0.094	0.724	0.730	0.499	0.750	0.419	0.113	0.733	0.647	1		
Hg	0.151	−0.678	−0.678	−0.365	0.579	0.379	0.554	−0.154	0.598	0.711	0.369	0.734	0.365	0.390	0.557	0.590	0.439	1	
Pb	0.231	−0.740	−0.740	−0.009	0.362	0.345	0.545	−0.263	0.792	0.664	0.577	0.656	0.287	0.456	0.490	0.715	0.423	0.442	1

Table 5
Comparison between metal concentrations in seawater and sediment samples.

Element	Average in seawater	Average in sediments	Sediments:seawater
Fe	3.54	7681.94	2170 times
Al	2.36	2041.00	866 times
V	1.26	250.24	199 times
Pb	0.04	5.22	124 times
Cr	1.34	50.88	38 times
Cu	5.18	180.06	35 times
Mn	4.30	116.06	27 times
Ni	4.33	75.94	18 times
Co	0.36	4.48	13 times
Sr	201.97	1634.83	8 times
Mo	1.10	7.75	7 times
Cd	0.11	0.24	2 times
Zn	16.31	53.53	3 times
Se	0.38	0.52	1.4 times
As	2.45	1.65	0.7 times

comparison to some worldwide ones may attribute to the in situ sediments, anthropogenic activities like landfill and oil spills. As well as the dust storms from the surrounding deserts.

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